NWRI-SCSC GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

DATE: November 1, 2016

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

Graduate Fellow: Ryan Gustafson

Advisor: Professor Amy Childress

Institution: University of Southern California

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 currently being 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].

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
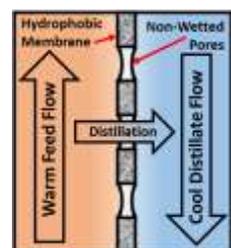

Figure 1: Membrane distillation diagram.

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 feed contaminants. 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

The initial phase of research has focused on development of a novel system for long-term testing of MD membranes under the conditions of elevated temperature and salinity. Traditionally, MD testing systems are built from a mixture of plastic parts and metallic parts, with the metallic parts being made of 316 stainless steel (316SS) for high corrosion resistance. The corrosion resistance of 316SS is greatly reduced when the steel exposed to elevated temperatures and salinity, causing the production of small amounts of rust over short periods of time. However, over time periods greater than 18 hours the amount of rust produced can be significant. In light of these considerations, a bench-scale MD system was constructed that uses only non-metallic and titanium components with very high corrosion resistance (Figure 2a). The system was designed to operate continuously over periods of weeks to months under constant temperature and feed solution salinity. Constant feed stream temperature and salinity is achieved through a cascade of room-temperature and heated replenishment tanks filled with deionized water (Figure 2b). Continuous operation is achieved with minimal operator support (emptying a tank twice per day). Temperature, conductivity, flow rate, pH, and produced water mass over time are recorded every ten minutes using a LabVIEW data acquisition system.
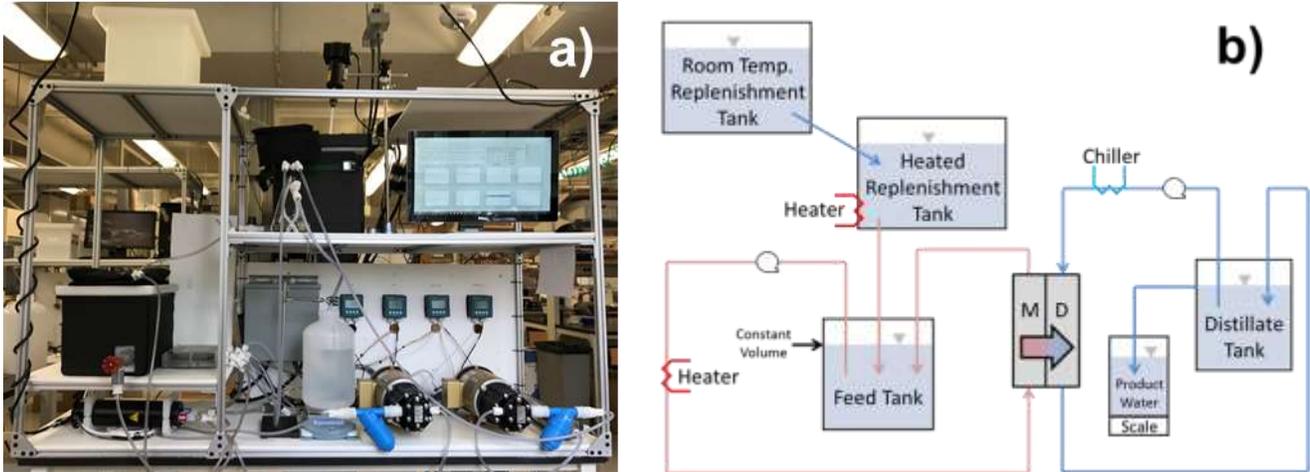
Figure 2: (a) Photo and (b) schematic of long-term bench-scale membrane distillation testing system.

Two experiments have been performed using the long-term MD testing system. A flat-sheet polytetrafluoroethylene (PTFE) membrane with an average pore size of 0.18 µm and a porosity of 0.801 was used in both experiments. The membrane was placed in a two-piece acrylic module with channels that are 146 mm long, 95 mm wide, and 0.787 mm deep. Turbulence-promoting spacers were placed in the flow channels and the experiments were operated in counter-current flow configuration.

The first experiment was operated using a 65 °C feed stream with 200 g/L NaCl, a 38 °C distillate, and 1.5 LPM flow rates on each side of the membrane. The experiment was operated continuously for 24 days before it had to be terminated early. The graph of water flux over time (Figure 3) shows three notable characteristics: a significant change in water flux on July 15, a slight decrease in water flux over time, and several small sections of missing data. The missing sections of data were caused by occasional electromagnetic interference between a solenoid valve and the signal being sent from the scale to the computer, which caused data acquisition to stop until the error was cleared in LabVIEW. After this experiment, the separation distance between the scale and the solenoid valve was increased to prevent further interference.
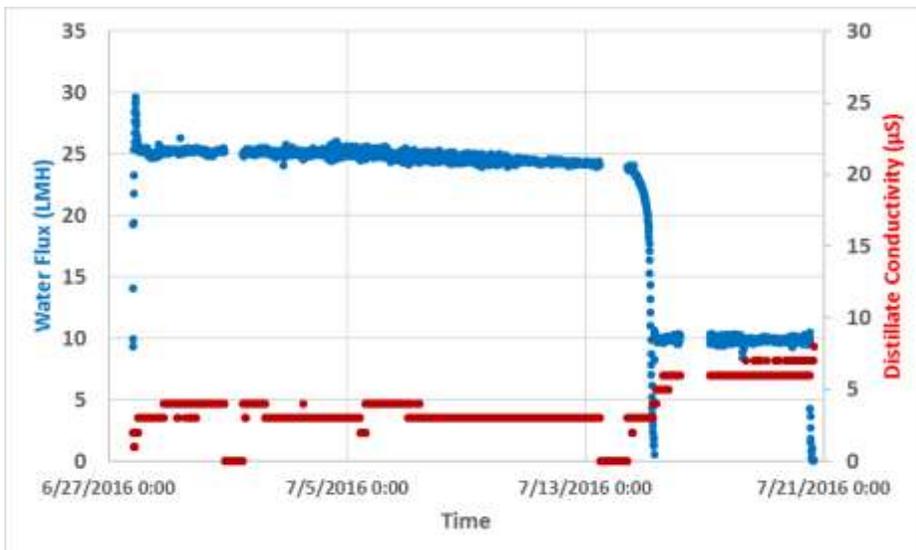

Figure 3: Water flux and distillate conductivity over time for 65 °C feed stream with 200 g/L NaCl and 38 °C distillate.

A 6.2% reduction in flux was seen over the 24 day period of operation, but the exact cause is currently unknown. A thin brown foulant layer was observed on the surface of the feed side of the membrane throughout the duration of the experiment, and it is expected that this layer was the cause of the flux decline. The layer is suspected to be due to biological growth, but the use of deionized water in the feed stream combined with the elevated temperatures and high NaCl concentration make it unlikely that it is a biofilm layer. The composition of the layer is currently being evaluated and will be discussed further in the next progress report. The graph of the distillate conductivity over time (Figure 3) shows no significant increase in conductivity, indicating that, even with the presence of a scale layer, there was no passage of salt from the feed stream to the distillate that would indicate a reduction in hydrophobicity. The significant change in water flux on July 15 occurred because the circuit that controls the feed tank replenishment system was accidentally left off, causing the feed solution to concentrate overnight. The feed solution concentration exceeded the solubility limit of NaCl, causing a layer of NaCl scale to form on the surface of the membrane, reducing water flux to less than 1 LMH. After the circuit was turned back on, the flux recovered only to 10 LMH before the experiment had to be ended due to a crack in the feed solution tank.

The second experiment is currently in operation using a 65 °C feed stream with 35 g/L NaCl, a 38 °C distillate, and 1.5 LPM flow rates on each side of the membrane. The experiment has been in continuous operation for 91 days. The graph of water flux over time (Figure 4) shows a slight decrease in water flux over time similar to that seen in the first experiment. The reduction in water flux in this experiment is currently 12.7%, and a thin brown foulant layer has been observed on the feed side membrane surface, similar to the first experiment. The reoccurrence of this foulant layer in the second experiment reinforces the need for analysis of the composition of this layer immediately after the experiment. The distillate conductivity data (Figure 4) does not indicate a significant increase in conductivity.
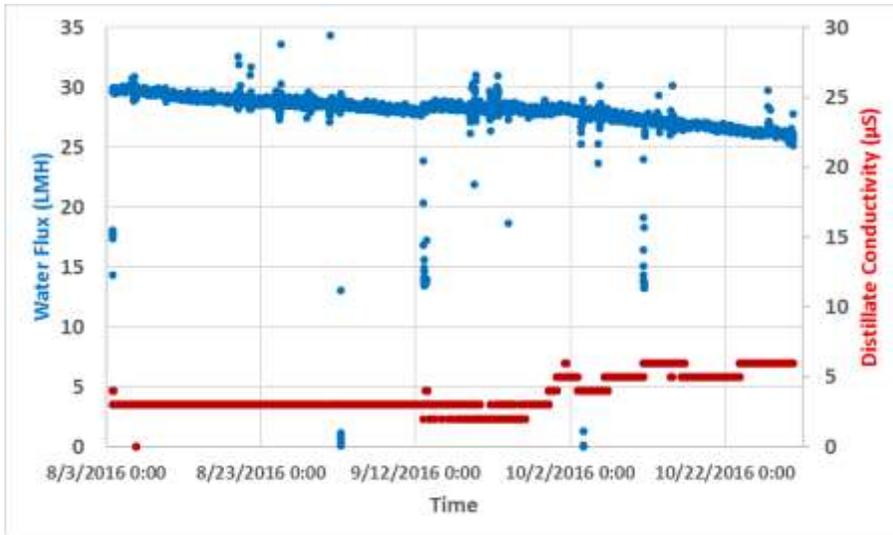

Figure 4: Water flux and distillate conductivity over time for 65 °C feed stream with 35 g/L NaCl and 38 °C distillate.

In addition to membrane fouling layer analyses after each experiment, contact angle and roughness measurements will be made before and after each experiment The contact angle measured before the first experiment was 141.5° and it was 70.5° after the experiment, showing a decrease in contact angle, as expected.

Conclusions

The research on long-term MD membrane hydrophobicity has focused on system design and construction, as well as data collection for two experiments. The similar results of the two experiments indicate the need for further analyses of the fouling layer's composition. The results of continued analyses will allow a comparison of the relative impacts of temperature and salinity on long-term MD membrane hydrophobicity and the membrane surface characteristics.

Addressing the objectives of the research described in this report will help MD researchers develop better 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

The unexpected presence of the thin membrane fouling layer in both experiments will be addressed by determining the fouling layer composition after the current experiment is completed. Additional experiments will be performed under different operating conditions in order to isolate variables and determine their relative impact on long-term membrane hydrophobicity.

References

[1] H. Cooley, M. Heberger, Key issues for seawater desalination in California: Energy and greenhouse gas emissions, Pacific Institute, California, (2013).
[2] R. Schwantes, A. Cipollina, F. Gross, J. Koschikowski, D. Pfeifle, M. Rolletschek, V. Subiela, Membrane distillation: Solar and waste heat driven demonstration plants for desalination, Desalination, 323 (2013) 93-106.
[3] H.J. Busscher, A.W.J. van Pelt, P. de Boer, H.P. de Jong, J. Arends, The effect of surface roughening of polymers on measured contact angles of liquids, Colloids and Surfaces, 9 (1984) 319-331.
[4] E. Guillen-Burrieza, A. Servi, B.S. Lalia, H.A. Arafat, Membrane structure and surface morphology impact on the wetting of MD membranes, Journal of Membrane Science, 483 (2015) 94-103.
[5] R.B. Saffarini, B. Mansoor, R. Thomas, H.A. Arafat, Effect of temperature-dependent microstructure evolution on pore wetting in PTFE membranes under membrane distillation conditions, Journal of Membrane Science, 429 (2013) 282-294.