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An advanced online monitoring approach to study the scaling behavior in direct contact membrane distillation

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Abstract

One of the major challenges in membrane distillation (MD) desalination is scaling, mainly CaSO_4 and CaCO_3 . In this study, in order to achieve a better understanding and establish a strategy for controlling scaling, a detailed investigation on the MD scaling was performed by using various analytical methods, especially an *in-situ* monitoring technique using an optical coherence tomography (OCT) to observe the cross-sectional view on the membrane surface during operation. Different concentrations of CaSO_4 , CaCO_3 , as well as NaCl were tested separately and in different mixed feed solutions. Results showed that when CaSO_4 alone was employed in the feed solution, the mean permeate flux (MPF) has significantly dropped at lower volume concentration factor (VCF) compared to other feed solutions and this critical point was observed to be influenced by the solubility changes of CaSO_4 resulting from the various inlet feed temperatures. Although the inlet feed and permeate flow rates could contribute to the initial MPF value, the VCF, which showed a sharp MPF decline, was not affected. It was clearly observed that the scaling on the membrane surface due to crystal growth in the bulk and the deposition of aggregated crystals on the membrane surface abruptly appeared close to the critical point of VCF by using OCT observation in a real time. On the other hand, $\text{NaCl} + \text{CaSO}_4$ mixed feed solution resulted in a linear MPF decline as VCF increases and delayed the critical point to

higher VCF values. In addition, CaCO_3 alone in feed solution did not affect the scaling, however, when CaSO_4 was added to CaCO_3 , the initial MPF decline and VCF met the critical point earlier. In summary, calcium scaling crystal formed at different conditions influenced the filtration dynamics and MD performances.

Keywords: Calcium sulfate; Mean permeate flux; Membrane distillation; Optical coherence tomography (OCT); Scaling.

1. Introduction

Membrane distillation (MD) is a thermal-driven separation process using hydrophobic micro porous membranes. The membrane prevents the pore from wetting due to repulsion forces between the hydrophobic wall and water, thus generating a liquid/vapor interface at the pore entrance and only allowing transportation of water vapor across the membrane. The driving force of the MD processes is the partial water vapor pressure difference resulting from the transmembrane temperature difference between the feed and permeate sides.

Scaling of the membrane surface is one of the major challenges for MD desalination systems [1], mainly caused by calcium sulfate (CaSO_4) and calcium carbonate (CaCO_3). MD membranes are sensitive to fouling and scaling which can affect the MD performance and wettability and can block the membrane pores due to crystal growth and the deposition of aggregated crystals on the membrane surface [2]. Particularly in a long-term operation these issues can drastically reduce the MD performance. Scaling and crystal growth in the pores can lead to severe membrane pore wetting resulting in water flooding across the membrane. Furthermore, the scaling layer not only impedes the mass transport of water vapor across the membrane but also reduces the membrane surface hydrophobicity [3-7]. It has been reported that scaling behavior strongly depends on the solubility of CaSO_4 and CaCO_3 and filtration conditions (i.e., concentration [5], velocity [8], temperature [9, 10]). In addition, the shape of the crystals formed can change as a function of solution temperature and the solubility of CaSO_4 [5, 11-14].

Recent studies have been conducted to achieve a better understanding of MD fouling and scaling with the aim of fouling mitigation and control [3, 15-18]. A study reported that scaling formed both on the membrane surface and inside the membrane pores in the direct contact membrane distillation (DCMD) operation [15]. Nghiem and Cath [3] investigated the scaling

tendencies, particularly the size of CaSO_4 crystals formed at different inlet feed temperatures, highlighting the interactions between induction time and saturation index. An experimental study made by Naidu et al. [16] was conducted to find the optimal inlet feed and permeate flow velocities in the DCMD process with bulk and surface crystallization tendencies. Curcio et al. [17] studied CaCO_3 scaling on the DCMD process and reported the role of the membrane on CaCO_3 scaling in the presence of humic acid. He et al. [18] examined an antiscalant to control MD scaling, reporting their effects on the induction period for the nucleation of the CaSO_4 and CaCO_3 crystals on the membrane surface.

