THE EFFECT OF FILTRATION AND PARTICULATE FOULING IN MEMBRANE DISTILLATION

Authors: David Martin Warsinger, Jaichander Swaminathan, Hyung Won Chung, Seongpil Jeong, and John H. Lienhard V

Presenter: David Martin Warsinger, PhD
Postdoctoral Associate, Mechanical Engineering Department, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
davidmw@mit.edu

Abstract
Fouling and scaling in membrane distillation (MD) is one of the significant barriers to its continued growth. Fouling in MD blocks the pores, causing a decline in permeate flux, and may eventually lead to wetting of a hydrophobic membrane by the saline feed, contaminating the permeate. Many previous studies on MD have observed that while MD is more fouling resistant than reverse osmosis (RO), inorganic salt precipitation on the membrane surface under supersaturated conditions may readily foul and cause wetting of the membranes. While most studies have assumed that crystal growth occurs directly on the membrane surface, precipitation of particles in the bulk which then migrate to the surface may play a significant or dominant role. In this study, membrane distillation experiments are run at varied supersaturated salinities with and without filtration in equivalent operating conditions to examine the effectiveness of particulate fouling in MD, and thus also the role of bulk precipitation in inorganic fouling. Conditions were designed to favor surface crystal growth over bulk nucleation, to examine the limiting case. The experiment is paired with heat and mass transfer and solubility numerical modeling to analyze the effects of concentration polarization to accurately calculate the saturation index (SI) in the bulk and at the membrane surface. The results show that the removal of particles precipitating in the bulk makes a tremendous difference in reducing flux decline, visible crystals on the membrane surface, and wetting. This implies that bulk nucleation followed by deposition, rather than surface crystal growth, dominates the scaling process in MD when the bulk is supersaturated.
I. INTRODUCTION
Membrane distillation is a thermal desalination technology which relies on porous hydrophobic membranes that repel liquid water but allow water vapor to pass. MD possesses relative fouling resistance compared to other membrane-based technologies such as reverse osmosis [1]. The process is driven by a difference in vapor pressure across the pores. Numerous studies have shown that MD membranes can withstand concentrations several fold higher than saturation without the onset of fouling [2, 3]. Indeed, materials used for MD are naturally scaling resistant, and are often used to coat heat exchangers to prevent surface scaling [4]. This advantage enables the use of MD in further desalinating brine from other desalination systems or to concentrate industrial waters. Understanding and control of fouling prevention is therefore imperative to the technology’s competitive advantage. Fouling in MD is generally categorized as scaling, which is the process of inorganic salts growing on the membrane surface, and particulate fouling, which generally refers to insoluble particles like silt, silica, and organic matter depositing on the membrane surface. While scaling is often described as largely crystal growth on the surface, this study investigates whether a particulate mechanism is substantially important in conditions thought of as scaling. Many studies have shown that inorganic fouling at high SI may block membrane pores, thus decreasing flux and wetting the hydrophobic membrane, causing saline feed water to contaminate the permeate [5, 6]. Therefore, it is highly desirable to determine the limiting supersaturation conditions that can allow MD to operate without fouling degrading performance. However, the literature lacks systematic studies determining which saturation conditions cause the fouling to originate at the membrane surface or in the bulk solution. The concentration of salts can be meaningfully compared across experiments with the saturation index, or SI, which is a log-based scale for the concentration compared to the saturation, where an SI = 0 indicates a saturated solution and SI = 1 is 10 times the saturated concentration.

Pretreatment with filtration can help address this question as it removes incoming particles from the bulk. Previous MD studies have shown that systems with filtration had low levels of fouling [7, 8], and a literature review study showed that filtration was among the most effective methods in reducing inorganic fouling [9]. Furthermore, additional studies found that incorporating filters in membrane distillation reduced flux decline [10, 11, 12, 13]. These studies lack a systematic examination of how the bulk SI and the SI at the membrane surface relate to both flux decline and wetting of the membrane, which the present study addresses. In this study, a range of experiments of supersaturated SI at the membrane surface are run in an Air Gap Membrane Distillation (AGMD) system, with and without a filter which removes particles that nucleate in the bulk before recirculation. The effects of nucleation and scaling are examined by measuring flux decline, increases in permeate conductivity caused by wetting, and polarized-light microscopy.

