Calcium Carbonate Scaling in Seawater Desalination by Ammonia-Carbon Dioxide Forward Osmosis: Mechanism and Implications

Zhenyu Li, Rodrigo Valladares Linares, Szilárd Bucs, Cyril Aubry, Noredine Ghaffour, Johannes S. Vrouwenvelder, Gary Amy

www.elsevier.com/locate/memsci

PII: S0376-7388(15)00076-9
DOI: <http://dx.doi.org/10.1016/j.memsci.2014.12.055>
Reference: MEMSCI13451

To appear in: *Journal of Membrane Science*

Received date: 17 July 2014
Revised date: 20 December 2014
Accepted date: 23 December 2014

Cite this article as: Zhenyu Li, Rodrigo Valladares Linares, Szilárd Bucs, Cyril Aubry, Noredine Ghaffour, Johannes S. Vrouwenvelder, Gary Amy, Calcium Carbonate Scaling in Seawater Desalination by Ammonia-Carbon Dioxide Forward Osmosis: Mechanism and Implications, *Journal of Membrane Science*, <http://dx.doi.org/10.1016/j.memsci.2014.12.055>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Calcium Carbonate Scaling in Seawater Desalination by Ammonia-Carbon Dioxide

Forward Osmosis: Mechanism and Implications

Zhenyu Li ^{a,*}, Rodrigo Valladares Linares ^{a,b}, Szilárd Bucs ^a, Cyril Aubry ^a, Noredine Ghaffour ^a, Johannes S. Vrouwenvelder ^{a,b,c}, Gary Amy ^a

^a Water Desalination and Reuse Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Al-Jazri Bldg 4, 4255 WS07, Saudi Arabia

^b Department for Biotechnology, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 67, 2628 BC Delft, The Netherlands

^c Wetsus, Centre of Excellence for Sustainable Water Technology, Agora 1, P.O. box 1113, 8900 CC Leeuwarden, The Netherlands.

*Corresponding author: Tel. +966 (2) 8082165 e-mail: zhenyu.li@kaust.edu.sa

ABSTRACT

Forward Osmosis (FO) is an osmotically driven membrane process, where the membrane separates a draw solution (DS) with high salinity from a feed solution (FS) with low salinity. There can be a counter direction flow of salt (i.e., salt leakage) that may interact with the water flux through the FO membrane. For the first time reported, this study describes a new calcium carbonate scaling phenomenon in the seawater FO desalination process using ammonium bicarbonate as the DS. The scaling on the membrane surface at the feed side is caused by the interaction between an anion reversely diffused from the DS and a cation present in the FS, causing a significant decline of the water flux. The composition of the scaling layer is dominated by the solubility (represented as solubility product constant, K_{sp}) of salt formed by the paired anion and

cation. Membrane surface morphology plays a crucial role in the reversibility of the scaling. If the scaling occurs on the active layer of the FO membrane, hydraulic cleaning (increasing crossflow velocity) efficiency to restore the water flux is up to 82%. When scaling occurs on the support layer of the FO membrane, the hydraulic cleaning efficiency is strongly reduced, with only 36% of the water flux recovered. The present study reveals the risk of scaling induced by the interaction of feed solute and draw solute, which is different from the scaling caused by the supersaturation in reverse osmosis and other FO studies reported. The scaling investigated in this study can occur with a very low solute concentration at an early stage of the FO process. This finding provides an important implication for selection of draw solution and development of new membranes in the FO process.

Keywords: Forward osmosis; Seawater desalination; Scaling; Calcium carbonate; Reversibility

1. Introduction

Scaling formed by mineral salts, such as calcium salts and silica, is an important aspect in high pressure membrane processes, i.e. reverse osmosis (RO) and nanofiltration (NF) [1-3]. Scaling is an impediment for the application of high pressure membrane process since it causes a significant decline of permeate flux and irreversible damage to the membrane. Generally, scaling in RO and NF process is due to the supersaturation of salts at the interface of the membrane and feed solution, followed by crystallization and growth [3]. Various factors, such as temperature, hydrodynamic conditions, pH, and interaction of solutes, can affect the formation of scaling [4-7].

