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Testing of ceramic membranes for PEG separation and preliminary design of a membrane cascade

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The Plasma Exhausts Gases (PEGs) proposed to reduce the power load over the plasma facing components are separated by the Plasma Exhaust Processing System of DEMO.

Two kinds of commercial ceramic porous membranes (top layer pore size 0.2 μm and 3-4 nm, respectively) have been tested. Experiments have been carried out at room temperature with feed pressure in the range 100-180 kPa and permeate pressure of 100 kPa by testing Ar, N₂, He and H₂. The experimental results validated a gas mass transfer model taking into account the permeation mechanisms of Knudsen and Poiseuille used to assess the permeance of the molecule DT.

According to the processing requirements for the PEG separation of DEMO, a membrane system consisting of ceramic membranes followed by a Pd-Ag permeator has been assessed. By vacuum pumping the permeate of the ceramic membrane cascade at 10 mbar maximum Ar concentration in the retentate is 99.95%, while higher Ar concentration of 99.995% can be achieved by vacuum pumping the permeate at 1 mbar. In both the cases, the Pd-permeator downstream the ceramic membrane cascade recovers about the 99% of the DT fed in form of ultrapure gas.

Keywords: plasma enhancement gas, membrane separation, gas mass transfer modelling.

1. Introduction

The Plasma Enhancement Gas (PEGs) are proposed to reduce the power load over the plasma facing components [1, 2]. Five gases have been considered as potential PEGs (Ar, Kr, Xe, Ne, N₂): in the ITER fuel cycle it is not foreseen to recover and purify the PEGs that are discharged by the exhaust processing system together with the other impurities, while fresh PEGs are fuelled in the plasma. In the DEMO exhaust processing system, the recovery of the PEGs is required because of their large amount (> 10 times more than in ITER).

In particular, the PEG Separation is a part of the Plasma Exhaust Processing System of DEMO [3]. In this study, the ceramic porous membranes have been taken into account among the several process options considered for separating the PEGs.

In a previous work, the mass transfer mechanisms of selected PEGs together with He and DT through ceramic porous membranes have been studied via the Poiseuille and Knudsen models [4]. The results of this work suggested the application to the PEG separation of the porous ceramic membranes of pore sizes around 1 μm operating at low temperature and low pressure (vacuum pumping in permeate side).

Following these activities, this work has been aimed to test porous membranes used commercially in the microfiltration of liquids in order to verify the results of the theoretical models developed previously. A preliminary assessment of a cascade of ceramic membranes coupled with a Pd-Ag permeator has been carried out according to the processing requirement defined in the the Plasma Exhaust Processing System of DEMO for the case when nitrogen is not used as PEG.

2. Experimental

The tests have been carried out on multichannel ceramic membranes produced by Atech Innovation gmbh (Germany) and provided by the MeTe Membrane Technology srl (Italy). In particular, two membranes type 19/3.3 from Atech have been tested:

- ATECH 02: a macro-porous support made up of alpha alumina and three 0.2 μm pores sintered layers made up of alpha alumina with an overall thickness of 35 μm , overall length 112 mm and useful length (the distance between the sealing at its two ends) of 100 mm,
- ATECH 3kD: a macro-porous support made up of alpha alumina and a top layer made up of ZrO₂ with a cut-off of 3000 D (3-4 nm), overall length 160 mm and useful length of 150 mm.

Both these membrane tubes have the external diameter of 24.5 mm and consist of 19 channels of diameter 3.3 mm.

The ceramic tubular membrane have been inserted into stainless steel modules to which the ceramic tube is gas-tight connected through silicone o-ring and the permeate stream is collected in the shell side. The fig. 1 shows the membrane module used for testing the membrane ATECH 02.

The permeation tests have been carried out by controlling the gas feed flow rate (via the mass gas controller MFC) while the retentate and permeate flow rates have been measured via mass flow meters (MFM). The feed pressure has been measured via the pressure



Fig. 1 – Views of the membrane module used for testing the tube ATECH 02.

gauge PG while the permeate side has been operated at atmospheric pressure. The feed pressure has been controlled both by setting the feed gas flow rate and by adjusting the control valve acting on the retentate stream leaving the membrane lumen. The scheme of the test rig for these experiments is reported in the fig. 2.

