



Comparison of MFI-ZSM5 and NaA zeolite-type tubular membranes for the separation of water vapour from helium for tritium processes in future fusion reactors

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ABSTRACT

Zeolite membranes have been increasingly used for gas separation applications, where the most studied are the MFI and NaA types. Typically, NaA membranes are used for dehydration applications whereas MFI are used for the separation of large/small molecules (e.g., CO₂/H₂). In the Tritium Laboratory Karlsruhe (TLK), both NaA and MFI-ZSM5 were selected for tritium processes where both molecular and oxidized tritiated species diluted in helium have to be processed in a continuous mode, as it is the case of the Tritium Extraction System of the Helium Cooled Pebble Bed breeding blanket. This paper presents and discusses the results obtained for the separation of a binary mixture of water vapour and helium, down to 0.2 vol%, where hydrogen replaces its radioactive counterpart. These experiments were performed in the temperature range between 25 and 100 °C. NaA demonstrates much better performances for feed concentrations ≥ 5 vol%, eventually reaching separation factors higher by a factor of 100 than that of MFI-ZSM5. However, the MFI-ZSM5 membrane must be selected instead when moisture levels are ≤ 1 vol%. In fact, at these conditions, the H₂O/He separation factor for NaA barely exceeds 2, whereas it can be as high as 9.6 for MFI-ZSM5. Moreover, rather high permeances for H₂O of around $1\text{--}2 \mu\text{mol m}^{-1} \text{s}^{-2} \text{Pa}^{-1}$ were measured for both membranes. In the case of helium, the permeances were highly dependent on the temperature for high water contents, reaching values as low as $1 \times 10^{-3} \mu\text{mol m}^{-1} \text{s}^{-2} \text{Pa}^{-1}$ for the NaA membrane.

1. Introduction

Compared to other conventional separation techniques and systems, membrane technology reduces the operation cost and size, and it is also more scalable [1,2]. In particular, over the last decades inorganic zeolite membranes have increasingly attracted the interest of the scientific community for gas separation applications [3–5]. Zeolites are crystalline, highly porous aluminosilicate materials with pore dimensions comparable to molecular dimensions, with superior thermal and chemical properties. The main separation mechanisms of these membranes result are three-fold: (i) molecular-sieving, (ii) adsorption and (iii) diffusion [6–8]. Molecular-sieving mechanism is available only when at least one of the molecules have comparable or larger size than the zeolitic pores, typically ranging from 0.2 nm to 0.5 nm (e.g., H₂/n-C₄H₁₀ separation with sodalite membranes [9]). Depending on the gas mixture-membrane system, species with different heats of adsorption are separated since the most adsorbable species hinders or partially blocks the motion of the other component (e.g., CO₂/H₂ separation [10]). The adsorption-diffusion transport mechanism throughout a

defect-free zeolite membrane can actually be described in five steps: (a) adsorption of the species on the external surface of the membrane, (b) mass-transport from the external surface into the zeolite pores, (c) intracrystalline zeolite diffusion, (d) mass-transport out of the zeolite pores to the external surface and (e) desorption from the external surface to the bulk [8,11,12]. (a) and (e) depend on operating temperatures, partial pressures, nature of the chemical species and the type of crystalline material; (b) and (d) can be described by considering the pore diameter, the size of the molecules and the mean-free path (i.e., molecular diffusion, Knudsen diffusion or configurational regime); (c) can be described using the Fickian (driving force given by concentration gradient) or Maxwell–Stefan (driving force given by the gradient of the thermodynamic potential). MFI-ZSM5 and NaA membranes are the most studied zeolite-type of membranes in the literature due to their applications and relatively high-quality synthesis. MFI-ZSM5 are typically studied and envisaged for applications for CO₂ sequestration [13], whereas NaA is widely used for dehydration applications [14,15]. Several authors have reported the production of high-quality MFI-ZSM5 membranes mainly constituted by intracrystalline zeolitic pores,

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whereas NaA membranes typically present intercrystalline, non-zeolitic pores as well [5].

Recently, zeolite membranes have been selected for tritium processes in the Tritium Laboratory Karlsruhe (TLK), where molecular and oxidized tritiated species diluted in helium have to be extracted in a continuous way, as proposed for the Tritium Extraction System (TES) of the Helium Cooled Pebble Bed [16,17]. In this concept, a purge gas composed by helium and 0.1 vol% hydrogen is used to extract the molecular and oxidized tritium species produced in the pebbles. Downstream of the blanket, the resulting He/H₂/HT/HTO stream, with HT/HTO concentrations down to ppm levels [18], has to be processed by the zeolite membranes followed by a membrane reactor. Due to the lack of experimental data, inactive experiments with different zeolite-type materials (MFI-ZSM5, NaA) purchased from Institute for Ceramic Technologies and Systems (IKTS, Germany) for the separation of H₂/He and H₂O/He have been performed [19]. The MFI-ZSM5 membrane demonstrated rather limited separation factors (below 2) for the H₂/He mixture, with interesting permeances of around 0.7 μmol m⁻¹ s⁻² Pa⁻¹ for H₂ at room temperature. Besides the zeolitic (intracrystalline) pores, NaA also has non-zeolitic (intercrystalline) pathways. Therefore, these membranes are typically non-selective for permanent gases mixtures [5].

This work aims to present the experimental results obtained for the separation of water vapour from helium with MFI-ZSM5 and NaA zeolite-type membranes synthesized on α-Al₂O₃ ceramic supports. To the knowledge of the authors, there is no published work where these two membranes are directly compared for the specific application of gas separation of vapor from helium. The experimental results presented below demonstrate the superior separation performances of these membranes, in comparison to H₂/He separation, due to the high chemical affinity between H₂O and the zeolite structure.

