


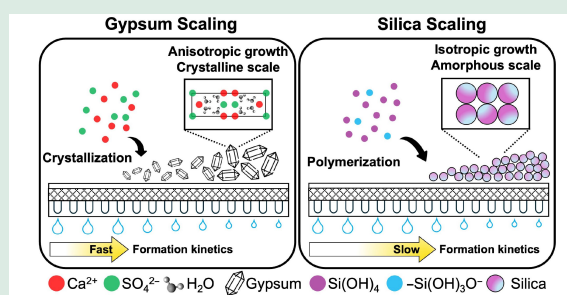
# A tale of two minerals: contrasting behaviors and mitigation strategies of gypsum scaling and silica scaling in membrane desalination

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## HIGHLIGHTS

- Gypsum scaling and silica scaling have distinct formation mechanisms.
- Gypsum and silica formation lead to distinct kinetics and mineral morphologies.
- Behaviors of gypsum scaling and silica scaling in desalination are different.
- Gypsum and silica interact with organic foulants differently.
- Gypsum scaling and silica scaling require different mitigation strategies.



**ABSTRACT:** Mineral scaling represents a major constraint that limits the efficiency of membrane desalination, which is becoming increasingly important for achieving sustainable water supplies in the context of a changing climate. Different mineral scales can be formed via distinct mechanisms that lead to a significant variation of scaling behaviors and mitigation strategies. In this article, we present a comprehensive review that thoroughly compares gypsum scaling and silica scaling, which are two common scaling types formed via crystallization and polymerization respectively, in membrane desalination. We show that the differences between scale formation mechanisms greatly affect the thermodynamics, kinetics, and mineral morphology of gypsum scaling and silica scaling. Then we review the literatures on the distinct behaviors of gypsum scaling and silica scaling during various membrane desalination processes, examining their varied damaging effects on desalination efficiency. We further scrutinize the different interactions of gypsum and silica with organic foulants, which result in contrasting consequences of combined scaling and fouling. In addition, the distinctive mitigation strategies tailored to controlling gypsum scaling and silica scaling, including scaling-resistant membrane materials, antiscalants, and pretreatment, are discussed. We conclude this article with the research needs of attain-

ing a better understanding of different mineral scaling types, aiming to inspire researchers to take scale formation mechanism into consideration when developing more effective approaches of scaling control in membrane desalination.

**KEYWORDS:** Membrane desalination, Membrane scaling, Gypsum scaling, Silica scaling, Scaling mechanism, Scaling mitigation

## 1 Introduction

Water scarcity is a global challenge that is getting intensified due to climate change. For example, four billion people are facing water shortage globally (Mekonnen and Hoekstra, 2016), and the water stress in arid and semi-arid regions poses a pressing threat to food production, energy generation, as well as ecological and human health (Brown et al., 2019). To address this grand challenge, a circular water economy, which leverages unconventional water sources like seawater, brackish groundwater, and wastewater, is becoming increasingly important to maintain water sustainability of our society (Mauter and Fiske, 2020).

Membrane desalination plays a vital role in our efforts of pursuing a circular water economy. A variety of membrane technologies, including reverse osmosis (RO), nanofiltration (NF), forward osmosis (FO), membrane distillation (MD), and electrodialysis (ED), are being used for water purification, resource recovery, and hypersaline brine treatment (Tong and Elimelech, 2016; Li et al., 2019; Razmjou et al., 2019; Mauter and Fiske, 2020; Zhao et al., 2021). However, all membrane-based processes are constrained by membrane fouling and scaling, which decreases the efficiency while increasing the cost of desalination systems (Tong et al., 2019a; Rolf et al., 2022). Compared to extensive studies of organic fouling and biological fouling (Potts et al., 1981; Pandey et al., 2012; Tijing et al., 2015; Jiang et al., 2017; Goh et al., 2018; Ly et al., 2019; Horseman et al., 2021), inorganic fouling (i.e., mineral scaling) is more complex and has received less attention. Different from organic foulants (mainly organic macromolecules) and biological foulants (mainly bacteria), mineral scales are usually not originally present in the feedwater. Rather, they start to form via various chemical reactions once the concentrations of their precursors exceed the mineral solubility at a certain threshold of water recovery (Tong et al., 2019a; Rolf et al., 2022). As a result, the mechanisms of mineral scaling are drastically different from those of organic and biological fouling, with the nature of mineral-forming reactions critical to determining the behaviors and consequences of mineral

scaling in desalination.

Mineral scales can be formed via two distinct mechanisms: crystallization and polymerization. On one hand, calcium- and barium-based minerals, such as calcite, gypsum, and barite, are formed via a crystallization process, which generates crystals with well-defined shapes (Prieto et al., 1990; Gebauer et al., 2008; Van Driessche et al., 2012; Stawski et al., 2016; Tong et al., 2019a). On the other hand, silica is formed via polymerization of silicic acid, resulting in amorphous silica scales (Milne et al., 2014). As demonstrated by our previous publications (Christie et al., 2020; Yin et al., 2020; Yin et al., 2021), such a difference in formation mechanism leads to different nucleation kinetics and mineral properties, as well as distinct consequences and mitigation strategies regarding mineral scaling in desalination. However, to the best of our knowledge, there is still a lack of review articles that systematically compare mineral scaling resulting from different formation mechanisms, despite their importance in guiding future research to advance our knowledge of mineral scaling and to develop more effective scaling mitigation strategies.

In this article, we present a comprehensive review that thoroughly compares gypsum scaling and silica scaling in membrane desalination. Gypsum scaling and silica scaling, which are among the most extensively studied scaling type in the literature (Tong et al., 2019a; Horseman et al., 2021; Rolf et al., 2022), are selected due to the common presence of their precursors in desalination feedwater as well as a sufficient number of relevant research articles for making a comprehensive comparison. The selection of these two scaling types is also due to the challenges of their mitigation in membrane desalination (Milne et al., 2014; Tong et al., 2019a). It is worth mentioning that other crystallization-induced scaling types, such as calcite, barite, and calcium phosphate scaling, are generally not included in this work, because a one-on-one comparison is clearer and more straightforward to make a contrast. We start from a description of the differences between mineral crystallization and polymerization, especially their effects on nucleation thermodynamics, kinetics, and mineral morphology. Then we review the literatures on

the distinct behaviors of gypsum scaling and silica scaling in a variety of membrane desalination processes, examining their varied damaging effects on desalination efficiency. Further, we discuss the different interactions of gypsum and silica with organic foulants, highlighting the contrasting behaviors between these two scaling types when coexisting with organic fouling. We also summarize mitigation strategies that are tailored to control gypsum and silica scaling, respectively, including scaling-resistant membrane materials, antiscalants, and pretreatment. We conclude this article with the research needs of attaining a better understanding of different mineral scaling types, aiming to inspire researchers to take scale formation mechanism into consideration when developing more effective approaches of scaling control.

## 2 Gypsum and silica are formed via distinct mechanisms

### 2.1 Formation mechanism of gypsum scaling

Gypsum (calcium sulfate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is a common mineral that forms in sedimentary settings such as evaporated seawater and groundwater (Reiss et al., 2021). A survey of water samples at the Brackish Groundwater National Desalination Research Facility that operates under the United States Department of Interior showed  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations of  $> 500$  mg/L and  $> 2,000$  mg/L (TetraTech, 2011), respectively, indicating high gypsum scaling potential when desalinating such groundwater. Also, another survey led by the US Geological Survey revealed that gypsum has the highest precipitation potential when desalinating groundwater from the Central Valley aquifer system, California (McMahon et al., 2016). Industrial wastewater can also have high potentials of gypsum scaling. For example, wastewater generated from power plants have high concentrations of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ , rendering gypsum scaling problematic to the treatment and reuse of such wastewater (Karanikola et al., 2018; Lee et al., 2018).

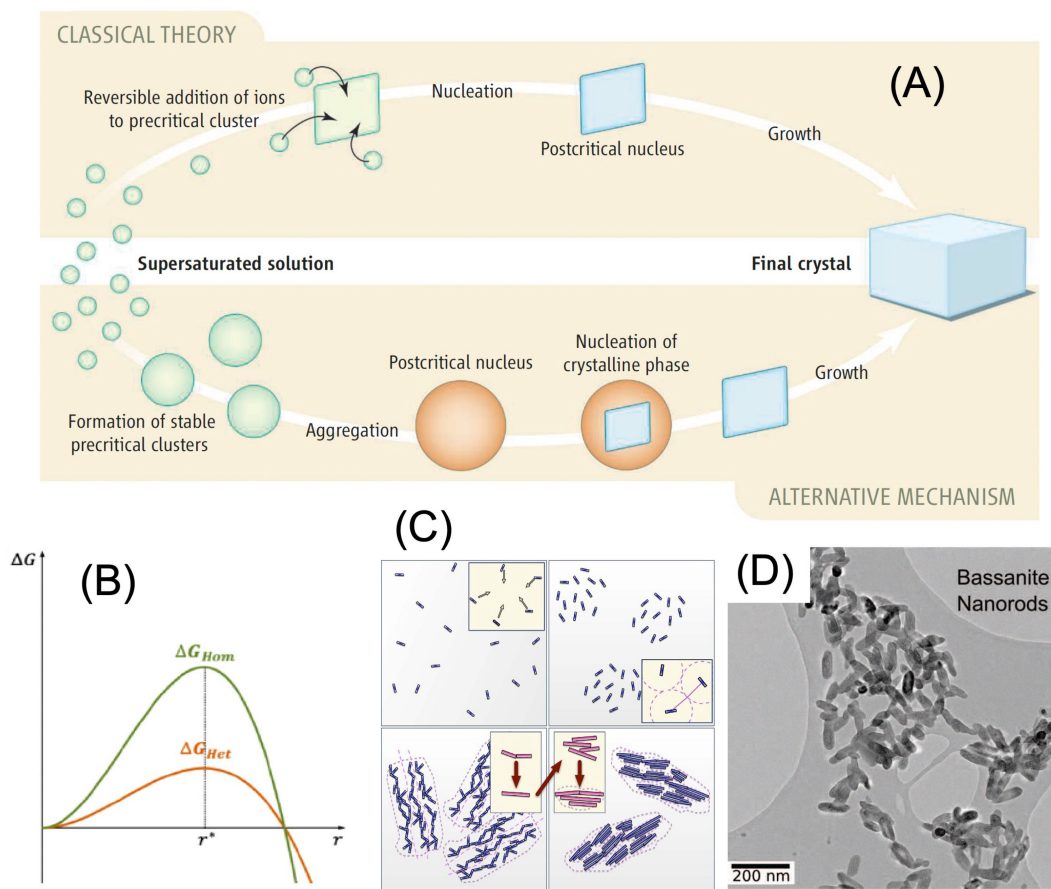
Gypsum is a challenging mineral scale for membrane desalination, partially due to its low sensitivity to pH (e.g., another calcium-based mineral scale, calcite, can be easily prevented by adjusting feedwater pH (MacAdam and Parsons, 2004)) (Shukla et al., 2008). The formation of crystal minerals including gypsum has been depicted by a “textbook” description that stems from the adaptation of classical nucleation theory (CNT, Fig. 1(A)). According to CNT, which describes

