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for desalination applications: A review*

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Scaling and fouling In membrane distillation for desalination

applications: A review

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Abstract

Membrane distillation (MD) has become an area of rapidly increasing research and development since the 1990s, providing a potentially cost effective thermally-driven desalination technology when paired with waste heat, solar thermal or geothermal heat sources. One principal challenge for MD is scaling and fouling contamination of the membrane, which has gained growing attention in the literature recently as well. The present paper surveys the published literature on MD membrane fouling. The goal of this work is to synthesize the key fouling conditions, fouling types, harmful effects, and mitigation techniques to provide a basis for future technology development. The investigation includes physical, thermal and flow conditions that affect fouling, types of fouling, mechanisms of fouling, fouling differences by sources of water, system design, effects of operating parameters, prevention, cleaning, membrane damage, and future trends. Finally, numerical modeling of the heat and mass transfer processes has been used to calculate the saturation index at the MD membrane interface and is used to better understand and explain some of trends reported in literature.

Keywords: Membrane distillation, fouling, scaling, biofouling, membrane cleaning, scale mitigation

Nomenclature

B	membrane distillation coefficient [$\text{kg}/\text{m}^2\text{s Pa}$]
$f()$	function of
h	heat transfer coefficient [$\text{W}/\text{m}^2\text{K}$]
h_{fg}	enthalpy of vaporization [J/kg]
J	mass flux [$\text{kg}/\text{m}^2\text{s}$]
k	mass transfer coefficient [m/s]
K_{sp}	solubility product constant
P	pressure [Pa]
\dot{q}	heat flux [W/m^2]
T	temperature [$^{\circ}\text{C}$]
x	salinity [g/kg]
ρ	density [kg/m^3]
$(\cdot)_f$	feed
$(\cdot)_b$	bulk/free stream
$(\cdot)_m$	membrane
MED	Multi-Effect Distillation
MD	Membrane Distillation
MSF	Multi-Stage Flash Distillation
RO	Reverse Osmosis
SI	Saturation Index

1 Introduction

Membrane distillation (MD) is a promising thermally driven desalination technology still in its infancy in terms of development and commercial deployment [1, 2]. The technology purifies water using a hydrophobic membrane, which is permeable to water vapor but which repels liquid water. In seawater desalination applications of MD, as hot saline feed solution flows over the membrane, the increased water vapor pressure from the higher temperature drives vapor through the pores ($d_p \approx 0.2 - 0.4 \mu m$) of the hydrophobic membrane, where it is collected on the permeate side [3]. MD possesses unique advantages over other desalination technologies, including pressure-driven methods such as reverse osmosis (RO) and thermally-driven methods such as flash distillation. MD is free of the specialized requirements of high-pressure RO systems, which includes heavy gauge piping, complex pumps, and maintenance demands [1]. Since MD is not a pressure driven process and only vapor is allowed to cross through the membrane, MD is more fouling resistant than RO [4] and has a potential 100% rejection of ions and macromolecules. MD can be run at lower temperatures than other thermal systems making untapped sources of waste heat usable, it requires significantly fewer parts, and can have a much smaller footprint as result of reduced vapor space [3]. Additionally, recent theoretical and computational work claims potential multistage DCMD configurations with efficiencies greater than that of other thermal technologies [5, 6, 7], assuming very large available heat exchanger areas. In practice, GOR values of practical state of the art MD systems with limited exchange areas are more modest [8]. Summers [9] has subsequently shown that multi-stage vacuum MD is thermodynamically identical to MSF, indicating that equivalent energy efficiencies can be achieved. The comparative simplicity makes MD more competitive for small-scale applications such as solar-driven systems for remote areas, especially in the developing world [3, 10, 11, 12]. However, significant advancements are needed in membrane technology for MD to reach the theoretical cost competitiveness and develop market share growth [13]. Fouling in MD is of particular importance, as fouling increases costs of energy consumption,

downtime, cleaning, required membrane area, required membrane replacement, and creates problems with product water contamination from pore wetting [14, 15].

The first patents on MD were granted in the late 1960s, but it wasn't technologically feasible until ultrafiltration membranes in the 1980s enabled sufficiently high trans-membrane fluxes [3]. Currently, most MD work is done in the laboratory, although a number of test beds across the world for small-scale solar thermal MD have already been deployed, and a few other projects exist [3, 11, 16].

While increased research interest in MD is relatively recent [17], scaling under high temperature conditions has been a key problem in systems with water heating since the advent of the steam engine. Research in the area, especially for metal heat exchangers, originated well before 1900 [18]. However, with respect to thermal efficiency, these studies mainly focus on conductive resistance due to scale formation, and often do not address the type of transport phenomena that are important in the context of fluid-membrane systems [18]. A somewhat more relevant area of scaling research is that for RO. However, RO membranes are not specifically hydrophobic, are virtually non-porous, are comprised of different materials, and operate at much lower temperatures but much higher pressures. Hence, RO membranes exhibit significantly different fouling characteristics than MD membranes [3, 14, 18, 19].

Studies focused on scaling in MD largely originated in the 1990s, and since then have become more numerous [13, 17]. Between 1991 and 2011, sixteen solar-driven MD systems were tested at the pilot or semi-pilot scale [20]. Limited fouling data from those plants constitute most of what we know about the fouling potential of MD membranes and the damage they may sustain under actual field operation conditions. Parallel to those pilot studies, a number of dedicated lab-scale studies were also conducted to understand fouling in MD. For many years, it was believed that the hydrophobic nature of the membrane, the maximum pore size and the low feed pressure in the MD process are sufficient to prevent the feed solution from penetrating the membrane pores (often referred to as pore wetting),

and from causing significant scaling on its surface. For example, in 2003, Koschikowski et al. [21] stated that *“the membranes used in MD are tested against fouling and scaling. Chemical feed water pre-treatment is not necessary. Intermittent operation of the module is possible. Contrary to RO, there is no danger of membrane damage if the membrane falls dry.”* Indeed, for years it was widely accepted that MD has this described ability to withstand dryout from intermittent operation. In fact, this is how most solar-powered MD plants operated, intermittently (shutting down overnight) and allowing the membranes to fall dry for hours every day [21, 22, 23, 24]. Intermittent operation can also result from unstable solar conditions or an uneven distribution of flux [24]. In contrast, the present review shows that while MD membranes are relatively resistant to fouling, they remain vulnerable to it and often require well engineered designs and operating methods to avoid and mitigate damage or destruction of the membranes by fouling. These design choices, especially in the case of inorganic scaling, are often related to maintaining the concentration of ions and the temperature at the membrane interface within limits where crystallization is not favored. Understanding temperature and concentration polarization effects (relative reduction in temperature and increase in solute concentration at the membrane interface compared to the feed bulk, due to the removal of energy and water mass through the membrane) therefore becomes key. Section 6.7 considers these factors in further detail while interpreting scaling data available in the literature.

Importantly, current MD membranes are adapted from microfiltration and similar markets, as yet there are no commercially available membranes specifically made for MD desalination [17]. An aim of this paper is to summarize differences in membrane properties for desalination from the literature so as to provide a background for the development of future, specialized membranes. The paper also aims to better understand fouling mitigation methods, and the effects and risks of different foulants.

2 Types of fouling in MD

Fouling is commonly defined as the accumulation of unwanted material on solid surfaces with an associated detriment of function. The types of fouling that can occur in membrane systems and therefore potentially found in MD systems can be divided into four categories: inorganic salt scaling or precipitation fouling, particulate fouling, biological fouling, and chemical membrane degradation [25, 26, 27, 28]. The appropriate mitigation methods vary dramatically for each of these [29, 30]. The causes also vary strikingly, although particulate fouling can be closely related to the others, as a result of coagulation. It is therefore most practical to analyze each of these four types separately. After MD was introduced in the late 60s, the first commercial applications for MD were in the food and semiconductor industries, not desalination [30, 31]. Since 1985, the number of publications dealing with MD desalination has increased [31, 32]. As a result, expectations for the types of scaling in MD are often inferred from other desalination technologies, particularly RO. While both technologies involve mass transfer through membranes, significant differences related to fouling exist, notably the significantly higher operating temperatures of MD, as well as the hydrophobic properties of MD membranes, the presence of temperature gradients in MD, and the larger pore sizes in MD [3, 33]. Also, MD lacks the high pressures of RO which are generally believed to aid the formation of compacted cake scales.

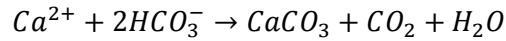
2.1 Inorganic scaling in MD

Study of inorganic scaling dominates the fouling literature for MD. Inorganic scaling, or simply scaling, in RO and MD generally falls into one of three categories: alkaline, non-alkaline, and uncharged molecule scale [14, 34]. Alkaline salts, or basic salts, have a tendency to make a solution more basic when added through hydrolysis, forming hydroxide ions. Generally, acidifying solutions below pH 7 decreases the tendency for many alkaline salts like calcium carbonate to scale or precipitate [35]. Non-alkaline salts include most other charged ions that dissolve in water without pH-raising tendencies [36].

Uncharged molecules that may scale, such as silica, are generally less soluble than salts because the charge on salts allows highly polar water molecules to break up and dissolve the salts. Uncharged scale can be considered with particulate scale [37], and is done so in this work.

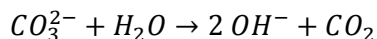
2.1.1 Alkaline scale in MD

Calcium carbonate is perhaps the most common scale in thermal desalination systems, often limiting operating conditions in brackish, groundwater, and seawater desalination [19, 38]. In thermal and RO desalination, CaCO_3 scale is regarded as a pervasive scale and among the first to reach supersaturated conditions in many feed solutions [38]. Calcium carbonate scale often forms after the breakdown of bicarbonate, HCO_3^- , as shown in the equation below:



For typical MD conditions, the breakdown of bicarbonate plays the dominant role in calcium carbonate precipitation [39]. However, the carbonate equilibrium and scaling is more complex than this simple equation implies. Increased pH and higher carbonate concentration are strongly associated with calcium carbonate scale [40]. The solubility of CaCO_3 changes dramatically with the concentration of CO_2 , and may decrease at higher temperatures as CO_2 comes out of solution, which raises the pH [19, 41]. Adding to this effect, CaCO_3 has inverse solubility, so high temperatures will decrease its solubility irrespective of CO_2 concentration [39]. According to Shams El Din, in typical thermal desalination systems such as MSF, a temperature of 37°C can be considered as the minimum temperature for the formation of CaCO_3 from mildly concentrated ocean water [42], which is well below the typical operation temperatures of MD ($60\text{--}80^\circ\text{C}$). However, the alkaline scaling process is strongly dependent on many factors such as heat transfer rate, brine concentration, residence time, flow conditions, etc. [19].

In general, bicarbonate dissociates more readily with increased temperatures. Notably, at higher temperatures carbonate has a tendency to hydrolyze into carbon dioxide [43], as follows:



This reaction makes the solution more basic, which influences the solubility of other scales, notably making $Mg(OH)_2$ more likely to precipitate. Carbon dioxide gas may come out of solution; this process is related to thermal water softening that can be used as a pretreatment strategy and has been discussed in the fouling mitigation (Section 5).

Calcium carbonate precipitates can take six different forms. Three anhydrous crystalline polymorphic forms may occur, known as calcite, aragonite and vaterite. These forms, all $CaCO_3$, differ in crystal morphology, color, hardness, and refractive index [44]. Three hydrated forms occur as well: amorphous calcium carbonate (ACC), calcium carbonate monohydrate (MCC), and calcium carbonate hexahydrate (CCH) [19, 45, 46, 47, 48]. Calcite is the most stable form found in MD system operation, but vaterite is common as well [49, 50]. In MD experiments, it was found that calcite formation was promoted by laminar flow [49]. Aragonite has been observed for MD as well [51], but it is relatively rare. The form of calcium carbonate is highly dependent on temperature, as seen in Figure 1 [39].

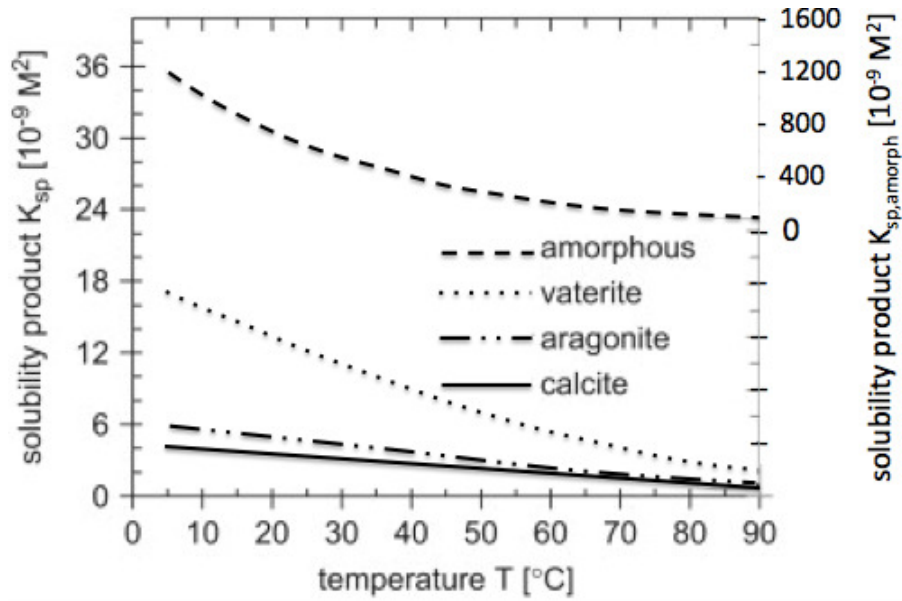


Fig. 1. Solubility of several forms of calcium carbonate in water as a function of temperature [52].

Importantly, calcium carbonate scale in MD is usually only observed at relatively high saturation indices (SI). However, the presence of a microporous membrane substantially reduces induction times in CaCO_3 precipitation, causing an increase in nucleation rate regardless of the SI index [53, 54]. With hollow fiber membranes, Gryta observed that for saturation indexes between 5 and 20 (supersaturated), which he considered low levels, the induction period for CaCO_3 scale exceeded 30 min for tests ranging from 20°C to 100°C [39, 55]. Fei et al. [50] found that the system required very high SI values for precipitation of CaCO_3 in MD, recording concentration 32 times higher than saturation concentration to initiate scaling for calcite [50]. Fouling of CaCO_3 may be highly variable. As solubility decreases significantly with temperature, Gryta recommended a feed temperature below 80°C to avoid calcium carbonate scale for experiments with lake water [39]. Although more common at higher temperatures due to reduced solubility, calcium carbonate scale has been an issue for MD even at low temperatures, such as 40°C in a study on untreated tap water with stacked membrane modules [56].

Calcium carbonate fouling can even occur at ambient temperatures such as in reverse osmosis at sufficiently high concentrations [38].

