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Effect of brine concentration on membrane distillation process for seawater desalination

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ABSTRACT

Membrane distillation (MD) process was systematically evaluated for concentrating brine of reverse osmosis process. Basic characteristics of MD membrane were first examined. Synthetic seawater brine was used as the feed solution of MD test. To investigate the flux variation of brine treatment process by the flow rate. In the MD process operated using high concentration artificial seawater, the flux was continuously decreased in both flow rates. However, the flux was rapidly decreased when the flow rate was high. The experimental result of membrane cleaning with deionized water and sulfuric acid solution showed that the flux was not affected by the membrane cleaning. The scanning electron microscope image analysis showed that the NaCl crystals were affected by cleaning but confirmed that pore block by the NaCl crystals is not significantly correlated with the decrease of the flux. Further studies will be conducted by using various kinds of cleaning agents to investigate the effect of cleaning the NaCl crystals.

Keywords: Membrane distillation; Brine; membrane cleaning; Seawater desalination; Flow rate

1. Introduction

Scarcity of water is one of the most critical global challenges [1]. Recently, membrane processes reveal that these systems are one of the viable options for water supply augmentation and water scarcity alleviation. Particularly, in terms of low energy requirement, easy operation, modular design, and small footprint demand [2,3] reverse osmosis (RO) process is used for seawater desalination [4–8]. However, RO system also leads to some critical problems such as brine after RO membrane. RO brine has serious detrimental impact on aquatic environments. Due to components of RO brine, accumulation of heavy metals, pH variation, and high salinity can occur in receiving waters [9].

Recently, membrane distillation (MD) process has also been attracting excellent attention for its potential applications in desalting highly saline waters system such as shale gas wastewater reuse [10] and concentration of RO brine [11–15]. MD system is a thermally driven separation process, in which only vapor molecules are able to pass through a porous hydrophobic membrane. Especially, the benefits of MD compared with other water treatment processes stem from not only 100%, theoretically, rejection of non-volatiles such as ions, colloids, macromolecules, and cells, but also lower operating temperatures than conventional thermal water treatment processes. The required heat for MD can be harvested from solar thermal convertors or industrial waste heat [16–20].

However, solutions of MD process should be aqueous and sufficiently dilute to avoid wetting of the hydrophobic MD membrane [21–23]. This limits MD to applications such as desalting process, currently dominated by concentration of RO brine, removal of trace volatile organic

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compounds from wastewater, and especially, concentration of ionic solutions. The purpose of this study was to evaluate MD processes for concentrating RO brine in an industrial RO plant. Basic characteristics of membrane processes were first examined, and then theoretical RO brine was treated by MD process. Finally, major causes of severe flux decline observed at high recovery were elucidated by analyzing the wetting membrane surfaces using scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy.

2. Materials and methods

2.1. Materials and equipment

Synthetic seawater brine, 70 g/L NaCl, was used as the feed solution of direct contact membrane distillation (DCMD) test. The DCMD module was employed in the experiment. Polyvinylidene fluoride (PVDF) flat-sheet membrane having a pore size of 0.22 μm was used. Tables 1 and 2 show the detailed specifications of the experimental apparatus and the properties of the membrane.

A constant temperature water bath (Lab Companion, Korea) was used to maintain the experimental temperature condition at both ends of the membrane. The membrane module was prepared by using acryl material. The size of the membrane inside the module was 3,096 mm^2 (86 × 36 mm), and the depth of the channel was 1 mm. The quantity of the produced water was measured by using a scale connected with a computer (Ohaus Explorer Pro, USA). The electric conductivity of the feedwater and the produced water was measured by using an electric conductivity meter (WTW, Germany) and the operating flow rate was determined as the lowest rate of the gear pump (Cole-Parmer, USA) that may be applied to the experiment and the highest rate that allows smooth long-term operation.

The MD process was established by using feedwater and product water reservoirs, a constant temperature circulation water bath, and a heat exchanger (Bakin Pipe, Korea), as shown in Fig. 1.

