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Reversing membrane wetting in membrane distillation: comparing dryout to backwashing with pressurized air

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Abstract

The critical failure mode for membrane distillation (MD) desalination is wetting through the pores of the hydrophobic membrane, which allows the saline solution to leak through and contaminate the permeate. The standard practice for reversing membrane wetting is to dry out the membrane for several hours before resuming the desalination process. An alternative method for mitigating MD membrane wetting is examined in this study, wherein pressurized air is pushed through the membrane from the permeate side for several seconds, forcing trapped water out before it can evaporate. To compare the wetting reversal methods, the Liquid Entry Pressure (LEP) was surpassed with saline water at varied salinity. Then, either a 24+ hour dryout, a 10 second pressurized air treatment, or both were applied, followed by remeasuring the LEP. Pressurized air backwashing restored the LEP to 75% of the original value for lower salinity feeds. The backwashing method is hypothesized to achieve this superior result because it removes saline solution from the membrane without separating water and salts by vaporization, whereas the dryout method causes seawater within the membrane to evaporate, leaving crystalline solutes trapped within the membrane. Such trapped particles may act as a path for rewetting, and also impair permeate flux and system energy efficiency. For all three methods, membranes tested with higher salinity water had lower LEP restoration irrespective of the restoration technique used. A method for testing LEP with more accuracy was also developed, using stepwise pressure increases. SEM images showed that the restoration methods did not alter the membranes themselves, although there remains a possibility that the air backwashing can cause superficial tears.

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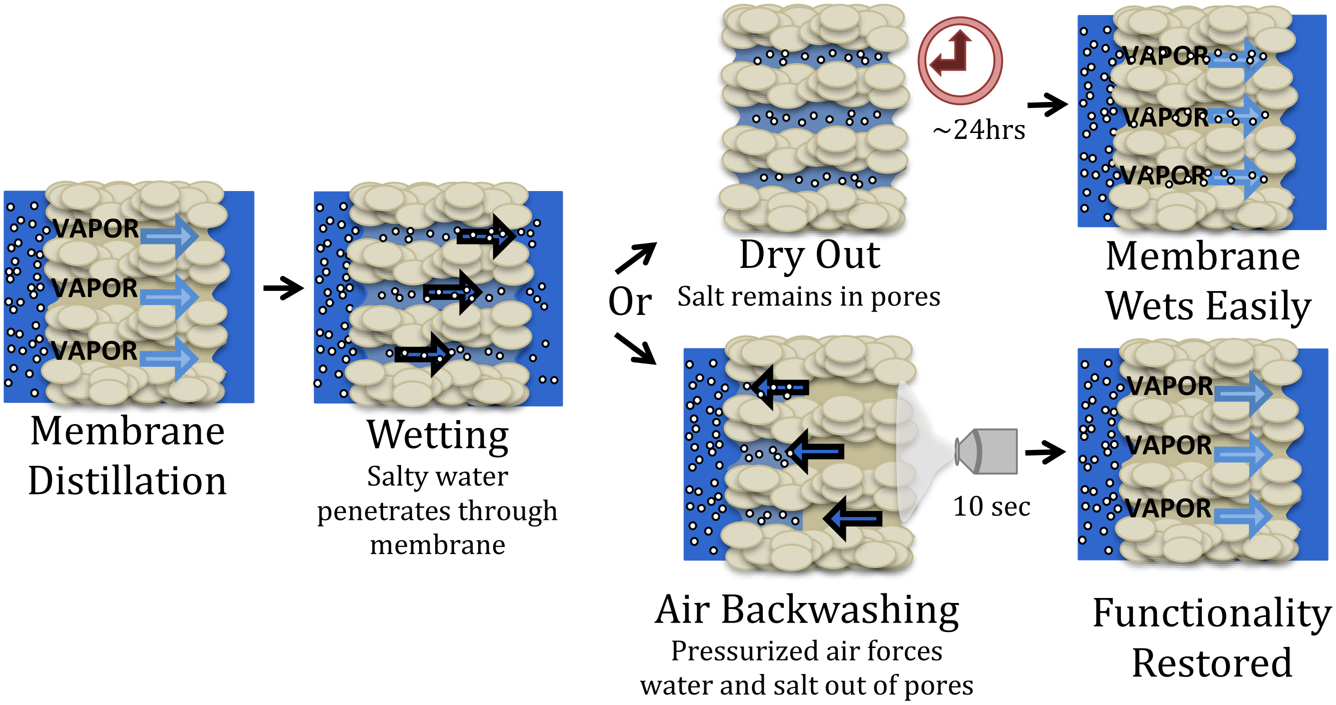
Keywords: *membrane distillation, wetting, dryout, air backwash, cleaning, crystallization*

Graphical Abstract



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1. Introduction

1.1 Membrane Distillation and its Failure Modes

Membrane distillation (MD) is a water desalination technology that is especially well suited for high salinity feed water [1, 2, 3]. MD is thought to be more fouling resistant than reverse osmosis, the dominant technology for brackish water and seawater desalination today [4, 5]. Membrane distillation utilizes a temperature difference and a porous hydrophobic membrane barrier to desalinate water. The membrane allows only pure water vapor through, which is then collected on the permeate side of the membrane [6]. This system can operate at relatively low temperatures, and has a similar efficiency to that of other thermal desalination systems [7, 8]. Additionally, although this system is not as energy efficient as reverse osmosis systems, MD can operate using low-grade thermal energy (so-called "waste heat") that may not otherwise be utilized [9, 10].