the free energy ( $\Delta G$ ) of mineral formation, an energy barrier needs to be overcome to form a stable nucleus that exceeds a certain critical size (Fig. 1(B)) (Tong et al., 2019a). However, researchers have recently realized the complexity of mineral nucleation processes, which contrasts CNT because of the discovery of stable, nano-scale intermediate species. There has been an increasing number of evidence that supports non-classical nucleation pathways, in which stable prenucleation clusters exist, especially for calcium-based minerals including calcite and gypsum (Meldrum and Sear, 2008; Van Driessche et al., 2012; Karthika et al., 2016; Stawski et al., 2016; Stawski et al., 2019). For example, (Stawski et al., 2016) report that gypsum formation is a result of formation, aggregation, rearrangement, and partial coalescence of elongated sub-3 nm  $\text{CaSO}_4$  clusters (Fig. 1(C)). By employing *in situ* high-energy X-ray diffraction techniques and molecular dynamics simulations, the authors revealed the structure of those clusters, which are found to be internally anhydrous but hydrated at their surface, contrasts the dihydrate structure of calcium sulfate crystals (Stawski et al., 2019). Also, (Van Driessche et al., 2012) discovered that nanocrystalline hemihydrate bassanite forms before the formation of gypsum crystals (Fig. 1(D)), and that the self-assembly of bassanite nanorods plays a crucial role in the transformation to dihydrate gypsum. The nucleation pathway of gypsum formation has significant implications to the design of scaling-resistant surfaces, which will be explained in detail in Section 5.2 below.

### 2.2 Formation mechanism of silica scaling

Silica is another common scale type in membrane desalination, which limits the water recovery of desalination systems (Milne et al., 2014). For example, the concentration of silica in brackish water ranges from 12 to 60 mg/L (Shemer et al., 2019), with a solubility of 100–150 mg/L at near neutral pH (Tong et al., 2017). However, due to the lack of effective methods of silica removal, silica is often the major constraint to the water recovery of brackish water desalination (Badruzzaman et al., 2011; Tong et al., 2017). Silica scaling has been also found to adversely affect the performance of membrane processes for the treatment of oil and gas produced water (Du et al., 2018) and refining wastewater (Chen et al., 2020). In addition, silica represents an important biogenic mineral, which is a key component of the cell wall of diatom (Kröger et al., 1999; Kröger and Sandhage, 2010).

Distinct from gypsum scaling, silica is not formed via a crystallization process. Instead, it is created by

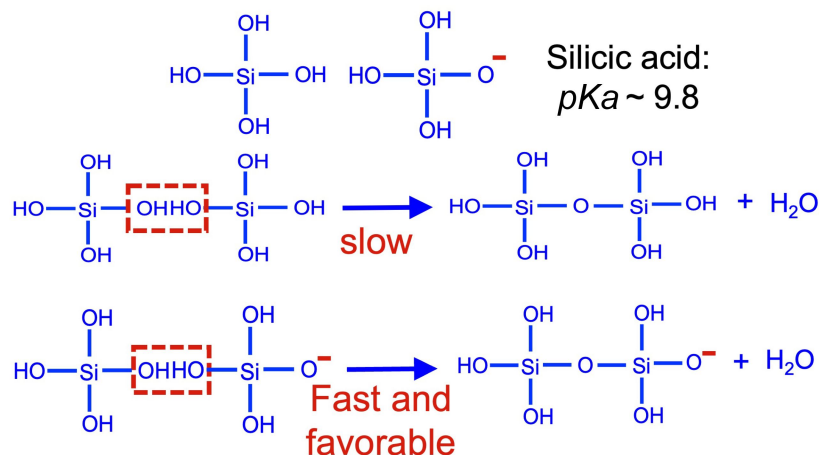


**Fig. 1** (A) Schematic of classical nucleation theory and non-classical nucleation pathway of mineral formation. (B) The change of free energy during mineral nucleation.  $\Delta G_{Hom}$  and  $\Delta G_{Het}$  refer to the free energy barrier to homogeneous nucleation and heterogeneous nucleation, respectively. (C) Schematic of four stages of gypsum crystal formation, including the formation, aggregation, self-assembly, and coalescence of CaSO<sub>4</sub> clusters. (D) Transmission electron microscopic image of bassanite nanorods formed before gypsum crystal formation. The figures are adapted with permission from Meldrum and Sear (2008), copyright American Association for the Advancement of Science; Tong et al. (2019a), copyright Elsevier; Stawski et al. (2016), copyright Nature Portfolio; Van Driessche et al. (2012), copyright American Association for the Advancement of Science.

polymerization reactions of silicic acid (Fig. 2). The ionization state of silicic acid plays a key role in regulating the kinetics of silicic acid polymerization. With a  $pK_a$  of  $\sim 9.8$  (Belton et al., 2012), a small fraction of silicic acid is ionized and carrying a negative charge in aqueous solutions. Despite its low abundance, ionized silicic acid is much more reactive in the polymerization reactions than its neutral counterparts (Belton et al., 2012). It is well accepted that polymerization of silicic acid proceeds mainly by the reaction of an ionized silicic acid molecule and a unionized, neutral silicic acid molecule (Fig. 2) (Shimada and Tarutani, 1980). As summarized by (Greenberg and Sinclair, 1955), the rate of silicic acid polymerization is the most rapid in the pH range of 8–9, where the concentrations of both ionized silicic acid and neutral silicic acid are reasonably high. A very

low pH results in a slow reaction of silicic acid polymerization due to the lack of ionized silicic acid, while a very high pH (e.g.,  $> 11$ ) also hinders silicic acid polymerization due to the dominance of ionized silicic acid molecules that tend to repel each other. It is noteworthy that as silicic acid polymerization proceeds, the  $pK_a$  value of silica species decreases (e.g., the  $pK_a$  of silanol groups of small silica nanoparticle is reported to be 6.8 (Belton et al., 2012)), creating more negative silica species that actively participate in silica formation. The importance of ionized silica species in governing the kinetics of silica scaling in membrane desalination will be further visited in Section 5.1, where the relationship between membrane surface charge and propensity to silica scaling will be discussed in detail.

It is worth mentioning that iron- and aluminum-rich silica scales have been found to form, especially from



**Fig. 2** Schematic of silicic acid polymerization that leads to silica formation.

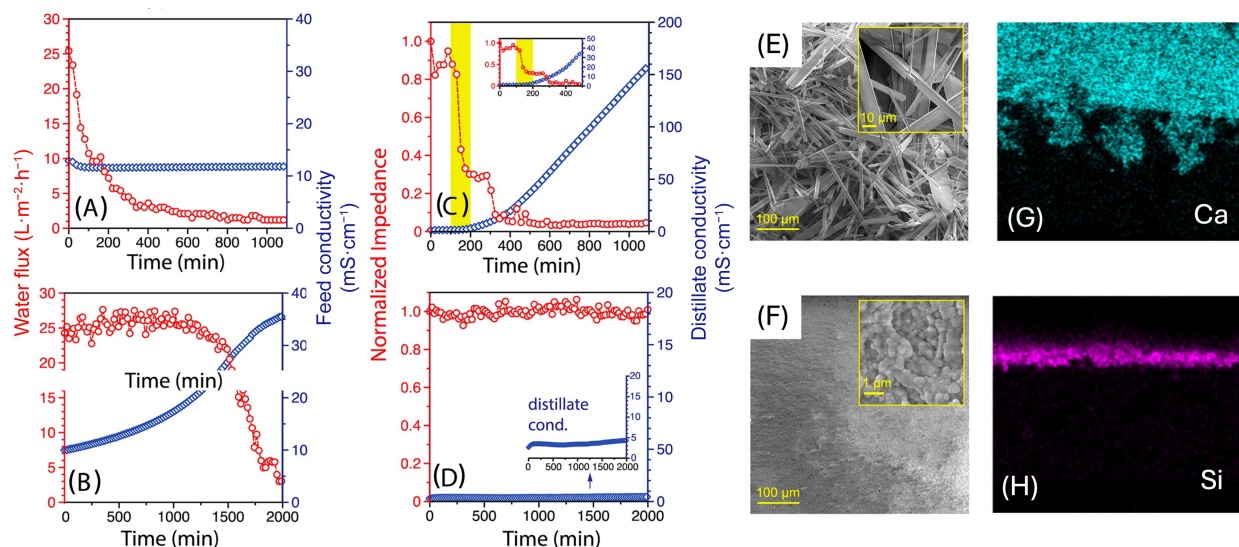
geothermal brines (Gallup, 1989; 1997; 1998). These siliceous minerals, which are often referred to as iron/aluminum silicate, are typically amorphous and mainly composed of  $\text{SiO}_2$  (Gallup, 1989; 1997; 1998). These metal silicates have been shown to have lower solubility than pure silica (Gallup, 1998), which are potentially formed in membrane desalination (e.g., when alum coagulation is applied prior to reverse osmosis) (Gabelich et al., 2005). To the best of our knowledge, most of existing studies on silicon-based scaling have focused on mineral scaling caused by pure silica, whereas the behaviors of metal silicate scaling in membrane desalination have been rarely reported in the literature (Tong et al., 2019b; Rolf et al., 2022) due to the complex nature of metal silicates (Milne et al., 2014). This knowledge gap makes it challenging to include metal silicate scaling in this article, despite the research needs of understanding the effects of metal silicates on membrane desalination.