In recent years, forward osmosis (FO) has been studied and applied as a novel membrane process to achieve a more sustainable solution of the water-energy nexus. FO is an osmotically driven membrane process. The driving force of the FO process is the osmotic pressure created by a salinity difference (gradient) between a feed water (FS) and draw solution (DS) which are separated by a FO membrane [8]. Given that researchers have identified the potential of FO or FO hybrid

systems for desalination [9, 10], scaling in the FO process is gaining more attention recently. So far, the amount of research about scaling in the FO process is still limited and most researchers have been focusing on gypsum scaling [11-14]. The similar feed conditions as the RO process were simulated in the FO process, with a near-supersaturated gypsum concentration in the FS. The mechanism of scaling formation in the FO process was found to be similar to RO process. The scaling in FO process can be induced by both concentration polarization and reversely diffused ions from DS, which lead to supersaturation of salts on the membrane surface. Furthermore, under the unique operational condition (driven by the osmotic pressure) of the FO process, the gypsum scaling on the membrane active layer (AL) was almost fully reversible when the AL faces the FS (AL-FS orientation) [11, 13]. However, when the active layer faced DS (AL-DS orientation) and the porous support layer faced FS, the scaling became partially irreversible, which was due to the formation of crystals of gypsum inside the porous structure of support layer [13]. In addition, membrane material also affects the formation of gypsum scaling and its reversibility. The gypsum scaling caused less water flux decline and the scaling was more reversible on a cellulose acetate (CA) membrane than a polyamide (PA) membrane in the FO process [11]. In addition to gypsum, silica scaling has also been observed in FO processes [15, 16]. The formation of silica scaling is dominated by silica polymerization and facilitated by the presence of hydroxyl groups on the membrane material or organic compounds in the FS. Therefore, silica scaling was more irreversible than gypsum.

On the other hand, ammonia-carbon dioxide (NH_3/CO_2) and ammonium bicarbonate (NH_4HCO_3) have been considered as a promising DS in the FO desalination process [17-19]. The attractiveness of this DS is that the fresh water can be recovered from the diluted DS after FO process by moderate heating (near 60°C). The solute is decomposed into NH_3 and CO_2 , which can easily be removed from water and used to regenerate the DS. In order to obtain a high concentration of ammonium salt, the DS can also be prepared by mixing NH_4HCO_3 and ammonium hydroxide (NH_4OH) in water at proper proportions [18].

In the present study, we reported a new scaling phenomenon in seawater desalination by the FO process using

NH_4HCO_3 as the DS. For the first time reported, this calcium carbonate (CaCO_3) scaling is different from the scaling caused by supersaturation of salts in RO and FO processes mentioned above. The mechanism of the scaling formation was investigated.

2. Materials and methods

2.1 FS, DS and FO Set-up.

All salts used in this study were purchased from Sigma-Aldrich (St. Louis, MO). The properties of natural seawater used in this study were reported in our previous publication [16]. This study was initially conducted as the post-treatment method for our previous FO study in which seawater could be diluted before desalination [20]. Therefore, the 50% diluted natural seawater (DSW, 50% diluted by deionized (DI) water) was employed as FS in this study. Natural seawater was pre-filtered by a capsule filter (pore size 0.45 μm , Polycap™ AS 36, Whatman®) before the dilution. 2% NaCl solution (synthetic diluted seawater, SDSW) were used as FS in baseline testing to compare with natural seawater while DI water was used as the FS to investigate the effect of scaling on the performance of membrane. The DS in this study was 2M NH_4HCO_3 . The experimental FO set-up was described in our previous publication [16]. In this study, the FO cell was installed vertically (Supporting Information, Figure S1). The pH of FS and DS in this study was weakly alkaline ($\text{pH } 8.2 \pm 0.2$). The variation of pH after the FO process was observed to be minor in both FS and DS ($\text{pH } 8.5 \pm 0.2$ after the FO process).

2.2 FO Membrane, and the Measurement of Intrinsic Permeability and Separation Properties.

The FO membrane was provided by Hydration Technology Innovations (HTI, Scottsdale, AZ, USA) and received as a flat coupon. The water permeability (A value) and salt rejection (R value) of the membrane was tested in a RO set-up (SEPA CF II, Sterlitech, Kent, WA, USA). The transmembrane pressure varied from 5 to 9 bar and the crossflow velocity was 10 cm/s. DI water was used as feed for the A value measurement. A cocktail of salts in solution (containing NaCl, KCl,

CaCl₂, FeCl₃, MgCl₂·6H₂O, SrCl₂·6H₂O, BaCl₂, Na₂O₃Si·9H₂O and H₃BO₃ with a concentration of 10 mg/L of each target ion at pH 6.8±0.5), was used as the feed to measure R for target ions listed in Table 1. The procedures to detect A and R value were discussed elsewhere [21].