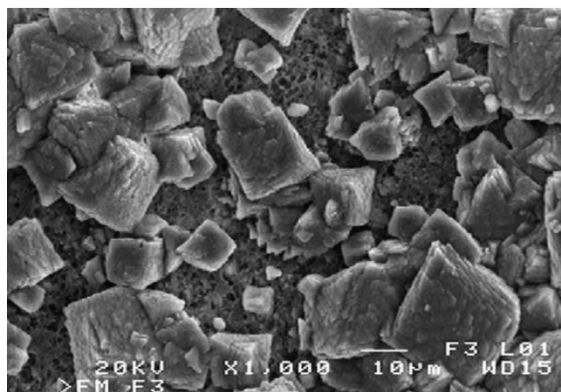


Fig. 2. SEM image of calcium carbonate scale on a polypropylene Accurel PP S6/2 membrane surface with tap water feed for long duration DCMD experiments. Experiment performed with 86°C feed and 20°C distillate [57].

Studies of calcium carbonate scale in MD have consistently found that pure calcium carbonate scale causes significant flux decline, and that it is generally nonporous in nature [39, 58]. However, it has also been found that the feed flow rate can modify the morphology of the carbonate deposits. Fig. 2 illustrates CaCO_3 crystal scale formation under small Reynolds number flow in hollow fiber membranes. In general, lower flow rates promote the growth of bigger crystals and more compact scaling layers, while higher flow rates reduce the size of the crystals and create comparatively more porous layers [39]. The flux decline varies widely, from zero or near zero to overall declines as high as 66% [59]. Furthermore, many experiments have found that calcium carbonate penetrates and scales in pores [58]. The scaling of calcium carbonate frequently causes wetting and thus results in contamination of the permeate by the feed [2, 49]. Long term performance studies, on the order of thousands of hours, found that calcium carbonate was consistently associated with wetted membranes, while deionized water experienced no such wetting [57]. Discussion of membrane damage from calcium carbonate scale can

be found in the following sections, and results of calcium carbonate experiments, including flux decline or fouling rate, are detailed in Table 1.

Notably, some studies have pointed out that the content of impurities in the CaCO_3 solutions used as feed can definitely play a role in flux decay. For example, He et al. [50] reported almost negligible impact on permeate flux using a very pure CaCO_3 solution. Fast homogeneous precipitation in the bulk solution and transport of CO_2 across the membrane explained the negligible membrane scaling, which is in good agreement with the results presented by Nghiem et al. [60].

Co-precipitation of foulants is common in desalination systems, and complicates the prediction of scaling behavior. Calcium carbonate co-precipitation has been frequently observed in MD systems, especially with calcium sulfate [58]. However, systematic studies of co-precipitation are lacking [25, 61]. Gryta found that CaCO_3 co-precipitation with CaSO_4 resulted in bimodal crystal size distribution, using scanning electron microscopy with energy dispersive X-ray spectrometers (SEM-EDS) post mortem analysis. Importantly, co-precipitation with CaSO_4 was found to weaken the negative effects of CaCO_3 , including reducing wetting and reducing membrane damage [58]. However, in a different paper, Fei found that co-precipitation of CaCO_3 and CaSO_4 caused an increased flux decline relative to CaCO_3 alone [50]. Studies on CaCO_3 and CaSO_4 precipitation kinetics have reported that an increased carbonate level may make CaSO_4 scale more tenacious and fine, but slows the rate of CaSO_4 precipitation [61]; this may explain the seemingly conflicting results in literature on the co-precipitation of these two compounds.

Curcio et al. [25] analyzed the fouling of CaCO_3 in the presence of humic acid (HA), with synthetic seawater concentrated 4 to 6 times. They found that the presence of other ions, including magnesium, sodium, sulfate, and HA, all inhibited the precipitation of CaCO_3 [25], which agrees with other studies [25, 62]. With 2 mg/L of HA present in hollow fiber membrane MD, the induction time of CaCO_3 was increased from 16 to 30 seconds [25]. It was found that HA increases the interfacial energy of

vaterite by 7%, from 45 to 48 mJ/m² [25, 62]. Other authors have shown that different humic substances, such as humin or fulvic acid, have dissimilar degrees of inhibition on calcite growth [25, 63].

Scaling literature predicts that the interactive effects of mixed salt solutions are significant and can alter the thermodynamics of precipitation [64]. Gryta found that when CaCO₃ co-precipitated with iron oxides, the scale was porous, and the flux reduction was not very high [26].

Several magnesium scales may also be a concern in MD for feed solutions with high levels of Mg²⁺. Magnesium hydroxide is another commonly observed alkaline scale in desalination applications, especially in groundwater, albeit not nearly as pervasive as calcium carbonate scale. Like CaCO₃, it exhibits inverse solubility with temperature, increasing its scaling propensity in MD [39]. Gryta tested lake-derived tap water with an Mg concentration of 15 mg/L in a Direct Contact Membrane Distillation (DCMD) system, and found that Mg(OH)₂ scaling occurred at above 348 K.

2.1.2 Non-alkaline scale in MD

Calcium sulfate is one of the most common non-alkaline scales that occur in membrane systems [19]. In thermal desalination, CaSO₄ scale is regarded as a tenacious and very adherent scale [58], and it has behaved as such in MD processes as well [58]. Cleaning calcium sulfate is relatively difficult compared to alkaline scales, so modifying operating conditions to avoid such scale is the most common method of mitigation [19]. Calcium sulfate scale may occur in one of two hydrate forms, the dihydrate CaSO₄·2H₂O (gypsum) and the hemihydrate CaSO₄·0.5H₂O (Plaster of Paris), or as an anhydrite, CaSO₄. The form precipitated depends strongly on temperature, with gypsum common around 20°C [19, 65], and the anhydrite form more common at higher temperatures. Calcium sulfate solubility peaks around 40 °C [58], but does not vary dramatically across typical MD operating conditions. A study by Gryta on calcium sulfate in MD found that the concentration of sulfate ions should not exceed 600 mg/L, but up

to 800 mg/L can be tolerated if bulk removal is available [58]. The study, specifically focused on CaSO_4 scaling in MD, found that membrane damage caused wetting and leaking and that it prevented further use of the membrane [58]. Gypsum scale was found to scale and penetrate the membrane pores. SEM images revealed needle-like gypsum crystals in typical orthorhombic and hexagonal prismatic needle. The crystals were tightly packed and tended to grow outward from initiated sites. As a consequence, exponentially worsening flux decline was observed, roughly experiencing a 29% decline over 13 hours [58]. Studies suggest that a supersaturated condition alone is not enough to start the crystallization of CaSO_4 on the membrane surface. Sufficiently long induction times (i.e., 53, 43, and 30 h for feed concentrations of 500, 1000, and 2000 mg/L of CaSO_4 , respectively) [60] are also a requisite [60]. This long induction time suggests a strategy to control the CaSO_4 membrane scaling.

Calcium phosphate, another potential scale, is a non-alkaline scale that has frequently occurred in wastewater treatment and in RO membranes [19, 66, 67, 68]. Phosphate often exists in water supplies as phosphoric acid, which is relatively weak and which dissociates through several stages; significant concentrations of phosphate ion do not occur until the pH becomes relatively basic. Therefore, maintaining a low pH is an effective method to avoid phosphate scale [19]. It is often treated with use of dispersants in nanoparticle form in the feed as well [19]. However, calcium phosphate scale has not been found in the MD desalination literature. A most likely potential risk of calcium phosphate scaling arises when phosphates additives are used as antiscalants. These additives prevent calcium carbonate precipitation by sequestering Ca^{2+} . However, under relatively high temperatures and neutral pH (MD conditions), the rate of polyphosphate hydrolysis increases [69] decreasing the scale inhibition efficiency and creating a potential for calcium phosphate scaling [70].

MD experiments on non-alkaline magnesium scale have been performed as well. Tung-Weng et al. [71] found that MgCl_2 and MgSO_4 scale significantly more on polytetrafluoroethylene (PTFE)

membranes compared to polyvinylidene fluoride (PVDF) membranes in a flat sheet module. They further report flux rate reduction of about a 86% of the initial value with the addition of 0.1% of either MgCl_2 or MgSO_4 to a 4.4% NaCl solution. In contrast, increasing the NaCl concentration to a 10% reduced the flux rate only to a 96% of the initial value, suggesting that the former registered decrease is a result of the Mg salts precipitating at the membrane surface rather than just a result of increased concentration and concentration polarization effect.

While not a common scale for most MD installations, sodium chloride, as the principal constituent of most desalination feeds, has been very widely used in MD literature including scaling studies. Sodium chloride, a non-alkaline scale, is characterized by a very high solubility and lengthy induction times. In scaling experiments by Tung-Wen Cheng et al. [71] under DCMD conditions at 50°C, increasing NaCl concentrations from 4.5% to 10% by weight only resulted in a 3-4% flux reduction, an expected level because of the decreased mole fraction of water at the membrane surface and not indicative of scaling-induced flux reduction, confirmed by the SEM micrographs which showed small levels of crystallization [71]. A MD paper by Fei He operating at 10% wt. NaCl reported similar results [7]. By contrast, extreme concentrations of NaCl, roughly 26-27.5 wt%, resulted in significant fouling [72]. After about 26% NaCl, the feed concentration seemed to asymptote while the flux dropped dramatically, indicating the onset of significant scaling. In the experiment, for roughly the first 250 min., 26% NaCl gave very good agreement to theory, indicating that even at this high concentration, the flux only dropped due to reduced vapor pressure, not scaling [73]. The extremely high solubility of NaCl relative to other salts and consideration of available sources of water indicates that virtually no natural source of water for desalination would have NaCl fouling as a concern. However, in cases of drying out membranes, NaCl will be among the salts to easily form on the membrane surface, as it will be discussed later. Other studies have shown that high concentrations of salts, exceeding saturation, can also cause wetting [58, 74].

2.2 Particulate and colloidal fouling in MD

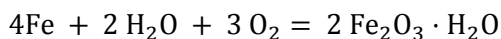
Particulate and colloidal fouling risk is common in many feed water solutions. Larger particles can often be addressed with modern filtration technology (i.e., UF, MF, NF), but smaller particles can be an issue in fouling. Notably, particles vary greatly by water source, and, in the case of surface water, by season. However, in many MD desalination pilots, the use of cartridge filters or screens is widespread and proves to be effective for particulate matter [75, 76, 77]. Compared to ocean water; lake, ground, and especially river water are more likely to have particulate fouling concerns. Particles and colloids include clay, silt, particulate humic substances, debris, and silica [78].

Silica is particularly notable because its small size makes it harder to remove with pretreatment stems such as microfiltration. Silica is generally found in water supplies in three forms: colloidal silica, particulate silica, and dissolved silica (or monosilicic acid). The latter can cause severe fouling in RO and FO systems when supersaturation is reached and the silica starts polymerizing on the membranes [19]. PH can also play a role in the ionization and polymerization of silica; nevertheless at most natural pH levels (including that of the SW, around 8.5) silica is relatively unionized, lowering the risk of scaling [79]. However, silica solubility increases with temperature and should be much less of a problem in thermal systems such as MD. In an MD experiment with hollow fiber membranes and tap water, Karakulski et al. [59] found precipitation of silica compounds on the membrane [59]. The silica clogged capillary membrane inlets, causing a gradual decline of the module efficiency. The flux declined by 30% after 1100 hours of operation, mostly during the first 200-300 hours. Removal of the foulant with acidification combined with drying the membranes restored the initial flow rates only briefly [59]. This happened despite nanofiltration of the feed upstream of the MD membranes [59]. SEM-EDS analysis indicated that the deposit consisted of silicon, with small amounts of iron, calcium, zinc, and chlorine. Unlike conventional fouling, which coats the surface and blocks the pores, the SEM analysis indicates that the

decline was not from a deposit layer, but from clogging membrane capillaries. The clogging reduced the feed flow rate, thus increasing temperature and concentration polarization, which reduced the module flux. The fibrous structure of the deposits blocked the foulants from further entry into the membranes capillary, stabilizing the flux [59]. This indicates that silica scale may be of significantly more concern in hollow fiber capillary MD systems than in flat sheet membranes. Silica fouling, while not causing a flux decline as fast as calcium carbonate, is a concern because it is difficult to clean. Acids that are commonly used to break down crystalline scale are not very effective on silica, which is uncharged [59]. When the feed has significant silica present, the authors recommend avoiding hollow fiber membranes with feed flow inside the capillaries.

An important and typically particulate foulant investigated in MD is iron oxide. Iron oxide fouling may consist of a variety of compounds, including iron oxides, iron hydroxides, and iron oxide-hydroxides [26]. These compounds are usually crystalline, and also may consist of hydrated forms. Iron oxide scale is not anticipated to be present in typical feed waters, but it is a risk of scaling due to the high propensity to rust on steel and even stainless steel parts in distillation systems. Corrosion fouling cannot only cause clogging problems, but also cause membrane damage by surface erosion (corroded flakes and chunks in motion through the narrow flow passages). Gryta found significant iron oxide fouling unexpectedly in a study on MD for treating effluents from regeneration of an ion exchange system in a water treatment plant [26]. However, the study found that iron oxide deposits did not significantly affect flux, undergoing only an 8% decline in permeate flux over 20 hours of operation. It was inferred that the iron scale was relatively porous. The composition of the iron oxides foulants was determined by x-ray diffraction, including maghemite, lepidocrocite, akaganéite, and hematite. It was found that the “iron oxides, hydroxides, and oxide-hydroxide” scales were crystalline [26]. These oxides exhibited high tendency to accumulate both on the membrane surface and within membrane pores.

The expected wetted corrosion reaction that causes iron oxide scale, also known as electrochemical corrosion, is as follows [26, 80]:



Corrosion reactions vary, but consist of oxidized forms of the metal and particles of positive, negative, or zero charge. Reactions also vary by oxygen content present [26]. In the various corrosion reactions, at least one of the products will be an oxidized metal, a metal cation, metal anion, or uncharged solid compound [26]. Oxidized metals may be Fe_2O_3 , FeO , or Fe_3O_4 ; iron metal cations are Fe^{2+} or Fe^{3+} ; metal anions include HFeO_2^- and FeO_4^{2-} ; and uncharged solid compounds include $\text{Fe}(\text{OH})_3$, Fe_3O_4 , and $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ [26]. The oxidation reactions are complex, and are affected by conditions in the feed, including salinity, feed composition, and oxygen content. Under oxygen limited conditions, black magnetite Fe_3O_4 is often formed. When other salts are present, such as Cl^- or SO_4^{2-} , they may be incorporated into iron oxides or hydroxides. Hydrolysis of Fe^{3+} ions may occur in basic conditions, from heating, or dilution of a salt with the ion. Hydrolysis may form hexaaquocation $\text{Fe}_3(\text{H}_2\text{O})_6^{3+}$, and its H_2O ligands again experience hydrolysis, creating FeOH or Fe_2O_3 . The oxides present and their crystalline structure generally vary by conditions of formation, including temperature, other ions present, and pH. The presence of water, high or low pH, and other dissolved ions are conditions existing in MD that encourage corrosion of steel elements [26].