### 3 The behaviors of gypsum scaling and silica scaling are different in membrane desalination

A number of publications have investigated the behaviors of gypsum scaling and silica scaling that occurred in membrane desalination. Although there are only a few works that directly compare gypsum scaling and silica scaling in a single study, the following differences between these two different types of mineral scaling can still be obtained by closely examining the literature.

First, the kinetics of gypsum scaling is faster than that of silica scaling. (Christie et al., 2020) compared the behaviors of gypsum scaling and silica scaling in MD desalination. They found that in the presence of saturated gypsum, the water vapor flux of MD decreased quickly from  $\sim 25 \text{ L}/(\text{m}^2 \cdot \text{h})$  to nearly zero within 600 min, whereas saturated silica at the same saturation index (SI) did not cause visible flux decline for more than 1000 min (Figs. 3(A) and 3(B)). Such a difference of scaling kinetics in MD was also observed by (Yin et al., 2020). In RO and FO, Mi and Elimelech (2010) reported that supersaturated gypsum at a SI (defined as the natural logarithm of the ratio between ion activity product and solubility equilibrium constant in this article) of 0.26 led to a flux decline of  $\sim 50\%$  within 1500 min, while a similar rate of flux decline was caused by supersaturated silica at a SI of 0.79 (Mi and Elimelech, 2013). Indeed, the slower kinetics of silica scaling compared to the rate of crystalline mineral formation has been shown in studies of mineralogy. For example, nano-scale, nascent silica nuclei were able to be observed after an hour using *in situ* tapping-mode atomic force microscopy (AFM) (Wallace et al., 2009), whereas it is very challenging (if not infeasible) to visualize nascent nuclei of gypsum due to its high growth rate (e.g.,  $\sim 0.05 \mu\text{m}/\text{min}$  for the most reactive [001] facet at a SI of gypsum at  $\sim 0.64$  (Mbogoro et al., 2017)).

Second, the growth of gypsum crystals is orientational and intrusive, whereas silica formation leads to amorphous scale but irreversible scaling. Gypsum crystal growth occurs preferentially along certain orientations, leading to gypsum crystals of high aspect ratios (Fig. 3(E)). In RO, a rosette morphology of gypsum was commonly observed on the surface of polyamide membranes, which is believed to be an



**Fig. 3** (A and B) Water vapor flux (red) and feed conductivity (blue) curves during MD desalination in the presence of (A) gypsum scaling and (B) silica scaling. (C and D) Normalized transmembrane impedance (red) and distillate conductivity (blue) during MD desalination in the presence of (C) gypsum scaling and (D) silica scaling. A decrease of normalized impedance and an increase of distillate conductivity indicate the occurrence of pore wetting. (E and F) Top-down SEM images of (E) gypsum and (F) silica scales formed in MD. (G and H) Cross-section energy dispersive X-ray spectroscopy mapping of membranes scaled by (G) gypsum and (H) silica. The figures are adapted with permission from [Christie et al. \(2020\)](#), copyright American Chemical Society.

indicator of surface-induced heterogeneous nucleation ([Shih et al., 2005](#); [Rahardianto et al., 2008](#); [Uchymiak et al., 2008](#)). In FO and MD, however, needle- or plate-shaped gypsum crystals were usually found ([Mi and Elimelech, 2010](#); [Xie and Gray, 2016](#); [Christie et al., 2020](#); [Yin et al., 2021](#)), which probably originated from bulk nucleation followed by surface deposition due to the high concentrations of scale precursors in the feedwater. In contrast, spherical silica particles are typically formed due to their isotropic growth ([Fig. 3\(F\)](#)) ([Mi and Elimelech, 2013](#); [Tong et al., 2017](#); [Xie and Gray, 2017](#); [Bush et al., 2018](#); [Lu and Huang, 2019](#); [Yin et al., 2019](#); [Christie et al., 2020](#); [Yin et al., 2021](#)), although silica particles formed in RO are smaller than those observed in MD. The fusion of silica particles into a gel layer has been discovered ([Yin et al., 2019](#)), which is responsible for the decrease of water flux.

The preferential growth orientation and high aspect ratio of gypsum crystals result in its intrusive nature, which causes pore wetting in MD. Pore wetting, which refers to a phenomenon where the saline feedwater permeates through the hydrophobic membrane, represents a major problem that constrains the performance of MD desalination ([Horseman et al., 2021](#)). As demonstrated by [Christie et al. \(2020\)](#), gypsum crystals were able to penetrate into the membrane substrate during MD desalination ([Fig. 3\(G\)](#)), leading to a rapid and dramatic

increase of distillate conductivity (i.e., leakage of feedwater to the distillate stream, [Fig. 3\(C\)](#)). However, pore wetting does not occur in the presence of supersaturated silica ([Fig. 3\(D\)](#)), which forms a thin scale layer that is confined on the membrane surface ([Fig. 3\(H\)](#)) ([Yin et al., 2019](#); [Christie et al., 2020](#)). Despite its slow kinetics and non-intrusive nature, silica scale layers are more adhesive to the membrane surface, resulting in a nearly irreversible decrease of water flux. For example, a majority (60%–90%) of water flux could be restored in RO by physical membrane cleaning (using deionized water) after gypsum scaling ([Mi and Elimelech, 2010](#)), whereas no water flux recovery was observed for silica scaling ([Tong et al., 2017](#)). Similarly, a remarkable water flux recovery of ~80% was achieved by physical membrane cleaning after gypsum scaling in MD with a superhydrophobic membrane ([Yin et al., 2020](#)). In contrast, physical membrane cleaning was unable to revive the water vapor flux after silica scaling ([Yin et al., 2020](#)). The irreversibility of silica scaling might be due to the gel nature of silica scale layer, which leads to stronger adhesion to the membrane surface.

In addition, gypsum and silica have different relationships between solubility and temperature. For gypsum, its solubility initially increases with temperature until reaching a maximum value at ~40 °C, after which the gypsum solubility decreases when temperature

further increases (Hulett and Allen, 1902; Rolf et al., 2022). Christie et al. (2022) systematically explored the effect of temperature on gypsum scaling in MD. The authors show that the critical water recovery, which corresponds to a 15% decline of water vapor flux due to gypsum scaling, decreases with feedwater temperature within a range of 50–80 °C. However, such a phenomenon is not only due to the decrease of gypsum solubility with temperature in this range, because the critical SI of gypsum at the membrane surface also decreases with temperature. They further demonstrate that an increase of temperature enhances the kinetics of gypsum formation by reducing the free energy barrier. For silica, its solubility increases with temperature within a wide range (e.g., from 8 °C to > 300 °C) (Gunnarsson and Arnórsson, 2000). In MD where an elevated temperature of feedwater is applied, temperature might influence the behaviors of mineral scaling by not only altering solubility of the mineral scale but also changing the water vapor flux. For example, although an increase of temperature increases silica solubility, it also increases the interfacial concentration of silicic acid at the membrane surface due to a higher extent of concentration polarization (as a result of a higher water vapor flux). The effect of temperature on silica scaling needs to be decoupled from that of water flux to isolate the role of temperature in governing MD performance, as what Christie et al. (2022) did for gypsum scaling as discussed above. However, to the best of our knowledge, such studies have not been reported in the literature and future research is needed to close this knowledge gap.

## 4 Gypsum and silica interact with organic foulants in different ways

In real-world membrane desalination systems, the feedwater typically contains a diverse mixture of organic foulants alongside mineral ions as precursors for scales such as gypsum and silica. The interactions of scale precursors with organic foulants have been shown to alter the behaviors of mineral scaling and the consequent impacts on the performance of the membrane desalination processes (Tong et al., 2023). However, the scalant-foulant interactions vary significantly between gypsum scaling and silica scaling due to their different formation mechanisms.

There are several studies on the interactions between organic foulants and the precursors of gypsum and silica in bulk solution (Benecke et al., 2018; Quay et al., 2018; Li et al., 2021a; Cao et al., 2022; Park et al.,

2024). For instance, Benecke et al. (2018) reported that humic acid and alginate, which represent humic substances and polysaccharides respectively, markedly prolonged the induction time of gypsum crystallization. The authors attributed this inhibitory effect to the adsorption of humic acid and alginate onto the gypsum nuclei or crystals, subsequently obstructing the active growth sites. Such an effect of organic foulants via adsorption was likely due to their abundance of carboxyl groups, which are known for their capability to bind with  $\text{Ca}^{2+}$  (Lioliou et al., 2006). This finding is supported by another study of (Cao et al., 2022), who also observed an extended induction time of gypsum nucleation in the presence of humic acid. These authors also reported that humic acid altered the morphology of gypsum from the characteristic needle-like shape to a polygon-like shape, providing more evidence on the adsorption of humic acid on the gypsum crystal surface. For silica scaling, (Li et al., 2021a) noted that silica could establish hydrogen bonds with the carboxyl groups of humic acid. However, when the concentration of silica exceeded a certain threshold (6 mmol/L with a humic acid concentration of 50 mg/L for this study), silica begin self-aggregating and the silica-silica interaction led to a bridged network of humic acid, resulting in a synergistic effect between silica scaling and humic acid fouling. Furthermore, proteins have been also reported to interact with gypsum and silica differently. (Park et al., 2024) reported that the bulk nucleation of gypsum was greatly affected by bovine serum albumin (BSA, a negatively charged protein), which extended the induction time of gypsum crystallization, whereas lysozyme (a positively charged protein) exhibited a negligible effect. In contrast, in the study by (Quay et al., 2018), the authors discovered that both BSA and lysozyme were able to facilitate silica aggregation, leading to the potential for fouling/scaling aggravation in membrane desalination.