II. METHODOLOGY

2.1 Experiment Design

The experimental setup for the study is a flat plate, air-gap MD (AGMD) module with turbulent flow conditions in the feed. The system has a small temperature drop over the feed and cooling channels (<0.2°C) to keep the conditions finely controlled. Numerous flow rate, temperature, and pressure sensors are arranged in the system as shown in Fig. 1. The system uses large 40 L tanks for the feed solution and cooling liquid to act as thermal masses, keeping the temperature constant. The module consists of a series of plates machined out of polycarbonate and aluminum. The module and its numerical modeling have been previously described and validated [14]. The system was designed with no metal parts
exposed to the flow, including the heater, since even resistant metal parts such as stainless steel may corrode when in contact with warm, saline feed [15], thus creating nuclei for crystallization. DI water and reagent grade chemicals were used to minimize contamination. This abated the availability of crystal growth nuclei in the bulk, making conditions adverse for bulk nucleation to play a significant role. When these opposing conditions of filtration and highly pure solutions still occur in tandem with significant bulk nucleation, it indicates that bulk nucleation plays a substantial role in MD fouling.

Figure 1. AGMD scaling test bed.

The AGMD system operated in a continuous mode with the SI and temperatures held constant throughout the experiment. The air gap size was 1 mm. The SI concentrations were determined with PHREEQC chemistry modeling software.

Error analysis was performed, and has been discussed in detail for this apparatus in the previous work by the authors [14]. The uncertainty in temperature for the thermistors was ±0.2 °C, and the temperature controllers cycled on and off to maintain a temperature range of ±0.1 °C. However, occasional temperature downward spikes caused by maintenance on the system was as large as 4 °C for a few minutes, causing slight variation in permeate flow rate, but not increasing or significantly effecting fouling. The permeate mass scale, measuring grams with intervals of 30 minutes each containing ~200 g thus had an uncertainty of around 0.5%. The uncertainty in the conductivity readings was <2%. The flow rate varied within ±0.6%. Feed static pressure was set to 1.5 bar, varying by ±3%, but static pressure has minimal effect in MD permeate flux and fouling. Two of the four experiments were performed twice (SI = 0.4, no filter; and SI = 0.2, with filter), and each produced the same results regarding whether notable flux decline or any wetting occurred, confirming repeatability of the system.
2.2 Mathematical Modeling

An Engineering Equation Solve (EES) discretized model based on finite difference method was used for determining the saturation index at the membrane surface, and estimating permeate flux [16]. The model balanced simultaneous heat and mass transfer through an AGMD system with approximately 300 computational cells over the length of 16 cm, as shown in Fig. 2. This balancing includes flow of the feed and permeate in and out of each cell, diffusion of the water vapor through the membrane and air gap, and convective heat transfer in the feed and permeate, advection of water vapor from the feed to the air gap, and conduction across the membrane. The model included the vapor flux equation through an MD membrane as a function of the membrane permeability $B$ and the vapor pressure difference across it, and modeled the condensation film of the permeate as a classic laminar condensation film on a vertical flat plate. The details and equations of this model have been previously published by the authors [14, 17].

![AGMD Computational Cell](image)

Saline Feed  MD Membrane  Air Gap  Condensate  Cooling Water

Figure 2. Computational Cell for AGMD Analysis and Concentration Polarization Calculation

2.3 Membrane and Filter

A commercial PVDF membrane was used with a nominal pore size of 0.2 μm and a thickness of 200 μm. The effective area of the membrane was 192 cm$^2$. The static contact angle of the membrane with water was 125°. The membrane was uncoated: improvement above the typical contact angle of PVDF (89°) can be attributed to surface features and roughness.

A filter was used for the feed to remove small nucleating particles, which could deposit on the membrane and serve as seeds for further growth within the AGMD module. The filter used was a Pentair pleated cellulose cartridge filter, with a 20 μm nominal pore size, allowing it to block large nucleated particles of CaSO$_4$. 
2.4 Scaling conditions

The experiments focused on calcium sulfate in a SI range from 0.2 to 0.4 at the membrane surface with a inlet bulk temperature of 70 °C. Calcium sulfate is among the most significant scales that may occur in concentrated seawater brine and other desalination applications [5, 18]. Unlike the common calcium carbonate scale, calcium sulfate does not have a strong pH dependence and has less complex chemistry, making the experimental study more tractable.

The setup was designed so that concentration polarization near the membrane surface caused further supersaturated conditions, increasing the concentration by 16%. Due to its inverse solubility behavior, the salt is supersaturated near the heater element in the feed tank as well, leading to nucleation and precipitation before the feed reaches the module. This effect was minimized by separating the heater from the feed solution with a plastic bag that acted as a thermal barrier. Real world MD systems also experience the precipitation near the heater, as salts such as CaCO$_3$ and CaSO$_4$ would be most supersaturated at higher temperatures.

Avoiding particles in the bulk was important to prevent alternative means of fouling the membrane. To achieve this, the water was created with DI water, and the feed was created by mixing two fully dissolved solutions: one with calcium chloride and another containing sodium sulfate, both of high purity from Sigma-Aldrich. Between experiments, system cleaning was performed by recirculating DI water. To avoid excessive supersaturation conditions near the heater, good mixing and heat transfer ensured that the heater temperature was close to that of the feed tank.