2.3 Experimental Protocol for FO Testing

The initial volumes of FS and DS were 1 liter each, and testing was terminated when 100 mL permeate was collected to the DS vessel. The bottom-up co-current fluid flow was operated at both the FS and DS side of the cell under the same crossflow velocity. All filtration processes were conducted at an ambient temperature of 21 ± 1°C. The variation of weight of DS solution was measured by a digital balance (Sartorius AG, Germany) and converted to flux. The reverse draw solute (NH₄HCO₃) from DS to FS was detected by measuring total nitrogen (TN) in FS and DS before and after the FO process, and subsequently converted to the amount of NH₄HCO₃. Specific reverse salt flux, J_{specific} is defined as the ratio of reverse NH₄HCO₃ flux (mmol/m²/h) and forward water flux (L/m²/h) to eliminate the effect of the draw solute concentration [22, 23]. DI water was used as the blank sample for TN measurement. In a parallel testing, after the FO process with DSW as the FS (i.e. 100 mL permeate was collected), both the FS and DS sides of the membrane were simultaneously flushed by DI water *in situ* at a crossflow velocity of 16.7 cm/s for 20 minutes. The recovery of DI water flux was measured with 2M NH₄HCO₃ as the DS at a crossflow velocity of 8.3 cm/s to investigate the reversibility of the scaling. In order to determine the composition of the scaling layer and the impact of water flushing on removal of the scalants, the membrane samples (2 × 2 cm) before and after hydraulic cleaning were collected and soaked in 10 mL 2% HNO₃ solution overnight with shaking to dissolve the scalants for further analysis.

2.4 Analytical Methods

The top surface (active layer, AL) and back surface (support layer, SL) of the original membrane were characterized by Fourier Transform Infrared Spectroscopy in the attenuated total reflectance mode (ATR-FTIR, Perkin Elmer Spectrum 100, USA). The cations were analyzed in 2% HNO₃ solution by Inductively Coupled Plasma/Mass Spectrometry (ICP-MS

7500, Agilent, USA). TN was measured by an Organic Carbon Analyzer (TOC-VCPH, Shimadzu, Japan). Adhesive force measurements were performed with an Atomic Force Microscope (Nano-Observer AFM microscope, CSI, France) using a 10 μm calcite probe (Novascan, USA). The roughness of AL and SL was measured by AFM. The membrane surfaces after scaling testing and water flushing were visualized by a Scanning Electron Microscopy-Energy Dispersive X-ray Apparatus (SEM-EDX, Magellan, FEI, USA) and an Optical Microscope (DP72, Olympus, Japan). The particle sizes in the feed DSW were analyzed by a particle size analyzer (Zetasizer, Nano Series, Malvern, UK).

3. RESULTS AND DISCUSSION

3.1 Characterization of FO Membrane

The commercial HTI FO membrane is made of cellulose triacetate (CTA) embedded about a polyester (PES) screen. There is no distinct porous support layer in this membrane [24]. Both AL and SL are relatively dense. The water permeability of CTA FO membrane and its rejection of the ions presenting in seawater are shown in Table 1. The membrane showed the rejection rates to cations following the order: trivalent (Fe^{3+}) > divalent (Ca^{2+} , Mg^{2+} , Sr^{2+} and Ba^{2+}) > monovalent (K^{+} and Na^{+}). The rejection of silica (in the form of monosilicic acid, $\text{Na}_2\text{O}_3\text{Si}\cdot 9\text{H}_2\text{O}$) was up to about 90%. The membrane showed a poor rejection of boron. This is due to diffusion of the non-ionic form of boron which passes through at the near neutral pH used in the study [25]. Figure 1 reveals that there is no distinct difference between AL and SL, except for the surface roughness. The AL is smoother than the SL (Figure 1).

Table 1

Figure 1

3.2 Water and Reverse Solute Flux.

The reverse NH_4HCO_3 flux indicated by J_{specific} was measured by analyzing TN, then converted to the amount of NH_4HCO_3 in different FSs, using different membrane orientations and crossflow velocities (Figure 2). TN can indicate the flux of NH_4^+ . According to Donnan exclusion mechanism and ion-pairing effect, the rejection of NH_4^+ approximately represents the rejection of NH_4HCO_3 [26]. The crossflow velocities varying from 2.1 to 16.7 cm/s under AL-FS did not show a significant effect on initial water flux as well as J_{specific} . Membrane orientation played a more important role on J_{specific} . Under the AL-FS mode, J_{specific} was 152.0 mmol/L while it was 76.4 mmol/L in the AL-DS mode when DI was used as the FS (Figure 2). This is attributed to the higher water flux and external concentration polarization at DS side in the AL-DS mode. Higher water flux induced more severe external dilutive concentration polarization at the interface between membrane and DS at DS side [22, 27]. The external dilutive concentration polarization at DS side reduced not only the effective osmotic pressure but also the amount of draw solute accessing to the membrane. Accordingly, a higher J_{specific} (i.e. reverse diffusion of draw solute) was observed with DSW compared to SDSW as FS under AL-FS mode.

