Pressure Retarded Osmosis: A Potential Technology for Seawater Desalination Energy Recovery and Concentrate Management

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Pressure Retarded Osmosis: A Potential Technology for Seawater Desalination Energy Recovery and Concentrate Management

by

Joshua Benjamin

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Environmental Engineering
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Keywords: Computational fluid dynamics, Process modeling, Optimization, Membrane fouling, Water reuse

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Dedication

I dedicate this dissertation to my wife, my parents, my grandparents, my sisters, and the rest of my family and friends. You have all helped me tremendously throughout this whole process, and for that, I will be eternally grateful.
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I would like to thank my advisors - Dr. Mauricio Arias and Dr. Qiong Zhang - for all of their guidance, mentorship, and support throughout this process. I would also like to thank my committee members, Dr. Nancy Diaz-Elsayed, Dr. Andres Tejada-Martinez, and Dr. Heather Rothrock for all of their guidance and feedback on this research.

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Abstract

Currently, a significant challenge with reverse osmosis-based desalination is reducing the energy consumption and environmental impacts of the process. This project analyzed the viability of using pressure-retarded osmosis (PRO) for energy recovery in seawater desalination facilities using brine concentrate (the draw solution) and other water sources (the feed solution) such as wastewater effluent. The primary goal of this project is to decrease the cost and overall energy consumption of seawater desalination through PRO-based energy recovery. Process modeling, statistical and sensitivity analysis, energy and cost analysis, geospatial and GIS analysis, laboratory-scale testing, water quality analysis, SEM-EDS microscopy, computational fluid dynamics (CFD), and optimization were used to create design schemes that help reduce the environmental impact and energy consumption of seawater desalination.

The first task involved creating a steady-state process model to inform the selection of draw/feed (high salinity/low salinity) solutions and membrane materials for a lab-scale reactor based on their potential for energy recovery and the results from a preliminary economic evaluation. It was found that using reverse osmosis concentrate and high-quality reclaimed wastewater can be economically viable as long as the plants are co-located. The second task involved using the process model to select potential sites in the United States where PRO would have the highest chance of succeeding. It was found that PRO could succeed in Santa Barbara California, where a desalination plant is located across the street from a wastewater plant, and on St. Thomas in the Virgin Islands, which has some of the highest electricity prices in the nation. The third task involved using a bench-scale PRO system to validate a developed CFD model that
could investigate the effect that membrane spacer configuration has on the internal hydraulics of a PRO membrane system. It was found that there is a tradeoff between decreased pressure buildup in the feed side of the membrane versus increased transport across the membrane, and that spacer manufacturers should place emphasis on keeping spacer strands more linear and decreasing the length of the sloped section of the thin cross-strand in a spacer to increase system performance. The fourth task focused on determining the impacts that spacer geometry and pretreatment have on membrane fouling and short-term performance. It was found that using a medium-sized diamond-oriented spacer combined with UV pretreatment was the most effective treatment protocol for minimizing the effects of membrane fouling.

Overall, the results from this study suggest that there is potential for PRO to be an economically viable form of energy recovery and brine management for seawater desalination. To maximize performance, PRO should be implemented using a pressure and foulant resistant integrated membrane/spacer combination, combined with source streams that require minimal pretreatment in areas where seawater desalination plants are co-located with wastewater plants and/or have high energy prices. It is recommended that future work focus on conducting additional physical experiments with different water quality and pressure levels, integrating fouling processes and additional water quality variables into the predictive models, and conducting more in-depth comparative analyses against alternative brine management and energy recovery technologies. These three tasks are recommended to be completed before a larger-scale system is constructed to investigate how the system would perform over an extended period. This study primarily used Tampa Bay (Florida) as a case study, although the information and models from this study can be used for other coastal water systems that seek to use seawater desalination that is augmented using PRO-based energy recovery and brine management technology.
Chapter 1: Introduction

1.1 Background and Motivation

Reverse osmosis (RO) is a treatment process widely implemented in desalination and advanced water reclamation facilities. Currently, a significant challenge with RO is reducing the energy consumption and environmental impacts of the process (Elimelech and Phillip, 2011). Elevated levels of energy consumption cause RO product water to be much more expensive than other conventional water sources and can prevent implementation of this crucial technology in areas that are under severe water stress, such as in Cape Town, South Africa (Oliver, 2017) and Orange County, California (Wisckol, 2018). While RO uses less energy than alternative desalination processes such as multi-effect distillation (MED) and multi-stage flash (MSF) (Ettouney et al., 2002), it is still a significant energy consumer, using 2.4 to 8.5 $kWh m^{-3}$ of product water (Yip et al., 2016). Furthermore, RO is also the principal technology implemented in seawater desalination facilities in the United States (combined capacity of 128 million $m^3 yr^{-1}$; (DOE, 2017)). Environmental impacts from RO primarily come from the emissions associated with energy input, especially if the energy is provided by thermoelectric power plants (Bruggen and Vandecasteele, 2002). Another primary environmental concern comes from RO concentrate disposal (Elimelech and Phillip, 2011). Depending on the temperature, salinity, and chemical input, RO concentrate disposal can negatively affect the oxygen content of the receiving water due to its salt content, and some RO discharge also contains biocides and anti-scaling additives (Sagle and Freeman, 2004).
These issues need to be addressed to make desalination a more effective technology for water strained regions. One option is to utilize the high osmotic pressure difference that exists when a highly concentrated solution, such as RO concentrate, is placed on the opposite side of a semipermeable membrane from a solution with a low concentration of solutes, such as wastewater treatment plant (WWTP) effluent. This concentration difference creates an osmotic pressure, which causes water to flow through the membrane to alleviate this pressure. If an external hydraulic pressure is applied to the concentrated side that is lower than the osmotic pressure, then this will result in an excess of diluted and pressurized concentrate. This excess can then be divided into two streams and used for both power generation in a hydropower turbine and for pressurizing incoming concentrate using an in-line pressure exchanger (Skilhagen, 2010). This technology is known as pressure retarded osmosis (PRO) and offers a potential solution to the issues of high energy consumption and brine management in desalination (Altaee et al., 2016; Altaee and Sharif, 2015; Saito et al., 2012). However, PRO-based energy recovery does have its challenges, as energy is needed to transmit and pretreat the solutions, as well as to backwash the system to mitigate membrane fouling, all of which necessitates a careful balance of energy expenditures and generation potential to maximize net energy recovery. Therefore, the primary goal of this project is to evaluate how PRO-based energy recovery can decrease the cost, overall energy consumption, and environmental impact of seawater desalination.

In general, two source streams need to be paired to create a concentration gradient for osmotic power to be successfully generated: a feed solution (low concentration), and a draw solution (high concentration) (Figure 1.1). For example, if freshwater is paired with saltwater, then the theoretical maximum specific energy (SE) can be as high as 0.34 kWh m\(^{-3}\) of mixed solution given a concentration gradient of 35 ppt of salt on the saline side and 0.001 ppt of salt on the
freshwater side (Lin et al., 2014b; Spiegler and El-Sayed, 2001; Yip and Elimelech, 2012). However, this is under an ideal situation, and neglects practical conditions, such as membrane and hydraulic inefficiencies, variable mixing ratios, turbine inefficiencies, and pretreatment requirements for draw and feed solutions, which can drop the $SE$ substantially (Sarp et al., 2016). Consequently, it can be surmised that a higher salinity difference is needed to make the process feasible. This energy density can be increased by using a higher concentration gradient, such as that found between RO concentrate (ROC) and tertiary WWTP effluent (Helfer and Lemckert, 2015). As the concentration gradient increases, so does the theoretical maximum specific energy (Table 1.1).

![General process diagram for PRO systems](image)

**Figure 1.1** General process diagram for PRO systems. Note that the presence of pretreatment systems is dependent on the source water quality for the draw and feed solutions.

**Table 1.1** Theoretical maximum specific energy for various salinity gradients.

<table>
<thead>
<tr>
<th>Draw Concentration ($M$)</th>
<th>Feed Concentration ($M$)</th>
<th>Salinity Gradient (Draw/Feed)</th>
<th>Maximum Theoretical Specific Energy ($kWh , m^{-3}$ of mixed solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.015</td>
<td>SW/RW</td>
<td>0.256</td>
</tr>
<tr>
<td>1.2</td>
<td>0.015</td>
<td>ROC/WW</td>
<td>0.551</td>
</tr>
<tr>
<td>5.7</td>
<td>1.2</td>
<td>Dead Sea/ROC</td>
<td>1.110</td>
</tr>
<tr>
<td>4.6</td>
<td>0.015</td>
<td>Great Salt Lake/RW</td>
<td>2.260</td>
</tr>
</tbody>
</table>

*RW stands for river water, SW stands for saltwater, ROC stands for RO concentrate, WW stands for wastewater effluent. Values from (Lin et al., 2014)
Aside from some localized high-salinity water bodies (the Dead Sea, the Great Salt Lake), the most common high-salinity gradient can be realized by combining ROC and wastewater effluent. Because of this, PRO is of significance in energy recovery and RO concentrate management, with potential power densities (W) reportedly as high as 21.3 $W \ m^{-2}$ of membrane surface (Song et al., 2013). When ROC with a salinity of 77 ppt is paired with freshwater, the theoretical maximum specific energy increases to approximately 0.7 $kWh \ m^{-3}$ of mixed solution. This can make the process feasible as long as the overall treatment process technologies, including membrane type, membrane spacer configuration, pretreatment technique, and turbine selection are optimized to maximize net energy generation (Sarp et al., 2016).

