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S Tosti et al.

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# **Ceramic membranes for processing Plasma Enhancement Gases**

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Fusion plasma exhaust is generally composed of unburned fuel (deuterium and tritium), helium and few impurities. However for a metal wall machine (like DEMO) that reaches elevated powers, a certain amount of plasma enhancement gas (nitrogen, Ar, Ne, etc.) could be used as seeding for enhancing the radiative power and decreasing the power load over the plasma facing components. The recovery of these Plasma Enhancement Gases (PEG) could be beneficial because of the high flow rates required, and to limit the load placed upon the exhaust detritiation system.

In this work, the application of ceramic porous membranes for the separation of PEG from other plasma exhaust gases is studied. The gas permeability through porous media of hydrogen, helium and a number of inert gases of potential interest ( $N_2$ , Ne, Ar, Kr, Xe) has been assessed via the models of Knudsen and Poiseuille.

A parametric analysis taking into account the effect of temperature (20 and 300 °C), pressure (100 kPa and 1 MPa) and pore size of the membranes (0.1 nm, 10 nm, and 1  $\mu$ m) has been undertaken to evaluate the capability of porous membrane systems to recover PEG from the exhaust gas in terms of separation factors. The preliminary design of a membrane module is also carried out.

Keywords: ceramic membranes, plasma enhancement gases, plasma exhaust treatment.

# 1. Introduction

Plasma exhaust gas (PEG) contains many kinds of impurity usually coming from the interactions of the plasma with the surfaces [1]. Moreover, with the aim to reduce the power load over the plasma facing components (PFCs) the technique of impurity seeding has been studied in several tokamaks (JET, JT-60U, Alcator C-mod) [2-5]. The presence of these impurities is aimed at reducing the amount of power reaching PFCs by using impurities that convert the plasma thermal energy to isotropic ultraviolet and soft X-ray radiation.

Several gases have been proposed as PEG: nitrogen, neon, argon and other inert gases. Nitrogen has interesting radiative properties but presents a significant chemical reactivity that involves the production of ammonia. Then, inert gases have been studied: mainly, Ne that increases the radiative power of plasma much more than Ar [2].

Among technologies for gas separation, membranes are attracting growing interest because of their reduced energy consumption, continuous operation, modularity and scale-up which can be combined with other traditional separation technologies [6-12]. The most used membranes are classified as polymeric, metallic and ceramic while glass membranes are not very important because of their low selectivity.

Ceramic membranes usually take the form of metal oxides and can be porous or dense [13, 14]: the oxides preferably used are alumina  $(Al_2O_3)$ , zirconia  $(ZrO_2)$ , titania  $(TiO_2)$ , and silica  $(SiO_2)$ . Mixtures of these metal oxides are frequently used, too. Their main advantages are good stability at high operating temperature and

resistance to chemicals. In order to obtain a high permeability and the desired selectivity, usually the porous ceramic membrane consists of a support with a very open pore structure, and a thin top-layer with smaller pores. Intermediate layers for bridging the support and top-layers may be also present. Due to their good chemical and thermal stability, this type of membranes is mainly used for applications in harsh circumstances of temperature (up to 600 °C) or aggressive chemicals.

This work assesses the permeability through ceramic porous membranes of plasma exhaust gases including DT, He and selected PEG (Ne, Ar, Kr, Xe,  $N_2$ ). Especially, a preliminary evaluation has been performed about the application of these membranes for separating: i) the DT from the PEG and He, and ii) the PEG from each other and from He.

# 2 Gas Permeation through porous media

The mass transfer of a gas through a porous membrane is expressed by the following formula [15]:

$$F = \frac{Pe}{d}(p_1 - p_2)A\tag{1}$$

Where:

F is the permeation flow rate, mol s<sup>-1</sup>

Pe is the permeability coefficient, mol m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1</sup>

d is the membrane thickness, m

p<sub>1</sub> is the upstream gas partial pressure, Pa

p<sub>2</sub> is the downstream gas partial pressure, Pa

A is the permeation area,  $m^2$ 

For porous ceramic membranes, gas separation can occur when the pore size is decreased to the same level as the mean free path of a gas, which is defined as the average distance between two successive collisions of a molecule [16-18]. In order to assess the permeability coefficient, the fluid-dynamics of the gas moving inside the porous membrane has to be established. The comparison of the mean free path of the gas molecules with the pore size defines the permeation regime:

- viscous (Poiseuille) regime when the mean free path is much smaller than the pore size,

- molecular (Knudsen) regime when the mean free path is larger than the pore size.