The AL-DS mode gave higher permeate water flux than the AL-FS mode when DI water was the FS (Figure 3). This can be explained by the reduction or elimination of dilutive internal concentration polarization (ICP) in the AL-DS mode [28]. When DI water is the FS, the dilutive ICP gives less impact on the drop of osmotic pressure in AL-DS mode than AL-FS mode since less salt (draw solute) can diffuse into the membrane when DS faces the AL of membrane. Water flux is not significantly affected by the membrane orientation when SDSW was used as the FS. When a saline water is used as the FS, the concentrative concentration polarization at FS side can be promoted by a rough or porous SL in the AL-DS mode, which may counteract the positive effect from the reduction or elimination of dilutive ICP mentioned above [18, 28]. Furthermore, a dramatic decline in the permeate flux was observed when DSW was employed as the FS in the AL-DS mode compared to the AL-FS mode. After 100 mL permeate was collected, the flux decline is about 47.1% under the AL-FS mode and 93.6% under the AL-DS mode. The membrane surface was fully covered by a scale-like layer under both modes.

Figure 2.**Figure 3**

3.3 Characterization of Scaling in Seawater Desalination using NH_3/CO_2 FO Process

A scaling layer was formed on the membrane surface at the FS side after the FO process with DSW as the FS under both AL-FS and AL-DS modes (Figure 4). The scalant showed acicular crystals which accumulated mainly in clusters. EDX spectra indicated that the scalant consisted predominantly of CaCO_3 . Generally, there are three polymorphs of anhydrous CaCO_3 , which include aragonite, calcite and vaterite. The scaling observed in this study showed a typical aragonite cluster which has a radial pattern. This is attributed to the high ratio of Mg/Ca in seawater [29]. Furthermore, the solubility product constant (K_{sp}) of CaCO_3 ($K_{\text{sp}} = 8.7 \times 10^{-9}$ at 25°C) is much lower than MgCO_3 ($K_{\text{sp}} = 1.0 \times 10^{-5}$ at 25°C) [30], thus Ca^{2+} in the FS has a greater tendency to pair with CO_3^{2-} to form the crystal. Meanwhile, the amount of Ca^{2+} in feed seawater is much greater than other elements (e.g., Fe, Sr, Ba) which have low K_{sp} value as well in the form of carbonate salts. Therefore CaCO_3 was the predominant compound of the scaling layer in this study.

Figure 4

In order to analyze the detailed composition of the scalant, the membrane sample with the scaling layer was soaked in HNO_3 solution and the dissolved salts were analyzed by ICP-MS (Table 2). A similar composition of the scaling layer was detected from the membrane samples under AL-FS and AL-DS modes. The large amount of Na and K is due to the residual seawater since the membrane was collected and soaked in the acid immediately after the scaling testing. Ca^{2+} is one of the

most abundant elements in the scaling layer. The presence of Mg and Sr was due to the incorporation of these elements into aragonite when the crystal formed and grew [31, 32].

Table 2

3.4 Reversibility of Scaling and Recovery of Permeate Water Flux by Hydraulic Flushing

After the scaling testing, the membrane was flushed by DI water *in situ* at a crossflow velocity of 16.7 cm/s for 20 minutes. The scaling layer formed in AL-FS mode was much easier to remove by hydraulic cleaning. The membrane surface was almost clean and only a few particles were observed on the membrane surface after hydraulic cleaning (Figure 4), and the recovery of DI water flux was up to 81.8% (Figure 3A). This result is consistent with previous study of gypsum scaling on the same membrane with AL-FS mode, in which the flux recovery was up to 96% after hydraulic flushing with higher crossflow velocity (21 cm/s) [11]. However, SEM image revealed that the scaling layer was still present on the membrane surface collected from the AL-DS mode and showed a more distinct needle/acicular crystal form after the hydraulic cleaning (Figure 4). The recovery of DI water flux was 36% with flushing (Figure 3B). This scaling layer could not be removed by mechanical brushing using a sterile brush. ICP-MS analysis confirmed that scaling in AL-DS mode is more irreversible than AL-FS mode. Most elements in the scaling layer formed in AL-DS mode were still present after the hydraulic cleaning (Table 2). This is different from the previous study of gypsum scaling on CTA FO membrane with AL-DS mode. Arkhangelsky et al. reported that the diffusion and accumulation of salt in the membrane was the main cause limiting the flux recovery after surface flushing while most scalants were removed from the membrane surface [13].

