Development of Tritium Monitor Using Hollow Filament Polyimide Membrane

A. Shimada¹, Y. Morimoto¹, K. Iguchi¹, K. Okuno¹,
S. Sasaki², T. Suzuki², and K. Kondo²
¹Faculty of Science, Shizuoka University,
836 Shizuoka, Shizuoka 422-8529 Japan
²High Energy Accelerator Research Organization,
1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

INTRODUCTION

At high-energy accelerator facilities, air in the beam-line tunnels is exposed to high-energy primary and secondary particles during machine operation. As a result, tritium nuclei are produced in the air together the other radionuclides such as ¹⁷C, ¹⁵N, ¹⁸F and ⁴¹Ar mainly through nuclear spallation of atmospheric elements (¹). Tritium is a relatively longer-lived isotope with a half-life of 12.3 y, while the half-lives of the other radioactive airborne species mentioned above are in the order of minutes. Some fractions of tritium produced are eventually released to the atmosphere through exhaust funnels or stacks, and accumulate in the environment.

With recent progress of higher-beam-power accelerators, where a large amount of tritium is produced, it becomes more and more important for preservation of the environment around them to establish an effective method for real-time measurements of tritium released from such facilities. However, a real-time measurement for small amounts of tritium has not been successfully made since tritium emits only low-energy beta ray with an average energy of 5.7 keV and its direct measurement is not so easy. In addition, it becomes more troublesome due to radiations from disturbing radionuclides mentioned above. Therefore, the separation and the enrichment of tritium from contaminated radionuclides would be essential for real-time measurements of tritium.

Among several methods of tritium separation, a hollow-filament type polyimide membrane is one of the most promising device because its high separation efficiency with low-cost. Especially it has one or two order higher permeability for water (vapor) and hydrogen than that for nitrogen or oxygen (³). Theoretically, the gas permeation through plane type polyimide membrane is expressed by the following equation,

\[ F_t = \frac{A_t}{\delta} \times Q \times (P_h - P_l), \]  

(1)

where \( F_t \) is the amount of gas permeated through membrane per unit time, \( A_t \) the surface area of membrane, \( \delta \) the thickness of membrane, \( Q \) the permeation coefficient, and \( P_h \) and \( P_l \) are the pressures at the inlet and at the permeant side of membrane, respectively. \( Q \) is largely different from gas to gas. So, gas with larger \( Q \) can be easily separated from gas with smaller \( Q \) in the permeant side. From Eq.(1), the flow rate of permeant gas also depends on \( A_t \) and a differential pressure \( (P_h-P_l) \). From a view point of obtaining larger processing capability, a hollow-filament type membrane is extremely attractive because of its larger surface area and thinner layer of membrane.

In the present work, we performed experiments to study separation and enrichment performance for various gases using a hollow-filament type polyimide membrane. Measuring the enrichment characteristics for hydrogen and deuterium and also investigating isotope effects in hydrogen isotopes, we discuss feasibility to apply hollow-filament type polyimide membranes to the real-time tritium monitors in large-scaled accelerator facilities.

RADIONUCLIDES PRODUCED IN ACCELERATOR TUNNEL AIR

The radionuclides observed mainly in accelerator tunnel air during its operation are tritium (¹H), ⁷Be, ¹¹C, ¹⁷N, ¹⁸F, ²⁴Na, ³⁶Cl, ³⁸Cl, and ⁴¹Ar (⁴). A chemical form of tritium in the tunnel air is HTO or HT, and the ratio of their relative abundance (HT/HTO) is known to be about 2.0 × 10⁻² (⁵), while the ratio in the atmosphere is to be 0.5. ⁷Be and ²⁴Na exist in the chemical forms of aerosol in the air, and the others are normally gaseous species such as CO, CO₂, O₂, N₂, and NO. These gaseous species are principally found in effluent gases from the accelerator tunnel. Principal radionuclides and their chemical species in the air of accelerator tunnels are summarized in Table 1.
Table 1 Principal radionuclides and their chemical species in the air of accelerator tunnels