The gas permeability for the Poiseuille regime (i.e. the amount of gas molecules permeating through the pores) is inversely proportional to the gas viscosity:

$$Pe = \frac{\varepsilon \eta r^2}{8\mu RT} p_{av} \tag{3}$$

Where:

E is the porosity

 $\eta$  is the shape factor

r is the pore radius, m

p<sub>av</sub> is the mean pressure, Pa

For the case of Knudsen regime:

$$Pe = \frac{2\varepsilon\eta rv}{3}\sqrt{\frac{8}{\pi MRT}}$$
(4)

### 3. Assessment of membrane separation

The gas permeability has been evaluated with reference to the membrane porosity of 1  $\mu$ m, 10 nm and 0.1 nm. The assessment of the gas permeability has been done for the case of ambient temperature (20 °C) and, in order to investigate the effect of the temperature, the calculations have been repeated at 300 °C.

The graphics of the gas permeabilities are reported in the figures 1 and 2. For the Knudsen regime, the gas permeation is unaffected by the pressure and depends linearly with the pore radius. This is the case when using membranes of pore size 10 nm and 0.1 nm that work under the Knudsen regime for all the operating conditions considered: the values of permeability vary linearly with the pore radius and do not depend on the pressure. For the membranes of pore size 1 µm the permeation regime is "mixed" (Poiseuille-Knudsen) for the operation at low pressure (upstream pressure 100 kPa and downstream under vacuum) and mostly Poiseuillekind for the high pressure operation (upstream pressure of 1 MPa and downstream pressure of 100 kPa). The values of the permeability for the mixed regime have been calculated as the average of the outputs of the equations (3) and (4).









In order to simulate the separation of PEG via porous membranes, the selectivity (or separation factor)  $\alpha_{AB}$  of the membranes for one component (A) over another component (B) is calculated by the formula [16]:

$$\alpha_{AB} = \frac{Pe_A}{Pe_B} \tag{6}$$

# 3.1 Membranes of pore size 1 $\mu m$

For the membranes of pore size 1  $\mu$ m the mass transfer mechanisms at low pressure (upstream pressure of 100 kPa and downstream under vacuum) are ruled by a mixed regime (Knudsen + Poiseuille). When operating at high pressure (upstream pressure of 1 MPa and downstream pressure of 100 kPa) the Poiseuille regime controls the mass transfer through the membranes of pore size 1  $\mu$ m.

At low pressure the selectivity of PEG (or He) over DT at 20 and 300 °C are reported in 1 and 2, respectively. In all these cases PEG can be separated effectively from DT, while the separation of DT from helium could be slightly more difficult. The selectivity of PEG (or He) over DT at high pressure at 20 and 300 °C are reported in

Table 3 and Table , respectively. Effective separation of all gases (PEG or He) takes place in all these cases.

At low pressure the effect of the temperature

(comparison of

Table 1 and

Table 3) is generally modest: by increasing the temperature from 30 to 300 °C, Ne and N<sub>2</sub> separate lightly worse from DT, while for the other gases considered the selectivity is a little higher at 300 °C. At

high pressure the effect of the temperature (comparison of Table and Table ) is also generally modest. By increasing the temperature from 30 to 300 °C, no significant change of selectivity for Ne and N<sub>2</sub> is observed, while the selectivity of DT towards the other gases (Ar, Kr, Xe, He) increases.

Table 1. Membranes of pore size of 1  $\mu$ m: selectivity of PEG (or He) over DT for the case of low pressure (upstream pressure of 100 kPa and downstream under vacuum), temperature 20 °C.

Ne	Ar	Kr	Xe	N <sub>2</sub>	He
0.391877	0.373741	0.298308	0.288406	0.460417	0.791037

Table 2. Membranes of pore size of 1  $\mu$ m: selectivity of PEG (or He) over DT for the case of high pressure (upstream pressure of 1 MPa and downstream pressure of 100 kPa), temperature 20 °C.

Ne	Ar	Kr	Xe	N <sub>2</sub>	He
0.281150	0.394619	0.35484	0.385965	0.500000	0.448980

Table 3. Membranes of pore size of 1  $\mu$ m: selectivity of PEG (or He) over DT for the case of low pressure (upstream pressure of 100 kPa and downstream under vacuum), temperature 300 °C.