Although the interactions between organic foulants and mineral scalants in bulk solutions have been explored as discussed above, it is crucial to investigate their impacts on membrane desalination systems because it has been reported that observations in the bulk solution may not accurately predict the combined phenomena of mineral scaling and organic fouling in crossflow desalination systems (Park et al., 2024). Several studies have demonstrated the RO performance of combined organic fouling and mineral scaling, which was compared to that of individual fouling and scaling (Quay et al., 2018; Wang et al., 2020a; Li et al., 2021a; Park et al., 2024). For example, (Park et al., 2024) observed that the water flux curve of combined gypsum scaling with humic acid or alginate fouling was close to the corresponding additive flux curve (i.e., the sum of

water flux decline caused by individual gypsum scaling and individual organic fouling), indicating an additive effect rather than a synergistic effect. However, different results were displayed in the case of combined humic acids/alginate fouling and silica scaling. Li et al. (2021a) revealed that, at a critical point (6 mmol/L of silica and 50 mg/L of humic acid), the mixture of humic acid and silica in feedwater resulted in a faster water flux decline than the additive flux behaviors of individual fouling and scaling, indicating a synergistic effect that was also observed by (Wang et al., 2020a) for combined silica scaling and alginate fouling. These findings demonstrate distinct behaviors of gypsum and silica in membrane systems when being combined with organic foulants such as humic acid and alginate.

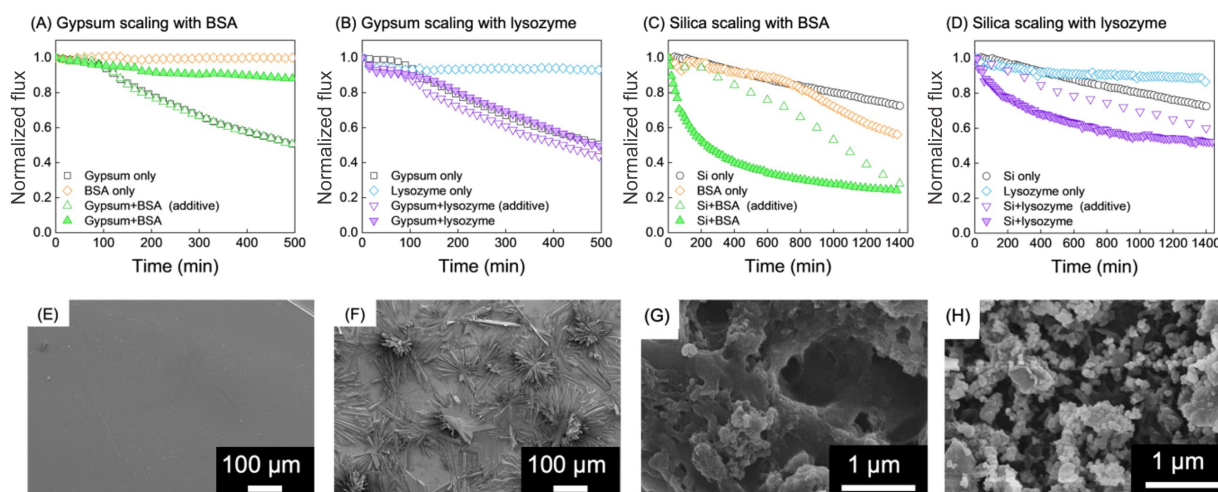
Furthermore, the differences between gypsum scaling and silica scaling are especially profound in case of combined mineral scaling and protein fouling. (Park et al., 2024) revealed that the presence of BSA significantly reduced the water flux decline caused by gypsum scaling (Fig. 4(A)), suggesting an antagonistic effect of BSA on gypsum scaling. However, a negligible effect was observed when lysozyme was present with supersaturated gypsum in the feed solution (Fig. 4(B)). These results are supported by SEM observations of the membrane surfaces after combined gypsum scaling and protein fouling. Gypsum crystals with defined shape were not observed after combined gypsum scaling and BSA fouling (Fig. 4(E)), whereas the morphology of gypsum scales displayed a typical rosette-like shape in the presence of lysozyme (Fig.

4(F)) (Park et al., 2024). In contrast, both BSA and lysozyme exhibited a synergistic effect on silica scaling (Figs. 4(C) and 4(D)), with the water flux of RO in combined silica scaling and protein fouling decreasing faster than those in individual scaling and fouling (Quay et al., 2018). SEM observations reveal that BSA and lysozyme resulted in distinct membrane surface morphologies after combined protein fouling and silica scaling. The membrane surface after combined BSA fouling and silica scaling showed both a dense BSA layer and silica particles (Fig. 4(G)), whereas only silica particles were observed on the membrane surface after combined lysozyme fouling and silica scaling (Fig. 4(H)) (Quay et al., 2018). The authors explained that such differences were attributed to BSA aggregation being enhanced in the presence of silica, while lysozyme facilitated silica particle formation (Quay et al., 2018).

## 5 Different mitigation strategies are required to control gypsum scaling and silica scaling

### 5.1 Scaling-resistant membrane materials

Developing fouling-resistant membranes, which does not require additional equipment and is compatible with existing desalination infrastructure, is a promising strategy of membrane fouling control. Although extensive



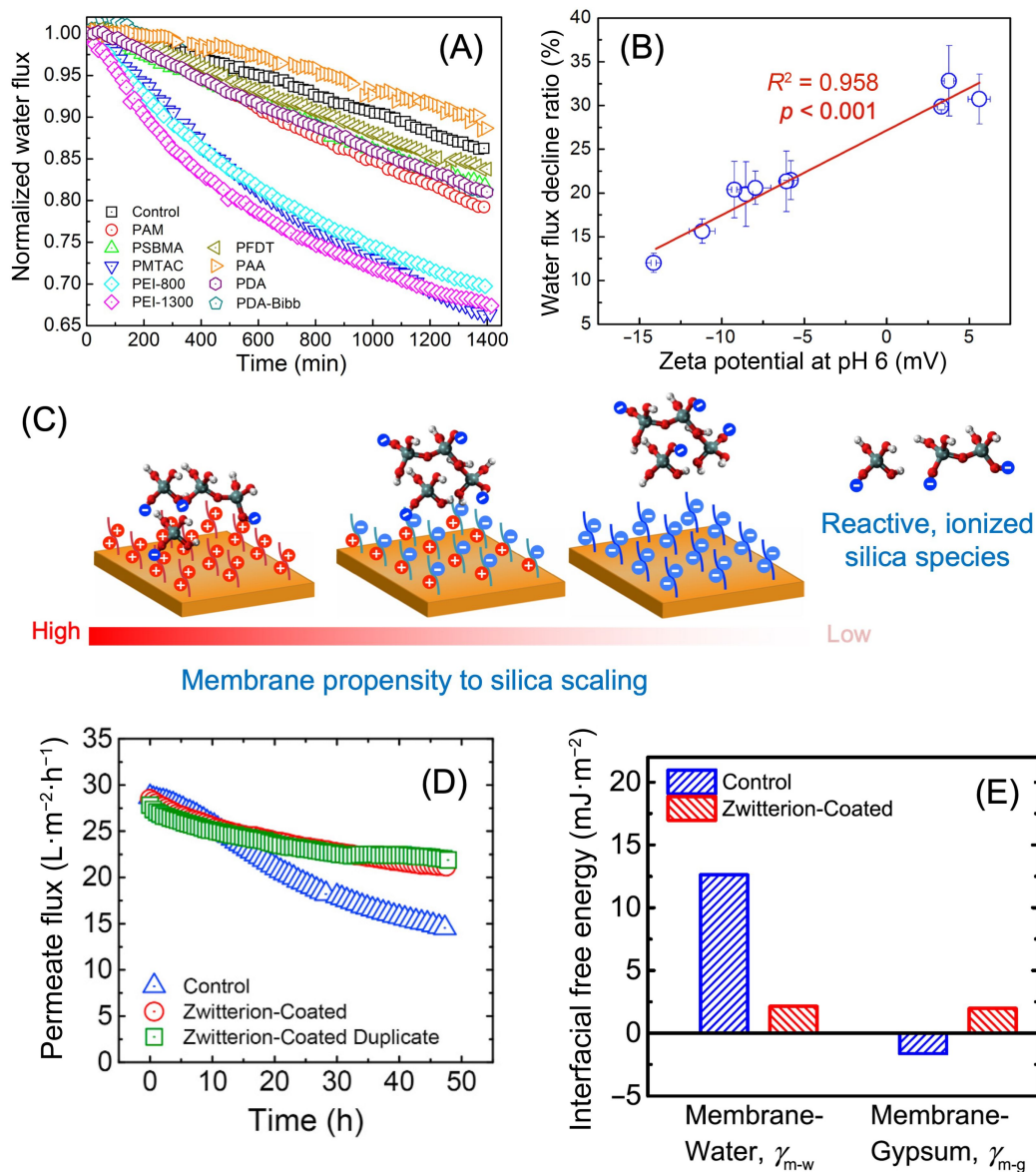
**Fig. 4** Representative normalized water flux decline curves for (A and B) gypsum and (C and D) silica scaling in the presence of proteins in RO. Each graph includes water flux curves of individual mineral scaling and organic fouling, the additive curve of individual scaling and fouling, and the actual water flux curve of combined scaling and fouling. (E and F) SEM images of the membrane surface after combined scaling and fouling experiments: gypsum scaling with (E) BSA and (F) lysozyme fouling, and silica scaling with (G) BSA and (H) lysozyme fouling. The figures are adapted with permission from Park et al. (2024) (A, B, E, F), copyright Elsevier; Quay et al. (2018) (C, D, G, H), copyright American Chemical Society.

studies have been performed to develop a variety of antifouling membranes for organic and biological fouling (Rana and Matsuura, 2010; Jhaveri and Murthy, 2016; Zhang et al., 2016), there are only a limited number of publications on the design and fabrication of membranes that are resistant to mineral scaling. In this section, we review the current status of developing scaling-resistant membranes, highlighting the distinct design principles and mechanisms associated with those for gypsum scaling and silica scaling.