Additional Iron Oxide fouling in Gryta's study occurred as a consequence of acid cleaning (HCl) of the feed side. The volatile acid was capable of getting through the membrane to a small degree as gaseous HCl, acidizing the permeate and causing oxidation of the stainless steel elements on the permeate side of the system. Even concentrations of less than 50 g/L HCl can lead to significant reaction with the stainless steel elements [26]. Therefore, Gryta recommends using acid resistant high-grade steel or plastic as materials for MD systems [26, 81]. However, it is important to note that Gryta

used very acidic conditions to clean the module, 18% and 36% HCl, which are relatively high compared to 3% or 5% HCl used in other experiments [26]. Therefore, acidic permeate may not be guaranteed to be a concern. The acid wash trials from the study are discussed in Section 5.7.7. The fouling layer was observed with SEM-EDS, as seen in Fig. 3, and small amounts of Cu, Zn, Ca, P, Al, Mg, Na, S, Cl and Si were also observed in the membrane.

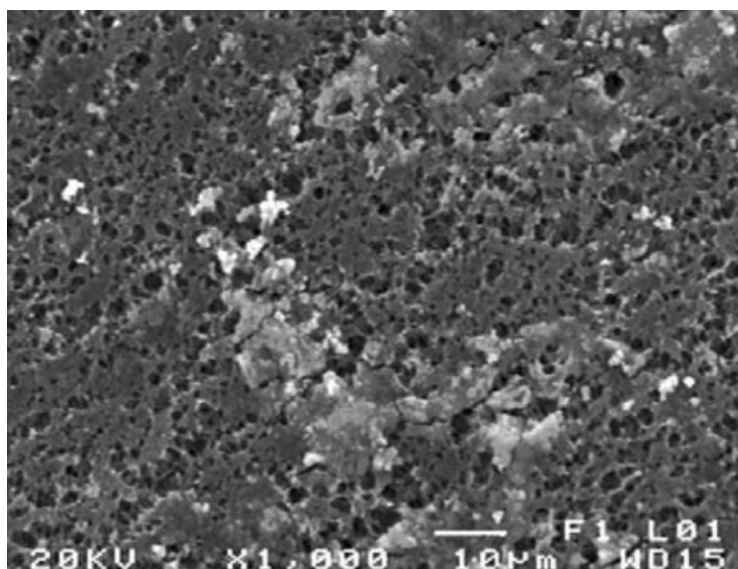


Fig. 3. SEM micrograph of the polypropylene membrane surface covered with iron oxides after cleaning with 18 wt.% HCl failed to remove them, with a 353 K feed and a 293 K distillate temperature [26].

Compared to other scale forms in MD, iron oxide can be judged as unlikely to occur with proper system design. It is relatively less harmful to permeate flux but still a major cause of wettability and very difficult to remove. The lower operating pressure typical of the MD process makes it possible to use plastic components, which can potentially eliminate most iron from the system.

2.3 Biofouling in MD

Biofouling of hydrophobic membranes applicable to MD has been a key research interest in the food, beverage, and wastewater industries [27, 82]. Many of the membranes used in MD originated in

these industries. The majority of these studies focus on very high chemical oxygen demand (COD) effluents, although recently MD biofouling studies have extended to MD for desalination [27]. The high COD content comes from using MD or similar systems for animal products processing, fermentation, and other processes [27]. For the sake of brevity, this review focuses only on biofouling relevant to clean water production.

Biofouling relevant to MD desalination includes bacteria, fungi, and biofilm studies. Biofouling is pervasive in most waters [78] and has been a critical issue for RO membranes [83] and it is likely to be a concern in practical MD systems. However, the operating conditions of the MD process, especially the high temperatures and salinity, can restrict to a great extent the microbial growth in MD installations [27]. As a consequence, the problems caused by biofouling in membrane processes including NF, UF or RO should not occur in such a high degree in MD systems. [84]. However, organic fouling can play a more important role in membrane wetting in MD.

2.3.1 Bacteria and biofilms in MD

Bacteria and microorganisms are pervasive in water systems. While chlorination is effective in killing bacteria, it can be damaging to many common MD membrane materials [78]. Bacteria can be very difficult to remove from membranes, as they excrete an extracellular polymer substance (EPS) to adhere to the surface [78]. In typical biofilm formation, bacteria colonize and excrete EPS, and then organic compounds accumulate in the film. These compounds are typically composed of polysaccharides, proteins, lipids, humic substances, nucleic acids and aromatic amino acids, and often contain trapped particles and absorbed substances [27]. These biofilms are typically 75-95% water and are relatively porous compared to alkaline scale [78].

Biofouling impairs MD process through wetting and pore blocking. Additionally, the relatively porous biofouling layers reduce diffusion and create a hydrodynamically stagnant layer of water at the

feed side [27]. Biofilms are mostly constituted by a hydrated EPS matrix which makes diffusion the main mass transport mechanism. Water diffusion coefficient in biofilms has been estimated to be 15% lower than that in bulk water [85], conferring biofilms an extra mass transfer resistance and increasing temperature and concentration polarization effect. As a consequence, they can hinder convective heat transfer to the membrane while favoring diffusion and conduction. The thermal conductivity of biofilms has been estimated to be around 0.57–0.71 W/mK (close to that of water), almost 75% less than that of inorganic scale (i.e. CaCO_3 and CaSO_4) [86].

In Krivorot et al.'s experiments on hollow fiber MD with ocean water and a high biological load (1×10^8 CFU/ml) at 40°C, permeate flux declined by 34% over 19 days [27]. However, minimal flux decline was detected in samples with normal biological loads. The high biological load was attributed to local wastewater spills to the sea. In the high biological load sample, a conditioning biofilm was formed in as little as 4 hours, and a recognizable biofilm was apparent after 28 hours. Over the 19 day experiment, all samples showed a biofilm. Temperature cycling to 70°C was found to reduce the biofouling behavior. In general, processes with a top brine temperature of 70°C minimized any biological presence [27].

In a study done by Gryta [84], MD was performed on a bioreactor with saline wastewater that contained yeast, *Pseudomonas* and *Streptococcus Faecalis* bacterium, and the fungi *Penicillium* and *Aspergillus*. The DCMD hollow fiber membranes failed to prevent *Streptococcus* bacteria from entering the distillate. With a temperature of 90°C and salts concentrated up to 300,000 ppm, no bacteria was detected at the membrane surface, indicating these conditions prevented bacterial growth. However, when the temperature was decreased to 80°C, bacteria and fungi were detected at the membrane (Fig.4).

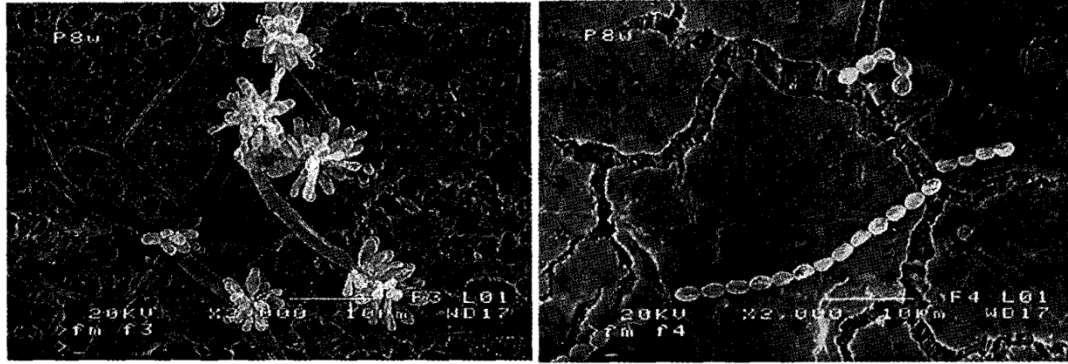


Fig. 4. Left: SEM image of *Aspergillus* fungi on MD membrane surface. Right: SEM image of *Streptococcus faecalis* bacteria, 65°C feed solution, at roughly 5 times the concentration of seawater [84].

Notably, while the anaerobic bacteria *Streptococcus* grew on the membrane, no aerobic bacteria were observed on the membrane, despite being present in the original feed. The same feed caused significant fouling in MSF and RO, but tolerable and unproblematic fouling in MD. Elevated temperature, significant salt concentrations, and low pH values all can hinder bacterial growth. Similar MD studies by Meindersma et al. using an AGMD system and pond water as feed, reported a flux decline after 800 h from biofouling. No organism break through was noted however [87]. In this same study, original flux was almost restored by reversing the direction of the flow.

Biofilms, especially in seawater settings, often contain more microorganisms in addition to bacteria. Although direct MD experiments with marine microorganisms couldn't be found in the literature, highly relevant superhydrophobic materials similar to MD membrane materials have been examined in seawater conditions. A study by Zhang [88] compared ocean fouling in submerged hydrophobic and superhydrophobic surfaces over 6 months. Polysiloxane and PTFE surfaces were examined. The results showed that the hydrophobic surface exhibited fouling within a day, but the superhydrophobic surface (contact angle 169°) resisted fouling for about three weeks. However, after 2 months, both surfaces were heavily fouled and wetted with 10-20% macroalgae, 5-10% barnacles, and

50-60% bryozoans, although they resisted the tubeworms, ascidians, and to some extent algae that covered the control plate. The loss of biofouling resistance was attributed largely to air bubble loss through the membrane, as the air dissolves into the surrounding water [88]. These results can be extended to MD surfaces, where seawater is passed on the feed side over a hydrophobic membrane.

Specific conditions for avoiding biofouling cannot be determined presently from the literature because biofouling depends on many factors such as: salt concentration, feed composition, residence time, pre-treatment, bacterium present, operating temperatures, membrane type and cleaning frequency [27].

2.3.2 Natural organic matter (NOM) in MD

NOM compounds at risk for MD are especially prevalent in wastewater and certain lake and ocean water samples. NOM includes various constituents such as proteins, amino sugars, polysaccharides, polyhydroxy-aromatics, and humic substances [89]. These compounds are often present where traditional biofouling is a concern, as they often provide sustenance to bacteria and may originate from similar processes. The fouling caused by NOM can affect both the permeability and the dissolved solids rejection of the membranes. Membrane fouling in the presence of organic compounds is affected by ionic strength, pH, ions present, membrane surface structure and chemistry, molecular weight, polarity, permeate flux, and hydrodynamic and operating conditions [34]. In general, hydrophilic surfaces are less susceptible to organic fouling [90, 91] but MD employs hydrophobic surfaces, making organic fouling a concern.

The principal NOM foulant is HA, a general term for complex mixtures of organic acids with carboxyl and phenolate groups [92]. HA is produced by biodegradation of organic matter, and it gives many swamps and rivers a characteristic yellow brown color [36]. HA are complex and vary greatly; molecular weights typically occur between 700 and 200,000 Daltons [93], and may even be above or

below this range. HA systems are thus typically measured with averages. For instance, the average HA particle in a solution may act as an acid with two and sometimes three free hydrogen atoms [92]. HA production in rivers and lakes is often seasonal, with large quantities produced annually from deciduous tree leaf decomposition. Importantly, HA may readily nourish bacteria, and thus may instigate significant bacterial fouling [27]. HA fouling in MD may vary based on feed composition, membrane hydrophobicity, temperature, membrane pore characteristics, and pH [94, 95]. For example, the addition of multivalent cations increases the electrolyte or ionic strength of the feed water and can favor the aggregation of the HA and therefore the fouling [96]. Divalent ions, including Ca^{2+} , act as binding agents to the carboxyl functional groups reducing the charge and the electrostatic repulsion between macromolecules and encouraging particulate precipitation [25, 97]. HA at 100mg/L concentration in a MD study with added CaCl_2 at 3.775 mM caused significant flux reduction of 40% on flat-sheet membranes [29]. This solution treated with MD produced a thick fouling layer, blocked pores, and increased heat transfer resistance [29]. In more acidic conditions, HA dissociates less because fewer Ca^{2+} ions are available [29, 98]. However, HA can also affect other types of scaling and has significant scaling inhibition effects on calcium carbonate (i.e. inhibit heterogeneous nucleation and increases induction time) as explained earlier [25].

Other metal ions (i.e., Fe^{3+} , Mg^{2+} , Al^{3+} , etc.) can also contribute to NOM fouling in a similar way: increasing the ionic strength and causing metal ion-induced aggregation [99]. In a study with UF hollow fiber polyethersulfone (PES) membranes, the presence of Fe^{3+} in the HA feed solution reduced the flux to one fifth of the original rate in one hour. The effects of Ca^{2+} and Mg^{2+} were similar but not as significant [100]. In this same study, the authors found that the use of EDTA as a chelating agent inhibited the crosslinking of HA induced by the presence of the metal ions and reduced the fouling.

HA deposits are typically loosely packed and porous and traditionally in UF and MF systems they are effectively eliminated through backwashing. In MD systems, they can be cleaned rather effectively with basic solutions. Srisurichan [29] found that HA fouling was easily removed with a 0.1 M NaOH solution, while still achieving full recovery of permeate flux. Alternating temperature changes, in one case between 25 °C and 35 °C, was found to clean HA as well, resulting in a flux recovery of 98.2% with proven repeatability [97].

3 Factors that influence scaling in MD

3.1 Temperature

Temperature is among the most dominant factors related to scaling and fouling of MD membranes. In particular, the solubility and crystal formation of salts vary widely over the temperature range relevant to the MD systems. Importantly, the solubility of individual salts may be positively or negatively correlated with temperature. For example, the solubility of sodium chloride increases with temperature, whereas those of calcium carbonate, magnesium hydroxide, and calcium phosphate decrease with temperature. This negative correlation of solubility with temperature is typical for alkaline salts, which depend on the breakdown of water into hydrogen and hydroxide in order to form scale; such dissociation increases at higher temperatures [36]. Salts such as calcium sulfate and calcium carbonate that exhibit inverse solubility are also often the closest to being saturated in desalination feed solutions (calcium sulfate concentration is higher in the case of seawater as a feed while calcium carbonate concentration is higher in ground water sources). Generally, for common feed solutions, increased temperature causes increased risk of scaling. Higher temperatures also reduce induction periods for some salts [101].