Table 1
Operating condition of DCMD test

Membrane material	PVDF
Feedwater temperature (°C)	60
Permeate water temperature (°C)	20
NaCl concentration (mg/L)	70,000
Feed volume (L)	1.0

Table 2
Properties of the membranes

Material	Polyvinylidene fluoride (PVDF)
Type	Flat-sheet
Manufacturer	Millipore
Pore size, μm	0.22
Porosity, %	75
Thickness, μm	125

2.2. DCMD experiments

Synthetic seawater brine, 70 g/L NaCl, was used as the feed solution of DCMD test. To investigate the flux variation of brine treatment process by the flow rate. These flow rates were 0.2 and 1.0 L/min. The temperature was set to be 60°C on the feedwater side and 20°C on the permeate water side.

A membrane cleaning experiment was conducted to verify if the effect of high concentration NaCl may be decreased in the MD process. In the membrane cleaning experiment, the membrane was cleaned by using deionized water and sulfuric acid (0.01 N) for 10, 30, and 60 min when the concentration of the feedwater was increased to about 200 mS/cm (Table 3). In addition, SEM analysis was performed to analyze the effect of the crystallization of concentrated seawater on the membrane. The SEM analysis was performed after drying the membrane used in the experiment for about 24 h.

3. Mechanism of vapor transmission on MD membrane

The amount of permeate water, which is proportional to the vapor pressure difference, may be expressed as in the following equation according to Darcy's law. In the equation, ΔP denotes the vapor pressure difference caused by the temperature difference between the two sides of the membrane and equals to the pressure at both ends of the pores.

$$J = C_m \cdot \Delta P = C_m \cdot (P_1 - P_2)$$
$$P_i = \exp\left(23.328 - \frac{3841}{T_i - 45}\right) \quad (1)$$

where i = 1, 2.

The driving force of MD process is the temperature difference between the two sides of the membrane. Heat loss is caused by the temperature difference at the interface between the solution and the membrane. Temperature polarization

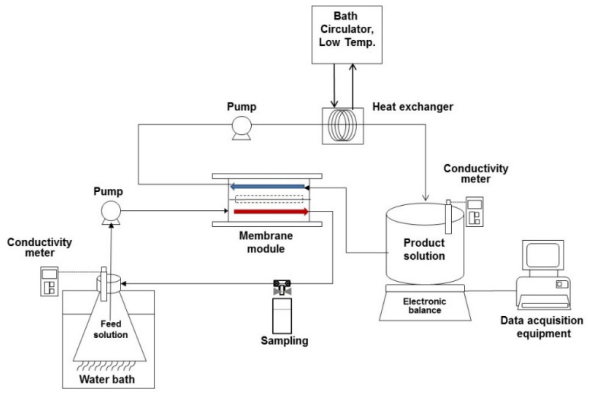

Fig. 1. Schematics of DCMD operation.

Table 3
Cleaning condition of DCMD crystallization test

Cleaning time, min	10, 30, 60
Cleaning materials	Deionized water, acid
Cleaning flow rate, L/min	0.2, 1.0, 1.5

is caused at the two sides of the membrane as the temperature of the solution is increased on the membrane surface. Temperature polarization is expressed by the following equation:

$$TPC = \frac{T_{m1} - T_{m2}}{T_{b1} - T_{b2}} \quad (2)$$

The heat transfer may be calculated by multiplying the temperature difference between the two sides of the membrane by the effective heat transfer coefficient of the membrane, which is expressed as the following equation [24]:

$$q_p = h_p(t_{pm} - t_p) \quad (3)$$

4. Mechanism of crystal growth

Nucleation should first take place in crystallization of a solution if the solution does not contain solid particles of the material to be crystallized or other materials. In addition, new nuclei should be continuously generated when the nucleus is growing. Growth based on a nucleus generated beforehand is the basic mechanism of a crystallization reaction (Fig. 2) [25].

