



# Theoretical framework for predicting inorganic fouling in membrane distillation and experimental validation with calcium sulfate



David M. Warsinger, Emily W. Tow, Jaichander Swaminathan, John H. Lienhard V\*

Rohsenow Kendall Heat Transfer Laboratory, Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA

## ARTICLE INFO

### Keywords:

Membrane distillation  
Fouling  
Calcium sulfate  
Nucleation  
Induction time

## ABSTRACT

A methodology for predicting scaling in membrane distillation (MD), which considers thermodynamics, kinetics, and fluid mechanics, is developed and experimentally validated with calcium sulfate. The theory predicts the incidence of scaling as a function of temperature, concentration, and flow conditions by comparing the nucleation induction time to the residence time and applying an experimental correction factor. The relevant residence time is identified by considering a volume of solution near the membrane surface that contains enough ions to form a nucleus of critical size. The theory is validated with fouling experiments using calcium sulfate as a model scalant over a range of temperatures (40–70 °C), saturation indices, and flow rates. Although the model is validated with a bench-scale MD system, it is hoped to be compatible with large-scale systems that may have significant changes in concentration, temperature, and flow rate along the flow direction. At lower temperatures, the saturation index can be as high as 0.4–0.5 without scaling, but the safe concentration limit decreases with increasing temperature. Increasing the feed flow rate reduces concentration polarization and fluid residence time, both of which decrease the likelihood of fouling. The model is translated into easily readable maps outlining safe operating regimes for MD. The theory and maps can be used to choose safe operating conditions in MD over a wide range of conditions and system geometries.

## 1. Introduction

Membrane distillation is a desalination technology thought to have relatively high fouling resistance in comparison to other membrane-based desalination technologies such as reverse osmosis (RO) [1]. MD relies on evaporation of water from a hot saline feed through a hydrophobic, porous membrane that allows the passage of vapor but not liquid water [2,3]. The fouling and scaling resistance of MD makes it a promising technology for high salinity applications. MD is especially promising where high osmotic pressure precludes the use of conventional RO, such as in zero liquid discharge systems and for some mining and industrial water treatment [4]. However, the cause of fouling resistance in MD is poorly understood. The literature offers many experimental studies but little fundamental explanation [5]; however, the hydrophobicity of the membrane is thought to minimize surface crystallization [6]. A fundamental understanding of MD fouling is needed, as is a practical approach to predicting the fouling limits of MD with complex solutions.

Previous studies have shown that MD can withstand significantly supersaturated conditions, and that filtration and membrane super-

hydrophobicity are the most effective existing methods to enhance the fouling resistance of MD [5,7]. Numerous pilot studies have found good resistance to fouling, but have documented significant flux decline and membrane wetting when fouling did occur [8–10]. The inorganic salts most likely to cause scaling in many cases are calcium sulfate and calcium carbonate [11], which are the found in seawater, groundwater, and mining applications. There is evidence that filters are extremely effective in reducing fouling-related flux decline [12–15] and directly observable fouling [5,16,17]. Some past studies have observed crystals only when the membrane dried out, not during operation [7,18]. This is evidenced by the absence of crystals when the system was allowed to drain, even under very saline conditions (e.g., saturation index (SI) between 1.08 and 1.93 on strongly hydrophobic membranes [7]). When fouled membranes that had flux decline during operation have been examined, the observed crystals are sparsely scattered over the membrane surface, with many areas remaining free of crystals [6].

Understanding the effect of surface properties on crystal nucleation is necessary for scaling prediction. As detailed by Warsinger et al. [19], the Gibbs energy barrier for heterogeneous nucleation on a surface can be expressed as a function of surface energies between the liquid,

\* Corresponding author.

E-mail address: [lienhard@mit.edu](mailto:lienhard@mit.edu) (J.H. Lienhard V).

**Nomenclature**

$a_{\pm}$	Mean ionic activity [dimensionless]
$a_{\pm, sat}$	Mean ionic activity at saturation [dimensionless]
$b, c$	Constants fit from nucleation time data [dimensionless]
$C$	Concentration of calcium sulfate at membrane [mol/m <sup>3</sup> ]
$C_{sat}$	Saturation concentration of calcium sulfate [mol/m <sup>3</sup> ]
$D_h$	Hydraulic diameter [m]
$f_d$	Darcy friction factor [dimensionless]
$\Delta G_V$	Volumetric Gibbs energy change [J/m <sup>3</sup> ]
$L$	Membrane length [m]
$M_w$	Solute molar mass [kg/mol]
$N_A$	Avogadro constant [mol <sup>-1</sup> ]
$n_{min}$	Minimum number of molecules in a stable nucleus [dimensionless]
$P$	Pressure [Pa]
$R$	Universal gas constant [J/mol-K]