The dominant membranes used in RO and NF are thin-film composite (TFC) polyamide membrane (Habib and Weinman, 2021; Li et al., 2021b; Liu et al., 2021a). Tong et al. (2017) systematically investigated the relationship between membrane surface properties and propensity of TFC polyamide membranes to silica scaling in RO. By exploring the correlation between water flux decline and several membrane properties including surface hydrophilicity, surface charge, and free-energy barrier for heterogenous nucleation, the authors discovered that the extent of silica scaling is strongly correlated to membrane surface charge, and that a more negatively charged surface reduces scaling and vice versa (Figs. 5(A) and 5(B)) (Tong et al., 2017). Such a fundamental relationship, which was further confirmed by Lu and Huang (2019), paves the way for the design and fabrication of several membranes with improved resistance to silica scaling. For example, Qi et al. (2020) modified a TFC polyamide RO membrane with ferric-phytic acid (PhA) complexes using layer-by-layer (LbL) assembly. PhA, a natural and nontoxic organic phosphate with abundant negatively charged phosphate groups, led to an increase of negative surface charge. The authors demonstrate that the PhA-modified polyamide membrane experienced a less extent of water flux decrease than the pristine membrane during silica scaling. Similarly, Wang et al. (2020b) reported that a polyamide membrane modified with acrylic acid enriched with negatively charged carboxyl groups displayed enhanced resistance against silica scaling compared to the unmodified membrane. Interestingly, the authors also observed a water flux recovery of ~20% by physical cleaning of the acrylic acid-modified membrane, despite the irreversible decrease of water flux for the unmodified membrane (Wang et al., 2020b). In addition to surface modification, altering the surface charge of polyamide membranes can also be attained by applying novel monomers in interfacial polymerization for creating the polyamide selective layer. Hao et al. (2023) used a novel monomer, namely 2,2'-benzidinedisulfonic acid (BDSA), as a co-monomer with the traditional *m*-phenylenediamine (MPD) to fabricate TFC polyamide

RO membrane. Due to the negatively charged sulfonic groups of BDSA, the fabricated membrane showed an enhancement of negative surface charge, which led to a mitigated extent of silica scaling. The higher resistance of more negatively charged membrane against silica scaling was due to the importance of negatively charged silica species in governing the kinetics of silicic acid polymerization, as discussed above. A more negatively charged membrane surface imposes a stronger electrostatic repulsion against the ionized, negatively charged silica species, thus resulting in a lower local concentration of reactive silica species near the membrane surface (Fig. 5(C)). As a result, the rate of silica polymerization is slowed, consequently reducing the tendency of silica scaling (Tong et al., 2017).

Regarding gypsum scaling, the first scaling-resistant RO membrane was reported by Lin et al. (2010). The authors reported that TFC polyamide membranes grafted with hydrophilic polymer brushes, such as poly(methacrylic acid) and poly(acrylamide), resulted in a significantly lower membrane propensity to gypsum scaling in RO than the unmodified membrane. The authors explain that partial local mobility of the dangling polymer brushes reduces the attachment of gypsum nuclei or crystals. Also, Jaramillo et al. (2021) fabricated a polyamide membrane coated with a zwitterionic polymer brush (poly(sulfobetaine methacrylate), PSBMA). The resultant membrane was found to mitigate gypsum scaling in RO compared to the uncoated pristine membrane (Fig. 5(D)). The authors show that the presence of zwitterionic coating renders the interfacial free energy between gypsum and membrane surface less negative (Fig. 5(E)), suggesting lower adhesion of gypsum nuclei or crystals to the zwitterionic coated surface. Such a finding was supported by another study where the extents of gypsum scaling for five RO membranes with various surface properties were tested (Yin et al., 2022a). To understand the mechanisms underlying surface resistance to gypsum scaling, Yin et al. (2022b) further explored heterogenous gypsum nucleation on an array of surfaces with different surface wetting properties. Their results show that more hydrophilic surfaces are less prone to gypsum scaling, which is consistent with those reported by Huang et al. (2020) who correlated surface wettability with gypsum scaling potential using quartz crystal microbalance with dissipation (QCM-D). Such results contradict the theoretical predictions of CNT, which indicates an opposite relationship between surface wettability and scaling potential (Yin et al., 2022b). Instead, the authors demonstrate that the affinity of  $\text{CaSO}_4$  clusters to surfaces of varied wetting properties is perfectly aligned with the experimental



**Fig. 5** (A) Water flux curve of RO desalinating feedwater containing supersaturated silica using membranes of different surface properties. (B) The water flux decline ratio of membranes shown in Fig. 5(A) demonstrates a strong correlation with surface charge, manifested by zeta potential, of the membranes. (C) Mechanisms underlying the relationship between membrane surface charge and propensity of silica scaling. (D) Water flux curve of RO desalinating feedwater containing supersaturated gypsum using a pristine polyamide membrane and membranes coated with zwitterionic polymer. (E) The membrane-water and membrane-gypsum interfacial free energies for the pristine polyamide and zwitterion-coated membranes. The figures are adapted with permission from Tong et al. (2017), copyright American Chemical Society; Jaramillo et al. (2021), copyright Elsevier.

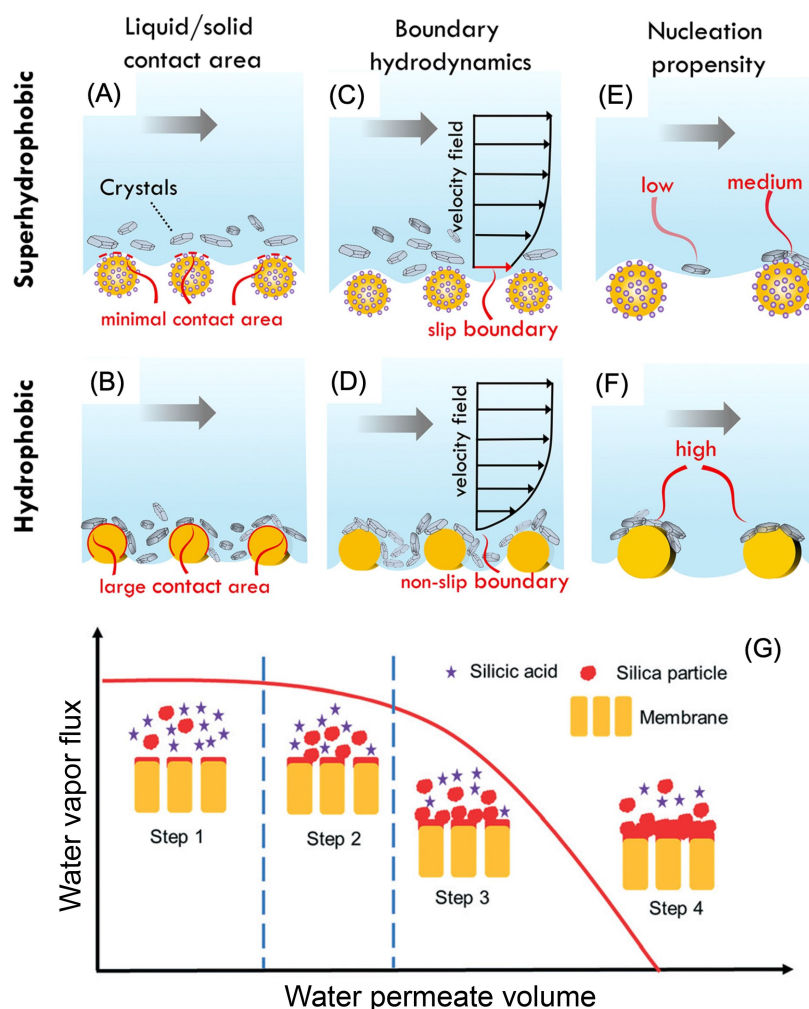
observations of surface scaling propensity (Yin et al., 2022b). This study provides additional evidence that supports not only the non-classical nucleation pathway of gypsum nucleation, but also the aforementioned mechanisms of scaling-resistant membranes modified with hydrophilic polymer brushes.

The first scaling-resistant membrane in MD was

reported by Karanikola et al. (2018), who fabricated a superhydrophobic membrane with slippery property as a result of both a re-entrant surface texture and low membrane surface energy. The developed membrane showed resistance to gypsum scaling and better performance in MD desalination of an industrial blowdown wastewater. Similarly, Xiao et al. (2019a;

2019b) created a superhydrophobic membrane with micro-pillar arrays by employing a micro-molding phase separation method. After  $\text{CF}_4$  plasma treatment, the fabricated membrane displayed both a high static contact angle ( $> 160^\circ$ ) and a very low sliding angle ( $\sim 3^\circ$ ). This membrane was able to resist mineral scaling caused by both gypsum and NaCl (it is worth mentioning that highly soluble salts such as NaCl cause mineral scaling in MD due to the elevated feedwater salinity and high-water recoveries). Since then, several studies have proved the excellent resistance of superhydrophobic membranes to gypsum scaling (Su et al., 2019; Zhu et al., 2021; Hu et al., 2023). Researchers have proposed three mechanisms underlying gypsum scaling mitigation by superhydrophobic

membranes (Fig. 6) (Horseman et al., 2021; Liu et al., 2021c). First, superhydrophobic membranes effectively decrease the liquid-solid contact area available for crystal nucleation, growth, and deposition (Figs. 6(A) and 6(B)). Second, superhydrophobic membranes create a favorable slip boundary condition (Figs. 6(C) and 6(D)) that (1) reduces the residence time for crystal growth and deposition and (2) creates a higher flow velocity and intensified turbulence, which mitigate concentration polarization and decreases the degree of mineral supersaturation. Furthermore, according to CNT, the free energy barrier to heterogeneous nucleation of minerals on superhydrophobic membranes is higher than that on conventional hydrophobic membranes (Figs. 6(E) and 6(F)). As discussed above,



**Fig. 6** (A–F) Three possible mechanisms underlying the resistance of superhydrophobic membranes against gypsum scaling in MD. It is worth mentioning that the mechanism shown by Figures 6E and 6F is unlikely to be the main mechanism because gypsum is described more appropriately by a non-classical pathway. (G) A four-step mechanism of silica scaling in MD. The figures are adapted with permission from Horseman et al. (2021), copyright American Chemical Society; Yin et al. (2019), copyright Royal Society of Chemistry.

however, an increasing amount of evidence has emerged that CNT is not applicable to gypsum scaling, which is more appropriately described by a non-classical nucleation pathway. Therefore, the first two mechanisms are likely to be responsible for the scaling resistance of superhydrophobic membranes.