Overall, to optimize the PRO process for ROC management and energy recovery, it is crucial to select the membrane type and configuration that properly balances energy generation potential and foulant resistance. When the PRO process was first experimented on by Sidney Loeb, modified reverse osmosis membranes were used (Loeb, 1976). These membranes were ineffective at producing the power densities necessary to make the process economically viable, and the technology was put on the wayside until membranes technology could improve. It was not until the 2000’s that PRO membrane development began again, due to the advances in membrane technology made in the reverse osmosis field (Achilli and Childress, 2010).

Modern PRO membranes can either be configured in a hollow-fiber orientation, or in a flat sheet/spiral wound orientation. Flat sheet/spiral wound configurations are currently preferred, as they can be crafted with thin support layers and have a lower potential for pressure loss on the draw side than hollow-fiber configurations (She et al., 2013a). For flat sheet/spiral wound configurations, another crucial aspect is the spacer matrix that exists between the membrane layers. Feed spacer geometry affects both fouling rates and membrane stability, with smaller spacer
widths increasing membrane power density by decreasing membrane deformation (She et al., 2013a). Feed spacer orientation (diamond vs. parallel) is also important, as the orientation can affect the deposition pattern of particles in the feedwater (Radu et al., 2010). Table 1.2 lists the advantages and disadvantages of the two most common membrane types (Gohil and Ray, 2017; Sagle and Freeman, 2004): cellulose triacetate (CTA) and thin-film composite (TFC) (polysulfone coated with aromatic polyamides).

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTA</td>
<td>Resistant to chlorine attacks and can tolerate Cl⁻ concentrations up to 5 ppm. Resistant to organic and colloidal fouling</td>
<td>Only stable in pH ranges from 4–6 and temperatures below 45°C, due to decrease in salt rejection with increase in temperature.</td>
<td>(Sagle and Freeman, 2004; She et al., 2013a)</td>
</tr>
<tr>
<td>TFC</td>
<td>Can reject low molecular weight organics. Stable at high temperatures and pH. Can suppress ICP using tailored porous support layers.</td>
<td>Highly sensitive to chlorine, and can only tolerate 1000 ppm-hours of Cl⁻ exposure Vulnerable to organic and colloidal fouling.</td>
<td>(Chou et al., 2012; Gerstandt et al., 2008; Helfer et al., 2014; Sagle and Freeman, 2004; Yip and Elimelech, 2013)</td>
</tr>
</tbody>
</table>

Since CTA membranes have been found to be more resistant to organic and colloidal fouling than TFC membranes (She et al., 2013a), and membrane fouling has been shown to be one of the primary detrimental factors to PRO performance, (Bar-Zeev et al., 2015) they were the membrane type chosen for this research.

1.1.1 Current State of PRO

PRO is currently in its pilot phase, with several experimental plants throughout the world (Song et al., 2013). The first pilot PRO plant was the Statkraft plant in Tofte, Norway (Skilhagen, 2010). The plant was built in 2009 and used river water as a feed solution and saltwater as the draw solution. The hydraulic pressure was 12.5 bar, and a spiral wound membrane developed by Hydronautics was used starting in 2011. The plant was operated until it closed in 2013, primarily due to high operational costs that would make the power generated from a full-scale plant
uncompetitive in the European power market. These high costs stemmed from pretreatment costs, low extractable work values, and inefficiencies in the hydraulic power generation system (Sarp et al., 2016; Yip et al., 2016). Projects that pair ROC with wastewater have been more successful, such as the Mega-ton Water System project in Japan, and the GMVP in South Korea. Both projects are currently in the pilot phase, with plans for eventual full-scale implementation (Kurihara et al., 2016; Kurihara and Hanakawa, 2013).

Currently, there have not been any studies investigating how PRO could be implemented in pre-existing desalination facilities and the effect that variations in source water quantity and quality, as well as how implementation of PRO and its cost and energy saving measures would affect the overall net energy consumption and financial cost of the desalination facility. Furthermore, while current models have focused on predicting the gross power density and specific energies of PRO systems (Anissimov, 2016), there have been limited studies on calculating net power densities and specific energies, as well as capital and operational costs that would be incurred in implementing a PRO system in a desalination plant (Sarp et al., 2016). Moreover, most models only consider single solute solutions (NaCl), with only a few having included the effect of multiple ions (Yaroshchuk et al., 2013). Being able to accurately predict how a system would function in pre-existing plants would enable plant managers to evaluate how PRO would function in their plants.

1.1.2 PRO Primary Issues

The primary issues with pressure retarded osmosis, and by extension, the main technical risks in this project, are concentration polarization, and membrane fouling (Figure 1.2) (Bogler et al., 2017; Thelin et al., 2013; Yip and Elimelech, 2013). Concentration polarization is caused by solutes building up on the membrane surface and reducing the overall concentration gradient and
is a consequence of thermodynamics and thus cannot be prevented. PRO membranes are usually oriented with the active layer (where diffusion occurs) facing the pressurized draw solution. This in turn maintains membrane integrity and preserves high salt rejection (over 99.8%) while the support layer is pressed onto the feed channel spacer, but also causes external concentration polarization (ECP) and internal concentration polarization (ICP) (Elimelech et al., 1997; She et al., 2013b). ECP effects are relatively minor, but ICP is one of the key limiting phenomena for PRO performance which can be suppressed using membranes with tailored porous support layers (Chou et al., 2012; Yip and Elimelech, 2013). While several membrane development studies have taken these (ICP and ECP) phenomena into effect, several studies that have made plant scale models have not included this factor (Helfer and Lemckert, 2015; Naghiloo et al., 2015). This is likely overestimating the potential specific energies using PRO, since ICP and ECP, and to a lesser degree, reverse solute diffusion, all have the potential of reducing the overall specific energy of a system.

Membrane fouling reduces the permeability of the membrane and prevents water from flowing through the membrane matrix, but it can be controlled through pretreatment and process optimization schemes. It is important for fouling to be controlled, as it is one of the primary factors increasing overall energy generation costs to the point of making PRO economically unfeasible (Yip et al., 2016). When RO concentrate is mixed with tertiary WWTP effluent, fouling primarily occurs on the feed side of the membrane surface, as RO concentrate has lower concentrations of potential fouling agents, and the water flux through the membrane prevents foulants from accumulating on the draw side (Saito et al., 2012). Membrane fouling can be divided into four distinct categories: colloidal/particulate fouling, mineral scaling, organic fouling, and microbial fouling (biofouling) (Bogler et al., 2017; Sagle and Freeman, 2004). In general, membrane fouling
happens on both the membrane support layer, which is a polymeric matrix that adds stability to the membrane active surface under high pressures, as well as in the gaps inside of the spacer matrix (Bogler et al., 2017; Radu et al., 2010; Vrouwenvelder et al., 2010). Overall, the dominant mechanism is determined by foulant type and support layer pore size. It has been found that primary compounds of concern are suspended solids and colloidal suspensions, which can cause colloidal/particulate fouling; microbes such as *Pseudomonas aeruginosa* and *Pseudoalteromonas atlantica*, which can cause biofouling; natural organic matters, such as fulvic and humic acids, which can cause organic fouling; and cations and anions such as calcium, phosphate, sulfate, and silica, which can cause inorganic scaling (Bar-Zeev et al., 2015; Bogler et al., 2017; Han et al., 2016; Saito et al., 2012).

![Figure 1.2](image)

Figure 1.2  Concentration polarization and membrane fouling in a ROC-WW system. Observe how concentration polarization decreases the concentration gradient across the membrane. $A_M$ is the membrane area, $s$ represents a discrete membrane element, $Q_{ROC}$ is the reverse osmosis concentrate flux, $Q_{WW}$ is the waste-water effluent flux, $b$ stands for bulk, $m$ represents the surface of the active layer of the membrane. All $c$’s are for solutes.
Biofouling and organic fouling have been shown to be the two most problematic types of foulants, as scaling can be controlled through the use of acids and scalant inhibitors such as EDTA, HEDP, and Poly(L-aspartic acid sodium salt), while colloidal/particulate fouling can be controlled using filtration-based pretreatment (Han et al., 2016; Picioreanu et al., 2009). Biofouling is caused by the growth of biomass on both the membrane and spacer surface and occurs under two different pathways that can occur simultaneously. The first pathway is the deposition of cells and organic matter due to the permeate water flux through the membrane, and the second pathway is from cell growth on the membrane surface (Bogler et al., 2017). Once established, bacteria create a biofilm, which begins by first creating a “conditioning film” that other bacteria can then attach to via van der Walls, hydrogen bonding, and hydrophobic interactions. Eventually, the initial colonies of bacteria excrete extracellular polymeric substances, which reinforces the bacterial communities and creates a functional biofilm (Song et al., 2013). While bio and organic fouling can be controlled using osmotic backwashing (Bar-Zeev et al., 2015), pressure-aided osmotic backwashing (Bar-Zeev et al., 2015), and chemical treatment (Han et al., 2016) none of these methods have been found to be 100% effective (Bogler et al., 2017). PRO is especially susceptible to fouling since the support layer faces the feed side, which allows bacteria to propagate inside of the porous structure of the support layer and cause severe ICP (Bogler et al., 2017). Reduced fouling will make membranes more cost-effective by extending their operational lifetime and lowering their energy requirements (Bogler et al., 2017).