Temperature can have a significant effect on biofouling due to microorganisms' lack of tolerance for high temperature and also because of thermal effects on organic compounds. According to M. Krivorot et al.'s experiments with hollow fiber membranes, at temperatures above 60 °C, most environmental organisms will not function and hence not grow on MD membranes [27]. Temperature increase causes the decomposition of HA and other biological compounds. In fact, for RO membrane systems, temperature increase may be used as an effective cleaning method for HA [97]. However, for MD at higher temperatures, permeate flux increases: this may lead to higher concentration of organic compounds at the membrane interface due to the concentration polarization effect. Srisurichan [29] found that at higher temperatures, flux decline was greater for solutions containing HA, observing a 16% decline at 50°C and a 43% decline at 70°C. Severe protein fouling was observed at temperatures higher than 20–38°C for aqueous solutions containing organic compounds at representative concentrations (i.e., wastewater, NOM, bovine serum albumin, etc.) [30, 84, 102] but it was practically absent at lower temperatures [103]. Notably, hydrophobic surfaces show an especially high tendency to get fouled by proteins [104], making MD membranes problematic for waters containing proteins, amino sugars or polysaccharides [105].

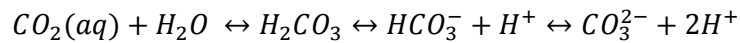
3.2 Dissolved gases

Dissolved gases are present in almost all feed waters of interest in desalination [36], and these gases may have some limited effects on scaling and fouling in MD. Gases dissolved in feed water, as well as those resulting from chemical processes such as the breakdown of bicarbonates, travel into the membrane along with the water vapor, providing an additional diffusive resistance for the water vapor [39, 72].

The effect of dissolved gases on fouling is indirect and small; dissolved gases impede the permeate flow process, reducing concentration polarization and scaling. This occurs because dissolved

gases in the feed stream may flow into the membrane pores, providing mass transfer resistance to water vapor, and may also contribute to mass transfer resistance in the air gap after the membrane (depending on the system configuration). The effect is to reduce the condensation heat transfer rate, possibly making the system mass transfer limited on the air-side, thus reducing the overall vapor flux [16]. On the other hand, the absence of dissolved gases can increase membrane wettability by removing the air trapped in the membrane pores, which was experimentally confirmed by Schofield et al. [106]. The presence of these gases in the membrane can act as a barrier to fouling. Therefore, reducing dissolved gases by deaeration or other means may be expected to increase fouling potential [16].

Dissolved gases, especially carbon dioxide, may alter the pH of the solution, affecting the solubility of various salts as described previously. Dissolved CO₂, common in many feed waters and often produced by breakdown of calcium carbonate in ground water, may acidify the water by the creation and dissolution of carbonic acid as follows [28]:



So despite increasing carbonate concentrations, typically increased dissolution of CO₂ reduces scaling by the associated pH decrease. This result may differ depending on temperatures, concentrations, and pH, as discussed in Section 5.1 (on thermal softening). Dissolved gases or lack of them may significantly affect biofouling, as the presence of dissolved oxygen supports aerobic bacteria and microorganism fouling. Therefore, deaeration of oxygen may be used to inhibit microbial growth.

3.3 Water source

As seen in previous sections, fouling likelihood and type of fouling in MD depend on the salts and other foulants present in the feed water and thus are highly dependent on the water source.

Generally, specific sources have fairly consistent conditions and thus consistent expectations for fouling, although surface waters' quality and algae blooms may be seasonal.

Possible water sources for desalination include lake, river, ocean, ground waters as well as industrial waste water. Generally calcium carbonate saturation is a significant concern in most water sources relative to other salts. However, water sources are variable enough that other insights on types of fouling susceptibility may not be comprehensive. Compared to ocean water, lake and river water are typically characterized by high silica content, biological compounds, suspended solids, and calcium concentrations, but vary widely between different rivers and lakes [107]. Due to the low salinity of these waters, MD use is unlikely, but electrodialysis desalination may be used if slightly reducing salt concentrations is desirable. Ocean waters often have relatively high scaling potential for calcium sulfate compared to other surface waters, as well as calcium carbonate, possible biological compounds and organisms, and a significant dry-out concern from very high levels of sodium chloride [36]. Groundwater sources are perhaps the most variable. Groundwater often has high levels of salts compared to non-ocean surface water [108], and may be especially rich in calcium, bicarbonates, magnesium and sulfate. Groundwater is also commonly rich in iron (reduced Fe^{2+}) that can oxidize in contact with air and form iron hydroxides (nearly insoluble in water), producing heavy fouling. Due to its variability, groundwater may cause some of the worst scaling and flux reduction seen in desalination systems. Finally, the composition of industrial wastewater varies depending on the source, but can be extremely saline with a variety of dissolved metals (as in, e.g., produced water from hydraulic fracturing operations). The compositional variability of these waters makes it difficult to single out problem-causing compounds in a general fashion.

Gryta investigated MD fouling for water from river, lake, and groundwater sources for hollow fiber MD [72]. In that study, within 20 hours of MD testing, river tap water experienced the largest flux

decline, lake tap water experienced the smallest flux decline, and groundwater had a flux decline in between. The flux decline was largely caused by calcium carbonate, with bicarbonate ion concentrations being the limiting factor for causing scale.

In contrast, seawater has very consistent constituents, generally has greatly more sodium chloride than other bodies of water, very high salt content overall, and lower concentrations of many other ions than some lake or river waters. Due to typically low concentrations of magnesium and organic HA, seawater may be less prone to fouling by these components than other sources of water. Like many tap water sources, calcium carbonate is a significant component of expected scale for ocean water, but is even more of an issue in ground and lake water. Calcium sulfate is also a concern for scaling in seawater [109]. Ocean water is susceptible to a variety of biological fouling types, including algae and microorganisms that may differ significantly from inland waters [27]. Curcio et al. found scaling of CaCO_3 in DCMD of seawater at concentration factors of 4-6 and 40°C [25]. The consistency of seawater salts and literature studies indicate that calcium sulfate, calcium carbonate, particulate fouling, and biofouling are the expected fouling concerns in seawater.

Wastewater treatment has also been attempted through MD, and fouling studies can even be found in literature. Wastewater contains numerous fouling compounds that may affect the flow significantly, especially biological compounds. In a study with hollow fiber MD membranes, a rapid decline in permeate flux was observed in solutions containing HCO_3^- , expected from CaCO_3 fouling [110]. The presence of bacterium *S. faecalis* was detected as well, but temperatures of 85°C prevented bacterial growth. Silica was detected as a deposit as well. Wastewater constituents vary dramatically by the source, so inorganic scale types may be hard to predict, although organic fouling of various kinds is common in wastewater.

4 Scaling and fouling effects on MD operating parameters

4.1 Wetting and permeate water quality change

An important requirement for the MD process to perform well is that the membranes have to remain hydrophobic, thus allowing only vapor and not liquid water to pass through. Wetting refers to the process whereby the membrane starts allowing liquid water to flow into the membrane pores. While wetting can be caused by the pressure in the feed channel exceeding the liquid entry pressure (LEP), fouling induced wetting is the concern for real MD systems. Hydrophobicity of the membrane material is the reason why the interior of the pores are not normally wetted. Scaling along the pores with salt crystals growing into the pore tends to reduce the net hydrophobicity and non-wetting character of the pores. Wetting caused by scaling is an important long-term performance issue for MD since the maximum concentration of the salts is expected to occur close to the pore openings where water evaporates, therefore the potential for precipitation is highest in this region.

Once wetting occurs, the MD process is affected in several ways. In several studies, water has been observed to more easily penetrate adjacent pores [25, [59, 57, 26, 84]. Further crystallization can also lead to accelerated wetting. Once the membrane is wetted, MD is no longer selective and hence doesn't achieve its goal of desalination or other types of separation. Figure 5 shows that scaling can occur within the membrane pores following wetting. The presence of this layer of salt deposits renders the top surface more hydrophilic, making it more prone to wetting [24, 111, 112]. In some cases, such propensity to wetting was shown to affect only the top-most portion of the pores of a polypropylene (PP) membrane, leaving the pores beneath un-wetted [112]. In other cases, wetting across the whole membrane thickness was reported, which has been seen in PTFE and PVDF membranes, evidenced by the presence of salt crystals at various depths of the membrane's cross section [24, 102].

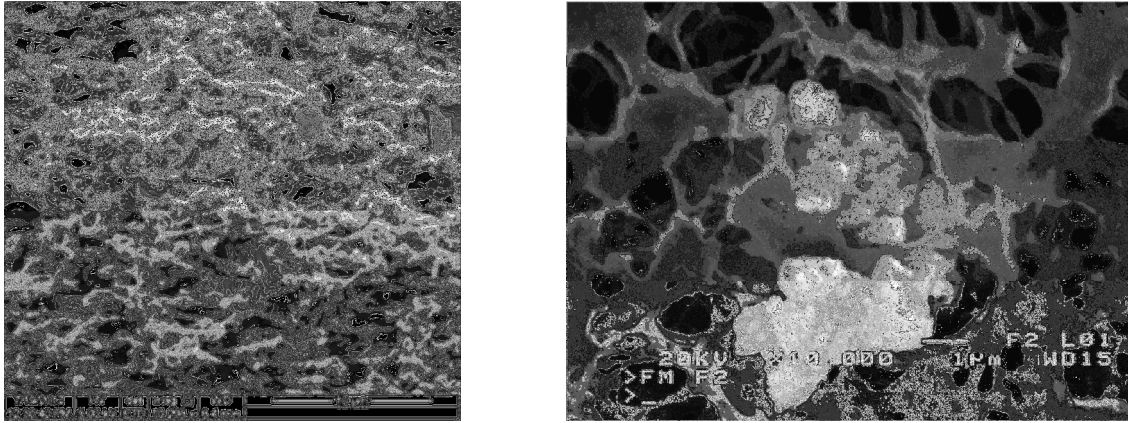


Fig. 5. Left: Cross sectional SEM image of salt deposits inside a PVDF membrane after the 4th week of real seawater exposure [51]. Right: Cross sectional SEM image of deposits located inside a PP MD membrane after rinsing with HCl solution [35].

Pore wetting may degrade the performance of the MD process either because it reduces the interface for evaporation and therefore the production of vapor, or because, once a pore is wetted, saline water may flow through and contaminate the distillate [24, 59, 57, 102, 112, 113].

Finally, one very interesting impact of scaling on MD membranes is the occurrence of “negative flux,” reported by Guillen-Burrieza et al. [24] in one of their PVDF membrane tests. According to Guillen-Burrieza et al. [24], one of their fouled PVDF membranes showed a flux from the permeate side to the feed side, until a minimum trans-membrane temperature gradient of 10°C was reached, after which a positive flux (from feed to permeate side) was obtained. They attributed this negative flux to the osmotic pressure created by the localized high salinity at the membrane surface on the feed side due to the deposited salt layer. Franken et al. [114] observed a 30% decay in DCMD flux over a period of one month and postulated that this must be a result of membrane wetting and possibly “back flow.” Laganá et al. [115] has also reported a similar phenomenon.

4.2 Permeate flow rate reduction

Relatively few studies report data on fouling and its effect on the MD process performance. Different experiments report fouling differently, so a comparative metric is desirable. The average percentage flux reduction is defined as the reduction in flux as a percentage of the initial flux. The rate of change of the flux reduction can be used to examine the rate at which fouling lowers flux, as shown:

$$fouling\ rate\ \left[\frac{\%}{hr}\right] = \frac{flux_{initial} - flux_{final}}{flux_{initial}} \times \frac{100}{t}$$

which may eventually level off at some system steady state. In a modeling context, flux decline is associated with a decrease in the MD coefficient B. The MD coefficient, or B coefficient ($\text{kg m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$), characterizes the permeability of a membrane under the MD process. The coefficient B is a function of the membrane material properties (i.e. pore size, thickness, etc.) and the operating temperature [116].

The degree of permeate decline varies widely by experiment. In some processes, no decay occurred after months of operation [3, 117], while in others flux decline was as high as 66% in less than two days [59]. Permeate decline is dependent on the porosity of the scale that occurs and the thickness of scale layer [26], thus it is largely dependent on the salt or type of scale, the local concentration, and the scale's solubility under the given operating conditions. Decline may be slow and gradual [118], or it can occur rapidly from rapid crystal growth after exceeding critical levels of supersaturation [73]. As discussed previously, uncharged fouling including biofouling and iron oxide fouling were found to be relatively porous, while inorganic scale such as calcium carbonate were relatively nonporous.

Theory on fouling in membrane systems suggests different profiles for decline in flux over time based on different models of fouling [119]. Srisurichan et al. [119] applied the cake model of scale deposition to DCMD experiments using HA as a foulant with NaCl and CaCO_3 in the feed and found that it was capable of explaining the decline in flux. This paper illustrates that previous research on the use of

additional transport resistances to model a fouling layer can be adapted to MD systems, accounting for the fact that the driving force in MD is a vapor pressure difference rather than a pressure difference.

Table 1 shows data gathered from publications that report fouling induced flux reduction. The program WebPlotDigitizer [120] was used to analyze the graphs and estimate initial and final flux values and the elapsed time between them. This data is used in subsequent analysis to draw conclusions about the effect of system parameters on rate of fouling.

Table 1: Fouling induced flux changes reported in the literature.

	Study	MD configuration	Feed	Feed, Permeate Inlet Temperatures [°C]. Permeate Pressure (P_p) [kPa] for VMD	Initial Flux [L/m ² day]	Final Flux [L/m ² day]	Time of experiment [hours]	Additional Information	Average Fouling Rate [% flux decrease/hr]
1	[121]	VMD	7 ppt NaCl solution	60, $P_p = 1.5$	680.2	597.4	150.0	$T_{ind} = 100.3$ hrs	0.08
2			7 ppt NaCl solution	40, $P_p = 3$	391.0	332.2	150.0	$T_{ind} = 90.4$ hrs	0.10
3			Ground Water	60, $P_p = 1.5$	529.7	376.1	75.0	$T_{ind} = 40.9$ hrs	0.39
4			Ground Water + 0.1 mol/l HCl	60, $P_p = 1.5$	529.8	506.9	70.0		0.06
5	[72]	DCMD-hollow	Ground water GW	85, 20	400.0	350.0	23.0	$v_f = 0.4$ m/s	0.54
6			Boiled GW	85, 20	395.0	383.0	23.0		0.13
7			Tap Water TW1	85, 20	418.0	247.0	44.0		0.93
8			Boiled TW1	85, 20	412.0	320.0	38.0		0.59
9			Tap water TW2	85, 20	795.0	705.0	65.0		0.17
10			Boiled TW2	85, 20	720.0	590.0	36.0		0.50
11			Tap Water TW1 +	85, 20	407	404	27.0		0.03

2			HCl pH = 4		.0	.0			
1			Tap Water (CaCO ₃)	90, 20	729	653			
3					.7	.1	24.7		0.42
1			Tap Water (CaCO ₃)	85, 20	612	577			
4					.0	.0	25.0		0.23
1			Tap Water (CaCO ₃)	80, 20	548	534			
5					.0	.0	24.4		0.10
1			Tap Water (CaCO ₃)	80, 20	414	242		$v_f = 0.3$ m/s	0.96
6					.4	.5	43.0		
1			Tap Water (CaCO ₃)	80, 20	476	416		$v_f = 0.6$ m/s	0.19
7	[39]	DCMD-hollow			.0	.1	66.0		
1			Tap Water (CaCO ₃)	80, 20	537	506		$v_f = 1.0$ m/s	0.06
8					.7	.4	89.8		
1			Tap Water (CaCO ₃)	80, 20	599	479		$v_f = 1.4$ m/s	0.24
9					.3	.5	82.9		
2			Waste water	85, 20	321	288			
1	[10	DCMD-hollow			.0	.0	47.5		0.22
2	2]		Waste water boiled	85, 20	364	348			
2					.4	.8	45.0		0.10
2			CaSO ₄ (batch mode)	60, 20	265	32.		$T_{ind} =$ 28.6 hrs	2.35
3					.3	9	37.3		
2			Na ₂ SiO ₃ (batch mode)	60, 20	265	172		$T_{ind} =$ 21.6 hrs	0.59
4					.3	.6	59.3		
2			CaSO ₄ (batch mode)	60, 20	739	38.		$T_{ind} =$ 4.4 hrs	6.12
5	[10	DCMD			.2	4	15.5		
2	1]		CaSO ₄ (batch mode)	50, 20	496	100		$T_{ind} =$ 8.5 hrs	4.40
6					.8	.8	18.1		
2			CaSO ₄ (batch mode)	40, 20	259	28.		$T_{ind} =$ 30.1 hrs	2.40
7					.2	8	37.0		
2	[11	DCMD	Seawater	60, 20	570	344		$v_f = 0.14$ m/s	0.05
8	8]				.2	.6	720.0		
2			MF treated Seawater	45, 20	350	276			
9	[11	DCMD			.0	.1	168.4		0.13
3	3]		Raw Seawater	45, 20	230	185			
0					.6	.0	167.3		0.12

4.3 Increased temperature and concentration polarization

Scaling may increase temperature and concentration polarization by creating a hydrodynamically stagnant or slow moving layer of water at the surface of the membrane [27, 111]. If scaling impedes flow velocity, which occurs particularly in hollow fiber membranes, the slower velocity will increase temperature polarization as the water residence time is lengthened [122]. The deposited

salt layer creates an additional thermal resistance, reducing the heat transfer coefficient from the feed bulk to the evaporation and condensation interfaces [105], and in some cases possibly accelerating the degradation of polymeric materials [111]. As explained in Section 2.3.1 Bacteria and Biofilms, a fouling layer impedes convective heat transfer in the bulk. Although fouling layers have greater thermal conductivities than the polymers composing the membrane, they do not increase temperature polarization directly. Instead, they impart mass transfer resistance, altering the heat transfer associated with evaporation and consequently increasing the temperature polarization [123].

The mass transfer coefficient close to the membrane surface is also often reduced due to the presence of biofilms or other foulants. This leads to an increase in the concentration of dissolved ions close to the membrane interface, reducing the local vapor pressure and thereby reducing flux, in addition to increasing tendency to precipitate [124].

Recent studies by Goh et al. [123] found that hydrophilic biofouling on membrane surfaces that reduce the average pore size of the evaporating surfaces can reduce the MD driving force by causing vapor pressure reduction, as described by the Kelvin equation.

4.4 Membrane damage and chemical degradation

Many studies, especially at the lab-scale, have reported physical damage to the membrane as a result of scaling [24, 35]. The damage to the MD membrane was observed to take several forms. These include: a reduction in hydrophobicity of the membrane surface by altering its chemistry [24, 112], 119]; alteration of the membrane's pore structure and pore size distribution [24]; reduction in the membrane's mechanical strength [24]; reduction in the membrane's permeability via surface blockage [24, 112]; and the formation of defects (e.g. cracks) within the membrane structure [24]. In most cases, the damage was associated with a deterioration of the distillate quality (lower salt rejection) [22, 23, 35,

57, 77]. The most frequently reported membrane damage when scaling occurs during MD is the formation of a scale layer on the membrane's top surface in contact with the feed (Figure 6). This layer is composed of insoluble salts, such as CaSO_4 , MgCO_3 and CaCO_3 [24], in addition to NaCl [24, 112].

Interestingly, membrane damage due to scaling can lead to either higher or lower flux than that of an intact membrane. While lower flux can be attributed to pore blockage by scale deposits on the surface [35, 112], higher flux is primarily due to pore wetting, usually accompanied by a lower salt rejection [24, 77]. For example, Hsu et al. [113] reported severe fouling and flux decline, but without permeate quality deterioration, when PTFE membranes were used to desalinate pre-treated sub-tropical seawater, with high NOM and biofouling potential. Ultrasonic cleaning was applied periodically in this study, which restored most of the flux. However, the data suggest a small degree of irreversible fouling, as evidenced by a slow reduction in the flux with time [113].

Guillen-Burrieza et al. [24] reported that the scale layer formed on the membrane surface during MD operation reduced the gas permeability of the membrane [24]. However, MD experiments showed apparently higher permeate fluxes for the fouled membranes which were attributed to heavy pore wetting processes caused by the inorganic scaling and membrane damage. Post-deposition washing with de-ionized water did very little to remedy that. Gryta et al. [112] reported similar findings for PP MD membranes exposed to NaCl solution as feed. A similar behavior was also reported for fouled membranes [105] when a biofouling protein layer was formed after concentrating saline wastewater.

Changes in membrane morphology upon fouling are the second observed damage in MD membranes. Gryta et al. [112] noticed only a minor change in membrane porous structure in PP membranes and concluded that the polymer material used for PP membranes production exhibited good thermal stability [112]. This was not the case for the PVDF and PTFE membranes studied by Guillen-Burrieza et al. [24], who conducted a study on the effect of cyclic wet-dry MD operation using

seawater. The latter reported a noticeable variation in membranes' porosities and a shift in their pore size distributions (PSD) upon fouling after two weeks of seawater exposure. The shift in PSD was more pronounced in the PVDF membranes (which had a broader PSD to begin with) than in PTFE membranes. They attributed this change to: i) buildup of a relatively thick (4-7 μm) salt deposit layer on the membranes' surface; and, ii) damage to the membranes, especially PTFE ones, in the form of cracked fibrils (Fig. 6) and altered structure. The cracks in PTFE membranes, described as being similar to those observed during shrinkage of dried clay, were attributed to the dry out periods. In PVDF membranes, on the other hand, a buildup of salt crystals within the membrane was observed. Guillen-Burrieza and co-workers concluded that PVDF and PTFE behaved differently in their reaction to a fouling medium under MD [24]. A series of AFM studies were also conducted by this group, which revealed that the two membrane materials behaved differently in terms of their attraction forces to CaCO_3 salt crystals, as well as their surface roughness [24]. Collectively, this strongly suggests that the nature of membrane material, in addition to its surface morphology, has an important role to play in resisting fouling in MD. The mechanisms behind this role are yet to be explored.

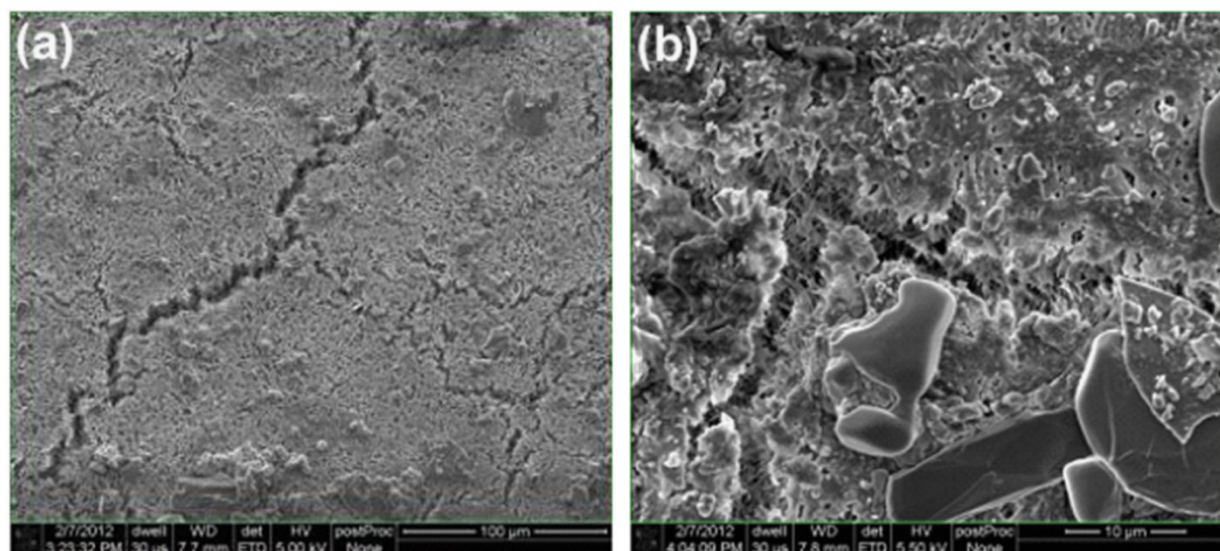


Fig. 6. (a) and (b): Cracking and thick salt layer deposit on two different PTFE membranes under intermittent drying conditions after 2 weeks of exposure to real seawater [24].

Using Mullen burst test, Guillen-Burrieza et al. [24] were able to demonstrate a third impact of fouling on MD membranes: the loss of their mechanical strength. They showed a difference between the Mullen burst pressure of PTFE and PVDF membranes before and after fouling. While PVDF membranes remained unaffected after seawater exposure and maintained their integrity, fouled PTFE membranes showed a decreasing trend in the pressure required to initiate the burst (even with the presence of the PP backer material). This strength deterioration was attributed to the fibril damage and crack formation seen in PTFE during the dry out processes.

Another reported form of membrane damage during MD operation is that which is due to chemical degradation. Using Accurel PP membranes, Gryta et al. [112] reported significant hydrophilization of the membrane surface, leading to increased rate of wetting. They found that the operating conditions of their MD process, including elevated temperature and the presence of oxygen, enabled the degradation of the PP polymer by forming hydrophilic groups (hydroxyl and carbonyl) on its surface [112]. These surface groups reacted with the concentrated NaCl solutions and consequently sodium carboxylate was formed. This was supported by FTIR analysis [112]. Attempting to regenerate the wetted membranes by rinsing and drying was found ineffective, since the presence of those hydrophilic groups caused a rapid membrane rewetting during the consecutive MD operation [112]. The presence of salt, according to Gryta et al. [112], has also stiffened polymer molecules (i.e. PP), preventing their chain disentanglement, and leading to chain scission. However, the quality of the distillate in their study was found to have remained unaffected [112].

5 Fouling mitigation in MD

The main scaling prevention tools employed in MD are feed pretreatment and chemical cleaning [1, 58]. Other fouling prevention methods attempted include increasing the feed flow rate, hydraulic cleaning, reducing surface roughness, changing the hydrophobicity of the membrane, magnetic water treatment, and changing surface charges on the membrane [16, 125]. The effects of the filtration and antiscalants have been studied in MD, as well as less commonly used technologies like feed heating or boiling, pH changes, flocculation, and magnetic water treatment [49, 59, 72, 82].

Pretreatment of the feed is standard practice in most desalination systems, and pretreatment needs vary significantly by technology and feed water quality. Common pretreatment methods include filtration, antiscalants, flocculation, and chlorination [107]. The market dominant desalination technology, RO, has intense pretreatment demands to protect the membranes, and some reports anticipate that MD will not need this level of pretreatment, as liquid water does not pass through the membrane and no cake compaction takes place. [107]

5.1 Thermal water softening

Certain water conditions, such as groundwater with high hardness, may benefit from the intentional breakdown of bicarbonate ions through high temperatures or boiling. This process is called thermal softening, and helps reduce scale by causing CaCO_3 and other salts to precipitate out in a heating step, and also reducing CO_2 , which is linked to bicarbonate ions as explained previously. For an MD system, M. Gryta boiled feed water for 15 min. and paper filtered it prior to undergoing hollow fiber MD, which lowered the bicarbonate ion content 2 to 3 times, to a concentration of $1.5 \text{ mmol HCO}_3^-/\text{L}$ [72]. While boiling is an expensive pretreatment option in terms of energy use, since MD needs a hot feed stream, the boiled water is used in the MD setup after some salts precipitate out of the solution. As a result, flux declined only 3% over 23 hours, instead of 12% without boiling. However, for tap water

with a concentration of 0.4-0.95 mmol HCO_3^-/L , CaCO_3 fouling was worse than in the untreated case [72]. A comparison of the rate of fouling is shown in Fig. 7. Although not addressed in the paper, boiling likely reduced the concentration of dissolved CO_2 , which in turn made calcium carbonate more likely to precipitate, and that may have been the cause of this non-intuitive result that contradicts other typical results. Boiling may therefore only be advisable with certain feed water solutions for certain durations.

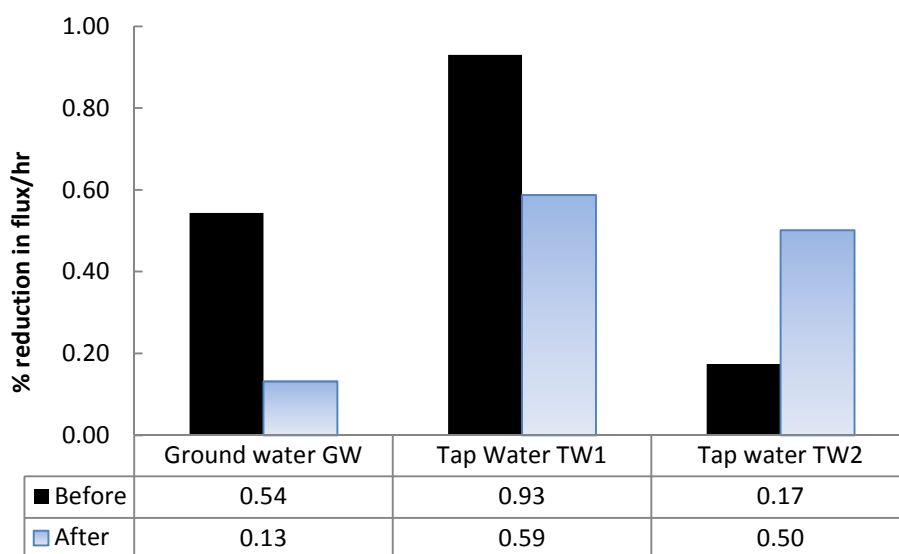


Fig. 7. Literature data. The effect of boiling as pretreatment on the fouling rate (represented as the % of flux reduction per hour) for different source waters (see Table 1 for references).