Membrane distillation has two primary failure modes: vapor flux decline, which can be caused by membrane pores blocking [11, 12, 13], and wetting of the membrane, where saline water leaks through the hydrophobic pores of the membrane and contaminates the permeate [14, 15]. The more serious failure mode is wetting, as it drastically reduces permeate quality. Some authors have pointed out inorganic fouling as the main cause of partial membrane wetting [16, 17, 18, 19], which some have claimed can also reduce vapor flux. Organic foulants may also play a role [16, 20, 21]. Additionally, the possibility of membrane wetting can limit the ability of MD to treat fouling-prone solutions. Fouling and wetting have been shown to be interrelated in membrane distillation: wetting causes increased fouling and fouling causes increased wetting. This cycle can cause rapid degradation of MD performance, increasing the frequency of membrane replacement.

In some studies, it has been shown that intermittent operation of membrane distillation facilities is the primary cause of fouling, especially when drying of the membrane is allowed to occur. Dryout can lead to salt particulates being left behind on the membrane as the water evaporates from the surface of the membrane, blocking pores and causing flux decline across the membrane as a result [22, 23]. If any wetting occurred during operation, after dryout, particulates would also remain in the membrane pores, further decreasing flux and increasing the possibility of future wetting, This intermittent operation occurs frequently when the system is driven by renewable energy sources without energy storage, including solar power [24, 25, 26, 27].

Despite these findings, the current baseline treatment of membrane wetting in MD is to stop operation and allow the membrane to dry out completely [28]. The MD system performance may decrease over time as a result of more salt particulate buildup within the pores and on the surface of the membrane, which leads to a lower resistance to wetting and a reduced vapor flux. A number of methods have been examined to mitigate such wetting concerns, including superhydrophobic membrane surfaces, surface oscillations, and a variety of cleaning techniques. [29, 30]. While many methods show promise in wetting prevention, wetting reversal and restoration has remained a pervasive challenge for membrane distillation.

1.2 Liquid Entry Pressure

Wetting occurs as a result of water pressure on the feed side overcoming the interfacial force caused by the hydrophobicity of the membrane. The membrane's ability to resist wetting is described by the Liquid Entry Pressure, or LEP. LEP is the pressure that the feed water must overcome in order to penetrate the membrane's pores, leading to wetting. The significance of LEP and its influence on membrane wetting have been discussed elsewhere [31, 32]. LEP is classically described by the following modified Young-Laplace equation [14, 33]:

$$LEP = \frac{4\mathrm{B}\sigma\cos\theta}{D_{max}} \tag{1}$$

where B is the geometric factor for the pore shape (B_g = 1 for perfectly cylindrical pores), σ is the surface tension of the feed solution, θ is the contact angle for the membrane and feed solution interface, and D_{max} is the maximum pore size (i.e., diameter) of the membrane.

1.3 Previous Work on Restoring Wetted Membranes

Dryout of the membranes is accepted as a poor solution for reversing the wetting of membranes in MD, although it is the primary method for doing so [34]. Cleaning the membrane surface with water and solvents to remove scalant deposits is used to reduce wetting in MD systems. However, the membrane continues to lose its resistance to wetting over time in feed solutions with common foulants, as the cleaning poorly restores performance [35]. Backwashing with pure water or pressurized distillate has been tried to reduce wetting as well [36], but is very limited because the hydrophobic nature of the membrane prevents penetration through the vast majority of the pores and space within the membrane [37]. To counter this issue, a study performed by McAlexander et al. treated wetted membranes by backwashing them with a non-aqueous solution having a low surface energy. The low surface-energy solution wets the membrane thoroughly, restoring hydrophobicity to the membrane after washing and removal of the solution through evaporative drying in an oven [38]. Those results showed moderate restoration of the membrane performance in most cases. However, this method may be costly to implement in practice owing to the expense of heating and consumption of the non-aqueous liquid, as well as the additional infrastructure needed to implement this solution. Additionally, because the removal of the non-aqueous solution was incomplete, there is potential to pollute the permeate. Moreover, the downtime incurred to treat the membrane with a non-aqueous solution exceeds the time needed for dryout: non-aqueous solution treatment required approximately 15 hours under lab conditions, whereas complete dryout of membranes can be faster [38]. Finally, backwashing may be less successful with more hydrophobic membranes because the surface energy of the non-aqueous liquid may not be low enough to wet the membrane.

1.4 Remediating fouling with air layers and air backwashing

In the present work, air backwashing is studied as an alternative to dryout. Air backwashing is a several-second periodic process aimed to restore the membrane from its wetted state and to largely regenerate the effective hydrophobicity of the membrane. By sufficiently exceeding the LEP with air backwashing, the high-pressure air stream may force out the water and any foulants trapped in the pores of the membrane. Excess pressure beyond LEP is needed, as LEP is defined by only the maximum pore size, and other smaller pores may also need to be dried. By removing the water rather than letting it evaporate from the surface of the membrane, salts are less likely to be left on or within the membrane. Manipulating air at the membrane surface holds promise for avoiding fouling. Past studies have looked at using membrane superhydrophobicity, spacers, and air addition on the feed side to reduce fouling. These studies have shown a reduction in adhered foulant [39, 40] and reduced membrane wetting from the surfactant SDS [41]. Additionally, past studies have used aeration and low pressure air backwash to mitigate salt deposition: in a study by Meng et al., the air backwash prevented permeate conductivity increases despite a complex supersaturated feed, while aeration did not [42]. While those air pressures were too low to push out trapped water through membrane pores, the air may have helped displace water at the membrane-water interface. Other filtration technologies with large pore sizes have also used air backwashing such as contact filtration [43], membrane bioreactors [44, 45], and ultrafiltration [46, 47], but these studies are limited and water backwashing is generally preferred. Previous studies have not used air backwashing for reversing wetting or in conjunction with LEP tests.

