NWRI-SCSC GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

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Project Title:	Impacts of Long-Term Exposure to Flow with Elevated Salinity and Temperature on Hydrophobicity of Membranes used for Membrane Distillation
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Background and Introduction

Drinking water sources throughout the world are becoming increasingly saline over time. This increase in water resource salinity has a number of different causes, including: urban runoff, residential water treatment systems (e.g., water softeners), industrial uses (e.g., cooling towers), agricultural practices (e.g., fertilizers and animal wastes), and water and wastewater treatment systems (e.g., brines and chemicals used in treatment). The increased salinity of drinking water sources has spurred interest in desalination technologies. Additionally, historic droughts like the one recently experienced in California reduce the reliability of traditional water systems that import water from water-rich regions to water-scarce regions. For these reasons, water managers in areas with scarce water resources are turning to water reuse and desalination to meet their water supply needs.

Although water reuse and desalination technologies are a viable option to enhance local water supplies, these processes can consume larger amounts of electrical energy than conventional water treatment technologies [1]. Consequently, these technologies may contribute more greenhouse gases to the atmosphere than conventional water treatment processes do, thereby exacerbating concerns regarding climate change. These concerns create the need for water treatment technologies that require low levels of electrical energy. To achieve this end, my research project focuses on an option for a low-energy desalination process.

Membrane distillation (MD) is an innovative water treatment technology that can be driven by alternative energy sources like solar energy or low-grade (waste) heat [2].

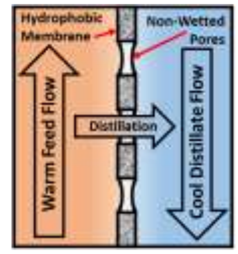

Figure 1: Membrane distillation diagram.

In direct contact MD, the feed solution (e.g., wastewater, seawater, or brine) is heated and passed along one side of a membrane, while a cooler pure water solution (the distillate) is passed along the other side of the membrane (Figure 1). The membranes used in MD are microporous–meaning that they have pore sizes less than one micrometer–and hydrophobic–meaning that they repel water. In MD, water evaporates at the feed membrane surface, passes through the membrane pores, and condenses upon contact with the cool distillate stream. Because the vapor pressure driving force is unaffected by salinity, MD can be used to treat high-salinity process streams that are challenging or impossible for conventional technologies to treat. The vapor phase separation results in a characteristically high rejection of non-volatile contaminants, but the high rejection of non-volatile contaminants can only be maintained as long as the hydrophobicity of the membrane is maintained. If the hydrophobicity is not maintained, the pores will become flooded with feed water, allowing passage of feed solution and its contaminants into the distillate solution.

Similar to how the flow of water in a river smooths the rocky surface of a riverbed, **it is my hypothesis that long-term exposure of MD membranes to viscous flow (e.g. wastewater, seawater, or brine) reduces surface roughness over time.** Because surfaces with a higher roughness are more hydrophobic [3], a reduction in MD membrane surface roughness would result in a reduction in membrane hydrophobicity and therefore a lower rejection of contaminants in the feed solution. Additionally, feed solution salinity and temperature impact membrane hydrophobicity. A smaller pore size and a higher liquid surface tension result in a higher liquid entry pressure and therefore a higher hydrophobicity, as described by the modified Young Laplace equation [4]. Because a higher salinity solution has a higher surface tension, membrane hydrophobicity would be expected to be higher for a higher salinity solution. However, higher temperatures have been demonstrated to result in pore size expansion [5], which would result in a lower membrane hydrophobicity. This indicates that the net effect on MD membranes of temperature, salinity, and potential changes in membrane surface roughness over time is unknown. The interplay between temperature, salinity, and surface roughness in affecting long-term MD membrane hydrophobicity is not well-described in the scientific literature, and my research addresses this concern.