5. Results and discussion

5.1. Flux variation by flow rate

Fig. 3 and Table 4 show the results of the PVDF flat membrane system operation until no more permeate water was produced. The operation was performed for about 1,500 min at the flow rate of 0.2 L/min. During the operation for 1,500 min, the flux was changed from 14.1 to 6.2 LMH, and thus the rate of flux decrease was 56.0%. As the feedwater was continuously concentrated, the volume concentrate factor (VCF) became 5.77.

The operation was performed for about 660 min at the flow rate of 1.0 L/min. The flux was changed from 34.7 to 9.7 LMH, and thus the rate of flux decrease was 72.1%. The VCF was 4.81 after the operation.

The initial flux was 2.46 times higher when the flow rate was 1.0 L/min than when the flow rate was 0.2 L/min. The flux was rapidly decreased when the flow rate was 1.0 L/min.

As the operation time was increased, the NaCl concentration of the feedwater was continuously increased and the flux was continuously decreased. This may be because of pore block, concentration polarization, and temperature polarization due to NaCl crystallization. A cleaning experiment was performed to verify the effect of crystallization on pore block.

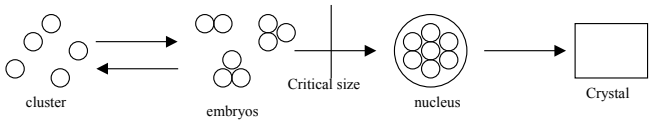

Fig. 2. Crystallized product process.

5.2. Flux recovery by membrane cleaning

Crystallization of NaCl in the feedwater tank was found when the NaCl concentration in the tank was 200 mS/cm, indicating that the feedwater was almost saturated with NaCl [26]. To verify the effect of NaCl crystals on pore block, the membrane was cleaned with deionized water by varying the cleaning duration and the deionized water flow rate.

Fig. 4 shows the cleaning results at the flow rate of 0.2 L/min. The cleaning efficiency was compared for 30 min after performing cleaning with deionized water at the flow rate of 0.2 L/min for 10, 30, and 60 min. The cleaning effect dependent on the flow rate was also investigated by performing the cleaning at the flow rate of 1.0 L/min for 60 min.

In the cleaning method for a pressurized membrane process where a hydrophobic membrane is employed, backwash may be performed to directly affect the scale blocking the membrane pores for efficient cleaning. However,

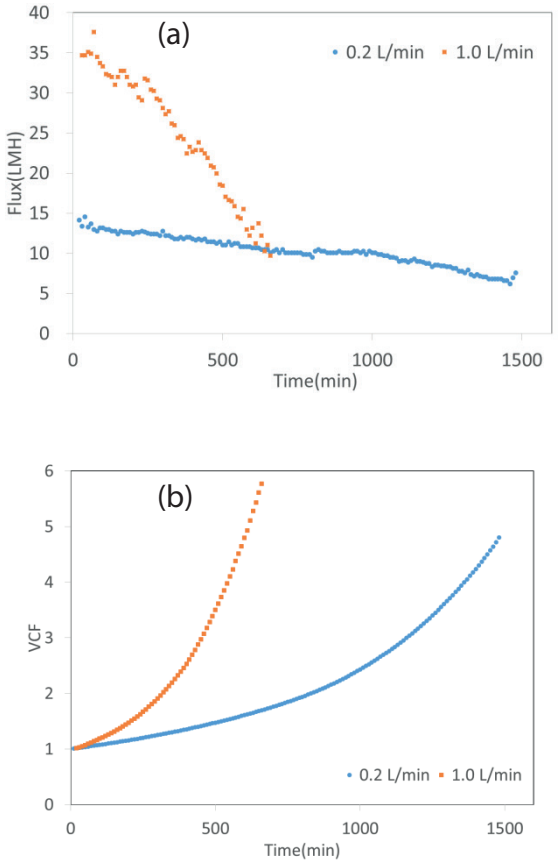

Fig. 3. Flux and VCF of MD flow velocity (no cleaning). (a) Flux of MD flow velocity and (b) VCF of MD flow velocity.