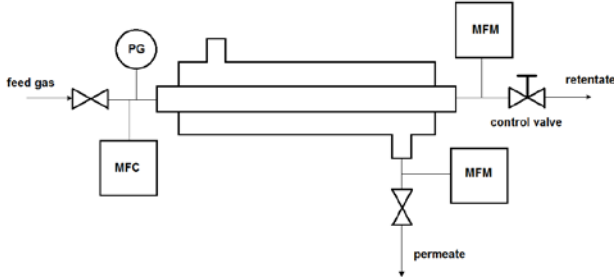


Fig. 2 –Scheme of the experimental setup for testing the ceramic membranes.

2.1 Permeation tests

From the measurement of the permeation flowrates and the upstream (lumen side) and downstream (shell side) pressure, the permeance of a single gas has been assessed through the formula:

$$Pe = \frac{F}{A(P_{up} - P_{down})} \quad (1)$$

where:

F is the permeation flow rate, mol s⁻¹

Pe is the gas permeance, mol m⁻² s⁻¹ Pa⁻¹

P_{up} is the upstream gas partial pressure, Pa

P_{down} is the downstream gas partial pressure, Pa

A is the permeation area, m²

For all the tests the operating conditions have been:

- flow rates (feed, retentate, permeate) up to 20 L min⁻¹,
- feed/lumen pressure up to 1 MPa,
- shell pressure of 100 kPa,
- ambient temperature.

The membranes have been characterized with N₂, He, H₂ and Ar.

The results of the permeation tests have shown in the figures 3 and 4 for the membranes ATECH 02 and ATECH 3kD, respectively.

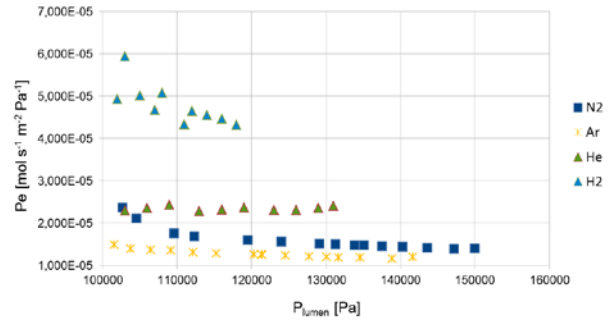


Fig. 3 – Gas permeance of the ceramic membrane ATECH 02 vs. the lumen pressure.

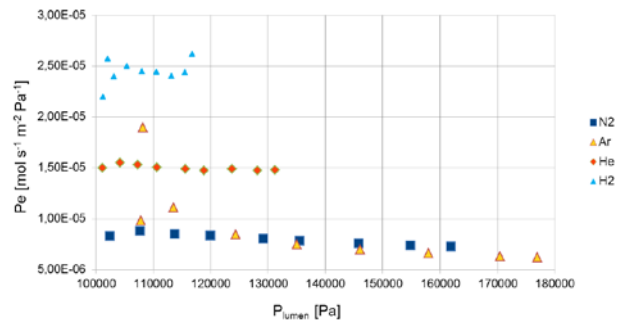


Fig. 4 – Gas permeance of the ceramic membrane ATECH 3kD vs. the lumen pressure.

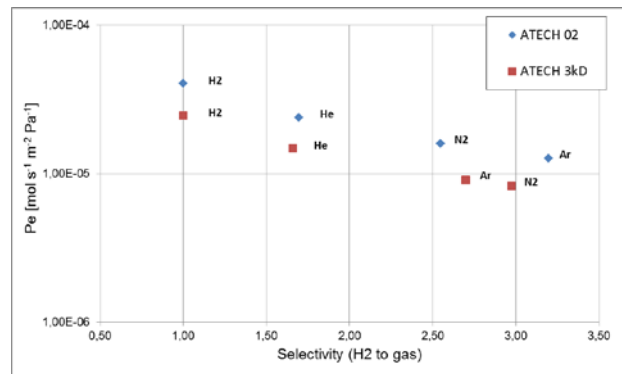


Fig. 5 – Permeance vs. selectivity of the hydrogen to the gas specified.

The selectivity (or separation factor) α_{AB} of the membranes for one component (A) over another component (B) is calculated by the ratio of their permeance through the formula [5]:

$$\alpha_{AB} = \frac{Pe_A}{Pe_B} \quad (2)$$

The selectivity of the gases tested have been calculated taking as reference gas the hydrogen. The results are shown in the graph of fig. 5 where the permeance values are reported vs. selectivity to hydrogen.