In the studies referenced above, various analytical methods were adopted to investigate the scaling mechanisms, such as monitoring flux decline pattern and permeate water quality, and analyzing the MD membrane after operation. These methods only allow an indirect analysis of scaling behavior in the MD processes. SEM image analysis of fouled membranes requires disassembly from the module and drying the membrane, after which it makes it difficult to observe the actual scaling structure without risk of collapse. In addition, the solution temperature significantly affects the scaling structures. Hence, an innovative and intuitive observation method is necessary to understand the scaling phenomena in real-time during the MD operation.

The optical coherence tomography (OCT) is an *in-situ* monitoring technique and it has recently been applied to observe fouling and scaling as well as biofouling in membrane systems [19-23]. In order to achieve a better understanding and strategies of scaling and its control in the MD process, a comprehensive analysis of scaling behavior was investigated in this study. The mean permeate flux (MPF) decline pattern, water quality, and scanning electron microscope (SEM) images as well as the OCT images were analyzed according to the operating conditions. Experiments were operated at different inlet feed temperatures ranging from 50-70 °C, inlet feed and permeate flow rates ranging from 0.4-1.2 L/min (LPM), and at a constant coolant temperature of 20 °C. A flat-sheet DCMD membrane module was used to assess the effects of physical parameters on the scaling formation.

2. Materials and methods

2.1 DCMD experimental set-up

Figure 1. A picture of windowed DCMD module for OCT imaging analysis. OCT is placed on the window for higher resolution images.

Table 1. Properties of flat sheet membrane.

	GE hydrophobic micro-porous membrane
Material	Polytetrafluoroethylene (PTFE)
Porosity (%)	75±5
Mean pore size (μm)	0.2
Thickness (μm)	179

As shown in **Fig. 1**, the MD module used in this study was made of acrylic plastic and designed with a window on the top side of the feed channel to monitor the scaling formation directly using the OCT technique. The module channel dimensions of both feed and permeate sides were 0.015 m × 0.06 m × 0.002 m, giving an effective membrane surface area of 0.0009 m². A new commercially available hydrophobic micro-porous membrane supplied by General Electric (GE, US) was used in each experiment. Properties of the membrane are summarized in **Table 1**.

Figure 2. A schematic diagram of the laboratory DCMD experimental set-up combined with OCT device.

Fig. 2 shows the lab-scale DCMD experimental set-up consisting of a closed-loop unit. The inlet feed temperature was maintained constant using a hot plate (C-MAG HS7, IKA) with temperature control unit (ETS-D5, IKA). The feed solution was kept well stirred by a magnetic bar (5 cm) to prevent the crystallized solute from sticking on the feed tank walls. MPF data was continuously recorded by measuring the permeate weight using a balance (ML3002, Mettler Toledo). The permeate temperature was set at 20 °C by using a chiller (1156D, VWR) coupled with a shell and plate heat exchanger. Two gear pumps (Micro gear pump (95211-35), Cole Parmer) were used to supply a constant volume flow rate to both feed and permeate channels. All the pipes and feed tank were well insulated to reduce the heat loss to the ambient. The pore wetting, or membrane leakage, were detected by using a conductivity sensor (SG78, Mettler Toledo) at the end of an experiment.

2.2. Experimental matrix

Experimental studies were conducted with CaSO_4 solution to investigate the effect of inlet feed temperature (related with the effect of CaSO_4 solubility) and inlet feed and permeate flow rates related with flow patterns (i.e. laminar and turbulent flow) on the scaling behavior. Milli-Q water was used to prepare the feed solutions. In addition, various solute components with CaSO_4 ,

CaCO₃, and NaCl (**Table 2**) present in seawater were tested at fixed operating conditions. To avoid pH change during the operation and exclude the effect of pH, all feed solutions were adjusted at pH 8.5 using 10 mM borate buffer in the feed solution before the experiments. All experiments were conducted more than three times to achieve reproducibility. The detailed experimental conditions are given in **Table 2**.

Table 2. Summary of feed solutions and operational conditions.

Feed type	Temperature (°C)		Feed and permeate	Volume(L)	pH
	Feed	Permeate	Flow rates (LPM)		
CaSO ₄ alone	50		0.4	1.0	
	60	20	0.4 and 0.8		
	70		0.4		
CaCO ₃ alone					8.5
NaCl alone					
CaSO ₄ and CaCO ₃	60	20	0.4	2.0	
CaSO ₄ and NaCl					
CaSO ₄ , CaCO ₃ and NaCl					

*Concentrations of CaSO₄, CaCO₃ and NaCl were 1,900, 140 and 35,000 mg/L, respectively, which are similar compositions present in seawater.