3.5 Mechanism of Scaling Formation in Seawater Desalination using NH_3/CO_2 FO Process

According to membrane surface properties (Figure 1) and the difference of the reversibility of scaling in AL-DS and

AL-FS modes, the membrane surface morphology may play a crucial role in the formation and reversibility of CaCO_3 scaling when the HTI CTA FO membrane is used. To confirm this, the AFM adhesion force measurement was performed using a commercial CaCO_3 probe (Figure 5) with SDSW which was a 2% NaCl solution. Figure 5 shows that the adhesion forces for the AL and SL of membrane were different. When the AL faced the CaCO_3 probe (simulating AL-FS mode in FO process), the rupture distance was much shorter than that with SL facing the CaCO_3 probe (simulating AL-DS mode in FO process). The larger rupture distance indicated the extensive long range attraction and stronger physical contact between CaCO_3 probe and the SL of membrane in the AL-DS mode [11, 33]. Therefore, the scaling on the SL of the FO membrane showed much less reversibility by hydraulic cleaning than that on the AL of the FO membrane. It has been proven in pressure driven membrane processes (e.g., NF, RO) that membrane surface roughness can significantly reduce electrostatic repulsion between foulants and the surface, and the valley regions experienced a greater adhesion force [34-36]. In addition, the CaCO_3 scaling was not observed inside the membrane inner structure even though AL-DS mode was applied. This is attributed to the unique structure of HTI CTA FO membrane. An embedded mesh provides the mechanical support to this membrane while a porous support layer is used in conventional RO and NF membranes. The relatively dense surfaces on both sides of this FO membrane prevent the scalant crystals from entering into the membrane. Similar phenomenon was also observed in the study of gypsum scaling during FO process using the same membrane in AL-DS mode [13].

Figure 5

CaCO_3 was not present in the pre-filtered seawater because of its low solubility. In addition, the concentration of Ca^{2+} in DSW (50% seawater) was much lower than the calcium saturation concentration which was studied in other FO scaling research [11-14]. However, there can be a counter direction flow of salts that may interact with the water flux through the membrane during the FO process since FO membrane separates the DS from FS [37-39]. Solute-solute interactions can

have a dramatic impact on the ion selective permeation in the FO process [39]. The formation of CaCO_3 scaling in this study was caused by the interaction between reverse salt flux (i.e., NH_4HCO_3) from the DS and CaCl_2 from DSW as the FS to form the insoluble CaCO_3 crystal and particle [40, 41], followed by the deposition or growth of these crystals and particles on the membrane surface at the feed side. The mechanism of scaling formation in the present study is different from RO and other FO processes reported, in which the scaling is due to the supersaturation of salts present in the feed water. In a previous study, calcium scaling was absent on the membrane surface during a seawater FO desalination when the NaCl solution was used as DS [16]. The absence of calcium scaling in the previous research can also be a proof for the scaling mechanism dominated by the formation of insoluble calcium salt via interaction between CO_3^{2-} from the DS and Ca^{2+} from the FS in the present study.

The scaling discovered in the present study can occur over a short time of FO process. It may cover the membrane surface in two different ways. The first, CO_3^{2-} carried by the reverse salt flux interacts with Ca^{2+} to form insoluble CaCO_3 crystal in the FS, then deposits onto the membrane surface by the drag force induced by the permeate flux. In this case, the scaling layer can be removed easily. The second, the solute-solute interaction with counter diffusion of CO_3^{2-} and Ca^{2+} occurs on the membrane surface and causes scaling on the membrane, subsequently, newly formed scaling (CaCO_3 crystals) with sharp edge penetrates into membrane matrix. Therefore, the scaling under this condition is more difficult to clean hydraulically. The penetration of scaling crystals into membrane matrix can damage the membrane, consequently reducing the membrane performance for the rejection of solutes [42]. In order to further demonstrate the mechanism of CaCO_3 scaling formation, the particle size was monitored along the FO process in AL-FS and AL-DS mode, respectively. Additional scaling tests (with DSW as the FS) were conducted and terminated when 15 mL permeate was collected, to observe the scaling development on the membrane surface in the initial stage of the FO process. It was found that the membrane surface was clean and no crystals were observed in the AL-FS mode while crystals started to grow on the membrane surface and form clusters in the AL-DS mode (Figure 6). The development of scaling may result in the different

flux patterns between AL-FS and AL-DS mode when DSW was FS (as shown in Figure 3). The flux with DSW as the FS approximated to SDSW during initial stage of FO in the AL-FS mode, which can be attributed to the slow formation and deposition of CaCO_3 scaling on the membrane active layer (Figure 6). In addition, the scaling is more reversible in the AL-FS mode (Figure 4). Conversely, a dramatic decline of flux with DSW as the FS can be observed from the beginning of FO process in the AL-DS mode (Figure 3). The particle size in the FS under AL-FS mode was larger than AL-DS mode from the beginning of the FO process. This could indicate that the formation of insoluble CaCO_3 crystals occurred in the FS under AL-FS mode while the crystals were initially formed on the membrane surface under AL-DS mode. It should be noted that the particle size in the FS was rapidly increased when 30 mL permeate was collected in both AL-FS and AL-DS modes. At this stage, membrane surfaces in both membrane orientations were fully covered by CaCO_3 crystals. The formed/deposited CaCO_3 crystal could be detached from the top of the scaling layer by the shear stress induced by the crossflow and suspended to the FS. Consequently, the particle size was quickly increased and was not much different afterward in both AL-FS and AL-DS modes.