The objective of the research described in this report is to determine (a) whether long-term exposure to viscous flow results in a reduction in MD membrane surface roughness over time, (b) the net effect of long-term exposure of MD membranes to viscous flow, elevated temperature, and salinity on membrane hydrophobicity, and (c) the relative contributions of each of these three variables to changes in membrane surface properties over time.

Progress to Date

Results from water flux and distillate conductivity for the experiment that was still underway during the last progress report are shown in Figure 2. This experiment was operated with a 35 g/L sodium chloride feed solution, a 65 °C feed solution temperature, a 38 °C distillate solution temperature, and 1.5 L/min flow rates on each side of the membrane for 100 days. The water flux decreased fairly linearly with a correlation coefficient of 0.9 and a flux decrease of 16%. The decrease in water flux was likely caused by dust entering the feed solution through the heated replenishment tank, which was slightly open to the environment. A chiller malfunction occurred on the night of Day 40, causing the chiller to turn off for 8.5 hours and the flux to decline during this time (data omitted) due to a lower driving force. When the chiller was turned back on the following morning, the driving force increased, causing the flux to increase slightly before returning to the pre-malfunction level.

The distillate conductivity showed no significant increase over the 100-day testing period. While a minor increase in the distillate conductivity was observed towards the end of the experiment, that value is significantly less than the feed conductivity, which is in the range of millisiemens. The stable value in conductivity indicates that the MD membrane maintained a high rejection of feed contaminants throughout the experiment.

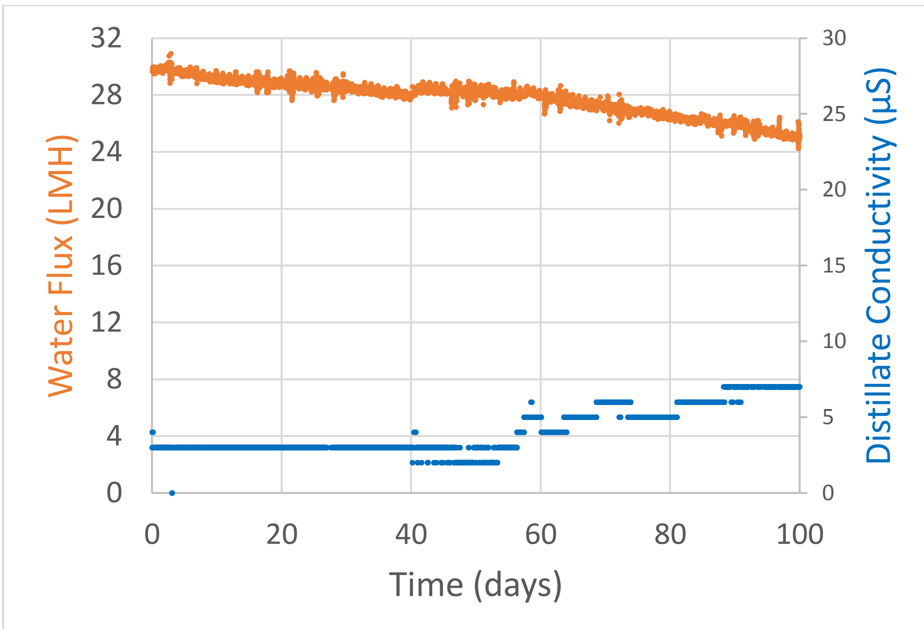

Figure 2: Water flux and distillate conductivity over time for 65 °C feed with 35 g/L NaCl and 38 °C distillate.

The post-experiment contact angle was measured for both the 100-day experiment described above and the 24-day experiment described in the previous progress report. Contact angle is the angle that a drop of water makes with the surface that it rests upon (Figure 3), and it is measured using a goniometer. The contact angle is used as a measure of hydrophobicity, with larger contact angles being indicative of more hydrophobic surfaces. We compared the pre- and post-experiment contact angles to determine whether the long-term exposure of the membrane to viscous flow with high temperature and high salinity (Table 1) caused the membrane hydrophobicity to decrease. The 100-day experiment showed a decrease of 56 and 26% for the feed- and distillate-side contact angles, respectively. The 24-day experiment showed a 65 and 19% decrease in the feed- and distillate-side contact angles, respectively.