In this study, we wetted membranes at three different NaCl salinities. Then, we attempted to reverse the wetting by dryout, air backwashing, or by air backwashing with dryout. Finally, we compared the LEP of the membranes before wetting to the LEP after wetting and dryout/air backwashing. This determined to what extent the membrane's hydrophobicity is restored by these methods.

2. Methodology

LEP was measured using a syringe-pump based LEP setup. The syringe pump was used to pressurize the saline solution until the pressure was high enough to overcome the hydrophobicity of the membrane. At this pressure, wetting of the membrane occured (Fig 1). This setup has previously been described in detail and proven to be successful for LEP experiments [31, 48, 49, 50, 51].

A PVDF membrane was chosen for this study: Millipore Immobilon-PSQ part # ISEQ 000 10 [52]. This membrane has a high advancing contact angle with water (125°), good porosity (~80%), a typical MD nominal pore size (0.2 µm), a suitable thickness for minimizing thermal conduction (~200 µm), and has been shown to be robust and fouling resistant over many experiments [39, 53, 54].

The procedure for testing each membrane's LEP was as follows [55]. A 13 mm diameter disk was cut out of the membrane, Then, the sample of new, unwetted membrane was held by the 13 mm syringe membrane holder (GE healthcare biosciences, Product Code 1980-001). Additionally, two O-rings held the membrane and the membrane support, a metal mesh support, within the membrane holder in a waterproof fit. First, the membrane was exposed to a saline solution (0.05%, 3.5%, or 20% NaCl by weight, from Sigma-Aldrich) on the top (feed) side, and to ambient air on the other side. Then, the syringe pump (PHD 22/2000, Harvard Apparatus), was set up to push the saline solution against the membrane at a constant volume rate of 0.02 mL/s until 0.2 mL of solution has been pushed through the syringe. This volume was held for 12 seconds to produce a stepwise increase in pressure, while the behavior of the membrane under pressure was observed. After 12 seconds, the process was repeated. The indication of when the LEP occurred was given by the rate of change of pressure (the slope of the pressure-time curve, dP/dt) during the pauses between steps. When wetting occurs, leakage of water through the membrane causes the pressure to decrease (negative dP/dt), whereas without wetting, the pressure remains fairly constant ($dP/dt \approx 0$) (see Fig. 5). This new methodology was compared to a standard methodology. In a standard test, the salinity is detected by a conductivity probe placed in a stirred DI solution outside the membrane (Fig. 1). That standard methodology identifies LEP as the maximum pressure reached during continuous pressurization, which occurs as pressure drops rapidly once leaking of a set volume becomes significant [49, 50, 51]. The new methodology gave very similar results to this standard one, but the new stepwise method had a standard deviation of LEP values less than half of that of the standard one, indicated more precise results. Additionally, the new step-wise method requires fewer parts, as the stirrer and submerged bath for the membrane are unnecessary (Fig. 1).

The pressure difference across the membrane was recorded using a pressure transducer with a precision of ±0.3 kPa (P409, Omega). The data received from the pressure transducer was received by the pump's default Symphony software, and measurements were recorded 10 times per second.