Figure 6

4. Conclusions

This study presents a novel FO scaling mechanism induced by the interaction of feed solute and draw solute. This scaling can occur at the beginning of the FO process with a low concentration of paired cation and anion from the FS and DS, respectively, and cause a dramatic and irreversible flux decline. Membrane surface morphology and roughness is crucial in the reversibility of CaCO_3 scaling reported. The study adds one more important criterion for the selection of DS in the FO process. In addition to the characteristics of a favorable DS, such as high osmotic pressure, non-toxic, low cost and easy separation/recycle, the risk of induced scaling should also be considered. Future work will focus on the impact of

membrane material and membrane surface modification. Furthermore, a deeper understanding of selective ion transport in the FO process and possible impact on scaling formation could contribute to the development of FO-based water treatment processes.

Acknowledgements

The authors appreciate the assistance offered by the Water Desalination and Reuse Center technical staff at KAUST to conduct this research work.

References

- [1] Al-Amoudi, A.S. Factors affecting natural organic matter (NOM) and scaling fouling in NF membranes: a review. *Desalination* **2010**, 259, 1-10.
- [2] Rahardianto, A.; McCool, B.C.; Cohen, Y. Reverse osmosis desalting of inland brackish water of high Gypsum scaling propensity: kinetics and mitigation of membrane mineral scaling. *Environ. Sci. Technol.* **2008**, 42, 4292-4297.
- [3] Antony, A.; Low, H.J.; Gray, S.; Childress, A.E.; Le-Clech, P.; Leslie, G. Scale formation and control in high pressure membrane water treatment systems: a review. *J. Membr. Sci.* **2011**, 383, 1-16.
- [4] Jawor, A.; Hoek, E.M.V. Effects of feed water temperature on inorganic fouling of brackish water RO membranes. *Desalination* **2009**, 235, 44-57.
- [5] Lee, S., Lee, C.H. Scale formation in NF/RO: mechanism and control. *Water Sci. Technol.* **2005**, 51, 267-275.
- [6] Rahardianto, A., Mccool, B.C., Chohen, Y. Reverse osmosis desalting of inland brackish water of high gypsum scaling propensity: kinetics and mitigation of membrane mineral scaling. *Environ. Sci. Technol.* **2008**, 42, 4292-4297.
- [7] Sheikholeslami, R. Mixed salts-scaling limits and propensity. *Desalination* **2003**, 154, 117-127.

- [8] Chung, T.S., Zhang, S., Wang, K.Y., Su, J.C., Ling, M.M. Forward osmosis processes: yesterday, today and tomorrow. *Desalination* **2012**, 287, 78-81.
- [9] Cath, T.Y., Childress, A.E., Elimelech, M. Forward osmosis: principles, applications, and recent developments. *J. Membr. Sci.* **2006**, 281, 70-87.
- [10] Coday, B.D., Cath, T.Y. Forward osmosis: novel desalination of produced water and fracturing flowback. *J. AWWA*. **2014**, February, E55-E66.
- [11] Mi, B.X., Elimelech, M. Gypsum scaling and cleaning in forward osmosis: measurements and mechanisms. *Environ. Sci. Technol.* **2010**, 44, 2022-2028.
- [12] Chen, S.C., Su, J.C., Fu, F.J., Mi, B.X., Chung, T.S. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) scaling on polybenzimidazole and cellulose acetate hollow fiber membranes under forward osmosis. *Membranes* **2013**, 3, 354-374.
- [13] Arkhangelsky, E., Wicaksana, F., Chou, S., Al-Rabiah, A.A., Al-Zahrani, S.M., Wang, R. Effects of scaling and cleaning on the performance of forward osmosis hollow fiber membranes. *J. Membr. Sci.* **2012**, 415-416, 101-108.
- [14] Zhang, M.M., Hou, D.X., She, Q.H., Tang, C.Y. Gypsum scaling in pressure retarded osmosis: experiments, mechanisms and implications. *Water Res.* **2014**, 48, 387-395.
- [15] Mi, B.X., Elimelech, M. Silica scaling and scaling reversibility in forward osmosis. *Desalination* **2013**, 312, 75-81.
- [16] Li, Z.Y., Yangali-Quintanilla, V., Valladares-Linares, R., Li, Q.Y., Zhan, T., Amy, G. Flux patterns and membrane fouling propensity during desalination of seawater by forward osmosis. *Water Res.* **2012**, 46, 195-204.
- [17] McCutcheon, J.R., McGinnis, R.L., Elimelech, M. A novel ammonia-carbon dioxide forward (direct) osmosis desalination process. *Desalination* **2005**, 174, 1-11.
- [18] McCutcheon, J.R., McGinnis, R.L., Elimelech, M. Desalination by ammonia-carbon dioxide forward osmosis: influence of draw and feed solution concentrations on process performance. *J. Membr. Sci.* **2006**, 278, 114-123.