As foreseen, the membrane ATECH 02 exhibits values of permeance higher than those of the membrane ATECH 3kD by about a factor 2. In these two membranes, the vales of the He selectivity are very close, while the Ar and nitrogen selectivities show an opposite behaviour. In fact, the membrane ATECH 02 separates better the Ar than the nitrogen exhibiting separation factors of 2.55 and 3.19, respectively. The separation factors of the membrane ATECH 3kD are 2.97 for Ar and 2.70 for nitrogen.

Based on the consideration that the values of the selectivities for the two ceramic membranes are not significantly different and that the membrane ATECH 02 shows larger permeances, the membrane design described in the following section will be carried out by using this kind of membrane.

3. Preliminary assessment of a membrane cascade

This analysis has adopted the permeance and selectivity values measured in the experimental tests before described while the permeance and selectivity of DT has been calculated by the model developed previously [4].

3.1 Calculation of the DT permeance

First, the model developed previously has been verified by comparing the values of the permeance calculated with those measured in the experimental tests carried out with hydrogen, Ar and He.

A parameter to be considered in order to establish the gas transport properties of porous membranes is the mean free path of the gas molecules [6]:

$$\lambda = \frac{3}{2} \frac{\mu}{p} \sqrt{\frac{\pi RT}{2M}} \quad (3)$$

Where:

μ is the viscosity, Pa s

p is the pressure, Pa

R is the gas constant, 8.314 J K⁻¹ mol⁻¹

T is the temperature, K

M is the gas molecular weight, kg mol⁻¹

The comparison of the mean free path of the gas molecules with the pore size defines the permeation regime [5-8]: i) viscous (Poiseuille) regime when the mean free path is much smaller than the pore size, and ii) molecular (Knudsen) regime when the mean free path is larger than the pore size.

The Knudsen number defined as $Kn = \lambda/r$ defines which transport mechanism is controlling the permeation. In case the pore size is similar to the mean free path, the gas permeability can be assessed as an average between the two values (Poiseuille and Knudsen).

The gas permeability for the Poiseuille and Knudsen regimes have been calculated according to the procedure described in the previous work [7].

The gas mass transport mechanisms have been studied for the macroporous support and the top layer of the membrane ATECH 02 based on the geometry characteristics reported in the Table 1.

From the analysis, for both the support and the top layer a mixed transport regime (Poiseuille-Knudsen) has been assessed being the values of the Knudsen number between 0.21 and 1.96.

Table 2 reports for the gases considered (H₂, Ar, He, DT) the Knudsen number and the calculated permeability according to Knudsen and Poiseuille regimes and to the mixed regime (Poiseuille-Knudsen) for both the support and the top layer. The calculated and measured permeance values of the membrane ATECH 02 are reported, too.

Table 1 – Characteristics of the support and top layer of the ceramic membrane.

	top layer	support
thickness, m	3.5E-05	1.0E-03
pore radius, m	2.00E-07	1.00E-06
porosity	0.5	0.5
Shape factor	0.1	0.5

3.2 Assessment of the membrane cascade

The use of nitrogen as PEG involves the formation of tritiated ammonia that rises up to 15.8% the impurity concentration of the stream to be treated by the PEG separation system [3]. For this reason, in this analysis the case where nitrogen is not used as PEG has been considered. Consequently, the PEG separation takes place upstream the Tritiated Impurities Processing that can be sized taking into account the modest amount of impurities present in the exhaust. Under these conditions, the characteristics of the feed stream sent to the PEG separation are the following [3]:

- DT: 4.98 Pa m³ s⁻¹,

- PEG: 235.3 Pa m³ s⁻¹,

- He: 2.73 Pa m³ s⁻¹,

- minor imp. (mainly H₂O, NH₃, CH₄): 0.005 Pa m³ s⁻¹,

- total flow rate: 243.0 Pa m³ s⁻¹.

The calculation of the ceramic porous membranes has been carried out under the hypothesis to use Ar as PEG.

Especially, being the permeance values of He and DT for the ceramic membrane very close under the operating conditions studied, it results that their selectivity to Ar is similar (1.97 and 1.89 for the He on Ar and the DT on Ar, respectively). Therefore, the PEG separation via the cascade membrane can be calculated by considering the virtual binary gas mixture consisting of “He+DT” and Ar: in practice, it is assumed that the He and DT behave as an unique gas that has to be separated from the Ar. Downstream the permeate of the ceramic membrane cascade, a permeator made up of self-supported Pd-Ag tubes separates selectively the DT from Ar and He. The presence of the minor impurities (about 0.002% of the total) is neglected in this assessment.

3.3 Ceramic membranes

A counter-current recycle cascade of ceramic membranes has been considered. Any time that a permeate stream becomes a feed stream to another stage, a compressor is necessary to increase the pressure.

Such a separation system behaves like a distillation column. In fact, the mass balances stage by stage lead to the calculation of the minimum number of stages (corresponding to the condition of maximum reflux ratio) through the same Underwood-Fenske equation developed for the case of a distillation column [9]. Particularly, the expression of the minimum number of stages is:

$$N = \frac{\log\left(\frac{x_d}{1-x_d} \times \frac{1-x_b}{x_b}\right)}{\log \alpha} \quad (4)$$

Where: x_d and x_b are the mole fractions of the more volatile component in the distillate (the permeate of the membrane) and in the bottom (retentate of the membrane), respectively, while α is the relative volatility.

Then the effective number of stages has been then calculated through the Gilliland correlation by fixing a finite reflux ratio corresponding to 1.5 times the minimum one [10].

Table 2 – Gas mass transfer properties of the ceramic membrane.

	DT		H ₂		Ar		He	
	top layer	support	top layer	support	top layer	support	top layer	support
Knudsen number	1.655	0.331	1.962	0.392	1.028	0.206	3.336	0.667
Poiseuille Perm. mol s ⁻¹ m ⁻¹ Pa ⁻¹	8.13E-10	1.02E-07	1.08E-09	1.36E-07	4.63E-10	5.79E-08	4.51E-10	5.64E-08
Knudsen Perm. mol s ⁻¹ m ⁻¹ Pa ⁻¹	3.05E-09	7.62E-08	4.82E-09	1.20E-07	1.08E-09	2.70E-08	3.41E-09	8.52E-08
Mix. regime Perm. mol s ⁻¹ m ⁻¹ Pa ⁻¹	1.16E-09	1.01E-07	1.79E-09	1.35E-07	5.21E-10	5.75E-08	1.42E-09	5.80E-08
Permeance calc. mol s ⁻¹ m ⁻² Pa ⁻¹	2.50E-05		3.71E-05		1.18E-05		2.39E-05	
Permeance meas. mol s ⁻¹ m ⁻² Pa ⁻¹	-		4.06E-05		1.27E-05		2.40E-05	

The membrane area of each stage has been calculated through the formula (1) applied to the permeation of the light components (He+DT). Other assumptions:

- use of tubular membranes;
- total constant pressure in both feed (retentate) and permeate sides;
- constant partial pressure of the two gases (DT and the other gas) in the permeate side.

Under these hypotheses, in the retentate side a partial pressure profile of the gases is established along the tubular membrane. In each membrane stage the permeation driving force has been calculated as “log mean partial pressure difference [11].

Finally, the overall membrane area of the system has been obtained multiplying the minimum number of stages by the area of one stage.

3.4 Pd-Ag permeato

The Pd-Ag permeator consists of a bundle of self-supported Pd-Ag tubes of diameter 10 mm, wall thickness of 0.150 mm and length 500 mm. Such a device is capable to separate selectively the hydrogen isotopes from the other gases. The Pd-tubes operate at 400 °C with a pressure of 17 bar and 10 mbar in the feed (lumen) and permeate (shell) side, respectively. The design of the permeator tubes has been verified according to the procedure described in literature [11].

3.5 Case studies

This assessment has been performed by considering the two cases of membrane cascades with permeate vacuum level of 1 mbar (case study 1) and 10 mbar (case study 2) followed by a Pd-separator capable to recover a stream of pure DT. These two case studies are schematically represented in the fig. 13 and 14.

When vacuum pumping the ceramic membranes at 1 mbar (case study 1), the Ar concentration in the retentate

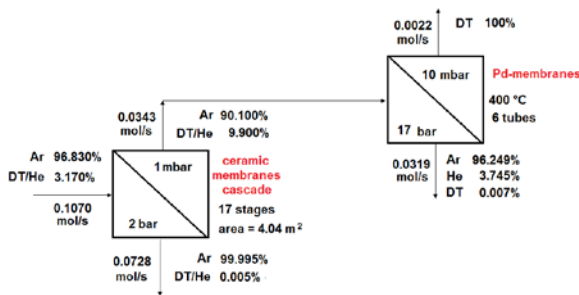


Fig. 6–Case study 1: membrane cascade with vacuum pumping in the permeate at 1 mbar.

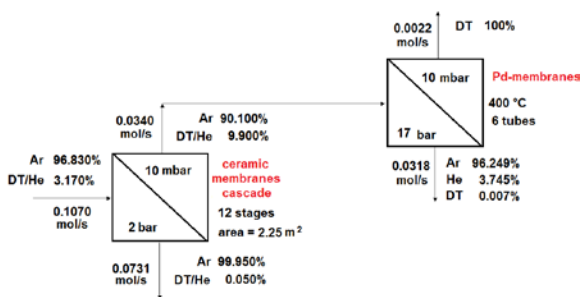


Fig. 7 – Case study 2: membrane cascade with vacuum pumping in the permeate at 10 mbar.

is 99.995% that corresponds to a recovery of the 70.2% of the Ar fed to the cascade. The remaining 20.8% of the fed Ar is recovered in the retentate of the Pd-tubes where its concentration is 96.249%. The total membrane area required is 4.04 m² in 17 stages.

In the case study 2, the ceramic membranes are vacuum pumped at 10 mbar and the Ar concentration is 99.950%: in this way, the 70.5% of Ar fed to the cascade is recovered in the retentate of the ceramic cascade (a little more than in the previous case). The cascade consists of 12 stages with an overall membrane area of 2.25 m².

In both the cases, the Pd-permeator downstream the ceramic membrane cascade consists of 6 tubes (membrane area of 0.094 m²) and separates pure DT in the permeate by recovering about the 99% of the DT fed, while its retentate stream contains DT in a very low concentration (0.007%).

5. Conclusions

The ceramic membranes tested have exhibited selectivity factors of interest for the separation of DT and He from PEGS such as Ar and N₂. The selectivity of He and DT to the Ar is 1.97 and 1.89, respectively.

A ceramic membrane cascade followed by a Pd-permeator has been studied. In the membrane cascade, Ar at 99.995% can be recovered in the retentate by vacuum pumping at 1 mbar, while a retentate with Ar at 99.950% can be recuperated by vacuum pumping at 10

mbar. In the first case (vacuum at 1 mbar) the membrane area is about 4 m² and reduces by half in the second case studied (vacuum at 10 mbar). In both cases, downstream the permeate of the ceramic membrane cascade there is a Pd-permeator consisting of 6 tubes (membrane area of 0.094 m²) that separates a pure DT stream corresponding to about the 99% of the DT fed to the membrane cascade.

Future work should be addressed to test the ceramic membranes with binary gas mixtures in order to verify the selectivity values assessed theoretically.

Acknowledgments

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References

- [1] T. Nakano, N. Asakura, H. Kubo, Contribution of Ne ions to radiation enhancement in JT-60U divertor plasmas, *Journal of Nuclear Materials* 438 (2013) S291–S296.
- [2] M.L. Reinke, J.W. Hughes, A. Loarte, D. Brunner, I.H. Hutchinson, B. La Bombard, J. Payne, J.L. Terry, Effect of N₂, Ne and Ar seeding on Alcator C-Mod H-mode confinement, *Journal of Nuclear Materials* 415 (2011) S340–S344.
- [3] R. George, Study of DEMO exhaust processing requirements, preliminary evaluation of technology solutions and evaluation of ENEA test rig for testing PEG separation, *Eurofusion Rep. EFDA_D_2MPGQA*, 2017.
- [4] S. Tosti, G. Bruni, M. Incelli, A. Santucci, Ceramic membranes for processing plasma enhancement gases, *Fusion Eng. Des.* 124 (2017) 928–933.
- [5] B.S. Massey, *Mechanics of fluids*, Chapman and Hall, London, 1989.
- [6] G.B. van den Berg and C.A. Smolders, Diffusional phenomena in membrane separation processes, *Journal of Membrane Science*, 73 (1992) 103–118.
- [7] K. Keizer et al., Gas separation mechanisms in microporous modified γ -Al₂O₃ membranes, *Journal of Membrane Science*, 39-3 (1988) 285–300.
- [8] E.A. Mason, A.P. Malinauskas, *Gas Transport in Porous Media*, Elsevier, Amsterdam 1983.
- [9] -B. Manson, T. Pigford and H. Levi, *Nuclear chemical engineering*, 2nd. Ed., McGraw-Hill Book Company, New York, 1981.
- [10] E.R. Gilliland, Multicomponent Rectification: estimation of number of theoretical plates as a function of reflux ratio, *Ind. Eng. Chem.* 32 (1940) 1220–1223.
- [11] G. Bruni, S. Cordiner, S. Tosti, A novel procedure for the preliminary design of dense metal membrane modules for hydrogen separation, *Int. J. of Hydrogen Energy* 41 (2016) 20198–20209.