	Ne	Ar	Kr	Xe	N <sub>2</sub>	He
0	.280164	0.356716	0.262629	0.233656	0.4398	0.910860

Table 4. Membranes of pore size of 1  $\mu$ m: selectivity of PEG (or He) over DT for the case of high pressure (upstream pressure of 1 MPa and downstream pressure of 100 kPa), temperature 300 °C.

Ne	Ar	Kr	Xe	N <sub>2</sub>	He
0.280164	0.363395	0.304444	0.326190	0.479021	0.360989

#### 3.2 Membranes of pore size 0.1 nm and 10 nm

The membranes of pore size 0.1 and 10 nm operate under the Knudsen regime at both low and high pressure and at the temperatures of 20 and 300 °C. Since the Knudsen permeability is unaffected by the pressure while the dependence on the temperature is the same for all the gases (it is proportional to  $1/T^{0.5}$ ), there is one selectivity matrix for all the operating conditions considered, as shown in

Table 5.

All PEGs are separated very well from DT and helium: in fact, the values of the selectivity of the PEG against DT and helium for these membranes are higher than those of the membranes of pore size 1  $\mu$ m (comparison of the

Table 1-4 with the

Table 5). Only the separation of DT from helium is better performed by the membranes of pore size 1  $\mu$ m. However, it is noteworthy that the separation effectiveness of the membranes of smaller pore size is hindered by their lower values of permeability. In fact, the permeability of the membranes of pore size 1  $\mu$ m is larger than that of the membrane of pore size 10 nm and 0.1 nm by about 3 and 5 orders of magnitude, respectively.

Table 5. Membranes of pore size of 0.1 nm 10 nm: selectivity of PEG (or He) over DT for the case of low pressure (upstream

pressure of 100 kPa and downstream under vacuum) and high pressure (upstream pressure of 1 MPa and downstream pressure of 100 kPa), temperature of 20 and 300 °C.

Ne	Ar	Kr	Xe	N <sub>2</sub>	He
0.497728	0.353783	0.244266	0.195143	0.422577	1.118034

### 4. Application to DEMO Exhaust processing

A preliminary assessment of the permeation area of a membrane separation unit has been carried out for binary mixtures of DT with another gas (PEG or He) by considering a counter-current recycle cascade of membrane separators. The minimum number of stages has been assessed by the Underwood-Fenske equation [19]. Particularly, the membrane area of each stage has been calculated through the formula (1) applied to the permeation of DT by assuming as permeation flowrate (F) the overall feed of 0.14 mol  $s^{-1}$  (conservative hypothesis). For the case of membranes of pore size of 0.1 nm and 10 nm separating the binary mixture of DT with He, the DT permeability is lower than that of other gas (He): therefore, in such a case the membrane area has been calculated by considering the permeation of He instead of 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.

#### 4.1 Low pressure case

In this case the total pressure in the feed (retentate) side is assumed to be fixed at 100 kPa, while in the permeate side the total pressure is assumed to be 1000 Pa (vacuum pumping).

With the input data for the DT mole fraction in the permeate and in the retentate side of 99.99% and 1.00% respectively, the number of membrane stages calculated via the Underwood-Fenske equation is reported in the Table . Due to the low selectivity for the DT-He mixture, the number of stages for this case is large, especially when operating at low pressure and/or with membranes with small pores (0.1 and 10 nm).

Table 6. Low pressure case: theoretical minimum number of stages for the case of a membrane cascade for separating of DT from binary mixtures with another gas.

	1 µm pores		10 - 0.1 nm pores
	20 °C	300 °C	
Ne	15	16	20
Ar	14	13	13
Kr	11	10	10
Xe	11	9	8
N <sub>2</sub>	18	17	16
He	59	148	124

According to the formula (1), the assessment of the permeation area is dramatically affected by the values of the permeability. In

Table the values of the permeation area for the case of low pressure are reported: the membrane area increases as the temperature increases and much more by reducing the pore size. The membrane area for the membranes of pore size 0.1 nm is two orders of magnitude higher than that of the membranes of pore size 10 nm and it is not reported in

Table . The values of the membrane area cannot be calculated for membranes of pore size 0.1 and 10 nm separating binary mixtures of DT with He: in fact, in this case, the partial pressure profile in the retentate side leads to values of  $p_{ret}$  lower than  $p_{perm}$ .

Table 7. Low pressure case: total membrane area  $(m^2)$  of the membrane cascade for separating DT from binary mixtures with another gas.