- [19] McGinnis, R.L., Hancock, N.T., Nowosielski-Slepowron, M.S., McGurgan, G.D. Pilot demonstration of the NH_3/CO_2 forward osmosis desalination process on high salinity brines. *Desalination* **2013**, 312, 67-74.
- [20] Valladares-Linares, R., Li, Z.Y., Abu-Ghdaib, M., Wei, C.H., Amy, G., Vrouwenvelder, J.S. Water harvesting from municipal wastewater via osmotic gradient: an evaluation of process performance. *J. Membr. Sci.* **2013**, 447, 50-56.
- [21] Wei, J., Qiu, C.Q., Tang, C.Y., Wang, R., Fane, A.G. Synthesis and characterization of flat-sheet thin film composite forward osmosis. *J. Membr. Sci.* **2011**, 372, 292-302.
- [22] Hancock, N.T., Cath, T. Solute coupled diffusion in osmotically driven membrane processes. *Environ. Sci. Technol.* **2009**, 43, 6769-6775.
- [23] Philip, W.A., Yong, J.S., Elimelech, M. Reverse draw solute permeation in forward osmosis: modeling and experiments. *Environ. Sci. Technol.* **2010**, 44, 5170–5176.
- [24] Wang, Y., Wei, J., She, Q., Pacheco, F., Tang, C.Y. Microscopic characterization of FO/PRO membrane - A comparative study of CLSM, TEM and SEM. *Environ. Sci. Technol.* **2012**, 46, 9995–10003.
- [25] Koseoglu, H., Kabay, N., Yüksel, M., Sarp, S., Arar, Ö., Kitis, M. Boron removal from seawater using high rejection SWRO membranes-impact of pH, feed concentration, pressure, and cross-flow velocity. *Desalination* **2008**, 227, 253-263.
- [26] Rice, G., Barber, A.R., O'Connor, A.J., Stevens, W.G., Kentish, S.E. Rejection of dairy salts by a nanofiltration membrane. *Sep. Purif. Technol.* **2011**, 79, 92-102.
- [27] Zhao, S., Zou, L., Mulcahy, D. Effects of membrane orientation on process performance in forward osmosis applications. *J. Membr. Sci.* **2011**, 382, 308-315.
- [28] Zhao, S.F., Zou, L.D. Relating solution physicochemical properties to internal concentration polarization in forward osmosis. *J. Membr. Sci.* **2011**, 379, 459-467.

- [29] Falini, G., Gazzano, M., Ripamonti, A. 1994. Crystallization of calcium carbonate in presence of magnesium and polyelectrolytes. *J. Crystal Growth* **1994**, 137, 577-584.
- [30] Atkins, P., Jones, L. *Chemical Principles.*; W.H. Freeman and Company: New York, U.S., 2010.
- [31] Brinza, L., Quinna, P.D., Schofield, P.F., Mosselmansa, J.F.W., Hodson, M.E. Incorporation of strontium in earthworm-secreted calcium carbonate granules produced in strontium-amended and strontium-bearing soil. *Geochim. Cosmochim. Acta* **2013**, 113, 21-37.
- [32] Fernandez-Diaz, L., Putnis, A., Prieto, M., Putnis, C.V. The role of magnesium in the crystallization of calcite and aragonite in a porous medium. *J. Sediment. Res.* 1996, 66, 482-491.
- [33] Mi, B.X., Elimelech, M. Organic fouling of forward osmosis membrane: fouling reversibility and cleaning without chemical reagents. *J. Membr. Sci.* **2010**, 348, 337-345.
- [34] Elimelech, M., Zhu, X., Childress, A.E., Hong, S. Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes. *J. Membr. Sci.* **1997**, 127, 101-109.
- [35] Bowen RW, Doneva TA. Atomic force microscopy studies of membranes: effect of surface roughness on double-layer interactions and particle adhesion. *J. Colloid Interf. Sci.* **2000**, 229, 544-549.
- [36] Vrijenhoek, E.M., Hong, S., Elimelech, M. Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes. *J. Membr. Sci.* **2001**, 188, 115-128.
- [37] Phillip, W.A., Young, J.S., Elimelech, M. Reverse draw solute permeate in forward osmosis: modeling and experiments. *Environ. Sci. Technol.* **2010**, 44, 5170-5176.
- [38] She, Q.H. Jin, X., Li, Q.H., Tang, C.Y. Relating reverse and forward solute diffusion to membrane fouling in osmotically driven membrane processes. *Water Res.* **2012**, 46, 2478-2486.
- [39] Irvine, G.J., Rajesh, S., Georgiadis, M., Phillip, W.A. Ion selective permeation through cellulose acetate membrane in forward osmosis. *Environ. Sci. Technol.* **2013**, 47, 13745-13753.