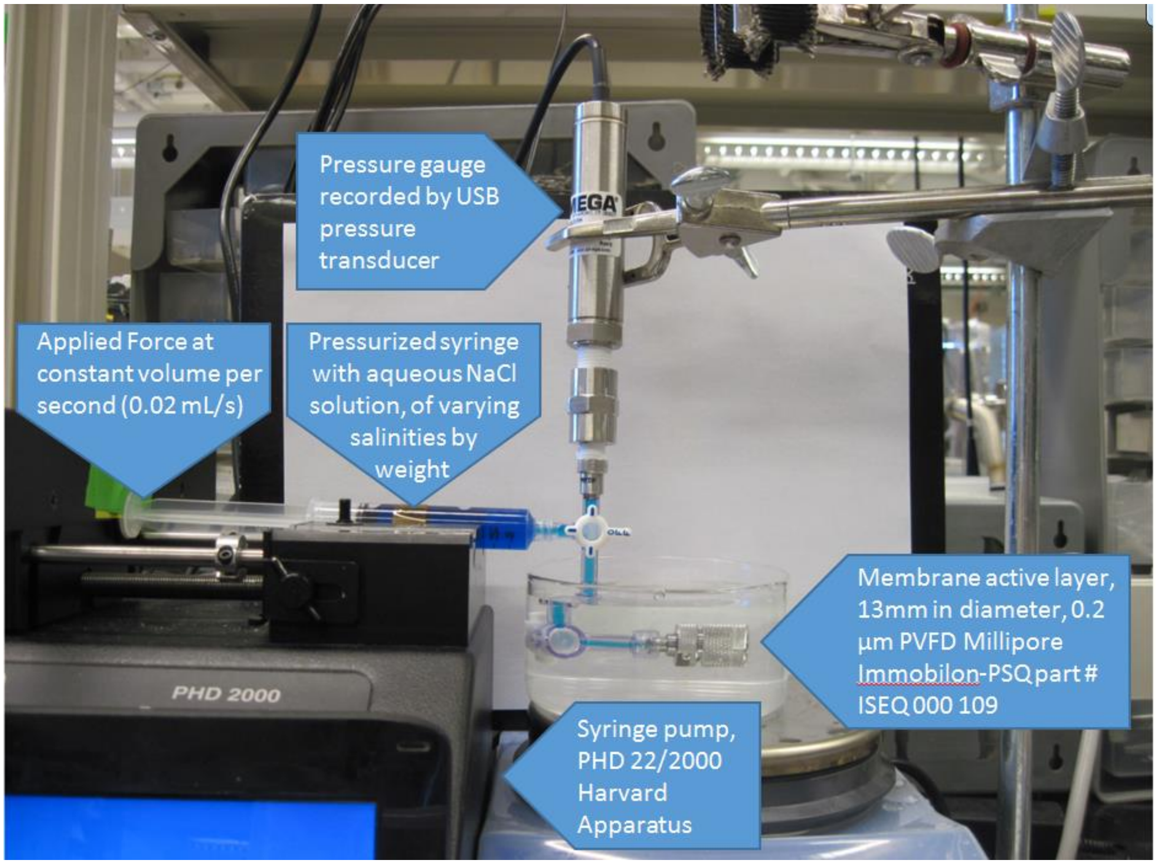

Figure 1. Liquid Entry Pressure (LEP) testing setup, using pressurized syringe, a saline solution, and a small membrane holder. Feed is dyed blue here for visibility. The submersion bath was used only to compare the new LEP method to other methods.

After wetting has occurred (when the feed pressure exceeded the LEP of the membrane, see section 3.2), the membrane was removed from the setup and subjected to one of the two recovery methods: the sample was either allowed to dry for a minimum of 48 hours, or it was immediately subjected to the air backwashing where pressurized air was forced through the permeate side of the membrane (Fig. 2). A few cases were tried using both methods, where the membrane was dried before being backwashed with pressurized air. For the air backwashing method, the air was pushed through the membrane for 10 seconds at approximately 450 kPa, a pressure significantly higher than the membrane's LEP. This excess pressure allows the forcing liquid out of smaller pores, but is not high enough to damage the membrane. Tests showed that at pressures exceeding ~1,000 kPa, our membranes started to rupture, so operation was limited to 450 kPa. The pressurized air line was coupled with the membrane holder by using a custom design made by modifying the original GE membrane holder (Fig. 2).

A Quanta FEG 250 (FEI, USA) microscope at an accelerating voltage of ~7-10 keV was used to perform the SEM analysis on the samples. Prior to SEM analysis, the samples were gold and palladium coated using an Etching Coating System (PECS Model 682 by GATAN, Japan).

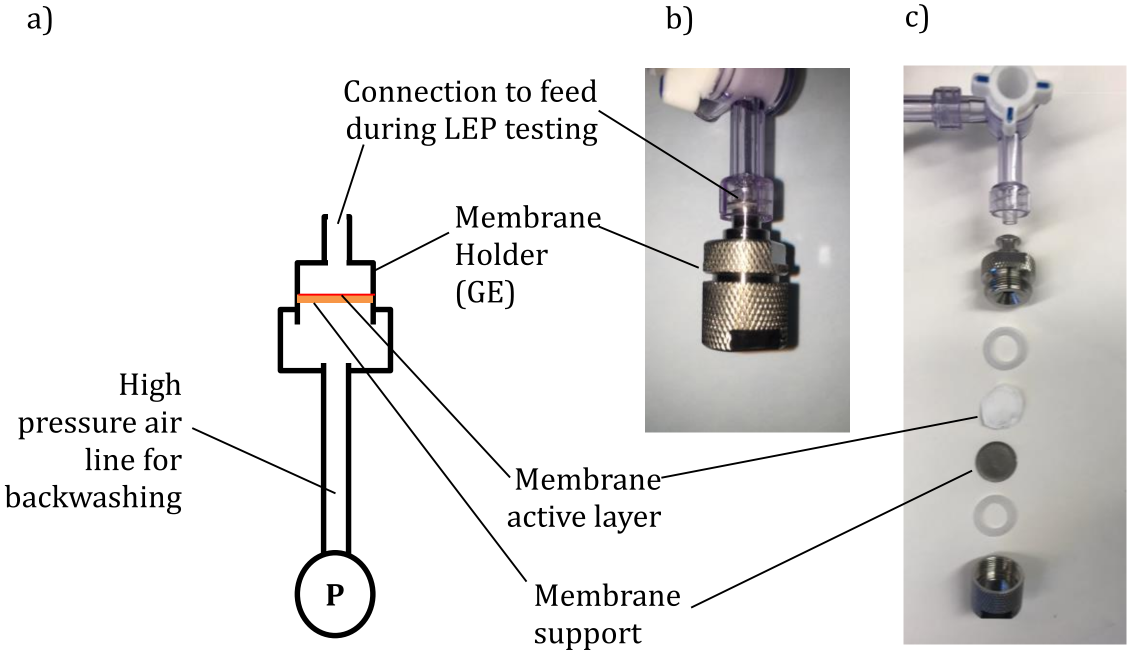

Figure 2. Setup for adding forced air into the gap side of the membrane holder. a) diagram of membrane holder with air recharging, b) photo of membrane holder for LEP testing, c) holder dismantled

3. Results and Discussion

3.1 Impact of Air backwashing vs Dryout

Overall, the air backwashing consistently restored LEP to a higher value than the 24-hour air dryout method (Fig. 3), but the percent LEP improvement was not much beyond the experimental error for some cases. The LEP measurements prior to wetting exhibited some variability, with an average standard deviation between all trials of 20.8 kPa (about 7% of LEP). This deviation was accounted for by minor impacts from equipment error and variation in the physical properties throughout the membrane, including pore size, thickness, and porosity. Membrane samples are known to vary, and this level of variation is actually relatively small. The trends and implications here are largely robust.