2.3. Saturation ratio (SR)

The MD process does not allow the transportation of ions through the membrane, thus the saturation ratio of Ca²⁺ concentration in the feed solution was measured immediately after filtration through a 0.45 µm syringe filter. Calculation of SR based on the permeate flux can be done by Eq. (1).

$$SR = [Ca^{2+}]_{brine} / [Ca^{2+}]_{initial} \quad (1)$$

The concentration of Ca²⁺ in the feed solution was measured using the inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis with respect to the flux decline pattern.

2.4 OCT monitoring

A spectral domain OCT system Ganymede I from Thorlabs, GmbH (Germany) armed with the scan lens (LSM 03BB) was used to assess the CaSO_4 deposition on the membrane surface. The DCMD module was positioned under the OCT probe allowing the scaling monitoring. 2D cross sectional OCT scans ($1000 \text{ pixel} \times 314 \text{ pixel}$), corresponding to $5.0 \text{ mm} \times 0.88 \text{ mm}$ (width $\times$ depth), were taken within a fixed rectangular area of $5.0 \text{ mm} \times 2.0 \text{ mm}$. Scans were acquired periodically over the duration of the experiment. The OCT scans were processed with the FiJi software. Images were filtered to reduce the noise, then the contrast and brightness were adjusted.

2.5 Scanning electron microscope (SEM)

To examine the surface of fouled membranes, samples were mounted on flat stubs and coated with 5 nm Iridium inside Q150TS sputter coater (Quorum Technologies). Quanta 200FEG SEM equipped with ETD secondary electron detector were used for SEM imaging. Secondary electron images were acquired at an accelerating voltage of 3.00 kv and working distances of 4.9 to 16.3 mm.

3. Results and discussion

3.1. Influence of inlet feed temperature

Figure 3. Effect of inlet feed temperature on (a) MPF and (b) SR versus VCF at various inlet feed temperatures (50-70 °C), at inlet permeate temperature of 20 °C, and inlet feed and permeate flow rates of 0.4 LPM.

The volume concentration factor (VCF) is defined as the initial feed volume divided by the current feed volume [24]. **Fig. 3a** represents the MPF as a function of the VCF at various inlet feed temperatures (50-70 °C) and inlet permeate temperature of 20 °C, at inlet feed and permeate flow rates of 0.4 LPM. MPF variation vs. VCF is an indirect observation of fouling and scaling behavior, where the effect of the solubility change and the various initial MPF were investigated. As shown in **Fig. 3a**, the initial MPF significantly increased from 22 to 50 kg/m²h when increasing the feed temperature from 50 to 70 °C due to the increase of the driving force. The water vapor flux is a function of the mass transfer coefficient and the partial water vapor pressure difference, which can be calculated by Antoine's equation, Eqs. (2-4) [25].

$$J = C_m(p_{f,m} - p_{p,m}) \quad (2)$$

$$p_{w,m} = \exp\left(23.1964 - \frac{3816.44}{T - 46.13}\right) \quad (3)$$

$$p_{f,m} = (1 - x_f) p_{w,m} \quad (4)$$

where J is the water vapor flux, C_m is the mass transfer coefficient, $p_{f,m}$ and $p_{p,m}$ ($p_{w,m}$) are the water vapor pressure of saline water and pure water respectively, T is the transmembrane temperature, and x_f is the molar fraction of non-volatile solute.