5.2 Micro/nano filtration pre-treatment

Microfiltration and nanofiltration (NF) is sometimes used before the MD process to remove particulate material and large molecules in the feed [87, 126]. Filtration may also be used to remove scaling the bulk, such as in the study by Kesime et al where a cartridge filter captured calcium scale, allowing high recovery of groundwater RO concentrate with MD [127]. While ultrafiltration is good for removing suspended solids and colloids, NF can be an effective pretreatment for rejecting organic matter and removing hardness from feed water. As commonly practiced in RO, some researchers have

also suggested using chemical coagulation followed by sand filtration or microfiltration to decrease fouling potential in MD [72]. Lawson and Lloyd [3] note that “several investigators ... reported a reduction in the degree of flux decay for pre-filtered ($\approx 1 \mu\text{m}$) process liquids” [3, 117, 128, 129]. Alkalaibi and Lior [130] have observed that following pretreatment with nanofiltration and acid addition to a pH of 5, the microorganism count in the water was close to zero even after 1400 hours.

Flocculation has been examined in conjunction with microfiltration for wastewater MD treatment, which found microfiltration to be very effective in reducing suspended solids, with relatively mild to weak improvement from FeCl_3 coagulation/flocculation [82].

5.3 Use of antiscalants

Antiscalants are a common tool to prevent inorganic scaling, and are potent for carbonate scales, as well as phosphate, sulfate, and fluoride, disperse colloids, and metal oxides [39, 131, 132]. Antiscalants act through a variety of mechanisms, including delaying nucleation, reducing the precipitation rate, distorting crystal structure, and altering CO_2 concentration [133]. They are generally the most common technique for scale control because of low costs, and usually require dosing of less than 10 ppm [133]. However, antiscalants molecules, typically organic, often reduce the surface tension of the water, which can promote membrane wetting [134].

A notable antiscalant study was performed for hollow fiber MD using a polyphosphate-based antiscalant designed for RO, and compared with laboratory grade sodium polyphosphate [28]. The particular antiscalant works by sequestering calcium, thus inhibiting precipitation. The name and composition of the commercial Polyphosphate based anti-scalant were not given. With the antiscalant, the formation of CaCO_3 crystals was virtually eliminated, but a thin amorphous non-porous layer deposited on the MD membrane. Surprisingly, the flux decline was worse when the antiscalant was

present. The higher the antiscalant concentration, the lower the permeate flux. However, the associated scale was mostly on the membrane surface, so periodic HCl cleaning was effective. Because of orthophosphate deposit risk from the breakdown of this antiscalant, residence times in MD were recommended not to exceed one hour [28]. Gryta concluded that regular HCl cleaning with an antiscalant system could make it useful in MD [28]. A different study by He et al. [135] found more positive results using polyacrylic acid antiscalants in MD, which were particularly effective in reducing calcium sulfate scale. Organo-phosphorus antiscalant compounds were also very effective in reducing calcium carbonate scale and mildly effective in reducing calcium sulfate scale [135]. An antiscalant blend of carboxylic and phosphoric acids was moderately effective in reducing both calcium carbonate and calcium sulfate [135]. Surface tension of the proposed antiscalant solutions (concentrations varying from 0.6 to 70 mg/L,) was very close to that of tap water (71.5 mN/m against 71.8 mN/m for tap water), and no wetting phenomena were detected under the experimental conditions.

5.4 pH Control of the MD feed

The pH control of the feed has been a common method to reduce or eliminate MD scaling. In almost all cases, this means acidifying the feed, as alkaline salts, the main component of scale, become drastically more soluble at acidic pH. However, according to Karakulski's findings, acidification of the feed failed to prevent silica scale [59, 110]. In one DCMD hollow fiber study with solutions of CaCO_3 at SI of 49 and CaSO_4 at SI 1.12, acidification to a pH of 4.1 fully prevented scale under conditions that experienced rapid scaling of MD membranes at neutral pH [50, 59, 110]. Numerous researchers found that bringing the feed to a pH of 4 with acid addition was sufficient to virtually eliminate calcium carbonate scale even at extreme SI indices [50, 72, 110]. Figure 8 shows the relative reduction in fouling rate (calculated as the rate of % flux decrease per hour, see Section 4.2) achieved by controlling the pH

of the feed solution. However, adding solution to modify the pH can quickly become prohibitively expensive, depending on the pH [136].

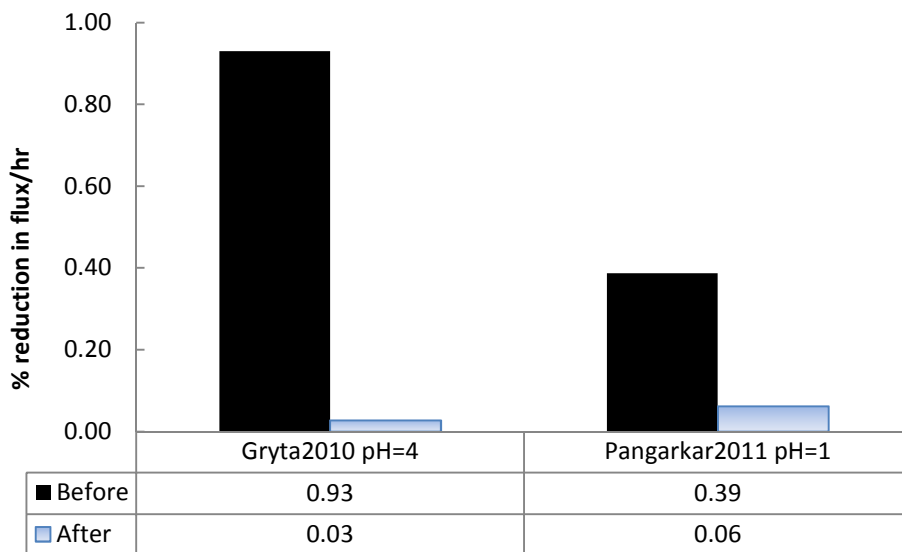


Fig. 8. Literature data. The effect of adding HCl to the feed solution and reducing pH as pretreatment on the fouling rate (represented as the % of flux reduction per hour) [72, 83].

5.5 Magnetic water treatment

Magnetic water treatment (MWT) is a technology developed for scale reduction in water treatment [49, 137, 138] and power plant heat exchangers [49]. The magnetic field slows nucleation while increasing crystal growth rate [112, 113, 139, 140], and it can alter the precipitate morphology and properties. Gryta performed a study with a commercially available MWT device called Magnetizer RWE-S on hollow fiber MD with a tap water feed [49]. The experiment ran with a 0.1 T magnetic field, feed temperature of 85°C, and alkalinities of concentrations of 2.72 and 3.61 mmol/dm⁻³ HCO₃⁻. The magnetic field caused significant changes in the morphology of crystal deposits on the membrane, causing crystals to be larger, but the deposits to be more porous. MWT caused the deposit layer thickness to be 10-25% smaller, and significantly mitigated flux decline. It was expected from previous studies that MWT would

shift CaCO_3 crystal type towards vaterite and aragonite forms, but under the temperature and slow laminar conditions, predominately calcite deposits occurred [49]. No effect on membrane wettability was found.

5.6 Tailoring MD membrane properties

Increased hydrophobicity of MD membranes has shown to have a dramatic effect in reducing scale formation. Hydrophobicity differences between materials may also account for different propensities to foul. For example, according to Gryta, polypropylene membranes do not have an optimal hydrophobicity, and undergo wettability readily, often after a few days in his experiments [111].

Superhydrophobic coatings provide an additional hydrophobic layer, which acts as a buffer layer from scale [141] by reducing the surface nucleation and the particulate attachment. Superhydrophobicity can reduce membrane wetting and improve membrane recovery from acid cleaning [125, 142]. One method of creating superhydrophobic MD membranes is depositing TiO_2 nanoparticles using LTH (low temperature hydrothermal synthesis). The superhydrophobic membranes generally have fluorosilicone coatings, and may achieve contact angles of 166° [125]. Coating the membranes with fluorosilicone for hollow fiber MD was found to create very long induction times of 194 minutes for gypsum [135], compared to no induction period otherwise. Other sources found significant CaCO_3 scale reduction [27, 50] and CaSO_4 scale [50] using fluorosilicone coatings [143]. These coatings can also reduce pore sizes, increasing resistance to scale [50].

As mentioned previously, superhydrophobicity also has shown to prevent microorganism fouling. However, more hydrophobic membranes are known to preferentially absorb HA [25]. Studies by Meng et al. found that superhydrophobic PVDF membranes fouled similarly to humic acid as ordinary PVDF, despite significantly reduced inorganic scaling [95]. According to Meng et al., humic acid fouling

on the superhydrophobic membrane occurred via an adsorption-desorption mechanism. A commonly used method to prevent biofouling is based on the hydrophilization of the membranes. Using sodium alginate hydrogel as coating may reduce the adsorption of organic compounds such as citrus oil on PTFE membranes [104]. Additionally, UV-induced grafting of zwitterionic polymers on PP membranes has been used to prevent protein fouling with very good results [144] as well as interfacial surface crosslinking of PP membranes [145] without compromising the rejection factor.

Increased surface porosity of membranes seems to be a factor in increased tendency to scale as well. Gryta performed a study of the effect of porosity on membrane performance using polypropylene capillary membranes and tap water. He found that the presence of larger pores on the surface allowed for the deposition of CaCO_3 crystals in the membrane interior, causing wettability, especially wetting during HCl cleaning [111]. The surface with higher porosity was found to have significantly increased wettability. However, no difference in flux decline was observed between the highly porous and non-porous surfaces of otherwise identical membranes, indicating that high porosity may not increase clogging or membrane blocking [111]. Gryta found that membranes with a low porosity coating 1 μm thick has significantly less tendency to wet, while exhibiting similar average properties and permeate production to the uncoated membrane [111]. Gryta inferred that crystal growth inside the membranes can be restricted by pore diameters much smaller than the crystal size. Such low porosity coatings may therefore be recommended to avoid wettability with only minor reduction in permeate production.

Finally, some studies suggest that membrane material type may have a significant impact on scaling. Curcio et al. found that in the presence of polypropylene hollow fiber membranes, the induction time for CaCO_3 was 18 seconds, compared with over 80 seconds for no membrane present [25, 53, 54]. Tung-Weng et al. [71] note that PVDF membranes wet more than PTFE. Non-polymer membranes such as glass membranes may have superior thermal and chemical robustness [142].

5.7 MD module design and operation

The conditions within the MD module may also significantly affect fouling. Temperature and concentration polarization may cause scaling preferentially at the membrane. Residence time in the module may have an effect as well, as stagnation areas can promote scalant precipitation from the bulk. Scaling is caused by conditions on the saline feed side rather than pure permeate, so system configuration (e.g., AGMD, DCMD, VCMD, or SGMD) plays a role only because they have different flux magnitudes [146]. Technologies with more conduction losses and with higher permeate flux, such as DCMD [116, 147] or VMD respectively, may be expected to have somewhat worse scaling issues from temperature and concentration polarization effects, as explained below. However, based on a numerical model developed by the authors elsewhere [148], the evolution of the Saturation Index (SI) as a methodology to predict extent of scaling, has been calculated and detailed. Understanding the theory associated with inorganic salt precipitation can help design safe operating conditions where the extent of precipitation can be controlled.

5.7.1 Temperature polarization

Temperature polarization is one of the most important secondary phenomena that affect the MD process. Water that evaporates into the pores of the MD membrane removes the corresponding latent heat of evaporation from the liquid feed stream. This cools down the fluid close to the membrane and results in a thermal boundary layer. Since the vapor pressure of water rises exponentially with temperature, any reduction in temperature of the water at the membrane interface leads to a significant drop in MD driving force. As a result, care is often taken in MD design to reduce and limit this effect as much as possible. At a given flux, the most important factor that determines the extent of temperature polarization is the effective heat transfer coefficient in the feed stream. At a higher heat transfer coefficient, a smaller ΔT is required across the thermal boundary layer to transfer the same

amount of heat of vaporization. The most common design strategies are to increase the flow rate of feed, operate in the turbulent regime or have turbulence promoters in the form of a spacer to increase the heat transfer coefficient on the feed side.

The simplest model for temperature polarization is given by Eq. 1, where h is the heat transfer coefficient in the feed channel and \dot{q}_{out} is the total heat loss across the membrane including sensible heat transfer and latent heat of evaporation of the vapor [12]:

$$T_{f,b} - T_{f,m} = \frac{\dot{q}_{out}}{h} \quad (1)$$

In general, temperature polarization reduces vapor flux, but it may also reduce scaling tendency since many critical salts' solubilities vary inversely with temperature. Conditions giving rise to a large temperature polarization may also create a large concentration polarization, which has the opposing effect of raising concentration near the membrane and potentially promoting scale formation.

5.7.2 Concentration polarization

The MD process allows only water vapor to pass through while retaining non-volatile salts, causing an increase in salt concentration near the membrane which is referred to as concentration polarization. A simple model of the concentration polarization process is the film model [17] described by Eq. 2:

$$\frac{x_m}{x_c} = \exp\left(\frac{J}{\rho k}\right) \quad (2)$$

where J is the water flux through the membrane, k is the mass transfer coefficient for the salt in solution, and x_m and x_c are the molar concentrations at the membrane interface and the bulk of the fluid streams, respectively.

Concentration polarization affects the MD driving force through its effect on vapor pressure, but this influence is minor relative to the effect of temperature polarization on vapor pressure. The more important effect of concentration polarization is that the elevated concentration may promote scaling formation on the membrane. As can be seen from Eq. 2, the effect rises with an increase in flux and falls with an increase in the mass transfer coefficient. It should be noted that temperature and concentration polarization are coupled phenomena since both depend on and influence the water vapor flux through the membrane.

5.7.3 Saturation index, numerical modeling

Thermodynamically, membrane fouling is expected to be a function of the salt supersaturation at the membrane surface. SI is a commonly used measure of supersaturation [149]:

$$SI = \log \left(\frac{\text{activity product}}{K_{sp}} \right) \quad (3)$$

$$K_{sp} = f(T, P) \quad (4)$$

According to these equations, temperature and concentration have an effect on the thermodynamic tendency for precipitation. These two parameters also influence the permeate flux and are in turn influenced by the flux and heat transfer rates (Eq. 1, 2). Engineering Equation Solver (EES) was used to numerically solve the implicit set of equations that connect these parameters along with the mass and energy balance equations, in order to predict the value of the SI on the membrane interface and feed bulk. The modeling methodology is described in detail in [12, 148]. In the following sections, results from the model are used to better understand the trends reported in literature. The numerical modeling provides a quantitative understanding of the competing effects and the reason for the overall trend observed. Data on changes in the extent of membrane fouling with modifications in feed flow velocity and feed inlet temperature are available in literature. In the following sections, data

from reference [39] is used to illustrate the effect of feed flow rate and feed inlet temperature on the extent of CaCO_3 fouling induced flux decline. Modeling results for an AGMD setup on the effect of system variables on SI at the membrane interface are also presented.