However, the mitigating effects of superhydrophobic membranes on silica scaling in MD were less profound than what were observed for gypsum scaling. For example, [Yin et al. \(2019\)](#) reported that a superhydrophobic membrane only moderately reduced the rate of water vapor flux decrease, while the induction time of flux decrease was not affected by membrane surface wettability. The authors further demonstrate that altering membrane surface wettability in MD was ineffective of enhancing either total water recovery or scaling reversibility under silica scaling, despite an effective extension of water recovery and high reversibility of gypsum scaling achieved by using superhydrophobic membrane ([Yin et al., 2020](#)). The low sensitivity of silica scaling to membrane surface wettability in MD is relevant to its scaling formation mechanism. Compared to gypsum scaling that is mainly attributed to heterogenous nucleation on the membrane surface ([Karanikola et al., 2018](#)), silica scaling is reliant more on bulk nucleation and the subsequent deposition of silica particles in MD. The decrease of water vapor flux was reported to be a result of silica particle deposition followed by the formation of a silica gel layer due to the reactions between the deposited silica particles on the membrane surface and soluble silica species in the solution ([Yin et al., 2019](#)). As a result, the change of membrane surface properties has a limited effect on silica scaling in MD. Instead, innovations in MD operational conditions such as adding antiscalants ([Yin et al., 2021](#); [Yao et al., 2023](#)) (which will be discussed in the following section) and applying a pulse flow ([Liu et al., 2021b](#)) were proven to effectively mitigate silica scaling in MD.

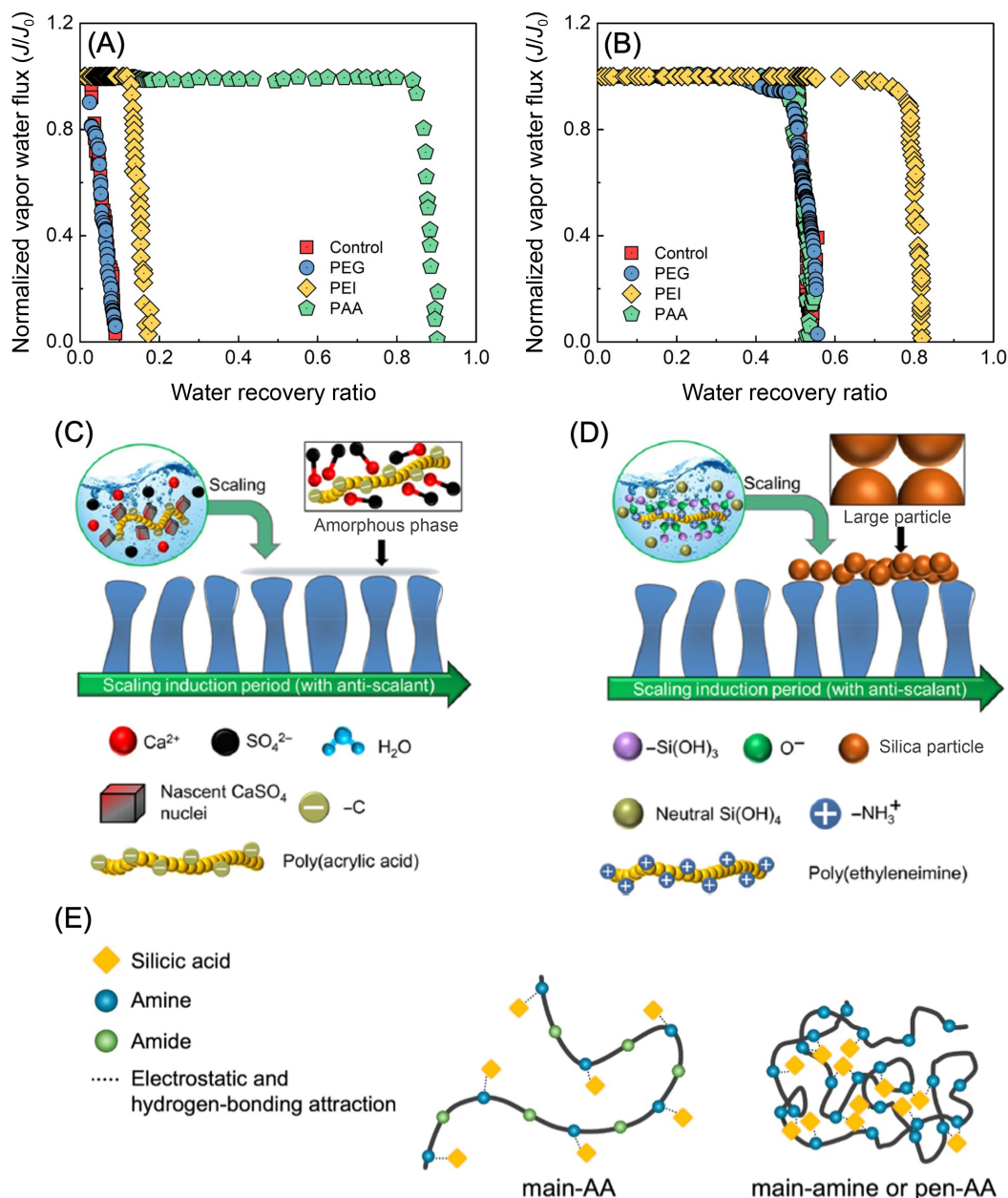
## 5.2 Antiscalants

The use of antiscalants is a common strategy of scaling mitigation applied by industries ([Yu et al., 2020](#)). Current antiscalants are predominantly designed for controlling mineral scaling induced by crystallization, such as calcite scaling and gypsum scaling ([Yu et al., 2020](#)). In contrast, antiscalants that enable effective mitigation of silica scaling in membrane desalination have been rarely reported in the literature.

Several antiscalants have been reported to hinder gypsum scaling, including carboxyl- and phosphonate-based compounds ([Weijnen and Van Rosmalen, 1985](#);

[Yu et al., 2020](#)). Carboxyl-based compounds such as polymaleic and polyacrylic compounds have been shown to inhibit the nucleation and growth of gypsum crystals ([Weijnen and Van Rosmalen, 1985](#); [Rabizadeh et al., 2019](#)). Similarly, phosphonate-based compounds such as sodium hexametaphosphate (SHMP) ([Rahman, 2013](#)), nitrilotri(methyl phosphonic acid) (NTMP or ATMP) ([Prisciandaro et al., 2006](#); [2009](#); [Rabizadeh et al., 2020](#)), and diethylenetriaminepentakis (methylphosphonic acid) (DTPMP) ([Dai et al., 2022](#)) have been reported to retard the nucleation kinetics of gypsum. These compounds have been found to have great potential as antiscalants by significantly increasing the induction time of gypsum formation and hindering the growth of gypsum crystals, thereby effectively reducing gypsum scaling in membrane desalination ([Yin et al., 2021](#); [2022a](#)).

In a study by [Yin et al. \(2021\)](#), who compared the molecular features essential for antiscalants between gypsum scaling and silica scaling, it was reported that the use of poly(acrylic acid) (PAA), which has abundant negatively charged carboxyl groups, was much more effective to mitigate gypsum scaling in MD than neutral or positively charged polymers such as poly(ethylene glycol) (PEG), poly(ethylenimine) (PEI), and poly(amidoamine) (PAMAM) ([Fig. 7\(A\)](#)). The authors further showed that adding a small concentration of PAA to a gypsum-supersaturated feedwater was able to nearly eliminate the water flux decline caused by gypsum scaling in RO, thereby greatly enhancing the total water recovery of a RO-MD treatment train ([Yin et al., 2022a](#)). The high anti-gypsum scaling efficiency of PAA is believed due to the strong interactions between carboxyl groups and  $\text{Ca}^{2+}$  on the surface of  $\text{CaSO}_4$  nuclei. The addition of PAA impedes the transformation of amorphous  $\text{CaSO}_4$  nuclei into gypsum crystals, and such inhibition results from the intercalation of PAA within the  $\text{CaSO}_4$  lattice by complexation between carboxyl groups and  $\text{Ca}^{2+}$ , inhibiting the crystalline transformation to gypsum ([Fig. 7\(C\)](#)) ([Yin et al., 2021](#)). Also, the adsorption of antiscalants to the surface of  $\text{CaSO}_4$  nucleus also plays a role in their antiscaling efficiency. As suggested by ([Dai et al., 2022](#)), the adsorption of carboxyl- and phosphonate-based antiscalants increases superficial surface tension of the nucleus and prolongs the induction time. Furthermore, ([Rabizadeh et al., 2020](#)) reported that the complexation between phosphonate-based antiscalants and  $\text{Ca}^{2+}$  reduces the activity of free  $\text{Ca}^{2+}$  and amorphous  $\text{CaSO}_4$  nuclei, thereby delaying the kinetics of gypsum crystallization. In addition, the greater the number of phosphonate functional groups in the antiscalants, the more effectively they are



**Fig. 7** (A and B) Normalized water vapor flux as a function of water recovery in MD for (A) gypsum scaling and (B) silica scaling in the presence of different antiscalant candidates. (C and D) Schematic illustration of the mechanisms of antiscalants for mitigating (C) gypsum scaling and (D) silica scaling in MD. (E) Schematic illustration of amino-containing polymers of different conformation hindering silica polymerization through interactions with silicic acid. The figures are adapted with permission from Yin et al. (2021), copyright American Chemical Society; Kaneda et al. (2024), copyright American Chemical Society.

complexed with Ca<sup>2+</sup>, thus retarding gypsum crystallization (Rabizadeh et al., 2020).