<table>
<thead>
<tr>
<th>Radionuclides</th>
<th>Half-life</th>
<th>Chemical Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H</td>
<td>12.3 y</td>
<td>$\text{H}_2\text{O}(98%), \text{H}_2(2%)$</td>
</tr>
<tr>
<td>$^{13}$N</td>
<td>9.96 m</td>
<td>$\text{N}_2, \text{NO}_x$</td>
</tr>
<tr>
<td>$^{11}$C</td>
<td>20.3 m</td>
<td>$\text{CO}_2(20%), \text{CO}(80%)$</td>
</tr>
<tr>
<td>$^{41}$Ar</td>
<td>1.82 h</td>
<td>$\text{Ar}$</td>
</tr>
<tr>
<td>$^{15}$O</td>
<td>2.03 m</td>
<td>$\text{O}_2, \text{CO}, \text{CO}_2$</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>109 m</td>
<td>$\text{HF}$</td>
</tr>
</tbody>
</table>

EXPERIMENTAL SETUPS

The separation and enrichment performance for various gases were investigated using hollow-filament type polyimide membranes fabricated by UBE Industries Ltd. Figure 1 shows a diagram of the experimental setups used in the present work. The apparatus consists of a membrane module, a metal-bellows pump (Senior Flexonics BP-158), a oil free scroll pump (Anest Iwata SP-250), a differential pressure gauge (MKS 223B), three mass-flow meter/controllers (MKS MF-100), a flow control valve (MKS 248A), three pressure transducers (MKS Baratron 127), a 250 L reservoir tank equipped with a rotary pump, and a quadrupole mass spectrometer (Balzers QMG 64) with a turbo molecular pumping system. Piping was made using stainless-steel pipes and Swagelock or VCR fittings.

Before the experiment the apparatus was evacuated to $10^{-1}$ Pa with the rotary pump, and then sample gases were introduced into the reservoir tank with a pressure of about $1.25 \times 10^5$ Pa. The gas was fed to the membrane inlet (the feed side) from the tank with the bellows pump through the mass flow controller (MF2 in Fig.1) and returned to the tank from the membrane outlet (the waste side) through the mass flow meter (MF1). The permeant gas was extracted from the membrane (the permeant side) through the mass flow meter (MF3) and the flow control valve (CV) with the scroll pump, and finally returned to the tank. The absolute pressures in three sides before/after the membrane were measured with the pressure transducers (PG). In the experiment, the gas flow rate in the feed side was kept constant by controlling it with MF2. The differential pressure between the feed and the permeant side was measured by the differential pressure transducer (DG) and controlled by CV to be kept constant during the measurement. In order to measure enrichment factors, gases flowing in the system were sampled at both the feed and the permeant side, and their composition were measured with a gas chromatograph (GCG) and the quadrupole mass spectrometer (QMS).

![Flow diagram of test loop for scaled polyimide membrane modules](image-url)

Fig.1 Flow diagram of test loop for scaled polyimide membrane modules

- PG : Pressure Transducer, CV : Flow Control Valve, DG : Differential Pressure Transducer,
- SP : Scroll Pump, MF : Mass Flow Controller or Mass Flow Meter, BP : Bellows Pump,
- RP : Rotary Pump, DM : Digital Manometer, QMS : Quadrupole Mass Spectrometer,
- IG : Ion Gauge, TCG : Thermocouple Gauge, TMP : Turbo Molecular Pump

2
In the present study, two types of the experiments using the above setups were carried out. One is to measure flow rates in the permeant side by changing those in the feed side, namely by changing the differential pressure between two sides. These experiments were performed for argon, air and helium using a high permeation-type membrane module (UBE TM-HB10). The flow rate in the feed side was changed from 0.25 to 9.75 with MF2, and the flow rate in the permeant side was measured with MF3. The other experiment is the measurement of the separation and enrichment performance for hydrogen, deuterium, argon, oxygen and carbon dioxide in nitrogen, as a function of differential pressure between the feed and the permeant side, where a high separation-type of membrane module (UBE UM-B2) was used. Typical experimental conditions for five gases are shown in Table 2. Changing differential pressures between the feed and the permeant side from about $2.0 \times 10^4$ Pa to $1.2 \times 10^5$ Pa, the composition of circulating gases at the two sides were measured with GCG for hydrogen and deuterium, and with QMS for oxygen, argon, and carbon dioxide.

