

DISSERTATION

ELUCIDATING THE MECHANISMS AND DEVELOPING MITIGATION STRATEGIES OF
MINERAL SCALING IN MEMBRANE DESALINATION

Submitted by

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ABSTRACT

ELUCIDATING THE MECHANISMS AND DEVELOPING MITIGATION STRATEGIES OF MINERAL SCALING IN MEMBRANE DESALINATION

Mineral scaling in membrane desalination, which is referred to as the accumulation of minerals on the membrane surface, has been considered as the primary constraint that limits the water recovery and efficiency of membrane desalination significantly. The occurrence of mineral scaling results in the decrease of water flux and compromises the lifetime of membrane materials, leading to increased needs of energy consumption and facility maintenance. Furthermore, the limited water recovery of membrane desalination due to mineral scaling also results in the production of high volumes of concentrated brines, which may require thermal-based technologies to further reduce the brine volume to achieve minimal liquid discharge (MLD) or zero liquid discharge (ZLD). However, these technologies are energy- and cost-intensive. Therefore, developing feasible and effective strategies to mitigate mineral scaling in membrane desalination is urgently needed to improve the resilience and performance of desalination systems, which will ultimately facilitate the implementation of desalination to mitigate global water scarcity and reduce the environmental risks and cost associated with brine management.

Gaining a fundamental understanding of mineral scaling mechanisms and the relationship between scaling behaviors and membrane surface properties are the key prerequisites to the rational design of scaling mitigation strategies in membrane desalination. First, I dedicated efforts to elucidate the scaling mechanism of silica in membrane distillation (MD), a hybrid

thermal-membrane desalination technology. Three PVDF membranes with different surface wettability were used to unveil underlying scaling mechanisms of silica in MD. The experimental results revealed that homogeneous nucleation played an important role in inducing silica scaling in MD, while heterogeneous nucleation facilitated the formation of silica scaling layer on the membrane surface. Additionally, I demonstrated that tuning membrane surface wettability was insufficient to reduce silica scaling in MD.

Next, I investigated the effect of membrane surface wettability on the scaling kinetics and reversibility of gypsum scaling and silica scaling in MD. Unlike the formation of silica that is regulated by polymerization reactions, the formation of gypsum is governed by crystallization reactions between Ca^{2+} and SO_4^{2-} ions. In this work, I demonstrated that superhydrophobic membrane was able to delay the induction time of gypsum scaling and enhanced scaling reversibility, which resulted in increased total water recovery. However, this strategy was not effective to mitigate silica scaling. Such distinct experimental observations between gypsum scaling and silica scaling were attributed to their different formation mechanisms and corresponding interactions with membrane surfaces.

Further, in addition to the development of novel membrane materials to resist scaling, the use of anti-scalants to mitigate gypsum scaling and silica scaling was also explored in MD. Although the use of anti-scalants has been widely adopted in the industry, the effectiveness of anti-scalants and the underlying factors that control the anti-scaling efficiency have not been systematically studied. Three anti-scalants with different functional groups were used to elucidate the efficiencies of anti-scalants in mitigating gypsum scaling and silica scaling in MD. Poly(acrylic) acid and poly(ethylenimine), which were enriched with carboxyl and amino groups, were shown to be effective to inhibit gypsum scaling and silica scaling, respectively. The

mitigating effect of poly(acrylic) acid molecules on gypsum scaling was due to their effects of stabilizing scaling precursors, whereas poly(ethylenimine) facilitated silica polymerization and altered the morphology of silica scale layer on the membrane surface. This work indicates that anti-scalants with different functional groups are needed for different mineral scaling types.

Finally, I compared the efficiencies of membrane surface modification and anti-scalants in mitigating mineral scaling in membrane desalination. The efficiencies of four types of membrane surface modification in mitigating gypsum scaling in reverse osmosis (RO) were compared with the use of anti-scalant poly(acrylic) acid. It was shown that membrane surface modification was only able to reduce the water flux decline caused by gypsum scaling moderately, whereas the use of anti-scalants greatly inhibited gypsum scaling. In addition, I also demonstrated that the use of anti-scalants was highly efficient in preventing gypsum scaling in a combined RO-MD treatment train, which dramatically increased the total water recovery. Therefore, a comparative insight on the efficiencies of different scaling mitigation strategies was provided, which has the potential to guide the selection of the most appropriate strategy to mitigate mineral scaling in membrane desalination.

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Lastly and the most importantly, I would like to present all my achievements to my mother, Youping Gou, my father, Zhi Yin and my dear wife, Xijing Liu. Without their standings on my back, it is impossible for me to pursue my Ph.D. study. Of course, I would like to share my dissertation with my son, Pascal Yin, who provides me the everlasting strength to overcome difficulties and challenges in my life.

“ I can do all this through him who gives me strength. ”

– *Philippians 4:13*

“ Do your best to present yourself to God as one approved, a worker who does not need to be ashamed and who correctly handles the word of truth. ”

– *2 Timothy 2:15*

“ In everything I did, I showed you that by this kind of hard work we must help weak, remembering the words the Lord Jesus himself said: ‘It is more blessed to give than to receive.’ ”

– *Acts 20:35*

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1.0 Introduction¹

1.1 Research Motivation and Research Background

In the past decade, the world has witnessed the escalation of the severity of freshwater shortage, which has been widely recognized as a major issue that exerts tremendous environmental, economic and public health impacts worldwide (Elimelech, 2006; Hoekstra, 2014; Vörösmarty et al., 2010). The fast urbanization and the continuous surge in global population further intensify the scarcity of freshwater, especially in the water-stressed inland regions such as sub-Saharan Africa, middle east districts and the West of the U.S. (Gober, 2010; Mekonnen and Hoekstra, 2016; Montgomery and Elimelech, 2007). For example, numerous people are sickened from waterborne diseases such as intestinal parasitic infection and diarrhea due to the lack of proper infrastructure in supplying clean and safe freshwater (Lima et al., 2000). Furthermore, countless new contaminants relevant to public health and environmental concerns are being detected in waters such as heavy metals and micropollutants (Lakherwal, 2014; Luo et al., 2014). Therefore, the demand for the development of efficient water management and technological solutions to address freshwater crisis becomes urgent to support freshwater sustainability globally (Shannon et al., 2010).

Recently, membrane-based desalination technologies have received great attention as one of the promising approaches in addressing freshwater scarcity (Gude, 2016; Werber et al., 2016). These technologies are capable of producing water with high quality and require a smaller

¹ Part of Section 1.1 has been accepted and published in a review article in the journal of *ACS ES&T Engineering*, in which I am the primary author, with the following citation:

Horseman, T., Yin, Y., Christie, K.S., Wang, Z., Tong, T. and Lin, S. 2021. Wetting, Scaling, and Fouling in Membrane Distillation: State-of-the-Art Insights on Fundamental Mechanisms and Mitigation Strategies. *ACS ES&T Engineering*, 1, 1, 117-140.

footprint compared with conventional water treatment technologies (Shannon et al., 2010). More importantly, the energy efficiency of membrane-based desalination is essentially higher than thermal-based desalination approaches such as mechanical vapor compression (MVC) (Elimelech and Phillip, 2011), making it more economically attractive to be implemented. Reverse osmosis (RO) is believed to be the most reliable and energy efficient desalination method using membranes to purify waters from inland brackish water or seawater (Elimelech and Phillip, 2011; Qasim et al., 2019; Xu et al., 2013). The energy requirement of RO in desalinating seawater to achieve a 50% water recovery could be as low as $\sim 2 \text{ kWh/m}^3$ (Elimelech and Phillip, 2011; Tong and Elimelech, 2016). Theoretically, the driving force of mass transport (i.e., water molecules) of RO is regulated by the difference between hydraulic pressure applied to the RO system and osmotic pressure of the feed solution (Elimelech and Phillip, 2011). Naturally, water molecules can spontaneously flow from the solution with low salinity across a semipermeable membrane to the solution with high salinity to reach osmotic equilibrium (Figure 1-1a and 1-1b) (Qasim et al., 2019). Nevertheless, this process can be reversed by applying an external hydraulic pressure, which is greater than the osmotic pressure, to the semipermeable membrane to force water molecules transported in the opposite direction across the membrane. This process is known as reverse osmosis (Figure 1-1c) (Qasim et al., 2019). Furthermore, due to its highly dense membrane structure, a relatively high salt rejection rate can be achieved in RO (Nataraj et al., 2009). However, the efficiency of RO in producing freshwater is greatly constrained by the salinity of water sources, which is up to $\sim 70,000 \text{ mg/L}$ (Chen and Yip, 2018), because of the maximum tolerable pressure of the RO membrane module (Shaffer et al., 2013). In addition, due to the salinity ceiling imposed by the limited pressure applied in the RO system, a large proportion of feedwater becomes hypersaline brines and it would cause significant

concerns if directly discharging into the environment (Jones et al., 2019). Therefore, it is necessary to develop innovative membrane desalination technology, which is less constrained by feedwater salinity, to further reduce the volume of the RO brine to enhance the overall water recovery efficiency.

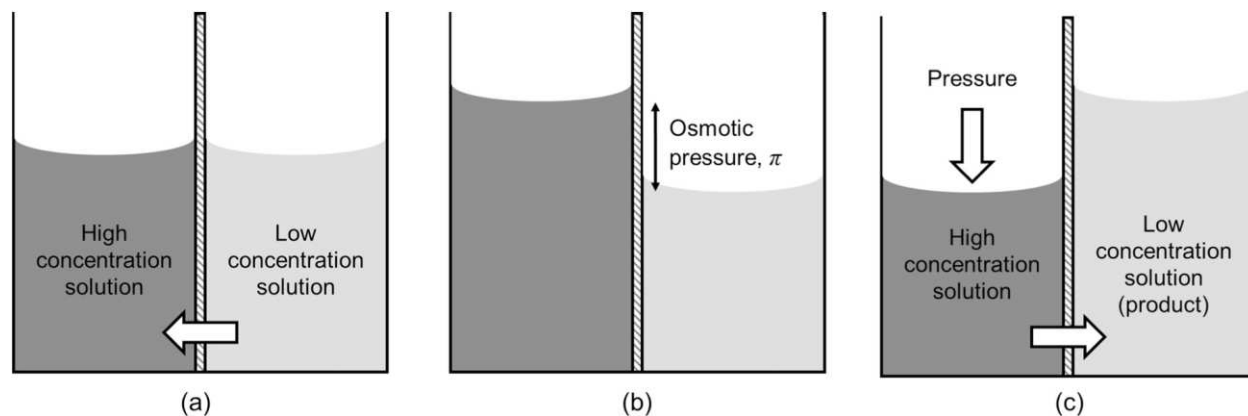


Figure 1-1. Schematic illustration of (a) osmosis (b) osmotic equilibrium and (c) reverse osmosis (Qasim et al., 2019)

One potential solution to the above question is the application of membrane distillation. Membrane distillation (MD) is a thermal-driven desalination technique (Alkhudhiri et al., 2012; Deshmukh et al., 2018; Lawson and Lloyd, 1997), in which a microscale porous hydrophobic membrane is applied to separate the warmer feed solution and the cooler distillate (Figure 1-2) (Zrelli, 2017). The mass transport of water in MD is driven by the difference of water vapor pressure resulting from temperature variation across the membrane barrier. Theoretically, due to such unique mass transport mechanism of MD, only volatile molecules (i.e., water molecules) is allowed to permeate across the membrane, whereas all non-volatile solutes such as inorganics and microorganisms are retained within the feed solution (Alkhudhiri et al., 2012; Lawson and Lloyd, 1997; Thomas et al., 2017; Tijning et al., 2015). However, these non-volatiles might still be able to penetrate across the membrane along with feed solution, when the hydrophobic property of the membrane is lost (Rezaei et al., 2018). This phenomenon is termed as membrane

pore wetting. Different from RO, MD is not limited by hydraulic pressure and feed solution salinity, which allows it to desalinate water sources with salinity higher than 70,000 mg/L (Tong and Elimelech, 2016). Yet, MD is more energy intensive than RO because phase change of water molecules takes place during the process, which results in a potential demand of large energy inputs (Deshmukh et al., 2018). Nevertheless, the operational temperature of MD is relatively low, rendering it capable of using low-grade thermal energy (Alkhudhiri et al., 2012; Deshmukh et al., 2018). Thereby, MD is a promising alternative desalination technology to treat water sources with high salinity such as RO brines (Tong and Elimelech, 2016), or combine with RO to achieve a high water recovery.

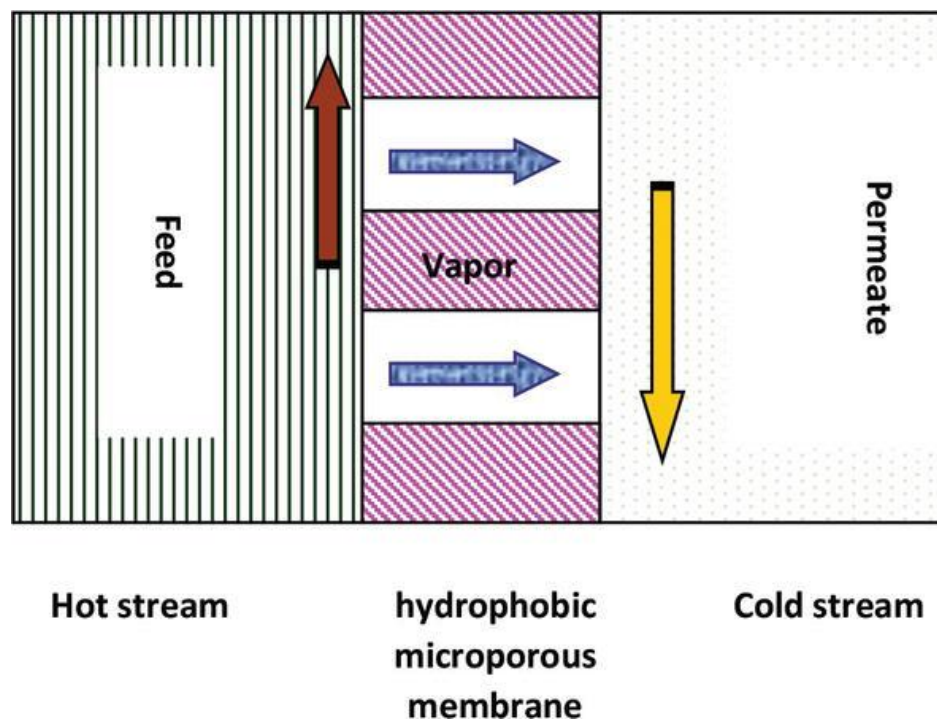


Figure 1-2. Schematic illustration of membrane distillation (Zrelli, 2017)

However, as RO and MD are practically intended for desalinating (i.e., removal of minerals from waters) high salinity waters, the formation of minerals during the desalination, which is also referred to as mineral scaling or membrane scaling, is a major challenge to both RO and MD

(Antony et al., 2011; Tijing et al., 2015; Tong et al., 2019b; Warsinger et al., 2015). Particularly, the increase of water recovery during desalination further increases the solute concentration, resulting in an elevation of the scaling potential (Tong et al., 2019a). Mineral scaling in membrane desalination occurs when solute concentrations exceed the solubility of sparingly soluble minerals in an aqueous solution due to the concentration of feed solution (Tong et al., 2019a). The formation of mineral scales such as calcite, gypsum and silica results in adhesion and coverage of the scale on the membrane surface (Figure 1-3), leading to enhanced resistance against the transport of the water through the membrane (Alkudhiri et al., 2012; Lawson and Lloyd, 1997; Tijing et al., 2015; Tong et al., 2019b). The occurrence of membrane scaling reduces water flux and the lifespan of the membrane materials, and thus the desalination efficiency is greatly compromised (Antony et al., 2011; Warsinger et al., 2015). For example, silica scaling was found to be firmly attached to the membrane surface in RO, causing a severe reduction in water flux (Tong et al., 2017). Also, consistent studies suggested that the presence of calcite scale could result in a significant flux decline and pore wetting in MD (Curcio et al., 2010; Gryta, 2005; 2008; 2011; He et al., 2009; Wang et al., 2008; Warsinger et al., 2015). Furthermore, mineral scaling has recently received more attention in membrane desalination because it is recognized as the main barrier that potentially prevents the achievement of zero liquid discharge (ZLD) or minimal liquid discharge (MLD) (Panagopoulos and Haralambous, 2020; Tong and Elimelech, 2016; Wang et al., 2020). Therefore, mineral scaling in membrane desalination has been identified as a major challenge that needs to be addressed properly. In addition, with increasing demands of using membrane desalination such as RO and MD to treat water sources with high scaling potential (Tong and Elimelech, 2016), systematic and

comprehensive research of mineral scaling in membrane desalination becomes paramount importance.

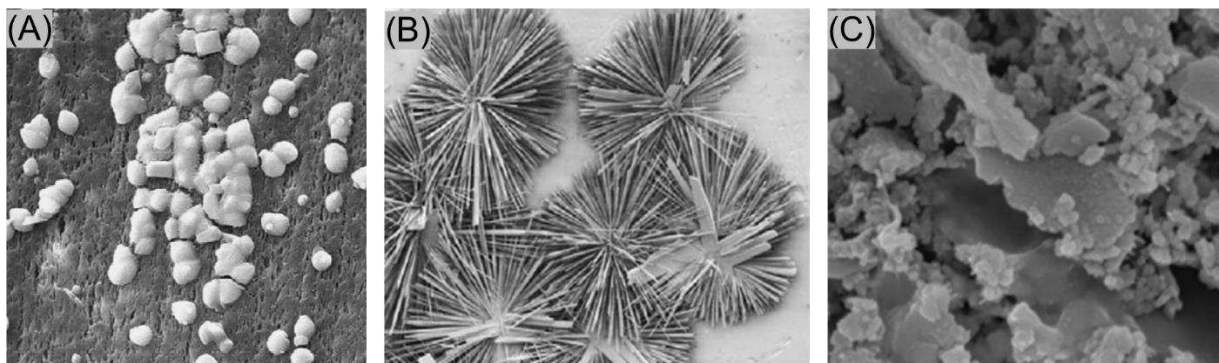


Figure 1-3. SEM micrographs of (A) calcite, (B) gypsum and (C) silica scales attached to the surfaces of the membranes used in MD and RO systems (Curcio et al., 2010; Shih et al., 2005; Tong et al., 2017).

Currently, the most widely accepted scaling mitigation strategy is dependent on effective removal of scaling precursors prior to releasing the feed solution contacting with membrane materials during desalination (Antony et al., 2011; Tong et al., 2019b). For example, ion exchange resins have been employed in the RO system to remove divalent ions such as Ca^{2+} and Mg^{2+} , softening the RO influent as well as decreasing the scaling potential during the process (Smith and SenGupta, 2015). Further, the introduction of specific mineral slurry could promote early mineral precipitation, which reduces the potential of mineral scaling in the feedwater (Gilron et al., 2005; Kedem and Zalmon, 1997; Oren et al., 2001). However, implementing additional pretreatments would increase the capital cost and facility footprint. Thus, it is necessary to develop more economical and effective strategies to control scaling. Inspired by the anti-fouling membranes that have been demonstrated to successfully mitigate organic fouling and biofouling in membrane desalination (Dong et al., 2017; Rana and Matsuura, 2010; Zhang et al., 2016), developing membrane materials with scaling resistance could be a promising means. For example, a Janus membrane with a hydrophilic surface has been demonstrated to be effective in mitigating organic fouling in MD (Li et al., 2019; Wang et al., 2016c; Wang and Lin, 2017).

Fabricating membrane surface with low-surface-energy brushes and a hydrophilic layer was able to mitigate both organic fouling and biofouling in RO (Wang et al., 2018). However, in comparison with extensive studies in fabricating anti-fouling membrane materials to mitigate organic fouling and biofouling (Gao et al., 2018; Huang et al., 2017; Kang and Cao, 2012; Wang et al., 2016a; Wang et al., 2017; Wang et al., 2018; Wang et al., 2016b; Wang and Lin, 2017; Zhang et al., 2016), few studies have been systematically conducted to explore the feasibility of designing scaling-resistant membrane to control scaling in MD. Such research blank spots result in a lack of understanding upon several critical aspects relevant to mineral scaling in membrane desalination. For example, the interplay of varying mineral scales with membrane surface possessing different functionalities has not been well understood, the role of homogeneous nucleation and heterogeneous nucleation play in inducing mineral scaling is still unidentified, and the extent of effectiveness of membrane surface modification in retarding mineral scaling has been rarely discussed. Therefore, in order to develop a scaling-resistant membrane to control scaling, addressing these knowledge gaps and questions properly is the prerequisite.

In addition to membrane materials innovation, an important consideration in regard to controlling scale formation using anti-scalants could potentially offer us an alternative to reduce the impact of membrane scaling economically. So far, the use of anti-scalants is the most straightforward approach of controlling mineral scaling in membrane desalination (Andrés-Mañas et al., 2018; Gryta, 2012; He et al., 2009; Minier-Matar et al., 2014; Peng et al., 2015; Qu et al., 2020; Yu et al., 2013; Zhang et al., 2015). For example, organic phosphonate derivative were found to mitigate precipitation of calcium scales in MD treatment of seawater RO brine (Zhang et al., 2015), while the application of a proprietary polymeric compound was reported to retard calcite scaling in MD treating coal seam gas RO brine as the feed water (Zhang et al.,

2018). Additionally, carboxylic-based polymeric molecules also inhibit the nucleation of calcite and gypsum in MD (He et al., 2009). Anti-scalants typically serve as nucleation inhibitors that hinder homogeneous nucleation in feed solutions. The two major mechanisms that are likely responsible for scaling inhibition are (1) the formation of soluble complexes in the bulk solution, which decreases the saturation index by reducing availability of the “free” ions for precipitation; and (2) the direct adsorption onto the nuclei surface, which retards the mineral growth (Tijing et al., 2015; Warsinger et al., 2015). Anti-scalants that are widely used in industry are weak acids such as phosphonate derivatives and polymeric molecules anchored with carboxylic groups. Under near-neutral conditions of desalination, such anti-scalants are partially or fully deprotonated, exposing negative active sites that are able to form complexes with multivalent cations in the solution (Deluchat et al., 1997; Duan et al., 1999; Lioliou et al., 2006; Sun et al., 2015). For example, polyacrylate acid (PAA), a carboxylic derivative polymer with pK_a of 4.4 (Battaglia et al., 2005), is highly deprotonated around pH of 7 and may strongly chelate with Ca^{2+} to reduce its activity for precipitating with CO_3^{2-} or SO_4^{2-} to form calcite or gypsum (Ben Ahmed et al., 2008; Liu et al., 2015). However, this complex formation mechanism is challenged by the fact that the anti-scalants can be highly effective at a very low concentration—much lower than the concentration of Ca^{2+} stoichiometrically (Le Gouellec and Elimelech, 2002; Shih et al., 2004).

Another possible mechanism for the role of anti-scalants in scaling inhibition is the adsorption of anti-scalant molecules onto the surface of crystal nuclei via either electrostatic interaction or ligand exchange (Ben Ahmed et al., 2008; Jain et al., 2019; Le Gouellec and Elimelech, 2002; Rabizadeh et al., 2019; Shih et al., 2004; Shih et al., 2006). Adsorption of anti-scalants may contribute to scaling mitigation in two different ways. First, the adsorption of anti-

scalants on the nuclei surface increases the interfacial free energy at the liquid-nucleus interface (Oh et al., 2009), thereby increasing the energy barrier of nucleation according to the classical nucleation theory as discussed in the following section. This consequently reduces the nucleation rate and extends the induction time of scaling (He et al., 2009; Jain et al., 2019; Oh et al., 2009). Second, the attachment of anti-scalants reduces the active nuclei surface area for crystal growth (Rosenberg et al., 2012; Weijnen and Van Rosmalen, 1986). However, the previous studies using anti-scalants to control scale formation have still not provided sufficient answers to several crucial aspects relevant to the use of anti-scalants. For example, although several theories have been proposed to elucidate the mechanisms that regulate the effectiveness of anti-scalants, a confusion of underlying factors that are responsible for their efficiency still exist. For example, the specific functionality requirement of anti-scalants to inhibit scale formation as a function of mineral types is still mysterious. Also, the specific requirements of anti-scalants dosage and type for different desalination systems are indeed another question. Therefore, it is now demanding to perform a systematic study to respond these uncertainties, so that we could pave a way to the successful mitigation of mineral scaling in membrane desalination.

In the following sections of this chapter, necessary knowledge background about mineral scaling will be described and discussed, serving as the basis of this study.

1.2 Knowledge Background Relevant to Mineral Scaling

1.2.1 Formation mechanisms of gypsum and silica

The inorganic constituents present in natural waters stem from the chemical weathering of the Earth's crust (Tong et al., 2019a). Due to the composition complexity of minerals within the crust, numerous inorganic chemical species including calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), barite (BaSO_4) and silica (SiO_2) co-exist in the feed solution that could lead to mineral scaling

during desalination (Tong et al., 2019a). In this study, I typically selected gypsum and silica as the representative scales because gypsum and silica are the most commonly found minerals in natural water. More importantly, the formation of gypsum and silica are regulated by two utterly different mechanisms at the molecular level, namely crystallization reaction and polymerization reaction (Gryta, 2009; Neofotistou and Demadis, 2004c; Tong et al., 2019a). These two mechanisms are responsible for the formation of the majority of minerals in membrane desalination, thus, it is critical to assess how the different mineral formation mechanisms affect membrane scaling.

Unlike other crystallization-induced scales such as calcite, the solubility of gypsum is insensitive to the pH adjustment (Compton and Pritchard, 1990; Tong et al., 2019a). To alter the pH of the solution is ineffective to remove gypsum from the water matrix. In addition, although the formation of gypsum scales is a result of hydration reaction between Ca^{2+} and SO_4^{2-} ions, the underlying formation mechanism is complex. According to Wang et al (Wang et al., 2012), the formation of gypsum consists of three steps, in which bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) serves as the intermediate stage to bridge crystalline transformation of gypsum from amorphous CaSO_4 (Figure 1-4). It is worth noting that the crystalline transformation of gypsum in aqueous solution via bassanite has been ignored in the previous studies (Van Driessche et al., 2012; Wang et al., 2012), which results in great confusion of interactions between gypsum and other constituents in water such as anti-scalants.

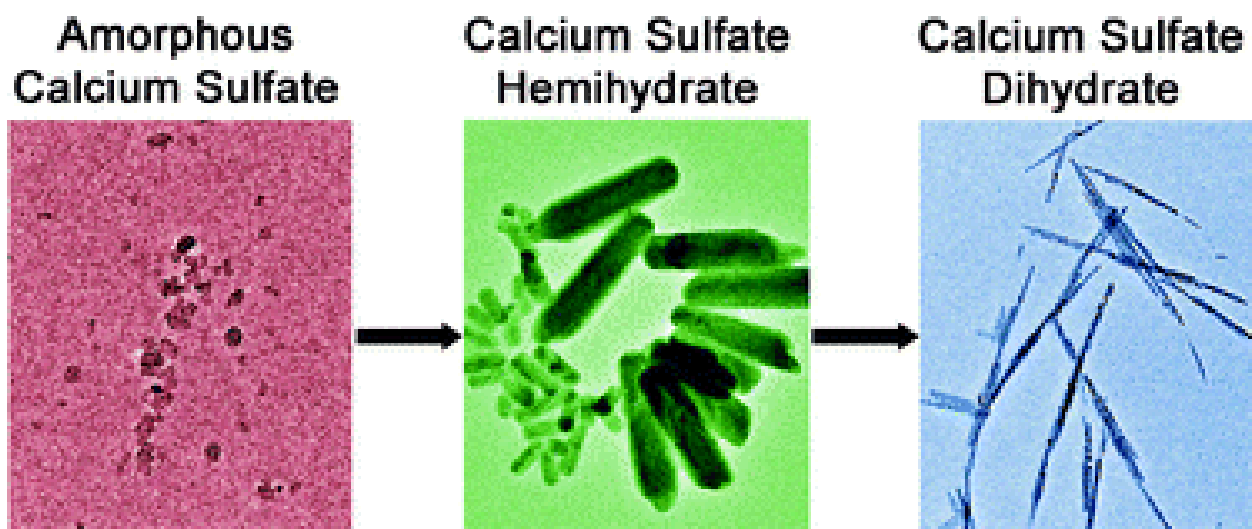


Figure 1-4. The crystalline transformation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) from amorphous CaSO_4 phase via bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) (Wang et al., 2012).

In contrast, silica behaves distinctly different from gypsum. For example, the solubility of silica is pH-sensitive when the solution pH beyonds 7 (Alexander et al., 1954). To increase the pH of the silica solution above 11 has been used as an effective means to prevent silica scaling in MD (Bush et al., 2018). However, this approach requires the addition of sodium hydroxide, which is likely to corrode membrane module and also induce additional scale precipitations such as forsterite (Mg_2SiO_4) (Chen et al., 2006). More notably, the formation of silica is induced by polymerization reaction between silicic acids in the solution, which results in the formation of silica particles with amorphous nature (Figure 1-5) (Currie and Perry, 2007; Makrides et al., 1980; Milne et al., 2014). As compared to gypsum, this fundamental difference could likely result in different interplays with membrane surfaces possessing different properties, as well as varying interactions with anti-scalants in the solution. Although previous studies suggest that a limited number of anti-scalants could stabilize silica species in the solution or reduce silica scaling during membrane desalination (Hater et al., 2011; Hater et al., 2013; Kempter et al., 2013; Neofotistou and Demadis, 2004a; b; Ning et al., 2009), most anti-scalants are still

ineffective to interfere with silica forming process because of the non-crystalline nature of silica (Tong et al., 2019a). Additionally, the anti-scaling mechanism and effectiveness of these molecules in inhibiting silica scaling in membrane desalination have yet to be fully understood.

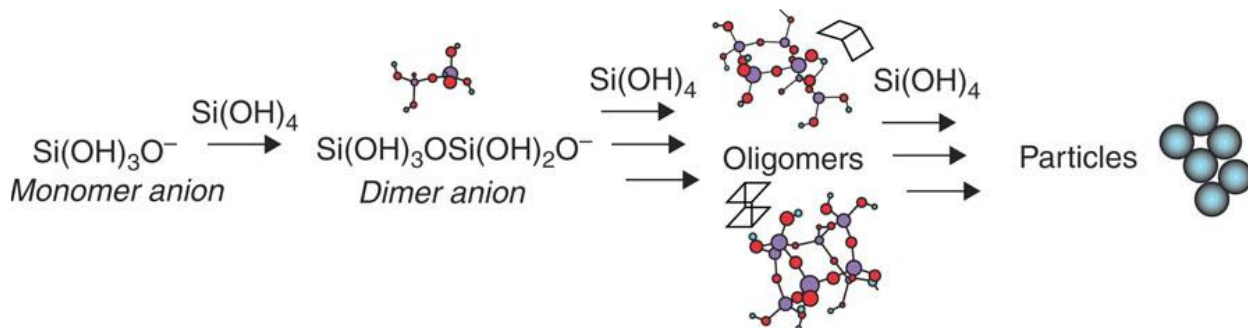


Figure 1-5. The formation of amorphous silica particles via polymerization reaction between silicic acids as the monomer in the solution (Currie and Perry, 2007).

1.2.2 Homogeneous nucleation and heterogeneous nucleation for mineral scaling

Despite different forming mechanisms (i.e., crystallization vs. polymerization) of gypsum and silica, both gypsum scaling and silica scaling are the result of homogenous nucleation and heterogeneous nucleation (Tong et al., 2019), which are two main mechanisms in controlling mineral scaling in membrane desalination (Figure 1-6) (Tang et al., 2017; Tong et al., 2019).

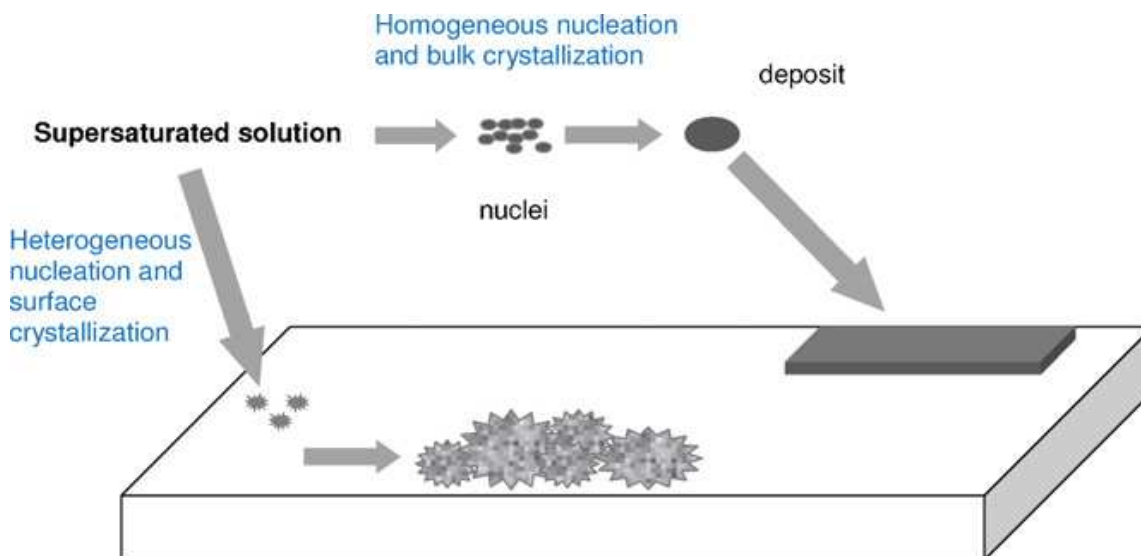


Figure 1-6. Schematic illustration of homogeneous nucleation and heterogeneous nucleation (Antony et al., 2011).

Mineral scaling induced via homogeneous nucleation in membrane desalination is initiated from the solution due to an oversaturation status of the corresponding minerals (Liu, 2000). As the concentration of scale-forming species reaches certain thresholds that exceed the solubility of soluble minerals, mineral precipitation takes place spontaneously within the aqueous solution, and then followed by the deposition unto membrane surfaces, which results in surface coverage of the scale that blocks effective membrane areas for water transporting (i.e., water flux reduction) (Antony et al., 2011; Tong et al., 2019). On the contrary, heterogeneous nucleation refers to the participation of foreign substrates such as membrane surfaces or suspended particles in the solution to occur (Liu, 2000). The *in-situ* growth of minerals on the membrane surface could result in the formation of scaling layers that attach to the membrane surface to obstruct water transport (Mi and Elimelech, 2010; Tong et al., 2019a). However, to distinguish the extent of contributions of each nucleation pathway in inducing scale formation in membrane desalination is relatively hard, because both of these two mechanisms are not only dependent on the saturation status of the solution, but also a dynamic process that might proceed simultaneously. Yet, based on the previous study (Shih et al., 2005), a subtle difference in morphology might be able to provide hints on how homogeneous nucleation and heterogeneous nucleation contribute to scaling in membrane desalination. As reported by Shih et al. (Shih et al., 2005), gypsum crystals formed via heterogeneous nucleation usually display needle-like morphology, while a platelet- or rod-like morphology in gypsum is believed to be resulted from homogeneous nucleation.

1.2.3 Theoretical frameworks established for mineral scaling

To predict the propensity of mineral scaling via either homogeneous nucleation or heterogeneous nucleation, the classical nucleation theory (CNT) has been widely used as a

thermodynamical framework in mineral crystallization (Karthika et al., 2016; Lundrigan and Saika-Voivod, 2009; Niu et al., 2018; Wette and Schöpe, 2007; Zanotto and James, 1985). CNT provides direct quantitative analysis of the energy barriers of mineral nucleation (ΔG), which is determined by the difference of the bulk free energy and energy penalty due to the increase of extra interfacial areas (Clouet, 2010), which is usually expressed as (Clouet, 2010):

$$\Delta G = -n\Delta\mu + Area_n\gamma \quad (1 - 1)$$

where n is the number of molecules in the nucleus, $\Delta\mu$ is the variation of chemical potential, γ refers to the interfacial surface tension between the nucleus and the surrounding medium, and $Area_n$ is the interfacial surface area of the nucleus with the medium.

For homogeneous nucleation, the free energy barrier (ΔG_{hom}) mainly depends on factors including the chemical potential difference ($\Delta\mu$), the physical property of the nucleus (Ω : molar volume of the nucleus) and the interfacial surface tension between the nucleus and the medium (i.e., water) (γ_{ln}) as (Kalikmanov, 2013):

$$\Delta G_{hom} = -\frac{4}{3}\frac{\pi r^{*3}}{\Omega}\Delta\mu + 4\pi r^{*2}\gamma_{ln} \quad (1 - 2)$$

where r^* stands for the critical size of the nucleus in the solution, which can be calculated as:

$$r^* = \frac{2\gamma_N\Omega}{\Delta\mu} \quad (1 - 3)$$

where γ_N is the surface energy of the nucleus.

For heterogeneous nucleation, the height of heterogeneous nucleation energy barrier can be correlated with homogeneous nucleation using a correction factor ($f(\Theta)$) as (Förster and Bohnet, 1999; Maris, 2006; Turnbull, 1950; Volmer, 1939):

$$\Delta G_{het} = \Delta G_{hom} f(\Theta) \quad (1 - 4)$$

where $f(\theta) = \frac{1}{4}(1 - \cos\theta)^2(2 + \cos\theta)$, θ represents the contact angle between the nucleus and the surface of the foreign substrate. The value of the correction factor $f(\theta)$ lies between 0 and 1, which implies that the free energy barrier of heterogeneous nucleation is always lower than homogeneous nucleation. Thus, the occurrence of heterogeneous nucleation is more thermodynamically favorable than homogeneous nucleation in the presence of membrane surface during desalination. Furthermore, it is evident that an increased contact angle between the nucleus and the surface (θ) could theoretically elevate the free energy barriers of mineral formation via heterogeneous nucleation. This interpretation serves as the theoretical basis for membrane surface modification to inhibit membrane scaling in this study.

In addition to the quantitative analysis of scaling potential based on CNT, the saturation index (SI) has also been used as a direct method to qualitatively predict the scaling propensity of mineral scaling, which can be calculated as (Tong et al., 2019a):

$$\sigma = \ln \frac{IAP}{K_{sp}} \quad (1 - 5)$$

where the σ is the SI, IAP is the ion activity product, K_{sp} is the solute solubility product. The ratio between IAP and K_{sp} corresponds to the chemical driving force for the mineral formation. Unlike the scaling potential prediction made by CNT, the saturation index can only provide rough estimates on scaling propensity (e.g., $\sigma < 1$ and >1 indicates undersaturation and oversaturation status of solutes, respectively), yet the SI is more convenient in practice because it requires fewer efforts in calculation than CNT.

1.2.4 Concentration polarization in membrane desalination

Concentration polarization in membrane desalination is an important concept (Antony et al., 2011; Tong et al., 2019). In membrane desalination, the membrane material only allows passages

of water penetrating through, which leaves solutes accumulated near the interface between membrane surface and feedwater, thus, the concentration of the solute adjacent to the membrane surface is much higher than the concentration in the bulk solution. Thus, it is important to quantify the effect of concentration polarization on membrane desalination. Classical film model has been used to calculate the extent of concentration polarization, which is expressed as (Kim and Hoek, 2005; Shirazi et al., 2010):

$$C_m = C_b \exp\left(\frac{J}{k}\right) \quad (1 - 6)$$

C_m represents the concentration of solute near the membrane surface, C_b is the concentration of solute from bulk solution and J is the water flux measured during the desalination process, and k is the mass transfer coefficient, which can be calculated as:

$$k = \frac{Sh \cdot D}{d_h} \quad (1 - 7)$$

where Sh is the Sherwood number, D is the solution diffusion coefficient, and d_h is the hydraulic diameter.

It is evident that the extent of concentration polarization is a function of the water flux and hydrodynamic conditions of the feed solution. As the water flux increases during desalination, the more severe effects of concentration polarization occur near membrane surface. The direct consequence of concentration polarization, even when the bulk feed solution is undersaturated, is facilitating the scale formation, particularly for heterogeneous nucleation. To reduce the effects of concentration polarization, reducing the water flux is the most straightforward approach. However, the reduction of water flux would inevitably decrease the desalination efficiency. Another possible means is to increase turbulence of the flow in the feed solution chamber to disrupt the concentration layer near the membrane surface (Naidu et al., 2014).

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2.0 Research Objectives

According to the review of the current status of mineral scaling in membrane desalination, mineral scaling has been considered as a major challenge that greatly compromises the desalination efficiency. However, the mechanisms and mitigation strategies of mineral scaling have yet to be well established. Four primary knowledge gaps have been identified and described below. Addressing these knowledge gaps would significantly advance our understanding of mineral scaling for membrane-based desalination processes, which facilitates the development of effective scaling control strategies.

- The mechanisms of membrane scaling as a function of different scaling types in membrane desalination have not been well understood.
- The relationship between mineral scaling and membrane surface property (e.g., surface wettability and surface charge) in membrane desalination has not been fully elucidated.
- The efficiencies of anti-scalants in suppressing mineral scaling and the underlying mechanisms for different scaling types have been rarely discussed in membrane desalination.
- Different scaling mitigation strategies have not been compared, resulting in the lack of criterion for the selection of scaling mitigation strategy in membrane desalination.

To close the above knowledge gaps, I performed a series of experiments with the following research objectives:

- **Unveil silica scaling mechanism in MD and explore the feasibility of membrane surface modification in inhibiting silica scale formation on the membrane surface.**

Silica scaling is detrimental to the performance of MD. Although the formation mechanism of silica, which is controlled by polymerization reactions, has been documented in the literature, the silica scaling mechanism in MD is still unknown. In addition, the scaling behaviors of silica with respect to membrane surfaces possessing different wettability has not been elucidated. Three PVDF membranes possessing different surface wettability were challenged by two silica solutions with varying saturation status (i.e., supersaturated and undersaturated) to investigate silica scaling mechanism in MD. The findings of this study identified the role of homogeneous nucleation and heterogeneous nucleation played in controlling silica scaling in MD.

- **Elucidate the effects of membrane surface wetting properties on membrane pore wetting and scaling reversibility associated with gypsum and silica in MD.**

Altering membrane surface wettability has been considered as an effective means to mitigate organic fouling and membrane wetting. However, its effectiveness has not been well understood for membrane scaling induced by different scaling types in MD. In addition, membrane pore wetting and scaling reversibility as a function of scaling type have been rarely discussed in the literature. A comparative study between gypsum scaling and silica scaling in MD was performed to elucidate the relationships between surface wetting properties with pore wetting and scaling reversibility. The results from this study provide valuable insights to link membrane surface chemistry with membrane performance in MD for different types of mineral scaling, which have the potential to guide the future development of effective scaling mitigation strategies.

- **Investigate the efficacies and mechanisms of anti-scalants in inhibiting gypsum scaling and silica scaling in MD.**

Anti-scalants is a common means to control scale formation. However, the regulating factors that govern the efficiencies of anti-scalants in MD have not been well understood. Furthermore,

the relationship between different scaling types with anti-scalant functionalities is still lacking. A comparative study on the efficiencies of anti-scalants with different functional groups to inhibit gypsum scaling and silica scaling was conducted. The data from this study demonstrate different scaling types require anti-scalants of varied functionalities. The finding of this work also provide mechanistic insights on the molecular design of anti-scalants that are tailored to different types of scaling in MD.

- **Compare the efficiencies of utilizing membrane surface modification and anti-scalants in inhibiting gypsum scaling to enhance the total water recovery with a combined reverse osmosis and membrane distillation treatment train**

Both the development of novel membrane materials and the use of anti-scalants have been applied as possible methods to inhibit scale formation in membrane desalination. However, we still lack a comparative understanding of their anti-scaling efficiencies. Furthermore, the effectiveness of using anti-scalants in a combined RO and MD treatment train to enhance the total water recovery has also not been evaluated. In this work, the anti-scaling efficiency of membrane surfaces modified with different functional groups to control gypsum scaling in RO was compared with that of anti-scalants. Furthermore, the effectiveness of anti-scalants to enhance the total water recovery of a combined RO and MD treatment train was assessed. The findings of this work provide comparative perceptions on the efficiencies of different strategies to control scaling and have the potential to guide the selection of the most appropriate method of scaling mitigation in membrane desalination.

3.0 Elucidating Mechanism of Silica Scaling in Membrane Distillation: Effects of Membrane Surface Wettability²

3.1 Introduction

Membrane distillation (MD) is a hybrid thermal, membrane-based technology for sustainable water purification. MD utilizes a partial vapor pressure difference generated between the hot feedwater and cold distillate to drive water vapor transport across a hydrophobic, microporous membrane (Alklaibi and Lior, 2005; Deshmukh et al., 2018; Lawson and Lloyd, 1997). The tolerance of MD to high salinity beyond the reverse osmosis (RO) limit renders this technology specifically suitable to desalinate and treat hypersaline wastewaters such as concentrated RO brines as well as produced water from shale oil and gas production (Du et al., 2018; Kim et al., 2017; Lokare et al., 2017; Martinetti et al., 2009; Shaffer et al., 2013; Tong and Elimelech, 2016; Zhang et al., 2019). Also, MD is able to leverage low-grade thermal energy (e.g., solar energy, industrial waste heat, and geothermal energy), thereby reducing the primary energy consumption and carbon footprint compared to electricity-driven technologies such as mechanical vapor compression (MVC) (Tong and Elimelech, 2016). As a result, MD has recently attracted great interests as a promising means to promote sustainability at the water-energy nexus.

Mineral scaling is a primary limiting factor that constrains MD performance (Tong et al., 2019). When water recovery reaches certain thresholds, scale-forming species will exceed their

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solubility and precipitate as sparingly soluble salts on the membrane surface (Antony et al., 2011). The formation of mineral scales results in severe flux decline and requires harsh chemical cleaning, thereby increasing the cost and reducing the energy efficiencies of MD desalination (Duong et al., 2016; Gilron et al., 2013; Guillen-Burrieza et al., 2014; Tijing et al., 2015; Warsinger et al., 2015). Mineral scaling is particularly problematic in the MD process due to the typically high salinity and scaling potential of MD feedwaters. Compared to other common types of mineral scaling (e.g., calcite scaling and gypsum scaling), silica scaling is more challenging to mitigate and considered as the “Gordian knot” of water treatment processes (Neofofistou and Demadis, 2004). Most commercially available anti-scalants, which typically disrupt the crystallization process of mineral scales (Antony et al., 2011), have poor performance in controlling silica scaling because of the amorphous nature of silica scale (Neofofistou and Demadis, 2004). According to Sandia National Laboratories (Brady et al., 2005), silica scaling often determines the water recovery in inland brackish water desalination. Previous studies have demonstrated that silica scaling reduced the water productivity of MD significantly (Bush et al., 2018; Gilron et al., 2013), and the presence of silica scales has been reported in MD desalination of both brackish RO brine (Martinetti et al., 2009) and shale oil and gas produced water (Du et al., 2018).

So far, the mechanisms of silica scaling in MD have not been elucidated, imposing a significant barrier to the development of effective mitigation strategies. Homogenous nucleation and heterogeneous nucleation represent two major mechanisms of mineral scaling (Tang et al., 2017; Tong et al., 2019). The former refers to the formation of mineral nucleus in the solution, while the latter is associated with surface nucleation in the presence of a foreign substrate (e.g., membrane surface). Previous studies indicated that gypsum scaling in forward osmosis (FO) was

dominated by heterogeneous nucleation on thin-film composite (TFC) polyamide membranes, while it was mainly driven by homogeneous crystallization on cellulose acetate membranes (Mi and Elimelech, 2010; Xie and Gray, 2016). Due to the differences between working principles of FO and MD, as well as between gypsum scaling and silica scaling, it is still unknown which mechanism plays a more important role in silica scaling during the MD process. The membrane surfaces are exposed to colloidal scale particles when homogeneous nucleation occurs, whereas interactions between soluble scale precursors and membranes dominate during heterogeneous nucleation. As a result, membrane materials play distinct roles in mineral scaling under different scaling mechanisms, to which different strategies of scaling mitigation should be tailored.

Understanding the interplay between membrane surface property and scaling propensity will promote our knowledge of mineral scaling mechanism in MD desalination. So far, membrane materials with varied surface properties have been developed to resist organic fouling and wetting in MD application, and the optimization of membrane surface wettability has been utilized as a primary approach (Deshmukh et al., 2018). For example, omniphobic membranes have been fabricated to mitigate membrane wetting caused by low surface tension contaminants such as surfactants (Boo et al., 2016a; b; Lee et al., 2016; Razmjou et al., 2012). A combination of materials with low solid surface energy (e.g., fluoroalkylsilane coatings) and a re-entrant structure is the key principle of creating such membranes (Tuteja et al., 2008; Wang et al., 2016a). On the other side, an in-air hydrophilic top layer is incorporated into MD membranes to mitigate organic fouling (Li et al., 2019; Wang et al., 2016b; Wang and Lin, 2017). The hydration layer formed with hydrophilic coating inhibits the attachment of organic foulants (such as oil) to the surface of membranes. As a result, a wide range of surface wettability (i.e., from

superhydrophobic to hydrophilic) has been created for MD membranes tailored to different feedwater compositions (Wang and Lin, 2017).

However, the relationship of membrane surface wettability with mineral scaling is emerging and has not been fully established. Recently, Karanikola et al. (Karanikola et al., 2018) reported that superhydrophobic membranes were able to mitigate gypsum scaling in MD desalination. The authors suggested that superhydrophobic surface provides a higher energetic barrier to the nucleation of gypsum, and minimizes the deposition of gypsum crystals via reducing the membrane-solution contact area. Similarly, Xiao et al. (Xiao et al., 2019a; Xiao et al., 2019b) reported that superhydrophobic membrane with micro-pillar arrays after CF₄ plasma treatment showed superior anti-scaling performance in saturated NaCl and gypsum feed solutions. However, silica scaling is distinct from both gypsum scaling and NaCl scaling. Gypsum and NaCl scales are formed in crystallization processes that create CaSO₄·2H₂O and NaCl crystals, respectively (Mi and Elimelech, 2010; Xiao et al., 2019b). In contrast, the generation of silica scale proceeds via polymerization of silicic acid, which is a non-crystallization process (Quay et al., 2018; Tong et al., 2017). Therefore, the responses of membrane surface property to mineral scaling are likely varied between gypsum/NaCl scaling and silica scaling. To the best of our knowledge, the effect of membrane surface wettability on silica scaling in MD desalination has not been reported in the literature.

In this study, we investigated the relationship of silica scaling with membrane surface wettability in MD desalination, in order to reveal the mechanism of silica scaling in MD. We modified a commercial hydrophobic polyvinylidene fluoride (PVDF) membrane with a hydrophilic polymer or fluorosilanized SiO₂ nanoparticles (SiNPs), generating membranes possessing varied surface wettability. The membranes were then challenged with silica-

containing feed solutions in a custom-built direct contact MD (DCMD) system. Two silica concentrations were employed to result in different initial saturation status, and membrane performance in silica scaling tests was compared among different membranes under both saturation conditions. Further, colloidal silica fouling was also conducted for comparison, and detailed characterization was performed to analyze the scaling layers formed on membrane surfaces. Finally, a four-step mechanism was proposed for silica scaling in the MD process.

3.2 Material and Methods

3.2.1 Materials and chemicals

Polyvinyl alcohol (PVA, 98% hydrolyzed, Mw 13,000–23,000), glutaraldehyde (GA, 50 wt% in H₂O), LUDOX HS-30 colloidal silica (30 wt% suspension in H₂O), (3-aminopropyl)triethoxysilane (APTES, ≥98%), and sodium metasilicate pentahydrate (Na₂SiO₃·5H₂O, >95.0%) were all purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide (NaOH) and sodium chloride (NaCl) were obtained from VWR BDH Chemicals (Radnor, PA, USA). A long-chain fluoroalkyl silane (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane, 17-FAS) was supplied by Gelest Inc (Morrisville, PA, USA). It should be noted that any experiments using 17-FAS were and should be performed with caution in the fume hood due to its potential toxicity and bio-accumulative property. Anhydrous ethanol was purchased from Decon Laboratories (200 proof, King of Prussia, PA, USA). Flat sheet polyvinylidene fluoride (PVDF) membranes with a nominal pore size of 0.45 μm (HVHP, Durapore) were purchased from Millipore Sigma (Burlington, MA, USA). In addition, deionized (DI) water was generated from a commercial water purification system (>18 MΩ·cm, Millipore, Burlington, MA, USA).

3.2.2 Membrane modification approaches

A hydrophilic coating of PVA was grafted on the surface of PVDF membranes to create a Janus PVDF membrane, using the protocol reported in our recent publication (Du et al., 2018). Briefly, 1 g PVA was dissolved in 100 mL DI water overnight at a temperature $> 90\text{ }^{\circ}\text{C}$ until PVA was dissolved. The PVA solution was then cooled down to the room temperature, after which the pH was adjusted to around 2. Then 1 mL of GA (50 wt%) solution was added into the 100 mL PVA solution as cross-linking agent (Zhang et al., 2008). After stirring, the PVA-GA mixture was decanted on the surface of a PVDF membrane, which was then incubated at $60\text{ }^{\circ}\text{C}$ for 1 h. The membrane modified with PVA (referred to as PVDF-PVA membrane) was rinsed with DI water and dried gently using nitrogen gas. This modification approach only provided hydrophilic coating on the PVDF membrane surface but maintained hydrophobicity of the PVDF membrane, because the PVA-GA aqueous solution was not able to wet the entire hydrophobic PVDF membrane.

Further, SiNPs modified with 17-FAS was incorporated into the surface of PVDF membrane, using the method of our publication and others (Boo et al., 2016b; Du et al., 2018; Karanikola et al., 2018). The combination of low surface energy with appropriate texture introduced by SiNPs rendered the imparted the PVDF membrane with superhydrophobic properties. In brief, the PVDF membrane was wetted with ethanol and then soaked in a solution of 7.5 M NaOH for 3 h at $70\text{ }^{\circ}\text{C}$. This alkaline treatment step created abundant hydroxyl functional groups on the PVDF membrane surface (Lu et al., 2018). The membrane was then immersed in 1% v/v APTES in ethanol for 1 h, which grafted the membrane surface with amine groups carrying positively charges. The APTES-modified PVDF membrane was rinsed with ethanol and dried at $60\text{ }^{\circ}\text{C}$ for 1 h. The membrane was then wetted with ethanol and soaked in an

aqueous SiNP solution (0.03% v/v in 10 mM NaCl solution) for 30 min, during which the SiNPs attached to the membrane surface via electrostatic attraction. The SiNP-modified membrane was rinsed with DI water and dried in the oven, after which the membrane was soaked in hexane containing 0.4% v/v 17-FAS at room temperature overnight. The resultant PVDF membrane (referred to as PVDF-SiNP-FAS membrane) was rinsed with hexane and dried at $> 80\text{ }^{\circ}\text{C}$ for > 10 hours.

3.2.3 Membrane characterization

Scanning electron microscopy (SEM, JEOL JSM-6500F) was employed to investigate the surface morphologies of pristine and modified PVDF membranes. Prior to imaging, the membranes were dried and coated with a thin layer of gold using a sputter coater (Denton Desk IV, Denton Vacuum, Moorestown, NJ, USA). The water contact angle of each membrane was measured by a contact angle goniometer (Ramé-hart Instrument Corporation, Succasunna, NJ, USA). An 8- μl water droplet was placed on the surface of each sample, and the photographs of the water droplet were taken and analyzed by imaging software (Drop Image Software, Ramé-hart Instrument Corporation, Succasunna, NJ, USA). Also, the dynamic surface wettability was measured by dropping a 7- μl water droplet from a height of 5 cm and recorded the motion of the water droplet in contact with the membrane by a high-speed camera (Photron FASTCAM SA3, Motion Engineering Company, Westfield, IN, USA).

3.2.4 Membrane distillation scaling experiments

The scaling behaviors of the pristine and modified PVDF membranes were tested using a bench-scale DCMD system. Two feed solutions containing different concentrations of silica were used to result in varied silica saturation status. NaCl (50 mM) and NaHCO_3 (1 mM) were used as the background electrolytes, and 1.5 mM or 6 mM $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ was added as the

scalants. The pH of both feed solutions was adjusted to 6.50 ± 0.05 . Thermodynamic calculations using PHREEQC (Parkhurst and Appelo, 1999) and the database WATEQ4F (PC Version) indicated that silica was the sole precipitate formed in the feed solutions. The saturation indices (defined as natural logarithm of the ratio of ion activity product to the product solubility, $\ln \frac{IAP}{K_{sp}}$) were -0.82 and 0.55 for amorphous silica in the feed solutions containing 1.5 mM and 6 mM $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, respectively. Also, additional feed solutions were made to induce gypsum scaling and colloidal silica fouling for comparison. The feed solution for gypsum scaling contained 20 mM CaCl_2 , 20 mM Na_2SO_4 , and 50 mM NaCl without adjusting pH, and the saturation index of the feed solution was -0.02 for gypsum; the feed solution of colloidal silica fouling contained 360 mg/L silica particles (equivalent to a molar concentration of 6 mM SiO_2 , LUDOX HS-30, Sigma Aldrich), 50 mM NaCl , and 1 mM NaHCO_3 with pH adjusted to 6.50 ± 0.05 .

In the DCMD scaling tests, membrane coupons were placed in a custom-built flow cell that possessed an effective membrane area of 20 cm^2 . For the PVDF-PVA membrane, the PVA-modified surface contacted the hotter feed solution, whereas the unmodified surface faced the colder distillate stream. The temperatures of feedwater and deionized distillate were maintained at 60°C and 20°C , respectively. The crossflow velocities of the feed and distillate streams were 9.6 cm/s (0.45 L/min) and 6.4 cm/s (0.3 L/min), respectively. The weight and conductivity of the solution in the distillate reservoir were monitored continuously with a digital balance (EW-10001-05, Cole-Parmer) and a calibrated conductivity meter (Oakton Instruments), respectively. Accordingly, the water vapor flux and salt removal efficiency were calculated. Dynamic light scattering (DLS, Zetasizer Nano S90, Malvern Panalytical) measurement was performed during the DCMD test, in order to monitor the changes of hydrodynamic diameter of the particles

formed in the solution containing 6 mM $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ with time. In brief, samples were collected from the feed reservoir every 90 minutes and analyzed immediately by DLS. Eight samples were measured with 5 independent measurements performed for each sample.

The membrane coupons after the scaling tests were gently rinsed with DI water (to remove the feed solution on the membrane surface) and dried in the air, followed by analysis using SEM coupled with energy-dispersive X-ray (EDX) spectroscopy (JEOL JSM-6500F). The top-view surface of the membranes was imaged to investigate the morphology, location, and chemical composition of scales present on the membrane surface.

3.3 Results and Discussion

3.3.1 Characterization of membrane surface wettability

The pristine PVDF membrane was modified with two approaches to tune the surface wettability. In the first approach, a hydrophilic polymer (i.e., PVA) was used to coat the membrane surface, resulting in a Janus PVDF membrane with a hydrophilic top layer. In the second approach, PVDF membrane with superhydrophobicity was fabricated by incorporating SiNPs onto the membrane surface followed by silanization with 17-FAS.

SEM was utilized to visualize the surface morphologies of pristine PVDF membrane, PVDF-PVA membrane, and PVDF-SiNP-FAS membrane. As shown in Figures 3-1, no difference was observed in the morphologies of pristine PVDF membrane and PVDF-PVA membrane, due to the ultra-thin PVA layer coated on the surface of PVDF substrate. In contrast, spherical nanoparticles with an average diameter of ~30 nm were clearly present on the surface of PVDF-SiNP-FAS membrane (Figure 3-1F). The introduction of SiNPs imparted the membrane surface with a hierarchical texture. After being treated with the fluorine-rich 17-FAS,

the combination of hierarchical texture and ultralow surface solid energy materials would provide the PVDF-SiNP-FAS membrane with superhydrophobic property (Kota et al., 2014).

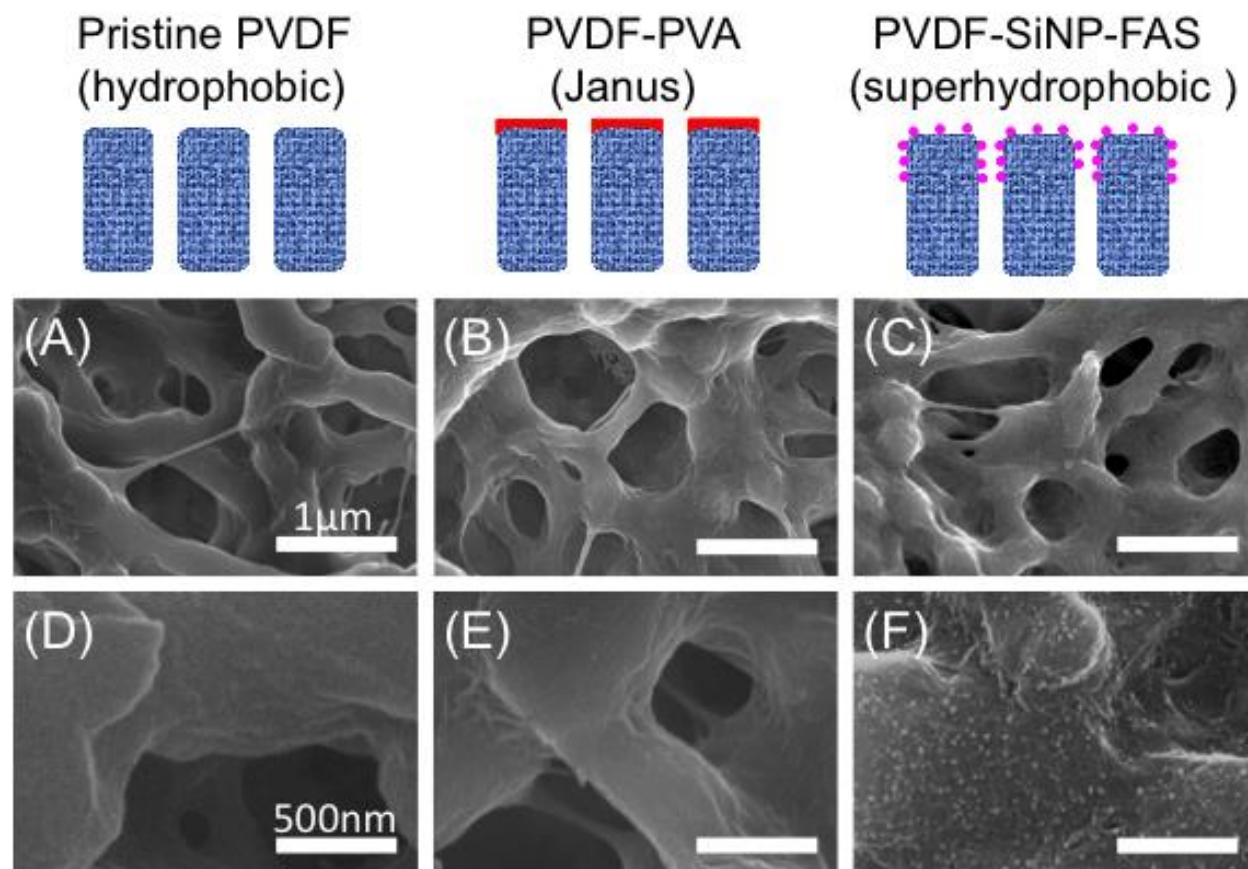


Figure 3-1. SEM micrographs of pristine PVDF (A, D), PVDF-PVA (B, E) and PVDF-SiNP-FAS (C, F) membranes, with magnifications of 30,000 $\times$ (A-C) and 80,000 $\times$ (D-F), respectively.

Surface wettability of all the three membranes was tested by measuring the static water contact angles and the sliding angles (Figure 3-2A). PVDF-PVA membrane had a static water contact angle of $56 \pm 5^\circ$, which was much lower than pristine PVDF membrane ($116 \pm 4^\circ$). As expected, PVDF-SiNP-FAS membrane possessed the highest static water contact angle of $150 \pm 1^\circ$. When measuring the sliding angle, the water droplet failed to move on the surface of the pristine PVDF membrane and PVDF-PVA membrane, both of which did not display sliding of water droplets. In contrast, the water droplet started to slide on the surface of PVDF-SiNP-FAS

membrane when the membrane was tilted around 17°. The unique slippery property of PVDF-SiNP-FAS membrane was also confirmed by the dynamic surface wettability test (Figure 3-2B). The pristine PVDF membrane and PVDF-PVA membrane showed no bouncing of the water droplet, which settled on the membrane surface stably during the test. However, the water droplet bounced back to the air immediately when contacting with the surface of PVDF-SiNP-FAS membrane, indicating the low adhesion between the water droplet and the membrane surface. The results above indicate that PVDF-SiNP-FAS membrane was able to repel water strongly, whereas the pristine PVDF membrane and PVDF-PVA membrane had higher adhesion to water.

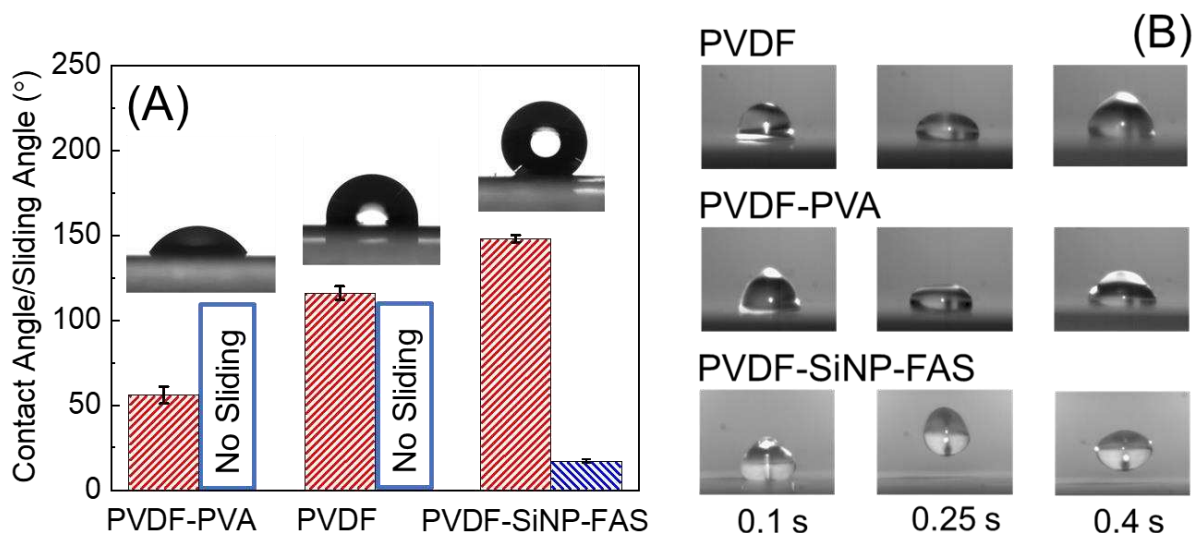


Figure 3-2. (A) Static contact angles (red column) and sliding angles (blue column) of PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes. (B) Dynamic surface wettability of the membranes assessed by recording the behavior of a water droplet on the membrane surface. The water droplets adhered to the PVDF and PVDF-PVA membrane surfaces upon contacting, while it completely rebounded on the PVDF-SiNP-FAS membrane surface.

3.3.2 Membrane performance in silica scaling and different saturation conditions

The performance of the pristine PVDF membrane, PVDF-PVA membrane, and PVDF-SiNP-FAS membrane was investigated by exposing the membranes to silica-containing feed solutions in dynamic DCMD experiments. The changes of water vapor flux and distillate

conductivity with time were used to monitor the extent of silica scaling and the potentially induced membrane wetting. Two different initial silica concentrations (saturation indices of -0.82 and 0.55) were used to investigate the effects of saturation condition on the membrane behavior. The initial water vapor fluxes were $30.8 \pm 0.6 \text{ L m}^{-2} \text{ h}^{-1}$, $32.2 \pm 0.9 \text{ L m}^{-2} \text{ h}^{-1}$, and $24.9 \pm 1.4 \text{ L m}^{-2} \text{ h}^{-1}$ for the pristine PVDF membrane, PVDF-PVA membrane and PVDF-SiNP-FAS membrane, respectively (Figure A1, Appendix A). Thus, normalized water fluxes are presented as functions of both time (Figures 3-3A and 3-3C; Figures A2A and A2C, Appendix A) and cumulative permeate volume (Figures 3-3B and 3-3D; Figures A2B and A2D, Appendix A) in order to better compare the membrane performance.

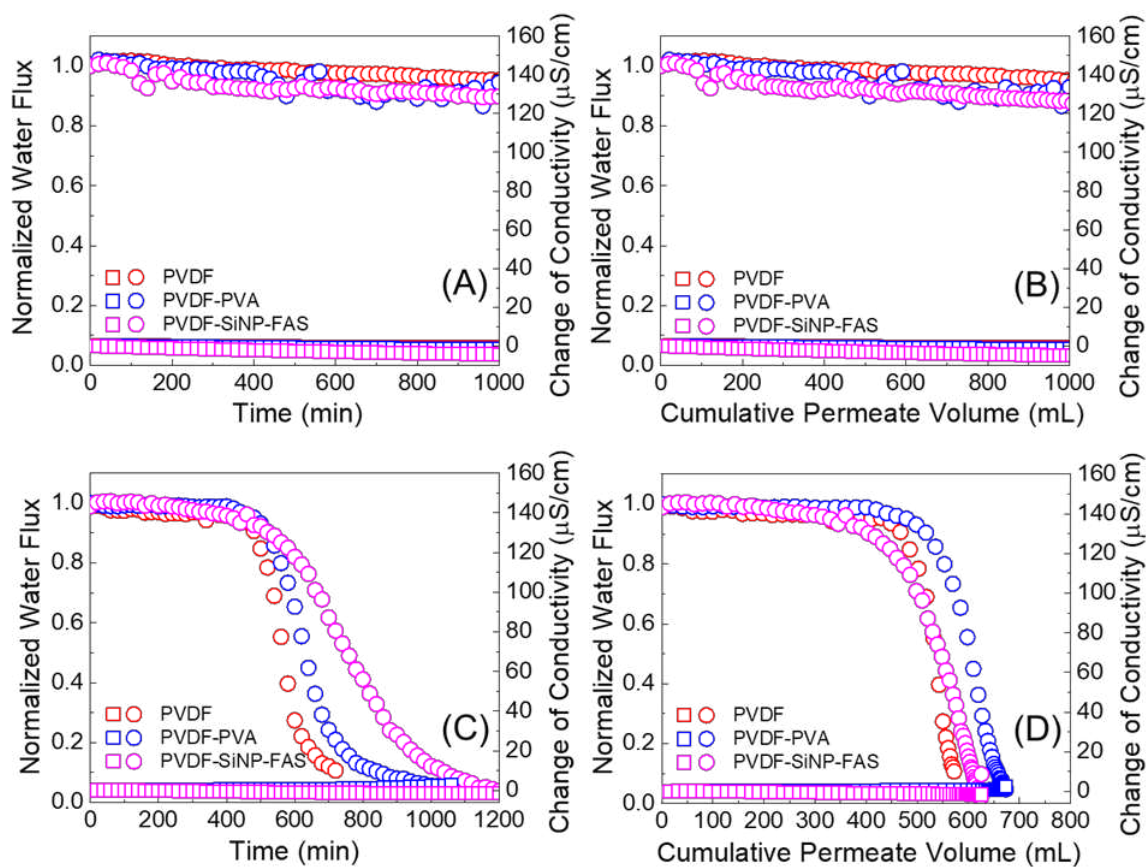


Figure 3-3. Normalized water flux and change of distillate conductivity of PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes during the DCMD scaling experiment. The feedwater contained 50 mM NaCl, 1 mM NaHCO₃, as well as 1.5 mM Na₂SiO₃·5H₂O (A, B) or 6 mM Na₂SiO₃·5H₂O (C, D) at pH of 6.50 ± 0.05 . The crossflow velocities in the feed and distillate streams were 9.6 cm/s and 6.4 cm/s,

respectively. The temperatures for feed and distillate streams were maintained at 60°C and 20°C, respectively. The initial volume of feed solution was 1500 ml. The initial water vapor fluxes were $30.8 \pm 0.6 \text{ L m}^{-2} \text{ h}^{-1}$, $32.2 \pm 0.9 \text{ L m}^{-2} \text{ h}^{-1}$, and $24.9 \pm 1.4 \text{ L m}^{-2} \text{ h}^{-1}$ for PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes, respectively.

When the initial saturation index of silica was -0.82, the water vapor fluxes of all the tested membranes remained >90% of the initial values for 1000 min, with no significant flux decline observed in the DCMD experiment (Figures 3-3A and A2A). Also, relatively stable water vapor fluxes were maintained when 1000 mL of deionized distillate had been collected (Figures 3-3B and A2B). Under this condition, the concentration of silica was under-saturated initially, while it became saturated (saturation index of 0.27 considering an initial feedwater volume of 1500 mL) at the conclusion of the experiment. Therefore, considering concentration polarization (Uchymiak et al., 2008) and the facilitating effect of a foreign substrate (Tong et al., 2019) (i.e., membrane surface in this study) on mineral nucleation, heterogeneous nucleation was easier to occur than homogeneous nucleation during the scaling test. As shown in Figures 3-4A – 3-4C, numerous particles were clearly present on the surface and in the pores of all the tested membranes after the scaling tests, and SEM-EDS analysis confirmed that the chemical compositions of those particles were silica (Figure 3-5A – 3-5C). Therefore, silica scales were indeed formed on the membrane surface (which was more likely due to heterogeneous nucleation), though the formation of silica scales did not significantly affect the water vapor flux during the DCMD experiments. The feedwater and/or water vapor might still be able to penetrate through the scale layer, due to the loosely connected silica particles on the membrane surface.

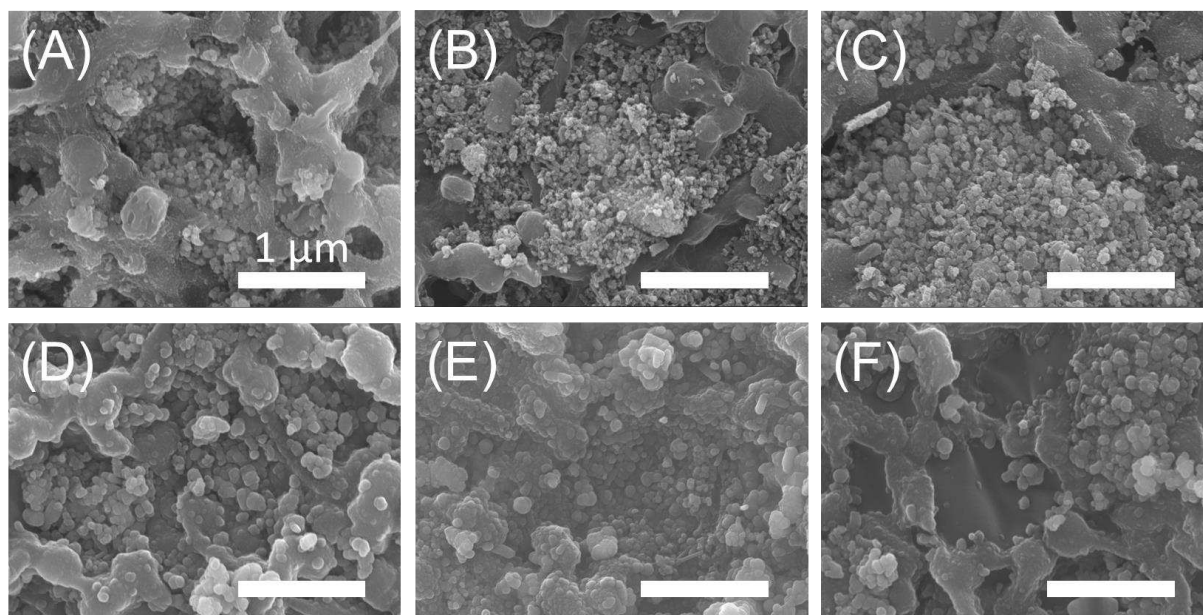


Figure 3-4. SEM micrographs of PVDF (A and D), PVDF-PVA (B and E) and PVDF-SiNP-FAS (C and F) membranes after DCMD silica scaling experiments. The concentrations of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ were 1.5 mM (A to C) and 6 mM (D to F).

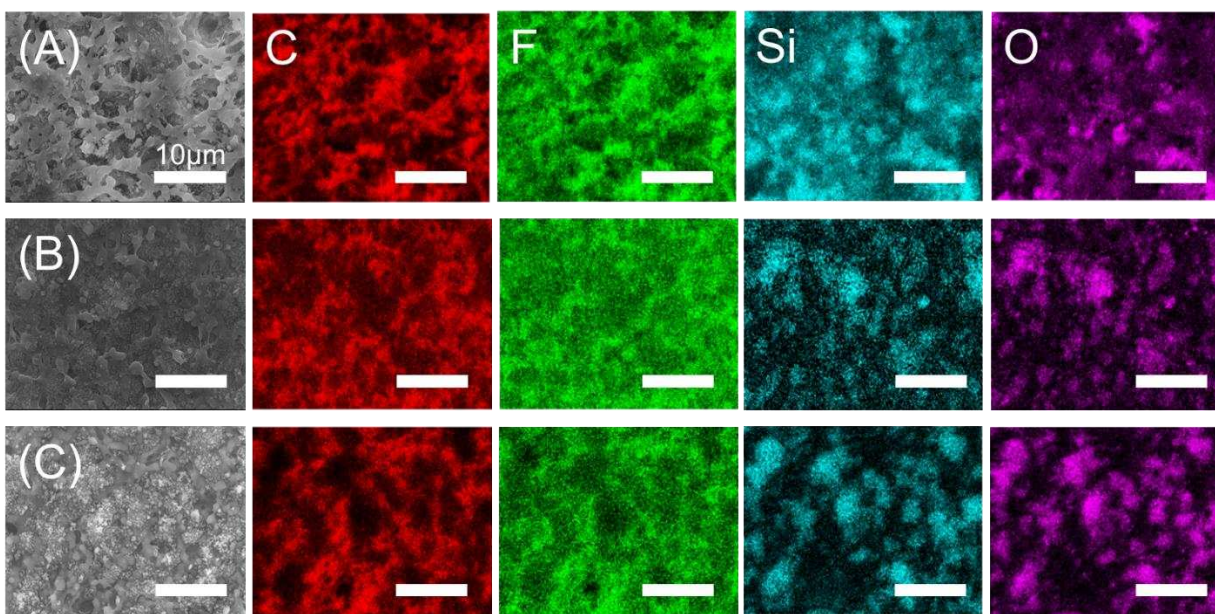


Figure 3-5. SEM-EDS elemental analysis of the PVDF (A), PVDF-PVA (B) and PVDF-SiNP-FAS (C) membranes (top-view) after DCMD silica scaling experiments. The concentration of silica in the feed solution was 1.5 mM. The SEM-EDS analysis of scaled membranes exposed to 6 mM silica is presented in Figure A4 of the Supporting Information.

When the initial saturation index of silica was 0.55, a rapid reduction of water vapor flux as a function of both time and cumulative permeate volume was observed for all the membranes in MD (Figures 3-3C and 3-3D; Figures A2C and A2D). Under this condition, silica particles were able to form in the bulk solution via homogeneous nucleation at the onset of the DCMD tests, as evidenced by the DLS measurement (Figure A3, Appendix A). Although the water flux decline started at almost the same time for the tested membrane materials, PVDF-SiNP-FAS membrane displayed a slower rate of flux decline with time than the pristine PVDF membrane and PVDF-PVA membrane (Figures 3-3C and A2C). This phenomenon was likely due to the lower initial water flux of PVDF-SiNP-FAS membrane, which resulted in a lesser extent of concentration polarization (the concentration polarization moduli of Na_2SiO_3 for the pristine PVDF membrane, PVDF-PVA membrane, and PVDF-SiNP-FAS membrane were 1.7, 1.7, and 1.5, respectively, with the calculation detailed in the Appendix A). However, when the water vapor fluxes are presented as a function of cumulative permeate volume (Figures 3-3D and A2D), PVDF-PVA membrane performed slightly better than the pristine PVDF and PVDF-SiNP-FAS membrane in terms of total water recovery, because of its highest initial water vapor flux (Figure A1). This phenomenon was different from the recent results reported by Karanikola et al. (Karanikola et al., 2018) that superhydrophobic, slippery membrane showed superior resistance against gypsum scaling even as evaluated by cumulative permeate volume. Therefore, we also compared the MD performance between pristine PVDF membrane and PVDF-SiNP-FAS membrane in gypsum scaling. As shown in Figure 3-6, PVDF-SiNP-FAS membrane possessed better resistance to gypsum scaling when the water vapor flux was expressed as a function of both time and cumulative permeate volume. This result suggested that the scaling resistance of superhydrophobic, slippery membranes is more notable in gypsum scaling than in

silica scaling. Although this discrepancy is beyond the scope of the current study (i.e., focusing on the mechanism of only silica scaling), the difference between gypsum and silica scaling as well as the associated mechanisms are being investigated in our ongoing work.

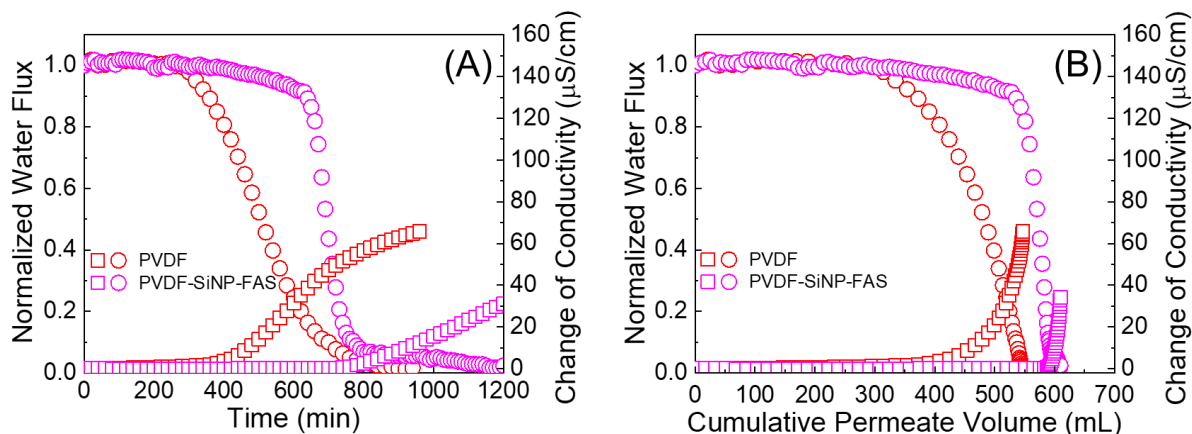


Figure 3-6. Normalized water flux and change of distillate conductivity of PVDF (red) and PVDF-SiNP-FAS (pink) membranes during DCMD experiments with gypsum scaling. The feed solutions contained 20 mM CaCl_2 , 20 mM Na_2SO_4 , and 50mM NaCl . The crossflow velocities in the feeding and permeating streams were 9.6 cm/s and 6.4 cm/s, respectively. The temperatures for feed and distillate streams were maintained at 60°C and 20°C, respectively. The initial volume of feed solution was 1500 ml. The initial water vapor fluxes were $30.9 \text{ L m}^{-2} \text{ h}^{-1}$ and $25.5 \text{ L m}^{-2} \text{ h}^{-1}$ for PVDF and PVDF-SiNP-FAS membranes, respectively.

As shown in Figures 3-4D – 3-4F, the scale layers formed under a high initial silica concentration (i.e., saturation index of 0.55) displayed different morphologies from those formed under a lower initial silica concentration (i.e., saturation index of -0.82). Larger particulate scales were observed on the membrane surface, with the structure of PVDF membrane not visible (Figures 3-4D – 3-4F). The sizes of scale particles (100–200 nm) were consistent with the hydrodynamic diameters measured by DLS (Figure A3), indicating that those particles might be formed in the bulk solution and deposited onto the membrane surface. Further, the scale layer formed under high silica concentration exhibited a compact and gel-like morphology, which completely covered the membrane surface and was likely responsible for the dramatic flux decline during the DCMD experiments. The results of SEM-EDS analysis confirmed the

chemical composition of silica for the scale layers (Figure A4, Appendix A). Under both silica concentrations, the electrical conductivity of the distillate stream remained unchanged throughout the DCMD experiments, indicating that membrane wetting did not occur regardless of silica concentrations present in the feedwater or the water flux behaviors of the tested membranes. The negligible wetting in silica scaling was consistent with the observations by Bush et al. (Bush et al., 2018)

3.3.3 Proposed mechanisms of silica scaling in membrane distillation

In the current study, we compared MD behaviors of PVDF membranes with varied surface wettability in silica scaling under two different saturation conditions. With an initially under-saturated feed solution (saturation index of silica at -0.82), the water vapor fluxes of all the tested membranes were not significantly affected during the experiments (Figures 3-3A and 3-3B), despite the formation of silica scales likely due to heterogeneous nucleation. With a higher silica concentration in the feedwater (initial saturation index of silica at 0.55), all the membranes showed dramatic reduction of water vapor flux, with the starting point of water flux decline independent of membrane surface wettability (Figures 3-3C and 3-3D). Hence, the flux decline caused by silica scaling in the MD process seemed to be controlled by the feed solution rather than membrane material. As a result, homogeneous nucleation of silica in the feed solution, instead of heterogeneous nucleation on the membrane surface, was likely to play a more important role in initiating the water vapor flux decline due to silica scaling during MD desalination.

In order to further investigate the specific roles that homogeneous nucleation and heterogeneous nucleation play in MD silica scaling, we performed additional DCMD tests of colloidal silica fouling, in which 360 mg/L silica particles (equivalent to a molar concentration of

6 mM SiO_2) rather than silicate salts (i.e., $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) was added into the feed solution. By doing so, membrane-mediated heterogeneous nucleation was excluded in the MD experiments. As shown in Figure 3-7 and Figure A5 (Appendix A), all the membranes were subjected to a sharp flux decline after a period of relatively stable water vapor flux, which was similar to the water flux profiles observed in the silica scaling experiments. Also, no membrane wetting was observed during colloidal silica fouling. However, the rates of water vapor flux decline caused by colloidal silica fouling were slower than those caused by silica scaling. Compared to the scaling layer formed from silica scaling with 6 mM $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, the foulant layer formed by colloidal silica particles with the same molar content (Figure 3-8) was consisted of smaller particles without the gel-like morphology as observed in Figures 3-4D – 3-4F. These differences observed between silica scaling and colloidal silica fouling suggested that the water flux decline caused by silica scaling in MD was not exclusively due to the deposition of silica particles from the feed solution. In silica scaling experiments, the silica particles deposited on the membrane surface were still able to react with silicic acids and other soluble silica species in the solution, forming a cross-linked silica layer (between the silica particles) that demonstrated the compact and gel-like morphology. This self-inducing silica-silica interaction, which was absent in colloidal silica fouling, facilitated water vapor flux decline in silica scaling, because the compact silica layer prevented the penetration of feed solution or water vapor. As a result, both homogeneous nucleation and heterogeneous nucleation were responsible for water flux decline caused by silica scaling in the MD process.

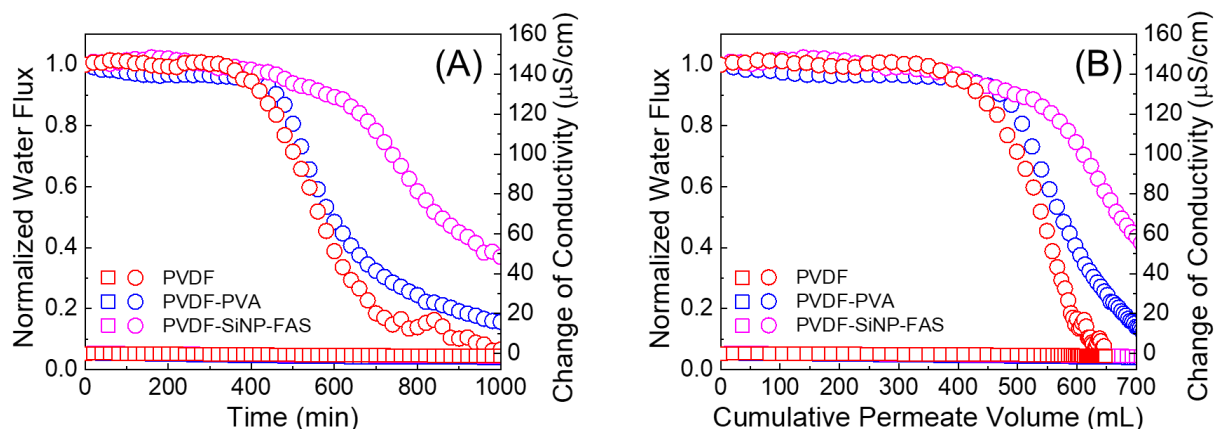


Figure 3-7. Normalized water flux and change of distillate conductivity of PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes during DCMD experiments with colloidal silica fouling. The feed solutions contained 50 mM NaCl, 1 mM NaHCO₃, and 360 mg/L silica colloidal particles at pH of 6.50 ± 0.05 . The crossflow velocities in the feed and distillate streams were 9.6 cm/s and 6.4 cm/s, respectively. The temperatures for feed and distillate streams were maintained at 60°C and 20°C, respectively. The initial volume of feed solution was 1500 ml. The initial water fluxes were 30.7 L m⁻² h⁻¹, 31.7 L m⁻² h⁻¹, and 25.3 L m⁻² h⁻¹ for PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes, respectively. The replicate results from independent MD experiments are presented in Figure A5 of the Appendix A.

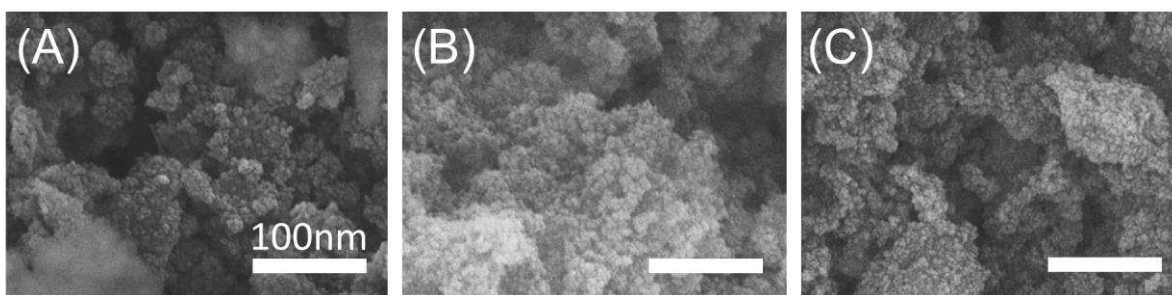


Figure 3-8. SEM micrographs of PVDF (A), PVDF-PVA (B) and PVDF-SiNP-FAS (D) membranes after DCMD experiments with colloidal silica fouling. The concentration of silica particles was 6 mM. Note that in contrast to silica scaling (Figure 3-4D – 3-4F), no compact and gel-like scale layer was observed.

Furthermore, PVDF-SiNP-FAS membrane exhibited better MD performance than the other two membranes in colloidal silica fouling, even when the membrane performance was evaluated as a function of cumulative permeate volume (Figures 3-7 and A5). This phenomenon, which was different from what had been observed in silica scaling, also indicated the mechanistic difference between silica scaling and colloidal silica fouling. In colloidal silica fouling, all the silica was in the form of particles at the beginning of the MD experiments. The deposition of

silica particles onto PVDF-SiNP-FAS membrane, which was responsible for the water flux decline, was mitigated due to the reduced contact of feed solution with the superhydrophobic and slippery surface. In contrast, a majority of silica was initially in the form of soluble precursors (i.e., $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) in silica scaling experiments. The accumulation of sufficient silica particles to induce water flux decline required a certain time, during which the surface of PVDF-SiNP-FAS membrane become more hydrophilic due to the adsorption of silicic acids and silica particles. In order to test this hypothesis, we performed additional silica scaling experiments with PVDF-SiNP-FAS membrane for 3 hours, well before the onset of water vapor flux decrease (Figure A6, Appendix A). When the membrane was taken out of the flow cell, it was found that the membrane surface exposed to the feed solution became not superhydrophobic, although the surface facing the permeate stream maintained its original surface property (Figure A7, Appendix A). At this point, the contact with feed solution for PVDF-SiNP-FAS membrane was similar to that for the pristine PVDF and PVDF-PVA membranes, and thus the flux decline started at almost the same time for all the three tested membranes.

Based on the discussions above, we propose a four-step mechanism of silica scaling in the MD process, which is schematically presented in Figure 3-9. In the first step, silica particles are formed via polymerization of silicic acid if the bulk solution is supersaturated (homogenous nucleation), while heterogeneous nucleation also takes place on the membrane surface. At this stage, the number of silica particles is insufficient to cause flux decline, and heterogeneous nucleation poses a negligible impact on water vapor flux. As a result, the water vapor flux was maintained stably. In the second step, enough silica particles have been accumulated and deposited on the membrane surface after a certain “induction time”, when the water vapor flux starts to decrease. Afterwards, the water flux keeps decreasing due to continuous deposition of

silica particles (Step 3). Meanwhile, the reactions between the deposited silica particles and remaining silica species in the feed solution (heterogeneous nucleation, Step 4) form a cross-linked silica network on the membrane surface, resulting in the compact and “gel-like” silica layer that further reduces the water vapor flux. This proposed mechanism indicates that the water flux decline caused by silica scaling in MD is due to a combined effect of both homogeneous nucleation and heterogeneous nucleation. Homogeneous nucleation plays a major role to initiate water flux decline, followed by the occurrence of heterogeneous nucleation that expedites the decrease of water productivity. As a result, membrane surface wettability did not impose a significant influence on MD water productivity in the presence of silica scaling in our study. However, it should be noted that our findings do not depreciate the efforts of developing MD membranes with improved scaling resistance. Recently, membranes with superior slippery property have demonstrated exceptional resistance to mineral scaling in MD (Xiao et al., 2019a; Xiao et al., 2019b). Since these membranes have ultra-low sliding angles of $< 5^\circ$, which were smaller than that of the superhydrophobic membrane used in the current study, it is possible that such “super-slippy” membranes would display improved silica scaling resistance, if their superhydrophobicity could be maintained when sufficient silica particles have been accumulated in the feed solution. In those two studies, micro-pillar arrays with spacing of $>5\text{ }\mu\text{m}$ were used to create re-entrant structure. Such long spacing resulted in a high volume of air pocket between the pillars, creating exceptional slippery property that could not be achieved by our PVDF membrane that has a nominal pore size of only $0.45\text{ }\mu\text{m}$. Alternatively, other strategies that delay or prevent the formation and deposition of silica particles, such as altering the hydrodynamic condition and removing silica from feedwaters prior to MD, are also worthy of investigation in future efforts of mitigating silica scaling in MD desalination.

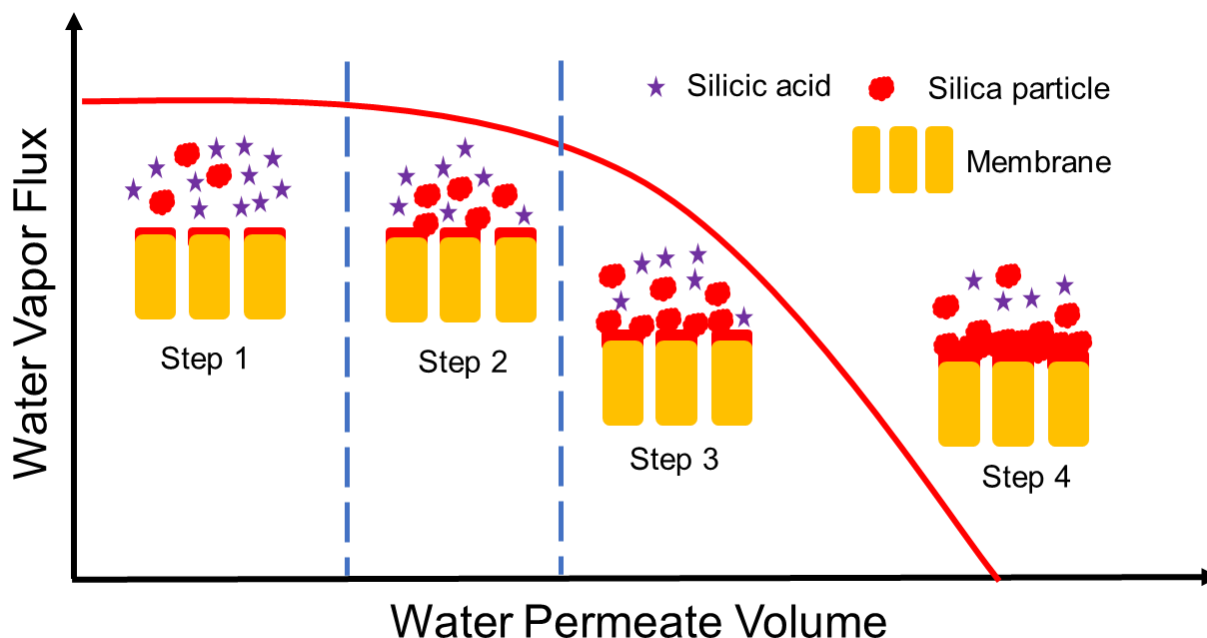


Figure 3-9. Schematic description of silica scaling mechanisms in membrane distillation. A four-step mechanism is proposed, including (1) formation of silica particles in the bulk solution and heterogeneous silica nucleation on the membrane surface; (2) deposition of silica particles on the membrane surface; (3) further deposition and accumulation of silica particles on the membrane surface; and (4) formation of ‘gel-like’ silica layer due to the interactions between silica particles on the membrane surface and soluble silica precursors in the solution. Note that Steps 3 and 4 could occur at the same time.

3.4 Conclusions

The effects of membrane surface wettability on silica scaling in MD were investigated by comparing the performance of three PVDF membranes with varied surface wettability, which revealed the underlying scaling mechanism. With an initially under-saturated feed solution (saturation index = -0.82), the water vapor fluxes of all the tested membranes were maintained relatively stable during the experiments, despite the formation of silica scales likely due to heterogeneous nucleation. With a supersaturated feed solution (saturation index = 0.55), all the membranes experienced a dramatic reduction of water vapor flux, which started at almost the same time regardless of membrane materials. Thus, silica particles formed in the feed solution via homogenous nucleation were likely to play a major role in initiating the water vapor flux

decline. The slippery superhydrophobic membrane exhibited the slowest flux decline rate with time, but the Janus membrane with hydrophilic surface coating displayed the best water productivity. Microscopic observation of the scale layer morphology, along with the comparison between silica scaling and colloidal silica fouling, provided explicit evidence that homogenous nucleation was not the exclusive scaling mechanism, and indicated that the interaction of silica particles deposited on the membrane with soluble silica species in the feedwater facilitated water flux decline. Accordingly, a four-step mechanism was proposed for silica scaling in MD, involving both homogenous and heterogeneous nucleation. As a result, hydrophilic coating or superhydrophobic surface with the slippery degree in this study was unable to markedly mitigate silica scaling in MD. Other strategies, which delay or prevent the formation and deposition of silica particles in the feed solution (e.g., altering the hydrodynamic conditions and removing silica from the feedwater), is worthy of investigation in future efforts of mitigating silica scaling in MD desalination.

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4.0 The Effects of Membrane Surface Wettability on Pore Wetting and Scaling Reversibility Associated with Mineral Scaling in Membrane Distillation³

4.1 Introduction

Membrane distillation (MD) is a thermal-driven membrane desalination technique, which is able to treat hypersaline wastewater and leverage low-grade heat (Alkhudhiri et al., 2012; Deshmukh et al., 2018; Lawson and Lloyd, 1997). The temperature difference between feed and distillate streams generates a gradient in vapor pressure that drives the transport of water vapor through microscale pores of a hydrophobic membrane (Alkhudhiri et al., 2012; Lawson and Lloyd, 1997; Thomas et al., 2017; Tijing et al., 2015). Compared to pressure-driven desalination technologies such as reverse osmosis (RO), MD is less constrained by feedwater salinity due to its thermal nature, allowing complete rejection of nonvolatile components (Deshmukh et al., 2018). However, mineral scaling in MD, which refers to the deposition or formation of inorganic scales on the membrane surface, is a major challenge that compromises MD performance in practical (Tijing et al., 2015; Tong et al., 2019). Membrane scaling in MD results in the decline of water vapor flux and membrane pore wetting (Karanikola et al., 2018; Su et al., 2019; Tong et al., 2019; Xiao et al., 2019b), causing a significant obstacle for commercial implementation of MD technology.

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Mineral scaling of MD involves the adhesion and coverage of minerals on the membrane surface, leading to enhanced resistance against the transport of water vapor through the porous membrane (Alkudhiri et al., 2012; He et al., 2008; Lawson and Lloyd, 1997; Tijting et al., 2015; Tong et al., 2019). The intrusion of feedwater, along with the in-pore scale crystallization, can also result in membrane wetting and subsequent contamination of the distillate (Christie et al., 2019; Rezaei et al., 2018). Crystallization and polymerization are two major mechanisms that govern the formation of mineral scales (Christie et al., 2019). For example, gypsum (i.e., calcium sulphate dihydrate) scaling is a representative type of scaling that is formed by a crystallization process, in which gypsum crystals are created on the membrane surface via the hydrated reaction between Ca^{2+} and SO_4^{2-} ions (Christie et al., 2019; Gryta, 2009; Mi and Elimelech, 2010; Rice et al., 2020; Warsinger et al., 2017). In contrast, amorphous silica scale layer, which also causes damaging effects in MD, is produced via a polymerization process between silicic acid molecules and gelation of silica particles (Mi and Elimelech, 2013; Sheikholeslami et al., 2002; Yin et al., 2019). In addition, depending on the initial concentrations of scale precursors, the scaling process might be a combination of homogeneous nucleation and heterogenous nucleation (Antony et al., 2011; Shaffer et al., 2017; Tijting et al., 2015). Distinct scaling mechanisms can result in dramatically different membrane performance. In our previous study (Christie et al., 2019), we compared the behaviors of gypsum and silica scaling in MD desalination. The fundamental difference in mechanisms of gypsum and silica scaling led to a more rapid kinetics of gypsum scaling than silica scaling. More importantly, due to the oriented growth of gypsum crystals that deforms the membrane structure, the in-pore invasion of gypsum crystals could induce membrane pore wetting, which was not noticed in silica scaling (Christie et al., 2019).

Recently, tuning membrane surface wettability has been utilized to mitigate mineral scaling in MD. Superhydrophobic membranes with slippery property were found to reduce the extent of water vapor flux decline caused by gypsum scaling (Karanikola et al., 2018; Su et al., 2019; Xiao et al., 2019a). The smaller contact area of membrane surface with the feedwater reduces the area available for scale formation on superhydrophobic membranes, while the slippery property decreases the local residence time for scalant-membrane interaction (Su et al., 2019; Xiao et al., 2020). According to the classical nucleation theory, surface with lower surface energy also provides a higher thermodynamic energy barrier to scale formation from heterogeneous nucleation (Erdemir et al., 2009; Karanikola et al., 2018). However, such mitigating effect is uncertain for silica scaling. In our recent publication (Yin et al., 2019), superhydrophobic membrane failed to reduce the water flux decline caused by silica scaling. Therefore, the relationship between membrane surface wettability and mineral scaling as a function of scaling type in MD needs further investigation. A comparative investigation of gypsum and silica scaling on membranes with varied surface wettability is of great value to provide further insights on membrane design and scaling mitigation for MD applications.

In addition to water flux decline and pore wetting, the reversibility of membrane scaling is also an important parameter to evaluate membrane performance in MD. Scaling reversibility refers to whether the decrease of water vapor flux caused by scaling could be reversed after simple membrane cleaning. In other desalination processes such as RO, nanofiltration (NF), and forward osmosis (FO), the reversibility of organic, inorganic and biological fouling has been extensively investigated, and membrane cleaning successfully restored water flux after fouling occurred (Ang et al., 2006; Creber et al., 2010; Li and Elimelech, 2004; Matin et al., 2011; Mi and Elimelech, 2010; 2013). Recently, the performance of membrane cleaning in eliminating

organic fouling layer has also been evaluated in MD (Guillen-Burrieza et al., 2014; Martinetti et al., 2009; Nghiem and Cath, 2011). However, to the best of our knowledge, the reversibility of inorganic scaling in MD has not been well documented in the literature. Understanding the reversibility of different scaling types, in particular for membranes with varied surface wettability, is an essential step to improve the total water recovery and membrane lifespan of MD desalination.

In this study, we compared the scaling behaviors of gypsum and silica for membranes with varied surface wettability in MD. The effects of membrane surface wettability and scaling type on total water recovery, membrane pore wetting, and scaling reversibility were investigated systematically. A hydrophobic polyvinylidene fluoride (PVDF) membrane, a Janus PVDF membrane with a hydrophilic surface coating, and a superhydrophobic PVDF membrane were used as model membranes to analyze the scaling behaviors in direct contact membrane distillation (DCMD). The membranes were challenged with feed solutions containing gypsum and silica with the same saturation status. We evaluated water vapor flux, distillate conductivity, as well as flux recovery after membrane cleaning during scaling experiments. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were applied to analyze the morphology and intrusion of scales on and into the microporous membranes. Our study demonstrates that superhydrophobic membrane was able to delay scaling induction time, reduce membrane wetting, and enhance scaling reversibility of gypsum scaling. However, such mitigating effects were not applicable to silica scaling due to its different scaling mechanism. As a result, “fit-for-purpose” strategies of scaling mitigation might be needed for MD applications to the treatment of hypersaline wastewater containing different scalants.

4.2 Materials and Methods

4.2.1 Materials and chemicals

Polyvinyl alcohol (PVA, Mw of 13,000-23,000), glutaraldehyde (GA, 50wt% in water), (3-aminopropyl)triethoxysilane (APTES, $\geq 98\%$), LUDOX HS-30 colloidal silica (30 nm, 30% suspension in water), sodium sulfate (Na_2SO_4), sodium metasilicate pentahydrate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) and sodium bicarbonate (NaHCO_3) were all supplied by Sigma-Aldrich (St. Louis, MO, USA). Silica nanospheres of 120 nm were purchased from NanoComposix (San Diego, CA, USA). (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)-triethoxysilane (17-FAS) was obtained from Gelest Inc (Morrisville, PA, USA). Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), sodium chloride (NaCl), sodium hydroxide (NaOH), hexane, and hydrochloric acid (HCl , 36%) were acquired from Fisher Chemical (Hampton, NH, USA). Pure anhydrous ethanol (200 Proof) was provided by Decon Laboratories (200 proof, King of Prussia, PA, USA). PVDF membranes (HVHP, Millipore Sigma, Burlington, MA, USA) with a nominal pore size of 0.22 μm were used as the control MD membranes. Deionized (DI) water was supplied from a water purification system ($>18\text{M}\Omega$, Millipore, Burlington, MA, USA).

4.2.2 Approaches of membrane surface fabrication

A hydrophilic layer of PVA was coated onto the surface of the pristine PVDF membrane in order to make a Janus membrane possessing hydrophilic surface and hydrophobic substrate (Zhang et al., 2008). In brief, the dissolution of 1 g PVA in 100 mL DI water was completed for at least 12 h with a temperature $> 90\text{ }^\circ\text{C}$. The pH of the PVA solution was adjusted to 2 by 1 M HCl and 1 M NaOH solutions after the PVA solution cooled down to the room temperature. Then, 1 ml of GA was added into the 100 mL PVA solution. After stirring for 10 min, the PVA-GA mixture solution was poured onto the surface of the pristine PVDF membrane, which was placed in the heating oven under $60\text{ }^\circ\text{C}$ for 1 h. The membrane was then rinsed with DI water and

dried by flushing the membrane gently with nitrogen gas. The fabricated membrane is referred to as PVDF-PVA membrane in this study.

The superhydrophobic surface of the membrane was created by incorporating materials with ultra-low surface energy (i.e., 17-FAS) and a hierarchical texture provided by the grafting of two layers of silica nanoparticles (SiNPs) on the membrane surface (Boo et al., 2016b). The grafting of multi-layer particles is important to create PVDF membrane with a high level of slippery property (i.e., low contact angle hysteresis, CAH) (Luo et al., 2017). In brief, the pristine PVDF membrane was immersed into 7.5 M NaOH solution for 3 h at 70 °C after being fully wetted by ethanol. Then the membrane surface was imparted with positive charges by grafting amine groups via immersing the membrane in 1% v/v APTES ethanol solution for 1 h. The PVDF-APTES membrane was rinsed with ethanol and dried at 80 °C for 30 min. Then the membrane was fully wetted by ethanol and soaked in the solution of SiNPs (120 nm, 0.03wt%% in acetic buffer solution of pH 4) for 1 h. The membrane with one layer of SiNPs was washed by DI water and dried under 80 °C for 1 h. Then the modification procedures associated with APTES and SiNPs were repeated to graft a layer of 30 nm SiNPs on the membrane surface. The membrane grafted with two layers of SiNPs was rinsed with DI water and dried in the oven. A hexane solution with 0.5% v/v 17-FAS was then applied to the membrane and incubated overnight. The membrane was then washed with hexane and dried on a hotplate at > 80 °C overnight. The fabricated membrane is referred to as PVDF-SiNP-FAS membrane in this study.

4.2.3 Membrane characterization

The water contact angles (WCA) of membranes were measured by a contact angle goniometer (Ramé-hart Instrument Corporation, Succasunna, NJ, USA) using a sessile drop method. The sliding angle (SA) was also recorded when the water droplet started sliding on the

tilted membrane surface. Morphology analysis of top-view and cross-section of membranes as well as the corresponding elemental distribution were performed using SEM coupled with EDX spectroscopy (JEOL JSM-6500F, Peabody, MA, USA). The SEM samples were fully dried and coated with a 10-nm gold layer by a sputter coater (Denton Desk IV, Denton Vacuum, Moorestown, NJ, USA).

4.2.4 Experimental setup for scaling in membrane distillation

A lab-scale DCMD system with a membrane coupon of 20 cm² was used to evaluate the scaling performance of the pristine and modified PVDF membranes. The changes of electrical conductivity and weight in the distillate reservoir were monitored by a conductivity meter (Oakton Instrument, Vernon Hills, IL, USA) and a digital balance (EW-100001-05, Cole-Parmer, Vernon Hills, IL, USA) throughout the experiment. The real-time water vapor flux and salt rejection were calculated accordingly. Two feed solutions were used to compare the scaling behavior of gypsum (1000 mL) and silica scaling (1500 mL). The first solution contained 18 mM CaCl₂·2H₂O and 18 mM Na₂SO₄, while the second solution contained 3.2 mM Na₂SiO₃·5H₂O, 50 mM NaCl and 1 mM NaHCO₃. The initial saturation indices (SI, defined as the ratio of the ion activity product to the product solubility, IAP/K_{sp}) of both solutions were 0.93, calculated using the PHREEQC software and database WATEQ4F (PC Version). The solution pH for gypsum scaling was unadjusted, while the solution for silica scaling was adjusted to 6.5 ± 0.05. The temperatures were maintained at 60 °C and 20 °C for feed and distillate streams, respectively. The crossflow velocities of feed (9.6 cm s⁻¹) and distillate (6.4 cm s⁻¹) streams were maintained throughout the experiment. The feed and permeate streams were continuously circulating to mix the solutions throughout the experiments, and the MD distillate did not return to the feed solution but was collected in the distillate reservoir.

4.2.5 Scaling reversibility after physical membrane cleaning

The scaling reversibility was evaluated by performing physical membrane cleaning with DI water. At the conclusion of the DCMD scaling experiment, the feed solution was replaced with DI water and the membrane was rinsed with DI water under a high flow rate of 21.3 cm s^{-1} for 15 min in order to remove the scale layer on the membrane surface. After membrane cleaning, the feed solution was switched back to the previous feed solution containing scalants and continued the DCMD experiment. The water flux recovery rate (R) was measured using Eq. (4-1):

$$R = \frac{J_{0,r}}{J_{0,i}} \quad (4-1)$$

where $J_{0,r}$ is the recovered water vapor flux after membrane cleaning in MD, and $J_{0,i}$ is the initial water vapor flux before membrane scaling occurs.

The membrane samples after the scaling experiments (both with and without membrane cleaning) were rinsed gently with DI water for 30 s in removing the solution residual on the membrane surface. The membranes were then dried in air and preserved for SEM-EDX analysis, which was performed to evaluate the scale morphology and the elemental composition of membrane surface and cross-section before and after membrane cleaning.

4.3 Results and Discussion

4.3.1 The characterization of membrane surface properties

The membrane surface morphologies of the pristine PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes were evaluated by SEM (Figure 4-1). No morphological difference was noticed between PVDF-PVA membrane and the pristine PVDF membrane, indicating an ultra-thin coating of the PVA layer (Park et al., 2018; Zhang et al., 2008) (Figures 4-1A, 4-1B, 4-1D and 4-1E). In contrast, a significant change in surface morphology caused by the adhesion of the SiNPs on the membrane surface was observed for the PVDF-SiNP-FAS membrane (Figures 4-1C and

4-1F). Further, the hydrophilic property of the PVDF-PVA membrane surface was indicated by the WCA of $62.8 \pm 1.2^\circ$ (inset of Figure 4-1E), which is much lower than the WCA of the pristine PVDF membrane ($122 \pm 0.3^\circ$, inset of Figure 4-1D). The creation of a re-entrant structure by the attachment of SiNPs is crucial to provide the membrane with superhydrophobicity (Boo et al., 2016a; Tuteja et al., 2007), and the coating of 17-FAS on the membrane surface lowered the surface energy of the membrane. Such a synergetic effect of re-entrant structure and low surface energy led to a superhydrophobic membrane surface with a high WCA of $153 \pm 1.1^\circ$ (inset of Figure 4-1F). In addition, the incorporation of two different sizes of SiNPs (120 nm and 30 nm) was used to enhance the movement of water droplet on the surface of PVDF-SiNP-FAS membrane, which resulted in a slippery property that was proposed to be critical in scaling mitigation (Karanikola et al., 2018; Xiao et al., 2019a; Xiao et al., 2019b). The PVDF-SiNP-FAS membrane exhibited a low SA of $9 \pm 2.9^\circ$ (inset of Figure 4-1F), while the SA was unmeasurable ($> 90^\circ$) for the pristine PVDF and Janus PVDF-PVA membranes.

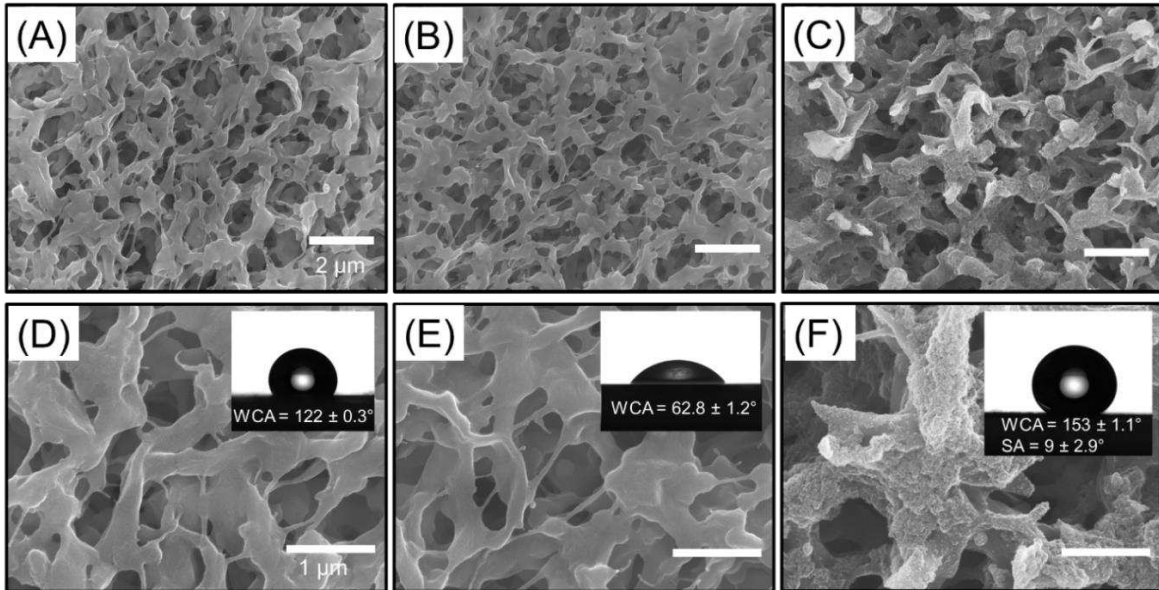


Figure 4-1. Top view SEM micrographs of (A, D) the pristine PVDF membrane, (B, E) PVDF-PVA membrane and (C, F) PVDF-SiNP-FAS membrane, with magnification of 10,000X and 30,000X. The

scale bars represent 2 μm (A-C) and 1 μm (D-F). The static water contact angle (WCA) and sliding angle (SA, if measurable) of the corresponding membranes are presented as insets.

4.3.2 The extent and reversibility of gypsum scaling in membrane distillation

The scaling performance of membranes with different surface wettability was assessed in gypsum-containing solution with an initial SI of 0.93. As shown in Figure 4-2A, all the membranes were subject to a water flux decline caused by gypsum scaling. The pristine PVDF and Janus PVDF-PVA membranes exhibited a similar performance in water vapor flux, with the flux started to decline at ~ 400 min (Figure 4-2A). However, the PVDF-PVA membrane suffered from membrane pore wetting at a very early stage of the experiment, indicated by the early increase in distillate conductivity (Figure 4-2C). In contrast, membrane pore wetting was not noticed for the pristine PVDF membrane until ~ 600 min (Figure 4-2C). The vulnerability of the PVDF-PVA membrane to pore wetting was likely due to the hydrophilic property of PVA coating. The easy contact of PVDF-PVA membrane with feedwater resulted in an early feedwater intrusion that led to in-pore crystal growth. The pristine PVDF membrane, which was benefited from its hydrophobic property, reduced the invasion of feedwater into membrane pores and delayed pore wetting. Comparing to both pristine PVDF and PVDF-PVA membranes, the superhydrophobic PVDF-SiNP-FAS membrane postponed the induction of water flux decline by ~ 100 min (Figure 4-2A). This phenomenon was consistent with the mitigating effect of membrane superhydrophobicity on gypsum scaling as reported in the literature (Karanikola et al., 2018; Su et al., 2019). However, since the PVDF-SiNP-FAS membrane exhibited a lower initial water vapor flux than the pristine and PVDF-PVA membranes, such a delay of water flux decline could also be partially due to the less extent of concentration polarization (CP, the CP moduli of $\text{CaCl}_2/\text{Na}_2\text{SO}_4$ for the pristine PVDF, PVDF-PVA, PVDF-SiNP-FAS membranes were 1.46/1.68, 1.48/1.70 and 1.37/1.54, respectively; the detail of calculation is described in the Appendix B).

In addition, no pore wetting was observed for the PVDF-SiNP-FAS membrane, which managed to maintain a high permeate quality without an increase in distillate conductivity throughout the experiment (Figure 4-2C). Therefore, our results demonstrate that superhydrophobic membrane, which has shown wetting resistance against amphiphilic or low-surface tension contaminants (e.g., surfactants and oil) (Hou et al., 2020; Huang et al., 2017; Wang and Lin, 2017), could also mitigate membrane pore wetting caused by gypsum scaling.

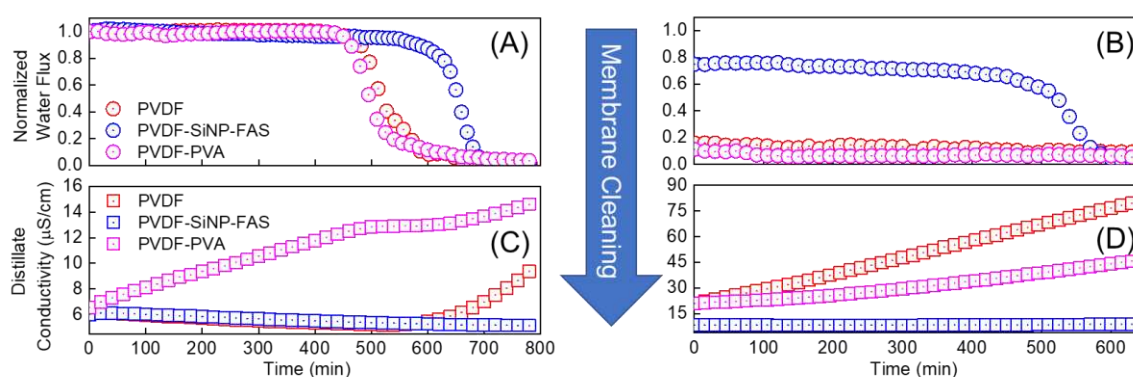


Figure 4-2. Normalized water vapor flux and distillate conductivity of the pristine PVDF, PVDF-SiNP-FAS and PVDF-PVA membranes as a function of time (A and C) before and (B and D) after physical membrane cleaning. The feed solution contains 18mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 18mM Na_2SO_4 . The temperatures of the feed and distillate solutions were maintained at 60 °C and 20 °C, respectively. The crossflow velocities of feed and distillate solutions were 9.6 cm/s and 6.4 cm/s, respectively. The initial water vapor fluxes of the pristine PVDF, PVDF-SiNP-FAS and PVDF-PVA membranes were 26.3 $\text{L m}^{-2} \text{h}^{-1}$, 21.9 $\text{L m}^{-2} \text{h}^{-1}$ and 27.7 $\text{L m}^{-2} \text{h}^{-1}$, respectively. These flux values are used to normalize the fluxes in all the figures. The recovered water vapor fluxes after membrane cleaning were 4.2 $\text{L m}^{-2} \text{h}^{-1}$, 16.4 $\text{L m}^{-2} \text{h}^{-1}$ and 3.1 $\text{L m}^{-2} \text{h}^{-1}$ for PVDF, PVDF-SiNP-FAS and PVDF-PVA membranes, respectively.

Scaling reversibility is an important factor to evaluate membrane performance in scaling tests, because higher scaling reversibility corresponds to a longer membrane lifespan and a higher degree of total water recovery. Therefore, physical membrane cleaning was applied to investigate the effect of membrane surface wettability on the reversibility of gypsum scaling. At the end of the first MD cycle, membrane cleaning was implemented with a high flow rate of 21.3 cm s^{-1} on both sides of the membrane for 15 min, after which the second MD cycle was initiated using the residual feed solution from the first cycle. As shown in Figure 4-2B, a remarkable flux

recovery of nearly 80% was achieved by physical membrane cleaning for the PVDF-SiNP-FAS membrane, which was able to continue MD desalination for another ~500 min. In contrast, the pristine PVDF and PVDF-PVA membranes exhibited low flux recoveries of below 25%. Compared to the pristine PVDF membrane, the PVDF-PVA membrane had an even lower flux recovery (21% for pristine PVDF membrane and 13% for PVDF-PVA membrane). At the conclusion of MD experiment with two MD cycles, a concentration factor (CF, defined as the ratio of initial volume to the final volume of the feed solution) of ~4.3 was achieved for the PVDF-SiNP-FAS membrane, which was higher than those obtained by the pristine PVDF (CF ~2.3) and PVDF-PVA (CF ~2.2) membranes (Figures B1A and B1B, Appendix B). Therefore, the scaling reversibility and total water recovery followed the order of PVDF-SiNP-FAS membrane > pristine PVDF membrane > PVDF-PVA membrane, which was inversely correlated to the surface hydrophilicity of the membranes. Further, the PVDF-SiNP-FAS membrane was still resistant to membrane pore wetting in the second MD cycle, with almost a constant distillate conductivity during the experiment. Yet, the distillate conductivities for the pristine PVDF and PVDF-PVA membranes kept increasing, indicating that these membranes were still subjected to pore wetting after physical cleaning. The slower increase of distillate conductivity for the PVDF-PVA membrane than that of the pristine PVDF membrane in the second MD cycle was probably due to its lower water vapor flux. Therefore, our results demonstrate, for the first time, that the reversibility of gypsum scaling is a function of membrane surface wettability, and that the superhydrophobic membrane is favorable to possess both improved wetting resistance and scaling reversibility, which result in a higher extent of total water recovery.

4.3.3 Characterization of gypsum scales on and into MD membranes

Gypsum scaling on the membrane surface is resulted from crystallization, which is either via homogeneous nucleation followed by the deposition of crystals from solution or *in-situ* growth of crystals on the membrane surface via heterogeneous nucleation (Cao et al., 2018). The morphological feature of crystals formed via heterogeneous nucleation is displayed mostly as needle-like crystals, whereas the platelet- and rod-like crystals with monoclinic structure are typical characteristics of crystals that are formed via homogeneous nucleation (Shih et al., 2005).

The morphologies of gypsum crystals formed on the membrane surfaces were characterized via SEM (Figure 4-3). The gypsum crystals on the surface of the pristine PVDF membrane exhibited needle-like morphologies, indicating a major contribution of heterogeneous nucleation to membrane scaling (Figure 4-3A). The role of heterogeneous nucleation played in gypsum scaling was promoted with the PVDF-PVA membrane due to its hydrophilic nature, because the sizes of gypsum crystals with needle-like morphology were generally larger than those on the pristine PVDF membrane (Figure 4-3B). On the contrary, gypsum found on the PVDF-SiNP-FAS membrane surface consisted of smaller crystals in the shape of rods and platelets (Figure 4-3C), which were more likely formed from homogeneous nucleation. This observation was consistent with the fact that compared to hydrophobic and hydrophilic surfaces, superhydrophobic membrane surface possesses a higher energy barrier against heterogeneous nucleation (Karanikola et al., 2018).

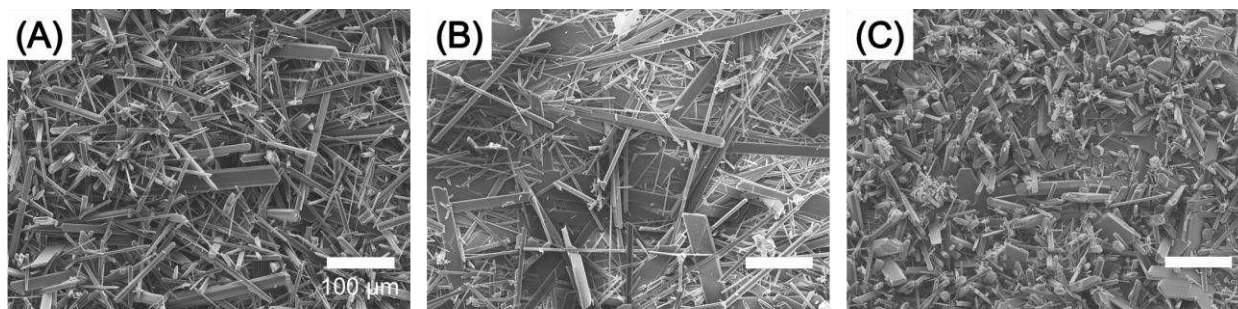


Figure 4-3. Top-view SEM micrographs of (A) pristine PVDF, (B) PVDF-PVA and (C) PVDF-SiNP-FAS membranes scaled with gypsum. The magnification of the SEM micrographs is 200X with the scale bar representing 100 μm .

Furthermore, we investigated the intrusion of gypsum crystal into the membrane substrate in order to better understand the different wetting resistance of membranes with varied surface wettability. SEM-EDS was applied to obtain elemental mapping of the cross-section of scaled membranes before and after membrane cleaning (Figure 4-4). As shown in Figure 4-4A, the elements Ca and S were clearly present within the membrane substrate of the pristine PVDF membrane, indicating the intrusion of gypsum scales into the membrane pores. By further analyzing the gypsum scales inside the membrane substrates (Figure B2, Appendix B), flaky gypsum crystals were observed, which was different in morphology from those on the membrane surface. Similarly, significant intrusion of gypsum scale into the membrane substrate was observed for the PVDF-PVA membrane (Figure 4-4C). Furthermore, although physical membrane cleaning removed most gypsum scales from the surface of the pristine PVDF and PVDF-PVA membranes, the presence of gypsum scales within the membrane substrates was still noticed after cleaning (Figures 4-4B and 4-4D), suggesting the embedding of those minerals in the membrane pores. These phenomena provide mechanistic understanding of the membrane wetting caused by gypsum scaling as shown in Figure 4-2. In our recent publication (Christie et al., 2019), we demonstrate that the intrusion of gypsum scales into membrane substrates results in pore deformation, which is caused by a “crystallization pressure” due to the oriented growth of

gypsum crystals within confined space. The pore deformation increases membrane pore size and reduces the liquid entry pressure (LEP), inducing membrane pore wetting (Christie et al., 2019). This explained membrane wetting observed for the pristine PVDF and PVDF-PVA membranes. The membrane damage caused by gypsum scaling could not be mitigated by physical membrane cleaning, as evidenced by the gypsum scales that were remained in the membrane substrates. As a result, membrane wetting continued to occur during the second cycle of MD desalination (Figure 4-2D).

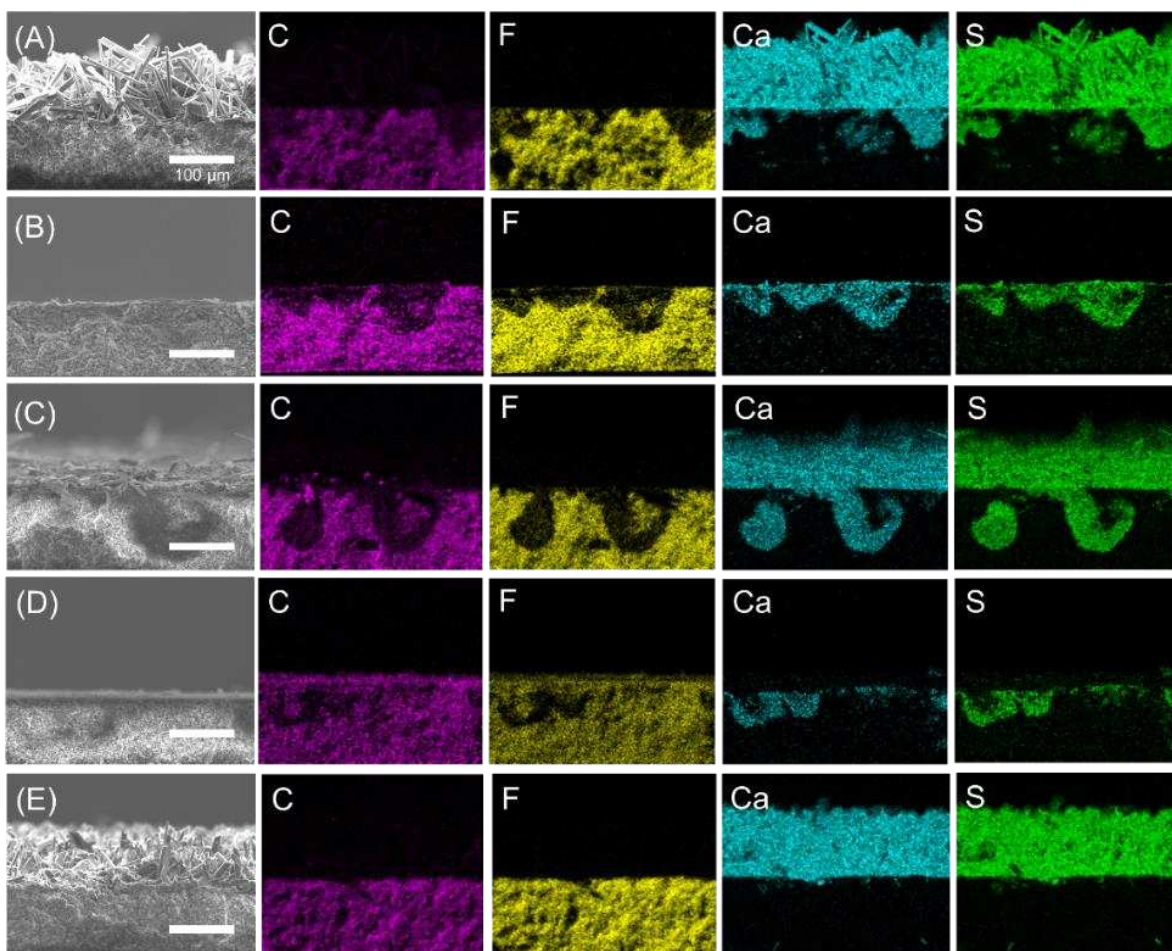


Figure 4-4. SEM-EDS elemental analysis of the cross-section of the pristine PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes for the DCMD gypsum scaling experiments. (A) PVDF membrane before membrane cleaning; (B) PVDF membrane after membrane cleaning; (C) PVDF-PVA membrane before

membrane cleaning; (D) PVDF-PVA membrane after membrane cleaning; (E) PVDF-SiNP-FAS membrane before membrane cleaning.

In contrast, gypsum crystals associated with the superhydrophobic PVDF-SiNP-FAS membrane were only observed on the membrane surface before physical membrane cleaning (Figures 4-4E and 4-5), indicating that in-pore gypsum intrusion was prevented. This result was in accordance with the exceptional wetting resistance of PVDF-SiNP-FAS membrane in MD. Due to the pore size heterogeneity of PVDF membrane, feedwater is able to penetrate into some pores with relatively large pore sizes and correspondingly low LEPs during MD desalination (Wang et al., 2019). Such pores are likely where in-pore crystallization is initiated. However, the high water repellency of superhydrophobic membrane, resulted from the synergy of hierarchical texture and low surface energy, effectively increased the LEPs of membrane pores, thereby preventing the intrusion of feedwater and reducing the possibility of in-pore gypsum crystallization. This explanation is also consistent with the inverse relationship between membrane surface hydrophilicity and membrane wetting propensity in MD scaling experiments.

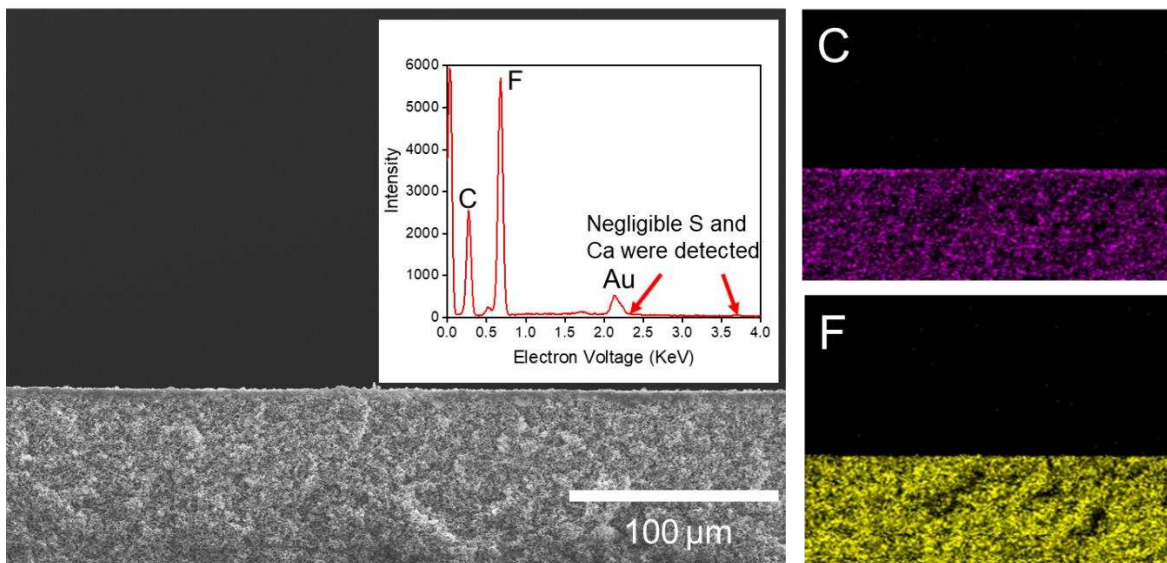


Figure 4-5. SEM-EDS elemental analysis of the cross-section of PVDF-SiNP-FAS membrane after membrane cleaning during the MD gypsum scaling experiment. The elemental spectra of EDS are presented as the inset. The Ca α and S α peaks are located at 3.69 KeV and 2.307 KeV, respectively.

Note that negligible Ca and S elements were observed for PVDF-SiNP-FAS membrane after membrane cleaning, indicating no gypsum was present on or inside the membrane.

4.3.4 Silica scaling performance and reversibility in membrane distillation

The performance of the membranes under silica scaling was also evaluated in silica-containing solution with SI of 0.93, which was identical to that used in gypsum scaling. As shown in Figure 4-6A, the pristine PVDF and PVDF-PVA membranes displayed a similar scaling behavior as a function of time, with a stable water vapor flux until ~1200 min followed by a rapid reduction. The longer induction time for silica scaling as compared to gypsum scaling (~500 min) was likely the result of slower kinetic of silicic acid polymerization than that of gypsum crystallization. For the PVDF-SiNP-FAS membrane, the onset of water flux decline was almost the same to those of the pristine PVDF and PVDF-PVA membranes (Figure 4-6A), which was different from the scenario of gypsum scaling. However, the rate of water flux reduction for PVDF-SiNP-FAS membrane was slower, which was probably due to its lower water vapor flux that imposed a less extent of CP (the CP moduli of Na_2SiO_3 for the pristine PVDF, PVDF-PVA, and PVDF-SiNP-FAS membranes were 1.54, 1.56, 1.43, respectively; the detail of concentration is described in Appendix B). Furthermore, throughout the first MD cycle, the electrical conductivity of the permeate slightly decreased in silica scaling for all the tested membranes (due to the diluting effect of distillate), indicating an exceptional salt rejection without membrane pore wetting (Figure 4-6C).

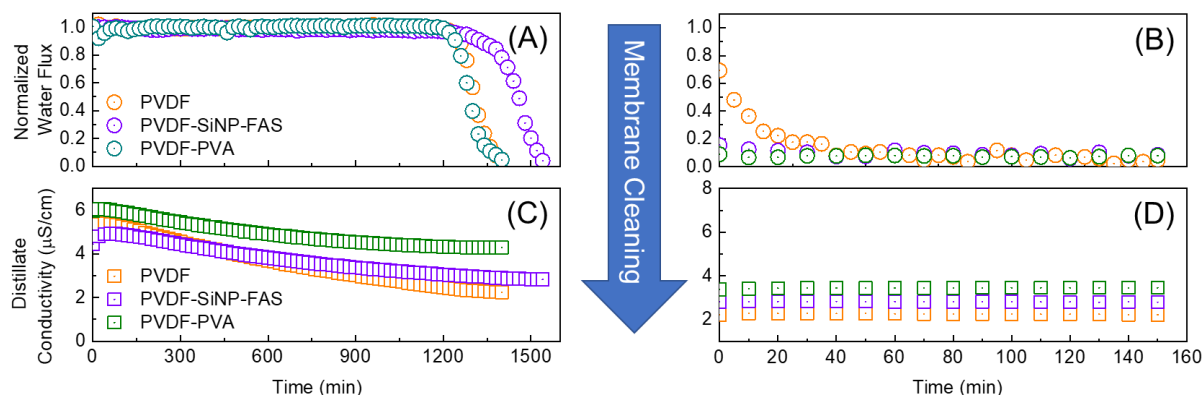


Figure 4-6. Normalized water vapor flux and distillate conductivity of the pristine PVDF, PVDF-SiNP-FAS and PVDF-PVA membranes as a function of time (A and C) before and (B and D) after physical membrane cleaning. The feed solution contains 50mM NaCl, 1mM NaHCO₃ and 3.2mM Na₂SiO₃·5H₂O. The temperatures of the feed and distillate solutions were maintained at 60 °C and 20 °C, respectively. The crossflow velocities of feed and distillate solutions were 9.6 cm/s and 6.4 cm/s, respectively. The initial water vapor fluxes of the pristine PVDF, PVDF-SiNP-FAS and PVDF-PVA membranes were 25.9 L m⁻² h⁻¹, 22.9 L m⁻² h⁻¹ and 26.1 L m⁻² h⁻¹, respectively. These flux values are used to normalize the fluxes in all the figures. The recovered water vapor fluxes after membrane cleaning were 17.7 L m⁻² h⁻¹, 3.3 L m⁻² h⁻¹ and 2.2 L m⁻² h⁻¹ for PVDF, PVDF-SiNP-FAS and PVDF-PVA membranes, respectively.

Physical cleaning was also performed to investigate the reversibility of silica scaling for different membranes in MD. As shown in Figure 4-6B, the pristine PVDF membrane displayed an initial water flux recovery of ~70% after membrane cleaning was executed on the silica-scaled membranes after the first MD cycle. But it was subjected to an immediate reduction in water vapor flux at the beginning of the second MD cycle. On the contrary, the water vapor fluxes of the PVDF-PVA and PVDF-SiNP-FAS membrane were only restored by less than 20% after physical cleaning. Further, the electrical conductivity of the distillate in the second MD cycle was unchanged (Figure 4-6D), consistent with the lack of pore wetting in the first cycle. The total CF achieved within the two MD cycles was similar (CF ~3.8–4.2) for all tested membranes (Figures B3A and B3B, Appendix B), indicating that none of the tested membranes were benefited from membrane cleaning. Therefore, the results in our study reveal that physical membrane cleaning was futile in reviving the membranes suffered from silica scaling, which resulted in a robust scaling layer that resisted the shear force during the cleaning process.

Besides physical cleaning, chemical cleaning has been applied in the literature to recover water flux after silica scaling. For example, Koo, et al. (Koo et al., 2001) investigated the cleaning effectiveness of water and two commercial cleaners (MT 5010 and MT 3100) in recovering water flux from RO membrane after silica scaling. Also, Beyer et al. (Beyer et al., 2010) studied the cleaning effect of caustic solution and sodium dodecyl sulfate (SDS) surfactant on membrane fouling by colloidal silica in nanofiltration. Unfortunately, these methods were found ineffective in silica scaling mitigation. To the best of our knowledge, the only study that reported effective membrane cleaning was by Bush et al. (Bush et al., 2018), who demonstrated that by coupling flow reversal with membrane cleaning using caustic solution (pH 11), a high flux recovery could be achieved after silica scaling during the MD process. However, this practice required flux reversal and corrosive cleaning agent, which complicated the operational process of MD in practical. Therefore, silica scaling is a knotty issue that requires more investigations and efforts to address than gypsum scaling.

4.3.5 Characterization of silica scales on and into MD membranes

The SEM characterization of scaled membranes after silica scaling indicates that all the tested membranes were fully covered with a layer of particulate silica scales (Figure 4-7). There was no significant morphological difference among the silica particles formed on different membrane surfaces. After physical membrane cleaning, the silica particles were still visible on the membrane surface. This phenomenon was surprising because a relatively high (although temporary) water flux recovery was achieved by physical cleaning for the pristine PVDF membrane. A closer look at the scaling layers revealed that the silica particles on the pristine PVDF membrane were less densely packed than those on the PVDF-PVA membrane after cleaning (Figures 4-7G and 4-7H). It was possible that the space between silica particles could

allow water penetration due to the hydrophilic nature of silica, resulting in water flux recovery after membrane cleaning. In contrast, the hydrophilic surface of the PVDF-PVA membrane promoted heterogeneous nucleation, forming a densely packed silica particle layer with high resistance to water transport. Interestingly, physical membrane cleaning detached some silica particles on the PVDF-SiNP-FAS membrane surface, exposing the silica scale layer underneath those particles (Figure 4-7I). The silica scale layer showed a smooth and nonporous morphology, suggesting that this layer was remarkably impervious. This phenomenon, which was consistent with our previous study (Yin et al., 2019), explained the low water flux recovery observed for PVDF-SiNP-FAS membrane after membrane cleaning, although the superhydrophobic property of this membrane should mitigate heterogeneous nucleation of silica scale. However, we acknowledge that the mechanism underlying the unique morphology of silica scales for PVDF-SiNP-FAS membrane is still unclear and requires further investigation.

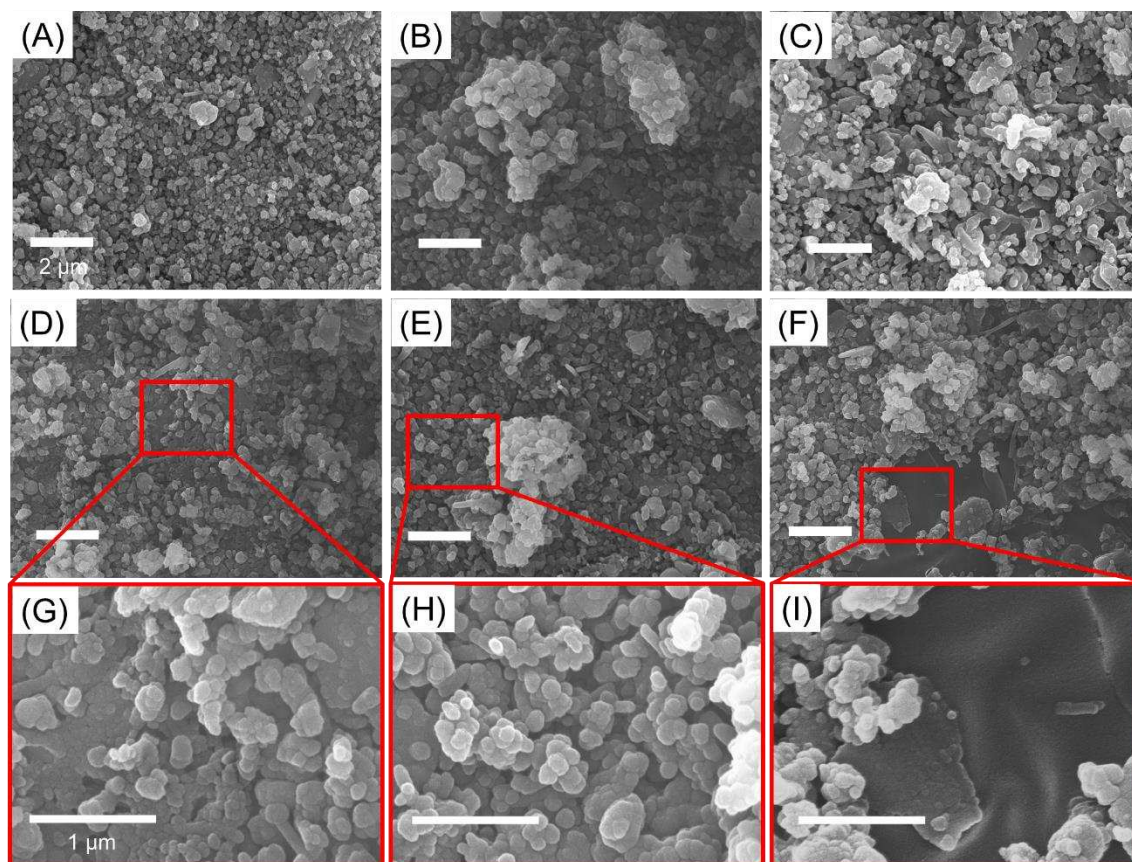


Figure 4-7. Top-view SEM micrographs of (A, D and G) the pristine PVDF, (B, E and H) PVDF-PVA and (C, F and I) PVDF-SiNP-FAS membranes (A-C) before and (D-F) after membrane cleaning for the DCMD silica scaling experiments. The magnification of the SEM micrographs in A-F is 10,000X with the scale bar representing 2 μm . The G, H and I are the magnified views that show the particle-like and gel-like silica scales formed on the surface of PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes. The magnification of the SEM micrographs in G-I is 40,000X with the scale bar representing 1 μm .

The extent of scale intrusion into membrane substrates was assessed via SEM-EDS analysis. As shown in Figure 4-8, the elements Si and O were only detected on the membrane surface regardless of membrane surface wettability, indicating that the silica scalants did not invade into the membrane substrates. The lack of scale intrusion was valid before and after membrane cleaning. In addition, the much thinner thickness of silica scale layer than that of gypsum layer suggests that the kinetics of silica scale formation was much slower (especially considering the longer induction time of silica scaling). The slow kinetics and the lack of orientation of silicic acid polymerization render silica scaling not intrusive and forming a thin film layer on the

membrane surface, explaining the lack of membrane pore wetting during silica scaling experiments. Unlike what was observed in gypsum scaling, the EDS signal intensities from the elements Si and O were unchanged after membrane cleaning, suggesting that physical membrane cleaning was ineffective in removing the silica scaling layer.

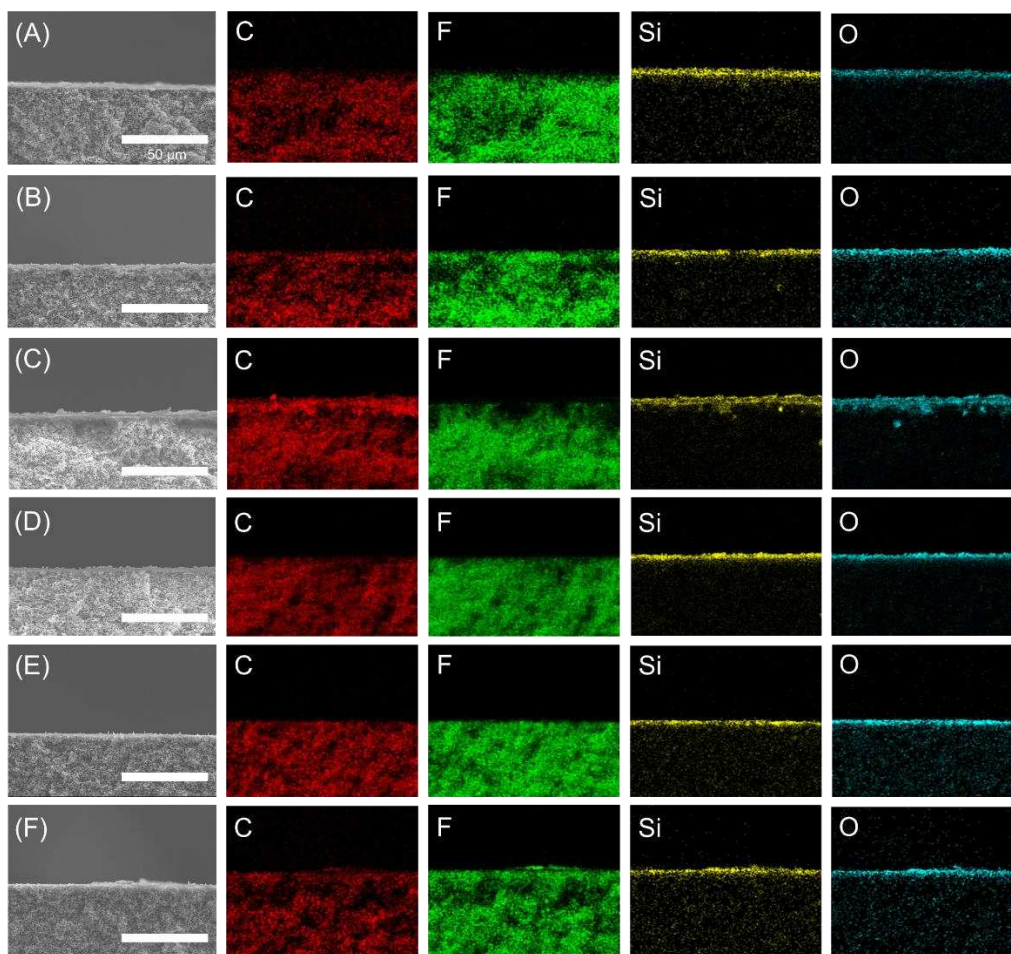


Figure 4-8. SEM-EDS elemental analysis of the cross-section of the pristine PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes for the DCMD silica scaling experiments. (A) PVDF membrane before membrane cleaning; (B) PVDF membrane after membrane cleaning; (C) PVDF-PVA membrane before membrane cleaning; (D) PVDF-PVA membrane after membrane cleaning; (E) PVDF-SiNP-FAS membrane before membrane cleaning; (F) PVDF-SiNP-FAS membrane after membrane cleaning

4.3.5 Implications for MD desalination

We have demonstrated that the effects of membrane surface wettability on gypsum scaling and silica scaling are different in terms of both membranes wetting and scaling reversibility.

Although gypsum scaling is able to induce pore wetting during MD desalination, its adverse effects on membrane performance could be mitigated by employing superhydrophobic membrane. Previous studies have reported that superhydrophobic membranes were able to delay the induction of gypsum scaling (Karanikola et al., 2018; Su et al., 2019). Our study further showed, for the first time, that superhydrophobic membrane could also reduce pore wetting and enhance scaling reversibility associated with gypsum scaling. On the other hand, silica scaling did not cause membrane wetting during MD desalination. However, silica scaling was irreversible for all the tested membranes regardless of their surface wettability, indicating that tuning membrane surface wettability alone is not an effective approach to mitigate silica scaling. The development of scaling mitigation strategies, therefore, should consider the varied mechanisms of different scaling types. For mineral scaling formed via crystallization processes such as gypsum scaling, superhydrophobic membranes could be used to reduce the scaling extent and improve total water recovery (Karanikola et al., 2018; Su et al., 2019; Xiao et al., 2020). However, other membrane design approach, such as tuning membrane surface charge (Qi et al., 2020; Rao et al., 2020; Rathinam et al., 2019; Tong et al., 2017), might be considered to improve scaling resistance of MD membranes against silica scaling. In addition, our study suggests that the problem of mineral scaling in MD might not be eliminated by only altering membrane surface properties, due to the complexity of scaling mechanisms for diverse scalants present in the feedwater. Recent work has shown that a combination of membrane design and process innovation (such as the use of gas purging and pulse flow) could result in stable water vapor flux and desalination performance under mineral scaling (Horseman et al., 2019; Liu et al., 2020). Therefore, it will be valuable to investigate whether such a hybrid strategy, which is not

dependent on only membrane materials, would be universally effective to all types of scaling regardless of the scaling mechanisms.

In addition, besides innovations in membrane materials and processing, the application of anti-scalant, which aims at disrupting mineral formation in the feed solution, might be also feasible to mitigate mineral scaling during membrane desalination (He et al., 2009; Qu et al., 2020; Shi et al., 2017). Particularly, anti-scalant could be attractive to mitigate silica scaling that could not be reduced by tuning membrane surface wettability. However, although anti-scalant has been commonly applied to pressure-driven desalination process such as RO (Benecke et al., 2018; Le Gouellec and Elimelech, 2002; Lee et al., 2020; Shih et al., 2006; Yu et al., 2019), the application and understanding of this strategy is still limited in MD. Further, the use of anti-scalants might also result in an increase of cost and cause organic fouling and biofouling (Turek et al., 2017). Hence, a comparison between membrane-based approaches and the use of anti-scalants for the mitigation of mineral scaling in MD needs to be performed to identify the best practices of realizing the full potential of MD desalination for the treatment of hypersaline wastewater with high scaling potential.

4.4 Conclusions

In this study, we demonstrated that the effects of membrane surface wettability on pore wetting and scaling reversibility caused by mineral scaling in MD varied for scaling types with different mechanisms. Three PVDF membranes with distinct surface wettability were selected as model membranes that were challenged with gypsum- and silica-containing feed solutions. Compared to hydrophobic and surface-hydrophilic Janus membranes, superhydrophobic membrane not only delayed scaling induction but also enhanced scaling reversibility of gypsum scaling. Both the extent of scaling reversibility and total water recovery were inversely related to

membrane hydrophilicity in gypsum scaling experiments. In addition to its wetting resistance to low-surface-tension and amphiphilic contaminants, superhydrophobic membrane also displayed excellent resistance against membrane pore wetting caused by gypsum scaling, due to its capability of preventing feedwater intrusion into membrane pores. On the contrary, no membrane wetting was observed for all tested membranes in silica scaling experiments, in which tuning membrane surface wettability was ineffective to improve either scaling reversibility or total water recovery. The distinct behaviors and responses to membrane wettability between gypsum and silica scaling were attributed to their different scaling mechanisms. Gypsum scaling, which was formed via crystallization with an oriented and intrusive nature, led to membrane pore wetting and discrete crystals that could be removed by physical membrane cleaning. Silica scaling, however, was generated via polymerization of silicic acid. The slow kinetic and lack of growth orientation associated with silica polymerization resulted in a thin-film, less intrusive, and cross-linked scaling layer that was firmly attached to the membrane surface. Our results demonstrate that it is challenging to address the problem of membrane scaling in MD by only tuning membrane surface wettability, and that it is important to consider different scaling mechanisms when designing scaling mitigation strategies in MD desalination.

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5.0 Contrasting Behaviors Between Gypsum and Silica Scaling in the Presence of Anti-scalants During Membrane Distillation⁴

5.1 Introduction

Membrane distillation (MD) is a thermal-driven and membrane-based desalination process that is suitable for the treatment of hypersaline wastewater. (Alkhudhiri et al., 2012; Deshmukh et al., 2018; Lawson and Lloyd, 1997) Different from reverse osmosis (RO), MD is not constrained by hydraulic pressure, and is thus able to treat hypersaline wastewaters containing salinities higher than the RO salinity limit. (Deshmukh et al., 2018) Due to its capability of leveraging low-grade thermal energy (e.g., waste heat, geothermal and solar energy), MD has the potential to reduce the primary energy consumption and the cost of wastewater treatment. (Robbins et al., 2020; Shaffer et al., 2013, Wang et al., 2019) However, MD is vulnerable to mineral scaling that imposes detrimental effects on its performance. (Tong et al., 2019; Wang and Lin, 2017) Mineral scaling refers to the development of mineral precipitates on the membrane surface, resulting in water vapor flux decline and membrane pore wetting that compromise the efficiency and reliability of MD in practice. (Alkhudhiri et al., 2012; He et al., 2008; Lawson and Lloyd, 1997; Tijing et al., 2015; Tong et al., 2019)

Mineral scaling occurs by either a crystallization or polymerization mechanism. (Christie et al., 2019; Horseman et al., 2020; Yin et al., 2020) For example, gypsum (calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) scaling is a result of crystallization via the hydration reaction of Ca^{2+}

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and SO_4^{2-} in aqueous solutions, (Christie et al., 2019; Gryta, 2009; Mi and Elimelech, 2010; Rice et al., 2020; Warsinger et al., 2017) whereas silica scale is created via the reaction of silicic acid polymerization. (Mi and Elimelech, 2013; Yin et al., 2019) The formation of mineral scales in membrane desalination could also be attributed to either homogeneous nucleation or heterogeneous nucleation. (Antony et al., 2011; Shaffer et al., 2017; Tijing et al., 2015) As a high water recovery is being achieved, the supersaturated status of scale precursors in the feed solution provides strong momentum to initiate homogeneous nucleation, (Yu et al., 2020) and the formation of nascent nuclei offers further nucleating sites for scale growth. (Sumper, 2004; Yu et al., 2020) In the presence of membrane materials, the formation of scale nuclei can also take place heterogeneously on the membrane surface. (Nghiem and Cath, 2011; Tong et al., 2019) According to the classical nucleation theory (CNT), heterogeneous nucleation occurs more easily than homogeneous nucleation at the membrane-water interface due to its lower energy barrier. (Liu, 2000; Sear, 2006; Tong et al., 2019) However, homogeneous nucleation also plays an essential role in mineral scaling. As the concentration of calcium sulfate exceeds its solubility, gypsum formation proceeds via multiple stages of phase transformation in the solution, from amorphous phase to crystalline phases of calcium sulfate. (Wang et al., 2012) The formed gypsum crystals could deposit on the membrane surface and participate in the formation of a scale layer. Similarly, in our recent publication we demonstrate that the deposition of silica particles formed via homogeneous nucleation onto the membrane surface is the prerequisite for further scale formation responsible for water flux decline in MD. (Yin et al., 2019)

The use of anti-scalants is the most common strategy to prevent scaling in industry including membrane-based desalination. (Antony et al., 2011; Tong et al., 2019) Anti-scalants usually serve as inhibitors to interfere with homogeneous nucleation of scaling precursors and delay

mineral precipitation. (Yu et al., 2020) Two major mechanisms are proposed to govern the effectiveness of anti-scalants. First, the chelating effect, (Yu et al., 2020) in which the anti-scalants form a highly soluble complex with the scaling precursors stoichiometrically to extend the scaling induction time. (Ben Ahmed et al., 2008; Miyajima et al., 1997; Travers and Marinsky, 1974) Second, the anti-scalants directly adsorb onto the surface of scale nuclei via a ligand-exchange mechanism or electrostatic attraction to disrupt the nucleation process. (Rabizadeh et al., 2019; Tijing et al., 2015) The effectiveness of anti-scalants resulting from nuclei surface adsorption is attributed to the increase of nucleation energy barrier or the blockage of the active sites for crystal growth. (He et al., 2009; Jain et al., 2019; Oh et al., 2009) However, such fundamental knowledge on anti-scalants has been mostly derived from studies pertaining to static experiments (i.e., without membranes). Compared to a rising number of literatures on developing membrane materials with scaling resistance, (Karanikola et al., 2018; Su et al., 2019; Xiao et al., 2019) less work has been performed on understanding the performance and mechanisms of anti-scalants in MD. The limited number of relevant studies have focused on practical application rather than elucidating the underlying mechanisms. (Hou et al., 2013; Peng et al., 2015; Qu et al., 2020) Further, the findings from prior studies on anti-scalants in MD presented inconsistent results, where not all the anti-scalants improved membrane performance despite of their inhibiting effects on mineral formation. (Gryta, 2012; He et al., 2009) Therefore, an in-depth understanding on the selection and mechanisms of anti-scalants for MD desalination has yet to be established.

The efficiencies of anti-scalants are type-specific, and anti-scalants with distinct properties might be needed to mitigate different types of scaling. (Neofotistou and Demadis, 2004; Tong et al., 2019) For example, polyacrylic acid (PAA), a negatively charged polymer with abundant

carboxylic groups, showed promising effects in retarding crystalline scales such as gypsum and calcite. (Ben Ahmed et al., 2008; Liu et al., 2015) However, due to the amorphous nature of silica, its efficiency in delaying silica scaling remains questionable. (Neofotistou and Demadis, 2004) To mitigate silica scaling, the knowledge in the field of biomineralization sheds light on the selection of anti-scalants. (Kröger et al., 2000; Kröger et al., 1999; Kröger et al., 2002; Sumper et al., 2005; Sumper and Kröger, 2004) Amino-enriched molecules such as polyamine derivatives are capable of catalyzing silica polymerization, which offers a foreign template for silica precipitation in the solution. (Coradin et al., 2002; Sumper, 2004) Also, hydrogen bonding between silanol group and ethereal oxygen of the neutrally charged poly(ethylene oxide) (PEO) was reported to hinder silica polymerization and stabilize silica precursors in the solution. (Demadis et al., 2009) Although those prior studies suggest that the kinetics of mineral precipitation could be controlled by applying molecules with specific functionality, the role of different functional groups in determining the efficiencies of anti-scalants have not been systematically investigated in membrane desalination. Such an investigation will not only provide valuable insights to guide the design of effective anti-scalants, but also promote fundamental understanding of scaling (mitigation) mechanisms.

In this work, we performed a comparative investigation on the inhibiting effect of several anti-scalant candidates with different functional groups to mitigate gypsum scaling and silica scaling in MD. PAA, sodium polyphosphate (PP), and poly(ethylene glycol) (PEG) were used to represent anti-scalant candidates with anionic or neutral moieties, while poly(ethyleneimine) (PEI) and poly(amidoamine) (PAMAM) dendrimers were used as representatives of anti-scalant candidates with cationic amino groups. A hydrophobic polyvinylidene fluoride (PVDF) membrane was challenged with gypsum- and silica-supersaturated solutions with and without the

anti-scalant candidates in MD desalination. The performance of each anti-scalant candidate in scaling mitigation was evaluated by investigating its effects on regulating scale precursor status in the solution, extending water recovery, and preventing membrane wetting in MD. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were employed to analyze the morphology, crystallinity, and bonding chemistry of the scales precipitated on the membrane surface comprehensively. Our study reveals, for the first time, that anti-scalants with distinct functionalities are required to mitigate gypsum and silica scaling in MD, suggesting that tailored selection and design of anti-scalants are needed for MD applications to the treatment of wastewaters with different scaling types.

5.2 Materials and Methods

5.2.1 Materials and chemicals

Sodium sulfate (Na_2SO_4), sodium bicarbonate (NaHCO_3), sodium metasilicate pentahydrate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$), ammonium molybdate ($(\text{NH}_4)_2\text{MoO}_4$), and oxalic acid ($\text{HO}_2\text{CCO}_2\text{H}$) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), sodium chloride (NaCl), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were supplied from Fisher Chemicals (Hampton, NH, USA). PAA with a molecular weight (MW) of 1800, sodium polyphosphate with a MW of 2000, PEG with a MW of 1500, branched PEI with a MW of 800, as well as PAMAM dendrimers with a MW of 1430 (all supplied from Sigma Aldrich, St. Louis, MO, USA) were used as anti-scalant candidates in the MD experiments. A hydrophobic PVDF membrane with a nominal pore size of 0.22 μm (acquired from Millipore Sigma, Burlington, MA, USA) was used as the MD membrane. Deionized (DI) water was provided from a commercial water purification system ($>18\text{M}\Omega$, Millipore, Burlington, MA, USA).

5.2.2 The measurement of gypsum and silica precursors in static scaling experiments

A static scaling experiment was performed to assess the effectiveness of anti-scalants to delay the scale formation (gypsum and silica scale) without membrane materials. Such static scaling experiments have been commonly used to evaluate the efficiencies of anti-scalants. (Jain et al., 2019; Lioliou et al., 2006; Rabizadeh et al., 2019; Yu and Yang, 2020) The volumes of both gypsum- and silica-supersaturated solutions (1000 mL) in static scaling experiments were maintained constant throughout the experiments. The solution temperatures were maintained at 60 °C. The solution pH was adjusted to 6.50 ± 0.05 by using 1M HCl and 1M NaOH after all the solution constituents (including the anti-scalant candidates) were dissolved.

For gypsum scaling, two 500 mL solutions containing 60 mM Na_2SO_4 and 60 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ were prepared individually and then mixed together, followed by immediate insertion of the conductivity electrode into the mixture after pH adjustment. The final solution contained 30 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 30 mM Na_2SO_4 , corresponding to a saturation index (SI, defined as the natural logarithm of the ratio between ion activity product and solubility equilibrium constant, $\ln(\frac{IAP}{K_{sp}})$) of 0.55 as calculated by PHREEQC software and database WATEQ4F (PC Version). For experimental groups with anti-scalant candidates, 80 mg/L of anti-scalant candidate was added into the Na_2SO_4 solution, resulting in 40 mg/L of each candidate in the gypsum-supersaturated solution. A concentration of 40 mg/L for anti-scalant candidates was used in all experiments, because it resulted in the best anti-scaling performance in our preliminary screening tests. The concentrations of scale precursors for gypsum in the solution were indicated by monitoring the electrical conductivity using a conductivity meter (Oakton Instrument, Vernon Hills, IL, USA). The electrical conductivity decreases when the formation of CaSO_4 starts due to the consumption of Ca^{2+} and SO_4^{2-} ions.

A silica-supersaturated solution containing 50 mM NaCl, 1 mM NaHCO₃, and 6 mM Na₂SiO₃·5H₂O was used as the control (with SI of silica at 0.55), while the experimental groups also contained 40 mg/L anti-scalant candidates. The silicomolybdate method was applied to measure the concentration of silica scale precursors in the silica-supersaturated solutions. The chromogenic reaction between ammonium molybdate and reactive silica precursors produces yellow heteropoly acids in the harsh acidic range (pH ~ 1-2). (Coradin et al., 2004; Neofotistou and Demadis, 2004) The molybdate-reactive silica detected in this method is predominantly monomeric silicic acid (H₄SiO₄), (Milne et al., 2014) which might also contain a small fraction of disilicic acid (H₆Si₂O₇). (Preari et al., 2014) The first five samples were taken for measurements every 30 min within a period of 2 h, after which a time interval of 2 h was applied for the sampling. All the samples were filtered by a 0.45 µm cellulose acetate filter (GE Healthcare Life Science, Whatman, Sigma Aldrich, St. Louis, MO, USA). Then the quantification of molybdate-reactive silica was performed following the procedure used by Quay et al. (Quay et al., 2018) The concentration of molybdate-reactive silica in solution was proportional to the absorbance at 420 nm measured by an ultraviolet–visible (UV–vis) spectrophotometer (VWR, UV-1200, Radnor, PA, USA).

5.2.3 Dynamic MD scaling experiment with varied anti-scalants

Dynamic MD scaling experiments were performed to assess the effectiveness of anti-scalant candidates in mitigating gypsum and silica scaling in crossflow MD conditions. A custom-built, crossflow DCMD unit (20.02 cm² effective membrane area), which has been described in our previous work, (Yin et al., 2019) was used, equipped with a hydrophobic PVDF membrane that separated the feed and permeate streams (Figure C1, Appendix C). The initial volumes of the gypsum- and silica-supersaturated feed solutions were 1000 mL, with their pH adjusted to 6.50 ±

0.05 after all solution constituents were dissolved and well mixed. The temperatures of feed and permeate streams were maintained at 60 °C and 20 °C throughout the MD experiment, respectively. The feed and permeate streams were continuously circulated with crossflow velocities of 9.6 cm s⁻¹ and 6.4 cm s⁻¹, respectively.

The gypsum-supersaturated solutions containing 30 mM CaCl₂·2H₂O and 30 mM Na₂SO₄ were used as the control feedwater for gypsum scaling, while the feed solutions for silica scaling consisted of 50 mM NaCl, 1 mM NaHCO₃ and 6 mM Na₂SiO₃·5H₂O. Such feedwater compositions resulted in an initial SI of 0.55 for both gypsum and silica. Additional 40 mg/L of anti-scalant candidate (i.e., PAA, PP, PEG, PEI, or PAMAM) was added individually for the experimental groups. The water vapor flux (calculated by the change of the weight of distillate tank) and salt rejection rate (calculated by the change of distillate conductivity) were monitored along the experiments. At the conclusion of the MD experiments, the membrane coupons were collected and air dried carefully before being preserved for further analyses.

5.2.4 Mineral scale characterization

The top-view morphology of the mineral scales on the membrane surface was analyzed using SEM (JEOL JSM-6500F, Peabody, MA, USA). The samples were coated by a 10 nm-layer of gold using a sputter coater (Denton Desk IV, Denton Vacuum, Moorestown, NJ, USA). The crystalline feature of the scales was characterized using XRD (Bruker D8 Discover Series I, Billerica, MA, USA). The XRD pattern of each sample was compared with the RRUFF Mineral Project database (RRUFF ID: R040029). In addition, the local chemical environment of the mineral scales was investigated using XPS analysis, which was performed using a PHI-5800 spectrometer (Physics Electronics, Chanhassen, MN, USA) with a monochromatic Al-K X-ray source. All the spectra were referenced to C 1s signal from the adventitious carbon. The C-C

peak of the adventitious carbon, which is assigned to the value of 284.8 eV, was used for spectra calibration. (Greczynski and Hultman, 2017)

5.3 Results and Discussion

5.3.1 Efficiencies of anti-scalant candidates in mitigating gypsum scaling

We first compared the efficiencies of anti-scalant candidates with varied electric charges in retarding mineral precipitation in static experiments (i.e., without membranes) at pH of 6.50 ± 0.05 . At this pH, PAA molecules with a pKa value of 4.4 are negatively charged due to the deprotonation of carboxyl groups, (Battaglia et al., 2005) whereas PEI molecules with a pKa value of 7.1 displayed cationic nature that resulted from the protonation of amino groups. (Mady et al., 2011) In contrast, PEG molecules possess near-neutral electric charge at the solution pH of our study. (Liufu et al., 2004; Xu et al., 2015) For gypsum scaling, the change of soluble scaling precursors (i.e., Ca^{2+} and SO_4^{2-} ions) was monitored by measuring the solution conductivity. As shown in Figure 5-1A, an immediate and rapid reduction of solution conductivity was observed initially within ~15 min in all the experiments, which was probably due to the fast kinetics of CaSO_4 nucleation that led to the formation of nascent CaSO_4 nuclei. (Huang et al., 2020; Mbogoro et al., 2017) As compared to the control group (i.e., without the addition of anti-scalant candidates), the presence of PEG and PEI was able to delay the onset of further conductivity decrease. The solution conductivity was maintained relatively stable for ~60 min and ~170 min with PEG and PEI, respectively. Notably, after the initial reduction in solution conductivity, the presence of anionic PAA molecules was able to maintain a constant solution conductivity along our experiment for more than additional 280 min. This stabilizing effect was likely due to the strong affinity between carboxyl moieties of PAA and calcium ions embedded on the surface of CaSO_4 nuclei. (Israelachvili, 2011) It should be noted that the complexation of PAA with Ca^{2+}

ions in the solution was unlikely to be responsible, because the concentration of carboxyl groups (~0.55 mM in total for the added PAA) was too low to be stoichiometrically comparable to the concentration of free Ca^{2+} ions (30 mM) added into the solution. Therefore, all the anti-scalant candidates used in our study were able to delay CaSO_4 precipitation. However, their different molecular structures resulted in varied efficiencies in stabilizing the scale precursors of gypsum in solution, following the order of PAA > PEI > PEG.

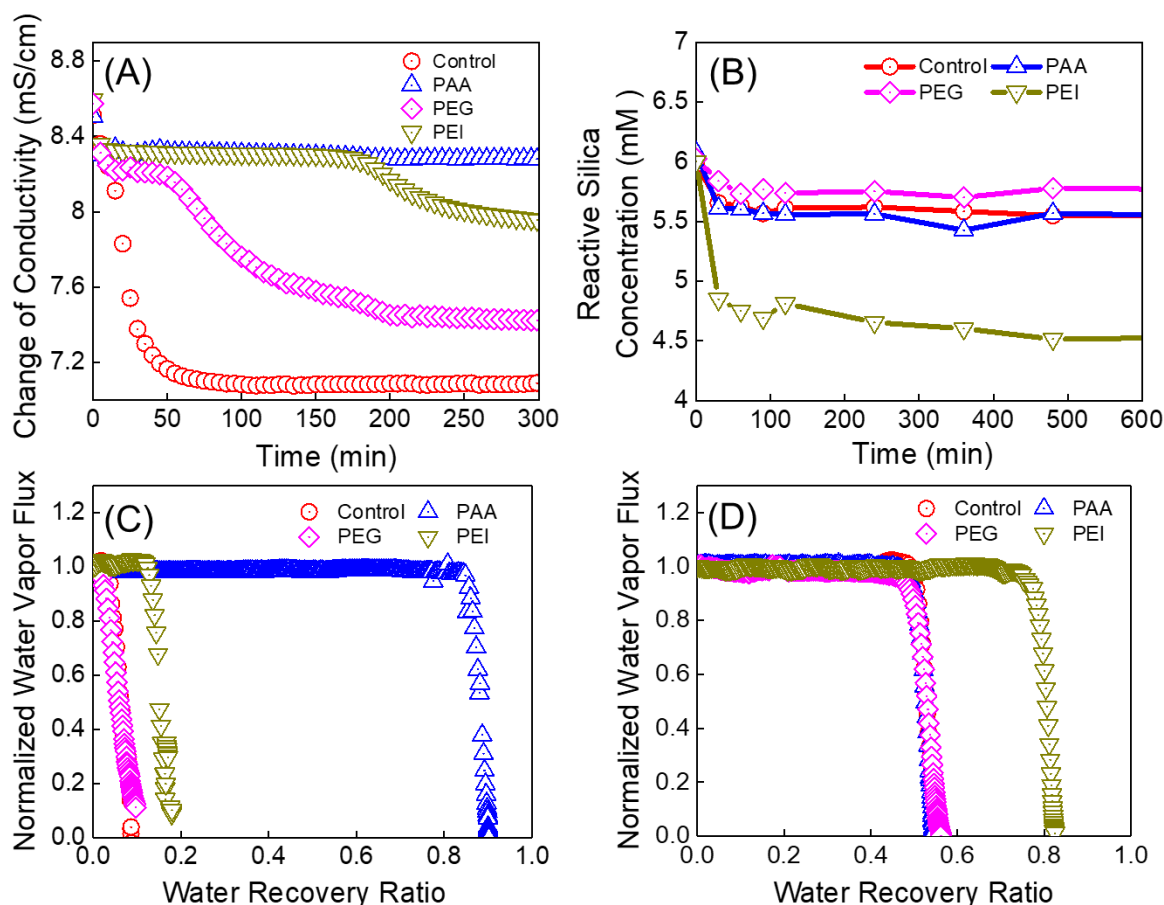


Figure 5-1. The change of contents of scaling precursors as a function of time for (A) gypsum- and (B) silica-supersaturated solutions from static scaling experiments. Normalized water vapor flux as a function of water recovery ratio in dynamic MD scaling experiments with (C) gypsum scaling and (D) silica scaling. The initial SI of both gypsum and silica feed solutions was 0.55, and the concentration of anti-scalant candidates was 40 mg/L in all experiments. The temperatures of feed and permeate streams were maintained at 60 °C and 20 °C, respectively. The feed and permeate streams were continuously circulated at crossflow velocities of 9.6 cm s⁻¹ and 6.4 cm s⁻¹, respectively. The initial water vapor flux of PVDF membrane was 25.5 ± 1.3 L m⁻² h⁻¹, which was used to normalize the water vapor fluxes in the figure.

The effectiveness of different anti-scalant candidates in mitigating gypsum scaling in MD was examined by challenging a hydrophobic PVDF membrane with gypsum-supersaturated solutions under dynamic and crossflow conditions. As shown in Figure 5-1C, the neutral PEG was ineffective to retard the onset of water vapor flux decline caused by gypsum scaling, resulting in a low water recovery ratio (~10%) that was the same as the control group. The positively charged PEI exhibited a limited mitigating effect on gypsum scaling, extending the water recovery ratio to ~20%. Notably, the negatively charged PAA displayed an exceptional anti-scaling efficiency, which extended the water recovery ratio remarkably to ~90%. In the presence of PAA, the water vapor flux was maintained stable (i.e., no water flux decline) until a high water recovery of ~80% was achieved (corresponding to SI of 2.75 if not considering gypsum precipitation). Furthermore, pore wetting caused by gypsum scaling (as indicated by the increase of distillate conductivity with time) was observed in the control group and in the presence of PEG and PEI (Figure C3A, Appendix C). In contrast, no pore wetting occurred in the presence of PAA (Figure C3A). Therefore, negatively charged PAA was highly effective to achieve high water recovery and prevent pore wetting caused by gypsum scaling in MD desalination. The order of anti-scalant efficiency in mitigating gypsum scaling in MD was consistent with that of stabilizing scale precursors as observed in Figure 5-1A.

To further assess the role that negative electric charge of anti-scalants plays in mitigating gypsum scaling in MD, sodium polyphosphate was used as another anti-scalant candidate. Sodium polyphosphate has a pKa value of 1 – 2 and thus exhibited an anionic nature under the solution pH of our study (6.5 ± 0.05). (Lee and Whitesides, 2010) Compared with the control group, the presence of negatively charged sodium polyphosphate was able to extend the water recovery in MD by ~20%, which was less effective than the presence of PAA (Figure C4,

Appendix C). Therefore, although both negatively charged anti-scalants (PAA and sodium polyphosphate) were capable of retarding gypsum scaling in MD, their anti-scaling efficiencies varied due to their different functional groups. Such a difference was attributed to the higher affinity of carboxyl group to Ca(II) than that of phosphate group (Hacht, 2008; Popov et al., 2001).

We also evaluated the effect of salinity on the anti-scaling efficiency of PAA by varying the feedwater salinity. In the absence of PAA, increasing the background electrolyte (NaCl) from 0 M to 1 M postponed the decline of water vapor flux, leading to an extension of MD water recovery from ~10% to ~75% (Figure C5A, Appendix C). This was due to the dependence of gypsum solubility on the feedwater salinity. (Tanji and Doneen, 1966) As the content of background NaCl raised from 0 M NaCl to 1 M NaCl, the solubility of gypsum increased, with the corresponding SI decreasing from 0.55 to -0.62. When PAA was added in the feedwater containing 1 M NaCl, PAA still showed a promising effectiveness to retard gypsum scaling, extending the water recovery of MD from ~75% to ~95% (Figure 5-2B). However, we could not conclude whether the efficiency of PAA varied at different salinities, as the alteration of feedwater salinity changed both gypsum solubility and the interactions of PAA with scalants. The suitability of PAA in mitigating gypsum scaling under a high feedwater salinity indicates that electric charge might not be the key molecular feature that determines the effectiveness of anti-scalants for gypsum, because electrostatic interactions of anti-scalants with scalants are suppressed under high salinities. Indeed, the surface of gypsum is negatively charged (zeta potential of -4.8 ± 1.2 mV in our study, consistent with the literature), (Chen et al., 2015) which in theory, repels anionic molecules. Along with our results that negatively charged anti-scalants could exhibit distinct anti-scaling efficiencies (Figure C4), we suggest the strong binding

between functional group (e.g., -COO^-) with Ca(II) embedded within CaSO_4 nuclei via complexation, rather than electrostatic interaction, plays a more important role in gypsum scaling mitigation (more detailed mechanisms will be discussed below).

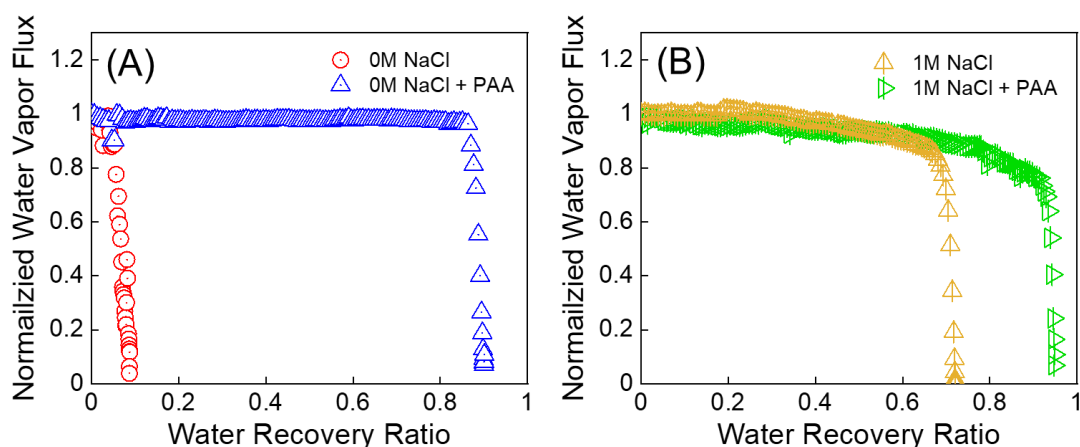


Figure 5-2. Normalized water vapor flux as a function of water recovery ratio in MD gypsum scaling experiments under different feedwater salinities. (A) Gypsum scaling under 0 M NaCl, and (B) gypsum scaling under 1 M NaCl. The initial SI of gypsum under 0 M NaCl and 1 M NaCl were 0.55 and -0.62, respectively. The initial SI of gypsum under 0 M NaCl and 1M NaCl were 0.55 and -0.62, respectively. The temperatures of feed and permeate streams were maintained at 60 °C and 20 °C, respectively. The feed and permeate streams were continuously circulated at crossflow velocities of 9.6 cm s^{-1} and 6.4 cm s^{-1} , respectively. The initial water vapor flux of PVDF membrane was $23.7 \pm 0.8 \text{ L m}^{-2} \text{ h}^{-1}$, which was used to normalize the water vapor fluxes in the figure.

5.3.2 Efficiencies of anti-scalant candidates in mitigating silica scaling

In order to investigate how scaling mechanism affects the relationship between the molecular feature and efficiency of anti-scalants, we also performed static and dynamic anti-scaling experiments for silica scaling. The concentration of molybdate-reactive silica (majorly in the form of monomeric silicic acid) was used to monitor the extent of silica polymerization in the solution. (Preari et al., 2014) As shown in Figure 5-1B, an initial decline in molybdate-reactive silica concentration was noticed within ~50 min, after which a concentration equilibrium was reached (except for with PEI). Compared to the control group, PEG showed a moderate stabilizing effect that maintained a slightly higher concentration of molybdate-reactive silica than

the control group. In contrast, the presence of PAA and PEI did not stabilize molybdate-reactive silica in the solution. In particular, silica polymerization was catalyzed by PEI molecules, as indicated by the significantly lower concentration of molybdate-reactive silica remained in the solution after ~60 min (Figure 5-1B).

When the PVDF membrane was challenged by the silica-supersaturated solution in dynamic MD experiments, both PAA and PEG were unable to delay the water vapor flux decline caused by silica scaling, resulting in the same water recovery ratio (~55%) as compared to the control group (Figure 5-1D). On the contrary, a much higher water recovery ratio (~80%) was obtained when the PEI was used as the anti-scalant in the feed solution (SI of 2.75 if not considering silica precipitation). Such an exceptional anti-scaling efficiency of PEI was probably attributed to the presence of amino groups. In order to test this hypothesis, we performed an additional MD experiment with PAMAM, a dendrimer-structure polymer enriched with amino groups. Our result showed that PAMAM was also able to inhibit silica scaling in the MD experiment (Figure C6A, Appendix C), providing more evidence that amino groups play an important role in mitigating silica scaling. Interestingly, PEI and PAMAM were found to facilitate, rather than slow down, silica polymerization reaction (Figure 5-1B, Figure C6B, Appendix C). This result indicates that anti-scalants do not necessarily hinder the precipitation of scale precursors in the solution. For silica scaling, anti-scalants that catalyze silica polymerization in the solution were able to mitigate the negative effect of silica scaling on water vapor flux of MD desalination. Such a phenomenon was in contrast with what was observed for gypsum scaling, for which the best anti-scalant showed the highest efficiency of stabilizing Ca^{2+} and SO_4^{2-} in the solution. Further, membrane pore wetting was not noticed in any silica scaling experiments (Figure C3B,

Appendix C), which was consistent with our previous publications. (Christie et al., 2019; Yin et al., 2019)

To assess the potential effect of feedwater salinity on anti-scaling efficiencies of PEI and PAMAM for silica scaling, we performed additional MD experiments by varying the background concentration of NaCl from 50 mM to 1 M NaCl. The solubility of silica is inversely correlated to solution salinity. (Lunevich et al., 2016) The initial SI values of silica feed solutions with 50 mM, 0.5 M, and 1 M NaCl were 0.55, 0.71 and 0.92, respectively. In the absence of anti-scalants, the decline of water vapor flux caused by silica scaling was facilitated as the concentration of background electrolyte increased. The water recovery of MD was ~58%, ~40%, and ~32% in the presence of 50 mM, 0.5 M, and 1 M NaCl (Figure C5B, Appendix C). When PEI or PAMAM was added in the feedwater, PEI and PAMAM were able to enhance the total water recovery at each level of feed solution salinity (Figure 5-3A – 5-3F). Therefore, PEI and PAMAM are still effective to mitigate silica scaling in MD under high feedwater salinities. Therefore, similar to the scenario of gypsum scaling, electric charge might not be the key feature that is mainly responsible for the anti-scaling efficiencies of amino-enriched anti-scalants such as PEI and PAMAM in MD (more detailed mechanisms will be discussed below).

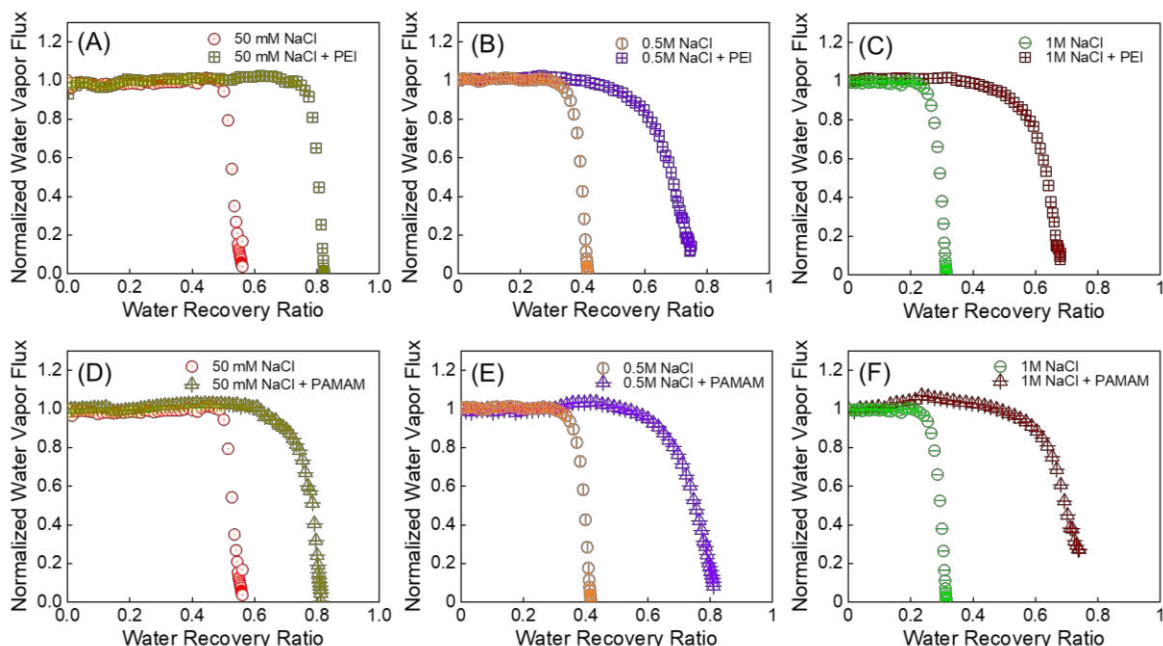


Figure 5-3. Normalized water vapor flux as a function of water recovery ratio in MD silica scaling experiments in the presence of 40 mg/L PEI and PAMAM under different feedwater salinities. (A-C) Silica scaling experiments with PEI as the anti-scalants. (D-F) Silica scaling experiments with PAMAM as the anti-scalants. The initial SIs of silica under 50 mM, 0.5 M, and 1 M NaCl were 0.55, 0.71 and 0.92, respectively. The temperatures of feed and permeate streams were maintained at 60 °C and 20 °C, respectively. The feed and permeate streams were continuously circulated at crossflow velocities of 9.6 cm s⁻¹ and 6.4 cm s⁻¹, respectively. The initial water vapor flux of PVDF membrane was 24.8 ± 1.1 L m⁻² h⁻¹, which was used to normalize the water vapor fluxes in the figure.

5.3.3 Morphological characterization of gypsum and silica scales on the membrane surface

The morphological features of gypsum and silica scales precipitated on the membrane surface were characterized by SEM (Figure 5-4). For the control group and in the presence of PEG, the scales formed with the gypsum-supersaturated feedwater exhibited a characteristic, needle-like crystal feature of gypsum (Figures 5-4A and 5-4C). Compared to the control group, longer and sharper gypsum morphology was observed when PEG was present in the feedwater. In the presence of PEI, platelet-like, smaller gypsum crystals precipitated on the membrane surface (Figure 5-4D). Thus, both PEG and PEI molecules distorted the formation of gypsum crystals while imposing different effects on the orientation of crystal growth. This was likely due

to the specific adsorption preference of PEG and PEI molecules onto varied gypsum crystal facets (the corresponding evidence will be provided in the next section). When PAA was added to the gypsum-supersaturated feed solution, the oriented gypsum crystals were not observed on the membrane surface, which was covered by a layer of amorphous-like scales (Figure 5-4B). Energy-dispersive X-ray spectroscopic (EDS) analysis showed that such amorphous scales were CaSO_4 (Figures C7 and C8, Appendix C). This remarkable alteration of scale morphology suggests that PAA significantly suppressed gypsum crystallization, rather than simply distorting the crystal morphology. Such suppression was in accordance with the exceptional performance of PAA in mitigating water vapor flux decline caused by gypsum scaling in MD (Figure 5-1C).

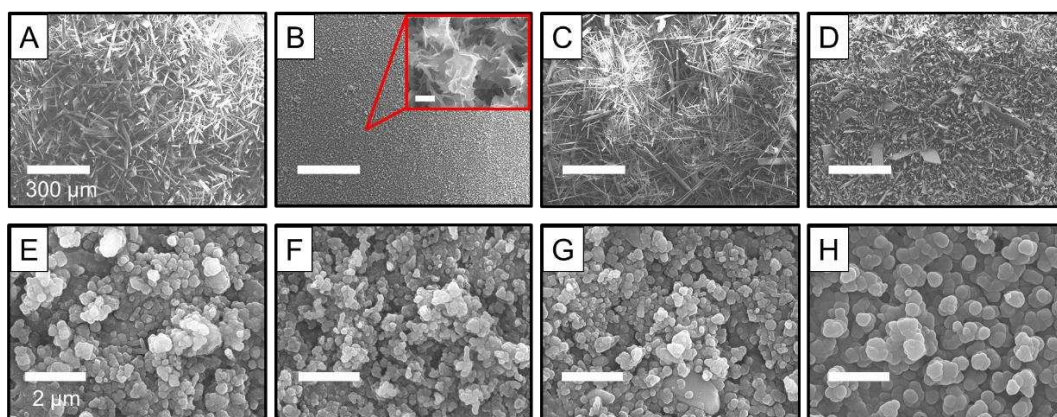


Figure 5-4. SEM micrographs of scales formed in gypsum- (A-D) and silica- (E-H) dynamic MD scaling experiments. (A and E) the control group, (B and F) in the presence of 40 mg/L PAA, (C and G) in the presence of 40 mg/L PEG, and (D and H) in the presence of 40 mg/L PEI. The magnifications of the SEM micrographs are 200X for A-D (9000X for the inset image in B) and 5000X for E-H. The scale bars represent 300 μm and 2 μm for A-D and E-H, respectively (the scale bar in inset of B represents 2 μm).

SEM characterization was also performed to observe the morphologies of silica scale on the membrane surface. Regardless of the type of anti-scalant candidates, silica particles were observed on the membrane surface (Figures 5-4E – 5-4H). There was no significant morphological difference between the silica scales formed in the control group and those in the presence of PAA or PEG. This similarity paralleled with the fact that PAA and PEG did not affect silica scaling behaviors in MD experiments (Figure 5-1D). On the contrary, when PEI or

PAMAM was used in the feed solution, larger silica particles with a clearer round-shape were observed (Figure 5-4H, Figure C9, Appendix C). The more regular and enlarged silica morphology was consistent with what have been observed in the field of biomineralization, in which amino-enriched molecules such as polyamines control silica morphology. (Kröger et al., 2000) Therefore, the alteration of silica morphology induced by PEI might relate to its exceptional anti-scaling efficiency in silica scaling MD experiments.

5.3.4 The crystalline feature and molecular structure of gypsum scales

To further understand the effects of anti-scalants on scale formation, XRD analysis was performed to characterize the crystalline feature of gypsum scales. As shown in Figure 5-5A, the XRD spectra of the control group indicated the presence of gypsum on the membrane surface, displaying characteristic peaks that correspond to the (020), (021), (040) and (041) facets of gypsum crystal. (Ben Ahmed et al., 2008; Rabizadeh et al., 2020) In the presence of PEG, the peaks for the (020), (021), and (040) facets either disappeared or were significantly reduced. This was likely attributed to the preferential adsorption of PEG molecules onto those facets of gypsum crystals, prohibiting their growth at the corresponding orientations. Such a hindering effect could result in the dominant growth of gypsum crystals upon specific orientation, explaining the longer and sharper gypsum morphology in the presence of PEG. When PEI was added into the feed solution, only the peak intensity of (020) facet was inhibited, suggesting a higher affinity of PEI molecules with this facet of gypsum crystals. In the presence of PAA, the small peaks for (301) and (400) facets of bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) indicate that limited phase transformation from amorphous CaSO_4 to this intermediate crystal phase towards gypsum might occur (Figure 5-5A). (Wang et al., 2012) Most characteristic peaks associated with gypsum crystal were not observed in the presence of PAA, consistent with the amorphous-like morphology of CaSO_4 on the

membrane surface observed in Figure 5-4B. Therefore, both PEG and PEI distorted the formation of gypsum crystal via adsorbing on specific crystal facets, while the crystalline nature of gypsum scales was maintained. In contrast, PAA imposed an essentially different mechanism to inhibit gypsum formation by completely constraining the transformation of metastable amorphous CaSO_4 to its most stable crystalline form (i.e., gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

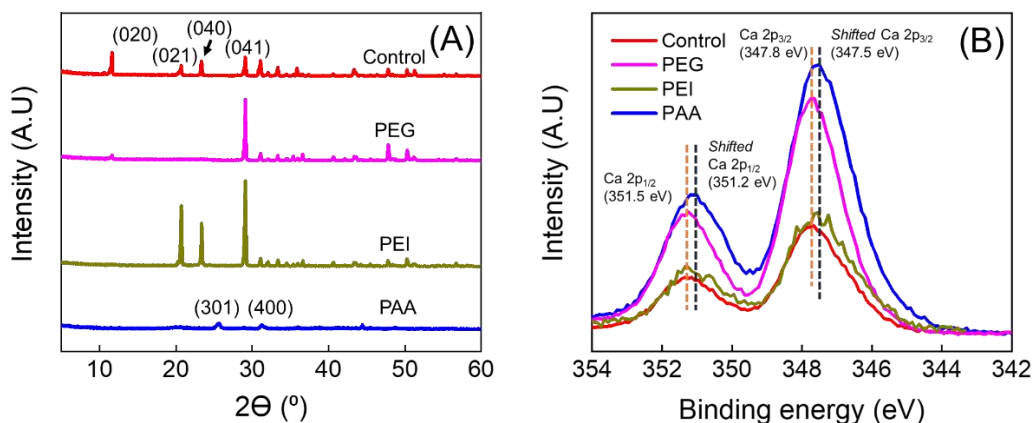


Figure 5-5. (A) XRD spectra of CaSO_4 precipitates on the PVDF membrane surface in the absence (i.e., control) and presence of anti-scalant candidates. (B) High resolution XPS spectra of Ca element of CaSO_4 precipitates on the PVDF membrane surface.

Furthermore, XPS analysis was performed to investigate the local chemical environment of CaSO_4 scales on the membrane surface. The high-resolution C 1s spectra confirms that the anti-scalant candidates used in this study coexisted with the CaSO_4 precipitates (Figure C10 and detailed explanation is in the Appendix C). As shown in Figure 5-5B, the high-resolution photoelectron spectra of element Ca for the control group displayed binding energies at 347.8 eV and 351.5 eV, which are assigned to the Ca 2p_{3/2} and Ca 2p_{1/2} spectral lines. (Demri and Muster, 1995) Compared with the control group, the presence of PEG and PEI resulted in negligible peak shifts of binding energies, suggesting that calcium was unlikely involved in any binding with the adsorbed anti-scalants. However, in the presence of PAA, both the binding energy of Ca 2p_{1/2} and Ca 2p_{3/2} shifted from 351.5 eV and 347.8 eV to lower energy of 351.2 eV and 347.5 eV,

respectively. Such a shift implies that calcium was binding with PAA molecules and such binding altered the chemical environment of calcium in the CaSO_4 scale. (Rabizadeh et al., 2019) Therefore, although the adsorption of anti-scalant candidates (i.e., PEG and PEI) onto the gypsum surface caused morphological distortion of the crystal, no chemical binding occurred between calcium and these organic molecules. In contrast, PAA molecules, which enriched with carboxyl groups, formed chemical binding with calcium. This could contribute to the disruption of gypsum crystallization as observed in Figures 5-4B and 5-5, resulting in the stabilization of CaSO_4 precursors in the solution (Figure 5-1A) and the mitigation of water vapor flux decline caused by gypsum scaling in MD desalination (Figure 5-1C).

5.3.5 The crystalline feature and molecular structure of silica scales on the membrane surface

The silica scale layers on the surface of PVDF membranes were also characterized via XRD. For all the experiments, the PVDF membranes subjected to silica scaling exhibited similar XRD spectra to the pristine PVDF membrane (i.e., without scaling), indicating the amorphous nature of silica scales (Figure 5-6A). Amorphous silica scales have been reported in both RO and MD, (Milne et al., 2014; Tong et al., 2017; Yin et al., 2019) which are in contrast with the crystalline gypsum scale. This difference resulted in different behaviors of gypsum and silica scaling in MD, which has been described in our recent published work. (Christie et al., 2019)

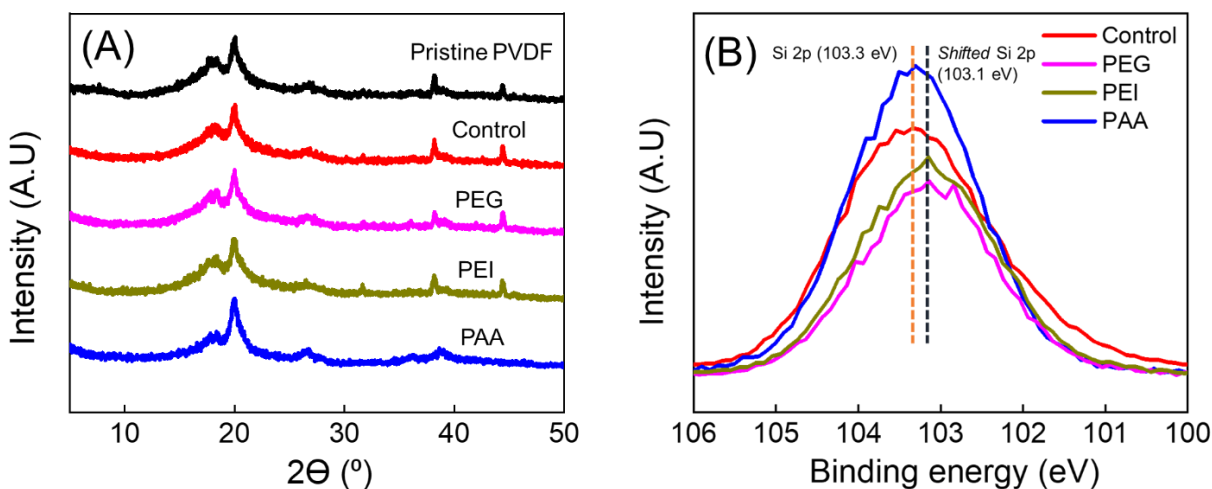


Figure 5-6. (A) XRD spectra of scaled and pristine PVDF membrane surfaces for silica scaling experiments. (B) High-resolution XPS spectrum of Si element of silica precipitates on the PVDF membrane surface.

The silica scale was further examined by XPS characterization. The presence of PAA, PEG, and PEI molecules in the silica scale layer was evidenced by the high-resolution C 1s spectra (Figure C11 and detailed explanation is in the Appendix C). To understand the changes in the local environment of element Si, the high-resolution Si 2p spectra were analyzed (Figure 5-6B). In the control group, the Si^{4+} oxidation state was confirmed by the typical peak at 103.3 eV that is assigned to the Si-O binding. (Wagner et al., 1982) The same peak binding energy in the presence of PAA indicates that PAA did not participate in silica formation during the scaling process, which paralleled with its negligible effect on silica polymerization and scaling behavior observed in Figures 5-1B and 5-1D. However, in the presence of PEG and PEI, the binding energy of Si 2p showed a negative shift from 103.3 eV to 103.1 eV. Although PEG and PEI resulted in the same binding energy shift of Si, the underlying mechanisms were different. PEG is able to form hydrogen bonding between the oxygen atom in ether groups of the PEG backbone and the hydrogen atom of the silanol group, (Preari et al., 2014) whereas catalyzing interaction between PEI molecules and silica species resulted in the formation of PEI-O-Si bonding. The

binding of PEG with silanol group was responsible for the moderate stabilization of molybdate-reactive silica in the solution, which was also observed by Preari et al. (Preari et al., 2014) In contrast, the presence of PEI catalyzes silicic acid polymerization and silica precipitation (Figure 5-1B), which will be explained in detail in the next section.

5.3.6 Mechanisms of anti-scalants to mitigate gypsum and silica scaling in membrane distillation

In this section, we intend to explain the mechanisms underlying the different requirements in functional groups of anti-scalants between gypsum and silica scaling. For gypsum scaling, we attribute the effectiveness of anti-scalants to their direct adsorption onto gypsum crystals, rather than Ca^{2+} complexation in the solution, because the anti-scalant concentrations were insufficient stoichiometrically. As evidenced by XRD characterization (Figure 5-5), PEG and PEI molecules hinder gypsum crystals growth in varied orientations, due to their adsorption preference on different crystal facets. But such an adsorption does not disrupt the crystallization process. As a result, although PEG and PEI are able to stabilize Ca^{2+} and SO_4^{2-} in the solution during a limited time period, they are unable to prevent the formation of gypsum crystals on the membrane surface or extend the water recovery of MD significantly. In contrast, PAA disrupts gypsum crystallization as evidenced by the amorphous-like CaSO_4 scale observed on the membrane surface and the significantly suppressed XRD spectra. Such disruption is mainly due to the affinity between the carboxyl groups of PAA molecules with Ca(II) of CaSO_4 nuclei (Figure 5-5B) via complexation, resulting in mitigated gypsum scaling and remarkably extended water recovery during MD desalination.

The effects of anti-scalant candidates on silica scaling are more complex and intriguing. PEG was able to stabilize silica in the solution due to its formation of hydrogen bonding with the silanol group, (Preari et al., 2014) whereas PEI and PAMAM displayed an opposite effect to

promote silica polymerization (Figure 5-1B). Under the solution pH of our study (pH of 6.50), silica polymerization proceeds with the reaction between neutrally charged silicic acid and negatively charged, ionized silicic acid. (Bishop Jr and Bear, 1972) The capability of anti-scalants to interfere this process is critical to their anti-scaling effect in silica scaling. (Neofotistou and Demadis, 2004) The amino groups of PEI and PAMAM are able to receive protons from neutrally charged silicic acid, aiding in the formation of ionic silica species as acid-base catalysts. (Fleming, 1986; Kröger et al., 2000; Mizutani et al., 1998) This creates a high local concentration of reactive silica species near PEI and PAMAM molecules, resulting in a faster kinetic of silica polymerization. Interestingly, the facilitated silica polymerization induced by PEI or PAMAM does not expedite the water vapor flux decline caused by silica scaling in MD. Instead, the presence of PEI or PAMAM significantly extends the water recovery (Figure 5-1D). This phenomenon is in distinct contrast with what is observed for gypsum scaling, for which PAA that stabilizes scale precursors and hinders precipitation is the most effective to improve MD performance. Furthermore, the use of anti-scalants does not alter the amorphous nature of silica scale. Instead, PEI and PAMAM modify the size and shape of silica scale, resulting in the formation of larger and more spherical particles on the membrane surface. Thus, rather than disrupting the crystallization process (e.g., PAA for gypsum scaling), the most effective anti-scalants for silica scaling affect the kinetics and morphology of silica scale formation.

In order to further explain the contrasting properties of anti-scalants required by gypsum and silica scaling, we would like to compare how these two scaling types damage MD performance (Figure 5-7). Due to their crystalline and oriented nature, gypsum crystals are able to cover the membrane surface, intrude into and block the membrane pores, and initiate pore wetting that

eventually compromises the distillate quality (observed in the current study and our previous work (Christie et al., 2019; Yin et al., 2020)). In order to mitigate gypsum scaling, it is necessary to constrain the phase transformation of CaSO_4 into crystalline gypsum. Wang et al. (Wang et al., 2012) demonstrate that gypsum formation is a complex process that consists of several stages, in which amorphous CaSO_4 is the precursor that can be converted to gypsum via $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ as the intermediate phase. As the CaSO_4 nuclei is formed, the carboxyl groups of PAA molecules immediately create a strong affinity with the CaSO_4 nuclei via complexation (Figure 5-7C). The intercalation of PAA within the CaSO_4 lattice structure completely disrupts its long-range order, thereby inhibiting the crystalline transformation to the gypsum phase. Furthermore, the presence of water molecules within the crystal structure might contribute to the crystallographic stability of gypsum. (van der Voort and Hartman, 1991) Thus, the release of H_2O adsorbed with Ca(II) as a result of ligand exchange between $-\text{COO}^-$ of PAA and $-\text{OH}$ of H_2O adsorbed on the CaSO_4 nuclei surface is likely another factor that results in the capability of PAA molecules in preventing the transformation of amorphous CaSO_4 nuclei to gypsum crystals. (Massaro et al., 2011) Our results are similar to what have been observed in the pioneering work of Aizenberg et al., (Aizenberg et al., 1996; Aizenberg et al., 2002; Beniash et al., 1997) in which macromolecules enriched with carboxylic functional groups were shown to inhibit the transformation of amorphous CaCO_3 into crystalline calcite. Therefore, the key property of an effective anti-scalant for gypsum scaling in MD is its capability of stabilizing the scale precursors (as well as the nascent CaSO_4 nuclei) and preventing the crystalline transformation to gypsum. Such an effect is also supported by the fact that PAA prevents membrane wetting caused by gypsum scaling, a characteristic outcome of oriented gypsum crystallization. (Christie et al., 2019)

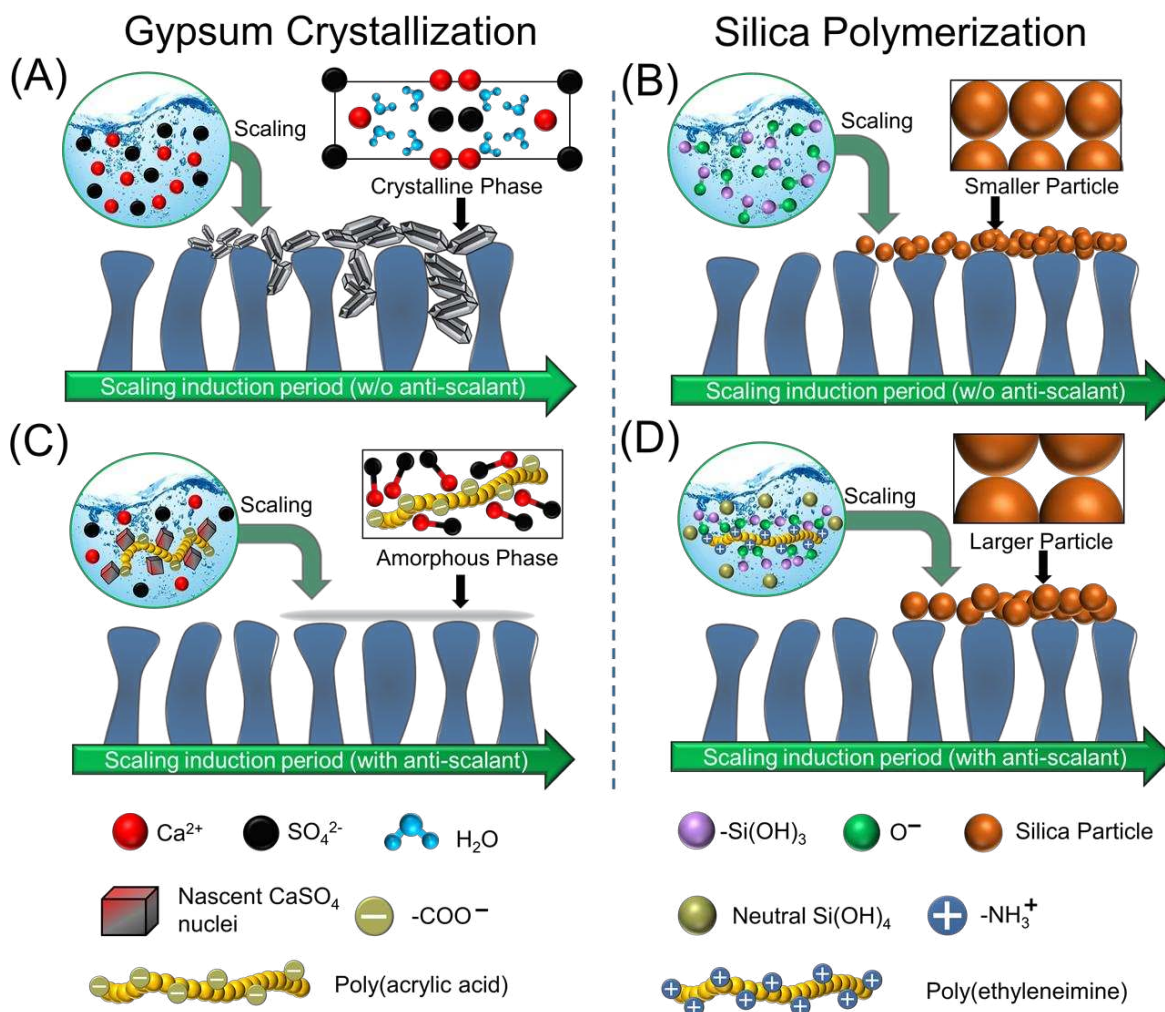


Figure 5-7. Schematics of the mechanisms underlying the effectiveness of anti-scalants to mitigate gypsum and silica scaling in MD. (A) Gypsum scaling formed via crystallization in the absence of anti-scalants. (B) Silica scaling formed via polymerization in the absence of anti-scalants. (C) PAA mitigates gypsum scaling by stabilizing scale precursors and CaSO_4 nuclei in the solution. (D) PEI mitigates silica scaling by promoting silica polymerization and immobilizing reactive silica precursors in the solution or as silica particles. It is worth mentioning that the PEI in Figure D could be replaced by PAMAM dendrimers.

In contrast to gypsum scaling, silica scaling is formed via polymerization reaction that is lack of orientation. In our previous publication, (Yin et al., 2019) we demonstrate that silica scales formed via heterogeneous nucleation do not cause water vapor flux decline in MD. Instead, silica particles formed via homogeneous nucleation are deposited onto the membrane surface, followed by further reactions of the deposited particles with the remaining silica species

in the feed solution to form a cross-linked silica gel layer (Figure 5-7B). The coverage of impermeable silica gel layer on the membrane surface, rather than its thickness (Figure C12, Appendix C), is directly responsible for the severe and irreversible decline of water vapor flux. (Christie et al., 2019; Yin et al., 2020; Yin et al., 2019) In the presence of PEI or PAMAM, as the process of silica polymerization is catalyzed, highly reactive, ionized silica species are accumulated near the amino-enriched molecules, where they are consumed to form larger silica particles. Therefore, there is a lack of reactive silica species available near membrane surface, and the formation of cross-linked silica gel layer is thus disrupted and slowed down. In other words, despite of its capability of catalyzing silica polymerization, PEI and PAMAM molecules “immobilize” the silica scale precursors in the solution or in the form of silica particles (Figure 5-7D). Further, due to the hydrophilicity of silica particles, the feed solution is still able to penetrate the space between the silica particles when the cross-linked silica gel layer has not been fully formed (Figure C13, Appendix C). A broader space exists between the larger silica particles formed in the presence of PEI or PAMAM (Figure 5-7D), indicating that a longer time might be needed to form an impermeable gel layer that completely covers the membrane pores. This could partially contribute to the significantly delayed induction of water vapor flux decline caused by silica scaling in the presence of PEI.

5.4 Conclusions

In this study, we performed a comparative investigation on the effectiveness of anti-scalant candidates with varied functionalities to mitigate gypsum and silica scaling in MD. We demonstrate that these two common types of mineral scaling, which result from distinct formation mechanisms (crystallization for gypsum vs. polymerization for silica), are alleviated by anti-scalants with different functional groups. Anti-scalants such as PAA that is enriched with carboxyl groups exhibited exceptional efficiencies to hinder gypsum scaling and remarkably extended the water recovery of MD desalination. In silica scaling, amino-enriched anti-scalants such as PEI and PAMAM showed promising capabilities of effectively reducing the adverse effect of silica scaling on the MD performance. Further, although PAA, PEI, and PAMAM possess different functional groups, all anti-scalants were still effective in mitigating gypsum and silica scaling in MD under high feedwater salinities.

In addition, our results also suggest that an effective anti-scalant does not always hinder the precipitation of scaling-forming species. Instead, preventing the scale precursors from blocking the membrane pores, either via stabilizing them in the solution or immobilizing them away from the membrane surface, is the key to delay the induction of mineral scaling and achieve high water recovery of MD under high scaling potential. Tailored molecular design of effective anti-scalants, which results from an in-depth understanding of scaling mitigation mechanisms, is needed for the applications of MD to the treatment of wastewaters with different scaling types. In addition, it is worth mentioning that commercial anti-scalants might contain a mixture of chemicals with proprietary compositions. The behaviors of these anti-scalants might differ from those used in the current study, which have well defined molecular structures. Also, the requirements of anti-scalants in MD might vary compared to those in RO and nanofiltration, in

which much lower concentrations of scalants could result in different scaling formation mechanisms. Therefore, future research should be directed to test the discoveries of this study for commercial anti-scalants and/or in other membrane processes such as RO and nanofiltration.

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6.0 The Use of Anti-scalants in Gypsum Scaling Mitigation: Comparison with Membrane Surface Modification and Efficiency in Combined Reverse Osmosis and Membrane Distillation⁵

6.1 Introduction

Membrane scaling, which results from the precipitation of minerals such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) on the membrane surface, is a major challenge that is detrimental to membrane-based desalination (Alkhudhiri et al., 2012; Antony et al., 2011; Horseman et al., 2020; Rahardianto et al., 2008; Tong et al., 2019). Membrane scaling is directly responsible for the reduction of water flux and salt rejection (Antony et al., 2011; Christie et al., 2019; Jaramillo et al., 2021; Karanikola et al., 2018; Tong et al., 2019). Further, as the membrane is covered by mineral scales, cleaning protocols are required to restore the water flux performance (Mi and Elimelech, 2013; Yin et al., 2020). However, membrane cleaning requires the use of corrosive chemicals or an extensive amount of electrical energy (Bush et al., 2018; Yin et al., 2020), which increases system maintenance costs and complicates the desalination process.

Reverse osmosis (RO) is the most energy efficient technology that is widely implemented for desalinating seawater, brackish water, and wastewater (Biesheuvel et al., 2019; Davenport et al., 2018; Elimelech and Phillip, 2011; Greenlee et al., 2009; Patel et al., 2021). In RO, a high hydraulic pressure is applied to the active layer of a thin-film composite (TFC) membrane to produce water flux (Greenlee et al., 2009). However, two major drawbacks exist and limit the

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performance of RO systems: membrane scaling and the generation of high-salinity brines. For example, the concentrations of scaling precursors for gypsum (Ca^{2+} and SO_4^{2-}) can be close to their solubility limit in brackish water (Sheikholeslami and Ong, 2003). Such scenarios, combined with concentration polarization that increases the solute concentration near the membrane surface, render RO membranes susceptible to membrane scaling (Chen et al., 2004; Chong et al., 2007). Furthermore, the continuing extraction of pure water from the feedwater in RO leads to the production of high-salinity RO brines, which are notoriously damaging to the environment upon discharge (Lattemann and Höpner, 2008). Therefore, effectively mitigating membrane scaling and improving water recovery (to reduce the brine volume) are highly desirable to improve the feasibility of RO in practical applications.

In order to further treat high-salinity RO brines, membrane distillation (MD), a thermal driven membrane desalination process, has recently attracted great attention because of its tolerance to high salinities and the capability to use low-grade heat as the energy source (Alkhudhiri et al., 2012; Deshmukh et al., 2018; Lawson and Lloyd, 1997). The strengths of MD make it suitable as a complement to RO for achieving minimal liquid discharge (MLD) or even zero liquid discharge (ZLD) (Martinetti et al., 2009; Panagopoulos and Haralambous, 2020; Tong and Elimelech, 2016). However, membrane scaling also occurs and compromises the efficiency of MD (Horseman et al., 2020; Tijing et al., 2015). In addition to severe reduction in water vapor flux caused by mineral scaling, membrane wetting, in which the saline feedwater floods into membrane pores, imposes additional deleterious impacts on MD performance by contaminating the permeate stream (Horseman et al., 2020). For example, the growth of gypsum crystals can occur on the membrane surface as well as inside the membrane pores (Christie et al., 2019). The in-pore crystal growth blocks the membrane pores and further causes pore

deformation that leads to membrane wetting (Christie et al., 2019; Gryta, 2009; Warsinger et al., 2017). Thus, a highly efficient and easily accessible strategy to mitigate scaling is crucial for both RO and MD to improve membrane desalination efficiencies.

Membrane surface modification has been studied extensively as a potential strategy to mitigate membrane scaling in RO and MD (Ashfaq et al., 2020; Cao et al., 2018; Jaramillo et al., 2021; Karanikola et al., 2018; Su et al., 2019; Xiao et al., 2019). Most recently, Jaramillo et al. reported that the thin-film composite (TFC) polyamide membrane modified with a layer of zwitterionic polymers was able to delay membrane scaling caused by gypsum formation (Jaramillo et al., 2021). In another study (Kim et al., 2010), hydrophilic poly(methacrylic acid) (PMAA) polymer chains anchored on the polyamide membrane surface demonstrated a reduction in membrane scaling propensity, likely due to a low probability of nuclei attachment on the membrane surface. However, membrane surface modification is only able to interfere with heterogeneous nucleation of scales on the membrane surface or hinder the attachment of nuclei. The deposition of scale particles formed from homogeneous nucleation in the bulk solution could still occur, which also leads to water flux decline (Horseman et al., 2020).

In addition to membrane surface modification, the use of anti-scalants is a viable method of scaling control. For example, anti-scalants enriched with phosphonate functional groups were found to greatly retard the precipitation of calcium minerals in desalination brines (Jain et al., 2019). Also, gypsum formation is largely constrained in the presence of poly(acrylic) acid (PAA) that contains carboxyl groups (Ben Ahmed et al., 2008; Le Gouellec and Elimelech, 2002; Rabizadeh et al., 2019). In RO, the application of anti-scalants has been a common component of pretreatment (Antony et al., 2011). Shmulevsky et al. reported that use of synthetic anti-scalants with carboxyl functional groups delayed the onset of water flux decline caused by gypsum

scaling (Shmulevsky et al., 2017). In another study, Shih et al. (Shih et al., 2006) investigated five types of anti-scalant candidates and found that the anti-scalant formulated with PAA as an active ingredient exhibited the best efficacy in mitigating gypsum scaling. In MD, applying anti-scalants to mitigate membrane scaling has received more attention recently (Elcik et al., 2020; He et al., 2009; Qu et al., 2020; Yan et al., 2020). Recently, we demonstrated that the effectiveness of anti-scalants in retarding mineral scaling mainly depends on the interactions between functional groups of anti-scalants and scale precursors or nuclei (Yin et al., 2021). Although both membrane surface modification and the use of anti-scalants have been shown to reduce mineral scaling, their efficiencies have not been compared. Such a comparison could provide valuable insights on the selection of appropriate strategies for scaling mitigation in membrane desalination.

In this work, we first compared the efficacies of membrane surface modification and the use of PAA (as anti-scalants) to minimize gypsum scaling in RO. The surface of a commercial TFC polyamide RO membrane was grafted with different polymer coatings, which imparted varying functionality, hydrophilicity, and electric charge to the membrane surface. The anti-scaling performances of the modified membranes and PAA were comparatively evaluated in a cross-flow RO system fed with gypsum-supersaturated solutions. Our results show that the use of PAA outperformed membrane surface modification in retarding gypsum scaling, and thus we further investigated the efficacy of PAA for gypsum scaling mitigation in a combined RO-MD treatment train. The total water recovery achieved by the combined RO-MD system was used to examine the effectiveness of PAA to enhance our capability of pursuing high water recovery from feedwaters with high scaling potential. The implications of our work in scaling mitigation for membrane desalination are also discussed.

6.2 Materials and Methods

6.2.1 Materials and chemicals

Sodium sulfate (Na_2SO_4), acrylic acid (CH_3CHCOOH), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, 99%), sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$, 99%), dopamine chloride, tris(hydroxymethyl)aminomethane (Tris, $\geq 99.8\%$), poly(acrylic) acid (PAA MW 1800), poly(ethylenimine) (PEI, MW 1800), 2-propanol (IPA, $\geq 99.5\%$), [2-(methacryloyloxy)-ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (also named as sulfobetaine methacrylate, SBMA, 95%), copper-(II) chloride (CuCl_2 , 99%), tris(2-pyridylmethyl)amine (TPMA, 98%), α -bromoisobutyryl bromide (BiBB, 98%), triethylamine (TEA, $\geq 99\%$), and N, N-dimethylformamide (DMF, $\geq 99.8\%$) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH) and hydrochloric acid (HCl, 36%) were acquired from Fisher Chemical (Hampton, NH, USA). L-ascorbic acid (98%) was purchased from Alfa Aesar (Haverhill, MA, USA). Commercial RO membranes (FILMTEC Flat Sheet XLE) and PVDF membranes (HVHP) with a nominal pore size of $0.22 \mu\text{m}$ were provided by DuPont FILMTEC and Millipore Sigma (Burlington, MA, USA), respectively. A water purification system ($> 18\text{M}\Omega$) manufactured by Millipore (Burlington, MA, USA) was used to provide deionized (DI) water.

6.2.2 Membrane surface modification of RO membrane

The Dupont XLE membrane was used as the control membrane for membrane modification. The membranes were immersed in a 25 v/v% isopropyl alcohol solution for 30 min, washed thoroughly by DI water, and then stored at 4°C until further use. Three surface modification approaches were used: activators regenerated by electron transfer-atom transfer radical polymerization (ARGET-ATRP), redox radical initiation, and dopamine-assisted direct grafting.

The procedures of these membrane modification approaches were adopted from our previous publication (Tong et al., 2017), with the principle of each approach briefly described below.