As silica is not formed via a crystallization process, the aforementioned antiscalants are not applicable to the mitigation of silica scaling. Compared to those for gypsum scaling, there are a smaller number of studies on the development of antiscalants for silica. So far,

amino-containing polymers (e.g., PAMAM and PEI) (Neofotistou and Demadis, 2004; Yin et al., 2021; Yao et al., 2023) and neutral polymers (e.g., PEG) (Preari et al., 2014; Yao et al., 2023) have shown capabilities of hindering silicic acid polymerization in the bulk solution. However, the mechanisms of antiscalants for silica scaling have yet to be fully revealed, although

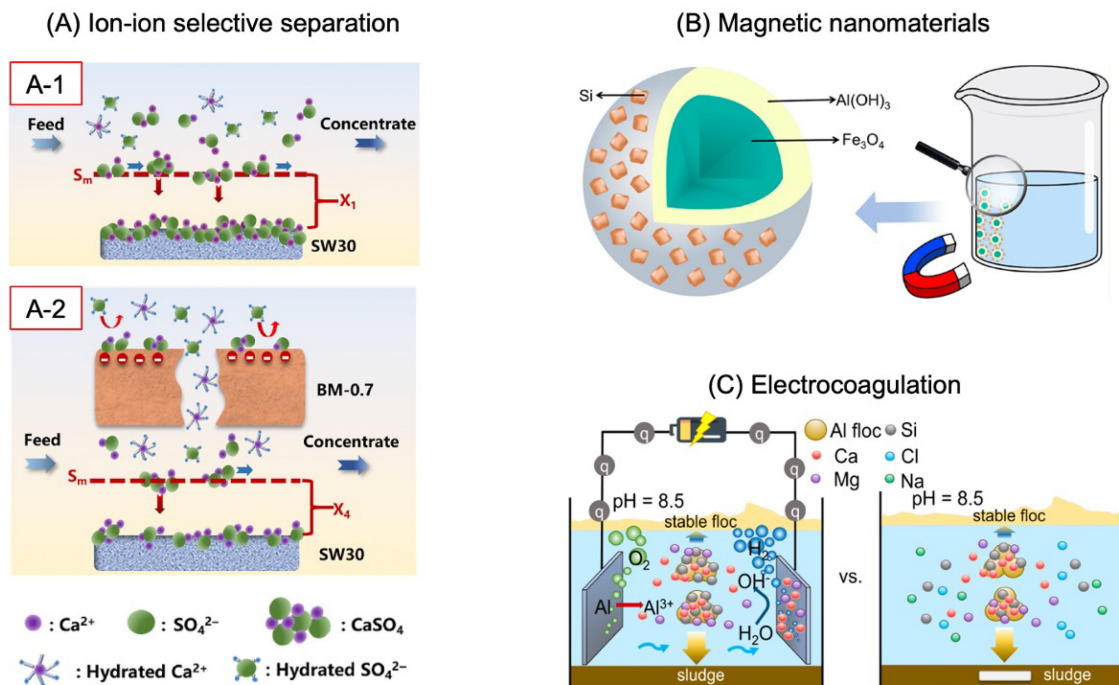
hydrogen bonding between antiscalants and silica species has been proposed to be the main mechanism (Kempter et al., 2013; Preari et al., 2014). Recently, Kaneda et al. (2024) synthesized an array of amine-containing polymers and explained the role of molecular structure in stabilizing silicic acid. The authors reported that polymers with both charged amine and uncharged amide groups possessed the highest efficiency of prohibiting silicic acid polymerization, whereas monomers of these polymers as well as polymers containing only amine or amide functionality were not effective. Molecular dynamics simulation reveals strong bindings between ionized, deprotonated silicic acids (reactive as mentioned above) and protonated amine groups of the polymer, and that an extended polymer conformation (as a result of the coexistence of amine and amide groups) plays an essential role in preventing proximity between the bonded silica species and subsequently facilitating inhibition of silica polymerization (Fig. 7(E)) (Kaneda et al., 2024).

Furthermore, although antiscalants that stabilize silicic acid in the bulk solution have been developed in the literature (Neofotistou and Demadis, 2004; Preari et al., 2014; Yao et al., 2023; Kaneda et al., 2024), antiscalants that are able to mitigate silica scaling in crossflow membrane desalination systems have been rarely reported. Yin et al. (2021) demonstrated that polymers enriched with cationic amino groups such as PEI and PAMAM significantly extended the water recovery of MD in the presence of silica scaling, whereas an anionic polymer PAA, which showed the best antiscaling efficiency for gypsum scaling, exhibited no effects of mitigating silica scaling (Fig. 7(B)). The authors suggest that the presence of PEI and PAMAM in the feedwater lead to larger silica particles, resulting in a broader particle-particle space that requires a longer time to form an impermeable gel layer (Fig. 7(D)). Yao et al. (2023) further proved the high efficiencies of PEI and PAMAM in reducing silica scaling during MD desalination, but they also showed that these amine-enriched polymers facilitated water flux decrease by silica scaling in RO. This phenomenon was probably due to the less negative membrane surface adsorbed with PEI and PAMAM in RO, consistent with the effects of membrane surface charge on silica scaling as shown by Figs. 5(A) and 5(B). Instead, the authors reported that high-molecular-weight PEG molecules and their derivatives were able to mitigate silica scaling in both MD and RO, despite that the presence of these antiscalants were unable to eliminate the water flux decline caused by silica scaling (Yao et al., 2023).

### 5.3 Pretreatment

Pretreatment is an effective strategy for minimizing membrane scaling, as it removes scaling precursors from the feedwater before it enters the membrane desalination stages, thereby reducing the potential of mineral scaling. Many studies have investigated various pretreatment techniques, such as coagulation/precipitation (Kim et al., 2009; Zhang et al., 2019; Jebur et al., 2024), ion exchange softening (Vermeulen et al., 1983; Ali et al., 2004), acidification (Prihasto et al., 2009; Bush et al., 2018), adsorption (Hingston and Raupach, 1967; Tokoro et al., 2014), magnetic treatment (Yang, 2005; Gryta, 2011), and nanofiltration (Hilal et al., 2005; Llenas et al., 2011; Ang et al., 2016). In this section, we review several recent studies that specifically focus on gypsum scaling, silica scaling, or both types of scaling.

Selective ion separation via NF has emerged as a promising strategy for controlling gypsum scaling. Indeed, one of the major applications of NF is softening, which effectively remove  $\text{Ca}^{2+}$ . Conventional NF using commercial membranes has been effectively adopted as a pretreatment step to reduce the concentrations of gypsum precursor ions in the feedwater (Hilal et al., 2005; Llenas et al., 2011; Ang et al., 2016), and novel NF membranes have been also developed to have high divalent/monovalent ion selectivity to retain calcium and sulfate ions (Cheng et al., 2018; Zhang et al., 2021; Zhao et al., 2024). However, it has been observed that gypsum scaling can also occur during NF pretreatment (Zhang and Zhang, 2021). Therefore, to prevent gypsum scaling in both NF and the following RO processes, it is favorable for the membrane to exhibit high ion-ion selectivity, allowing calcium ions to pass through while retaining sulfate ions. For example, Zhang and Zhang (2021) developed selective ion separation membranes by utilizing 2,2'-benzidine-disulfonic acid during interfacial polymerization for the synthesis of the polyamide active layer. Compared to a commercial TFC polyamide membrane, the synthesized membrane exhibited lower rejection for calcium ions due to the larger pore radius while retaining a large proportion of sulfate ions owing to the stronger electrostatic repulsion by the improved negative charge of membrane surface. When the NF membranes were employed in a hybrid NF-RO process (Fig. 8(A)), gypsum scaling was significantly reduced not only on the NF membrane due to the lower concentration of calcium but also on the RO membrane due to the lower concentration of sulfate compared to that in the raw feedwater. However, the efficiencies of NF in removing silicic acid as silica precursors have been rarely



**Fig. 8** Schematic illustrations of different pretreatment techniques. (A) Ion-ion selective separation process using NF for gypsum scaling mitigation. (B) Magnetic iron-aluminum hybrid nanomaterials for silica removal. (C) Electrocoagulation for removing silica and hardness. The figures are adapted with permission from (Zhang and Zhang, 2021) (copyright Elsevier), (Guan et al., 2019) (copyright American Chemical Society) and (Liu et al., 2022) (copyright American Chemical Society).

reported in the literature (So et al., 2023).

To alleviate silica scaling, utilizing nanomaterials for silica adsorption is getting attention as an effective pretreatment approach. There have been several studies on the use of aluminum hydroxide and iron hydroxide to remove silicic acid for silica scaling mitigation (Hingston and Raupach, 1967; Yokoyama et al., 1980; Tokoro et al., 2014), but the recovery of adsorbents remains an issue that needs to be addressed (Milne et al., 2014). As an attempt to tackle this challenge, Guan et al. (2019) developed  $\text{Al}(\text{OH})_3 @ \text{Fe}_3\text{O}_4$  magnetic nanomaterials with a core-shell design for efficient and recyclable removal of dissolved silica from water (Fig. 8(B)). The synthesized magnetic nanomaterials were able to effectively adsorb silicic acid from aqueous solutions and then recovered under a low magnetic field. After treating feedwater with the synthesized nanomaterials, silica scaling in the RO system was significantly mitigated. While further investigation into the long-term reusability of such nanomaterials is necessary, this work provided a novel direction for future design of engineered materials with improved efficiencies of silica removal.