As seen in Fig. 3, at the three salinities tested, air backwashing restored LEP to 55-79% of the original LEP value of 260 kPa. At 0.5wt% salinity, a 21% decrease from the original LEP of the membrane was observed. At 3.5wt% and 20wt% salinity, respectively, a 23% and 45% decrease from the original LEP was observed. In comparison, for the dryout test, for 0.5%, 3.5%, and 20%, LEP was restored to 73%, 59%, and 7% of the original value, respectively. These were all below the air backwash results. In the case of dryout followed by air backwash, some showed better while others showed worse LEP restoration. As the air backwash was done after dryout, where no water was present, it can be inferred that the important benefit is in removing saline water before salts are deposited.

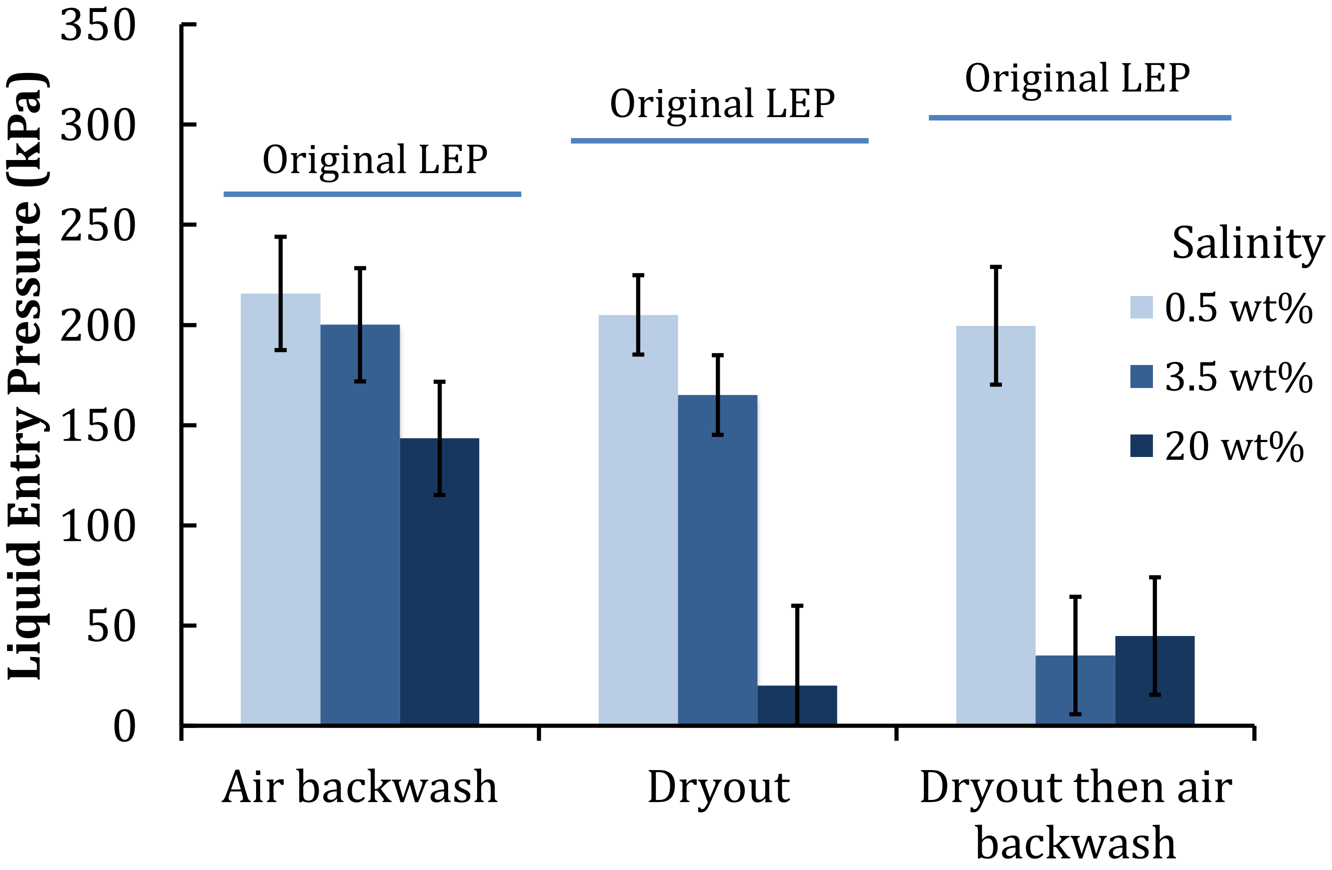

Figure 3. Restored LEP values of PVDF membrane distillation membrane after initial wetting for different restoration methods and NaCl concentrations. Dryout was done over 24 hours, and the air backwashing was done for 10 seconds.