ARGET-ATRP has been applied to synthesize well-defined polymeric molecules with narrow polydispersity, controllable architecture, and accurate composition (Matyjaszewski et al., 2007; Ye et al., 2015). This method was used to graft poly(sulfobetaine methacrylate) (PSBMA), a zwitterionic polymer, onto the membrane surface. Briefly, dopamine hydrochloride (DA) reacted with α -bromoisobutyryl bromide (BiBB) to initiate the formation of polydopamine-BiBB (PDA-BiBB) on the membrane surface. Then, the PSBMA polymer was grown on the PDA-BiBB modified membrane surface via polymerization in the presence of sulfobetaine methacrylate catalysed by Cu(II)/tris(2-pyridylmethyl)amine. The fabricated membrane is referred to as the PSBMA-RO membrane in this study.

Redox radical initiation was used to graft PAA, a negatively charged polymer at near neutral pH, onto the membrane surface. Oxidizing agents ($K_2S_2O_8$ and $Na_2S_2O_5$) were used to create oxygen-centered radicals by abstracting hydrogen from polyamide membrane surface (Belfer et al., 1998). The oxygen-centered radicals play a critical role in bridging vinyl monomers (i.e., acrylic acid) by attacking their double bond, which initiates the subsequent polymerization (Belfer et al., 1998). The fabricated membrane is referred to as the PAA-RO membrane in this study. Also, it is worth mentioning that PAA is the polymer on the membrane surface in this section, although it has the same chemical structure of the anti-scalant applied in this study.

PDA-assisted direct grafting was used to graft PEI, a positively charged polymer at near neutral pH, to the membrane surface. The oxidation of catechol groups from the PDA molecules results in formation of *o*-quinone groups. The *o*-quinone groups are highly reactive electrophilic moieties that readily initiate a secondary reaction with amine groups of PEI molecules,

subsequently creating a PEI layer on the membrane surface. The PEI modified membranes is referred to as the PEI-RO membrane in this study. In addition, a PDA-modified RO membrane was fabricated using dip-coating in a dopamine chloride solution buffered by tris(hydroxymethyl) aminomethane (pH 8.5) (Tong et al., 2017). This membrane, referred to as the PDA-RO membrane, was used to isolate the potential effect of PDA on membrane scaling propensity. After surface modification reactions, all the modified membranes were washed thoroughly by DI water and stored at 4 °C until further use.

6.2.3 Membrane characterization

The measurement of static water contact angles (WCA) of the RO membranes was performed using a sessile drop method (Ramé-hart Instrument Corporation, Succasunna, NJ, USA). The zeta potential of the membrane surfaces tested in this study was measured using an electrokinetic analyzer with an adjustable gap cell (SurPASS, Anton-Paar, Ashland, VA, USA). Each measurement was conducted using a 1 mM KCl electrolyte solution, with titration performed automatically over the pH range of 3-9. Scanning electron microscopy (SEM, JEOL JSM-6500F, Peabody, MA, USA) was used to analyze the membrane surface morphology. SEM coupled with energy dispersive X-ray spectrometer (EDX, Oxford Instrument, Concord, MA, USA) was used to analyze the morphology and elemental composition of the scale after scaling experiments. Also, the spectra of attenuated total reflectance-Fourier transform infrared (ATR-FTIR) were collected using a Nicolet spectrometer (Thermal Fisher Scientific, Waltham, MA, USA) in order to analyze the surface functionality of the membranes.

The water permeance of RO membranes used in this study were characterized with DI water in a custom-built RO system with a cross-flow velocity of 21.3 cm s⁻¹. Before characterization, the membrane was compacted under an applied pressure of 20.7 bar (300 psi) overnight with the

temperature maintained at 25.5 ± 0.1 °C. The water fluxes were then measured at different applied pressures (6.9, 13.8, and 20.7 bar). Then the DI water was replaced by a feed solution containing 50 mM NaCl in order to measure salt permeability of the membranes. The apparent salt rejection was determined at an applied pressure of 20.7 bar (300 psi) by comparing the electrical conductivity of the permeate to that of the feed solution. The water permeance, A , was calculated from the slope of the water flux as a function of the applied pressure (Jaramillo et al., 2021). The salt permeability coefficient, B , was determined with the water flux and intrinsic salt rejection rate according to Equation 6-1 (Werber et al., 2016):

$$\frac{R_{int}}{1 - R_{int}} = \frac{J_w}{B} \quad (6 - 1)$$

where J_w is the water flux, and R_{int} is intrinsic salt rejection, which was calculated by considering the effect of concentration polarization via equation:

$$R_{int} = 1 - \frac{C_p}{C_{f,m}} \quad (6 - 2)$$

where C_p is the solute concentration of the permeate, $C_{f,m}$ is the solute concentration at the feedwater-membrane interface, which was calculated using thin film theory (McCutcheon and Elimelech, 2006).

6.2.4 Gypsum scaling experiments

6.2.4.1 Reverse osmosis

A laboratory-scale, cross-flow RO system with an effective membrane area of 20.02 cm² was employed to perform gypsum scaling experiments. The change of water flux as a function of time was used to compare the anti-scaling efficiencies of membrane surface modification and the use of PAA in suppressing gypsum scaling in RO.

The gypsum-saturated solution contained 24 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 24 mM Na_2SO_4 , corresponding to an initial saturation index (SI, defined as the natural logarithm of ratio between the ion activity to the product solubility, $\ln(IAP/K_{sp})$) of 0.37 as calculated by PHREEQC software with the WATEQ4F database (PC Version). When the anti-scaling efficiencies of PAA were evaluated, different PAA concentrations (3.3 mg/L, 6.7 mg/L and 13.3 mg/L) were added individually in the above gypsum-saturated feed solution. It is worth mentioning that PAA was added into the feed solution prior to the mixing of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and Na_2SO_4 , in order to avoid the formation of gypsum nuclei before the addition of PAA. The pH value of all the feed solutions used in this study was adjusted to 6.50 ± 0.05 using 1 M HCl and 1 M NaOH.

The membranes were compacted overnight before the scaling experiments using DI water under an applied pressure of 13.8 bar (200 psi) at 25.5 ± 0.1 °C (controlled by a recirculating chiller, Polyscience, Niles, Illinois, USA). As the RO system was stabilized and operating with a stable water flux after membrane compacting, the prepared gypsum-saturated solution was added into the feedwater reservoir to replace the DI water. Due to the different water permeances among the tested membranes, varied hydraulic pressures of 10.3 ± 1.4 bar (150 ± 20 psi) were applied to create an identical initial water flux of $40.5 \pm 0.8 \text{ L m}^{-2} \text{ h}^{-1}$ (at a cross-flow velocity of 21.3 cm s^{-1}), in order to avoid the effect of concentration polarization on the membrane scaling propensity. The water flux was recorded automatically using a digital flowmeter (FlowCal 5000, Tovatech, Maplewood, USA) connected with a laptop (Lenovo, Morrisville, USA). The temperature of the feedwater was maintained at 25.5 ± 0.1 °C throughout the scaling experiment. A recirculating mode was applied, where both the feed and permeate streams flowed back to the feedwater reservoir. After the scaling tests, the membrane coupons were removed from

membrane cell, gently washed with DI water, and dried in air for further material characterization.

6.2.4.2 Combined reverse osmosis and membrane distillation treatment train

The experimental setup to assess the efficiency of PAA for scaling mitigation in a combined RO-MD system is schematically illustrated in Figure 6-1. A laboratory-scale RO system was first used to desalinate the gypsum-supersaturated solutions as described above. As the permeate was being collected in a separate reservoir, the RO feedwater was continuously concentrated to produce RO brine. At the end of the RO treatment, the RO brine was then transferred to the MD unit for further treatment. It is worth mentioning that the anti-scalants were only added in the feedwater of the RO unit. As the MD unit received RO brines, no additional anti-scalants were added to the MD feed solution.

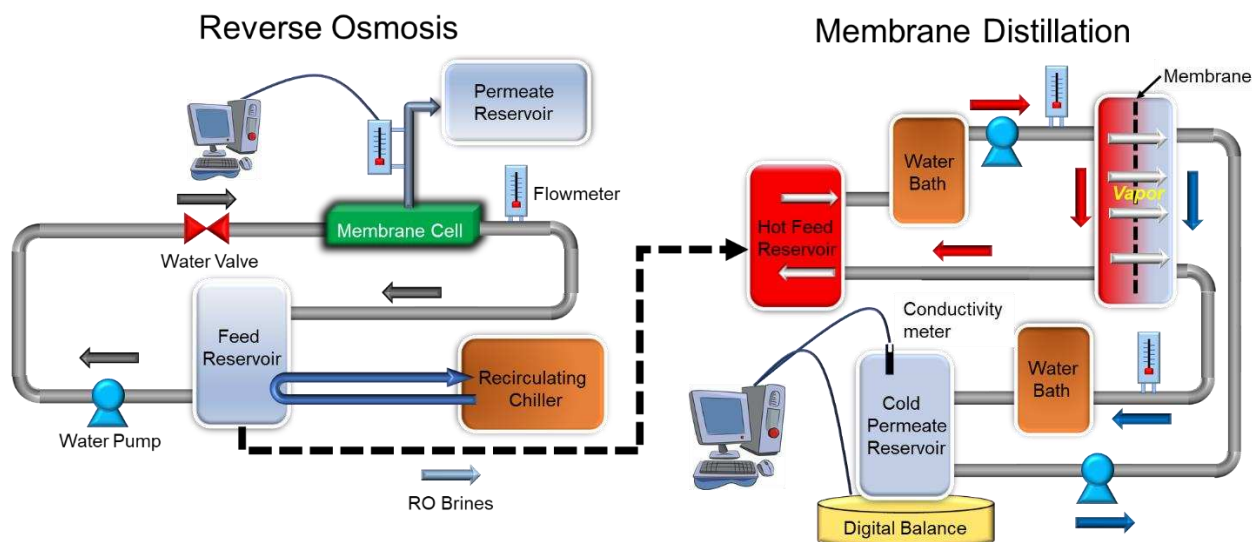


Figure 6-1. Schematic description of the combined RO-MD system. The brine produced by RO was collected after the experiment and then served as the feedwater for the subsequent MD system.

The gypsum-saturated solution containing 24 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 24 mM Na_2SO_4 (6000 mL) was used as the control group. For the experimental groups, 3.3 mg/L, 6.7 mg/L, or 13.3 mg/L of PAA was added individually to the feedwater. The pH of the feed solutions was

adjusted to 6.50 ± 0.05 using 1 M HCl and 1 M NaOH. The RO desalination was performed using the identical RO setup equipped with the commercial Dupont XLE membrane as described in Section 2.4.1, except that the RO permeate was collected separately to generate concentrated RO brines. Prior to MD, the RO scaling experiments were terminated when the water flux decreased more than 80% or the RO system had been run for 2000 minutes. After scaling experiments, the RO membrane coupons were removed from the system and washed with DI water gently, dried under ambient conditions, and then preserved for further analysis by SEM-EDX.

A custom-built, direct contact MD (DCMD) system equipped with a hydrophobic PVDF membrane was used to further treat the RO brines as received. The volume of the feed solution (RO brines) was 2000 mL, with the temperatures of the feed and permeate streams maintained at 60 °C and 20 °C, respectively. The cross-flow velocities were 9.6 cm s^{-1} and 6.4 cm s^{-1} for the feed and permeate streams, respectively. The real-time water vapor flux and salt rejection rate in MD were calculated based on the changes of weight and conductivity of the permeate reservoir. These values were measured using a top-loading digital balance (Cole-Parmer) and a bench-top conductivity meter (Oakton Instrument), respectively. Further, we performed two cycles of MD treatment, in which the PVDF membrane that was fully scaled in the first MD cycle (i.e., water vapor flux decreased to zero) was replaced with a new PVDF membrane to start another MD cycle. The efficiency of residual PAA from RO brines in suppressing gypsum scaling in MD was assessed in terms of water recovery ratio (defined as V_{rec}/V_{ini} , where V_{rec} is the volume of distillate recovered from the feed solution and V_{ini} is the initial feedwater volume before experiment). After scaling experiments, the membrane coupons were collected and preserved for further analysis by SEM-EDX (the same as the RO membranes above). In this study, both the

RO and RO-MD experiments were very reproducible, as shown in the Appendix D (Figures D1 and D2).

6.3 Results and discussion

6.3.1 Surface characterization of RO membranes

The surface morphologies of RO membranes investigated in this study were observed using SEM. A typical ridge-and-valley structure was observed on the surface of the pristine RO membrane (Figure 6-2A). After modifying the membrane surface with different polymers (e.g., PAA, PEI, PDA, and PSBMA), all modified membranes displayed an identical surface morphology to the pristine RO membrane (Figures 6-2B – 6-2E), indicating that only an ultra-thin polymer layer was coated onto the membrane surface.

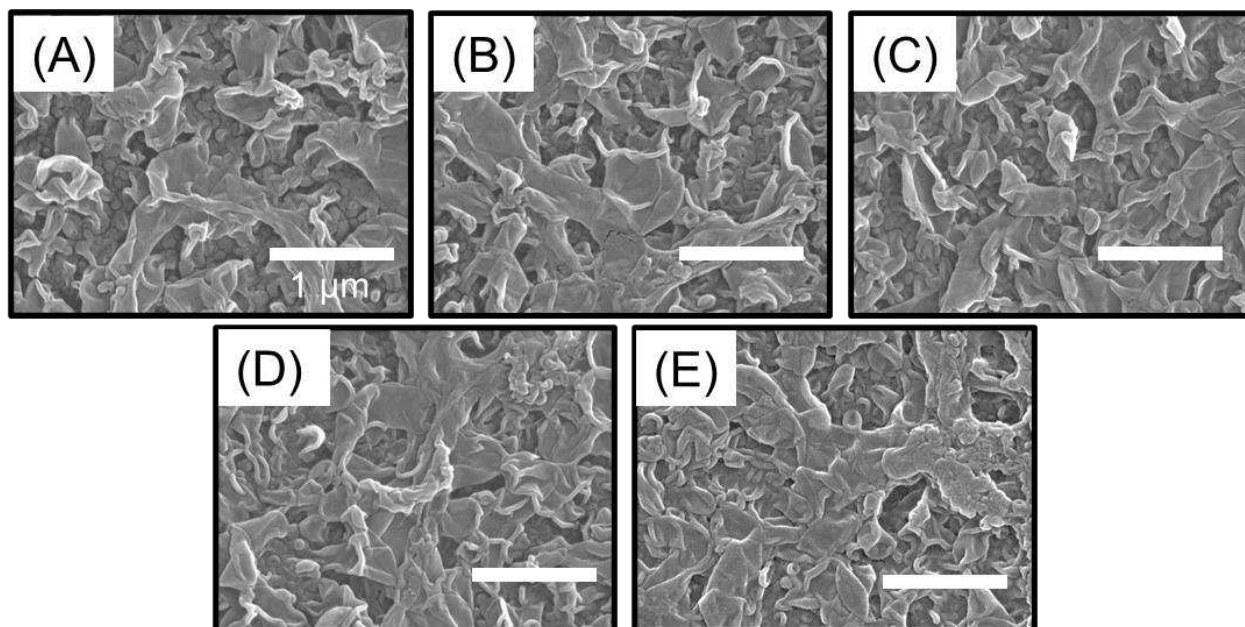


Figure 6-2. Top-view SEM micrographs of the RO membrane surface for (A) pristine RO membrane and membranes modified with (B) PAA, (C) PEI, (D) PDA, and (E) PSBMA. The magnification is 40000X and the scale bars represent 1 μm .

To prove successful grafting of polymers, ATR-FTIR spectroscopy was applied to characterize surface functionality of membrane surfaces (Figure 6-3). For all tested RO membranes, the peaks centered at 1543 and 1665 cm^{-1} are ascribed to the vibrations of C-N-H

and N-C=O functional groups of polyamide, while the peaks at 1150 and 1323 cm^{-1} are due to symmetric stretching and asymmetric stretching of $-\text{SO}_2-$ groups of polysulfone (the supporting layer) (Ye et al., 2015). A new peak at 1720 cm^{-1} was noticed for the PAA-RO membrane, which is assigned to the C=O stretching from $-\text{COOH}$ functional groups of PAA (Ma et al., 2015). For the PSBMA-RO membrane, the ATR-FTIR spectrum displays two additional peaks at 1039 and 1729 cm^{-1} , which are attributed to symmetric stretching of the sulfonate groups of SBMA molecules and the carbonyl moiety of the ester group, respectively (Ye et al., 2015). These observations indicate successful grafting of PAA and PSBMA polymers on the membrane surface. However, the indicative absorbance of the functional groups for other modified membranes was masked in the ATR-FTIR spectra because they were greatly overlapped with the functional groups of TFC polyamide membrane. Thus, no difference was observed for their ATR-FTIR spectra compared to that of the pristine RO membrane.

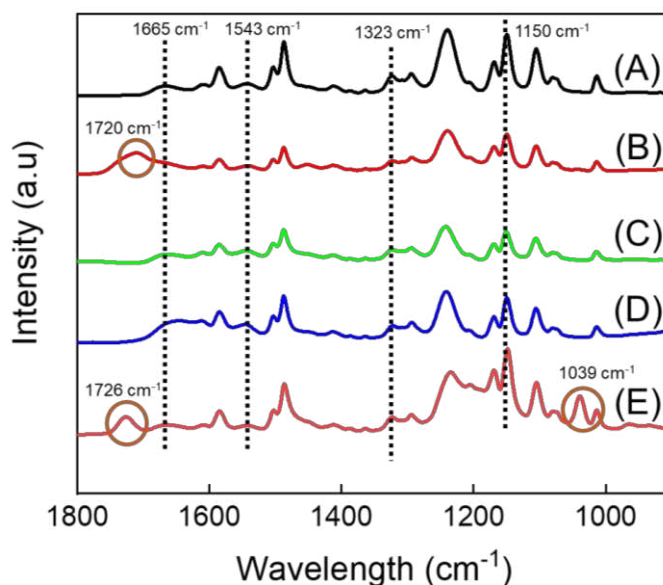


Figure 6-3. ATR-FTIR spectra of the (A) pristine RO membrane and the RO membranes modified with (B) PAA, (C) PEI, (D) PDA, and (E) PSBMA polymers. The peaks at 1150, 1323, 1543, and 1665 cm^{-1} are highlighted to indicate the presence of characteristic functional groups attributed to the polyamide selective layer and polysulfone supporting layer. The absorbance at 1720 cm^{-1} indicates carboxyl group

from PAA, while the peaks at 1039 and 1726 cm^{-1} are characteristic of sulfonate groups and carbonyl groups from PSBMA.

Further, the introduction of various functional groups via membrane surface modification is able to alter the hydrophilicity of the membrane surface. As shown in Figure 6-4A, the surface of the pristine RO membrane was hydrophilic, as indicated by a water contact angle of $\sim 52^\circ$. In comparison with the pristine membrane, the water contact angles were reduced to $\sim 40^\circ$, $\sim 28^\circ$, and $\sim 20^\circ$ for the membrane surfaces modified with PAA, PEI, and PSBMA polymers, respectively (Figure 6-4B, C, and E). The surface grafting of PAA molecules with strong hydrophilic carboxyl groups ($-\text{COOH}$) led to the increase of membrane hydrophilicity (Ding et al., 2005), while the highly hydrophilic surface with PEI was resulted from positively charged amino groups ($-\text{NH}_2$) that are inherently abundant in the PEI structure (Yang et al., 2014). In addition, the capability of zwitterionic PSBMA polymer to improve surface hydrophilicity was attributed to a strong binding of water with its localized charges (Yu et al., 2014). This unique interaction requires a higher energy than other hydrophilic materials to remove water molecules (Azari and Zou, 2013). Additionally, compared with the pristine membrane, the grafting of PDA polymer only led to a slight increase in surface hydrophilicity (WCA $\sim 48^\circ$) (Figure 6-4D).

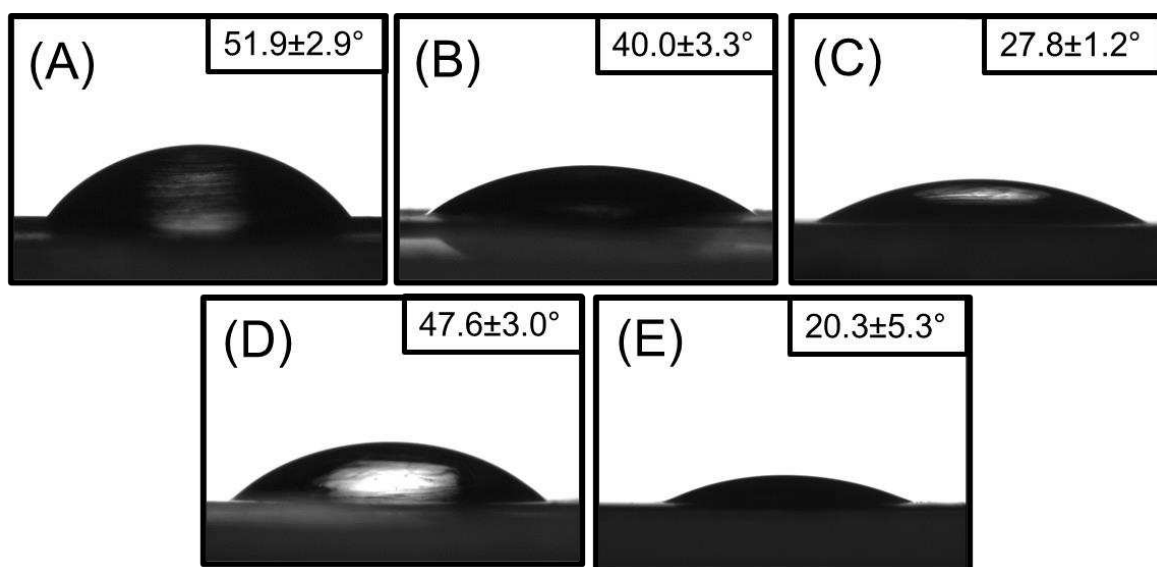


Figure 6-4. Water contact angles for (A) the pristine RO membrane, (B) PAA-RO, (C) PEI-RO, (D) PDA-RO, and (E) PSBMA-RO membranes.

The surface grafting with polymers (e.g., PAA and PEI) to the TFC RO membrane may also alter its surface charge property. The zeta potential is indicative to the surface charge of the membrane (Walker et al., 2002), which was determined from streaming current in the pH range of 3-9. As shown in Figure 6-5, the control membrane displayed negative surface charges within the tested pH range, which was due to the deprotonation of carboxyl groups on the membrane surface (Elimelech et al., 1994). In comparison with the control group, a more positively charged surface was observed for the membrane modified with PEI polymer, likely resulted from the protonation of amino groups from PEI molecules (Xu et al., 2015). In contrast, the PAA-RO membrane exhibited a more negatively charged surface than the unmodified RO membrane due to the presence of more -COOH groups from PAA. For the other membranes modified with PDA and PSBMA polymers, no significant alternation in surface charge property was observed. These results, along with ATR-FTIR spectra (Figure 6-3) and water contact angle measurements (Figure 6-4), indicate that PAA, PEI, PDA, and PSBMA polymers have been successfully grafted onto the active layer of the RO membrane.

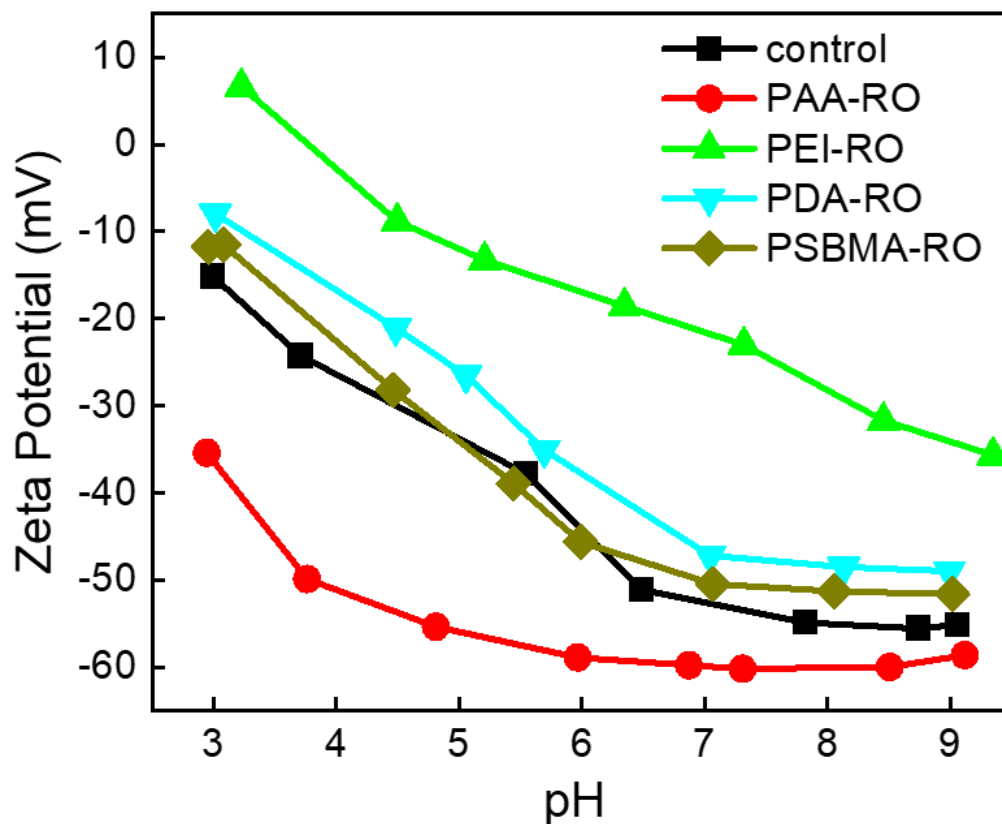


Figure 6-5. Zeta potential of membrane surface in the pH range of 3-9 for the control membrane and membranes modified with PAA, PEI, PDA, and PSBMA polymers.

6.3.2 Membrane transport properties

The effect of surface modification on the membrane transport properties was investigated by comparing the water permeance, A , and the salt permeability coefficient, B , between the pristine and modified membranes. As shown in Figure 6-6A, the water permeance of the pristine membrane was $5.6 \pm 0.4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which was slightly lower than the water permeance of membranes modified with PAA (A of $6.5 \pm 0.9 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) and PSBMA (A of $7.5 \pm 0.9 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$). The rest of the modified membranes (PEI-RO and PDA-RO membranes) did not display statistically different water permeances as compared to the pristine membrane. Therefore, the grafted polymer layers were too thin to hinder water transport within the membranes.

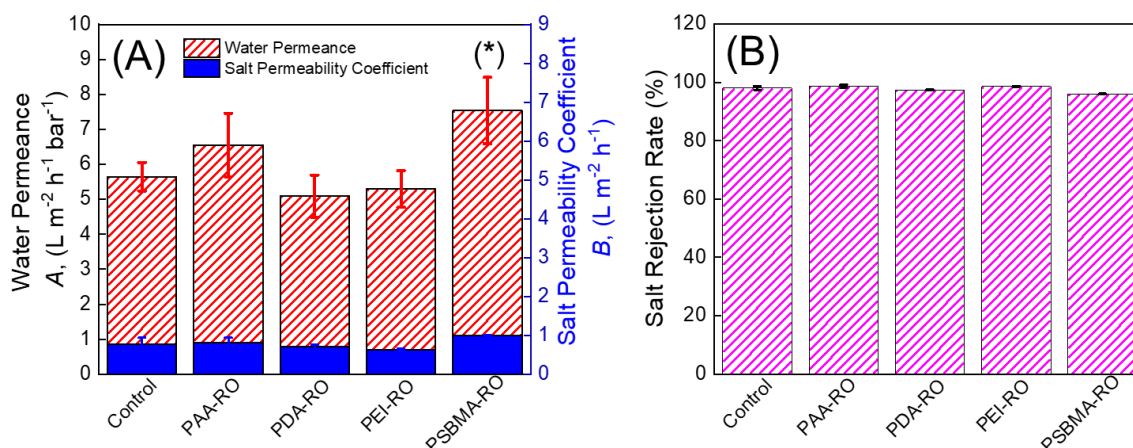


Figure 6-6. RO membrane transport properties. (A) Water permeance (A) and salt permeability coefficient (B) as well as (B) apparent salt rejection rate of the pristine membrane and membranes modified with various polymers. The asterisk sign (*) suggests that the water permeance of the PSBMA-RO membrane was statistically different from the pristine membrane ($\alpha < 0.05$). For (B), 50 mM NaCl solution was used as the feedwater.

The salt permeability coefficient (B) was calculated using water flux and intrinsic salt rejection values at an applied pressure of 300 psi after considering the effect of concentration polarization. The apparent salt rejection rates and the corresponding B values of most modified membranes did not differ from that of the pristine membrane (Figure 6-6B). The PSBMA-RO membrane with the highest water permeance displayed a slightly higher salt permeability, which is in accordance with the well-known permeability-selectivity tradeoff of polyamide membrane (Werber et al., 2016). Therefore, membrane surface modification did not significantly alter the transport properties of the RO membrane, consistent with our previous publication (Tong et al., 2017).

6.3.3 Comparison of membrane surface modification and the use of anti-scalants in mitigating gypsum scaling in RO

In this section, we compare the efficiencies of membrane surface modification and the use of anti-scalants (i.e., PAA) in mitigating gypsum scaling in RO desalination with a feed solution saturated with gypsum (with SI of gypsum at 0.37). As shown in Figure 6-7A, the tested membranes experienced varying levels of water flux decline caused by gypsum scaling in RO.

Since the factors that could potentially impact the rate of water flux decline (e.g., initial water flux, cross-flow velocity, temperature, and feedwater composition) were held constant for all scaling experiments, variations in water flux decline observed in this study can only be attributed to differences in membrane surface chemistry. After the 500-min experiment, the water flux of the pristine RO membrane decreased by ~80%. The membranes modified with polymers carrying different charges (PAA, PEI, and PDA) exhibited similar extents of water flux decline to the pristine membrane, suggesting that gypsum scaling is independent of membrane surface charge in RO desalination. However, the membrane modified with PSBMA polymer slightly reduced the rate of water flux decline, resulting in a water flux reduction of ~62% at the end of the experiments. The mitigating effect of grafting PSBMA polymers on gypsum scaling was consistent with the results of Jaramillo et al. (Jaramillo et al., 2021). The scaling-resistance capability of PSBMA was likely due to the repulsion between gypsum and PSBMA polymer brush, as both gypsum and PSBMA strongly interact with water molecules (Huang et al., 2020). Furthermore, the PSBMA polymer brush may provide an additional screening property to the underneath selective layer and reduce the rate of nuclei attachment due to partial local mobility of the dangling grafted chains within the solution (Lin et al., 2010). However, none of the membrane surface modification prevented gypsum formation. Regardless of the grafted polymer, the water flux decreased by more than 50%, indicating that gypsum scales were formed on the membrane surface despite the diverse surface properties (e.g., surface charge, hydrophilicity) of the membranes tested in this study.

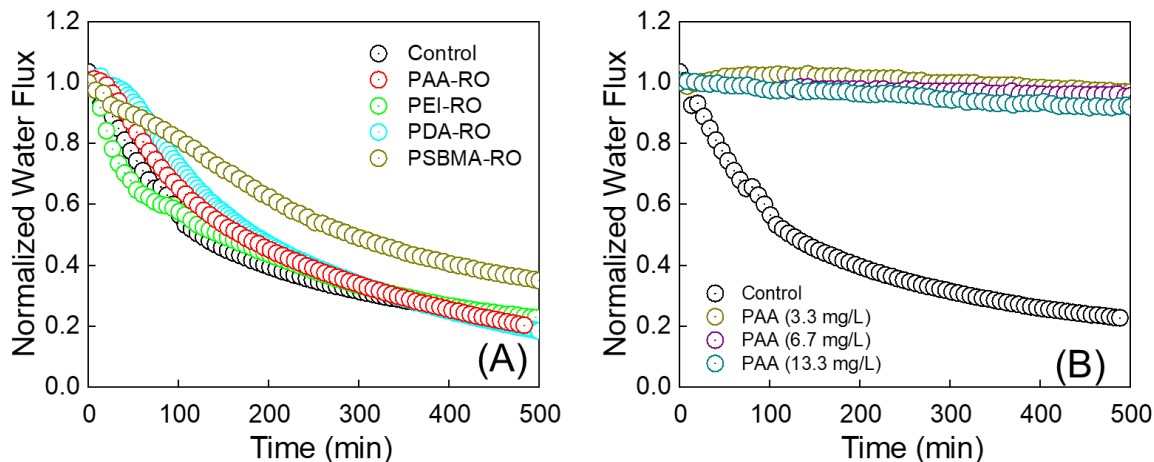


Figure 6-7. Normalized water flux as a function of time in RO gypsum scaling experiments (recirculating mode) when (A) membranes with different surface properties and (B) different concentrations of anti-scalants PAA were used. The gypsum scaling experiments were performed with an initial water flux of $40.5 \pm 0.8 \text{ L m}^{-2} \text{ h}^{-1}$ and a cross-flow velocity of 21.3 cm s^{-1} at temperature of $25.5 \pm 0.1 \text{ }^{\circ}\text{C}$. The feed solution contained 24 mM CaCl_2 and 24 mM Na_2SO_4 , with a SI of gypsum at 0.37. The concentrations of PAA were 3.3 mg/L, 6.7 mg/L and 13.3 mg/L, respectively.

In addition to membrane surface modification, we also explored the efficacy of PAA in controlling gypsum scaling in RO. As presented in Figure 6-7B, the addition of PAA dramatically reduced the water flux decline caused by gypsum scaling. We tested three different concentrations of PAA (3.3 mg/L, 6.7 mg/L, and 13.3 mg/L), and for all three concentrations the water fluxes remained $> 95\%$ of the initial value after 500-min scaling experiments. Therefore, the application of anti-scalants outperformed membrane surface modification in the mitigation of gypsum scaling in RO desalination. In our recent study (Yin et al., 2021), we demonstrated that PAA was able to effectively reduce gypsum scaling in membrane distillation by disrupting the formation of gypsum crystals. Such interruption could significantly alter the structure of scale layer on the membrane surface, thereby mitigating water transport inhibition imposed by the scale layer.

To prove our hypothesis, we performed SEM-EDX to analyze the membrane surface after RO scaling experiments. In the absence of PAA, the membrane surface was densely covered

with scales that displayed the characteristic rosette crystal morphology of gypsum (Rahardianto et al., 2008) (Red circles of Figure 6-8A). However, a loosely connected scale layer was observed in the presence of PAA at a concentration of 3.3 mg/L, with the rosette crystal morphology not observed (Figure 6-8B). The chemical composition of the scale layer was CaSO_4 as confirmed by EDX (Figure D3, Appendix D). The morphological distortion of the scale layer in the presence of a low concentration of PAA was likely due to the adsorption of PAA molecules onto the surface of CaSO_4 nuclei, which disrupted gypsum crystal formation (Rabizadeh et al., 2019). Such a distorted scale layer, as shown in Figure 6-8B, did not compromise the water flux of RO desalination, indicating that it was loose and permeable to water. Furthermore, as the concentration of PAA increased (from 3.3 mg/L to 6.7 mg/L or 13.3 mg/L), a reduced amount of scale was observed on the membrane surface (Figures 6-8C and 6-8D). The elemental analysis based on EDX confirms that the concentration of the element Ca (corresponding to CaSO_4 scale) was notably reduced with an increasing concentration of PAA, while the concentration of element C (corresponding to the RO membrane) increased (Figure 6-8E). Our previous study showed that a relatively high concentration of PAA was able to stabilize gypsum precursors (e.g., Ca^{2+} and SO_4^{2-}) in the solution (Yin et al., 2021), resulting in less CaSO_4 scale formation and deposition. Thus, PAA possessed the capability of not only altering the structure of the scale layer, but also reducing the amount of CaSO_4 scale on the membrane surface.

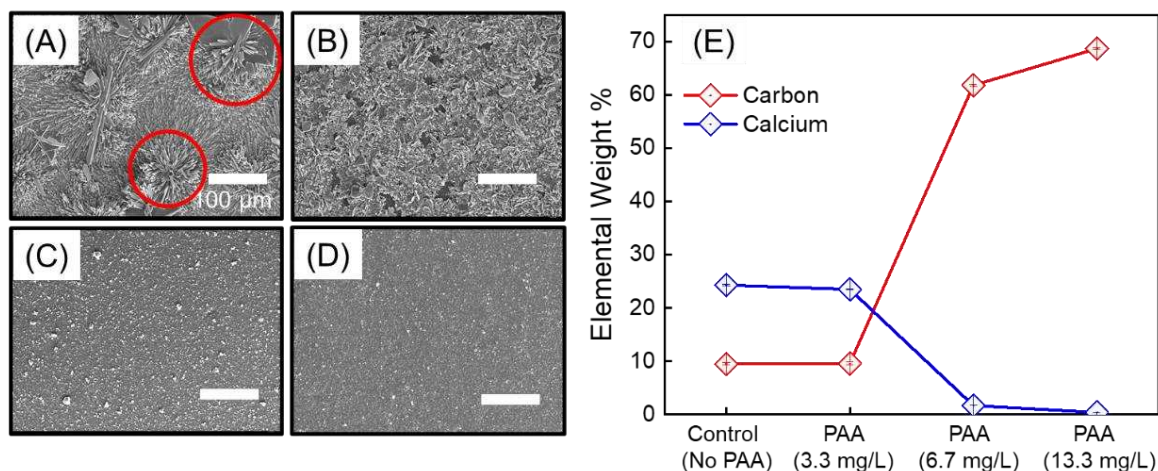


Figure 6-8. Top-view SEM micrographs of the RO membrane surfaces after gypsum scaling experiment for (A) the control group (i.e., no anti-scalants) and in the presence of (B) 3.3 mg/L PAA, (C) 6.7 mg/L PAA, and (D) 13.3 mg/L PAA. The red circles in (A) highlight the typical rosette crystal morphology of gypsum. (E) The change of elemental weight of C and Ca elements of the membrane surface as a function of PAA concentration as revealed by EDX.

The limited anti-scaling efficiencies of membrane surface modification is passively regulated by the membrane surface chemistry, which may affect heterogeneous nucleation or the deposition of gypsum nuclei in the feed solution (Jaramillo et al., 2021; Kim et al., 2010; Tong et al., 2017). However, because there is no disruption in the formation of gypsum crystals, scale can still form and hinder water flux. In contrast, the presence of anti-scalants such as PAA actively interacts with the gypsum precursors and/or nuclei, which prevents the formation of a dense gypsum scale layer on the membrane surface. Overall, anti-scalants were found to be more effective in mitigating gypsum scale formation, thereby preserving water flux and prolonging the lifespan of RO membranes.

6.3.4 The efficiency of PAA in combined RO-MD scaling experiments

Since the use of anti-scalant PAA outperformed membrane surface modification in suppressing gypsum scaling in RO, we further investigated the efficacy of PAA in improving water recovery for a combined RO-MD system. In this section, PAA was only added in the feedwater of RO, and the RO brines were then used as the feedwaters for the subsequent MD

unit. As compared to Section 3.3, the same feedwater (SI of gypsum at 0.37) and PAA concentrations (i.e., 3.3 mg/L, 6.7 mg/L and 13.3 mg/L) were used in the RO unit. However, the concentrations of PAA in the feedwater were higher in the subsequent MD experiments, which received the brine of RO desalination. Thus, in order to avoid potential confusion on the PAA dose from the readers, we denoted the control group and the experimental groups in the presence of PAA at 3.3 mg/L, 6.7 mg/L and 13.3 mg/L as PAA-0, PAA-a, PAA-b, and PAA-c, respectively.

Similar to what was observed in Figure 6-7B, the addition of PAA was found to drastically reduce water flux decline caused by gypsum scaling (Figure 6-9A). The difference between the RO scaling results depicted in Figure 6-7B and Figure 6-9A was that the RO permeate was not recirculated to the feed tank in the experiments of Figure 6-9A (concentrating mode vs. recirculating mode of Figure 6-7B). This was done to create concentrated RO brines that were fed to the following MD experiments. In the absence of PAA (the control group), the RO system experienced a rapid decline of water flux by more than 95% after ~1300 min, which only resulted in a water recovery of ~9.3% (~560 mL of permeate collected from 6000 mL feedwater). In contrast, in the presence of PAA (regardless of PAA concentration), a much slower rate of water flux decline was noticed, which led to a moderate flux reduction of only ~30% after a 2000-min experiment (Figure 6-9A). This decline in flux was probably due to the extraction of pure water, which gradually increased the osmotic pressure of the feedwater. Upon the conclusion of RO scaling experiments, the water recovery was ~40% (~2400 mL of permeate collected from 6000 mL of feedwater, Figure 6-9B). At this time, the SI of gypsum increased from 0.37 to 0.94 (without considering the precipitation of gypsum), implying that the PAA is a highly effective gypsum scale retardant. The presence of PAA is likely to allow for a higher

water recovery ratio in the RO unit. However, the experiments were terminated after 2000 min, in order to protect the RO system.

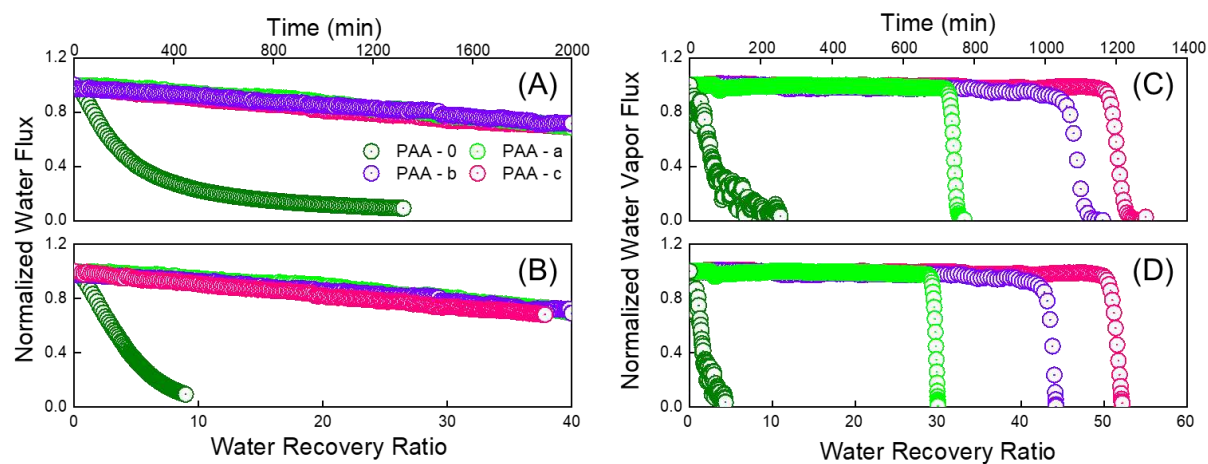


Figure 6-9. Normalized water flux for (A, B) RO scaling experiments (concentrating mode) and (C, D) MD scaling experiments as a function of time and water recovery ratio. The feed solution of RO contained 24 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 24 mM Na_2SO_4 , corresponding to an initial gypsum SI of 0.37. The concentration of PAA in RO were 3.3 mg/L, 6.7 mg/L and 13.3 mg/L, respectively. The initial water flux of RO was $40.5 \pm 0.8 \text{ L m}^{-2} \text{ h}^{-1}$ at a cross-flow velocity of 21.3 cm s^{-1} and temperature of $25.5 \pm 0.1 \text{ }^\circ\text{C}$. For MD, the temperatures of feed and permeate streams were maintained at $60 \text{ }^\circ\text{C}$ and $20 \text{ }^\circ\text{C}$, respectively. The cross-flow velocities of feed and permeate streams were 9.6 cm s^{-1} and 6.4 cm s^{-1} , respectively. The initial water vapor flux of MD was $24.7 \pm 0.8 \text{ L m}^{-2} \text{ h}^{-1}$.

We further used the RO brines as the feedwaters for the subsequent MD unit to test the efficiency of PAA in improving the water recovery of a combined RO-MD system. When desalinating RO brine in the absence of PAA (strictly speaking, such feedwater is not RO “brine” due to the low water recovery ratio of ~9%, Figure 6-9B), the water vapor flux decreased rapidly by ~95% due to gypsum scaling after ~200 min (Figure 6-9C), resulting in a very low water recovery ratio of ~4% by the MD system (Figure 6-9D). In contrast, when anti-scalant PAA was added in the RO unit, the onset of water vapor flux decline was greatly postponed, and much higher water recovery ratios were achieved (from ~30% to ~52%) by the MD unit (Figures 6-9C and 6-9D). These results suggest that PAA remaining in the RO brines were still effective in suppressing gypsum scaling in the MD process. Furthermore, the efficiency of PAA in gypsum scaling mitigation was positively correlated with its initial concentration. Water recoveries of

~30%, ~43%, and ~52% were achieved when 3.3 mg/L, 6.7 mg/L, and 13.3 mg/L of PAA was added in the RO unit (i.e., PAA-a, PAA-b, and PAA-c group), respectively. In addition, the presence of PAA in the feedwater prevented membrane wetting induced by gypsum scaling in MD (Figure D4, Appendix D). No increase in permeate conductivity was observed for PAA-a, PAA-b and PAA-c experimental groups throughout the experiments. However, an immediate and rapid elevation of permeate conductivity (an indicator of membrane wetting and reduction of salt rejection) was observed if no PAA was added in the RO step (Figure D4).

SEM was performed to examine the scales on the membrane surface after the MD scaling experiment. As shown in Figure 6-10A, a typical needle-like gypsum crystal morphology was clearly observed on the membrane surface in the absence of PAA. In contrast, the morphologies of CaSO_4 crystals were greatly altered even when relatively low PAA concentrations were present in the feedwater (PAA-a, and PAA-b), displaying rod- and platelet-like features with lower aspect ratios (Figures 6-10B and 6-10C). When the initial concentration of PAA in RO increased to 13.3 mg/L (i.e., PAA-c), crystal was not observed on the surface of the PVDF membrane; instead, the surface was covered with an amorphous-like scaling layer (Figure 6-10D). When observing this scaling layer using a higher SEM magnification, only tiny needle-like gypsum crystals were observed (Figure D5, Appendix D), which indicates that gypsum formation was significantly hindered by the residual PAA in the MD feedwater. Therefore, similar to what was noticed in RO (Figures 6-8A – 6-8D), PAA molecules disrupt the process of gypsum crystallization, leading to an increase of water recovery of MD desalination. This also explains the capability of PAA in preventing membrane wetting, as shown in Figure D4. The interaction of PAA with CaSO_4 nuclei and gypsum precursors (Ca^{2+} and SO_4^{2-}) disrupt gypsum

crystallization, preventing the in-pore, intrusive crystal growth that causes pore deformation (Yin et al., 2021).

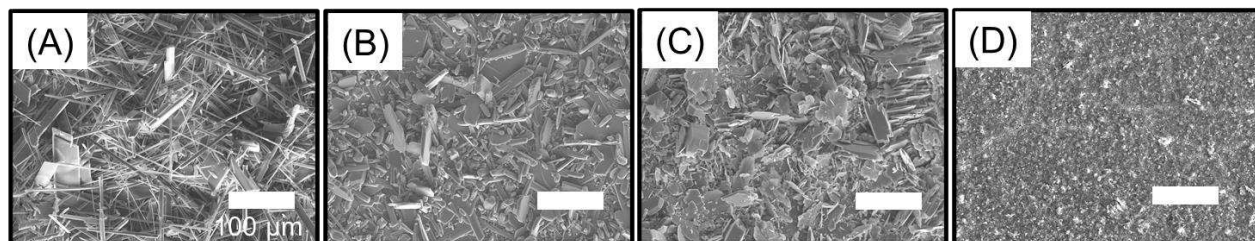


Figure 6-10. SEM micrographs of scales formed after the MD gypsum scaling experiments. (A) PAA-0 control group, (B) PAA-a experimental group, (C) PAA-b experimental group, and (D) PAA-c experimental group. The magnification of the SEM micrographs was 300X and the scale bars represent 100 μm .

6.4 Implications

In our study, the use of anti-scalant PAA was found to be more effective in mitigating gypsum scaling than membrane surface modification. Although the grafting of zwitterionic polymer (i.e., PSBMA) moderately reduced gypsum scaling, all the modified membranes displayed a significant decrease in water flux. In contrast, the presence of PAA greatly reduced the water flux decline, resulting in nearly stable water fluxes in RO desalination. Further, the PAA molecules retained in the RO brine were shown to effectively enhance the performance of the following MD desalination, leading to a greatly improved water recovery of the integrated RO-MD system. In contrary to the passive effect of membrane surface modification on gypsum scaling, anti-scalants actively disrupt gypsum crystallization, preventing the formation of a dense layer of gypsum on the membrane surface and resulting in a more stable water production. Therefore, at least in the current study, the use of anti-scalants outperformed membrane modifications in terms of gypsum scaling mitigation.

It is worth mentioning that our study does not intend to depreciate the importance of developing scaling-resistant membranes. Better surface modification approaches, if achieved,

have the potential to mitigate membrane scaling without the addition of additional chemicals. However, a rational framework of designing scaling-resistant membranes has not been established. Future work needs to be invested to fundamentally understand the interactions between membrane surface and scalants, in order to identify the membrane surface properties that effectively hinder membrane scaling. Further, although no membrane fouling was observed in this study when anti-scalant PAA was added, instances of organic fouling and biofouling induced or enhanced by the use of anti-scalants have been documented in the literature (Antony et al., 2011; She et al., 2016; Sweity et al., 2013; Sweity et al., 2014; Sweity et al., 2015). As a result, more investigations comparing membrane material innovation and the use of anti-scalants should be performed to provide necessary insights that guide the selection of the most appropriate strategies for scaling mitigation. Indeed, the combination of scaling-resistant membranes with anti-scalants may allow for a reduction in anti-scalant dosage, thereby reducing the cost and unintended risks associated with anti-scalants (e.g., membrane fouling).

Also, the application of anti-scalants will increase the operational cost of desalination. Using the data of Figure 6-9, the use of PAA as anti-scalants enhances the total water recovery of the RO-MD system significantly from 14% to 71% (such an increase is likely a conservative estimate because a higher water recovery could be potentially achieved by the RO system with anti-scalants). Considering the value of RO water product (\$0.3 to \$0.7 per m³ for brackish water RO using the data from the Texas Water Development Board (Arroyo and Shirazi, 2012)) and PAA (\$800 to \$1000 per ton), the cost of anti-scalants (even considering the highest dose used in this study) is only a small fraction of the economic benefits gained by harvesting a higher amount of purified water. Such an economic gain could be higher if considering the extended membrane lifespan due to the mitigation of mineral scaling by anti-scalants. Therefore, the

benefit of a higher water recovery should outweigh the cost increase due to the use of anti-scalants. We suggest that a more thorough techno-economic analysis (TEA) should be performed to assess the practical economic prospects and optimize the applied dosage of anti-scalants for scaling control in membrane systems that are designed for achieving MLD or ZLD.

6.5 Conclusions

In this work, we compared the anti-scaling efficiencies of membrane surface modification and the use of anti-scalants (i.e., PAA) in mitigating gypsum scaling in membrane desalination. Four types of polymers were selected to modify the surface of a commercial polyamide RO membrane, providing different surface functionalities and properties. We found that membrane surface modification displayed a limited effectiveness to mitigate the water flux reduction caused by gypsum formation in RO. On the contrary, the addition of PAA drastically reduced gypsum scaling, resulting in a stable water flux throughout the RO scaling experiments. The distinct anti-scaling behaviors between membrane surface modification and the use of PAA were attributed to their different responses to gypsum formation. In contrary to the passive effect of membrane surface modification on gypsum scaling, anti-scalants actively disrupt gypsum crystallization, preventing the formation of a dense layer of gypsum on the membrane surface and resulting in a more stable water production. Further, we demonstrated that the use of PAA was also effective in retarding gypsum scaling in a combined RO-MD system, which significantly enhanced the total water recovery. Therefore, more comparative investigations on the efficiencies of surface-modified membranes and anti-scalants in controlling mineral scaling are recommended to gain more knowledge that guides the selection of appropriate strategies to achieve resilient membrane desalination with exceptional system efficiencies.

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7.0 Conclusions and Future Recommendations

7.1 Conclusions

In my study, I aimed at elucidating the mechanisms of mineral scaling and developing strategies to mitigate mineral scaling in membrane desalination. To achieve this research goal, I decomposed my study into four studies to unravel the behaviors and mechanisms of gypsum scaling and silica scaling in MD, while exploring the feasibility of different mitigation strategies of scaling control in both MD and RO.

In the first work, three PVDF membranes with different extents of surface wettability were used to study silica scaling mechanism in MD. Based on the analyses of silica scaling behaviors under two solution statuses (i.e., undersaturated and supersaturated for the initial feedwater), I discovered that silica particles formed homogeneously in the aqueous solution were expected to be a primary role in causing the water vapor flux decline. Furthermore, with morphology analyses of silica scale layers after experiments, and a comparative experiment between silica scaling and colloidal silica fouling, it indicated that, in addition to homogenous nucleation, the interaction between silica particles deposited on the membrane and silicic acid in the feedwater also contributed to the water flux decline. Thus, I proposed a four-step mechanism to disclose the possible scaling pathway of silica in MD, involving both homogenous and heterogeneous nucleation.

In the second work, I demonstrated that the effects of membrane surface wettability on pore wetting and scaling reversibility were a function of mineral scaling types in MD. Superhydrophobic membrane was effective in not only delaying induction time, but also greatly enhancing scaling reversibility of gypsum scaling. In addition, superhydrophobic membrane displayed an excellent capability in resisting membrane pore wetting induced by gypsum scaling.

However, tuning membrane surface wettability was ineffective to mitigating silica scaling. Such distinct behaviors and responses of gypsum scaling and silica scaling associated with membrane surface wettability were attributed to their different formation mechanisms. Gypsum scaling was induced by crystallization reactions, while silica scaling was regulated by polymerization reactions. This work demonstrated that a combination of membrane surface modification with process innovation (i.e. membrane cleaning) was effective to reduce gypsum scaling and enhance the total water recovery. However, such a strategy was not an ideal solution to silica scaling in MD.

Further, the third work was built upon a comparative study that investigated the use of anti-scalants to mitigate mineral scaling in MD. I demonstrated that using anti-scalants to mitigate gypsum scaling and silica scaling in MD required different molecular functionalities of the anti-scalants. Such a finding was ascribed to the distinct scaling mechanisms between gypsum and silica. More importantly, this work introduces a novel concept to redefine the criterion of selecting anti-scalants for MD: an effective anti-scalant does not necessarily inhibit scale formation. Instead, immobilizing the scales (or their precursors) away from the membrane surface to prevent membrane pore blockage is the key to mitigating mineral scaling. Further, the mechanistic analysis of this work emphasizes the importance of molecular functionalities of anti-scalants in mitigating specific mineral formation and provides valuable insights into future research on designing effective anti-scalants with tailored molecular structure to scaling type.

Finally, in the last work, the anti-scaling efficiency of membrane surface modification was compared with that of using anti-scalants for mitigating gypsum scaling in a bench-scale RO system. I found that the effectiveness of using anti-scalants to inhibit gypsum scaling greatly outperformed membrane surface modification. The distinct anti-scaling efficiencies between

membrane surface modification and the use of anti-scalants were attributed to their different responses to gypsum formation. Membrane surface modification passively inhibited gypsum formation, while the anti-scalant actively disrupted gypsum crystallization in the aqueous solution. Further, I demonstrated the effectiveness of using anti-scalants in retarding gypsum scaling in a combined RO-MD system, which significantly enhanced the total water recovery. I also assessed the economic cost of anti-scalants, which was negligible to the economic benefits of the higher water recovery achieved in this work. But there is still a need to implement a more comprehensive techno-economic-analysis to fully evaluate the practical economic prospect of using anti-scalants to enhance the total water recovery in membrane desalination.

7.2 Recommended Future Research

Based on the findings of my thesis, several activities are suggested for the future research that could further enhance the scaling resistance of membrane desalination systems:

- More approaches to modify the membrane surface with improved scaling resistance need to be attempted. Strategies that have been used in other fields such as anti-icing coatings might provide inspirational insights on the development of more effective membrane surfaces to control scaling.
- More attentions need to be placed on tailoring the structure of the anti-scalant molecules to mitigate mineral scaling. Particularly, due to different mass transport mechanisms of varying desalination systems (e.g., RO and MD), the anti-scaling efficiency of anti-scalants might be varied. The molecular interactions of varying minerals with anti-scalant molecules need to be deeply unveiled for different desalination processes.

- A more thorough techno-economic analysis needs to be performed to evaluate the economic cost of different scaling mitigation strategies in membrane desalination to provide practical suggestions in selecting the most appropriate scaling control strategy.

Appendix A⁶

Calculation of concentration polarization of Na₂SiO₃ for different membranes

The concentration of Na₂SiO₃ on the membrane surface is higher than that of the bulk solution due to concentration polarization (CP). Since the extent of CP relates to the water flux across the membrane, we evaluated the CP modulus of Na₂SiO₃ for each membrane used in our study. According to the film model (Qin et al., 2017), the scalant concentration at the membrane surface (C_m) can be estimated using the following equations:

$$\frac{C_m}{C_b} = \exp\left(\frac{J_w}{k}\right) \quad (A - 1)$$

$$k = \frac{Sh \cdot D}{d_h} \quad (A - 2)$$

where C_b is the scalant concentration in the bulk solution, J_w is the measured water vapor flux, k is the mass transfer coefficient, Sh is the Sherwood number, D is the solution diffusion coefficient, and d_h is the hydraulic diameter.

However, we could not find the accurate D value of Na₂SiO₃ at 60 °C. In the reference of Reboreanu et al. (Reboreanu et al., 2008), the D values of dissolved silica in the temperature range of 2-30 °C were reported. Assuming a linear relation between temperature and diffusion coefficient, we obtained the D value of 1.9×10^{-9} m²/s for dissolved silica. As a result, the CP moduli of Na₂SiO₃ were calculated as 1.7, 1.7, 1.5 for pristine PVDF membrane, PVDF-PVA membrane, and PVDF-SiNP-FAS membrane, respectively.

⁶ This appendix has been published as the Supporting Information of a research article in the journal of *Environment Science: Water Research & Technology* with the following citation:

Yin, Y., Wang, W., Kota, A.K., Zhao, S. and Tong, T. 2019. Elucidating mechanisms of silica scaling in membrane distillation: effects of membrane surface wettability. *Environmental Science: Water Research & Technology* 5(11), 2004-2014.

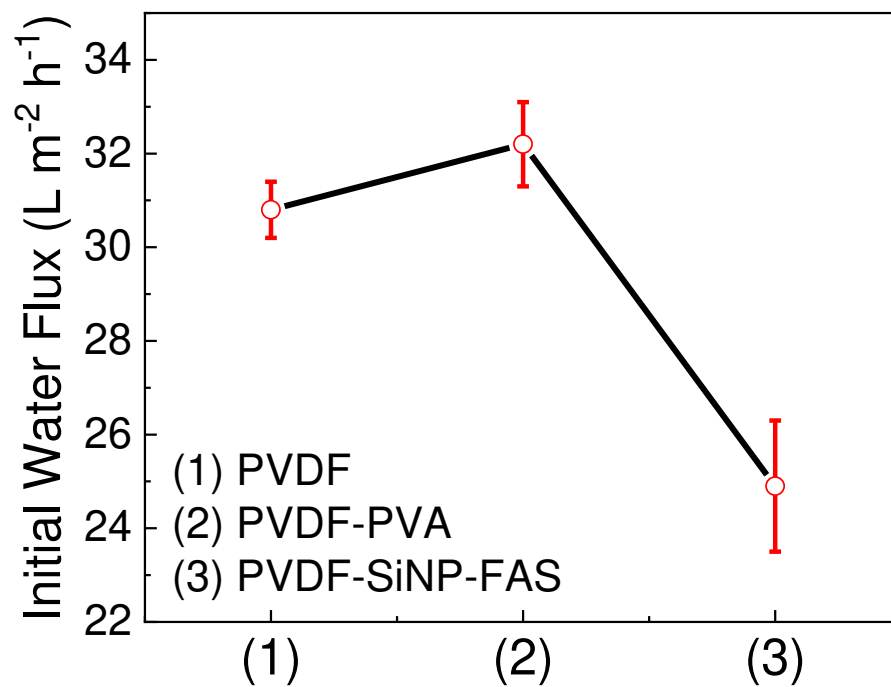


Figure A1. The initial water vapor fluxes of the PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes during direct contact membrane distillation (DCMD) experiments. The error bars were calculated from four independent experiments.

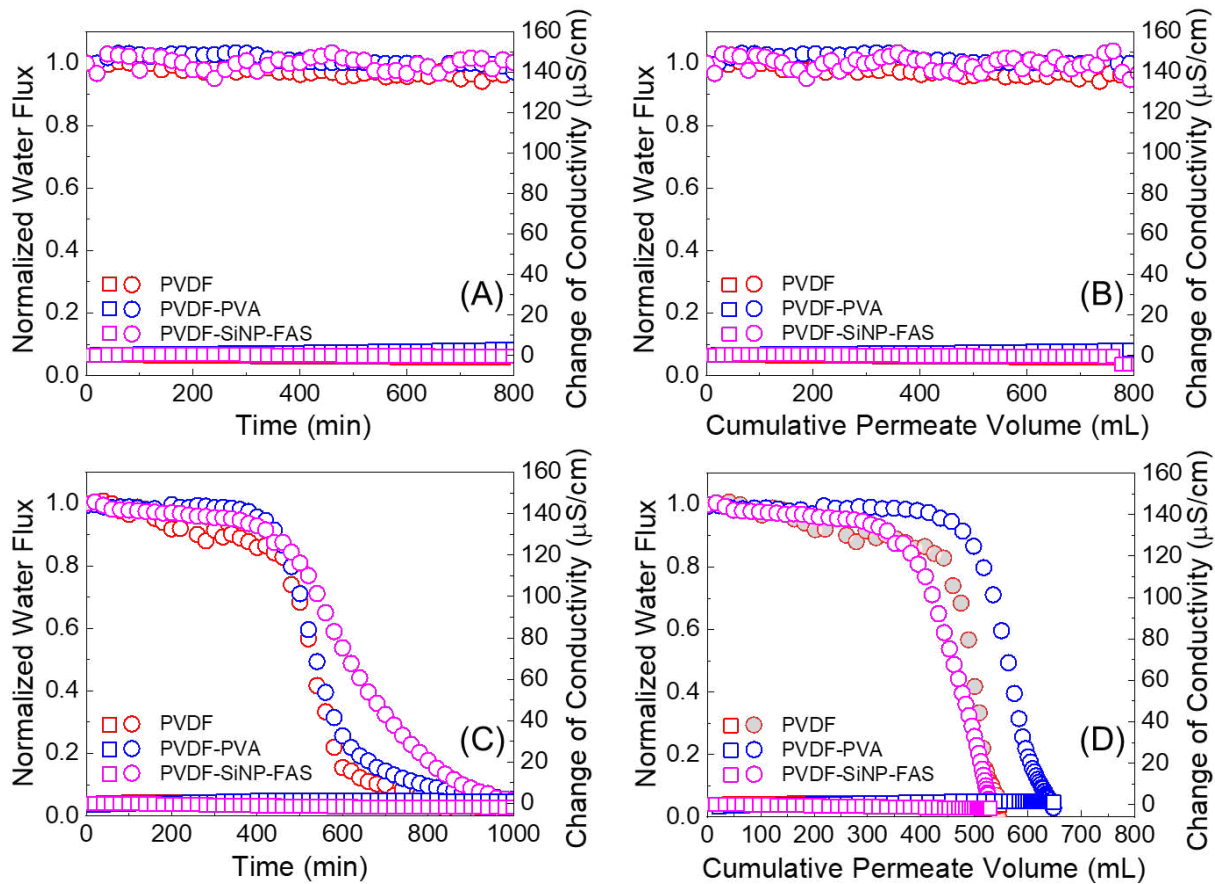


Figure A2. Normalized water flux and change of distillate conductivity of PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes during the DCMD scaling experiment. The feedwater contained 50 mM NaCl, 1 mM NaHCO_3 , as well as 1.5 mM $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (A, B) or 6 mM $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (C, D) at pH of 6.50 ± 0.05 . The crossflow velocities in the feed and distillate streams were 9.6 cm/s and 6.4 cm/s, respectively. The temperatures for feed and distillate streams were maintained at 60°C and 20°C , respectively. The initial volume of feed solution was 1500 ml. The initial water vapor fluxes were $30.7 \pm 0.2 \text{ L m}^{-2} \text{ h}^{-1}$, $33.2 \pm 0.25 \text{ L m}^{-2} \text{ h}^{-1}$, and $24.0 \pm 0.7 \text{ L m}^{-2} \text{ h}^{-1}$ for PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes, respectively.

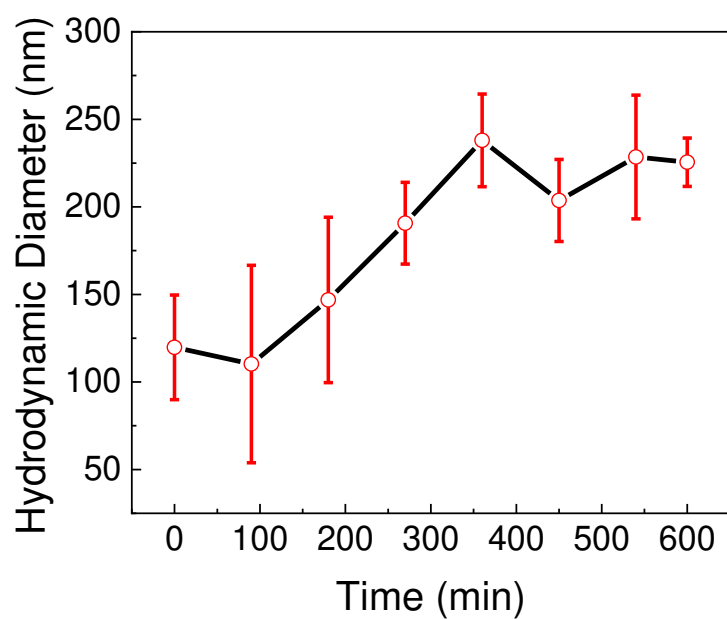


Figure A3. The hydrodynamic diameters of particles formed during DCMD of feedwater containing 6 mM of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$. The error bars were calculated from five independent measurements.

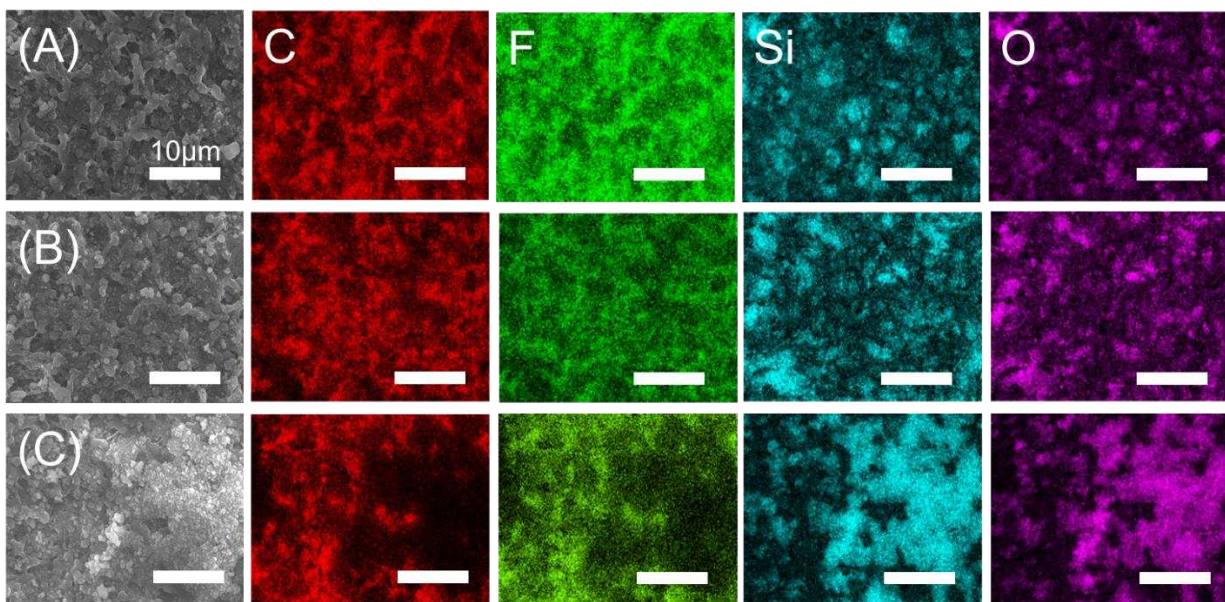


Figure A4. SEM-EDS elemental analysis of the PVDF (A), PVDF-PVA (B) and PVDF-SiNP-FAS (C) membranes (top-view) after DCMD silica scaling experiments. The concentration of silica in the feed solution was 6 mM.

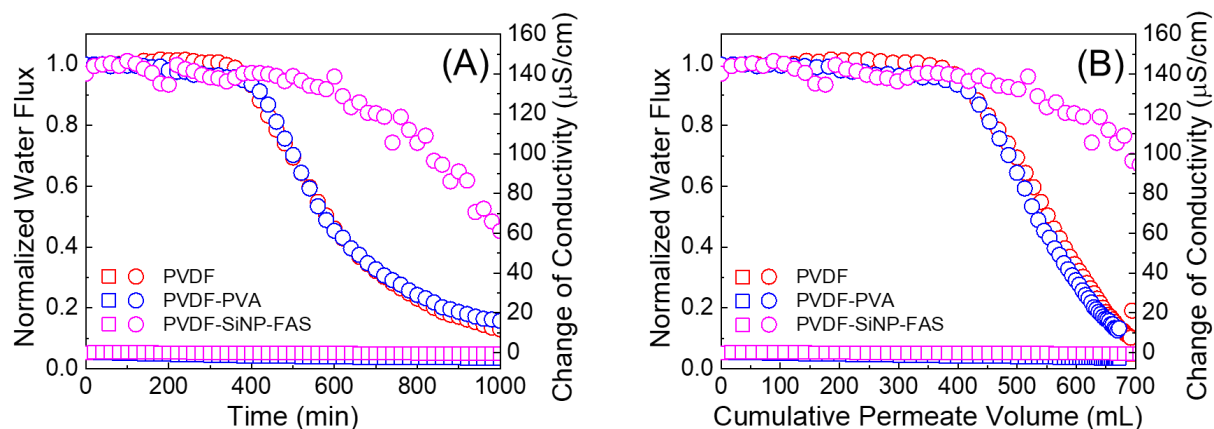


Figure A5. Normalized water flux and change of distillate conductivity of PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes during DCMD experiments with colloidal silica fouling. The feed solutions contained 50 mM NaCl, 1 mM NaHCO₃, and 6 mM silica colloidal particles at pH of 6.50 ± 0.05 . The crossflow velocities in the feeding and permeating streams were 9.6 cm/s and 6.4 cm/s, respectively. The temperatures for feed and distillate stream were maintained at 60°C and 20°C, respectively. The initial volume of feed solution was 1500 ml. The initial water fluxes were 30.3 L m⁻² h⁻¹, 30.4 L m⁻² h⁻¹, and 25.9 L m⁻² h⁻¹ for PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes, respectively.

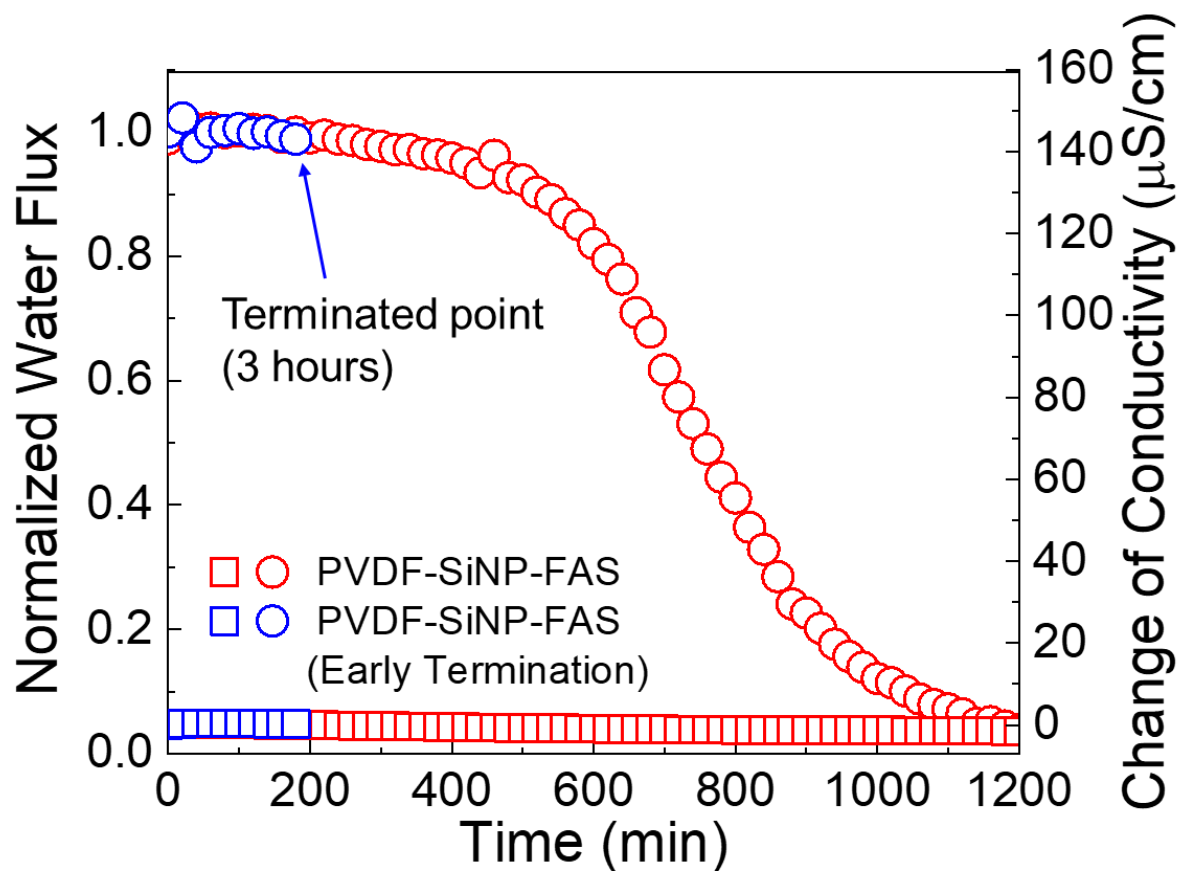


Figure A6. Normalized water flux and change of distillate conductivity for PVDF-SiNP-FAS membranes during DCMD experiments with silica fouling. The experiment was terminated at 3 hours (blue) for the analysis of membrane surface wettability after short-term scaling tests. A full scaling experiment (red), which was performed for > 1000 minutes, is presented for comparison. The feed solutions contained 50 mM NaCl, 1 mM NaHCO_3 , and 6 mM $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ at pH of 6.50 ± 0.05 . The crossflow velocities in the feeding and permeating streams were 9.6 cm/s and 6.4 cm/s, respectively. The temperatures for feed and distillate stream were maintained at 60°C and 20°C, respectively. The initial volume of feed solution was 1500 ml.

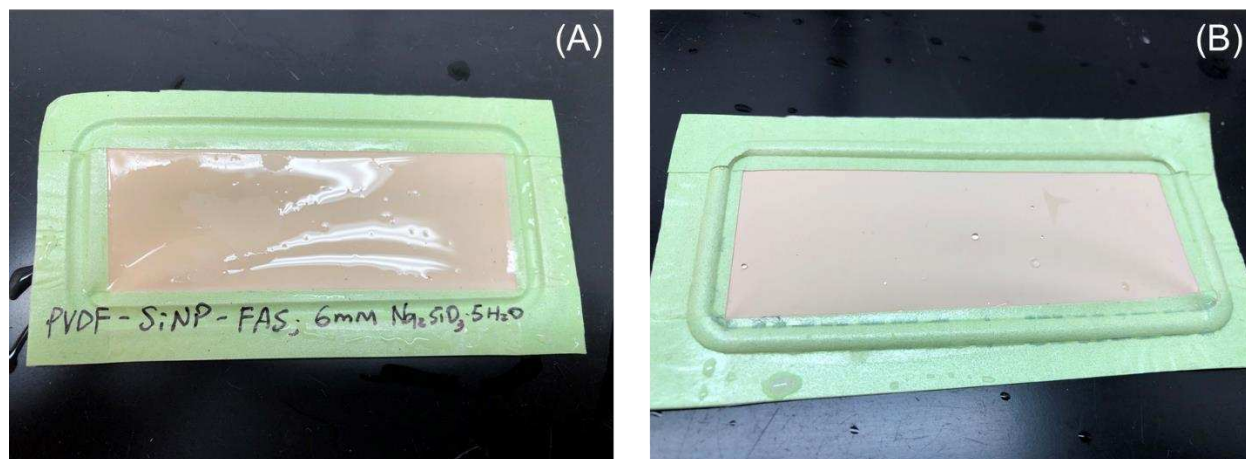


Figure A7. Photographs of PVDF-SiNP-FAS membrane after 3 hours of DCMD treatment of feed solution containing 6 mM $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (as shown in Figure A6). (A) The membrane side facing the feed stream; and (B) the membrane side facing the distillate stream.

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Appendix B⁷

Calculation of Concentration Polarization

Due to the effect of concentration polarization (CP), the concentration of each scalant on the membrane surface is higher than that in the bulk solution. Therefore, we quantified the effect of CP based on the film model (Qin et al., 2017):

$$\frac{C_s}{C_b} = \exp\left(\frac{J_w}{k}\right) \quad (B-1)$$

$$k = \frac{Sh \cdot D}{d_h} \quad (B-2)$$

where C_s is the scalant concentration at the membrane surface, C_b is the scalant concentration in the bulk solution, J_w is the measured flux of water vapor, k is the mass transfer coefficient, Sh is the Sherwood number, D is the solution diffusion coefficient, d_h is the hydraulic diameter.

Given the temperature dependency of diffusion coefficient, there is no information regarding the diffusion coefficients of CaCl_2 , and Na_2SO_4 , and Na_2SiO_3 at 60°C . Thus, we assumed the linear relation between temperature and diffusion coefficient from the literature (Derluyn et al., 2011; Reboreanu et al., 2008; Ribeiro et al., 2008; Soon et al., 1979), and estimated the D values of CaCl_2 , Na_2SO_4 , and Na_2SiO_3 as $2.3 \times 10^{-9} \text{ m}^2/\text{s}$, $1.5 \times 10^{-9} \text{ m}^2/\text{s}$, and $1.9 \times 10^{-9} \text{ m}^2/\text{s}$, respectively. Considering the bulk concentration of 18 mM and 3.2 mM for $\text{CaCl}_2/\text{Na}_2\text{SO}_4$ and Na_2SiO_3 in our MD experiments, the estimated CP moduli and scalant concentration at the membrane surface (C_s) are shown in Table B-1 below.

Table B-1. Concentration polarization moduli of gypsum and Na_2SiO_3

PVDF membrane	CaCl_2 (18 mM)	Na_2SO_4 (18 mM)	Na_2SiO_3 (3.2 mM)
CP moduli	1.46	1.68	1.54
C_s	26.28 mM	30.24 mM	4.93 mM
PVDF – PVA membrane	CaCl_2 (18 mM)	Na_2SO_4 (18 mM)	Na_2SiO_3 (3.2 mM)

⁷ This appendix has been published as the Supporting Information of a research article in the *Journal of Membrane Science* with the following citation:

Yin, Y., Jeong, N. and Tong, T. 2020. The effects of membrane surface wettability on pore wetting and scaling reversibility associated with mineral scaling in membrane distillation. *Journal of Membrane Science* 614, 118503.

CP moduli C_s	1.48 26.64 mM	1.70 30.60 mM	1.56 4.99 mM
PVDF – SiNP – FAS membrane	CaCl ₂ (18 mM)	Na ₂ SO ₄ (18 mM)	Na ₂ SiO ₃ (3.2 mM)
CP moduli C_s	1.37 24.66 mM	1.54 27.72 mM	1.43 4.58 mM

As shown in the Table B-1, the CP moduli of CaCl₂/Na₂SO₄ were calculated as 1.46/1.68, 1.48/1.70 and 1.37/1.54 for pristine PVDF, PVDF-PVA, and PVDF-SiNP-FAS membranes, respectively. The CP moduli of Na₂SiO₃ were calculated as 1.54, 1.56 and 1.43, for pristine PVDF, PVDF-PVA, and PVDF-SiNP-FAS membranes, respectively. The corresponding saturation indices (SI, defined as the ratio of the ion activity product to the product solubility, IAP/K_{sp}) of gypsum at the membrane surface were 1.58, 1.62, 1.45 for PVDF, PVDF-PVA and PVDF-SiNP-FAS membranes, respectively, after considering the different water vapor fluxes and CP. Similarly, the corresponding SI values of silica at the membrane surface were 1.45, 1.46, 1.32 for PVDF, PVDF-PVA, and PVDF-SiNP-FAS membranes, respectively.

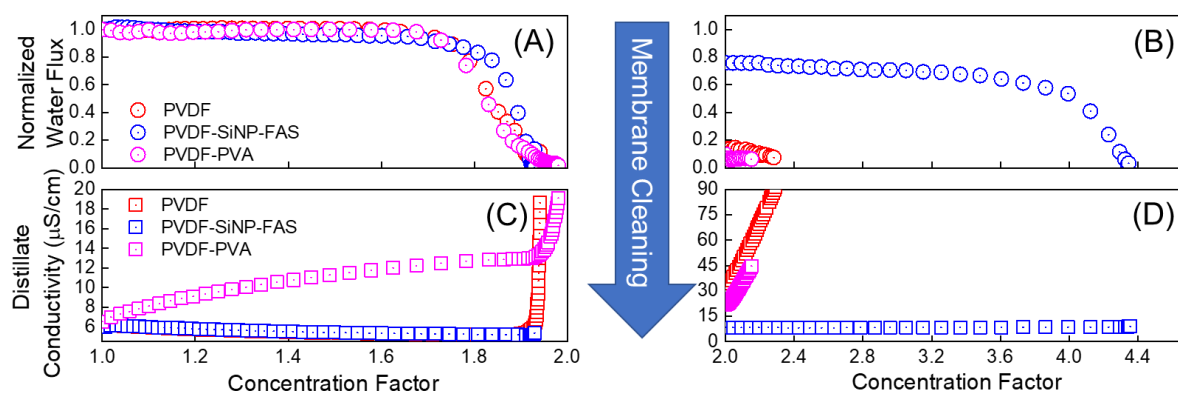


Figure B1. Normalized water vapor flux and the distillate conductivity of PVDF, PVDF-SiNP-FAS and PVDF-PVA membranes as a function of concentration factor (A and C) before and (B and D) after physical membrane cleaning.

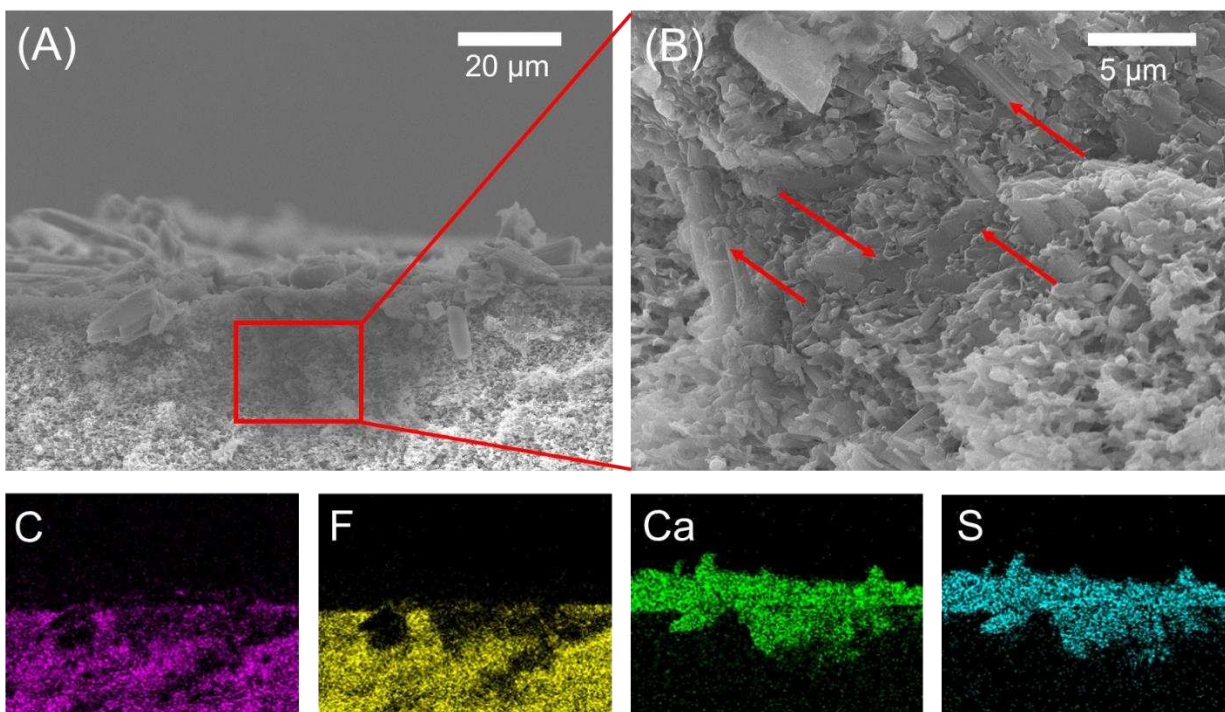


Figure B2. The morphology of gypsum scales formed inside the PVDF membrane substrate during MD scaling experiments. The EDS elemental maps correspond to Figure (A), which confirm the presence of gypsum in the area of (B). The red arrows indicate flaky gypsum crystals within the membrane substrates.

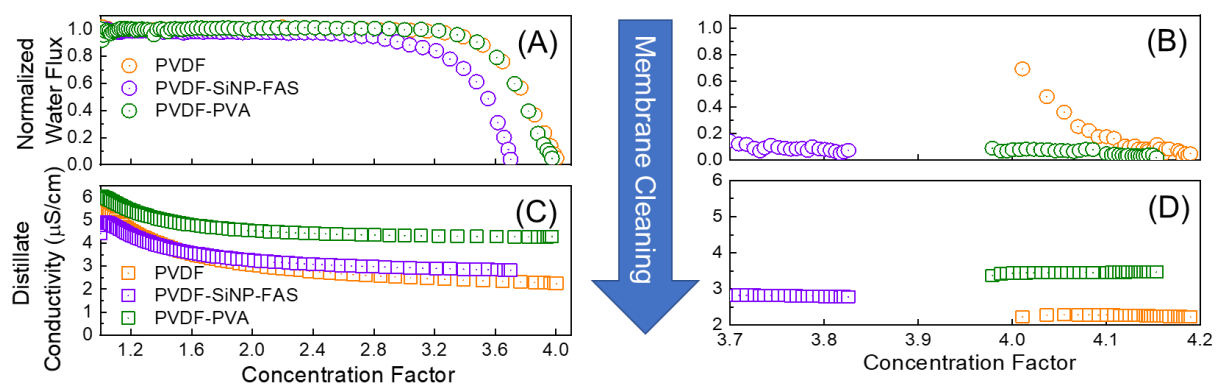


Figure B3. Normalized water vapor flux and the distillate conductivity of PVDF, PVDF-SiNP-FAS and PVDF-PVA membranes as a function of concentration factor (A and C) before and (B and D) after physical membrane cleaning.

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Appendix C⁸

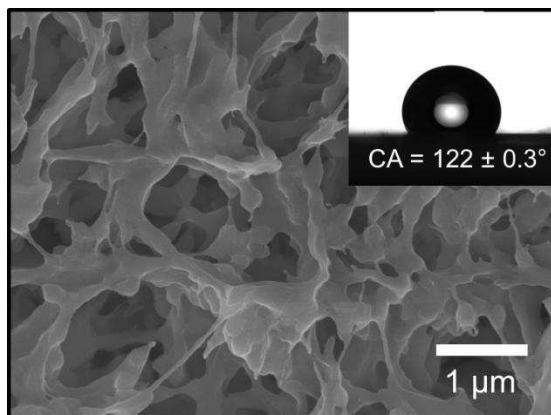


Figure C1. Top view SEM micrograph of the PVDF membrane used in this study. The static water contact angle (CA) is presented as inset. (Yin et al., 2020)

⁸ This appendix has been published as the Supporting Information of a research article in the journal of *Environmental Science & Technology* with the following reference:

Yin, Y., Jeong, N., Minjarez, R., Robbins, C.A., Carlson, K.H. and Tong, T. 2021. Contrasting Behaviors between Gypsum and Silica Scaling in the Presence of Antiscalants during Membrane Distillation. *Environmental Science & Technology* 55(8), 5335-5346.

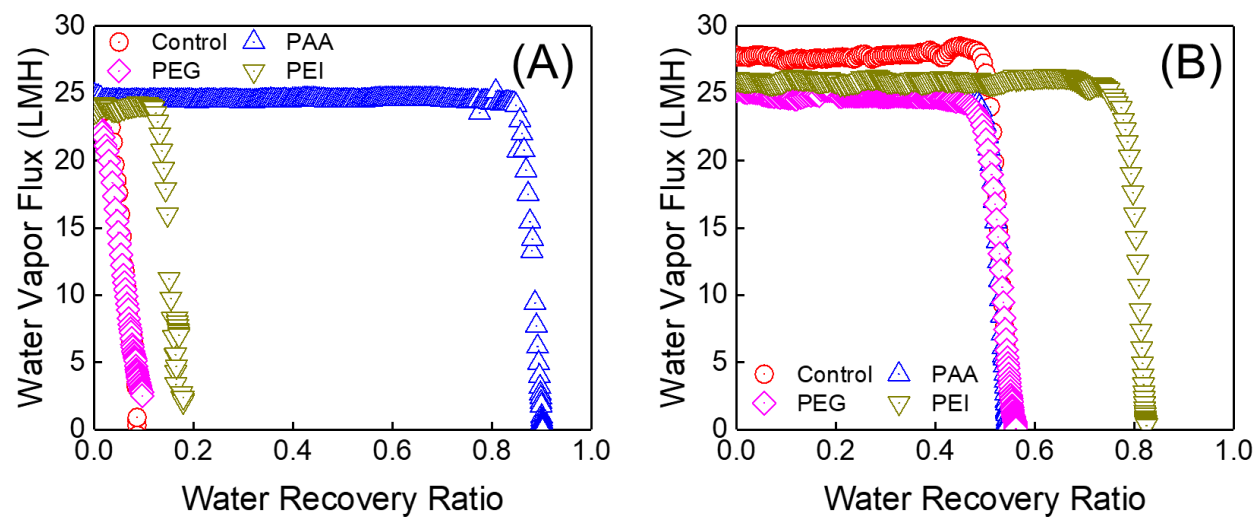


Figure C2. Water vapor flux as a function of water recovery ratio in dynamic MD scaling experiments with (A) gypsum scaling and (B) silica scaling.

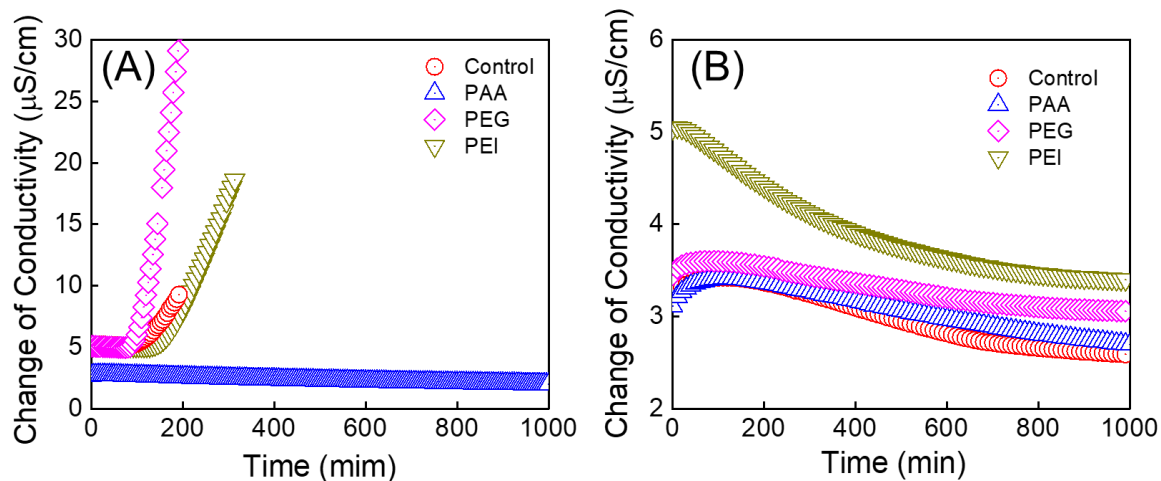


Figure C3. The change of distillate conductivity as a function of time in MD for (A) gypsum scaling and (B) silica scaling experiment. The initial SI of both gypsum and silica in the feed solution was 0.55, and the anti-scalant concentrations were 40 mg/L in all experiments. The temperatures of feed and permeate streams were maintained at 60 °C and 20 °C, respectively. The feed and permeate streams were continuously circulated at crossflow velocities of 9.6 cm s⁻¹ and 6.4 cm s⁻¹, respectively.

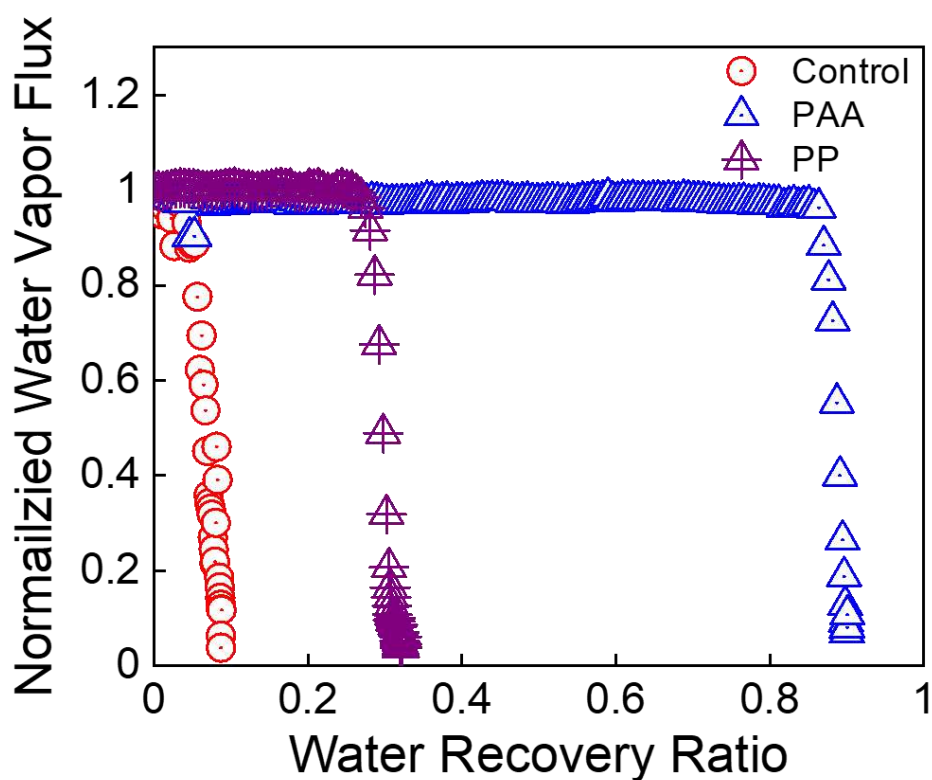


Figure C4. Normalized water vapor flux as a function of water recovery ratio in MD gypsum scaling experiments with different negatively charged anti-scalants. The initial SI of gypsum feeds solution was 0.55, and the concentration of anti-scalant candidates was 40 mg/L in the experiments. The temperatures of feed and permeate streams were maintained 60 °C and 20 °C, respectively. The feed and permeate streams were continuously circulated at crossflow velocities of 9.6 cm s⁻¹ and 6.4 cm s⁻¹, respectively. The initial water vapor flux of PVDF membrane was 23.6 ± 0.7 L m⁻² h⁻¹, which was used to normalize the water vapor fluxes in the figure.

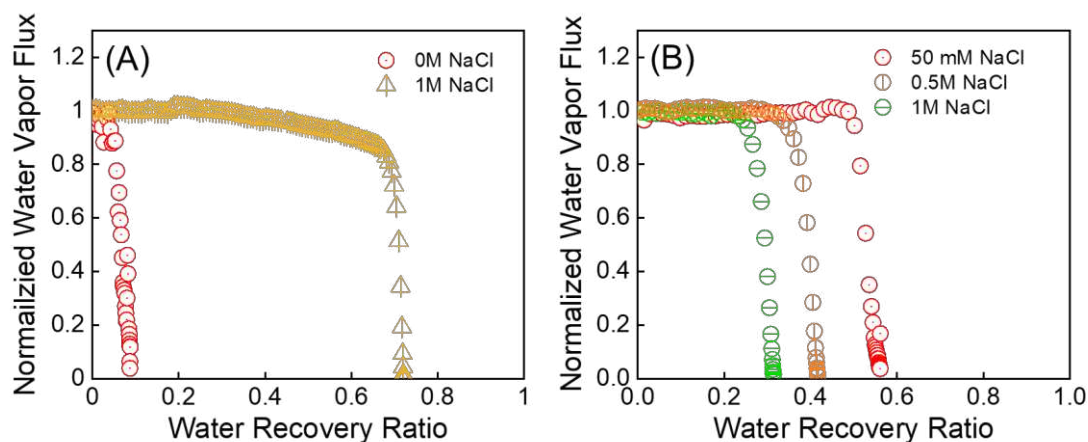


Figure C5. Normalized water vapor flux as a function of water recovery ratio in MD scaling experiments under different feedwater salinities with (A) gypsum scaling and (B) silica scaling. The initial SI of gypsum feed solution (with 0 M NaCl) and silica feed solution (with 50 mM NaCl) at low salinities was 0.55; the initial SI of gypsum with 1 M NaCl was -0.62; the initial SIs of silica with 0.5 M and 1 M NaCl were 0.71 and 0.92, respectively. The temperatures of feed and permeate streams were maintained at 60 °C and 20 °C, respectively. The feed and permeate streams were continuously circulated at crossflow velocities of 9.6 cm s⁻¹ and 6.4 cm s⁻¹, respectively. The initial water vapor flux of PVDF membrane was $24.5 \pm 0.6 \text{ L m}^{-2} \text{ h}^{-1}$, which was used to normalize the water vapor fluxes in the figure.

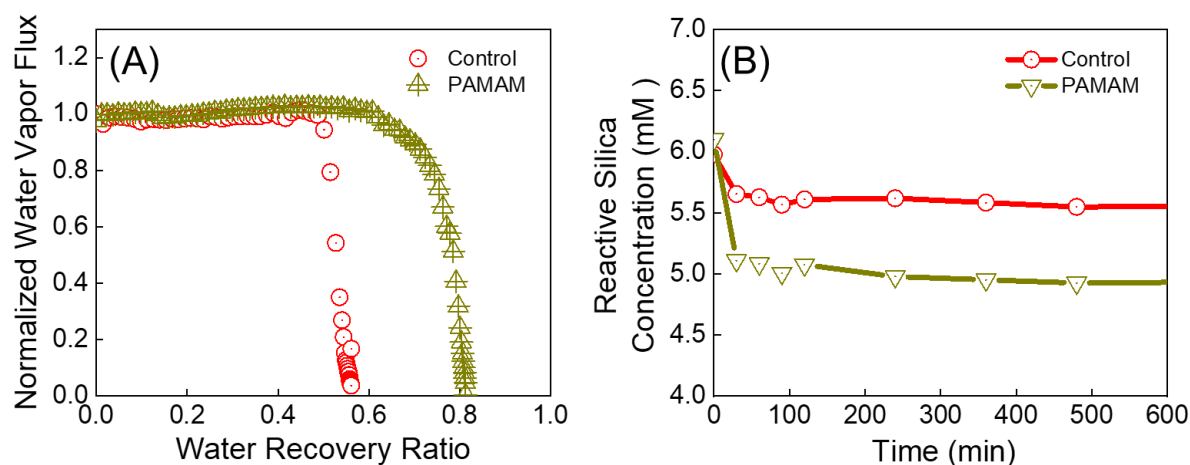


Figure C6. (A) Normalized water vapor flux as a function of water recovery ratio in MD silica scaling experiment with PAMAM. The initial SI of silica in the feed solution was 0.55, the concentration of PAMAM was 40 mg/L. The temperatures of feed and permeate streams were maintained at 60 °C and 20 °C, respectively. The feed and permeate streams were continuously circulated at crossflow velocities of 9.6 cm s⁻¹ and 6.4 cm s⁻¹, respectively. The initial water vapor flux of PVDF membrane was 26.3 ± 0.4 L m⁻² h⁻¹, which was used to normalize the water vapor fluxes in the figure. (B) The change of concentrations of scaling precursors as a function of time for silica-supersaturated solution in the absence and presence of PAMAM.

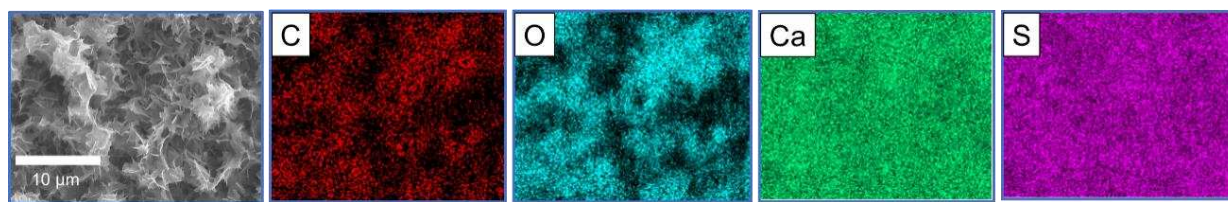


Figure C7. SEM-EDS elemental analysis of CaSO_4 scale on the membrane surface in the presence of PAA. The magnification of SEM is 3500X.

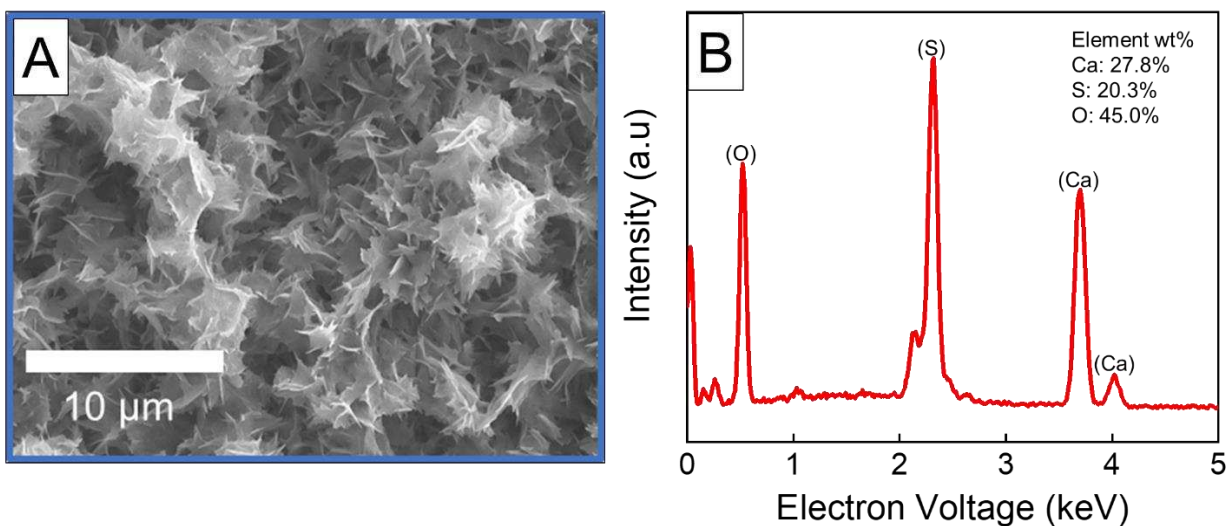


Figure C8. (A) SEM analysis of the top-view of PVDF membrane scaled with amorphous-like CaSO_4 after MD gypsum scaling experiment. (B) EDS elemental analysis of the PVDF membrane scaled with amorphous-like CaSO_4 . The EDS spectra indicate the Ca $\text{k}\alpha$ peaks at 3.69 and 4.01 keV, S $\text{k}\alpha$ peak at 2.31 and 2.46 keV, and O $\text{k}\alpha$ peak at 0.53 keV, respectively. Note that the element weight ratio of Ca: S: O revealed by EDS analysis was 1.3:1.0:2.2, which is roughly consistent to the elemental weight ratio in CaSO_4 (1.2:1.0:2.0). This indicates that the scale on the membrane surface was mainly consisted of CaSO_4 .

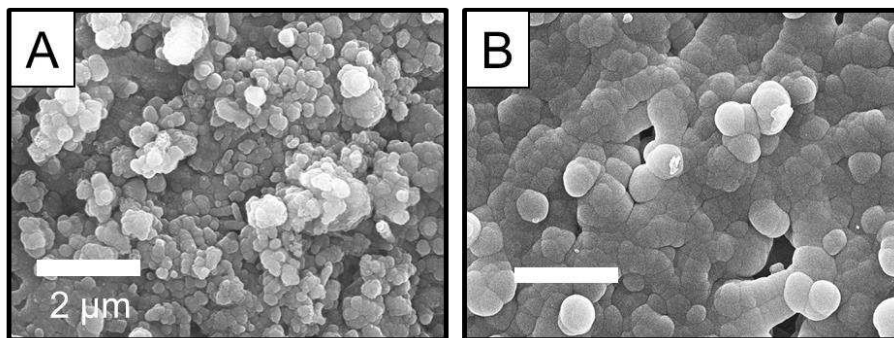


Figure C9. SEM analysis of silica scale on the membrane surface in the presence of PAMAM. The magnification of SEM is 15000X.

Characterization of scaled membrane surface using X-ray photoelectron spectroscopy

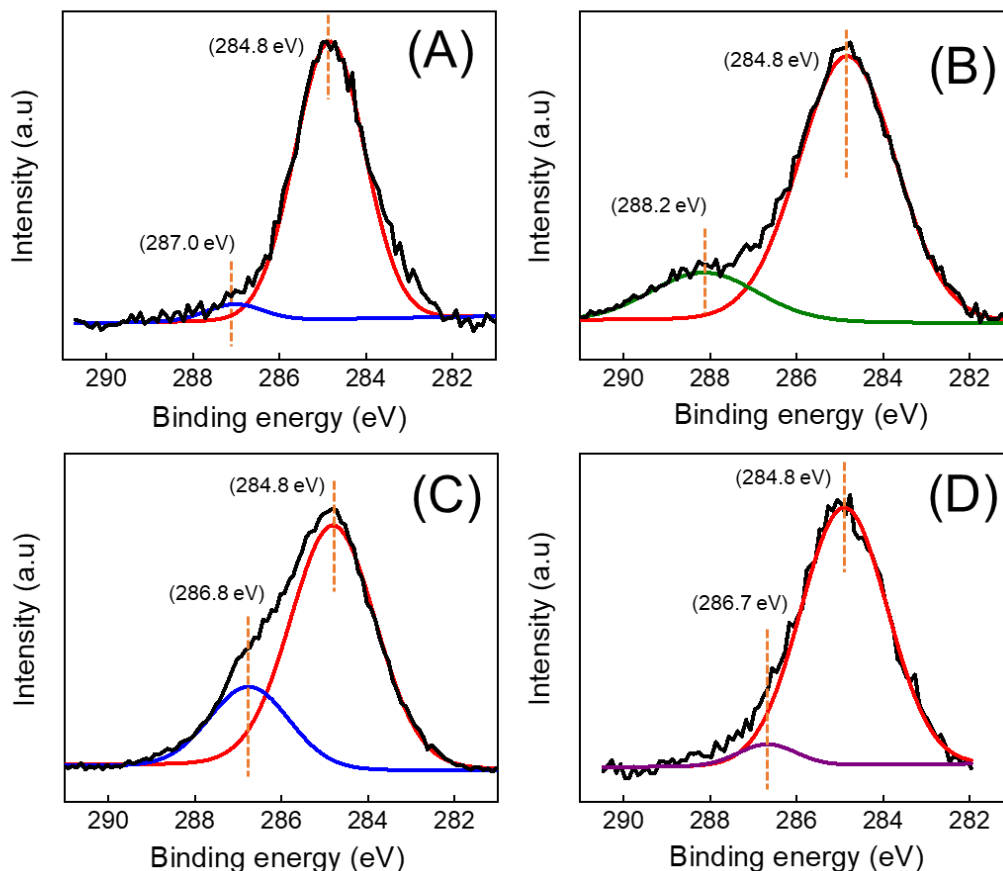


Figure C10. (A-D) High resolution C 1s XPS spectra of CaSO₄ scaled membrane surface. (A) the control group, (B) in the presence of 40 mg/L PAA, (C) in the presence of 40 mg/L PEG and (D) in the presence of 40 mg/L PEI.

C 1s spectrum originates from the adventitious carbon or the adsorbed anti-scalants coexisted with the CaSO₄ scale on the membrane surface. The decomposition of C 1s spectrum of the control group that originated from the adventitious carbon indicates two peaks at 284.8 eV and 287.0 eV, which are assigned to C-C and C-O-C bonds, respectively. (Figure C10A). (Greczynski and Hultman, 2017) The scaled membrane surface with PAA showed a peak at binding energy of 288.2 eV that corresponds to the O-C=O bond, (Greczynski and Hultman, 2017) indicating that PAA molecules coexisted with the CaSO₄ precipitates on the membrane surface (Figure C10B). Further, in the presence of PEG and PEI, peaks appeared at binding

energy of 286.8 eV and 286.7 eV (Figures C10-C and C10-D), corresponding to the C-O-C and C-N bonds. (Greczynski and Hultman, 2017; Louette et al., 2005) This provides evidence that PEG and PEI molecules coexisted with the gypsum scales on the membrane surface.

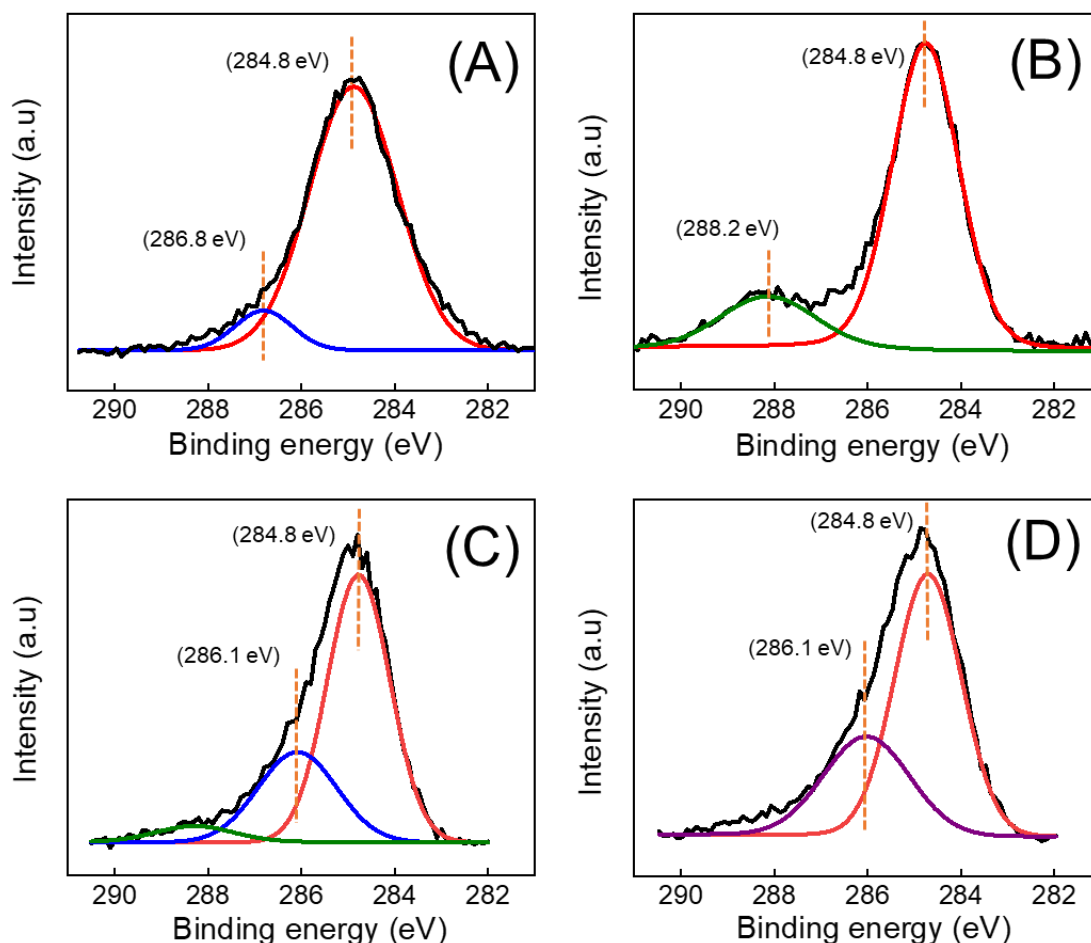


Figure C11. (A-D) High resolution C 1s XPS spectra of silica scaled membrane surface. (A) the control group, (B) in the presence of 40 mg/L PAA, (C) in the presence of 40 mg/L PEG and (D) in the presence of 40 mg/L PEI.

C 1s spectrum originates from the adventitious carbon or the adsorbed anti-scalants coexisted with the silica scale on the membrane surface. The decomposition of C 1s spectrum of the control group that originated from the adventitious carbon indicates two peaks at 284.8 eV and 286.8 eV, which are assigned to C-C and C-O-C bonds, respectively. (Figure C11-A). (Greczynski and Hultman, 2017) The scaled membrane surface with PAA showed a peak at

binding energy of 288.2 eV that corresponds to the O-C=O bond, (Greczynski and Hultman, 2017) indicating that PAA molecules coexisted with the silica scales on the membrane surface (Figure C11-B). Further, in the presence of PEG and PEI, peaks appeared at binding energy of 286.1 eV (Figures C11-C and C11-D), corresponding to the C-O-C and C-N bonds of PEG and PEI, respectively. (Greczynski and Hultman, 2017; Louette et al., 2005) The binding energies of C-O-C and C-N bonds in the presence of PEG and PEI were lower with silica than what were observed with CaSO₄ (Figure C11-C and C11-D).

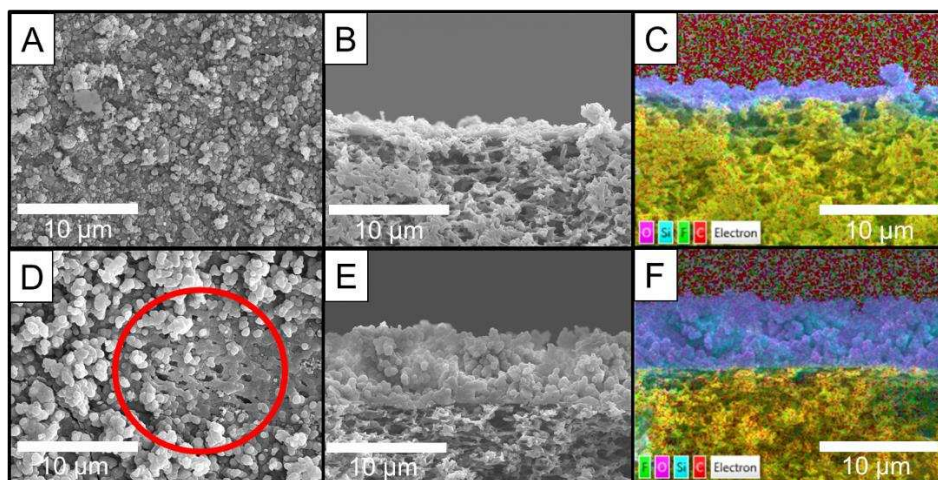


Figure C12. Top-view SEM micrographs of the scaled membranes at the conclusion of the MD silica scaling experiment. (A) The control group (no anti-scalants), (D) in the presence of 40 mg/L PEI. SEM-EDS elemental analysis of the cross-section of the scaled PVDF membrane. (B and C) The control group, (E and F) in the presence of 40 mg/L PEI. The magnifications of the SEM micrographs are 5000X for A, B, D and E. The red circle indicates the place where the silica gel layer had not covered the membrane surface.

We applied scanning electron microscopy (SEM) to compare the surface morphologies of silica scaled membranes with and without PEI at the conclusion of the MD scaling experiments (Figure C12). The silica particles were larger in the presence of PEI than what were observed from the control group (Figure C12-A, D). Further, comparison between Figures C12-A and C12-D shows the difference in space between the particles on the membrane surface. In some areas of the scaled membrane with PEI, the membrane structure underneath the silica scale layer was still observable (Figure C12-D, red circle). A SEM-EDS analysis of the membrane cross-section was also conducted (Figures C12-B, C, E and F). Due to the larger sizes of silica particles formed in the presence of PEI (i.e. facilitate silica polymerization), the thickness of the silica scale layer was thicker than that of the control group (without any anti-scalants) at the conclusion of the MD silica scaling experiments (Figures C12-C and C12-F). This result indicates that the delayed water vapor flux decline with anti-scalant PEI was not due to the change of scale layer thickness.

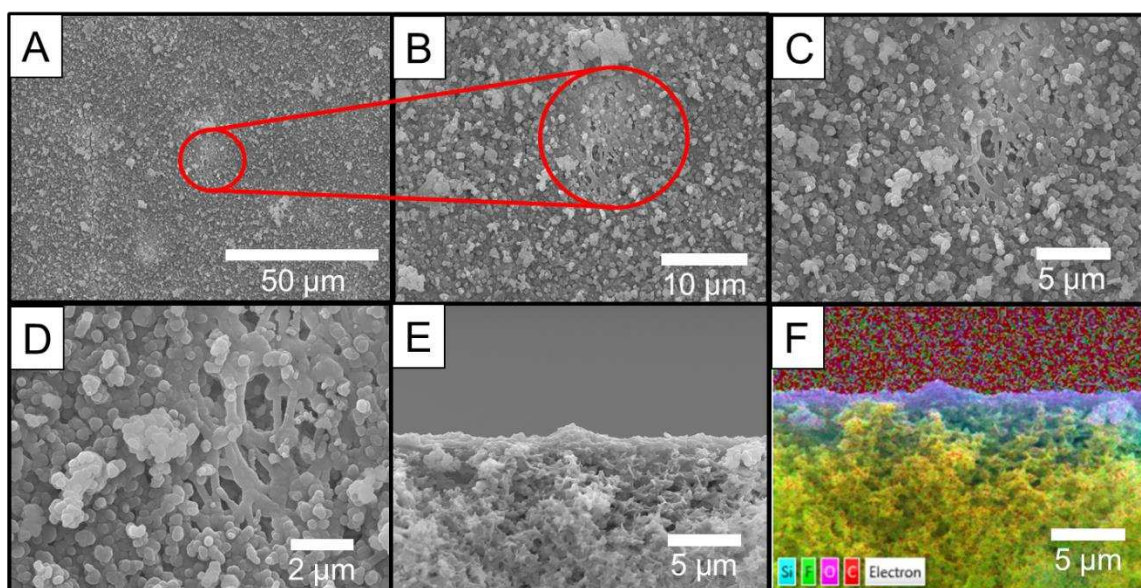


Figure C13. (A-D) Top-view SEM micrographs of the scaled membrane in the presence of 40 mg/L PEI, when the water vapor flux decreased by 35% in the MD silica scaling experiment. (E, F) SEM-EDS elemental analysis of the cross-section of the scaled PVDF membrane. The magnifications of the top-view SEM micrographs are 1000X, 3000X, 5000X, and 10000X for A-D, respectively. The magnification of the cross-section SEM micrograph is 5000X for E and F.

We also performed additional experiments to observe the extent of silica scale coverage on the membrane surface when the water vapor flux declined only by 35% compared to the initial water vapor flux (Figure C13, in the presence of PEI, less extent of flux decrease than Figure C12 above). While most of the membrane area was covered with silica scale, we could observe areas that were not fully covered by silica, with the underneath membrane structure clearly to discern (Figures C13-A – C13-D). The water vapor could penetrate the membrane from such areas, on which the cross-linked silica gel layer has not formed. Further, when the water vapor flux reduced by 35%, the thickness of the silica scale layer was comparable to the control group at the conclusion of the silica scaling experiments (when the water vapor flux decreased to zero) (Figures C13F and C13C). This result also supports that the thickness of the scale layer was not the factor that directly resulted in water vapor flux decline in MD. Instead, the formation of silica

gel layer, which covered the membrane surface, was responsible for the reduction of water vapor flux.

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- Louette, P., Bodino, F. and Pireaux, J.-J. 2005. Poly (ethylene imine)(PEI) XPS reference core level and energy loss spectra. *Surface Science Spectra* 12(1), 54-58.
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Appendix D⁹

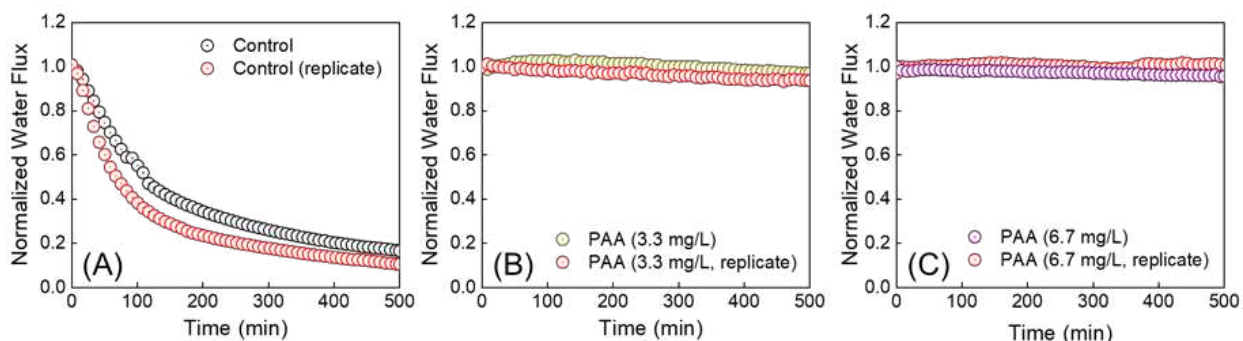


Figure D1. Duplicate runs of RO gypsum scaling experiments (recirculating mode) to demonstrate the results reproducibility of (A) the control group and the experimental groups with PAA concentrations at (B) 3.3 mg/L and (C) 6.7 mg/L. The experiments were performed in the RO system using commercial RO membranes. The gypsum supersaturated solution consisted of 24 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 24 mM Na_2SO_4 . The initial water flux and the cross-flow velocity were $40.3 \pm 0.4 \text{ L m}^{-2} \text{ h}^{-1}$ and 21.3 cm s^{-1} , respectively. The temperature was maintained constant at $25.5 \pm 0.1 \text{ }^\circ\text{C}$ throughout the experiment.

⁹ This appendix has been published as the Supporting Information of a research article in the *Journal of Membrane Science* with the following citation:

Yin, Y., Kalam, S., Livingston, J.L., Minjarez, R., Lee, J., Lin, S. and Tong, T. 2022. The use of anti-scalants in gypsum scaling mitigation: Comparison with membrane surface modification and efficiency in combined reverse osmosis and membrane distillation. *Journal of Membrane Science* 643, 120077.

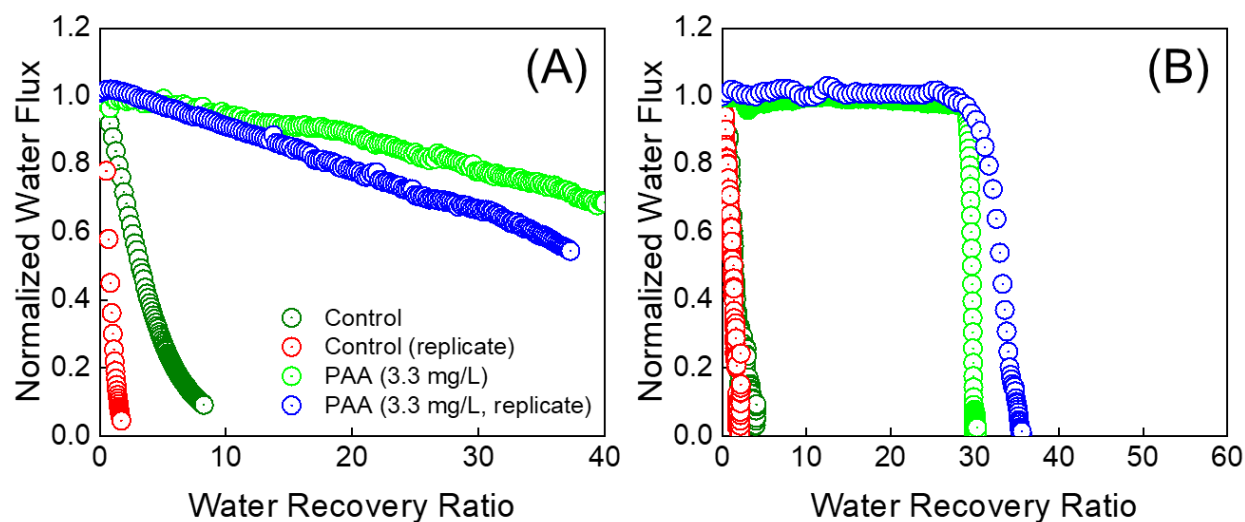


Figure D2. Duplicate runs of RO-MD gypsum scaling experiments to demonstrate the reproducibility of results for (A) RO scaling experiments (concentrating mode) for 2000 minutes and (B) MD scaling experiments as a function of water recovery ratio for the control group (with no anti-scalant) and the experimental group with PAA concentration at 3.3 mg/L. The gypsum-supersaturated solution used in RO consisted of 24 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 24 mM Na_2SO_4 . The initial water flux and the cross-flow velocity were $40.2 \pm 0.1 \text{ L m}^{-2} \text{ h}^{-1}$ and 21.3 cm s^{-1} , respectively. The temperature was maintained constant at $25.5 \pm 0.1 \text{ }^\circ\text{C}$ throughout the experiment. For MD, the temperatures of feed and permeate streams were maintained at $60 \text{ }^\circ\text{C}$ and $20 \text{ }^\circ\text{C}$, respectively. The cross-flow velocities of feed and permeate streams were 9.6 cm s^{-1} and 6.4 cm s^{-1} , respectively. The initial water vapor flux of MD was $24.9 \pm 0.4 \text{ L m}^{-2} \text{ h}^{-1}$.

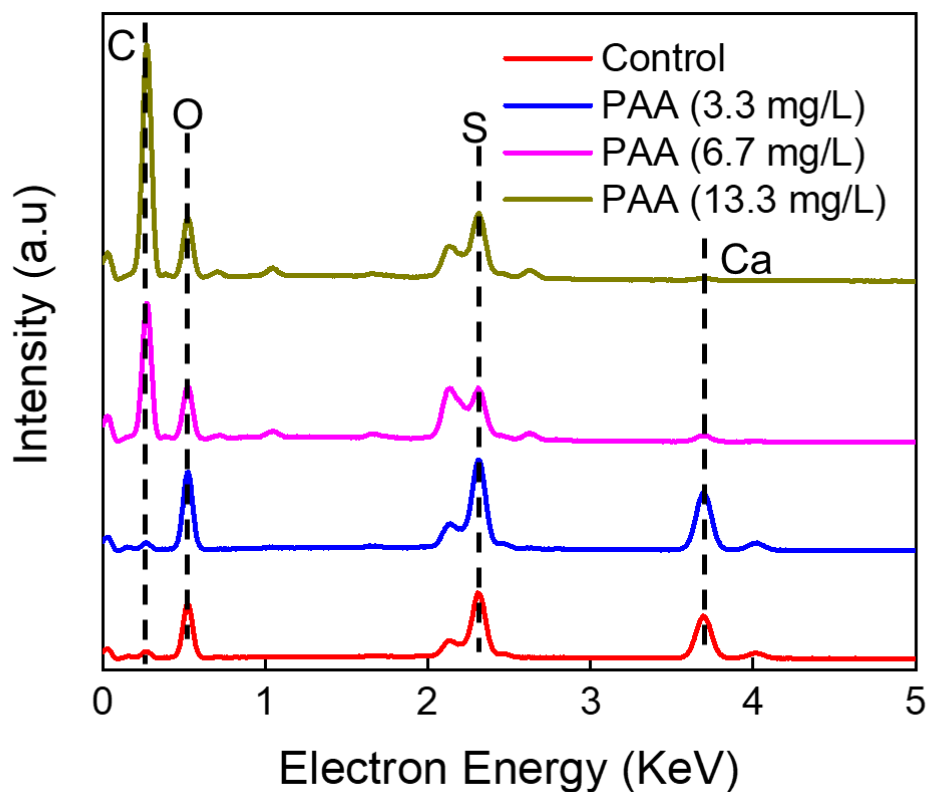


Figure D3. The elemental spectra of EDX for the scales on the membrane surfaces after RO gypsum scaling experiments. The C α , O α , Ca α and S α peaks are located at 0.28 KeV, 0.53 KeV, 3.69 KeV, and 2.31 KeV, respectively. Note that Ca element was negligible in the presence of PAA at the concentration of 6.7 mg/L and 13.3 mg/L.

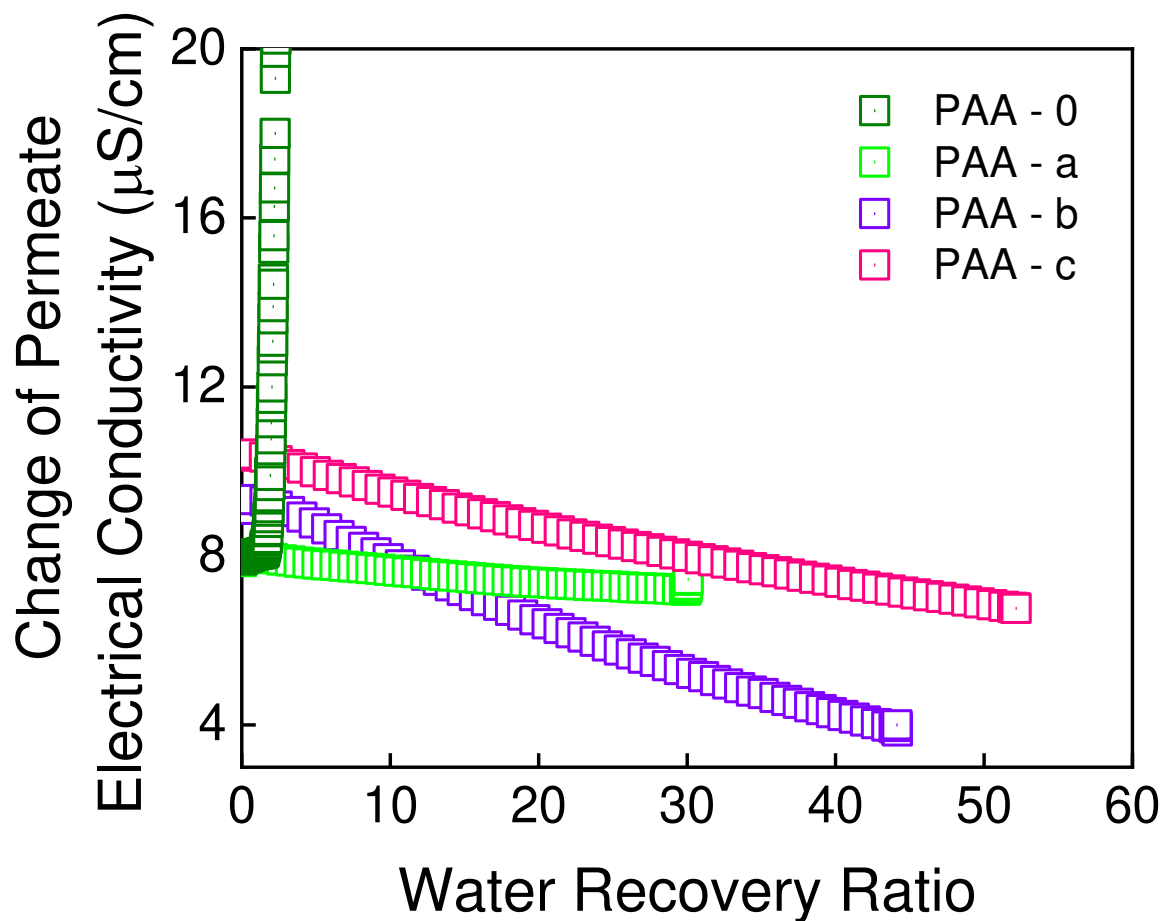


Figure D4. The change of permeate conductivity as a function of water recovery ratio for the MD experiments. The brines generated from RO served as the feedwaters of MD. PAA – 0, PAA – a, PAA – b, and PAA – c are the control group and experimental groups in the presence of PAA at 3.3 mg/L, 6.7 mg/L, and 13.3 mg/L, respectively.

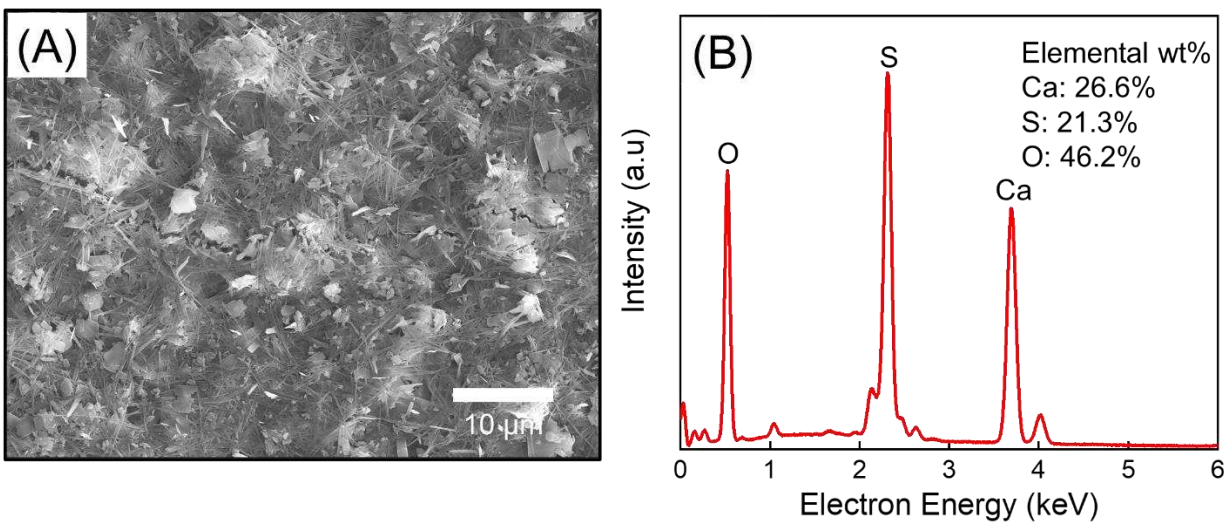


Figure D5. (A) Top-view SEM micrograph of PVDF membrane scaled with CaSO_4 after the MD scaling experiment for PAA-c experimental group (13.3 mg/L of PAA was added in RO). (B) EDX elemental spectra of the PVDF membrane surface after scaling. The Ca $\text{K}\alpha$ peaks at 3.69 keV, S $\text{K}\alpha$ peak at 2.31 keV, and O $\text{K}\alpha$ peak at 0.53 keV are labeled, respectively.