$r_c$	Critical radius [m]
$Re_{Dh}$	Feed channel Reynolds number= $\rho_l v D_h / \mu_l$ [dimensionless]
SI	Saturation index [dimensionless]
$t_{res}$	Residence time [s]
$t_{res}^*$	Relevant residence time for fouling prediction [s]
$u$	Local velocity [m/s]
$v$	Average velocity [m/s]
$V$	Volume [m <sup>3</sup> ]
$z$	Distance from membrane [m]
$z_{min}$	Distance from membrane containing enough ions to form a critical nucleus [m]
$\gamma$	Interfacial energy of crystal in saturated solution [J/m <sup>2</sup> ]
$\mu_l$	Liquid dynamic viscosity [Pa-s]
$\rho_l$	Liquid density [kg/m <sup>3</sup> ]
$\rho_x$	Scalant crystal density [kg/m <sup>3</sup> ]
$\varphi$	Experimental fitting parameter [dimensionless]

crystal, and substrate [20,21]. This energy barrier influences the nucleation induction time, which is the delay before observable nucleation occurs [21]. An overlapping set of surface energies dictates the liquid contact angle on the surface, thus linking hydrophobicity to induction time for crystal nucleation at the surface [19]. However, past work has shown that crystal nucleation in membrane distillation occurs largely in the bulk feed solution [6], rather than beginning on the membrane surface as in RO [11]. This difference results from the low surface energy of MD membranes, which are hydrophobic, in contrast to the high surface energy [22] of (hydrophilic) RO membranes [19].

Modeling scaling in MD is complex because of the fluid flow and gradients in temperature and concentration. While classical nucleation theory has focused on induction time in stagnant, heterogeneous solutions, this time can be compared to the fluid maximum residence time within a region of interest to determine whether bulk nucleation will occur. In the present work, we develop theory based on comparison of induction time and residence time, and we validate the theory with multi-day MD fouling experiments using calcium sulfate. From these results, we create regime maps in terms of temperature, saturation index, flow rate, and channel geometry that outline safe regimes for fouling-free operation (Section 4.4).

## 2. Theory development

Fouling can be approached from one of two standpoints: an Eulerian one, in which induction time theory suggests that crystallization at a given location will occur eventually for almost any supersaturated feed, and a Lagrangian approach that follows the solutes, recognizing that they may move through the membrane module without having time to crystallize. In previous induction time experiments [23–25], the supersaturated solution was in a closed system, and a model for conditions in a moving fluid was not needed.

Here, we take the Lagrangian approach, and we postulate that fouling will occur when the fluid residence time in the channel exceeds the nucleation time for any precipitate. However, evaluating the exact onset of fouling is not straightforward because both induction time and residence time vary within the channel. The highest residence times occur in the slow-moving boundary layer near the membrane surface (Fig. 1) and vary with distance from the wall.

### 2.1. Residence time

Near the channel wall, in the boundary layer, the velocity approaches zero and the residence time (inversely proportional to the velocity) of a fluid parcel in the channel approaches infinity. However, very close to the channel wall, there are not enough ions to form a

stable nucleus of a critical radius. We postulate that a group of ions large enough to form a critical nucleus must all be in residence long enough to allow for nucleation [26]. The number of molecules needed to form a critical nucleus of radius  $r_c$  is  $n_{min}$ :

$$n_{min} = \frac{V_{crit}}{V_{molecule}} = \frac{\frac{4}{3}\pi r_c^3}{\frac{M_w}{N_A \rho_x}} \quad (1)$$

where  $V_{crit}$  is the volume of a critical nucleus,  $V_{molecule}$  is the average volume of a salt molecule in solid form,  $M_w$  is the molar mass,  $N_A$  is the Avogadro constant, and  $\rho_x$  is the crystal density. The need for a critical nucleus for crystal growth arises from the high surface free energy per unit volume of small particles, as discussed in Ref. [23].

We assume that the relevant distance  $z$  from the membrane is very small compared to the thickness of the channel, so that the properties of the fluid (e.g., temperature, concentration) can be considered uniform in the nucleation region and equal to the value at the wall ( $z = 0$ ). A sphere of fluid containing  $n_{min}$  molecules in excess of the number that would be present at saturation has a diameter of  $z_{min}$ :

$$z_{min} = 2r_c \left( \frac{\rho_x}{M_w(C - C_{sat})} \right)^{1/3} \quad (2)$$

where  $C$  is the concentration near the wall of the crystal-forming molecule in moles per cubic meter and  $C_{sat}$  is the saturation concentration at the local temperature. The distance  $z_{min}$  from the wall is shown in Fig. 2.

Because enough ions are present locally to form a critical nucleus within a distance of  $z_{min}$  from the wall,  $z_{min}$  is the distance from the wall at which the residence time (based on the local velocity) will be compared to the nucleation time. The residence time at  $z_{min}$  can be computed using existing correlations for Darcy friction factor  $f_d$ ,

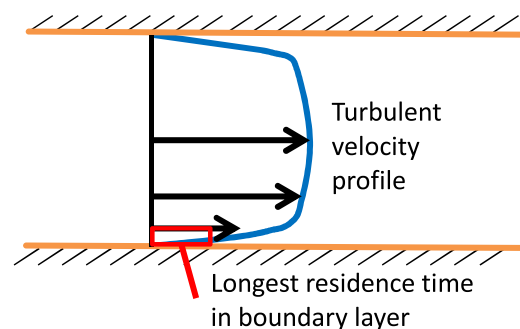


Fig. 1. The maximum residence time in the system occurs in the boundary layer near the membrane.

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