An important conclusion from these results is that salinity greatly impacted the results of the air backwash trials. Overall, the more saline the feed, the less the recovery of LEP (Fig. 3). Dissolved salts slightly decrease the surface tension [56] of water and thus impact LEP, but to a much smaller degree than the results seen in this study. Therefore, salt crystals forming on or in the membrane is a more likely explanation [2]. Salts like NaCl are hydrophilic, and would act to cause a net reduction in the LEP through the reduction of the surface tension between surface and solute (to which LEP is linearly proportional). This impact on LEP can be calculated with Cassie's law, which describes how coverage of another material (salt in this case) reduces the contact angle on the surface, where LEP is proportional to $\cos\theta$ as described in equation 1 (section 1.2). Feed water that intrudes into the pores forms the water/water-vapor interface. The evaporation of water at the interface induces supersaturation at the liquid-filled portion of the pore, which futher results in nucleation and growth of crystals adjacent to the evaporation spots and the growth of crystals in the direction of vapor phase. (This supersaturation will be rapid in the case of high saline water [2]. The results support this proposed mechanism of salt penetration, as higher concentrations impaired LEP more (Fig. 3). Flux is not fully restored in any case, likely because not all the salts are removed.

In order to further examine the impact of both air backwashing and dryout methods on restoration of LEP, the membranes were observed under SEM to seek any surface changes after treatment. Membranes from the air backwashing and the dryout trials appeared to be similar, with surface coverage of crystals having roughly the same total area fraction. This implies that air backwashing may prevent crystallization within the membrane, but does not keep the surface salt-free. As seen in Fig. 4 for 3.5 wt% NaCl, the membrane shows some deformation and superficial crystals after air-backwashing. In order to examine the membranes under SEM, both the forced air backwashing and the original dryout membranes had been left to dry, so there was salt left on the surface of the forced air and dryout membranes. This drying of the air backwashing membrane was necessary for SEM, but would not occur in situ in real systems, potentially resulting in fewer crystals on the surface.

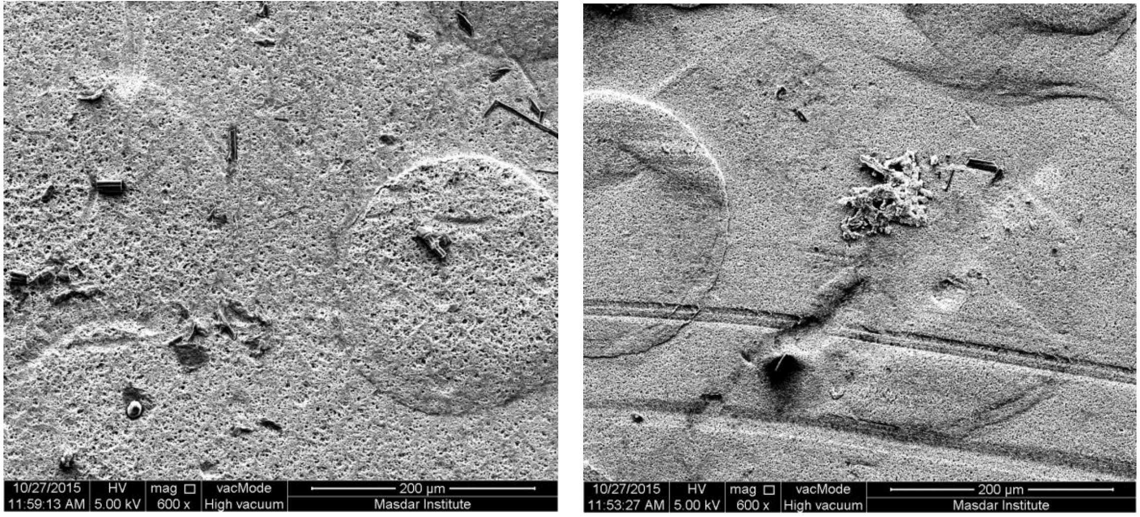

Figure 4. SEM image of feed side of membrane surface, in a trial with 3.5 wt% NaCl. Left: with forced air backwashing, and Right: with dryout

A peculiar membrane surface feature is the circular pattern seen in the SEM image of the membrane subject to air backwash (Fig. 4). This pattern is attributed to the metal spacer that serves as the membrane support during LEP testing. The metal spacer has small circular holes, which have created the same pattern within the membrane. This circular pattern was visible on membranes of both air backwashing and dryout experiments.

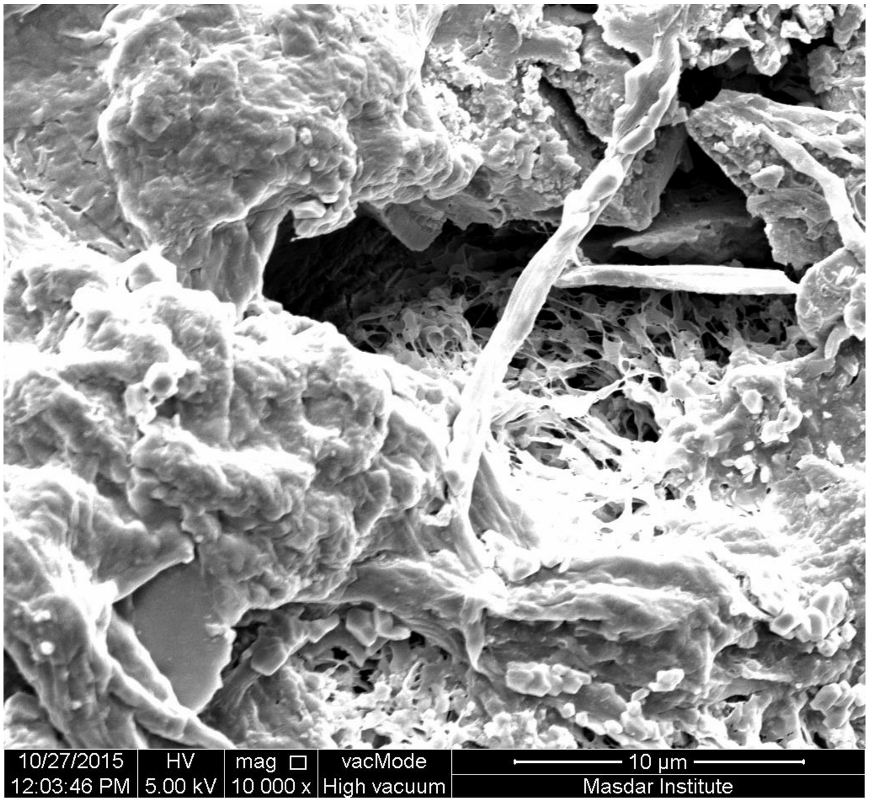

Figure 5. 3.5 wt% NaCl feed, after forced air backwashing. While the LEP restoration was superior to that of dryout, a possible tear may have occurred on the membrane surface (large dark area in center right of image)

We also examined the SEM images for evidence of structural changes to the membranes due to air-backwashing. Overall, the membrane appear nearly identical between the dryout and forced air backwashing trials (Fig. 4). This observation is notable because it suggests that the addition of high pressure has not significantly affected the membrane surface. However, in one sample under SEM, there was one surface feature seen for the air backwashing trial that was not seen in dryout. This feature is shown in Fig. 5, and it might be a tear, although the LEP of the membrane was still superior to that of the dryout membrane. In order to protect the membrane from tearing, a slow ramp up and down of the pressure may be preferable to a sudden blast of air. Further work should explore how best to support the membrane during air backwash and how much pressure is optimal for clearing membrane pores without tearing the membrane. Of interest for further work is examine the potential for repeated cycling to cause membrane damage under conditions typical of real systems. However, membranes are commonly subjected to high pressure air, especially during air scouring to remove fouling in bioreactors [46, 57, 45, 47].

The air backwashing process is expected to be highly applicable to most membrane distillation processes. The PVDF membrane in study is a good representation of membranes commonly used in MD systems [58]. The air backwashing method could be easily implemented in existing MD systems by connecting a high pressure air-line to the permeate output with appropriate valving.

3.2 Improved detection of LEP

An unexpected outcome of this study is an improved methodology for LEP detection, which was developed to reduce the variability standard methods. Typically, LEP measurement have been done simply by recording the maximum pressure reached during a test, while applying continuously increasing pressure. However, this can overestimate LEP, as LEP is taken as the point where leakage is rapid enough to cancel out ongoing pressurization. That approach is also highly variable and less repeatable because results depend on pressure ramp rates and the rates of leakage. Here, we have instead used a stepwise increase in pressure, monitoring for any slight decrease in pressure between steps (which occurs as a consequence of water leak, via wetting, out of the pressure chamber) as a sign of LEP.

The final region of a representative LEP trial is shown in Fig. 6. A stepwise pressure increase is used, with 12-second holding periods between increases.

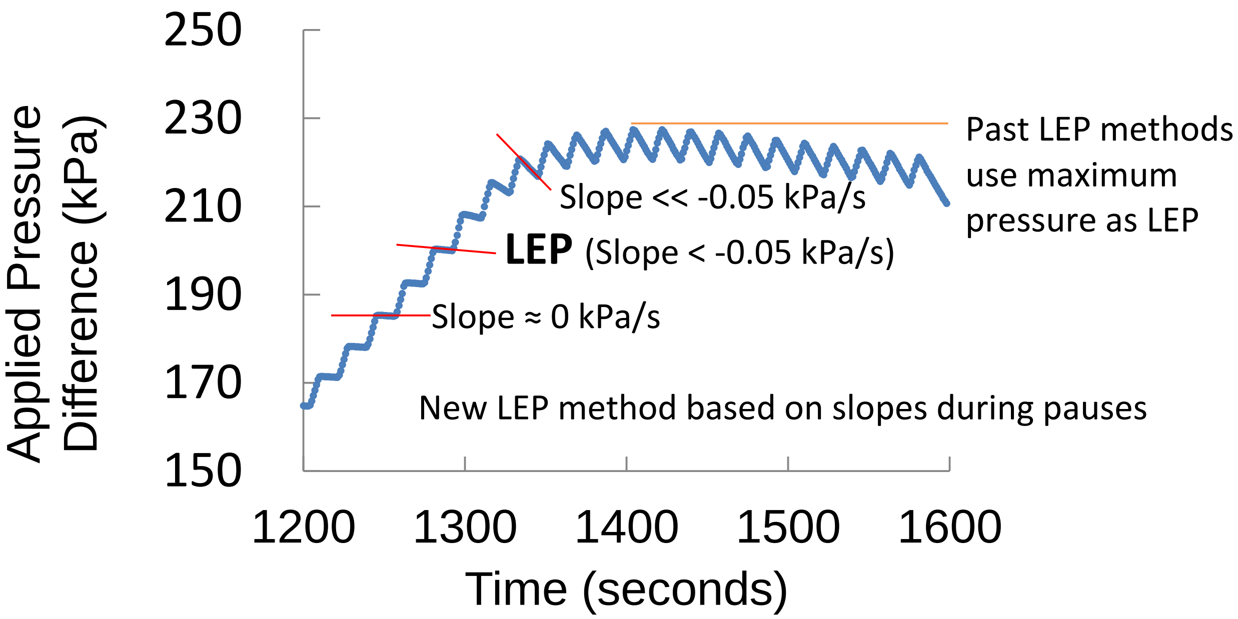

Figure 6 New methodology for determining LEP using stepwise pressure increases and defining LEP as the pressure at which the pressure begins decreasing during pauses. This test was performed at 3.5 wt% NaCl. A negative slope instead of a flat slope indicates