- [40] Chen J., Xiang, L. Controllable synthesis of calcium carbonate polymorphs at different temperatures. *Powder Technol.* **2009**, 189, 64-69.
- [41] Hernandez-Hernandez, A., Vidal, M.L., Gomez-Morales, J., Rodriguez-Navarro, A.B., Labas, V., Gautron, J., Nys, Y., Garcia Ruiz, J.M. Influence of eggshell matrix proteins on the precipitation of calcium carbonate (CaCO₃). *J. Cryst. Growth.* **2008**, 310, 1754-1759.
- [42] Li, Z.Y., Valladares, R., Muhannad, A.G., Amy, G. The process performance and fate of boron in a multi-stage forward osmosis process for integrated water management. *European Desalination Society (EDS) Conference and Exhibition on Desalination for the Environment: Clean Water and Energy*, Limassol, Cyprus. May 11-15, **2014**.

Table 1. Intrinsic water permeability and salt rejection of HTI CTA FO membrane.

Transmembrane Pressure (bar)	Water permeability ($\times 10^{-12}$ m/s.Pa)	Rejection (%)								
		K	Na	B	Ca	Mg	Fe	Sr	Si	Ba
5	1.95	81.88	89.43	19.14	92.90	92.58	99.18	92.61	89.90	92.75
6		83.38	85.33	19.53	91.54	92.63	98.82	92.66	84.71	92.48
7		86.89	87.08	14.01	91.67	92.75	97.81	92.57	86.88	92.10
8		87.23	88.22	21.51	92.81	93.12	98.25	92.76	90.04	92.50
9		88.25	89.66	24.61	93.21	93.70	98.21	93.58	86.83	93.36

Note: All measurements were conducted under RO mode with a constant feed flow linear velocity of 0.1 m/s. Membrane active layer faced the feed water.

Table 2. The composition of scaling on the membrane surface at the FS side before and after hydraulic cleaning under different membrane orientations.

Membrane orientation	Sample No.	Composition of the Scalant ($\times 10^{-3}$ mg/cm ²)								
		K	Na	B	Ca	Mg	Fe	Sr	Si	Ba
AL-FS	(1)	109	1147	0.14	891	366	6.5	200	17	0.30
	(2)	7.6	0.44	0	0.09	0	0	0	9.0	0
AL-DS	(1)	145	1459	0.97	1434	386	9.4	328	336	0.94
	(2)	90	300	0.54	963	237	6.3	223	45	0.49

Note: (1) Membrane sample after the scaling testing; (2) Membrane sample which was cleaned by DI water flushing after scaling testing.

Figure 1. The properties of virgin HTI CTA FO membrane. (A, The FTIR-ATR spectra of CTA FO membrane surface; B, The roughness of CTA FO membrane surface; C, SEM image of the membrane activate layer; D, SEM image of the membrane support layer)

Figure 2. Effects of feed water, membrane orientation and crossflow velocity on the specific reverse salt (NH_4HCO_3) flux.

Figure 3. Flux patterns during FO process under (A) AL-FS mode and (B) AL-DS mode. 2M NH_4HCO_3 was used as the DS for all flux measurements at the flow velocity of 8.3 cm/s. (■, DI water as the FS; ▲, SDSW as the FS; ●, DSW as the FS; ▼, DI water flux measured from the membrane which was cleaned by water flushing after the scaling testing)

Figure 4. SEM image and EDX spectra of scaling on the FO membrane surface at the FS side. (A and D, SEM image of the membrane after scaling testing; B and E, EDX spectra; C and F, SEM image of the membrane after hydraulic cleaning)

Figure 5. AFM force measurement using a CaCO_3 probe in 2% NaCl solution.

Figure 6. The particle size in the feed seawater in FO process and the membrane surface in the early stage (15 mL permeate collected) of FO process.

- CaCO_3 scaling was reported for the first time during seawater FO desalination.
- Scaling was induced by interaction between ions from feed and draw solution.
- Scaling can occur with a low calcium concentration at an early stage of FO process.
- Membrane surface morphology played a crucial role in the reversibility of scaling.

Accepted manuscript

Graphical Abstract: