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2016

Wang, Y.-N., Järvelä, E., Wei, J., Zhang, M., Kyllönen, H., Wang, R., et al. (2015). Gypsum scaling and membrane integrity of osmotically driven membranes: The effect of membrane materials and operating conditions. *Desalination*, 377, 1-10.

<https://hdl.handle.net/10356/80879>

<https://doi.org/10.1016/j.desal.2015.08.024>

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Gypsum scaling and membrane integrity of osmotically driven membranes: the effect of membrane materials and operating conditions

Yi-Ning Wang^{1,2}, Eliisa Järvelä², Jing Wei¹, Minmin Zhang^{1,3}, Hanna Kyllönen², Rong
Wang^{1,3}, Chuyang Y. Tang^{*4}

1. Singapore Membrane Technology Centre, Nanyang Technological University,
Singapore 637141
2. VTT Technical Research Centre of Finland, Jyväskylä, Finland, 40400
3. School of Civil and Environmental Engineering, Nanyang Technological
University, Singapore, 639798
4. Department of Civil Engineering, the University of HongKong, Hong Kong

* To whom correspondence should be sent,

Address: HW 6-19b, Haking Wong Building, Pokfulam Road, Department of Civil
Engineering ,the University of Hong Kong, Hong Kong SAR, China

Tel: +852 28591976;

Fax: +852 25595337;

Email: tangc@hku.hk

Abstract

The emerging thin film composite (TFC) forward osmosis (FO) and pressure retarded osmosis (PRO) membranes generally have better separation properties compared with their cellulose triacetate (CTA) counterparts. Nevertheless, their scaling performance has been rarely reported. In the current study, the phenomenon of membrane integrity loss as a result of scaling is reported for the first time for osmotically driven membrane processes (ODMPs). The results show that the TFC membrane suffered marked flux reduction during the scaling in the active-layer-facing-feed-solution (AL-FS) orientation, accompanied with the severe damage of the membrane active layer. The membrane integrity loss is attributed to the scale formation and growth in the confined space between the membrane and the feed spacer. Compared to the CTA membrane, the TFC was more prone to scaling and membrane damage due to its unfavorable physiochemical properties (presence of Ca^{2+} binding sites and ridge-and-valley roughness). Although antiscalant addition was shown to be effective for scaling control in AL-FS, it was ineffective in the active-layer-facing-draw-solution orientation. The current study reveals the critical need for scaling control in ODMPs processes in respect to the membrane integrity and flux stability. The results also have far-reaching implications for FO and PRO membrane design and process operation.

Keywords: Scaling; Forward osmosis (FO); Thin film composite (TFC); Cellulose triacetate (CTA); Membrane integrity

1 Introduction

Osmotically driven membrane processes (ODMPs) utilize the osmotic pressure difference between a concentrate draw solution (DS) and a dilute feed solution (FS) separated by a semi-permeable membrane to drive the permeation of water from the FS to the DS. Depending on the applied pressure in the DS, ODMPs can be classified into forward osmosis (FO, pressure = 0) and pressure retarded osmosis (PRO, pressure > 0). ODMPs have recently gained more and more research interests due to its potential applications in low-energy separation processes and power generation [1-7].

Membrane scaling is a critical challenge for ODMPs, particularly for applications involving scaling precursors at high concentrations (e.g., high $[\text{Ca}^{2+}]$ and/or $[\text{SO}_4^{2-}]$) [8-11]. From the experiences of pressure-driven reverse osmosis (RO), it is understood that inorganic scale starts to grow when the concentration of sparingly soluble salts in bulk or near membrane surface exceeds their solubility [12]. Their deposition on a membrane results in reduction of membrane permeability. Scaling can be influenced by various operating conditions, such as solution pH, temperature, crossflow velocity and permeation rate [12]. Although these experiences are applicable to ODMPs, the additional transport phenomena in ODMPs including internal concentration polarization (ICP) and reverse solute diffusion (RSD) may lead to more difficult scaling control. Despite that membrane water flux appears to be more easily restored in ODMPs compared with RO after cleaning [8, 10], a few FO/PRO scaling studies reported severe internal scaling when membrane support layer was facing the FS [9]. Furthermore, the RSD of scaling precursors from the DS plays an important role in

promoting scaling. In some cases, complete cease of water flux occurred within merely a few hours of scaling test [9, 10].