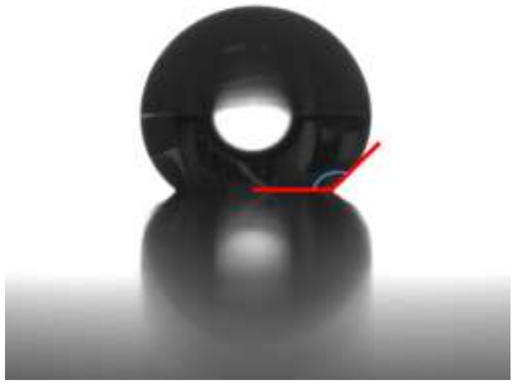

Figure 3: A goniometer image used to measure the contact angle of a drop of water on the membrane surface.

These results indicate a decrease in the hydrophobicity of both the feed- and distillate-sides of the membrane, but the high rejection maintained throughout each experiment indicates that the decreased hydrophobicity did not result in a significant decrease in membrane performance. While the feed-side contact angle decreased more for the 24-day experiment than for the 100-day experiment, the decrease was likely caused by the formation of the scaling layer on the feed-side membrane surface in the 24-day experiment. The scaling layer formed due to the feed replenishment electrical control circuit being accidentally left off overnight. The feed must be replenished with deionized water to replace the water that has transferred across the membrane in order to maintain a constant feed solution concentration. When the replenishment circuit was left off, the feed solution concentrated overnight, causing the sodium chloride to exceed its solubility limit and form a scale layer on the membrane surface.

Table 1: Comparison of water contact angle before and after the 100-day and 24- day experiments

	100-Day Experiment			**24-Day Experiment**		
Side	**Contact Angle Before**	**Contact Angle After**	**Percent Change**	**Contact Angle Before**	**Contact Angle After**	**Percent Change**
Feed	140 ± 3.96°	61.1 ± 9.09°	56%	139.8 ± 3.96 °	49.1 ± 3.18 °	65%
Distillate	140 ± 3.63°	104 ± 14.1°	26%	139.9 ± 3.63 °	114 ± 6.35 °	19%

Changes in membrane surface roughness were characterized for the 100-day experiment (Table 2), using measurements collected with atomic force microscopy. Surface roughness changed by 90 and 46% for the feed- and distillate-sides, respectively. These large changes in roughness likely explain the large changes in contact angle observed for each side of the membrane. However, to confirm that the changes in roughness were directly caused by changes in MD membrane surface properties, we took scanning electron microscopy (SEM) images.

Table 2: Surface roughness before and after the 100-day experiment.

Side	Surface Roughness		
	Before (nm)	After (nm)	Percent Change
Feed	31.0 ± 5.40	3.0 ± 0.88	90%
Distillate	27.1 ± 7.58	14.5 ± 3.11	46%

The SEM images of the unused membrane, the feed-side, and the distillate-side of the membrane after the 100-day experiment are shown in Figure 4. The feed-side SEM image clearly shows that the feed-side membrane surface is coated in a fouling layer. The presence of the fouling layer in the feed-side SEM image explains why the feed-side contact angle and roughness decreased but the rejection remained high: The changes in contact angle and roughness are due to the water's contact with the fouling layer rather than the membrane surface. While the fouling layer may have a lower hydrophobicity than the membrane, the membrane surface underneath the fouling layer may be able to maintain the high hydrophobicity that allows for the high rejection that was observed.