Previous research on membrane fouling in PRO has primarily focused on characterizing and controlling foulant propagation rates. In this area, there have been studies on controlling inorganic fouling and gypsum scaling when using DI water and NaCl (Zhang et al., 2014), characterizing fouling rates with various river water and seawater solutions (Abbasi-Garravand et
al., 2018), investigating the effect of hydraulic pressure and \( pH \) on organic fouling when using synthetic ROC and wastewater effluent (Jihye Kim et al., 2015b), and investigating the impact of biofouling on membrane performance when using synthetic ROC and wastewater effluent (Bar-Zeev et al., 2015). In particular, the paper by Bar-Zeev et al. (2015) indicated that spacer blockage plays a significant impact on foulant propagation rates, and that studies were needed to quantify the appropriate combination of feed pretreatment and spacer orientation necessary to minimize membrane fouling. Another challenge with PRO is knowing where it should be implemented, and how it compares against alternative technologies. How PRO compares in terms of energy performance and economic cost against other renewable energy technologies has been outlined as a gap in the literature, as there has yet to be a comprehensive technological comparison for PRO energy recovery and brine management systems (Achilli et al., 2014; Sarp et al., 2016). The main gaps in the research that will be addressed in this study are summarized below in Table 1.3.

<table>
<thead>
<tr>
<th>Area</th>
<th>Current gap</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process Modeling</td>
<td>Most process models have focused primarily on designing PRO systems in isolation, and do not consider how external factors (pretreatment, influent transmission) will affect the overall net energy density. Furthermore, most studies have not had rigorous sensitivity analyses conducted that showcase the limits of the modeling processes.</td>
<td>(Anissimov, 2016; Naghiloo et al., 2015)</td>
</tr>
<tr>
<td>Area of Applicability</td>
<td>There are no clear guidelines as to the necessary water quality and quantities that are necessary for a PRO system to be economically and energetically feasible. Furthermore, there have not been any studies on how regional variation in terms of energy pricing, climate, and distance to feed water sources effects PRO system performance.</td>
<td>(Helfer and Lemckert, 2015; Sarp et al., 2016)</td>
</tr>
<tr>
<td>Internal Hydraulics</td>
<td>There has not been a CFD study on understanding the influence that spacer geometry has on increasing mass transfer and reducing the internal pressure drop in PRO applications, or how optimization can be used to improve existing spacer designs.</td>
<td>(Aschmoneit and Hélix-Nielsen, 2021; Hayashi and Okumura, 2016)</td>
</tr>
<tr>
<td>Fouling Studies</td>
<td>Most fouling studies have focused on the impact that fouling has on the membrane itself and have not considered the impact that varying the spacer matrix in terms of geometry and material could have on system performance. Furthermore, there have not been any comprehensive comparisons of how different combinations of pretreatments impact the net specific energy of a PRO system.</td>
<td>(Bar-Zeev et al., 2015; Bogler et al., 2017)</td>
</tr>
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</table>
1.2 Research Questions and Hypothesis

1.2.1 Research Questions

The primary goal of this project was to evaluate how PRO can best be applied to decrease the cost and overall energy consumption of desalination. This dissertation aims to address the question of how effective PRO is at improving the energy efficiency of desalination by analyzing the technical aspects and economic costs of the technology.

The guiding question behind this research is: Under what cases is PRO a viable form of energy recovery and brine management for desalination? The primary variables that were investigated include salinity gradient, membrane characteristics, spacer geometries, pretreatment technologies, local geography, process configurations, influent quality and quantity, and economic conditions.

Membrane characteristics and spacer geometry were studied to inform how the PRO system should be designed to maximize gross specific energy generation, while pretreatment technologies, local geography, and process configurations were looked at to see how net specific energy can be maximized. Influent quality and quantity were looked at to gauge long-term system performance, and economic conditions were analyzed to see what the expected cost of implementation and payback period is for PRO-based systems. To investigate the full effect that all of these variables may play, this research is divided into four tasks, each with its own guiding question:

1. How can system characteristics such as salinity gradient and membrane type be configured to optimize a PRO system in terms of baseline net specific energy and economic performance?
2. What impact do local geography and economic conditions have on the viability of a PRO system?

3. What effect does membrane spacer geometry have on PRO membrane hydraulic performance, and how can it be improved?

4. What effect does membrane spacer geometry and pretreatment have on bio and organic fouling rates and the net energy density of the system?

Answering these questions will help reduce the uncertainty as to how PRO could be implemented as a full-scale technology by providing baseline projections in terms of plant process designs (Figure 3), operational requirements, expected costs, and potential economic incentives. Successful initial implementation of this technology will help generate positive public perception and pave the way for widespread implementation across the United States as an energy recovery and brine management technology. This will help reduce the cost and increase the overall viability of desalination, which will allow for enhanced resilience in the face of uncertainty, especially in areas of projected severe water stress like Florida and the Southwestern United States (Spencer and Altman, 2010).

Figure 1.3 Overview of a conceptual pressure retarded osmosis (PRO) system in the context of water and wastewater treatment facilities in the Tampa Bay area.
1.2.2 Hypothesis

The hypothesis of this dissertation is: When applied correctly, PRO-based energy recovery is a viable option for reducing the overall cost and net energy consumption of seawater desalination. In terms of what defines the “correct” conditions, this depends on how the variables (salinity gradient, membrane characteristics, process configurations, local geography, economic conditions, spacer geometries, pretreatment technologies, influent quality and quantity) that are relevant to PRO operations are configured to maximize long-term system performance in terms of net energy generation potential. In terms of the membrane system, it is hypothesized that net energy generation potential can be maximized by using ultraviolet radiation to treat WWTP effluent, before running it through a CTA membrane with a diamond lattice spacer. In terms of geography, it is hypothesized that PRO systems will fare best in areas with the following conditions: co-location of a seawater desalination plant with a wastewater treatment plant in order to minimize transmission distance, poor solar and wind potential, high electricity costs, the existence of discharge permits that regulate the salinity of the brine effluent, and renewable energy credits that could be adapted to help cover the initial start-up cost of a PRO system.

1.3 Dissertation Outline

The dissertation is divided into four tasks. No task is performed in isolation, as each successive task builds upon design decisions that were made in the previous tasks (Figure 1.4).

The first task involved conducting a preliminary analysis that investigated how a PRO system could be designed by simulating plant performance and estimating capital costs and potential payback periods for plants operating under baseline (steady-state) conditions. This was done by creating a Python-based model that determined the ideal salinity gradient for desalination energy recovery operations, produced ranges of variation for how a PRO system could potentially
perform through a sensitivity and uncertainty analysis, and validated the estimated results using thermodynamic limits and performance data from the literature.

Figure 1.4 The four tasks of the dissertation

The second task focused on identifying the ideal locations where PRO could potentially be implemented by examining preexisting seawater desalination plants in the United States. Once the sites were identified, they were evaluated using the Python-based model developed for the first task, and geographic and economic constraints were identified that would need to be met if a future seawater desalination plant wanted to use PRO-based energy recovery and brine management systems.

The third task focused on analyzing the internal hydraulics of PRO systems in order to design more effective membrane spacers that minimized the impacts from concentration polarization and internal pressure loss. This was done using a physical bench scale system to calibrate and validate a computational fluid dynamics membrane model and compare different membrane spacer geometries. Once the highest performing geometry was identified, it was then improved upon through integrated CFD-based optimization using the open-source optimization toolkit, DAKOTA.
The fourth and final task investigated how membrane spacer configuration, cleaning strategies, and additional feed water pretreatment affected the fouling rate of the membranes using a laboratory bench-scale test reactor. The parameters that were tested were membrane spacer configuration and feed water pretreatment - which was broken down into microfiltration, adding an antiscalant, or disinfecting the water with UV - with the pretreatments applied both individually and sequentially. Close attention was paid to how the concentration of salts and organic material changed as the water underwent the PRO process. These tests were used to develop foulant propagation curves, which were used to determine potential net energy densities for the various process configurations.

Table 1.4 lists the details and status of the publications associated with the research chapters. My contribution to those publications was through conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; resources; software; supervision; validation; visualization; roles/writing - original draft; and writing - review & editing.