LEP has been exceeded. Here, LEP is estimated at 199.6 kPA (occurring at *t*~1290 seconds).

The point at which the slope of pressure vs. time begins to become observably negative during holding periods (defined here as dP/dt < -0.05 kPa/s) is taken as the LEP, rather than the maximum pressure attained. This slope is appropriate because it is large enough to exceed experimental measurement error, but still an order of magnitude smaller than the maximum wetting rate, allowing for early detection of wetting.

Notably, system variables such as component warping under pressure can cause very slight negative slopes in unwetting conditions, so studies should test systems to ensure the cutoff slope for indicating LEP significantly exceeds the natural negative decline rate of a given apparatus. These slopes for selected trials are graphed in Fig. 7.

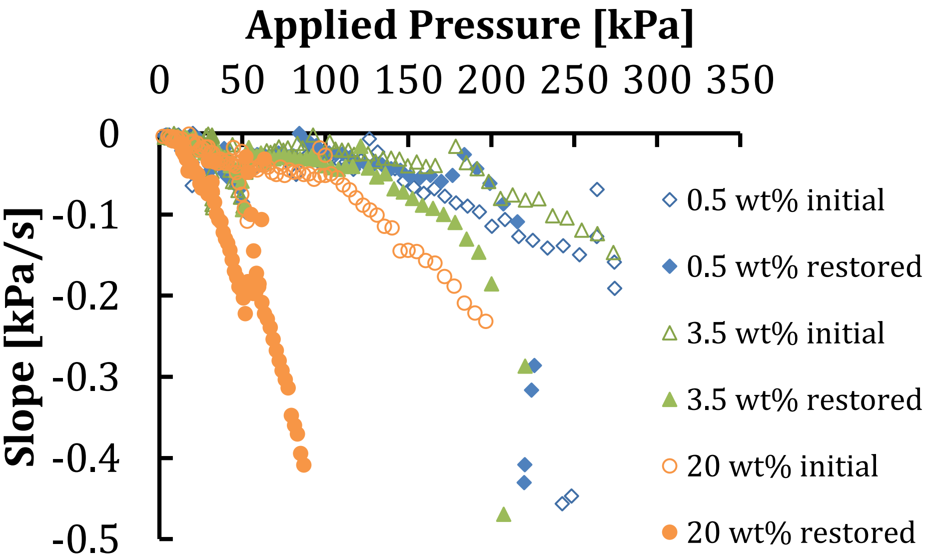

Figure 7. Rate of pressure decrease during flat periods of applied pressure step increases, for air backwashing. Values below -0.05 kPa/s are considered exceeding LEP.

Fig. 7 shows the slopes of the rate of pressure decline for air backwashing trials. Consistently, the curves remain flat (with slope very close to zero) until an LEP point has been reached, then the slope becomes steeper and negative. For example, for 0.5 wt% restored with air backwashing (solid blue diamond), the slope becomes very steep not long after 200 kPa is exceeded. For more saline trials (e.g., 20% wt), the rate of decline is steeper. These deformations are consistent between trials, and often create certain artifacts in the slopes at given pressures. The conclusion from Fig. 7 is simply that pressure decline rates increase near LEP points, but are otherwise small enough that the step-wise method of LEP measurement works across a significant range of conditions.

4. **Conclusions**

The air backwashing method (10 seconds of pressurized air) for restoring the LEP was consistently more effective than the traditional 24-hour dryout method, providing higher restored LEP's in all cases. The improvement was modest for low salinities and significant for high salinities. The backwashing method was able to restore the LEP of a membrane wetted with 0.5 wt% saline to up to 75% of the original value. In all cases, higher salinity solutions led to lower initial LEP values and significantly worse restored LEP values. This salinity trend, and the success in LEP restoration using air to remove water from inside wetted membranes, suggest that salt within the membrane pores is a key factor in wetting. The membranes subject to both LEP restoring tests were viewed under SEM, where no differences between the dryout or air backwashing method were observed from the membrane; neither case had large-scale deformation of the membrane. The high-pressurized air did not significantly damage the membrane, although the possibility of superficial tears may exist. Additionally, a more accurate methodology for LEP determination was developed: stepwise pressure increases, with a focus on any decline in between pressurization steps, provides a more precise and repeatable measure of LEP. Overall, the results suggest that high-pressure air backwashing can be used to improve membrane longevity and enable operation with more-fouling prone feed solutions.

Future work on MD air backwashing should should include the following:

- Examination of the impact of repetitive pressurization on membrane performance under realistic operating conditions
- Specific spacer and membrane design to accommodate high pressure backwash, including the addition of a feed spacer

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6. **Conflicts of interest**

The authors declare no conflicts of interest for this work.

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