2. Experimental description

2.1. Experimental setup

The schematic diagram of the ZIMT (Zeolite Inorganic Membranes for Tritium) experimental facility erected in the TLK is depicted in Fig. 1. The MFI-ZSM5 (thickness ≤30 μm) and NaA (thickness of few μm) zeolite-type membranes tested in our facility are synthesized on the inner surface of a ceramic Al₂O₃ tube (250 mm long, inn./out. diameter = 7/10 mm). The membranes are installed in the facility by inserting them into a stainless steel membrane module (ZMM) sealed by two EPDM O-rings, that can be heated up to ~120 °C using heating wires (Horst GmbH). H₂O/He mixtures are prepared with properly calibrated mass flow controllers (MFC, MKS Inst./Bronkhorst), where vapor is produced via a vaporizer (Bronkhorst aSteam DV2) after the water tank. Moreover, the cut can be varied by using downstream MFCs, whereas the permeate pressure is controlled by using a pressure regulator (Bronkhorst EL-Press) associated with a vacuum pump (Oerlikon DIVAC 0,8T). A quadrupole mass spectrometer (QMS, Pfeiffer-Vacuum QMG 220) is installed to analyse the retentate and permeate downstream flows, whereas cold traps (CT) at 77 K are used to remove

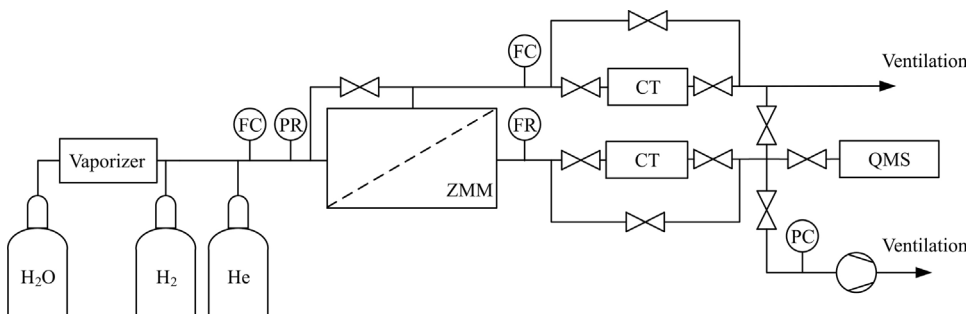


Fig. 1. Schematic diagram of the ZIMT facility erected in the TLK for gas separation experiments with zeolite membranes. ZMM – zeolite membrane module, CT – cold trap, QMS – quadrupole mass spectrometer, FR/C – flow register/controller, PR/C – pressure register/controller.

Table 1

Experimental conditions of the H₂O/He gas separation experiments performed with MFI-ZSM5 and NaA membranes at the ZIMT facility. It should be mentioned that the flows given are at standard conditions of pressure and temperature.

Dilution degree (vol%)	He feed flow (ml/min)	H ₂ O feed flow (ml/min)
0.207 ± 0.001	10,000 ± 73	20.8 ± 0.4
1.00 ± 0.01	5185 ± 51	51.9 ± 0.4
5.00 ± 0.06	3799 ± 45	199.9 ± 0.4
10.0 ± 0.2	1799 ± 37	199.9 ± 0.4

the moisture. The pipes of the facility are properly heated to avoid vapor condensation.

2.2. Experimental procedure

The H₂O/He experiments were performed at different dilution degrees of water in helium in the feed stream: 0.2–10 vol%. The different molar concentrations were prepared by varying the He and H₂O flows between ~2000–10,000 ml/min and ~20–200 ml/min, respectively. The presence of water in the feed stream hinders the control of the cut (ratio of permeate-to-feed flow) due to its adsorption onto the membrane's surface. Therefore, the MFCs downstream of the ZMM are set to their highest setting points. The permeate pressure is set below 0.2 bar, while the retentate is open to the atmosphere. In this configuration the feed pressure is always at ~1 bar. The operating conditions are summarized in Table 1.

As procedure the H₂O/He mixture is fed into the membrane module and the moisture present in the permeate and retentate streams is frozen out by the cold traps. At the end of an experimental run (~2–7 h) the cold traps are weighed and the average moisture concentration in the downstream flows is calculated. This procedure was repeated for temperatures applied on the surface of the ZMM between 25 and 100 °C. These experiments allow the study of the membranes' performances in terms of the H₂O/He separation factor ($\omega_{\text{H}_2\text{O,He}}$), permeance (Π_i) of the gas species i and both recovery fraction (RF_i) and enrichment factor (EF_i), given by the equations below, as a function of the temperature and concentration. The results are presented and discussed in the following section.

$$\omega_{\text{H}_2\text{O,He}} = \frac{y_{p,\text{H}_2\text{O}} x_{f,\text{He}}}{y_{p,\text{He}} x_{f,\text{H}_2\text{O}}} \quad (1)$$

$$\Pi_i = \frac{F_p y_{p,i}}{(x_{f,i} p_f - y_{p,i} p_p) A} \quad (2)$$

$$RF_i = 100 \times \frac{F_p y_{p,i}}{F_f x_{f,i}} \quad (3)$$

$$EF_i = \frac{y_{p,i}}{x_{f,i}} \quad (4)$$

where $y_{p,i}$ and $x_{f,i}$ denote the permeate and feed concentrations of species i , F_p and F_f are the total permeate and feed flows, p_p and p_f the

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