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Publication</th>
<th>Status</th>
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Chapter 2: A Techno-Economic Process Model for Pressure Retarded Osmosis Based Energy Recovery in Desalination Plants

2.1 Abstract

Existing desalination plants face the challenges of high energy costs and environmental impacts from brine disposal. Pressure retarded osmosis (PRO) is a technology that could mitigate these issues. PRO works by capturing the potential energy in the salinity gradient between brine and dilute (e.g. freshwater/wastewater) solutions. In this study, we developed a Python-based model called Propmod that uses both internal and user-defined inputs to simulate how a full-scale PRO system performs energetically and economically. The Tampa Bay Seawater Desalination Plant was used as a case study, and if a PRO system was installed in this plant, it could potentially save 9% of the energy consumed per $m^3$ of permeate, while also diluting the brine from 66 to 41 ppt. Sensitivity and uncertainty analysis on the net present value of potential full-scale PRO systems indicated that the most influential parameters on PRO system performance are membrane characteristics (salt permeability, water permeability, and structural parameter), as well as energy price and feed water transmission pipe size and length. Overall, PRO systems were found to be competitive with other forms of renewable energy in areas that allow systems to be designed with higher rates of energy generation and minimal capital and operational costs.

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2.2 Introduction

Reverse osmosis (RO) is a treatment process widely implemented in desalination and advanced water reclamation facilities. Currently, a significant challenge with RO is reducing the energy consumption and environmental impacts of the process (Elimelech and Phillip, 2011). Elevated levels of energy consumption cause RO product water to be much more expensive than other conventional water sources and can prevent the implementation of this crucial technology in areas that are under severe water stress. Another primary environmental concern comes from RO concentrate disposal (Elimelech and Phillip, 2011). Depending on the temperature, salinity, and chemical input, RO concentrate disposal can negatively affect the oxygen content of the receiving water due to its salt content, and some RO discharge additionally contains biocides and anti-scaling additives (Sagle and Freeman, 2004). These issues need to be addressed to make desalination a more effective technology for water strained regions.

One option is to utilize the high osmotic pressure difference that exists when a highly concentrated solution, such as RO concentrate, is placed on the opposite side of a semipermeable membrane from a solution with a low concentration of solutes, such as freshwater or wastewater treatment plant (WWTP) effluent. This concentration difference creates an osmotic pressure difference, which causes water to flow through the membrane to alleviate this pressure difference. If an external hydraulic pressure is applied to the concentrated side that is lower than the osmotic pressure difference, then this will result in an excess of diluted and pressurized concentrate. This excess can then be divided into two streams and used for both power generation in a hydropower turbine and for pressurizing incoming concentrate using an in-line pressure exchanger (Skilhagen, 2010). This technology is known as pressure retarded osmosis (PRO) and offers a solution to the
issues of high energy consumption and brine management in desalination (Altaee et al., 2016; Altaee and Sharif, 2015; Saito et al., 2012). The general process is illustrated in Figure 2.1.

![Figure 2.1 General process diagram for Pressure Retarded Osmosis (PRO) systems. Water flows from the feed side (low concentration) to the draw side (high concentration), where it then goes through a turbine to generate electricity, as well as through a pressure exchanger to maintain system pressure. Note that the presence of pretreatment systems is dependent on the source water quality of the draw and feed solutions.](image)

The primary issues with PRO are concentration polarization and membrane fouling (Bogler et al., 2017; Thelin et al., 2013; Yip and Elimelech, 2013). Concentration polarization is caused by an increasing gradient of solutes towards the membrane surface that reduces the overall concentration gradient; this is a transport phenomenon and thus cannot be prevented. PRO membranes are usually oriented with the active layer (where diffusion occurs) facing the pressurized draw solution. This maintains membrane integrity and preserves high salt rejection (over 99.8%) while the support layer is pressed onto the feed channel spacer, causing external concentration polarization (ECP), whose effects are relatively minor when compared with internal concentration polarization (ICP) (Bar-Zeev et al., 2015; Kim et al., 2016; She et al., 2013a; Straub et al., 2014a). ICP is one of the key limiting phenomena for PRO performance but can be suppressed using membranes with tailored porous support layers (Chou et al., 2012; Yip and...
Elimelech, 2013). While several membrane development studies have considered ICP and ECP, plant scale modeling studies have not included this factor (Helfer and Lemckert, 2015; Naghiloo et al., 2015). Neglecting these factors can overestimate the potential specific energies using PRO, since ICP and ECP, and to a lesser degree, reverse solute diffusion, all have the potential of reducing the overall specific energy of a system. Membrane fouling reduces the permeability of the membrane and prevents water from flowing through the membrane matrix, but it can be controlled through pretreatment and process optimization schemes. It is important for fouling to be controlled, as it is one of the primary factors increasing overall energy generation costs to the point of making PRO economically unfeasible (Yip et al., 2016).

PRO is currently in its pilot phase, with several experimental plants throughout the world (Jihye Kim et al., 2015a). The first pilot PRO plant was the Statkraft plant in Tofte, Norway (Skilhagen, 2010). The plant was built in 2009 and used river water as a feed solution and salt water as the draw solution. The hydraulic pressure was 12.5 bar, and a spiral wound membrane developed by Hydronautics was used starting in 2011. The plant was operated until it closed in 2013, primarily due to high operational costs that would make the power generated from a full-scale plant uncompetitive in the European power market. These high costs stemmed from pretreatment costs, low membrane power densities, and inefficiencies in the hydraulic power generation system (Sarp et al., 2016; Yip et al., 2016). Projects that pair RO concentrate with wastewater have been more successful, such as the Mega-ton Water System project in Japan, and the Global MVP project in South Korea. Both projects are currently in the pilot phase, with plans for eventual full-scale implementation (Kurihara et al., 2016; Kurihara and Hanakawa, 2013).

While advancements have been made in both membrane design and fouling mitigation techniques, progress in moving PRO from the pilot phase to the commercial phase has been
hindered by a lack of understanding regarding how a PRO system would perform both energetically and economically when implemented at full scale (Yasukawa et al., 2018). This is further hindered by the differing performances that PRO systems have at different membrane sizes, with a majority of experimental trials done on coupon-scale membranes, which do not incorporate the effect of variable draw and feed concentrations across the length of the membrane chamber caused by water and reverse salt fluxes that exist in a commercial scale module (Bar-Zeev et al., 2015; Kim et al., 2016; She et al., 2013a; Straub et al., 2014a). Furthermore, there are limited studies investigating how PRO could be implemented in pre-existing desalination facilities, and how the implementation of PRO and its cost and energy saving measures would affect the overall system performance in terms of energy consumption per unit volume of product water (kWh m$^{-3}$). Also, while current predictive models have focused on estimating gross power density and specific energies of PRO systems (Anissimov, 2016), there have been limited studies on calculating net power densities and specific energies, as well as capital and operational costs that would be incurred in implementing a PRO system in a desalination plant (Sarp et al., 2016). Most process models have focused primarily on designing PRO systems in isolation, and do not consider how external factors (e.g., pretreatment, influent transmission) could affect the overall net energy density. Furthermore, most studies have not had rigorous sensitivity and uncertainty analyses conducted that showcase the limits of the modeling processes (Anissimov, 2016; Naghiloo et al., 2015). Being able to accurately predict how a full-scale system would function in pre-existing plants would enable plant managers to evaluate the feasibility of implementing PRO in their plants and give a baseline for comparison against other energy reduction and brine management technologies.
Overall, to further advance and eventually implement the PRO process for desalination energy recovery, it is crucial to select the membrane type and configuration that properly balances energy generation potential and foulant resistance. In this study, we developed a plant-scale process model called Propmod that can simulate how a PRO system could perform both energetically and economically. Propmod can be used as an evaluation tool with an overall goal of reducing the energy consumption of desalination using PRO-based energy recovery. The different criteria that were evaluated in this investigation were membrane characteristics and configurations, salinity gradients, pretreatment options, energy prices, interest rates, and site locations. Through this evaluation, the range of potential net specific energies and expected payback periods for different plant configurations can be categorized, which can be used to enhance future plant design schemes. Propmod is designed to simulate any saltwater-based PRO process and has been tested with salinities ranging from DI water to RO concentrate (ROC). Overall, Propmod is designed to be as general as possible in order to extend its applicability to multiple scenarios.

2.3 Methods

Propmod includes a sequence of modules to calculate membrane processes, feed water requirements, energy generation potential, and costs (Figure 2.2). The model first calculates the membrane flow fields, then the membrane system is sized and priced. Next, the energy consumption and additional cost of transmission and pretreatment systems are added in if needed, and the net specific energy is calculated. If the net specific energy is greater than 0, then the power, total cost, unit cost ($ kW\(^{-1}\) of installed capacity), payback period, and net present value are calculated, and $SysCon_2$ is set to 1 to represent a system with a net positive specific energy. If the net specific energy is less than or equal to zero, then $SysCon_2$ is set to 0. This represents a system with a net negative specific energy, which means that that configuration would not be energetically
feasible. The following sections will go into detail on the specifics as to how the system is designed and priced.

Figure 2.2 Solution algorithm for Propmod. The presence of both transmission and pretreatment affects the overall net specific energy. SysCon2 is a variable that indicates whether a scenario has a net positive specific energy. If the net specific energy is less than 0, then placeholder values are used for values that require a positive net specific energy to calculate.