Most existing ODMP scaling studies used the commercially available cellulose triacetate (CTA) membranes (Hydration Technology Innovations [HTI], Albany, OR) [8, 9, 13, 14]. On the other hand, the more recently developed thin film composite (TFC) polyamide (PA) FO/PRO membranes are believed to be promising replacement to CTA membranes, thanks to their better chemical and biological stability and improved separation properties (higher water permeability and salt rejection) [15-18]. To date, very few papers have investigated the scaling of TFC FO/PRO membranes [8]. Although the PA layer has high selectivity, the carboxylic surface functional groups of the PA layer are presumably the effective binding sites for divalent cations such as Ca^{2+} [19], which may promote subsequent crystal growth on the TFC membranes. In addition, the thickness of a typical TFC PA rejection layer is on the order of 100 nm, which is much thinner compared with that of CTA membranes (a few μm) [15]. One potential concern is the mechanical stability of the PA layer. The deposition and growth of scalant crystals may introduce local mechanical stress, leading to potential loss of membrane integrity. To the best knowledge of the authors, such phenomenon has not yet been systematically reported in the literature.

The objectives of the current study are 1) to systematically compare scaling behavior between TFC and CTA membranes and 2) to investigate the factors that affect the mechanical integrity of FO/PRO membranes under the influence of scaling.

2 Materials and Methods

2.1 Chemicals and solution chemistry

Analytical grade chemicals (purity > 99%) were used as received without further purification. CaCl_2 and Na_2SO_4 were used as scaling precursors to study gypsum scaling. NaCl was used for conductivity adjustment and draw solution (DS) preparation. A typical feed solution (FS) contained 26.1 mM CaCl_2 , 72 mM Na_2SO_4 and 10 mM NaCl . It had an osmotic pressure of 7.5 bar and a saturation index (SI) of gypsum of 2.0, as calculated using OLI Stream Analyzer 3.1 software (OLI systems, Inc., Morris Plains, NJ) [9]. Another FS prepared with 163 mM NaCl was used as control for baseline tests (SI = 0, osmotic pressure = 7.5 bar). No pH adjustment was performed (pH = ~ 6.0).

Polyacrylic acid (sodium salt) (PAA, KemGuard 5804, Kemira, Finland) was used as the antiscalant (AS), and it had an average molecular weight of 2200 Da. Where the effect of AS was studied, 2 ppm PAA was dosed into the FS.

2.2 FO membranes

A polyamide (PA) based thin film composite (TFC) FO membrane and a cellulose triacetate (CTA) asymmetric FO membrane were employed in this study. Both were received from HTI (Albany, OR) as dry flat sheet coupons and stored in 4 °C fridge in dark. Prior to FO experiment, membrane coupons were cut into smaller size and soaked in ultrapure water for 1 day.

2.3 FO filtration experiments

FO tests were performed with a bench-scale crossflow filtration system (Appendix A) and the experimental procedures were adapted from prior studies [20, 21]). Briefly, the FO membrane cell (CF042-FO, Sterlitech) had an effective membrane area of 42 cm². Diamond-patterned spacers (65 mil (1.651 mm) spacer, GE Osmonics) were placed in both the FS and DS channels unless otherwise specified (e.g., where the effect of FS spacer was evaluated, the feed channel was not filled with any spacer). An FS of 3.5 L and a DS of 3 L were circulated by two variable speed peristaltic pumps (Watson-Marlow, Cornwall, UK) to generate a crossflow of ~10 cm/s in both channels. The DS tank was placed on a digital balance (Sartorius U4100 S, Germany) that was connected to a computer for water flux acquisition. The FS was well mixed by a magnetic stirrer and its conductivity was monitored by using a conductivity meter (SevenGo™ portable conductivity, Mettler Toledo). FO scaling experiments were performed in both active layer-facing-feed solution (AL-FS) and active layer-facing-draw solution (AL-DS) orientations. Unless specified otherwise, both FS and DS were freshly prepared prior to each test. The DS concentration was adjusted to achieve an identical initial FO water flux of $9 \pm 1.5 \text{ L/m}^2\cdot\text{h}$.

Membrane cleaning and flux reversibility tests were performed immediately after the FO scaling experiments. The ultrapure water flushing was carried out in both FS and DS flow channels at 15 cm/s for 30 min. The recovered flux after cleaning was measured with 2 M NaCl DS and ultrapure water FS, and was compared with the clean membrane flux obtained under the same testing condition (i.e., 2M NaCl (DS), ultrapure water (FS) and same

orientation). All the FO experiments and membrane cleaning were performed at room temperature (22 ± 1 °C).

2.4 Reverse osmosis (RO) tests for A , B , S values

The membrane water permeability and NaCl rejection were evaluated in RO experiments using a laboratory-scale crossflow filtration setup [22, 23]. Pure water flux (J) was measured under an applied pressure (ΔP) of 7 bar (101 psi) with ultrapure water as the feed. NaCl rejection (R) was obtained by filtering 10 mM NaCl feed solution (10 L) at 7 bar and a crossflow velocity of 20 cm/s. The water permeability (A) and NaCl permeability (B) were determined from the following equations:

$$A = \frac{J}{\Delta P} \quad (1)$$

$$B = J \left(\frac{1}{R} - 1 \right) \quad (2)$$

The structural parameter (S) of the membrane support layer was calculated from Equations 3 and 4, which describe the FO water flux (J_v) is affected by the internal concentration polarization (ICP) as well as the external concentration polarization (ECP) [24].

$$\text{AL-DS: } J_v = \left(\frac{1}{k_F} + \frac{1}{k_m} + \frac{1}{k_D} \right)^{-1} \ln \frac{A\pi_D + B - J_v \exp(J_v / k_D)}{A\pi_F + B} \quad (3)$$

$$\text{AL-FS: } J_v = \left(\frac{1}{k_F} + \frac{1}{k_m} + \frac{1}{k_D} \right)^{-1} \ln \frac{A\pi_D + B}{A\pi_F + B + J_v \exp(-J_v / k_F)} \quad (4)$$

where π_D and π_F are the osmotic pressures of the DS and FS, respectively; k_F , k_D and $k_m \equiv D/S$ are the mass transfer coefficient of the draw solution stream, feed solution stream and in the membrane support layer. D is the solute diffusion coefficient (1.6×10^{-9} m²/s was

used for NaCl in this study [25]). J_v was measured in both the AL-DS and AL-FS orientations using 2 M NaCl DS against ultrapure water FS. The hydrodynamic conditions were similar to that used for FO scaling tests (i.e., 10 cm/s crossflow velocity and feed/draw spacers were applied).

2.5 Membrane characterization

A field-emission scanning electron microscopy (FESEM, JSM-7600F, JEOL, Japan) was employed to characterize the virgin and scaled membranes. All membrane samples were gently rinsed with ultrapure water (to remove unbound crystals or dirt), dried in vacuum at room temperature for 24 h, and sputter coated with a thin layer of platinum using JFO-1600 auto fine coater. They were imaged at accelerating voltage of 5 kV.

The membrane active surface roughness was characterized using an atomic force microscopy (AFM, Park Systems XE-100, USA) with a scan area of $10\ \mu\text{m} \times 10\ \mu\text{m}$. The contact angle of the active surface was measured using an optical contact angle measurement system (OCA, DataPhysics Instruments GmbH) [20]. The zeta potential of clean membranes was analyzed with Electro Kinetic Analyzer (EKA, Anton Paar, Graz, Austria).

3 Results and Discussion

3.1 FO membrane characteristics

The properties of the TFC and CTA membranes are presented in Table 1. The RMS roughness of the TFC and CTA are 80.5 and 6.4 nm, respectively, suggesting that the TFC

membrane has a significantly rougher active surface due to the ridge-and-valley morphology of the polyamide (PA) surface. This is consistent with the traditional TFC PA RO membranes [26] as well as the lab fabricated TFC PA FO membranes [27]. TFC has a lower contact angle, indicating a more hydrophilic surface. The more negative zeta potential of TFC active surface is likely due to the presence of the deprotonated carboxylic groups at neutral pH [28]. In addition, the TFC membrane has significantly higher intrinsic water permeability (6.49×10^{-12} m/s.Pa) at comparable salt rejection. The structural parameters of TFC and CTA membranes are 1.38 mm and 1.06 mm, respectively, suggesting that this TFC membrane may suffer more severe ICP during osmotically driven processes.

3.2 Effect of membrane materials and operational conditions on scaling and membrane integrity

3.2.1 Active layer facing feed solution (AL-FS)

This section presents the scaling flux behavior of both TFC and CTA membranes in the AL-FS orientation (i.e., the FO orientation). To enable a fair comparison between the two membranes, an identical initial flux of ~ 9 L/m²·h was applied (achieved by using 2.5 M NaCl DS for TFC and 1.9 M NaCl DS for CTA). Figure 1 shows the normalized water flux (normalized with respect to the initial flux) of the TFC and CTA membranes during FO scaling by gypsum in the AL-FS orientation. For both membranes, the presence of Ca²⁺ and SO₄²⁻ in the FS (SI 2.0) led to significantly more flux decline compared to the respective baseline (no scaling) condition, which can be attributed to membrane scaling. Compared to the CTA scaling with $\sim 12\%$ flux decline (relative to the baseline flux) over the 18-h duration,

the TFC scaling experienced a far more severe relative flux loss of $\sim 70\%$. Figure 2 presents the FESEM micrographs of scaled membranes (Figures 2a-c for TFC and 2d-f for CTA; also see the micrographs of clean membranes in Appendix B). As expected, no internal scaling was observed for both membranes since the dense active layer was facing the FS. However, crystals were clearly visible on the fouled TFC membrane surface, and these crystals occurred mainly at the valley regions in the ridge-and-valley roughness structure (inset of Figure 2b). In comparison, far fewer crystals can be identified on the scaled CTA membrane (Figure 2e). Thus, both the flux performance and FESEM results strongly indicate that the TFC membrane was more prone to gypsum scaling, which can be partly explained by its surface chemistry and morphology. Prior studies have reported that the carboxylic groups of the PA layer have strong affinity to Ca^{2+} [19, 29], which could potentially promote the initial crystal nucleation on the membrane. Meanwhile, the rough ridge-and-valley structure could provide a local hydrodynamic condition that favors the anchorage of the crystals to the surface [26].

In addition to the active layer chemistry and morphology that tend to promote scaling, we further observed the formation of numerous defects (pinholes with sizes on the order of a few μm to a few tens of μm) for the scaled TFC membrane (Figure 2a and [Appendix C](#)). These defects were highly localized and only found around the spacer filaments. The scaled membrane was rinsed in ultrapure water and its integrity was evaluated by filtration in RO test mode. The result showed that the membrane had no rejection to NaCl, which indicates the loss of mechanical integrity as a result of membrane scaling. This loss of membrane

rejection (and thus loss of osmotic driving force) was probably the main cause of the severe water flux loss for the TFC membrane in the current study (The severe flux decline was also observed in a replicate test (See Appendix C)). In contrast, there was no noticeable damage on the CTA active surface (Figure 2d).

The localization of defects formation near the spacer filaments can be explained by the hydrodynamic dead zones near the filaments. Gao et al. [30] observed little vortex mixing in the spacer shadows to the cross flow using a novel optical coherence tomography technique. In our previous study on FO particulate fouling, we observed preferential particle accumulation under the spacer filaments [31]. The current observation is also consistent with the existing RO scaling literature that the crystal formation and precipitate deposition occurred preferentially at the spacer induced hydrodynamic dead zones [32-35]. For the case of CTA, its favorable surface properties (no binding sites for calcium and smooth surface) do not allow the initiation of severe scaling and thus cause little damage to membrane structure. However, the combination of the unfavorable surface properties (the presence of carboxylic functional groups and ridge-and-valley roughness structure) and the relatively thin PA active layer makes the TFC membrane much more vulnerable to scaling. The growth of crystals in the confined space between the spacer filaments and the membrane surface can create localized mechanical stress, which is a likely cause for the membrane damages observed in the current study. To further understand the role of feed spacer on FO scaling and membrane damage, additional FO scaling experiments were performed for the TFC membrane in the absence of feed spacer (Appendix C). The flux loss at the end of 18-h scaling was relatively

milder (~ 19% relative to the baseline flux) and the flux was stabilized after 8 h. No apparent sign of membrane damage was observed. These results confirm the role of spacer confinement on membrane integrity loss due to scaling.

Since the membrane damage was caused by the crystal growth in the confined space between the spacer and membrane surface, one effective way to protect membrane is to control the crystal growth. In the current study, a 2 ppm PAA AS was dosed for scaling control. The measurements of bulk crystallization induction time showed good evidence of crystallization suppression in the presence of PAA (Appendix D). The 18-h scaling test results also indicated that the dosage of 2 ppm PAA effectively prevented membrane flux loss in the AL-FS orientation (Appendix E). Meanwhile, the membrane did not suffer integrity loss during the scaling test.

3.2.2 Active layer facing draw solution (AL-DS)

Scaling tests were also performed in the AL-DS orientation to understand the membrane performance in PRO applications. In this orientation, about 80-90% flux reduction occurred for the TFC membrane within the first hour. A similar phenomenon was also observed for the CTA with approximately 50% flux loss. The flux decline occurred much faster in AL-DS compared to AL-FS. The scaling in AL-DS also appeared to be significantly faster than the bulk crystallization (induction time ~1.5 h at gypsum SI of 2.0, see Appendix D). Under this orientation, the severe ICP of scaling precursors (Ca^{2+} and SO_4^{2-}) can occur to result in a greatly elevated effective saturation index ($\text{SI}_{\text{effective}}$) in the support layer [9]. Based on the

balance of solute convection and diffusion, the Ca^{2+} and SO_4^{2-} concentrations inside the support layer were estimated with taking account of initial water flux of $\sim 9 \text{ L/m}^2\cdot\text{h}$ (Table 2 and Appendix F). The estimated $\text{SI}_{\text{effective}}$ value for the TFC membrane (~ 17.2) was also greater than that of the CTA membrane (~ 10.7) due to the larger structural parameter of the TFC membrane. In both cases, the $\text{SI}_{\text{effective}}$ values were an order of magnitude higher than the bulk SI value of 2. Therefore, both membranes suffered remarkable flux reduction at the beginning, with more severe flux drop for the TFC membrane as a result of its higher $\text{SI}_{\text{effective}}$ in the support layer.

The FESEM micrographs of the scaled membranes in the AL-DS orientation are shown in Figure 4. In contrast to the clean cross-sections in Figure 2 (AL-FS), the membrane support layers are filled with gypsum scale (Figure 4c and 4f) after scaling in the AL-DS orientation. The severe ICP of scaling precursors was responsible for the remarkable internal scaling and corresponding flux reduction. The microscopic examination of membrane top surfaces revealed severe deformation of the active rejection layers for both the TFC and CTA membranes (Figure 4a-b for TFC and 4d for CTA). The convex appearance of membrane deformation can be attributed to the gypsum crystal growth in the space-confined porous support layer. The AL-DS orientation is usually applied in PRO processes to achieve a higher water flux and thereby the high power density [36, 37]. However, such severe deformation of the active layer in the presence of uncontrolled scaling will be challenging to the membrane long-term stability. Hence proper scaling control can be very critical for PRO processes.

The use of PAA for scaling control was also tested in the AL-DS orientation (see Appendix E). Unfortunately, a 2 ppm dosage of PAA had no or only marginal effects in reducing membrane scaling. In the AL-DS orientation, the elevated $SI_{\text{effective}}$ values rendered the PAA less effective in retarding scaling, which is consistent with the bulk crystallization induction time experiments (see Appendix D).

3.2.3 Flux reversibility evaluation

After 18-h FO scaling, the TFC and CTA FO membranes were further evaluated based on the flux reversibility in this section. A comparison of the fluxes after 18-h scaling with respect to the respective baseline flux is shown in Figure 5a. The relative flux drop of the CTA at 18 h was about 15% and 24% in the AL-FS and AL-DS orientations, respectively. The TFC membrane suffered more severe flux reduction, i.e., over 70% flux drop in both orientations. The recovered flux for the two membranes after cleaning (relative to the clean membrane flux at the same test condition) is presented in Figure 5b. After flushing with ultrapure water for 30 min, the CTA could restore ~90% flux in both orientations, which were consistent with the high flux recovery of FO membrane reported in other studies [8]. However, the TFC membrane showed zero flux in the AL-FS orientation after ultrapure water flushing. Consistent with the previous discussion in Section 3.2.1, the scaling-damaged TFC membrane in the AL-FS orientation completely lost its salt rejection and was not able to effectively establish an osmotic pressure driving force across the membrane. In the AL-DS orientation, the TFC membrane was only able to restore ~50% flux. The difficulty to restore the TFC membrane performance after scaling combined with the greater risk of membrane