Furthermore, electrocoagulation pretreatment has been reported to be effective in mitigating both gypsum scaling and silica scaling (Zhang et al., 2019; Liu et al.,

2022; Jebur et al., 2024). For instance, Liu et al. (2022) recently demonstrated the effectiveness of an aluminum-based electrocoagulation pretreatment system for removing dissolved silica and hardness (Fig. 8(C)). The authors attributed silica removal to charge neutralization with positively charged species such as aluminum hydroxides or poly-hydroxide like  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Al}(\text{H}_2\text{O})_5\text{OH}^{2+}$ , and  $\text{Al}(\text{H}_2\text{O})_4\text{OH}^+$ . However, as discussed above, only a small fraction of silicic acid is ionized and negatively charged and silica species in solutions are mostly present in a neutral form. Thus, further studies are required to investigate the mechanism by which silica is removed by electrocoagulation processes. In addition to silica removal, hardness removal is also achieved during electrocoagulation via co-precipitation reactions at the cathode. Consequently, electrocoagulation as a pretreatment step was able to simultaneously remove the majority of silica ( $95\% \pm 4\%$ ) and a significant amount of hardness (40%–60%) from a synthetic groundwater solution. Further, the authors conducted a techno-economic analysis to show that electrocoagulation has the potential of reducing the cost by 6 times compared to chemical coagulation, while maintaining more stable effluent pH and conductivity levels (Liu et al., 2022).

In addition, while the above recent developments

**Table 1** Comparison between gypsum scaling and silica scaling in membrane desalination

	Gypsum scaling	Silica scaling
Formation mechanism	Crystallization	Polymerization
Formation kinetics	Fast	Slow
Crystal growth	Anisotropic	Isotropic
Membrane surface property – scaling propensity relationship in RO	Grafting of hydrophilic polymer brushes reduces scaling	More negative charged membrane reduces scaling
Membrane surface property – scaling propensity relationship in MD	Superhydrophobic membranes reduce scaling	Not sensitive to membrane surface wettability
Inducting pore wetting in MD	Yes	No
Interactions with organic foulants	Antagonistic or additive effects (e.g., the presence of BSA reduces scaling)	Amplifying effects (e.g., the presence of BSA facilitates scaling)
Antiscalants in RO	Carboxyl- and phosphonate-based molecules (elimination of water flux decline is achievable)	Poly(ethylene glycol)-based molecules (elimination of water flux decline has not been achieved)
Antiscalants in MD	Carboxyl- and phosphonate-based molecules	Amine-enriched molecules and poly(ethylene glycol)-based molecules

show promise, more mature methods are widely used in major desalination plants to remove mineral scalants. For example, lime-soda softening and ion exchange softening are common practices (Sheikholeslami et al., 2001; Antony et al., 2011; Anis et al., 2019). Lime-soda softening involves adding lime (i.e., calcium hydroxide) and soda ash (i.e., sodium carbonate) to the water, causing calcium and magnesium to form sparingly soluble precipitates that can then be filtered out. Although its primary purpose is to control hardness (thus effective in gypsum scaling mitigation), lime-soda softening has been reported to reduce dissolved silica at a similar efficiency (to calcium removal), showing potential in alleviating silica scaling (Sheikholeslami et al., 2001). Another example is ion exchange softening, which typically uses cation exchange resins to remove calcium and magnesium ions via exchange with sodium adsorbed on the ion exchange resins. Additional to its effectiveness in reducing water hardness, ion exchange has also shown the potential of removing silicic acid (Ali et al., 2004). The key difference in using ion exchange resins for removing gypsum versus silica scalants lies in the type of resin used: cation exchange resins are used to remove calcium, while anion exchange resins are used to remove reactive silica. Especially, the anion exchange resin for silica removal is a strong base resin in the hydroxide form (Ali et al., 2004), as the silica precursors (i.e., silicic acid) is a weak acid. This highlights the different scaling mitigation mechanisms and challenges between gypsum scaling and silica scaling.

## 6 Conclusions and outlook

In this Review article, we closely examine and compare

the formation mechanisms, behaviors, and mitigation strategies associated with gypsum scaling and silica scaling, two common types of mineral scaling in membrane desalination. We demonstrate that due to their distinct formation mechanisms (crystallization for gypsum scaling vs. polymerization for silica scaling), gypsum scaling and silica scaling lead to drastically different consequences in membrane desalination and require distinctive means of scaling control. The main differences between gypsum scaling and silica scaling are outlined in Table 1. We are aware that other types of mineral scales, such as calcite, barite, and calcium phosphate are potentially present in membrane desalination (Tong et al., 2019b; Rolf et al., 2022). Although these mineral scales are crystals, their scaling behaviors and mitigation strategies can be different from that of crystalline gypsum (e.g., the solubility of calcite increases significantly with pH (Gal et al., 1996), whereas the solubility of gypsum is not sensitive to pH (Shukla et al., 2008). Thus, pH adjustment might be used to mitigate calcite scaling but not gypsum scaling). Therefore, we constrain ourselves from applying the conclusions of this work to other scaling types, whose systematical comparisons are still needed. Furthermore, although this article focuses on the differences between gypsum and silica scaling, we would like to remind the readers that mitigation strategies of these two scaling types do not exclude each other. As discussed above, for example, pretreatment such as electrocoagulation has the potential of removing scale precursors for both gypsum and silica, despite to different extents. Even though, the findings from the literature when comparing gypsum scaling and silica scaling, as summarized in this article, suggest that the mitigation of mineral scaling in membrane desalination needs to be tailored to the scaling type and built upon in-depth knowledge of scale formation mechanism. However, knowledge gaps are

identified in existing studies. We propose that future research on membrane scaling can be directed in the following topics.

First, molecular interactions of scale precursors with membrane surfaces, co-existing foulants, and antiscalants have not been fully elucidated. Because of their different molecular features (e.g., functional groups, charge, size), the precursors of gypsum (i.e.,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ ) and silica (i.e., silicic acid) interact with surrounding substances differently, and such interactions play an important role in determining the scaling behaviors and developing effective scaling mitigation approaches such as scaling-resistant membranes and antiscalants. However, experimental approaches are limited to reveal such interactions at the molecular level, and the rapid development of computational simulations (e.g., molecular dynamics simulation) have made the exploration of these interactions possible. The combination of experimental and computational approaches has great potentials to advance our fundamental knowledge on the molecular interactions of scale precursors in membrane desalination.

Second, gypsum can be effectively controlled by the use of antiscalants or pretreatment (e.g., softening and ion exchange), but silica scaling represents a more intractable problem that requires more research efforts. Currently, there is still a lack of effective antiscalants that successfully eliminate water flux decline caused by silica scaling (especially in RO), and the efficiencies and mechanisms of silica removal by pretreatment have not been fully understood. Thus, future research of designing highly efficient antiscalants for silica scaling and pursuing more effective approaches for silica removal is highly desirable. Indeed, such efforts need to be built upon a better understanding regarding the regulating factors of silica formation as well as the interactions of silicic acid with co-existing materials (e.g., antiscalants, adsorbents, etc.).

Last but not least, considering the distinctions between different types of mineral scaling, as highlighted in this article, it is important to identify the specific scaling types on membrane surfaces in real desalination applications. Current studies on mineral scaling are predominantly using feedwaters with simple and defined water chemistry, in which a known type of mineral (e.g., gypsum or silica) is typically added and reaches a supersaturated state. However, analyzing scale types formed from feedwaters with more complex water chemistry, which represents real-world applications, has been rarely performed by the literature (Butt et al., 1997; Abada et al., 2023; Niemann et al., 2023). As a result, more studies are needed to focus on more complex feedwaters, especially those collected from

full-scale desalination facilities. Such studies will not only deepen our understanding of the differences among various scaling types, but also promote our knowledge that help predict the dominant types of scaling occurring in membrane desalination. Ideally, a predictive model should be established to forecast mineral scale formation based on the chemical compositions of the feedwater. Such a model will guide the design of proper scaling mitigation strategies tailored to feedwaters in various desalination scenarios, thereby increasing the water recovery and energy efficiency of membrane desalination for a wide range of applications.

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## Author Biography



Dr. Tiezheng Tong is currently a tenured Associate Professor in the School of Sustainable Engineering and the Built Environment (SSEBE) at Arizona State University (ASU). Before joining ASU, he was a tenured Associate Professor of Civil and Environmental Engineering at Colorado State University (CSU). He completed a postdoc position in the Department of Chemical and Environmental Engineering at Yale University and received his Ph.D. degree in Civil and Environmental Engineering from Northwestern University. Prior to his Ph.D. study, he graduated from Beijing Normal University (with the highest honor) and Tsinghua University with B.S. and M.S. degrees, respectively, both of which are in Environmental Engineering. He has published nearly 80 peer-reviewed journal articles, which have been cited by ~6,000 times globally with an H-index of 37. He is the recipient of many academic and professional awards, including the Super Reviewer Award from *Environmental Science & Technology* (2024), the James J. Morgan Early Career Award from American Chemical Society (honorable mention, 2024), the George T. Abell Outstanding Early-Career Faculty Award and Faculty Award for Excellence in Research from CSU (2023), the CAPEES/UCEEF Early Career Award from Chinese-American Professors in Environmental Engineering and Science (2023), the CAREER Award from National Science Foundation (2022), the 40 under 40 Award from American Academy of Environmental Engineers and Scientists (2022), *ACS ES&T Engineering Best Paper Award* (2022), the Young Membrane Scientist Award from North American Membrane Society (2020), a student award from Sustainable Nanotechnology Organization (2013), and Environmental Chemistry Graduate Student Award from American Chemistry Society (2012). He is currently an editorial board member of *Journal of Membrane Science* and the President-Elect of Chinese-American Professors in Environmental Engineering and Science. His current research interests include (1) achieving energy-efficient treatment of hypersaline brines for circular water economy, (2) elucidating fundamental phenomena at the water-membrane interface, and (3) applying data-driven approaches to promote water sustainability.