2.3.1 PRO Membrane System

In general, two source streams need to be paired to create a concentration gradient for osmotic power to be successfully generated (Figure 2.3). PRO membrane systems can either be oriented in a co-current orientation, where both the draw flow \( Q_D \, [L\ hr^{-1}] \) and feed flow \( Q_F \) are in the same direction, or in a counter-current orientation, as shown in Figure 2.3. The support layer is where ICP occurs and is located on the feed side of the membrane. The draw side is where ECP occurs. These systems can be described using a series of mass-balance equations that trace the mass of water and the mass of solutes. For a co-current system, the mass balances for salt
concentration and water volume are shown below in Equations (2.1A)–(2.1D) (Bar-Zeev et al., 2015; Kim et al., 2016; She et al., 2013a; Straub et al., 2014b):

\[
\frac{dQ_D(s)}{ds} = J_w(c_D(s), c_F(s), \Delta p) \tag{2.1A}
\]

\[
\frac{dQ_F(s)}{ds} = -J_w(c_D(s), c_F(s), \Delta p) \tag{2.1B}
\]

\[
\frac{d(Q_D(s)c_D(s))}{ds} = -J_S(c_D(s), c_F(s), \Delta p) \tag{2.1C}
\]

\[
\frac{d(Q_F(s)c_F(s))}{ds} = J_S(c_D(s), c_F(s), \Delta p) \tag{2.1D}
\]

Equations (2.1A) and (2.1B) represent the water mass balance, and Equations (2.1C) and (2.1D) represent the solute mass balance. \(c_D\) is the solute concentration on the draw side [g kg\(^{-1}\)], \(c_F\) is the solute concentration on the feed side [g kg\(^{-1}\)], \(J_w\) is the water flux through the membrane [L m\(^{-2}\) h\(^{-1}\)], \(J_S\) is the solute flux through the membrane [g L m\(^{-2}\) h\(^{-1}\) kg\(^{-1}\)], \(\Delta p\) is the hydraulic pressure difference [bar], and \(s\) represents a two-dimensional discrete membrane element [m\(^2\)]. These four equations must be solved in unison, with \(J_w\) and \(J_S\) being functions of \(c_D\), \(c_F\), and \(\Delta p\). In a counter-current system, the flow direction of the feed solution is counter to the flow direction of the draw solution, and so the polarity of the feed Equations (2.1B) and (2.1D) are reversed, making both \(J_w\) equations positive, and both \(J_S\) equations negative.

The water flux through the membrane is calculated according to (He et al., 2015):

\[
J_w = A \left[ \frac{iRT}{M} \left( \frac{\rho_D c_D \exp \left( -\frac{I_w}{k} \right) - \rho_F c_F \exp \left( \frac{I_w S}{D} \right)}{1 + B J_w \left\{ \exp \left( \frac{I_w S}{D} \right) - \exp \left( -\frac{I_w}{k} \right) \right\}} \right) - \Delta p \right] \tag{2.2}
\]

\(A\) is the water permeability of the active layer [L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)], \(B\) is the salt permeability of the active layer [L m\(^{-2}\) h\(^{-1}\)], \(k\) is a mass transfer coefficient [L m\(^{-2}\) h\(^{-1}\)], \(D\) is the diffusion constant [m\(^{-2}\) s\(^{-1}\)], \(M\) is the molecular weight of NaCl, \(\rho_D/F\) is the density of the draw and feed
solutions \([kg \ L^{-1}]\), \(R\) is the ideal gas constant \([L \ bar \ mol^{-1} \ K^{-1}]\), \(S\) is a structural parameter \([\mu m]\), \(T\) is temperature \([K]\), and \(i\) is the Van't Hoff factor for NaCl \((2)\). This equation was modified from the one found in \((He \ et \ al., \ 2015)\) to include the effect of variable densities on both sides of the membrane due to differences in solute concentration.

In a similar form, the salt flux can be represented as \((Straub \ et \ al., \ 2014a)\):

\[
J_S = B \left( \frac{c_D \ exp \left( -\frac{J_w}{k} \right) - c_F \ exp \left( \frac{J_w S}{D} \right)}{1 + B J_F \ \{exp \left( \frac{J_w S}{D} \right) - exp \left( -\frac{J_w}{k} \right)\}} \right) \tag{2.3}
\]
The membrane system itself is divided into a series of membrane elements, which are then stored in pressure vessels organized into skids. In desalination applications, there are typically seven elements per pressure vessel and fourteen pressure vessels per skid, with each membrane element having an eight-inch (20.32 cm) diameter, 440 ft² (40.88 m²) of surface area \(A_{m,elem}\), a length \(L_{elem}\) of 40 in (1.016 m), and a width \(w_{elem}\) of 132 ft (40.24 m) \cite{26}. This configuration is used for the design of the PRO system, with membrane element dimensions based on the DOW FILMTEC™ SEAMAXX™ RO membrane, which is an 8040 spiral wound TFC (thin-film composite) membrane. Internally, it is assumed that the channel height \(h_c\) is 700 μm and 1:3 ellipse type spacers are used, with 4.5 mm between each spacer \cite{Feinberg et al., 2015}. Note that Propmod has been preloaded with several different spacer geometry types, and the 1:3 ellipse type spacer was chosen due to its low hydraulic resistance \cite{Guillen and Hoek, 2009}.

The hydraulic pressure difference \(\Delta p\) is initially set at half of the available osmotic pressure difference \(\Delta \pi /2\) in order to achieve maximum power density \cite{Ramon et al., 2011}. Hydraulic pressure loss inside the membrane system is calculated as \cite{Feinberg et al., 2015}:

\[
\frac{dp}{dx} = \frac{\lambda \rho_D u_D^2}{2d_h}
\]

(2.4)

where \(x\) is a one-dimensional discrete membrane element [m] (calculated as \(s/w_{elem}\)), \(u_D\) is the draw side velocity [m s\(^{-1}\)] (calculated as \(Q_D/(h_c \times w_{elem})\)), \(d_h\) is the hydraulic diameter [m] (which is based on spacer geometry \cite{Guillen and Hoek, 2009}), and \(\lambda\) is the friction factor coefficient, which is calculated as:

\[
\lambda = \alpha + \frac{\beta}{Re^\gamma}
\]

(2.5)

where \(Re\) is the Reynold's number, and \(\alpha, \beta,\) and \(\gamma\) are fitting parameters obtained from computational fluid dynamics \cite{Guillen and Hoek, 2009}.
Once the water flux across the system is calculated, it can be used to calculate the power density, \( W \) \([W \ m^{-2}]\), and the specific energy \( SE \) \([kWh \ m^{-3}]\). The power density is calculated as (Straub et al., 2014a):

\[
W = \frac{\Delta p_{avg} \Delta Q_D}{36 * A_{m,PV}}
\]  

(2.6)

where \( A_{m,PV} \) is the total membrane area in the pressure vessel \([m^2]\), \( \Delta p_{avg} \) represents the average hydraulic pressure difference, \( \Delta Q_D \) represents the total amount of solution transferred to the draw side \([L \ h^{-1}]\) and 36 is a coefficient used to convert from bar to kWh m\(^{-3}\). Note that for a coupon-scale system, the power density can be calculated by multiplying \( J_w \) by \( \Delta p \) (Achilli et al., 2009). This assumption holds due to the limited size of coupon-scale systems keeping \( J_w \) constant across the length of the membrane. The overall specific energy \([kWh \ m^{-3}]\) of mixed solution is dependent upon the amount of feed solution transferred to the draw side. Due to this, the gross specific energy is calculated as:

\[
SE_{gross} = \frac{\Delta p_{avg} \Delta Q_D}{36(Q_{D,in} + Q_{F,in})}
\]  

(2.7)

where \( Q_{D,in} + Q_{F,in} \) represents the total amount of solution in the system. The theoretical maximum amount for specific energy would replace \( \Delta Q_D \) with \( Q_{F,in} \), since that would mean all of the feed solution would transfer to the draw side. Propmod simulates the membrane system by first solving Equations (2.1A)–(2.7) for an individual membrane pressure vessel in one dimension along the membrane length axis. The differential equations are solved numerically by discretizing each membrane pressure vessel into \( N \) finite elements, where \( N \) is equal to the length of a membrane element \( (L_{elem}) \) divided by the distance between spacers \( (L_{spacer}) \). Using the given geometry, this makes \( N \) equal to 226. To determine the total number of membrane skids required \( (N_{skid}) \), the total amount of draw solution influent, \( Q_{D,in,Tot} \), is divided by the amount of draw solution influent that
can flow through an individual pressure vessel, \( Q_{D,in,PV} \). This amount is then divided by \( N_{PV/skid} \), which is the number of pressure vessels per skid \((14)\), and rounded up to the nearest whole number. Once \( N_{skid} \) is calculated, it can be used to calculate the total membrane area as shown below:

\[
A_{m,Tot} = N_{skid}N_{PV/skid}N_{elem/PV}A_{m,elem}
\] (2.8)

where \( N_{elem/PV} \) is the number of elements per pressure vessel \((7)\) and \( A_{m,elem} \) is the area of an individual membrane element \((37.1 \text{ m}^2)\). In a similar fashion to the gross specific energy \((SE_{gross})\), the gross power generation potential, \( P_{Tot,gross} \ [\text{MW}] \), is calculated as:

\[
P_{Tot,gross} = \frac{\Delta p_{Eff}\Delta Q_{D,Tot}}{36 \times 10^{-6}}
\] (2.9)

Note that in this case, \( \Delta p_{Eff} \) is used, since power generation is an external process.