For the numerical model the following assumptions have been made: an inlet salinity of 13 mg/kg is assumed which is approximately equal to the solubility of CaCO_3 at room temperature; diffusivity of CaCO_3 is assumed to be $1.469 \times 10^{-9} \text{ m}^2/\text{s}$ and the dependence of solubility product of aragonite on temperature is modeled as in [39] (T is temperature in K):

$$K_{sp} = -171.9773 - 0.077993T + \frac{2903.293}{T} + 71.595 \log T \quad (5)$$

It is important to note that only the trends in SI variation with changing system parameters are being compared with the reported experimental fouling data. The actual value of SI in the experiment is likely to be different due to differences in concentration of the feed water, presence of other ions in the feed and differences in geometry and MD configuration.

5.7.4 Effect of temperature

As discussed previously, temperature has a dominating effect on scale formation due to salt solubility variation with temperature. Similarly, temperature polarization may have a significant effect on scaling and fouling since the solubilities of common foulants are highly temperature dependent, and since biological fouling as discussed previously can be limited by temperature. Also, the effect varies greatly depending on the salt. Reduced membrane temperature due to temperature polarization might prevent precipitation of CaCO_3 and CaSO_4 which are less soluble at higher temperatures, but may make non-alkaline salts scale more readily. Higher temperatures as stated previously may limit bacteria growth, so high degrees of temperature polarization may enable biofouling. Figure 9 shows data on the effect of temperature on fouling rate in an experiment where the major scalant was CaCO_3 [39].

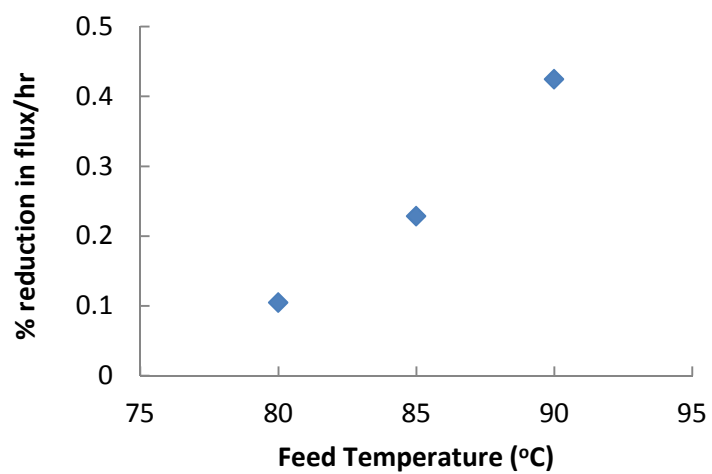


Fig. 9. Literature data by Gryta. The effect of the feed temperature on the fouling rate (represented as the % of flux reduction per hour) for Lake water with bicarbonates for hollow fiber DCMD [39].

Due to the inverse solubility of the salt and increased flux contributing to higher concentration polarization in the feed stream, there is a significant increase in fouling rate with change in feed temperature. The rate of fouling induced flux reduction is four times higher at 90°C than at 80°C.

To numerically explain this behaviour, the previously described EES model was used to estimate the effect of increasing feed temperature on the SI at the membrane interface and feed bulk. The simulations were carried out for a system with a feed flow rate of 0.1575 kg/s in a feed channel with a depth of 4 mm and a width of 12 cm. Figure 10 shows the predicted variation in SI at the membrane interface and in the bulk of the feed stream.

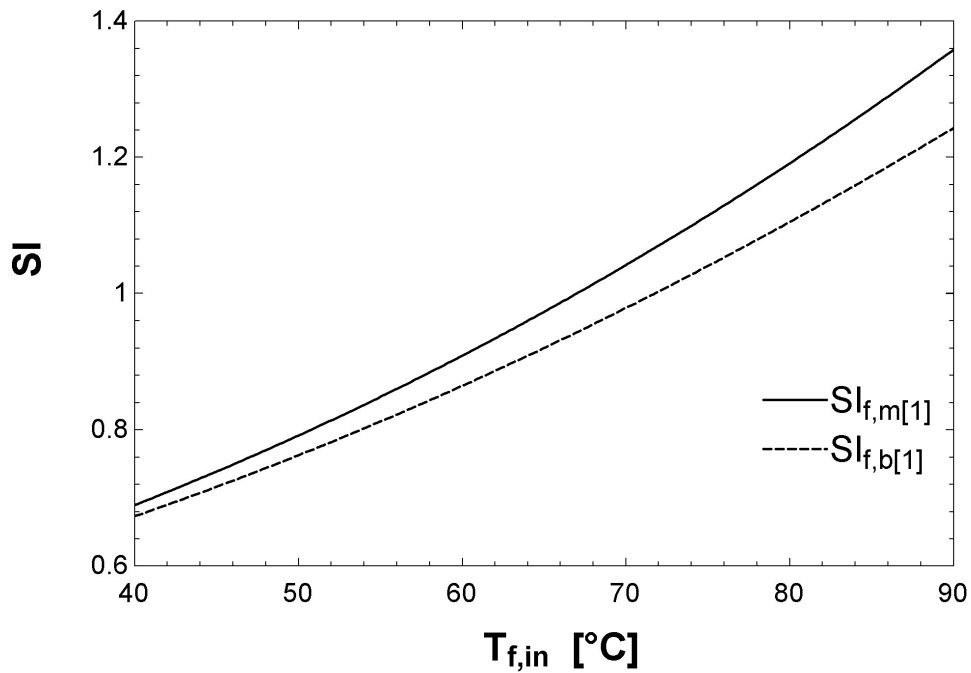


Fig. 10. Simulation results at fixed $\dot{m}_{f,in} = 0.1575$ kg/s. Saturation Index of CaCO_3 in the feed stream at the membrane interface ($SI_{f,m}$) and in the bulk ($SI_{f,b}$) as a function of feed inlet temperature. Increase in $SI_{f,m}$ correlates with higher scaling observed. $SI_{f,m}$ increases faster than $SI_{f,b}$ illustrating the effect of higher concentration polarization.

With an increase in feed inlet temperature, the SI of the bulk fluid increases associated with a reduction in the K_{sp} for CaCO_3 (Aragonite). At the membrane surface, the increase in SI is higher, since there is a larger water flux and an associated increase in membrane concentration of ions compared to the bulk. The increase in predicted SI at the membrane surface correlates well with the increased fouling rate at high temperatures as illustrated in Fig. 9.

5.7.5 Polarization abatement: feed flow rate and bubbling

Feed flow velocity has a direct influence on the heat and mass transfer coefficients in the feed channel. With an increase in feed velocity, both heat and mass transfer coefficients increase, and transition from laminar to turbulent flow may cause this change to be discontinuous. As a result, with an increase in flow rate, flux increases as a result of reduced temperature and concentration polarization.

For inverse solubility salts such as CaSO_4 , K_{sp} decreases with an increase in temperature (Fig. 1). Since the heat transfer coefficient (h) increases with flow rate, the temperature at the membrane surface increases. At the same time, an increase in mass transfer coefficient will lead to a decrease in salt ion concentration at the membrane surface. Since both the numerator (activity product) and the denominator (K_{sp}) of Eq. 4 decrease, the relative change in SI is determined by the rate at which the two quantities change.

Numerical modeling was again used to understand the overall effect of increasing the feed velocity on the SI at membrane interface. The parameters used for the study were the same as mentioned earlier, with the feed inlet temperature fixed at 80°C. Results are shown in figures 11 and 12.

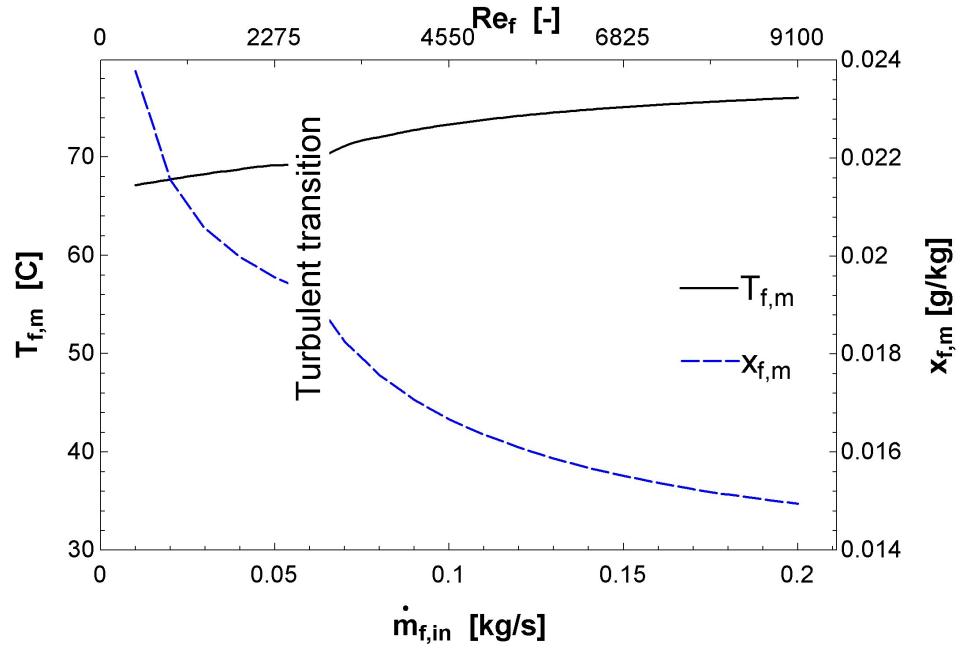


Fig. 11. Simulation results at fixed $T_{f,in} = 80$ °C. Effect of feed mass flow rate ($\dot{m}_{f,in}$) and Reynolds number (Re_f) on temperature ($T_{f,m}$) and $CaCO_3$ concentration ($X_{f,m}$) at the membrane interface. Increase in temperature would increase tendency for precipitation of $CaCO_3$, whereas decrease in concentration would reduce tendency for scaling.

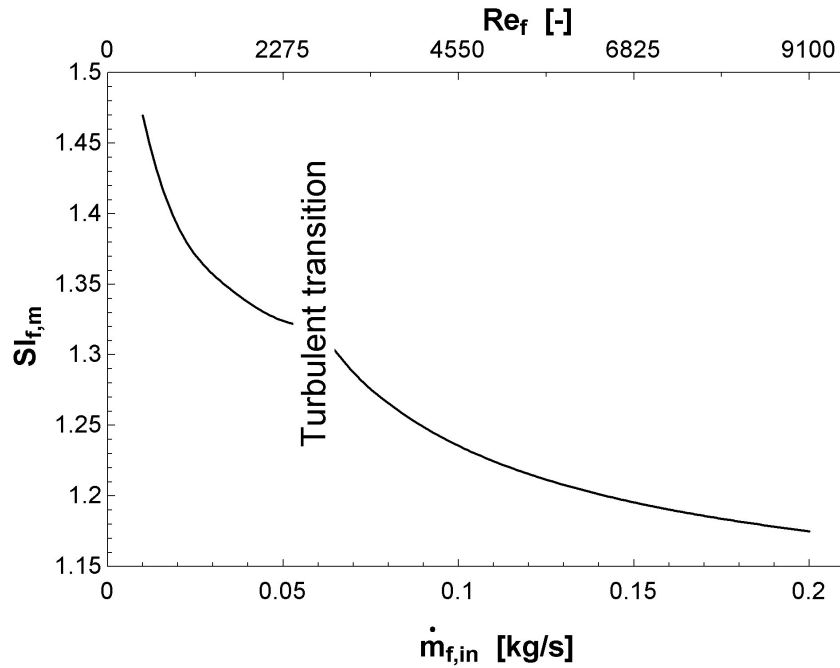


Fig. 12. Simulation results at constant $T_{f,in} = 80\text{ }^{\circ}\text{C}$. Overall effect of the feed mass flow rate ($m_{f,in}$) and Reynolds number (Re_f) on the SI at the membrane interface ($SI_{f,m}$). Decrease in SI correlates with experimentally observed decreased rate of fouling (Fig. 13).

Salt ion concentration decreases and temperature at membrane surface increases with increase in feed flow rate (Fig. 11). The overall effect of these two opposing effects was a decrease in SI at the membrane surface with increased feed flow rate, as shown in Fig. 12, since the reduced concentration polarization leads to a larger decrease in ion activity product as compared to the decrease in K_{sp} associated with lower temperature polarization. This result is consistent with data from Gryta [39] (Table 1, Fig. 13) which shows that an increase in feed velocity from 0.3 m/s to 1 m/s leads to a reduction in the rate of flux decline.

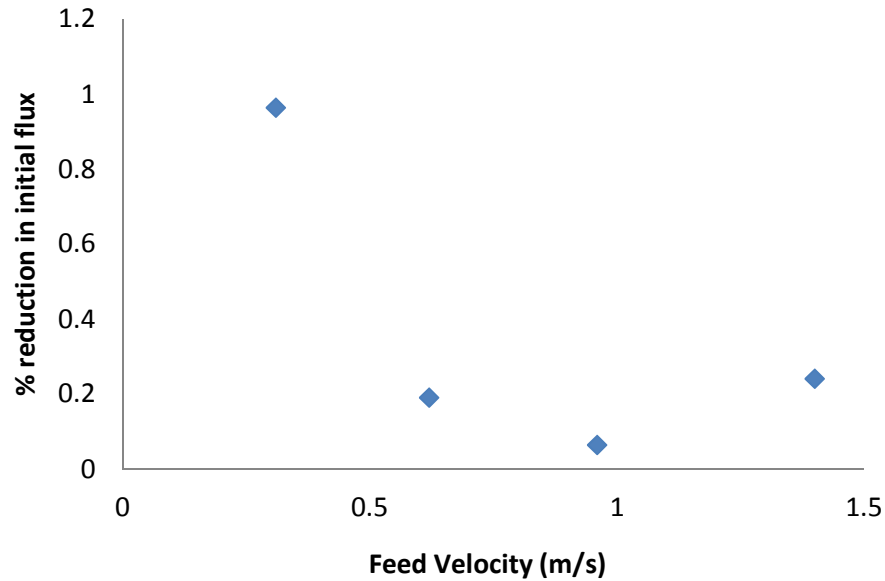


Fig. 13. Literature data. The effect of the feed flow velocity on the fouling rate at constant feed inlet temperature of $80\text{ }^{\circ}\text{C}$ (represented as the % of flux reduction per hour). Decrease in fouling rate with increase in feed velocity is shown [39].

The marginal increase in fouling rate between 1 m/s and 1.5 m/s (feed flow velocity), is inconsistent with the theory presented above and could be associated with transition to turbulence that is expected to happen at these velocities in the experiment.

In addition to the thermodynamic effects discussed above, at higher flow rates, the shearing action of the water in removing deposited precipitates is higher. This can help reduce the overall membrane scale deposition and fouling rate. Gryta [39] also reported that the size of salt crystals observed was much larger at the lower flow rates (0.31 m/s) as compared to higher flow rates (0.62 m/s), which can be explained by considering the kinetics of the fouling process as explained above.