III. RESULTS AND DISCUSSION

Experiments of CaSO$_4$ membrane fouling were performed at varied super-saturated SI at the membrane surface. These experiments, ranging from 24-60 hours in duration, identified fouling by permeate flux decline and an increase in permeate conductivity caused by wetting. By studying the effect of using or excluding a filter, the experiments can determine how significant a role bulk nucleation plays in MD membrane fouling. These experiments are detailed in the order of more adverse fouling conditions to less susceptible conditions. All experiments were run with an AGMD module with a hot feed temperature of 70°C and a coolant temperature of 20°C.
Figure 3. Permeate flux decline averaged over 0.5 hours for CaSO₄, SI = 0.4, no filter. The increase in flux between 25 and 35 hours corresponds with wetting through the membrane, as seen in Fig. 4.

Figure 3 shows that in the more highly saturated experiments without a filter, at SI = 0.4, permeate flux declines significantly by about 11%, as a result of foulant deposition clogging the membrane pores.

Figure 4. Permeate conductivity for CaSO₄, SI = 0.4, no filter. Flux increase between 28 and 35 hours corresponds to wetting of the feed through the MD membrane.

The increase in permeate flux in Fig. 3 corresponds to the amount of feed water that would leak through to cause the conductivity (and thus salinity) results seen in Fig. 4. There is a slight time delay between flux increase and conductivity rise (~3 hours), which is due to the piping after the module containing a significant volume of water, thus causing a time gap between water being flushed out and measured and water at the membrane surface.

This saline experiment without the filter experienced significant wetting of the membrane and contamination of the permeate. By the end of the experiment, the rate of leaking feed into the permeate
accounted for ~8% of the total permeate flux leaving the module. This represents a failure of the MD process, unless the standards for permeate quality are not high.

Figure 5. Cold side and hot side inlet and outlet temperature readings.

The temperature results shown in Fig. 5 indicate minimal variation in system temperatures, and represent those found in all the other trials. The dips in temperature in Fig. 5 at t = 32 and 46 hours and result from water addition to make up for evaporation losses and maintain inlet feed salinity constant. This process resulted in minor and brief flux declines observed throughout the permeate flux data for all experiments.

Figure 6. Permeate flux decline averaged over 0.5 hours for CaSO₄, SI = 0.4, with a filter.
As seen in Figs. 6 and 7, in the high SI case (0.4), the flux declined significantly less when a filter was in place. Furthermore, no wetting was observed with a filter. The results indicate that even filters with fairly large pore sizes (20 micrometers) significantly reduce scaling in MD.

**Figure 7.** Flux comparison with and without filter, CaSO$_4$, SI = 0.4

**Figure 8.** Permeate flux decline averaged over 0.5 hours for CaSO$_4$, SI = 0.2, without a filter.
Figure 9. Polarizing microscopy image of MD membrane surface after SI = 0.2 experiment without a filter. The crystals on the surface clog the membrane pores, reducing the permeate flux.

Microscopy with polarizing light helps make the white CaSO$_4$ scale visible on the white PVDF MD membrane. The scale occurs in discrete crystals, with most of the membrane remaining unscaled. This indicates that heterogeneous nucleation on crystals in the bulk and on the surface are much more favorable than growth on the PVDF surface itself. In cases with the filter, relatively few crystals were observed.

Figure 10. Permeate flux decline averaged over 0.5 hours for CaSO$_4$, SI = 0.2, with a filter.
Figure 11. Permeate conductivity for CaSO$_4$, SI = 0.2, with a filter. No significant flux declined occurred.

The permeate and conductivity graphs for the lower SI (0.2) experiment with a filter showed neither significant flux decline nor membrane wetting. Under these conditions, even for a long duration experiment, the scaling is minimal enough to not affect the performance of the MD process. The flux is slightly lower than the other experiments because the hot side temperature was maintained at 1.2 °C lower than those in the hottest experiments, where variability between experiments was caused by changes in heat losses. The first two hours were at 71.4°C, which caused higher initial flux.

In testing and commissioning the system, experiments were tried with subsaturated (SI<0) and saturated (SI = 0) solutions under the same conditions with CaSO$_4$ without a filter, and no effects of fouling were observed, which included no flux decline, no wetting, and no visually observable crystals on the membrane surface. It should be noted that all the SI values reported are those at the membrane surface, which are calculated via the numerical modeling explained previously.

Table 1. Summary of the effects of filtration and salinity on fouling in membrane distillation.