The total cost of the membrane system is:

\[
Cost_{Memb} = A_{m,Tot}C_{ms}
\] (2.10)

where \( C_{ms} \) is the cost per \( m^2 \) of membrane, which has been estimated to range from $5.80 (Naghiloo et al., 2015) to $14.18 (Helfer and Lemckert, 2015). This estimated price range for the cost of PRO systems is based on current and projected RO membrane prices for 8040 spiral wound TFC membranes purchased in bulk. RO membrane price estimates were used since there is currently no large-scale producer of PRO membranes that we know of. However, Propmod does have the flexibility of setting the membrane price as either a range or specific number, and so the membrane price can be adjusted as needed.

In Propmod, systems are configured based on membrane performance criteria collected from the literature. Overall, 30 different membranes were evaluated and compared to see which membrane has the best performance characteristics. A description of the algorithm used to solve
the membrane flow fields (Equations (2.1A)–(2.7)), information on how the algorithm was calibrated, and a table describing the 30 different membranes can be found in Appendix D.1.

2.3.2 WWTP Effluent Transmission

For the scenarios where ROC will be mixed with WWTP effluent, the impact of transporting the WWTP effluent to the desalination plant must be included. Note that it is more advantageous to transport the WWTP effluent to the desalination plant than the other way around, since ROC’s high salinity has a greater corrosion potential (Schorr et al., 2019). The power, $P_{Tra}$ [kW], consumed in pumping the WWTP effluent can be calculated as:

$$P_{Tra} = \frac{\rho g Q_{F,in} H}{\eta_{Tra}}$$  \hspace{1cm} (2.11)

where $\eta_{Tra}$ is the pump efficiency (Hammer and Jr., 2012), $\rho$ is density $[kg \ m^{-3}]$, $g$ is the acceleration due to gravity $[m \ s^{-2}]$, and $Q_{F,in}$ is the flow rate of the solution being transported $[m^3 \ s^{-1}]$. The hydraulic equations used to solve for the pump head ($H$) can be found in Appendix D.2.

The cost of installing the transmission system in US$ can be estimated as:

$$Cost_{Tra} = (a \times (1.341 P_{Tra})^n \times inf_1) + [L \times (362.34 d^2 + 78.5 d + 15.478) \times inf_2]$$  \hspace{1cm} (2.12)

where $a$ [US$ \ hp^{-1}$] and $n$ are coefficients, $inf_1$ is the US inflation rate from September 2007 – November 2018 (1.2089), $inf_2$ is the inflation rate from March 2007 – November 2018 (1.2273) (BLS, 2018), 362.34 [US$ \ m^{-2}$], 78.5 [US$ \ m^{-1}$], and 15.478 [US$] are empirical coefficients and 1.341 converts kW to horsepower (hp). The first term in the equation represents the cost of installing the pump station (McGivney and Kawamura, 2008), the second term represents the cost of installing a water main per linear meter (Quiroga et al., 2007). Note that this calculation assumes that installation is trench-based, and includes the cost of pavement removal, excavation, backfilling and compacting with native material.
2.3.3 Pretreatment System

In order to prevent the occurrence of membrane fouling, it is important to pretreat the source streams. Specific energy consumption from pretreatment, \( SEPT \ [kWh \ m^{-3}] \) is calculated as:

\[
SE_{PT} = SE_{PT,gen} \frac{Q_{F,in}/D,in}{Q_{M,in}} \tag{2.13}
\]

where \( SE_{PT,gen} \ [kWh \ m^{-3}] \) is the generalized specific energy consumption of a pretreatment technique (EPRI, 2013) and \( Q_{F,in}/D,in \) can either be the feed or the draw flow [\( L \ hr^{-1} \)]. Similarly, the power consumed by the pretreatment system, \( P_{PT} \ [MW] \), can be found by multiplying \( SE_{PT,gen} \) by \( Q_{F,in}/D,in \) and dividing by \( 10^6 \) to convert from \( W \) to \( MW \).

The capital cost [\$] is estimated as:

\[
Cost_{PT,MF} = a * Q_{F,in}/D,in * inf_1 \tag{2.14}
\]

where \( a \ [\$ \ hr \ L^{-1}] \) is a cost coefficient (0.6946). Propmod includes capital cost equations for pretreatment techniques using cost models from (AWWA, 2008) for microfiltration and ultrafiltration, and (McGivney and Kawamura, 2008) for all other pretreatment techniques listed. In the scenarios where seawater is applied, microfiltration will be used as the pretreatment technique due to microfiltration's ability to remove most bacteria. Ultrafiltration was also considered, but for this case, it is too energetically intensive to be feasible as a form of pretreatment. Note that in this study, pretreatment was only used in the scenarios with seawater, as it was assumed that ROC and WWTP effluent have been polished enough by their respective systems that further treatment at the PRO plant would not be necessary.

2.3.4 Net Energy Production and Generation/Circulation System

After the draw solution leaves the PRO membrane system, the flow is diverted into the generation and pressure recovery system. The purpose of the pressure recovery system is to
transfer the high system pressure from the draw effluent back into the draw influent so that energy
does not have to be spent re-pressurizing the system. In this case, the draw effluent is divided so
that an amount equal to $Q_{D,in}$ is sent to the pressure exchanger, while the amount passing through
the Pro membrane, $\Delta Q_D$, is sent to the generation system. The power consumed in recirculating
the draw solution, $P_{circ}$ [MW], is estimated as:

$$
P_{circ} = \frac{(\Delta p_{in} - \Delta p_{eff} \eta_{PX}) Q_{D,in}}{36 \times \eta_{BP} \times 10^6}
$$

where $\eta_{PX}$ is the efficiency of the rotary pressure exchanger (0.97), $\eta_{BP}$ is the efficiency of the
booster pump (0.89), and 36 and $10^6$ are unit conversion factors (Feinberg et al., 2015).

The generation system can either be a hydro turbine, or a rotary pressure exchanger. While
a rotary pressure exchanger can operate with efficiencies exceeding 97% (Stover, 2005), its
primary disadvantage is that for that efficiency to be achieved, it would need to feed the effluent
from the PRO system back into the desalination plant. This is possible in scenarios where only
brine and seawater are used, but it is not recommended for scenarios where WWTP effluent is
used, due to regulations barring direct potable reuse of WWTP effluent (Payne, 2017). Net energy
production is found by taking the gross amount of energy produced and subtracting the energy
consumption from transmission, pretreatment, and process inefficiencies. Thus, specific energy
($SE_{net}$) is represented as:

$$
SE_{net} = SE_{gross} \eta_{Gen} - SE_{Tra} \frac{Q_{F,in}}{Q_{M,in}} - SE_{PT} - \frac{P_{circ}}{Q_{M,in}}
$$

where $\eta_{Gen}$ is the efficiency of the generation turbine. $SE_{net}$ is then used to calculate the net power
($P_{Tot,net}$) [MW]:

$$
P_{Tot,net} = P_{Tot,gross} \eta_{Gen} - \frac{P_{Tra}}{1000} - P_{PT} - P_{circ}
$$
To calculate the cost of the generation/circulation system, the cost of the generation turbine/pressure exchanger, the recirculation pressure exchanger, and the booster pump must be included. The cost of the booster pump ($Cost_{BP}$) is calculated using the first term in Equation (2.12), where $P_{Tra}$ is replaced with $P_{Circ} \times 1000$ (to convert from MW to kW). The cost of the generation turbine/pressure exchanger and the recirculation pressure exchanger is calculated as (Aggidis et al., 2010):

$$Cost_{Gen} = \left[ 2600 \times \left( P_{Tot,net/Circ} \times 1000 \right)^{0.54} \times ex \right] \times inf_3$$

(2.18)

where $ex$ is the exchange rate between Euros and US$ in November 2008 (1.26), $inf_3$ is the US inflation from November 2008 to November 2018 (1.1865) (BLS, 2018), and $P_{Tot,net/Circ}$ represents either the net power for the generation turbine/pressure exchanger or the power consumed by circulation for the recirculation pressure exchanger. Note that the cost of all three systems (the booster pump, the generation turbine, and the pressure exchanger) is included in Propmod. Also note that this equation is contingent on $P_{Tot,net}$ being a positive number. Due to this, scenarios in Propmod that yield a negative $P_{Tot,net}$ have $P_{Tot,net}$ set to zero and are also removed from consideration as a viable option.