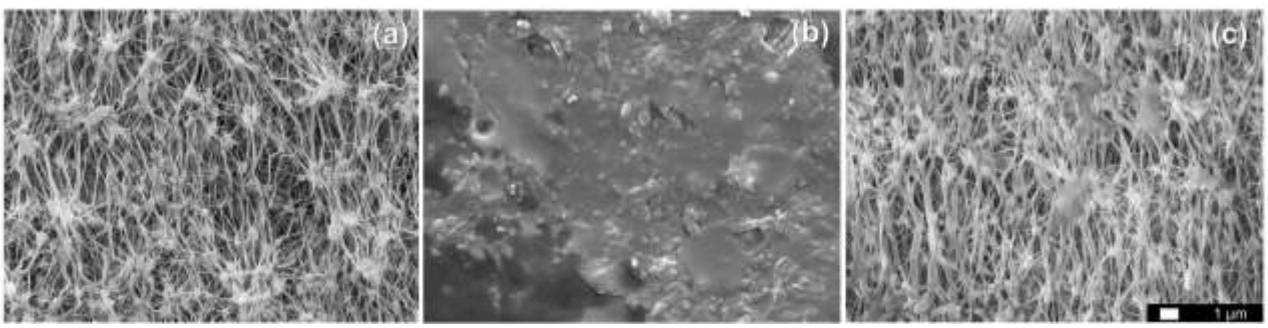

Figure 4: Scanning electron microscopy images for the (a) unused membrane,
(b) feed-side of the membrane after the experiment, and
(c) distillate-side of the membrane after the experiment, for the 100-day experiment.

Contact angle and roughness measurements on the feed side of the membrane could not indicate whether the feed-side membrane surface characteristics changed, due to the presence of the fouling layer. However, the lack of a fouling layer on the distillate side of the membrane allowed the changes in membrane surface properties during the experiment to be assessed. Comparison of images of the unused membrane surface and the membrane surface exposed to the distillate stream shows a clear change in the distillate-side membrane characteristics in the absence of a fouling layer. The changes observed on the distillate side of the membrane relate to the membrane fibrils – long and thin strands of membrane material – and the nodes – the locations where multiple fibrils meet. The distillate-side SEM image shows wider fibrils and larger, flattened nodes, which may be responsible for the observed decrease in contact angle and roughness. The comparison of feed- and distillate-side SEM images to the unused SEM image indicates that long-term exposure of MD membranes to viscous flow with high salinity and high temperature causes a change in membrane surface characteristics and membrane hydrophobicity. By confirming that long-term exposure of MD membranes to viscous flow with high temperature and high salinity can cause changes in membrane surface roughness and hydrophobicity, we have met the first two objectives of this research project. The third objective of this project is still unaddressed because the relative contributions of solution viscosity, temperature, and salinity to changes in membrane surface characteristics and hydrophobicity are still unknown. A series of 30-day experiments have been planned to investigate the relative impacts of solution viscosity, temperature, and salinity on long-term MD membrane hydrophobicity so that the final research objective can be met.

Conclusions

Two of the three research objectives have been met during this reporting period, while one objective requires further research.

We confirmed the following:

1. Long-term exposure of MD membranes to viscous flow with elevated temperature and high salinity reduces membrane surface roughness over time.

2. Long-term exposure of MD membranes to viscous flow with elevated temperature and high salinity reduces membrane hydrophobicity.

The third objective, which is still under investigation, is to determine the relative contribution of these variables (viscous flow, temperature, and salinity) to reduced membrane surface roughness and hydrophobicity.

The research described in this report will help MD researchers develop membranes that are able to maintain hydrophobicity for longer periods of time. These membranes can be used in future MD treatment systems to remove salt and other contaminants. This research serves the greater good by answering questions that will lead to improvements in a technology that is poised to make water reuse, desalination, and brine management more efficient, all while being driven by alternative energy sources such as solar energy or low-grade (waste) heat.

Next Steps

One research objective remains unaddressed, and that objective will be addressed by performing a series of 30-day experiments. Solution viscosity, temperature, and salinity will be isolated in each experiment, and the results of each experiment will be compared to determine the relative contributions of solution viscosity, temperature, and salinity to reductions in contact angle and surface roughness. These experiments will be performed on a modified version of the system that does not include the heated replenishment tank, in order to avoid dust contamination in the feed solution.

References

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