Table 4
Permeate flux and decrease rate of various flow velocity

Flow velocity, L/min	0.2	1.0
Initial flux, LMH	14.1	36.7
End flux, LMH	6.2	9.7
Flux decrease rate, %	56.0	72.1

cleaning should be performed by cross-flow in the MD process. Cleaning is not effective if backwash is not performed by using a hydrophobic substance or steam.

Therefore, although the cleaning time was gradually increased, the cleaning efficiency was not increased. Inorganic scale was expected to be washed out as it was dissolved in deionized water, but even inorganic scale was not effectively eliminated. The cleaning time was increased up to 1 h, because spending one or more hours in general cleaning may be ineffective in terms of economic feasibility and process efficiency in comparison with the current pressurized membrane process. However, the experimental result showed that the flux may not be recovered despite the variation of the cleaning time and flow rate.

Fig. 5 shows the result of cleaning at the flow rate of 1.0 L/min. The cleaning efficiency was compared for 30 min after performing the cleaning with deionized water at the flow rate of 1.0 L/min for 10, 30, and 60 min. In addition, the cleaning was also performed at an increased flow rate of 1.5 L/min to verify the cleaning effect depending on the flow rate.

The result shows that the flux was continuously decreased even after several times of cleaning.

Since the flux was not increased by the cleaning performed using deionized water and varying the flow rate and cleaning time, cleaning was performed using 0.1 N sulfuric acid at the flow rate of 1.0 L/min. However, the cleaning was discontinued in 30 min because of wetting, which might have taken place as the high concentration sulfuric acid affected the membrane pores. Then, cleaning was performed in the order of 10-min cleaning at 1.0 L/min, 30-min process operation, 30-min cleaning, 30-min process operation, and 60-min cleaning by using 0.01 N sulfuric acid. However, the flux was continuously decreased despite the cleaning performed using sulfuric acid (Fig. 6).

If pore block was caused by the crystallization of NaCl due to the continuous increase of the NaCl concentration in the MD process, the flux should have been changed by the cleaning performed using deionized water or sulfuric acid. However, no change in the flux was found even after the cleaning. Therefore, the decrease of the flux following the increase of the NaCl concentration in the MD process may not be recovered by cleaning.

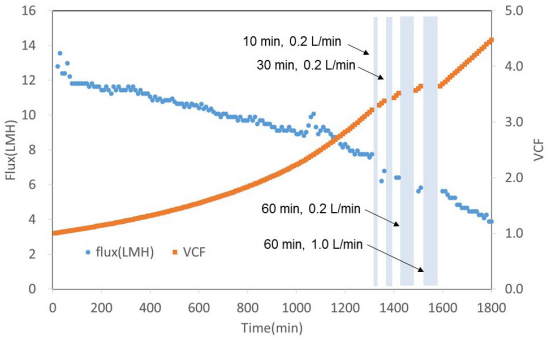

Fig. 4. Flux and VCF at 0.2 L/min of deionized water cleaning test.

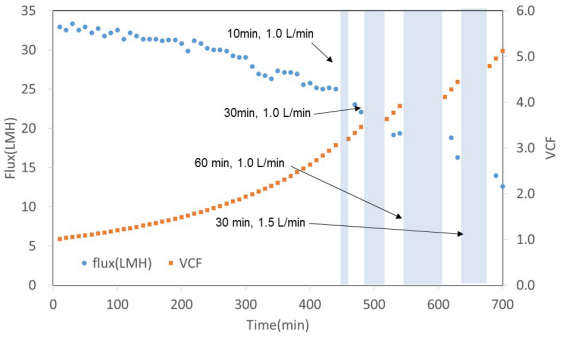

Fig. 5. Flux and VCF at 1.0 L/min of deionized water cleaning test.

5.3. SEM analysis

SEM analysis was performed after drying the membrane for about 24 h. When the membrane after the operation at the flow rate of 0.2 L/min was observed at a magnification of 1,000, the membrane was similar to the raw membrane. However, the membrane observed after the operation at the flow rate of 1.0 L/min showed a considerable amount of NaCl crystals on the membrane surface. The observation of the membrane at a magnification of 50,000 showed various shapes of NaCl crystals attached to the membrane surface (Fig. 7).

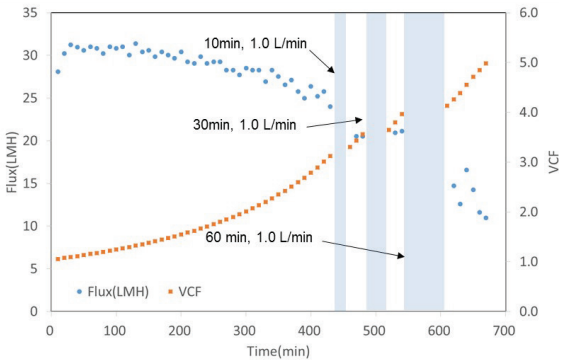

Fig. 6. Flux and VCF at 1.0 L/min of acid cleaning test.

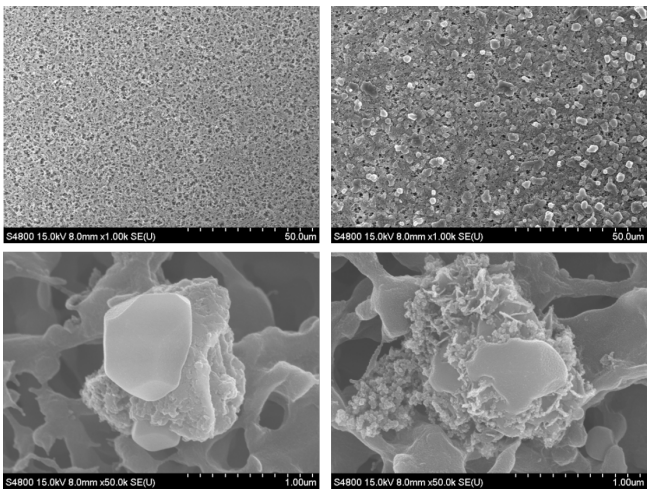

Fig. 7. Scanning electron microscope pictures for crystals on the membrane surface: (a) flow rate at 0.2 L/min and (b) flow rate at 1.0 L/min.

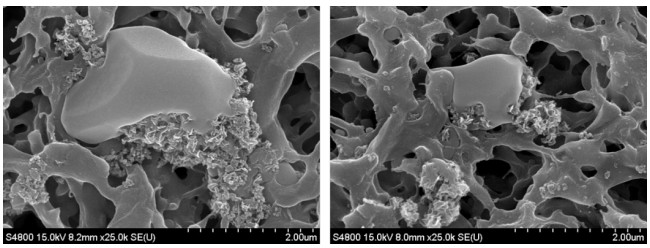

Fig. 8. Scanning electron microscope pictures for crystals on the membrane surface after cleaning: (a) flow rate at 0.2 L/min and (b) flow rate at 1.0 L/min.

The membrane cleaned by using deionized water also analyzed using the SEM images. The NaCl crystals were dissolved by the cleaning performed for various cleaning durations. This indicates that the pore block by NaCl crystals did not have an effect on the decrease of the flux (Fig. 8).

6. Conclusions

In the present study, the effect of NaCl crystals and membrane cleaning on the change of the flux was investigated in the concentrated seawater treatment of the MD process. Following conclusions were made from the present study.

- In the MD process operated using high concentration artificial seawater, the flux was continuously decreased in both flow rates. However, the flux was rapidly decreased when the flow rate was high. This may be the effect of concentration polarization, temperature polarization, or pore block by inorganic crystals.
- If pore block was caused by the crystallization of NaCl, the flux should have been increased by the cleaning performed by using deionized water or sulfuric acid. However, the experimental result showed that the flux was not affected by the membrane cleaning. Therefore, pore block by the NaCl crystals is not the main cause of the flux decrease.
- The SEM image analysis showed that the NaCl crystals were affected by cleaning but confirmed that pore block by the NaCl crystals is not significantly correlated with the decrease of the flux. Further studies will be conducted by using various kinds of cleaning agents to investigate the effect of cleaning the NaCl crystals.

Acknowledgment

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