integrity loss suggests that scaling control shall be a critical aspect to be addressed by future FO/PRO studies. The implications and potential controls of scaling in ODMPs are presented in the next section.

4. Conclusions and Implications

This study investigated the ODMP scaling using commercial CTA and TFC FO membranes. Our results generally show that the TFC membrane was more vulnerable to scaling. In the AL-FS orientation the active layer of the TFC membrane underneath the spacer filament was severely damaged, due to the deposit/formation of scale crystals in the hydrodynamic dead zones and the subsequent scale growth within the confined space between the spacer filament and membrane surface. The feed spacer filament was responsible for the mechanical stress created on the membrane surface. The vulnerability of the TFC membrane can be explained by its surface chemistry (containing carboxylic groups as binding sites for Ca^{2+}) as well as its physical properties (the ridge-and-valley surface roughness and the significantly thinner active layer). These factors shall be considered in order to design a more robust membrane against scaling. In the AL-DS orientation, the severe internal scaling resulted in remarkable flux drop for both TFC and CTA membranes. The use of AS could effectively prevent the scaling and thus membrane damage in the AL-FS orientation, but it had little effect in the AL-DS orientation.

Based on the findings from the current study, some potential control measures for FO/PRO scaling are proposed. In FO processes (AL-FS orientation), the use of spacer may be avoided

by adopting submerged membrane configuration and/or hollow fiber membranes to effectively eliminate membrane damage caused by scaling under spacer. It is also recommended to use appropriate dosage of AS as a precautionary measure for the prevention of scaling and severe membrane damage. Membrane surface modification (such as surface coating or graphing) could be adopted to avoid the unfavorable interaction of scalants and the membrane surface [38, 39]. In the case of PRO (AL-DS orientation), one may consider the use of a second skin on the porous substrate [40] to prevent internal scaling. The second skin shall be designed in such a way that it has nanofiltration-like rejection properties to mitigate the ICP of scaling precursors without significantly affecting the PRO water flux and power density [41]. The double-skinned membrane design can be further combined with AS dosage for effective scaling control. Finally, although the conventional wisdom in PRO is to use the AL-DS orientation, future studies may consider testing PRO in the AL-FS orientation [42] for the benefit of a more stable long term flux performance.

Acknowledgements

The authors thank the financial support from Tekes, the Finnish Funding Agency for Innovation and the Academy of Finland for the research work carried out in this manuscript. The work is also partially funded by the Ministry of Education of Singapore under the Tier 2 Research Grant (no. ARC3/12). The technical support from the Singapore Membrane Technology Centre is also acknowledged.

Appendices

A. Schematic of FO setup

The schematic of FO setup is presented in Figure A1.

B. FESEM micrographs of clean membrane surfaces

The SEM images of clean TFC and CTA membranes are shown in Figure B1.

C. Effect of feed spacer on TFC FO membrane scaling in the AL-FS orientation

To have a complete understanding of the effect of feed spacer on FO scaling with the TFC membrane, the scaling experiment was also performed in the absence of feed spacer. Figure C1(a-b) present the flux performance during the FO scaling with and without a feed spacer. The flux decline trend was duplicable for the FO scaling in the absence of feed spacer, while that was hardly repeatable when the feed spacer was used. This could be explained by the uncontrollable membrane damage occurred during the FO scaling with feed spacer (refer to the discussion in Section 3.2.1). The damaged membrane surface after the scaling in the presence of feed spacer can be clearly observed in Figure C1(c), in contrast to the intact surface after baseline test.