Other methods to reduce concentration and temperature polarization have also been explored. Recently, Chen et al. [150] have demonstrated the effectiveness of gas bubbling through the feed as a means of promoting mixing and thereby improving flux and reducing scale deposition. Traditional methods to promote better mixing include increased flow rate and the use of spacers to induce turbulence in the feed channel and to improve mixing. Chen et al. compare three different configurations of hollow fiber membrane MD with feed outside the fibers: no-spacer, spacer and air bubbling without spacer. Figure 14 shows the type of spacer used in that study.

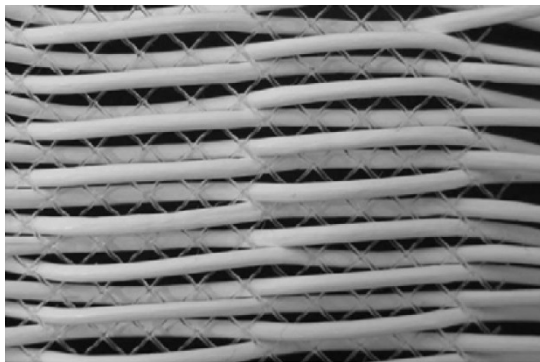


Fig. 14. Example of mesh spacers used in hollow fiber MD experiments [150].

The flux is lower for the no spacer case as compared to the other two. With time (about 7 hours of experiment), when the bulk NaCl concentration by weight is about 23%, a significant fouling layer and associated decline in flux rate is observed in all three cases. While the air bubbling case showed less scale formation, the spacer actually leads to more scaling than the no-spacer case, since it enables local trapping of NaCl close to the membrane. Air bubbling achieves the goal of mixing the feed stream and improving performance, while at the same time retards local scale formation. Amongst the air bubbling cases, performance improvement is higher for cases where significant temperature or concentration polarization is expected (at higher feed water temperature and laminar flow conditions). Air bubbling will also increase the dissolved gas concentrations in the feed which has potential impact on gas content in the membrane pores, permeate-side mass transfer resistance (for AGMD or SGMD), and on the formation of salts depending on the gas chemistry (e.g., CO₂ content) [88].

5.7.6 Types of module

Several MD module configurations have been designed and studied for fouling, with significant differences. Although direct comparisons are lacking, evidence from similar feed solutions indicates dramatic differences in fouling risk. The types of MD modules include: hollow fiber membranes which consist of small tubular capillaries; flat plate modules; tubular modules which consist of concentric cylinders that resemble flat plate membranes; and spiral wound membrane modules, which consist of a membrane and spacer wrapped around a collection tube [1]. The largest differences can be found between hollow fiber membranes, which have been studied for MD fouling relatively extensively, and all the rest. Hollow fiber membranes are known to have higher fouling potential [50], but the present review has found that their fouling potential is often extremely high, occurring under many conditions for which other units have not been known to foul, and they have even experienced fouling with bulk concentrations well below saturation conditions, which is highly unusual [3, 151]. Crucially, this high degree of fouling has generally been found in the experimentally more common setup in which feed is

inside the capillary tubes [28]; in other experiments with distillate inside the capillary tubes, fouling was in some cases regarded as unlikely [143], although it still can occur, as shown in Fig. 15.

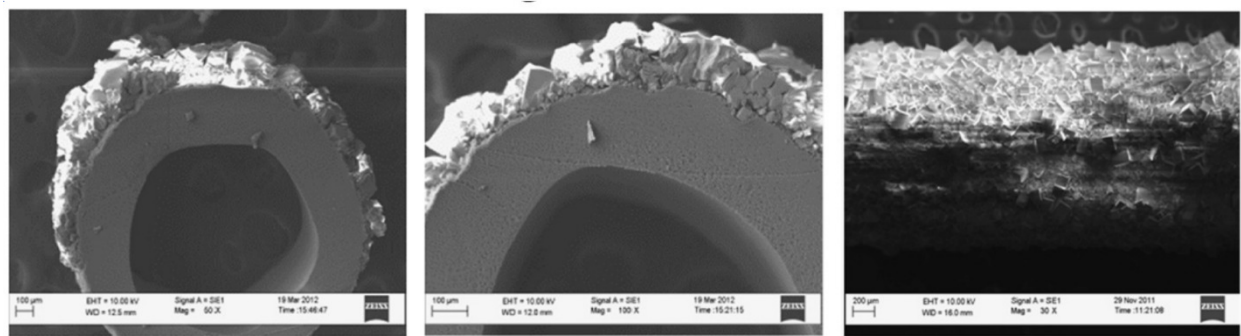


Fig. 15. SEM images of PVDF Hollow Fiber DCMD fouled modules in cross-section with NaCl taken from 18 wt.% to saturation after 7 hours of operation with feed external to the capillary tubes [150].

In the case of hollow fiber membranes, the fine fibers cause slow internal laminar flow and often extreme concentration polarization. They are also known to clog readily by colloidal particles in the feed. Additionally, hollow fiber MD modules are difficult to clean and maintain [1], and if the feed penetrates through the membrane pores, the whole module should be replaced.

Flat plate modules have been examined thoroughly as well in this review, and while tubular and spiral wound modules have been investigated less, they are essentially flat plate systems with mild curvature, and should not behave much differently. Flat plate modules are relatively easy to clean [1]. However, since hollow fiber and spiral wound modules can hold greater membrane areas they are regarded as more cost effective MD modules. Therefore, cleaning protocols should be adapted to the most commercially successful module option.

The various types of MD operation, including DCMD, AGMD, SGMD, and VCMD are not thought to significantly affect MD scaling, but their differences on permeate flux and heat conduction alters

concentration and temperature polarization effects. These configurations differ on the permeate side, not the saline feed side, so effects on fouling are secondary feed design [1].

5.7.7 Membrane cleaning

Acid cleaning is one of the most common methods used for fouled membrane reclamation. Several studies have used different types of acids (both strong and weak) to remove scale components from the membrane surface. HCl is by far the most commonly used acid in MD experiments for membrane cleaning. It is particularly effective in removing basic salts such as CaCO_3 by dissolving them [39, 57]. Acid cleaning is carried out as a batch process with the feed water being replaced by an acidic solution. During this period, the permeate should be discarded, as noted by Gryta [26, 152] since HCl is volatile and can be carried into the permeate side along with water vapor. This was observed in a DCMD experiment with hollow fiber membranes [26].

Gryta [28, 114] reported the efficacy of HCl rinsing in restoring flux back to original value in the case of membranes with CaCO_3 scale layer. However, after repeating the washing procedure with 2-5% HCl, Gryta found that maximum restored flux declined [111]. Yang et al. [56] were able to restore flux completely by cleaning with a 5% HCl solution following the use of untreated 'tap water' in their experiments. Curcio et al. [25] used a two-step cleaning strategy using a citric acid solution followed by a NaOH solution, allowing each of them to act for 20 minutes. They reported complete recovery of both flux and hydrophobicity in an MD experiment using synthetic seawater. Some authors [29] have also reported cleaning using bases such as 0.1 M NaOH for 20 minutes followed by pure water run for 2 hours. While pure water achieved 87.5% flux recovery, the NaOH solution was able to restore the flux to the initial value. Gryta et al. found that pretreatment using Ca(OH)_2 helped mitigate fouling from silicates and sulfates [102].

Gryta [26] used HCl also to clean a membrane with iron oxide scale layer. It was found that 18% HCl solution cleaning brought the flux close to the initial value and did better than 5% or 36% HCl. The experiment showed that iron oxides were very difficult to remove from the MD hollow fiber membrane, requiring high levels of acidification (36 wt. %) for 1 hour cleaning duration to obtain full removal, which damaged the membrane [26]. Complete removal of the iron oxide scale did not eliminate all the negative effects of fouling, which included decreased membrane flux after cleaning and increased membrane wettability. Moreover, drying was needed to actually recover the flux and restore the distillate quality because both were hindered (i.e., flux reduction from 800 to 650 dm³/m²-day and distillate electrical conductivity of 20 µS/cm) after the acid cleaning. Therefore, Gryta recommends only partial removal of iron oxide scale.

Table 2 shows data gathered from literature on the effectiveness of various cleaning protocols for restoring permeate flux.

Table 2. Common cleaning methods used in MD and reported flux recovery.

S No	Ref	Membrane Material	Solution type	Cleaning method	Recovery %
1	[121]	PTFE	7 g/L NaCl	Water wash	98.48
2			7 g/L NaCl	Water wash	97.48
3			Ground Water	Water wash	94.43
3	[72]	PP-hollow fiber	Ground Water (CaCO ₃)	3 wt.% HCl	98.75
4			Tap water (CaCO ₃)	3 wt.% HCl	98.56
5			Boiled TW (CaCO ₃)	3 wt.% HCl	98.79
6	[25]	PP-hollow fiber	Seawater (HA, CaCO ₃)	20 min citric acid followed by 20 min NaOH two stage cleaning	≈100
7	[113]	PTFE	Seawater	Piezoelectric transducer at 35kHz used to induce cavitation and cleaning of membrane. Initially flux restored.	91.20

8	[27]	PP-hollow fiber	Microbial Biofilm	NaOH at pH=12, 40C distilled water, 70% ethanol for disinfection, distilled water	≈100
9	[39]	PP-hollow fiber	Ground Water (primarily CaCO ₃ , CaSO ₄)	2-5 wt.%HCl	≈100
10	[58]	PP-hollow fiber	Tap Water (CaCO ₃)	5 wt.% HCl	Recovery reduces with number of cleaning cycles: Cycle 1 - 99.9 Cycle 6 - 96.5

The effectiveness of acid washing is known to vary dramatically by the type of fouling. Alkaline solutions that are more soluble at lower pH have been found to be very effectively removed by acid cleaning, including the most common scale, CaCO₃. Other crystalline scale, like iron oxide, has required very strong acid to remove, [26] as described above. Silica scale has proven to be similarly difficult to remove. Acid cleaning has caused mild but incomplete removal in cleaning organic matter on MD membranes [30].

Sometimes cleaning has been achieved by simply running de-ionized (DI) water through the system. DI water readily absorbs salts, and is even known to leach salts from surroundings [121]. Mericq et al. [109] for example, completely restored membrane flux using RO permeate water to remove and re-dissolve scale deposits from synthetic seawater in their VMD system.

In terms of other cleaning methods, a common and simple approach is reversing the flow direction, which successfully restored flux from biofouling in AGMD Memstill experiments with pond water performed by Meindersma et al. [87].

6 Trends in scaling in MD

Future developments in MD technology and industrial applications will create new issues and areas needing investigation for MD fouling. Multi-stage designs of MD promise much better efficiency, with some theoretical studies claiming lower energy consumption than the existing state-of-the-art thermal technologies, such as MSF and MED [7]. Fouling in staged systems and for energy recovery devices that recirculate fresh feed into later stages needs further research [26, 84]. As MD is developed industrially, field experience and optimization of pretreatment requirements will be developed. Additionally, as membranes designed specifically for MD are created, studies fouling with those materials, porosities, B values, and other properties will be critical. MD use will continue to grow as well in non-desalination areas such as the food, chemical, and dye industries [153], which were not considered in this review. One final area of for further study is monitoring of scale development in plants operations and long-term experiences.

7 Conclusion

Scaling and fouling in MD are found to be pervasive, but design and mitigation methods have proven effective at making MD technology resistant to scaling and fouling. Four principal types of fouling and membrane damage have been found in MD: inorganic salt scaling or precipitation fouling, biofouling, particulate fouling, and chemical degradation. Inorganic scaling risk, the primary focus of academic studies, varies greatly with the salts present. Alkaline salts such as CaCO_3 , the most common scale by far, have proven to be readily prevented by decreasing feed pH or removed through acidic cleaning, while other scale has proven more tenacious and must be generally be limited by avoiding supersaturation. Biofouling has also been observed in MD, but can be largely mitigated through control of operating conditions. Particulate fouling in MD has proven difficult to remove, but it can largely be prevented by ultra- or microfiltration. Chemical degradation and damage to the membrane has proven

to be a concern as well, but can be mitigated by selecting operating conditions that avoid fouling, extreme pH, and certain salts. The choice of membrane material and properties can also help to avoid chemical degradation; PTFE and PVDF membranes exhibited different fouling characteristics, such as in wetting, internal crystal growth, cracking, and mechanical strength [24]. A study on glass membranes claimed glass membranes had superior thermal and chemical robustness than polymer membranes [142]. However, there is a general lack of information about the effect of the polymer type on the prevention of fouling/scaling in MD processes.

Fouling tendency had been perceived to be highly variable and perhaps unpredictable, but some consistent patterns are seen. Studies with extreme susceptibility to fouling have almost exclusively been performed with hollow fiber capillary membranes with the feed internal to the capillary tubes. These modules have fouled within hours to days in unsaturated conditions that would not cause fouling in other modules. Likewise, the studies showing high resistance to fouling tended to have highly hydrophobic membranes or coatings, and include hollow fiber studies with permeate in the capillaries [143]. Numerous studies have found substantial reduction in scale from superhydrophobic fluorosilicone coatings, and while the individual papers may question how large a role the coating played in the often complete lack of scale [50], the literature overall proves consistently that these coatings have a dramatic effect. More hydrophobic membranes show higher resistance to wetting and associated internal crystal precipitation. Since internal fouling often leads to further wetting, this too is reduced. Studies have shown that increased hydrophobicity increases LEP and, in experiments, is associated with reduced wetting, fewer fouling deposits, and purer condensate [125].

Micro, nano, or ultrafiltration has proven effective in stopping particulate scale. Modifying pH in the feed or with cleaning may prevent or remove certain types of fouling very effectively as well. Keeping feed temperature above 60 °C has proven very effective in mitigating biofouling, with some

exceptions. Removal of oxygen via deaeration may be expected to reduce biofouling and the authors recommend further investigation into the effectiveness of this technique. Rinsing with a basic solution such as with NaOH may resolve fouling for some substances, including HA. Mildly effective fouling prevention methods include boiling for removal of carbonate, ultrasonic cleaning, magnetic water treatment, flocculation, covering the membrane surface with a less porous smaller pore size layer, and for HA, oscillating the feed temperature. Antiscalant effectiveness studies in MD have been inconclusive; both strong reduction in scaling and actual decreases in permeate flux have been reported.

System design characteristics also influence fouling. Concentration polarization, closely related to feed Reynolds number and rate of permeate production, is critical in causing fouling, and can be mitigated by increasing the feed flow rate, or mixing technologies such as bubbling [150]. Temperature also remains important, as the most likely foulants have inverse solubility with temperature. Simple computational models were applied by the present authors to illustrate the effect of coupled heat and mass transfer on scaling. A correlation between theoretical prediction of higher SI at the membrane interface and increased rate of fouling induced flux decline was observed. Choice of safe operating conditions should therefore consider temperature and concentration polarization effects and solubility characteristics of the salts. Finally, stagnation zones or high residence times in the module may contribute to fouling as well.

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