At all feed temperatures tested (50-70 °C), the observed flux decline patterns were found to be similar. For instance, there was no MPF decline with increase of VCF from 1.0 to 1.9 at 60 °C, and then MPF started decreasing slightly at VCF of around 1.98 leading to a subsequent dramatic decrease, especially at high feed temperatures. Results show that an increase in the water vapor flux contributes to more scaling on the membrane surface. The crystal may be formed more near the membrane surface because the water evaporation occurs near the surface. In addition, the scaling with CaSO_4 crystals, grown in bulk flow on the membrane surface occurs due to the decrease of CaSO_4 solubility with an increase in the temperature. The flux decline trends of CaSO_4 solution observed are in good agreement with results of Nghiem and Cath [3]. Moreover, this pattern can be clearly found from the SR curve (**Fig. 3b**). The induction time (*i.e.* when crystal formation starts) was similar at 50 and 60 °C, and about VCF 1.9 (SR of 50 and 60 °C was 1.75 and 1.73, respectively). This indicates that before bulk crystallization occurs, a small quantity of calcium ion is precipitated without deposition on the membrane surface (initial stage). For all temperatures tested, SR was about 1.5 at VCF 1.6. However, at VCF 2.3, the amount of crystallized calcium at 60 °C (124 mg) was slightly higher than that at 50 °C (115 mg). Interestingly, this only represents about 6% of total calcium used. On the other hand, at 70 °C the induction time of CaSO_4 was much shorter, compared to the lower temperatures. The formation of bulk crystals started at about VCF 1.6. In this case, a higher amount of calcium (186 mg of Ca ion) was associated with crystal formation and removed from the feed water at VCF 2.3 and SR 1.46. In summary, as feed temperature increases the induction time decreases resulting in an increased amount of crystallized calcium which further impacts the flux pattern observed in DCMD operation.

SEM images of membrane samples collected at the end of experiments are presented in **Fig. 4**. Based on results of the current study, the CaSO_4 crystals on the membrane surface have a needle shape, however, their sizes increased remarkably with increasing inlet feed temperatures from 50 °C to 70 °C, showing the formation of larger crystal sizes occurring at higher feed

solution temperatures, which also have the lower solubility. Here, crystal size influenced by feed temperature could affect the scaling structure and subsequently the water filtration dynamics and flux (**Fig. 3**).

In addition, sharper crystal forms are expected to accelerate the membrane wetting because it can damage faster the polymeric membrane surface. However, based on our experimental results, that effect on the membrane wetting was not observed maybe because of the shorter experimental time for such phenomenon to occur.

Magnitude 2,500×

Magnitude 25,000×

(a)

(b)

(c)

Figure 4. SEM images of membrane surface with respect to the inlet feed temperatures (a) 50 °C, (b) 60 °C, and (c) 70 °C, at inlet permeate temperature of 20 °C and inlet feed and permeate flow rates of 0.4 LPM.

3.2. Influence of inlet flow rate

(a)

(b)

Figure 5. Effect of inlet feed and permeate flow rates from 0.4 to 0.8 LPM on (a) MPF and (b) SR vs. VCF at inlet feed and permeate temperatures of 60 °C and 20 °C, respectively.

Fig. 5a represents the effect of inlet flow rates on the MPF vs. VCF. The effect of laminar flow (0.4 LPM, $Re=1,651$) and turbulent flow (0.8 LPM, $Re=3,302$) on the MPF pattern and $CaSO_4$ scaling behavior was investigated for inlet feed and permeate temperatures of 60 °C and 20 °C, respectively. A modeled solution ($CaSO_4$, 1,900 ppm) was employed. The Reynolds number was calculated by Eqs. (5) and (6).

$$Re = \frac{\rho D_h v}{\mu} \quad (5)$$

$$D_h = \frac{2ab}{a+b} \quad (6)$$

where ρ is the density of solution, D_h is the hydraulic diameter, v is the velocity, μ is the dynamic viscosity, a is channel width, and b is channel depth. Higher initial MPF (43.53 kg/m²h) was found with higher inlet feed and permeate flow rates (both 0.6 LPM) as higher flow rates can achieve a higher convection heat transfer in the channel flow (**Fig. 5a**) [26]. The higher convection heat transfer can lead to lower temperature polarization [25-28].

A similar trend on the MPF vs. VCF is seen for same inlet feed temperature but varying flow

rates (**Fig. 5b**). The MPFs at both flow rates did not declined till a VCF 1.9, where a sharp decreased is observed after this point, as shown in **Fig. 5a**. This is supported by SR pattern (**Fig. 5b**). By VCF 1.9, SR was similar at the different flow rates. However, after VCF 1.9 a relatively significant decline of SR at 0.8 LPM is seen compared with the 0.4 LPM flow rate. At VCF 2.3, the SR at 0.4 and 0.8 LPM flow rates were 1.73 and 1.51, respectively, corresponding to an increase of the amount of crystallized calcium from 124 to 173 mg. Another interesting point is that although the MPF increased due to the increase of inlet feed and permeate flow rates, its decline occurred at almost the same VCF value. In addition, the induction times at 0.4 and 0.8 LPM were measured at around 17 h (VCF 1.91) and 12 h (VCF 1.87), respectively. This indicates that flow rate or hydrodynamic condition is associated with crystal formation and affects the flux decline in terms of the induction time. SEM images clearly show this effect. The CaSO_4 crystal size formed on the membrane surface at 0.4 LPM seems to lead to a higher proportion of small size crystal compared to that at 0.8 LPM (**Fig. 6**). In addition, the rate of MPF decline is less with the smaller CaSO_4 crystal size at the lower flow rate (0.4 LPM). Consequently, higher inlet flow rates could lead to an increase in the MPF due to the enhancement of the convection heat transfer, which reduces the temperature polarization effect. In addition, although the increase in the inlet feed and permeate flow rates does not significant effect the flux decline related to the MD scaling in terms of VFC, the increase in inlet feed velocity from 0.4 LPM to 0.8 LPM can reduce the induction time from 17 h (VCF 1.91) to 12 h (VCF 1.87).

Figure 6. SEM images of membrane surface with respect to the inlet feed and permeate flow rates (a) 0.4 LPM, and (b) 0.8LPM at inlet feed and permeate temperatures of 60 °C and 20 °C, respectively.

3.3. Influence of sodium chloride (NaCl)

Figure 7. Effect of NaCl on CaSO_4 scaling in terms of MPF vs. VCF at inlet feed and permeate flow rates of 0.4 LPM and inlet feed and permeate temperatures of 60 °C and 20 °C, respectively.

Fig. 7 represents the MPF patterns of DCMD tested with three different solutions: NaCl alone (35,000 ppm), CaSO_4 alone (1,900 ppm), and CaSO_4 (1,900 ppm) with NaCl (35,000 ppm). The MPF of NaCl solution decreased by about 27% as VCF increased from 1.0 to 4.5. This trend is consistent with a DCMD experimental study using high salinity feed solution by Yun et al. [29]. However the CaSO_4 + NaCl mixed solution showed a lower MPF compared to that of NaCl alone. Moreover, there was a sharp MPF decline at the initial VCFs with the mixed solution. This may be because the salt concentration near the membrane surface at the feed side suddenly increased due to the decrease of NaCl solubility with CaSO_4 . It may also be due to particularly high concentration near the membrane surface in the feed side [30]. The MPF of CaSO_4 and NaCl mixed solution was observed to have a similar MPF decline pattern with NaCl mixed solution. This is because the decrease in the NaCl solubility with CaSO_4 may led to the initial flux decline which continued to decrease due to the relatively high NaCl concentration

change compared to the change of CaSO_4 concentration as VCF increases. Furthermore, the presence of NaCl in the solution delayed the CaSO_4 scaling. However, right after VCF 4.45 the MPF with $\text{CaSO}_4 + \text{NaCl}$ mixed solution dramatically decreased by approximately 75% due to CaSO_4 scaling which suddenly formed and deposited on the membrane surface. It should be noted that the VCF at which MPF starts to decline the $\text{CaSO}_4 + \text{NaCl}$ mixed solution was delayed compared to that for the CaSO_4 alone (**Fig. 3**). The high concentration of NaCl postponed the formation of gypsum (CaSO_4) because in the presence of NaCl in the feed solution, the gypsum (CaSO_4) solubility increases [31] due to the decrease in the activity coefficient and the increase in NaSO_4^- complexation [32].

Figure 8. SEM images (magnitude, 10,000 $\times$) of membrane surface for (a) NaCl solution and (b) $\text{CaSO}_4 + \text{NaCl}$ mixed solution at inlet feed and permeate flow rates of 0.4 LPM, inlet feed and permeate temperatures of 60 °C and 20 °C, respectively.

Figure 9. SEM images ((a) magnitude $\times 1,000$ and (b) magnitude $\times 25,000$) of membrane surface with $\text{CaSO}_4 + \text{NaCl}$ mixed solution at inlet feed and permeate flow rates of 0.4 LPM, inlet feed and permeate temperatures of 60 °C and 20 °C, respectively.

Fig. 8 shows a SEM image of the membrane surface tested with (a) NaCl and (b) $\text{CaSO}_4 + \text{NaCl}$ mixed solution at inlet feed and permeate flow rates of 0.4 LPM, inlet feed and permeate temperatures of 60 °C and 20 °C, respectively. **Fig. 9** represents SEM images with (a) magnitude $\times 1,000$ and (b) magnitude $\times 25,000$) under the same operating conditions. When $\text{CaSO}_4 + \text{NaCl}$ mixed solution was used, more deposition on the surface was observed compared to NaCl solution alone, as shown in **Fig. 9**. The decrease in MPF for NaCl alone was not significant compared to $\text{CaSO}_4 + \text{NaCl}$ mixed solution, meaning that the NaCl solution alone did not give a significant impact on the flux decline while NaCl affected the CaSO_4 scaling formation, which is not observed in other processes [33].

Comparing the SEM images of the membrane surface (**Figs. 4 and 6**) and the effect of inlet feed and permeate flow rates on the system performance, such as MPF, SR vs. VCF with the CaSO_4 solution and the $\text{CaSO}_4 + \text{NaCl}$ mixed solution (**Figs. 8b and 9a and b**), the membrane surface was less covered with $\text{CaSO}_4 + \text{NaCl}$ mixed solution and it resulted in the delay of VCF of MPF decline started to occur at around VCF 4.3. In addition, the meniscus of membrane pores were observed not to be completely covered with CaSO_4 crystals as shown in **Fig. 9**.

3.4. Influence of calcium carbonate (CaCO_3)

Fig. 10 shows the effect of CaCO_3 on CaSO_4 scaling in terms of MPF vs. VCF. In addition, the effect of $\text{CaCO}_3 + \text{CaSO}_4 + \text{NaCl}$ mixed solution as a function of VCF is highlighted. The MPF with only CaCO_3 solution did not decrease with increasing VCF, shown in **Fig. 10**. This indicates that if the concentration of CaCO_3 (140 ppm) is alone in the feed solution is low, it has an insignificant effect on the MD scaling. This is in agreement with a previous study [3]. In addition, no leaking or pore wetting was found, detected using a conductivity meter in the distilled permeate tank at the end of experiments. **Fig. 11** presents SEM images ((a) magnitude $\times 1,000$ and (b) magintude $\times 25,000$) of the membrane surface with CaCO_3 solution at inlet feed and permeate flow rates of 0.4 LPM, inlet feed and permeate temperatures of 60 °C and 20 °C, respectively. The SEM image with CaCO_3 also appears to have a more porous structure on the membrane surface than that with CaSO_4 , shown in **Fig. 11a** and **b**.

Figure 10. Effect of CaCO_3 in mixed solution on the MPF vs.VCF at inlet feed and permeate flow rates of 0.4 LPM, inlet feed and permeate temperatures of 60 °C and 20 °C, respectively.

Figure 11. SEM images ((a) magnitude $\times 1,000$ and (b) magnitude $\times 25,000$) of membrane surface with CaCO_3 solution at inlet feed and permeate flow rates of 0.4 LPM, inlet feed and permeate temperatures of 60 °C and 20 °C, respectively.

In the case of the mixed solution $\text{CaSO}_4 + \text{CaCO}_3$, the MPF was similar as for CaSO_4 alone. However, at initial range of VCF, the MPF decline with $\text{CaCO}_3 + \text{CaSO}_4$ mixed solution was slightly higher. This is because CaCO_3 scaling formation crystals could block some parts of the membrane pores. In addition, solubility of CaCO_3 is much lower than CaSO_4 . The co-precipitation of $\text{CaCO}_3 + \text{CaSO}_4$ may also cause a sharp MPF decline at the initial VCF where the solubility of CaCO_3 decreases with an increase in CaSO_4 concentration and the feed temperature. The presence of a common Ca^{2+} ion, due to the Le Châtelier's principle, reduces the solubility of the CaSO_4 salt. Furthermore, due to the decrease of CaSO_4 solubility, the MPF decline with $\text{CaCO}_3 + \text{CaSO}_4$ mixed solution was observed at an earlier VCF values compared to CaSO_4 solution. The MPF decline pattern with $\text{CaCO}_3 + \text{CaSO}_4 + \text{NaCl}$ mixed solution is similar with the MPF decline pattern with $\text{CaSO}_4 + \text{NaCl}$ mixed solution. As shown in **Fig. 10**, when the $\text{CaCO}_3 + \text{CaSO}_4 + \text{NaCl}$ mixed solution is employed, the initial MPF decreased from 36.53 to 33.00 $\text{kg/m}^2\text{h}$ when compared to the $\text{CaCO}_3 + \text{CaSO}_4$ mixed solution. This is because the high NaCl concentration near the membrane surface may reduce mass transfer across the membrane. The significant MPF decline with $\text{CaCO}_3 + \text{CaSO}_4 + \text{NaCl}$ mixed solution was observed around VCF 4.2, earlier than the VCF (4.42) with $\text{CaSO}_4 + \text{NaCl}$ mixed solution. This is because the addition of CaCO_3 may reduce the CaSO_4 solubility or the co-precipitation of CaCO_3 and CaSO_4 .

[11], causing the sharp MPF decline at the initial VCF.

In summary, when a low concentration of CaCO_3 (140 ppm) is used in the feed solution it does not significantly affect the MPF decline (**Fig. 10**). However, if CaCO_3 is mixed with CaSO_4 or CaSO_4 and NaCl , a dramatic MPF decline starts at an earlier VCF. In addition, the high concentration of NaCl (35,000ppm) alone in solution led to a small MPF decline with an increase in the VCF. However, when NaCl is mixed with CaSO_4 or CaCO_3 and CaSO_4 , it was found that the effect of NaCl could delay the VCF at which a significant MPF decline occurs.

Figure 12. SEM images (from magnitude 1,000x to magnitude $\times 10,000$) on the membrane surface after experiment with $\text{CaCO}_3 + \text{CaSO}_4 + \text{NaCl}$ mixed solution at inlet feed and permeate

flow rates of 0.4 LPM, inlet feed and permeate temperatures of 60 °C and 20 °C, respectively.

SEM images of membrane surface after experiments of $\text{CaCO}_3 + \text{CaSO}_4 + \text{NaCl}$ mixed solution were almost similar with CaSO_4 solution (**Fig. 12**). However, several NaCl and CaCO_3 have a porous structure while CaSO_4 has a dense crystal form covering the membrane surface.

3.5. OCT monitoring

Fig. 13 represents cross-sectional images of the membrane taken by OCT at specific points of the MPF pattern during the DCMD operation with the CaSO_4 solution only at inlet feed and permeate temperatures of 60 °C and 20 °C, respectively, and inlet feed and permeate flow rates of 0.4 LPM. As shown in **Fig. 13 (a)**, the cross-sectional image of a clean membrane is characterized by a certain roughness. Around VCF 1.9, no deposition of CaSO_4 crystal was observed on the membrane surface, although some calcium (around 26 mg) was removed from the feed solution. This suggests that a slight amount of CaSO_4 scaling formation has taken place in the VCF range from 1.0 to 1.9. However, it was not significantly enough to affect the MPF due to the negligible small amount. No deposition was observed in the OCT image because the small size was assumed to be below the OCT resolution limit. Deposition of CaSO_4 scaling on the membrane surface was clearly observed during the MPF decrease from 30.53 to 5.13 $\text{kg/m}^2\text{h}$, and was further enhanced in the VCF range of 2.1 to 2.3, as shown in **Figs. 13 (c) and (d)**, where the MPF decreased asymptotically from 5.13 $\text{kg/m}^2\text{h}$ to 1.67 $\text{kg/m}^2\text{h}$.

Figure 13. Cross-sectional images of membrane taken by OCT and MPF versus VCF from 1.0 to 2.3 using the CaSO_4 solution only at inlet feed and permeate temperatures of 60°C and 20°C , respectively, and inlet feed and permeate flow rates 0.4 LPM.

The cross-sectional images of the membrane taken by OCT at specific points of the MPF pattern during the DCMD operation with $\text{CaCO}_3 + \text{CaSO}_4 + \text{NaCl}$ mixed solution at inlet feed and permeate temperatures of 60°C and 20°C , respectively, and inlet feed and permeate flow rates of 0.4 LPM are presented in **Fig. 14**. The initial MPF slightly decreased due to the decrease in NaCl solubility in the solution by CaSO_4 . However, right after VCF 1.8 the MPF decreased linearly till the induction point (VCF 4.1). **Fig. 14 (a)** shows a brighter layer compared to the

OCT image of **Fig. 13 (a)**, which may be due to a thin deposition of NaCl on the membrane surface at VCF 1.4. Then, from VCF 1.4 till VCF 3.6 (**Fig. 14 (a)-(c)**) the bright layer thickness did not change significantly. Afterwards, the MPF decreased linearly as VCF increases. In addition, the depositions of CaSO_4 and CaCO_3 were not observed till VCF 3.6 (**Fig. 14(a)-(e)**). It means that the scaling, which is occurred by CaSO_4 and CaCO_3 , was not dominant till VCF 3.6. A drastic decline in the MPF was observed right after VCF 4.1 which represents the induction point corresponding to the formation of crystals in the bulk feed solution and the subsequent deposition on the membrane surface. However, due to the limited resolution of this generation of OCT technology, it was not possible to distinguish between the deposited scaling layers formed by CaSO_4 or CaCO_3 using OCT only.

This is the first attempt to investigate CaSO_4 scaling and $\text{CaCO}_3 + \text{CaSO}_4 + \text{NaCl}$ mixed scaling in the DCMD process using OCT technique. Although the cross-sectional membrane images with CaSO_4 and $\text{CaCO}_3 + \text{CaSO}_4 + \text{NaCl}$ scaling obtained by OCT have a low resolution due to the small crystallization sizes or scaling layers, the scans were acquired in real-time under continuous operation. The potential for real-time monitoring of membrane scaling or fouling in the process is important and essential for better understanding this phenomenon because MD operates under completely different conditions compared to other membrane processes, mainly the high operating feed temperature, the membrane nature (superhydrophobic material) and mass transfer through the membrane structure (water vapor transport). This opens for the possibility of monitoring and characterizing the changes in fouling structure and property with varying temperatures and water contents. Conventional methods to analyze fouling are performed after finishing the experiments (not under operation conditions) and by using certain protocols/procedures, which may change the fouling layer structure and its properties, especially in the MD process as the membrane will be cooled down and dried.

Figure 14. Cross-sectional images of membrane taken by OCT and MPF versus VCF ranging from 1.0 to 4.4 with $\text{CaCO}_3 + \text{CaSO}_4 + \text{NaCl}$ mixed solution at inlet feed and permeate flow rates of 0.4 LPM, and inlet feed and permeate temperatures of 60 °C and 20 °C, respectively.

4. Conclusions

In order to better understand the calcium-based scaling phenomenon in the MD process and establish an improved control strategy, comprehensive scaling analyses were conducted coupled with online image analysis using a novel observation method, namely OCT, which enables

images to be recorded in real-time and *in-situ* during operation at various feed temperatures and feed and permeate flow rates. MPF decline and SR patterns as well as image analyses using OCT and SEM were employed to investigate the scaling behavior in the MD process. Feed solutions containing different concentrations of CaSO_4 , CaCO_3 , and NaCl employed separately or mixed were investigated. The key findings obtained from this study are summarized as follows:

- The significant MPF decline and critical point of VCF at which the MPF decline started with CaSO_4 alone in feed solution were attributed to the changes in CaSO_4 solubility as a function of various inlet feed temperatures.
- Inlet feed and permeate flux rates affected the initial MPF values (e.g. increasing MPF with increasing rate), but did not affect the critical point of VCF. This is due to the severe crystal growth and deposition of aggregated crystals on the membrane surface that occurred close to the critical point of VCF, as observed by the OCT.
- SEM image analysis enabled finding the size of bulk crystals deposited on the membrane surface and the influence of inlet feed temperature and inlet feed and permeate flow rates. In SR analysis, the induction time decreased and the amount of crystallized calcium increased with an increase in the inlet feed temperature and feed and permeate flow rates.
- The mixed $\text{NaCl} + \text{CaSO}_4$ solution could lead to a linear MPF decline by decreasing vapor pressure as VCF increases and delay the critical point of VCF. In addition, CaCO_3 alone in feed solution did not affect the scaling, however, CaCO_3 caused the initial MPF decline and meet the critical point of VCF earlier.
- This clearly shows that the physic-chemical conditions affected the CaSO_4 scaling behavior, subsequently leading to the variation of MD performance with different filtration dynamics.

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Highlight

- A comprehensive analysis of calcium-based scaling behavior in DCMD was investigated.
- OCT was employed to monitor the scaling behavior in real-time during MD operation.
- CaSO_4 , CaCO_3 , and NaCl were tested separately and in mixed feed solutions.
- CaSO_4 scaling occurred by deposition of bulk crystal on the membrane surface.
- A critical point of VCF at which MPF decreased significantly has been observed.