PTFE Hollow Fiber Membrane Designed for Membrane Distillation

Hiroki MIYATA*, Satoshi YAHAGI, Atsushi FUKUNAGA, Yuta SUZUKI, Arata ISHIODORI, and Sinsuke KAWABE

Sumitomo Electric Industries, Ltd. developed polytetrafluoroethylene (PTFE) porous membranes ahead of the world. In the early 2000s, utilizing the membranes, the Company develop hollow fiber membrane water modules with excellent chemical resistance and strengths. The modules have been widely applied to water purification, sewage treatment, and industrial wastewater treatment around the world. With the increasing demands for the recovery of salt components, we focused on the application of these modules to membrane distillation for the separation of trace components such as salt in seawater and rare-earth elements in water resources, taking advantage of the excellent hydrophobicity of PTFE. This paper reports on the development of a PTFE hollow fiber membrane with superior water pressure resistance and gas permeability, both of which are critical for membrane distillation.

Keywords: PTFE, porous membrane, hollow fiber membrane, membrane distillation, water purification

1. Introduction

Sumitomo Electric Industries, Ltd. developed a porous membrane named "POREFLON," utilizing a drawing process on the fluororesin polytetrafluoroethylene (PTFE) ahead of our global competitors.(1) In the early 2000s, we developed a water treatment module containing hollow fiber membranes made of POREFLON. Taking advantage of the excellent chemical resistance and strength of PTFE, the modules have been used in various regions, including Asia and North America, for applications such as water purification, sewage treatment, and industrial wastewater treatment.(2)

In recent years, there has been a growing demand for the separation of salts, such as through seawater desalination, and the recovery of rare-earth elements from water resources. However, the demand has not been met by the combination of POREFLON and existing water purification technology relying on membrane filtration. As a solution, we focused on membrane distillation that utilizes the hydrophobicity (low surface tension) of PTFE. Membrane distillation requires high water pressure resistance*1 because wet membranes lose their separation capacity. This paper reports on the development of a PTFE hollow fiber membrane with superb salt separation performance without compromising either water pressure resistance or gas permeability.

2. Membrane Distillation

Figure 1 illustrates the differences between conventional membrane filtration and membrane distillation.(3) In conventional water purification, micropores in POREFLON are treated to be hydrophilic by Sumitomo Electric's original method. These micropores prevent solid content from passing through and allow only water to pass through, producing cleanly filtered, treated water. In comparison, in membrane distillation, hydrophobic POREFLON prevents water and any solids from passing

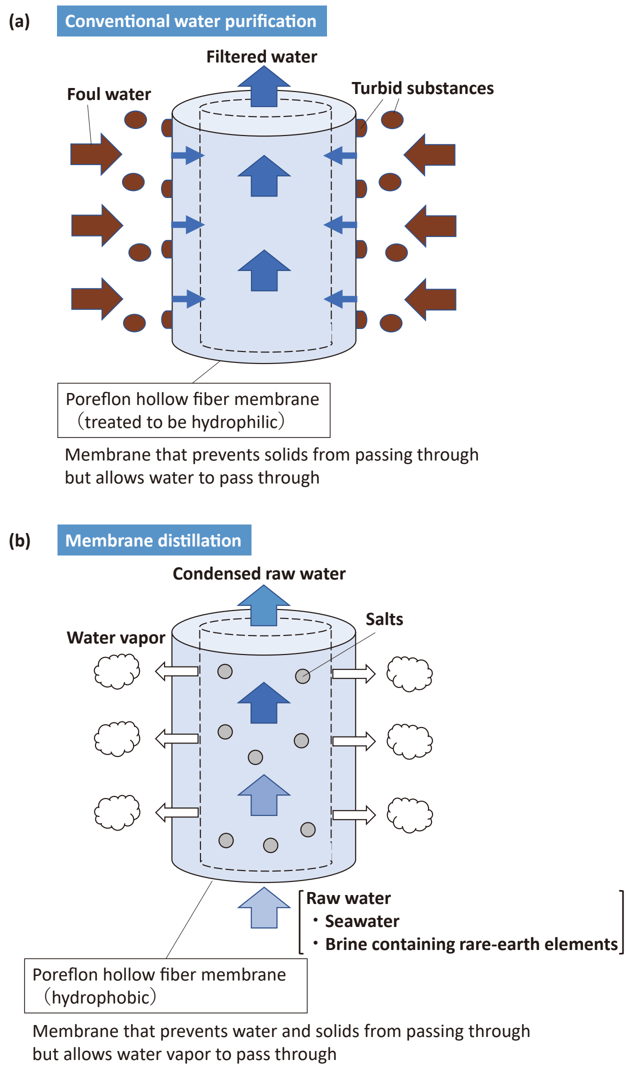


Fig. 1. Schematic illustration of (a) Water purification by conventional membrane filtration and (b) membrane distillation

through and allows only water vapor to pass through the membrane. Therefore, membrane distillation can separate salts and other dissolved materials from seawater.

In addition to membrane distillation, several kinds of operation systems are used to separate salts such as evaporation*2 and filtration by reverse osmosis membranes.*3 Table 1 lists their respective features. Compared to these techniques, membrane distillation offers advantages, such as superb water quality achieved by porous membranes, water vapor produced at low temperatures below 100°C without the need for high energy including high temperatures and high pressure, and minimal footprint requirements for operation.[(4),(5)]

Table 1. Features of Different Separation Processes

	Evaporation	Reverse osmosis membrane filtration	Membrane distillation
Water quality	fair	good	good
Energy efficiency	fair	good	excellent
Equipment size	fair	good	good

In membrane distillation, water vapor permeation is principally driven by the difference in saturated water vapor pressure*4 between the heated raw water side and the cooling side. Membrane distillation is categorized into several types according to the water vapor recovery system.[(6)] Three typical methods are shown in Fig. 2. Their strengths and drawbacks are listed in Table 2. In evaluating them, we employed vacuum membrane distillation (VMD), in which water vapor generated from heated raw water that has passed through the membrane is recovered by evacuation.

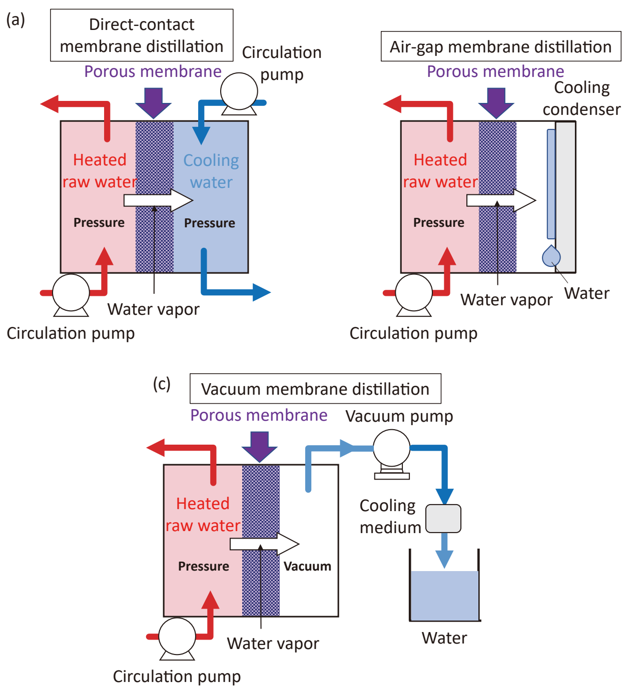


Fig. 2. (a) Direct-contact membrane distillation, (b) air-gap membrane distillation, and (c) vacuum membrane distillation

Table 2. Strengths and Drawbacks of Different Methods of Membrane Distillation

	Direct-contact membrane distillation	Air-gap membrane distillation	Vacuum membrane distillation
Strength	• Simple mechanism • Low resistance to water vapor mobility	• Little heat loss	• Litle heat loss • Low resistance to water vapor mobility
Drawback	• Large heat loss	• High resistance to water vapor mobility	• Membrane required to have high water pressure resistance

As its features, VMD offers little heat loss because it avoids direct contact between the raw water side and the cooling side, and provides high water vapor recovery efficiency. However, it requires the membrane to have high water pressure resistance.

Membrane distillation has been studied extensively, exploring the use of materials such as polypropylene (PP) and polyvinylidene fluoride (PVDF).[(7)] These materials are, however, difficult in terms of hydrophobicity required in membrane distillation. Accordingly, few porous membranes made of these materials are used on a commercial basis for membrane distillation. POREFLON is made of PTFE, which with very low surface free energy has the highest hydrophobicity among general polymeric materials. Therefore, presuming that it would be highly suitable for membrane distillation, we undertook the development of a POREFLON hollow fiber membrane tailored for membrane distillation.

3. Development of a PTFE Hollow Fiber Membrane Tailored for Membrane Distillation

3-1 Specifications for hollow fiber membranes

The VMD method requires hollow fiber membranes to have high water pressure resistance. With low water pressure resistance, the membrane becomes wet and begins to leak to the cooling side. Under this condition, a pass line is made for the raw water via the membrane, resulting in loss of the dissolved materials separation capacity. When operating VMD, the heated raw water side of the membrane is under positive pressure due to the raw water circulation pump; the cooling side is under a vacuum due to the vacuum pump for water vapor recovery. In light of these mechanisms, we assumed that the hollow fiber membrane would be fit for actual use without making a wet pass line if it has a water pressure resistance of over 150 kPa. In the present development, we sought a porous hollow fiber membrane made of PTFE and a hollow fiber membrane module that would have water pressure resistance of 150 kPa or more and high gas permeability, achieved owing to suitably designed inside and outside diameters of the hollow fiber membrane as well as to the well-designed filling of the module with hollow fiber membranes.

3-2 Development of hollow fiber membrane manufacturing technology

Figure 3 shows the process followed to manufacture PTFE hollow fiber membranes. First, PTFE powder and a molding aid are homogeneously blended. A cylindrical preform is formed through compression molding in advance and is loaded in an extrusion cylinder. It is then extruded with a piston into a hollow fiber. The extruded piece becomes porous through a drawing process and is subjected to sintering to become a hollow fiber membrane.

Table 3 presents the consideration results on the inside and outside diameters of the newly developed hollow fiber membrane for membrane distillation, and a comparison with a conventional water purification membrane not treated to be hydrophilic. The newly developed hollow fiber membranes all exhibited water pressure resistance of 150 kPa or more.

Photo 1 shows cross-sectional SEM images of a conventional hollow fiber membrane and newly developed hollow fiber membrane B. Compared to the conventional hollow fiber membrane, newly developed hollow fiber membrane B features a shorter PTFE fiber length and a smaller pore size, contributing to considerably improved water pressure resistance.

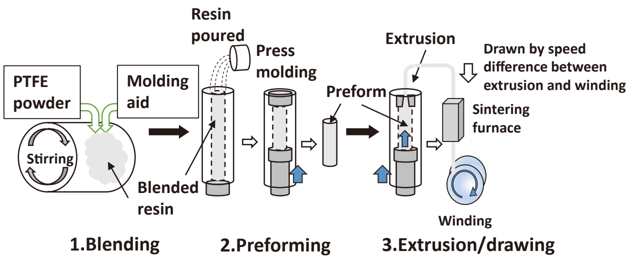


Fig. 3. PTFE hollow fiber membrane manufacturing process

Table 3. Properties of Hollow Fiber Membranes for Membrane Distillation

	Conventional membrane	Newly developed membrane A	Newly developed membrane B	Newly developed membrane C
Application	Water purification	Membrane distillation	Membrane distillation	Membrane distillation
Outside diameter [mm]	2.3	1.4	1.6	2.2
Inside diameter [mm]	1.1	1.0	1.0	1.5
Thickness [mm]	0.6	0.2	0.3	0.35
Porosity [%]	80	40	53	52
Water pressure resistance [kPa]	30	240	200	200

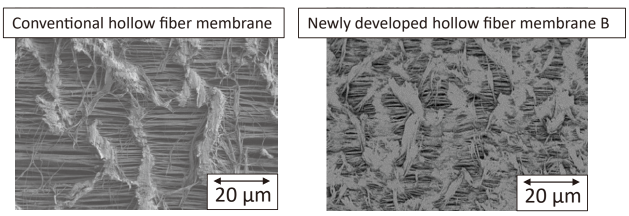


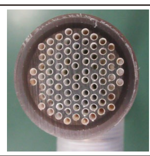
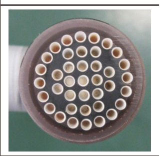
Photo 1. Cross-sectional SEM images of hollow fiber membranes for membrane distillation

Photo 2 illustrates the exterior of a module used for membrane distillation experiment and evaluation. A cylinder 22 mm in inside diameter contains an array of hollow fiber membranes 200 mm in effective membrane length, while avoiding contact between them. Thermosetting plastic is used to secure the ends.

Table 4 provides the membrane distillation evaluation results for the module tested at a raw water temperature of 75°C and a transmembrane pressure*5 of 115 kPa. The water flow rate was a value determined by the quantity of the cool recovered water, and normalized by the internal area of the membrane. Three types of module were compared and evaluated. The results showed that the module using newly developed hollow fiber membrane B marked the highest water flow rate.

Photo 2. Module used for membrane distillation experiment and evaluation

Table 4. Module Used for Membrane Distillation Experiment and Evaluation

	Module containing newly developed membrane A	Module containing newly developed membrane B	Module containing newly developed membrane C
Cross section of module for experiment and evaluation			
Number of membranes [pieces]	82	66	39
Filling rate [%]	33	35	39
Internal area of membrane [cm^2]	1030	829	735
Water flow rate [L/(m^2·h)]	8	16	13

3-3 Examination of membrane distillation using simulated seawater

We examined membrane distillation using a module containing newly developed hollow fiber membrane B and commercially available simulated seawater at a salt concentration of 3.5%. Figure 4 presents the operation results obtained at a raw water temperature of 75°C and a transmembrane pressure of 115 kPa. The salt removal rate was determined by measuring the electrical conductivity of the water obtained from the recovered water vapor. In a principle verification operation, the salt removal rate proved to be high at 99% or more. The average water flow rate was 17 L/(m^2·h).

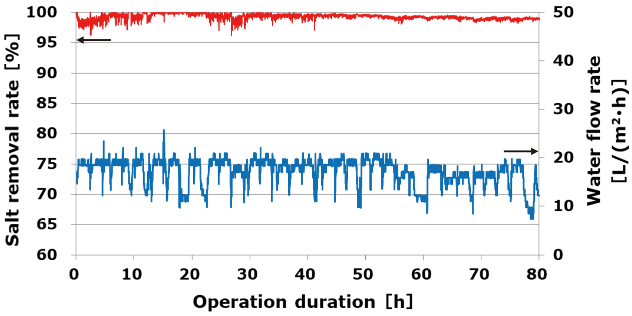


Fig. 4. Salt removal rate and water flow rate in a membrane distillation operation using simulated seawater

4. Conclusion

A porous PTFE hollow fiber membrane suitable for membrane distillation was developed taking advantage of the hydrophobicity of PTFE to meet the growing demand for recovering salts.

A module filled with hollow fiber membranes without compromising either water pressure resistance or gas permeability achieved a water flow rate of 17 L/(m^2·h) and a salt removal rate of 99% or more when operated in the membrane distillation of simulated seawater.

The hollow fiber membrane is anticipated to play an active role in a wide range of applications such as seawater desalination and recovering rare-earth elements.

Technical Terms

*1 Water pressure resistance: A value that indicates the water wettability of a porous membrane; above this pressure, water permeates the pores in the porous membrane.

*2 Evaporation: The method of obtaining water by heating raw water and cooling water vapor without a membrane.

*3 Filtration using a reverse osmosis membrane: When the condensed raw water side and the diluted liquid side are separated by a porous membrane having a pore size in the order of nanometers, and a pressure exceeding the osmotic pressure is applied on the condensed raw water side, water alone passes through the pores and flows to the diluted liquid side.

*4 Saturated water vapor pressure: With air containing saturated water vapor, that part of the total air pressure accounted for by the water vapor.

*5 Transmembrane pressure: The total pressure determined by adding the pressure intended for raw water circulation applied to the inner side of a membrane and the vacuum pressure intended for evacuation of water vapor applied to the outer side of the membrane.

References

(1) Sumitomo Electric Industries, Ltd. https://sumitomoelectric.com/products/electronics/poreflon

(2) Sumitomo Electric Industries, Ltd. https://sumitomoelectric.com/id/project/v04/01

(3) Sumitomo Electric Industries, Ltd. https://sumitomoelectric.com/id/topics/2021/09/002

(4) M. Taniguchi, "Current Status and Future Prospects of Seawater Desalination Technology Using RO Membrane," Bull. Soc. Sea Water Sci., Jpn., 63, pp214-220 (2009)

(5) R. Schwantes, K. Chavan, D. Winter, C. Felsmann, J. Pfafferott, Techno-economic comparison of membrane distillation and MVC in a zero liquid discharge application, Desalination 428, pp. 50-68 (2018)

(6) A. Alkhudhiri, N. Darwish, and N. Hilal, Membrane distillation: A comprehensive review, Desalination 287, pp. 2-18 (2012)

(7) Global & Regional Membrane Distillation Market, Credible Markets. Ltd. pp.48, 57 (2022)

Contributors The lead author is indicated by an asterisk (*).

H. MIYATA*
• Assistant Manager, Energy and Electronics Materials Laboratory

S. YAHAGI
• Assistant Manager, Energy and Electronics Materials Laboratory

A. FUKUNAGA
• Ph.D.
Group Manager, Energy and Electronics Materials Laboratory

Y. SUZUKI
• Water Processing Division

A. ISHIODORI
• Group Manager, Water Processing Division

S. KAWABE
• Group Manager, Water Processing Division