2.3.5 Effluent Quality and Total Capital Cost

Total system cost is calculated by summing up the costs of the transmission system, pretreatment system, membrane system, and generation/circulation system, and then multiplying by 1.35 to account for the costs of yard piping, sitework landscaping, and site electrical and controls (McGivney and Kawamura, 2008). The total system cost is then multiplied again by 1.35 to account for non-capital costs, which are engineering, legal, and administrative costs (McGivney and Kawamura, 2008). This can be represented as:
\[ \text{Cost} = \left[ (\text{Cost}_{\text{Tr}} + \text{Cost}_{\text{PT}} + \text{Cost}_{\text{Memb}} + \text{Cost}_{\text{Turb/Circ}}) \right]^{1.35} \cdot 1.35 \] (2.19)

To calculate \( V_{SP} \), the present value of energy cost savings generated by the PRO system [$], the yearly savings generated must be summed up (Naghiloo et al., 2015):

\[ V_{SP} = \sum_{n=1}^{N} \left( E_{\text{net}} \cdot 10^3 \cdot EP \cdot (1 + \Delta EP)^n \right) \frac{1}{(1 + r)^n} \] (2.20)

where \( E_{\text{net}} \) is the net amount of energy recovered by the system per year \([\text{MWh yr}^{-1}]\), \( EP \) is the energy price \([\$ \text{kWh}^{-1}]\), \( \Delta EP \) is the change in energy price per year \([\$]\), \( r \) is the interest rate in decimal form, \( N \) is the total number of years the system will be installed \([\text{yr}]\), and \( n \) is the iteration year \([\text{yr}]\). Finally, the capital cost of the system is subtracted from \( V_{SP} \) to determine \( V_{NP} \), the net present value. The number of years that it takes for \( V_{SP} \) to become positive determines the payback period for the PRO system.

2.3.6 Primary Assumptions

The primary assumptions made in Propmod are that (1) the system operates at steady-state conditions; (2) pretreatment completely removes any potential foulants; (3) the draw and feed solutions are already at system pressure when they enter the PRO system; and (4) seawater can be pretreated with microfiltration, as this can remove most bacteria, algae, humic acids, and colloids that could potentially cause biofouling.

2.3.7 Simulation Validation Method

All model inputs were sourced from either the literature or from interviews with plant personnel. Propmod was validated using data from (Straub et al., 2014b). To evaluate the accuracy of the model validation, the Nash-Sutcliffe Coefficient (NS) (Nash and Sutcliffe, 1970), the ratio of the standard deviation of observations to the root mean square error (RSR), and the mean square error (MSE) were all calculated.
Furthermore, the expected specific energy levels were cross-checked with the thermodynamic maxima for reversible processes as well as the maxima for both co-current circulatory processes and counter-current circulatory processes (Lin et al., 2014a; Spiegler and El-Sayed, 2001; Yip and Elimelech, 2012). A description of the validation coefficients and the thermodynamic equations can be found in Appendix D.3.

2.3.8 Sensitivity and Uncertainty Analysis Method

Due to the inherent uncertainty that lies in any numerical model, sensitivity and uncertainty analyses were conducted. The purpose of the sensitivity analysis was to investigate how the variation in the output of the model could be attributed to variations in individual input factors. The sensitivity and uncertainty analyses were conducted using the SALIB python library (Herman and Usher, 2017). The analysis used the Saltelli sampler method to generate $N \times (2D + 2)$ sample sets, where $N$ is the number of arguments supplied, and $D$ is the number of model inputs (Campolongo et al., 2007; Saltelli, 2002). From this sample set, it is also possible to conduct the uncertainty analysis, which evaluates the overall range of variation of the model outputs.

In order to identify which input variables caused the largest variation in model output, it is important to conduct a global sensitivity analysis that can capture both the variation caused by individual variable variations (the local variation, which can be found using one-at-a-time, or OAT methods), but also from variations caused by changing sets of variables. In this study, the Sobol method was used (Sobol, 2001). The Sobol method works by calculating sensitivity indices and confidence intervals (with a typical confidence level of 95%) for first order (local), second order (combined variables), and total (global) variations.

The analysis was done by varying the nineteen coefficients listed in Table D.2. The range of variation for the membrane parameters was based on the membrane performance parameters
from the membranes found to have a positive net power in the initial case study. For plant and economic characteristics, data were based on interviews with plant personnel and extracted from the literature and were chosen to represent the expected range of variation that could be found in the United States.

In order to generate a wide range of sample sets, each variable was sampled 168 times, which was chosen to minimize the potential for computational error while also limiting the total number of sample sets to prevent excessive computational runtime. Using the Saltelli sampler method, this ended up generating 6720 individual sample sets for each salinity gradient in order to see which inputs had the greatest effect on the output. After that, sensitivity indices were generated using the Sobol method for the net present value, $V_{NP}$, which was chosen as the most critical final output, since the net present value requires all nineteen variables to be calculated.

2.4 Case Study Background

A case study on how to retrofit the Tampa Bay Seawater Desalination Plant (TBSDP) with a PRO-based energy recovery system was performed to demonstrate the applicability of Propmod. The TBSDP is one of the largest seawater desalination plants in the United States and provides up to 25 million gallons daily (MGD; $1.1 \text{ m}^3\text{ s}^{-1}$) of desalinated water to the region. The plant is essential during the dry season and ensures that the Tampa Bay area has a robust and continuous water supply. The system is located next to the TECO Big Bend Power Station, which captures 1.4 billion gallons a day ($61 \text{ m}^3\text{ s}^{-1}$) of seawater for cooling purposes. The TBSDP then captures up to 44 MGD ($1.9 \text{ m}^3\text{ s}^{-1}$) of that warm seawater when it exits the power plant and treats the water through a five-stage treatment scheme consisting of coagulation, flocculation, sand filtration, dichotomous earth filtration, and cartridge filtration. The water then enters an RO treatment scheme which consists of a first pass and a partial second pass through the RO membranes. Finally,
the effluent water is stabilized before it is distributed to the Tampa Bay area. When running at full capacity, the plant requires 11.67 MW of power to operate and produces 19 MGD (0.83 m³ s⁻¹) of RO concentrate (ROC). On average, the plant consumes 3.43 kWh m⁻³ of product water and has an average production cost of $0.79 per cubic meter of drinking water. For context, in the Tampa Bay area, this production cost can be up to five times as expensive as surface water and ten times as expensive as groundwater. Operational data for the plant was collected from TBSDP staff (Aleix Martorell Cebrian, personal communication).

Figure 2.4 The distance between the South County Regional Wastewater Treatment Plant (bottom) and the Tampa Bay Desalination Plant (TBSDP) (middle). It is assumed that a transmission pipe with a length of 9382 m would be placed underneath the dotted line, and so the calculated transmission distance also includes four 90° turns and two 45° turns. On top is the Howard F. Curren Wastewater plant, which is farther away from TBSDP, with a total distance of 23,500 m. However, due to its proximity to Tampa Bay, it is where the seawater–wastewater configuration was tested.

In this study, different solutions available for generating salinity gradient energy were evaluated to see which gradient would produce the most energy for the lowest cost. Three scenarios
were tested: The first scenario paired the ROC from the TBSDP with the wastewater treatment plant effluent (WW) from the nearby South County Regional Wastewater Treatment Plant, (SCRWWTP) (ROC-WW); the second scenario paired the ROC with seawater (SW) from Tampa Bay (ROCSW); the third scenario paired seawater from Tampa Bay with the WWTP effluent from the Howard F. Curren Wastewater Treatment (HCWWTP) Plant (SW-WW). Note that the WWTP effluent from the HCWWTP was used for the SW-WW scenario because the SCRWWTP is not located next to the shoreline (Figure 2.4). The primary inputs specific to the Tampa Case Study are listed in Table 2.1. Individual membrane characteristics are collected in Table D.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Range of Values</th>
<th>Unit</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbine Efficiency*</td>
<td>$\eta_{Gen}$</td>
<td>90–98</td>
<td>%</td>
<td>(Feinberg et al., 2015; Stover, 2005)</td>
</tr>
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<td>WWTP Elevation</td>
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<td>m</td>
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<tr>
<td>Desalination Plant Elevation</td>
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<td>3.1</td>
<td>m</td>
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<td>Transmission Pipe Length</td>
<td>$L$</td>
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<td>m</td>
<td>(USGS, 2019)</td>
</tr>
<tr>
<td>Transmission Pipe Diameter</td>
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<td>0.46</td>
<td>m</td>
<td>(Quiroga et al., 2007)</td>
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<td>Draw Flow Rate#</td>
<td>$Q$</td>
<td>0.2–2.29</td>
<td>$m^3 \cdot s^{-1}$</td>
<td>(EPRI, 2013)</td>
</tr>
<tr>
<td>Draw Concentration**</td>
<td>$c_D$</td>
<td>27–66</td>
<td>g kg$^{-1}$ [ppt]</td>
<td>(EPRI, 2013)</td>
</tr>
<tr>
<td>Feed Concentration**</td>
<td>$c_F$</td>
<td>0.256–27</td>
<td>g kg$^{-1}$ [ppt]</td>
<td>(FDEP, 2013)</td>
</tr>
<tr>
<td>Energy Purchase Price</td>
<td>$EP$</td>
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<td>$\text{kWh}^{-1}$</td>
<td>(EPRI, 2013)</td>
</tr>
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<td>Annual Energy Price Change</td>
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<td>$\text{s}$</td>
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<td>%</td>
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<td>Annual Plant Operation Time##</td>
<td>$OT$</td>
<td>80–100</td>
<td>% yr$^{-1}$</td>
<td>(EPRI, 2013)</td>
</tr>
<tr>
<td>Cost per m$^2$ of membrane</td>
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<td>$\text{$/m}^2$</td>
<td>(Naghiloo et al., 2015)</td>
</tr>
<tr>
<td>Water Temperature</td>
<td>$T$</td>
<td>31.6</td>
<td>°C</td>
<td>(TBEP, 2019)</td>
</tr>
</tbody>
</table>