The enrichment factor EF is defined by the following equation;

$$EF = \frac{M_{fp}}{M_{ff}}$$

where $M_{fp}$ and $M_{ff}$ are the mole fractions of interested gas in the permeant in the feed side, respectively.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Pressure and Flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \text{H}_2$(0.53%) + $\text{N}_2$ Feed side</td>
<td>$-1.247 \times 10^5$ Pa, 12 L/min</td>
</tr>
<tr>
<td></td>
<td>Permeated side</td>
</tr>
<tr>
<td></td>
<td>$4.433-0.5158 \times 10^4$ Pa, 18-25 mL/min</td>
</tr>
<tr>
<td>$2 \text{D}_2$(0.53%) + $\text{N}_2$ Feed side</td>
<td>$-1.254 \times 10^5$ Pa, 12 L/min</td>
</tr>
<tr>
<td></td>
<td>Permeant side</td>
</tr>
<tr>
<td></td>
<td>$6.465-0.5264 \times 10^4$ Pa, 13-26 mL/min</td>
</tr>
<tr>
<td>$3 \text{O}_2$(0.62%) + $\text{N}_2$ Feed side</td>
<td>$-1.251 \times 10^5$ Pa, 12 L/min</td>
</tr>
<tr>
<td></td>
<td>Permeant side</td>
</tr>
<tr>
<td></td>
<td>$10.49-0.5105 \times 10^4$ Pa, 13-26 mL/min</td>
</tr>
<tr>
<td>$4 \text{Ar}$(0.62%) + $\text{N}_2$ Feed side</td>
<td>$-1.251 \times 10^5$ Pa, 12 L/min</td>
</tr>
<tr>
<td></td>
<td>Permeant side</td>
</tr>
<tr>
<td></td>
<td>$10.46-0.5078 \times 10^4$ Pa, 4-23 mL/min</td>
</tr>
<tr>
<td>$5 \text{CO}_2$(0.64%) + $\text{N}_2$ Feed side</td>
<td>$-1.238 \times 10^5$ Pa, 12 L/min</td>
</tr>
<tr>
<td></td>
<td>Permeant side</td>
</tr>
<tr>
<td></td>
<td>$10.33-0.5425 \times 10^4$ Pa, 4-26 mL/min</td>
</tr>
</tbody>
</table>

**ANALYTICAL MODELS**

Simulations for gas enrichment performance of membranes were made using the cross flow model. The separation characteristics of the membrane module have been studied elsewhere. In the cross flow model, flow patterns of the permeant gas are assumed as cross flows as schematically shown in Fig.2, where $f_r, f_p$ is the flow rate of feed gas and that of out side, $x_{i1} \cdots x_{in}$ mole fraction of each constituent in feed gas, $y_{i1} \cdots y_{in}$ that of waste gas, $y_{p1} \cdots y_{pn}$ that of permeant gas, and $x_1 \cdots x_n y_1 \cdots y_n$ that of any small part of membrane, respectively.

![Fig. 2 Schematic diagram of cross-flow model](image)

In the calculation, the followings are assumed. The permeant gas flows orthogonal to the membrane.
At any small part of membrane, a decrease of flow rate in the feed side agrees with an increase of flow rate in the permeant side because mass balance should be held, and the permeant-flow rate should be described by Eq. (1). The equations used in the present works are found in the literature(6).

From the above assumption, the mole fraction at any small part of membrane can be obtained, and mole fraction in the permeant side is calculated by integrating the values from one end to the other of membrane. In the calculation, we used the permeant coefficient for plane membrane because that for a hollow-type polyimide membrane was not obtained.