It is noteworthy that the membrane flux without feed spacer demonstrated a sharp decrease and recovery from 2.5 to 6 h, presumably explained by the crystallization process (i.e., scale nucleation and subsequent growth on/near the membrane surface). The small crystals formed on the membrane surface (Figure 2b) at the beginning of crystallization may cause significant

flux reduction, whereas the formation of large crystals (that can be washed away from membrane surface easily) at a later stage could lead to an increased water flux. This is further confirmed by Figure C2, as the aged FS with suspended large gypsum crystals (after the crystallization process) did not cause much flux loss.

D. Induction time of gypsum nucleation with and without antiscalant (AS)

The anionic nature of the polyacrylic acid (PAA) AS (in a neutral pH solution) makes it a good chelator for multivalent cations and leads to dispersion of precipitates and lattice distortion [12]. The effect of AS on the gypsum nucleation induction time is presented in Figure D1. The kinetics of gypsum crystallization was monitored by on-line turbidity measurements. Increasing gypsum SI resulted in a shorter induction time. The induction time was about 0.1, 0.4, and 1.5 hour respectively for the solution of SI = 2.0, 2.3 and 3.17 in absence of AS. The induction time can be prolonged in the presence of AS. Results show that 2 ppm AS dosage was sufficient to retard gypsum formation at $SI \leq 2.0$ based on 2-day observation; while the same dosage was only marginally effective for the solution with SI greater than 3.17.

E. FO/PRO scaling control with AS

2 ppm dosage of PAA AS did not cause additional flux reduction (Figure E1), indicating no adverse effect of AS (e.g., gelation related membrane fouling [12]) on the two membranes. Upon the addition of AS into the FS, no gypsum precipitation could be observed in the bulk FS during the 18-h run, which was consistent with the results from the induction time test.

The effect of AS on membrane flux performance during FO scaling run is shown in Figure E2(a-d). It can be observed that the presence of AS retarded gypsum growth and maintained a

similar water flux level as the baseline condition for both TFC and CTA membranes in the AL-FS orientation (Figure E2(a-b)). This agrees with the effect of AS on RO/NF scaling control – a low dosage of AS could inhibit scale growth [43, 44]. In contrast, the AS had marginal influence on retarding flux decline in the AL-DS orientation (Figure E2(c-d)). The flux decline rate was slightly slowed down for the case of CTA membrane; however, this beneficial effect was almost negligible to the TFC membrane. The ineffectiveness of AS in the AL-DS orientation could be explained by the severe ICP of Ca^{2+} and SO_4^{2-} ions in the membrane support layer, resulting in a remarkably high $\text{SI}_{\text{effective}}$ (Table 2). Even if the concentration of AS was also elevated in the support layer as a result of the ICP of AS, the enhanced $\text{SI}_{\text{effective}}$ in the support layer still rendered the AS ineffective, likely due to the upper saturation limit of gypsum ($\sim \text{SI } 4$) with AS [12, 45]. The TFC membrane of larger structural parameter suffered more ICP, which may explain the even less beneficial effect. For both membranes, the fluxes under the conditions with AS and without AS nearly converged (at 1.5 h for TFC and 12.5 h for CTA), indicating that the use of AS was merely to delay the crystal formation but not to eliminate the scaling constituents [12].

F. Internal concentration polarization of scaling precursors in the AL-DS orientation

In the AL-DS orientation, the solutes in the feed solution accumulate in the porous support layer as a result of the transport discontinuity (i.e., rejection by the active layer), resulting in concentrative internal concentration polarization (ICP). In the current study, the amount of solutes in the support layer was balanced by the solutes entering the support layer via convection and the solutes diffused back to the bulk solution due to concentration gradient [9]:

$$J_v C - D \frac{dC}{dx} = 0 \quad (\text{F1})$$

By integrating the Equation F1 across the boundary layer thickness (the boundary layer is in between the active layer and bulk FS), i.e., from the $x=0$ representing the interface of the

boundary layer and the FS, where the solute concentration is C_b , to the $x=S$ representing interface of the boundary layer and the membrane active layer, where solute concentration is C_i , the below equation is obtained:

$$C_i = C_b \exp\left(\frac{J_v S}{D}\right) \quad (\text{F2})$$

where S is the structural parameter representing the length scale for concentration polarization, J_v is the volumetric water flux and D is the solute diffusion coefficient.

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