<table>
<thead>
<tr>
<th>SI (membrane surface)</th>
<th>Filter</th>
<th>Flux Decline</th>
<th>Wetting</th>
<th>Duration [hr]</th>
<th>Final Permeate Conductivity [μS/cm]</th>
<th>Permeate Flux Decline Percent</th>
<th>$T_h$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>27</td>
<td>4.9</td>
<td>3.5%</td>
<td>69.8</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>47</td>
<td>4.0</td>
<td>0.6%</td>
<td>69.5</td>
</tr>
<tr>
<td>0.4</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>29</td>
<td>367</td>
<td>12.6%</td>
<td>71.8</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>23</td>
<td>[not recorded]</td>
<td>3.3%</td>
<td>70.9</td>
</tr>
</tbody>
</table>
Table 1 summarizes the experimental results for all trials performed. Filtration was extremely effective in reducing membrane fouling, indicating bulk nucleation of crystals plays a very significant role in these experiments.

The pore size of the filters was still quite large. The theoretical critical size for stability of a CaSO₄ crystal in the bulk solution is much smaller than the 20 µm pore size of the filter, so smaller crystals can presumably still pass through. Nanofiltration would be required to entirely remove smaller but stable crystals. Nevertheless, the use of a filter made a more significant difference in reducing flux decline than did changes in the saturation index. This indicates that bulk nucleation is likely dominant in the present MD system, and that it may be important in other system configurations. System design to reduce that process, including filtration and control of residence times, may therefore be effective in mitigating MD fouling.

The results also have important implications for MD systems that use brine recirculation. Since MD typically has low recovery (e.g., 6-10%), recirculation is common, especially for systems trying to reach high water recovery or zero-liquid-discharge. Such systems will have substantial residence time for potentially supersaturated brine, which would allow significant bulk nucleation to occur. The effective residence time for long term operation could be an order of magnitude or more larger than for the present experiments.
IV. CONCLUSIONS

Experiments were conducted by separately mixing Na$_2$SO$_4$ and CaCl$_2$ in DI water and then combining these solutions to form the feed. With the concentrations, the measured temperature and flow rates, and an Engineering Equation Solver (EES) numerical model, the concentration and temperature polarization effects were estimated, and the saturation index of CaSO$_4$ was evaluated at the feed-membrane interface, SI$_{f,m}$.

Table 2. CaSO$_4$ fouling effects summary for the filtration experiments

<table>
<thead>
<tr>
<th>SI</th>
<th>Filter</th>
<th>No Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>none</td>
<td>Flux Decline</td>
</tr>
<tr>
<td>0.4</td>
<td>Flux Decline</td>
<td>Wetting and Flux Decline</td>
</tr>
</tbody>
</table>

The experiments have shown that filtration can significantly reduce flux decline at high saturation index as seen in Table 2, which indicates that precipitation in the bulk may play a dominant role in the flux decline and wetting of MD membranes by inorganic fouling. This occurred despite conditions that were favorable to surface scaling over nucleation, including a weakly hydrophobic membrane material (PVDF), notable concentration polarization at the membrane surface, the minimize of available crystallization nuclei provided by lab-grade purity solutions and avoiding of metal parts, and a minimization of temperature elevation at the heater. Therefore, bulk heterogeneous nucleation, not surface crystallization, is indicated as the dominant fouling mechanism in the present system.

For the conditions studied, the presence of the filter reduced flux decline by an amount similar to decreasing the saturation index to SI =0.2 from 0.4. The present experiments have shown that bulk precipitation dominates at both low and high SI (0.2-0.4). Significantly, the study implies that real MD systems using brine recirculation without filtration may suffer a significant penalty in performance under supersaturated conditions, as brine residence times are effectively endless. Additionally, benchtop experiments using recirculation may not properly represent real systems without recirculation.
V. REFERENCES


VI. ACKNOWLEDGEMENTS

This work was funded by the Cooperative Agreement between the Masdar Institute of Science and Technology, Abu Dhabi, UAE and the Massachusetts Institute of Technology (MIT), Cambridge, MA, USA, Reference No. 02/MI/MI/CP/11/07633/GEN/G/00. We would also like to thank Mathias Kolle, Jocelyn Gonzales, Sarah Van Belleghem, Ann McCall Huston, and Priyanka Chatterjee for their contributions to this work.

VI. AUTHOR AFFILIATIONS

David Martin Warsinger\textsuperscript{a,}\textsuperscript{1}, Jaichander Swaminathan\textsuperscript{a,}\textsuperscript{1}, Hyung Won Chung\textsuperscript{a}, Seongpil Jeong\textsuperscript{b}, and John H. Lienhard V\textsuperscript{a}

\textsuperscript{a} Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA
\textsuperscript{b} Center for Water Resources Cycle Research, Korea Institute of Science and Technology, Seoul, Republic of Korea
\textsuperscript{1} These authors contributed equally to this work