RESULTS AND DISCUSSION

1) Flow rate of permeant gas

The flow rates of the permeant gas measured for air, argon and helium are shown in Fig. 3 as a function of differential pressure between the feed and the permeant side. The flow rate of permeant gas increases in proportion with increasing differential pressure. The results can be fitted well with a least-squares method. The flow rate of the permeated air, argon, and helium is $0.282 \times 10^4$, $0.353 \times 10^4$, and $4.36 \times 10^4$ L / min Pa, respectively. Then the ratio of permeation coefficient of helium and air to that of argon is calculated to be 15.4 and of 1.25, respectively.

![Fig.3 Change of flow rate at permeated side](image)

2) Separation and enrichment experiments in high separation-type membrane

Separation and enrichment experiments were carried out for hydrogen, deuterium, argon, oxygen, and carbon dioxide in nitrogen. The experimental results of hydrogen and deuterium are shown in Fig. 4. It can be seen in the figure that the enrichment factor increases with increasing the differential pressure between the feed and the permeant side. In particular, rapid increments in the factor can be observed at the differential pressure more than $1.0 \times 10^5$ Pa. The enrichment factor of deuterium is almost the same as that of hydrogen, and the factors obtained at the maximum differential pressure of about $1.2 \times 10^5$ Pa, which is the maximum attainable in the present setups, are 22.3 and 22.9, respectively. It should be concluded that there is no observable isotope effect in the hydrogen isotopes enrichment within fluctuations of the experimental data (about 3%).

![Fig.4 Enrichment factors for H$_2$ and D$_2$](image)
Figure 5 shows the measured enrichment factors for argon, oxygen, and carbon dioxide in nitrogen. It can be seen from the figure that these enrichment factors also increase with increasing the differential pressure, and those of oxygen and carbon dioxide increase steeply at the differential pressure more than \(1.0 \times 10^{5}\) Pa. On the other hand, the increase of the factor in argon is very small. At the differential pressure of about \(1.2 \times 10^{5}\) Pa, the factors of argon and of oxygen increase up to 1.9 and 8.3, respectively. The enrichment factor of carbon dioxide is large and almost same of that for hydrogen. The separation of hydrogen isotopes from carbon dioxide is supposed not to be sufficiently made with membrane. It may be necessary that any conventional methods, such as a temperature distillation and a separation due to absorbent, may be additionally used in order to separate carbon dioxide.

The enrichment factors calculated by using the cross flow model are also indicated in Fig.4 and Fig.5. The calculated factors are all in good agreement with the experimental results. It seems that the cross flow model would simulate permeation processes successfully. In the calculation, the permeation coefficient for plane polyimide membrane was used. This implies that the permeation coefficient of plane membrane may be almost close to that of hollow type membrane.

CONCLUSION

As demonstrated above, a hollow-filament type polyimide membrane has sufficiently high efficiency for separation and enrichment of hydrogen isotopes from air constituents. The difference between the enrichment factors of hydrogen and deuterium was not clearly observed in the present study, and it may be concluded that there exist no remarkable isotope effects in the separation characteristics. The calculation using the cross flow model was found to explain well measured enrichment factors for many gases examined in the present study. The model can be utilized in designing practical systems.

In the present work, however, we could not make experiments in higher differential pressure more than \(1.2 \times 10^{5}\) Pa, though the enrichment factors of hydrogen isotopes are expected to increase more steeply above the pressure. As a next step, such experiments should be made. We also plan separation and enrichment experiments for moisture, because tritium exist mainly as tritiated water vapor (HTO) in the accelerator tunnel air as previously mentioned. Since water is known to have quite larger permeation coefficient than any other gases in the membrane, larger enrichment factor of tritium can be expected for HTO in comparison with the case of gaseous tritium.

Thus, the polyimide membrane may be potentially applicable for a real-time tritium monitor in effluent gases from accelerators, though more detail studies on its separation characteristics are necessary.

ACKNOWLEDGEMENTS

The authors wish express their thanks to Mr. Hayashi. We would like to thank High Energy Accelerator Research Organization for providing our experimental apparatus.

REFERENCES


(4) Hayashi T., Yamada M., Suzuki T., Matsuda Y. and Okuno K. Gas separation performance of a hollow-