	Total membrane area m <sup>2</sup>						
	1 μm	pores	10 nm pores				
	20 °C	300 °C	20 °C	300 °C			
Ne	$8.53 \times 10^{1}$	$2.01 \times 10^{2}$	$1.50 \times 10^{4}$	$2.10 \times 10^4$			
Ar	$7.73 \times 10^{1}$	$1.34 \times 10^{2}$	$6.78 \times 10^{3}$	$9.48 \times 10^{3}$			
Kr	$5.11 \times 10^{1}$	$7.96 \times 10^{1}$	$3.68 \times 10^{3}$	$5.15 \times 10^{3}$			
Xe	$4.84 \times 10^{1}$	$6.73 \times 10^{1}$	$2.74 \times 10^{3}$	$3.83 \times 10^{3}$			
N <sub>2</sub>	$1.24 \times 10^{2}$	$2.11 \times 10^{2}$	$9.86 \times 10^{3}$	$1.38 \times 10^{4}$			
He	$1.36 \times 10^{3}$	$1.63 \times 10^{4}$	-	-			

#### 4.2 High pressure case

Operating the feed (retentate) side at 1 MPa and the permeate side at 100 kPa, the retentate stream cannot be depleted in DT below the concentration of 10%. Accordingly, for the high pressure case the DT concentration in the retentate is fixed at 10%: the number of membrane stages is reported in the Table 8. The membrane areas shown in

Table are smaller than those of the low pressure case since in this case the separation is less effective (the DT concentration in retentate is 10% instead of 1%). Also, the values of the membrane area cannot be calculated for membranes of pore size 0.1 and 10 nm separating binary mixtures of DT with He. In fact, in such a case, the partial pressure profile in the retentate side leads to values of  $p_{ret}$  lower than  $p_{perm}$ .

Table 8. High pressure case: theoretical minimum number of stages for the case of a membrane cascade for separating DT from binary mixtures with another gas.

	1 µm pores		10 - 0.1 nm pores
	20 °C	300 °C	_
Ne	9	9	16
Ar	12	11	11
Kr	11	10	8
Xe	12	10	7
N <sub>2</sub>	16	15	13
He	14	11	102

Table 9. High pressure case: total membrane area  $(m^2)$  of the membrane cascade for separating DT from binary mixtures with another gas.

	Total membrane area m <sup>2</sup>						
	1 μm	pores	10 nm	pores			
	20 °C	300 °C	20 °C	300 °C			
Ne	$3.28 \times 10^{-1}$	$9.98 \times 10^{-1}$	$9.33 \times 10^{2}$	$1.30 \times 10^{3}$			
Ar	$6.10 \times 10^{-1}$	$1.86 \times 10^{0}$	$4.21 \times 10^{2}$	$5.88 \times 10^{2}$			
Kr	$4.92 \times 10^{-1}$	$1.50 \times 10^{0}$	$2.29 \times 10^{2}$	$3.20 \times 10^2$			
Xe	$5.82 \times 10^{-1}$	$1.77 \times 10^{0}$	$1.70 \times 10^{2}$	$2.38 \times 10^{2}$			
N <sub>2</sub>	$1.10 \times 10^{0}$	$3.34 \times 10^{0}$	$6.12 \times 10^2$	$8.56 \times 10^2$			
He	$8.23 \times 10^{-1}$	$2.51 \times 10^{0}$	-	-			

#### 4. Conclusions

This paper reports the application of porous ceramic membranes to the separation of PEG from plasma exhaust. Assuming a feed flow rate of 0.14 mol s<sup>-1</sup> with composition of DT = 99% and PEG (or He) = 1% the main results are:

- by operating at 100 kPa in the feed (retentate) and vacuum (1000 Pa) in the permeate side it is possible to obtain a permeate rich in DT (99.99%) and a retentate rich in PEG or He (99%) by using a cascade of membranes for a total membrane area of some tens of  $m^2$  (for He about 1300 m<sup>2</sup>) for the case of membrane pore size of 1  $\mu$ m;

- at the same conditions the membrane area rises up to several thousands of  $m^2$  for the membranes of pore size 10 nm;

- the membrane area increases a little with the temperature;

- when operating at 1 MPa in the feed (retentate) and 100 kPa in the permeate side the concentration of the PEG (or He) in the retentate cannot be smaller than 10%.

In summary, this study would suggest the application to the PEG separation of the porous ceramic membranes used in microfiltration be assessed in more detail. Operation at low temperature and low pressure (vacuum pumping in permeate side) is also advised.

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