*Efficiency is 90% for a Hydro turbine and 98% for a rotary pressure exchanger.
**For the ROC-WW scenarios, $c_D = 66 \text{ ppt}$ and $c_F = 0.256 \text{ ppt}$. For the ROC-SW scenarios, $c_D = 66 \text{ ppt}$ and $c_F = 27 \text{ ppt}$. For the SW-WW Scenarios, $c_D = 35 \text{ ppt}$ and $c_F = 0.431 \text{ ppt}$.
$Q_D$ is 0.2 $m^3 \cdot s^{-1}$ for the ROC-WW scenario due to the smaller flow from the SCRWWTP, 0.83 $m^3 \cdot s^{-1}$ for the ROC-SW scenarios, and 2.29 $m^3 \cdot s^{-1}$ for the SW-WW scenarios due to the larger flow from the HCWWTP.
##$OT$ is 80% of the year for the ROC-WW and ROC-SW scenarios, and 100% of the year for the SW-WW scenario.
2.5 Results and Discussion

2.5.1 Model Validation

Propmod was validated using data from (Straub et al., 2014b) using the co-current flow method solver, with a membrane area of 0.002 $m^2$, a membrane length of 0.077 $m$, an $A$ of 2.49 $L m^2 h^{-1} bar^{-1}$, a $B$ of 0.39 $L m^2 h^{-1}$, an $S$ of 564 $\mu m$, a $D$ of 5.328E-6 $m^2 h^{-1}$, a $k$ of 99 $L m^2 h^{-1}$, a $cF$ of 0.0003 $g kg^{-1}$ (representative of DI water), and a $T$ of 25 °C. The results of the validation at \( c_D \) concentrations of 0.6 $M$, 1 $M$, 2 $M$, and 3 $M$ are in Figure 2.5. Note that for \( c_D = 0.6 \) $M$ and 1 $M$, the concentrations were converted to ppt using Millero-Poisson Method (Millero and Poisson, 1981). Since this equation is only valid for concentrations from 0.5 to 43 ppt, it was not used for \( c_D = 2 \) $M$ and 3 $M$, since they represent concentrations more than three times higher than the maximum value tested (The Millero-Poisson method was used for \( c_D = 1 \) $M$, since it is close to the maximum value tested). Instead, these values were converted by multiplying their molarities by the molecular weight of NaCl. In this case, Propmod had a Nash-Sutcliffe coefficient score of 0.969, an RSR value of 0.176, and an MSE value of 8.414. All three values were within their respective acceptable ranges, although the MSE was higher than the other two coefficients and is due to some of the larger values at the tail end of the $W$ curve for \( c_D = 1 \) $M$ and 2 $M$ increasing the total mean. Since all three performance indicators were within acceptable ranges, it is likely that the model produces realistic results in terms of membrane performance under steady-state conditions with limited fouling. Furthermore, during model testing, it was found that the calculated gross specific energies never exceeded their maximum thermodynamic values, which indicates that the results are consistent within the laws of thermodynamics.
Figure 2.5 Model validation results. $c_D$ stands for draw concentration, $J_w$ stands for water flux, $W$ stands for power density, $\Delta p$ stands for the hydraulic pressure difference, NS stands for Nash-Sutcliffe, RSR stands for the ratio of standard deviation of observations to root mean square error, and MSE stands for mean square error. Note that while NS and RSR remain steady across the four concentrations, the MSE value increases with increasing concentrations due to higher power densities.

2.5.2 Case Study Results

For this analysis, 30 different membrane types from across the literature were tested in order to evaluate how the PRO system would function with each membrane. As shown in Figure 2.6, there is a clear relationship between the net specific energy generation potential and the unit net present value of the project, where the unit net present value increases as the net specific energy increases, especially for the ROC-WW scenario. Furthermore, there is a clear divide between the overall performance of ROC-WW solutions and other solutions, as the ROC-WW scenarios have a wider range of net specific energy values and higher unit net present values.
Figure 2.6 Net specific energy vs unit net present value for each tested membrane. SW is seawater, ROC is reverse osmosis concentrate, and WW is wastewater treatment plant effluent. Trials where net specific energy was less than 0 due to energy losses from pretreatment and transport were filtered out of this graph, since calculating net present value requires a positive net specific energy (Equations (2.16) & (2.18)). The starred points are the membranes with the lowest unit cost for each solution. Note that an interactive version of this figure that identifies which membrane each point represents upon hovering over it is available at https://tinyurl.com/DSPROF6.

From this point, only the best performing membrane from each scenario – which was the Oasys forward osmosis 4040 membrane module used by (Achilli et al., 2014) – was considered for further analysis. In terms of net vs gross specific energy, even though energy is lost to transmission in the ROC-WW scenario, the difference in energy generation potential makes up for this energy loss (Figure 2.7), with the net specific energy being 0.25 kWh m\(^{-3}\) of mixed solution.
Figure 2.7 Net and gross levels of energy generation and consumption for the lowest unit cost ($kWh^{-1}$) system for each salinity gradient. SW is seawater, ROC is reverse osmosis concentrate, and WW is wastewater treatment plant effluent.

In terms of capital cost, the ROC-WW system has the lowest unit cost (Figure 2.8) at $11,249 kW^{-1}$, and is the only system to have a positive net present value (Figure 2.6). This is primarily because an additional pretreatment system is not needed due to the high source water quality of ROC and WWTP effluent, as the presence of additional pretreatment significantly increases the cost for the other two scenarios. Note that this is contingent on the treatment quality of the WWTP plant and the desalination plant and may need to be amended after pilot scale testing with the source water. If the ROC-WW system were to include pretreatment, the unit cost would increase to $13,278 kW^{-1}$ and the net specific energy would decrease to 0.24 kWh m$^{-3}$ if microfiltration was used, and $14,831 kW^{-1}$ and 0.16 kWh m$^{-3}$ if ultrafiltration was used, with both systems having a payback period greater than 30 years.
Overall, the best-case scenario for implementing a PRO system in the Tampa Bay Seawater Desalination Plant is to use the membrane used in (Achilli et al., 2014) with a ROC-WW salinity gradient. This system has a power density of 16.7 $W m^{-2}$ of membrane, runs at an initial pressure difference of 29.8 $bar$ with a pressure loss of 0.4 $bar$, a net specific energy of 0.25 $kWh m^{-3}$ of mixed solution, and dilutes the salinity of the draw side (the ROC) from 66 ppt to 41 ppt. Since the salinity of the draw-side effluent is similar to seawater, it can either be disposed of in the ocean or reused as cooling water for nearby industrial processes that are already designed to use seawater. In addition, the final salinity of the feed water effluent is 2 ppt, with the increase being due to reverse salt transport. This stream can also be captured and reused, or it can be mixed with the draw-side effluent to further dilute it to 38 ppt. This system would have a total cost of $4.64 million and a payback period of 28 years. This assumes that a new transmission line is placed between the SCRWWTP and the TBSDP, minimal pretreatment is needed for both water sources, the TBSDP
operates 80% of the time, the interest rate remains at 3%, and that electricity prices remain fairly steady at $0.09 kW$ with a $0.003$ increase per kW per year.

In regard to the overall energy recovery rate of the RO system at the TBSDP, the RO system currently has a 57% permeate recovery rate, a 0.76:1 ROC to permeate ratio, and a specific energy consumption of $3.43 \text{ kWh m}^{-3}$ of permeate produced (SERO). Meanwhile, the PRO system has a 1.61:1 ROC effluent to influent ratio and a net specific energy production of $0.25 \text{ kWh m}^{-3}$ of mixed solution. Overall, this means that the PRO system could recover 9% of the energy used per m$^3$ of drinking water produced. This energy recovery percentage ($ERP \%$) was calculated as:

$$ERP = \frac{SE_{net} \left( \frac{Q_{D,eff}}{Q_{D,in}} \right) \left( \frac{Q_{ROC}}{Q_{Perm}} \right)}{SE_{RO}}$$  \hspace{1cm} (2.21)

where $Q_{ROC}$ is the ROC flow rate from the RO system, and $Q_{Perm}$ is the RO permeate flow rate. Assuming the PRO system is at full capacity, it could generate up to $0.41 \text{ MW}$ and can use $0.30 \text{ m}^3 s^{-1}$ (6.8 MGD) of ROC, which is 36% of the ROC produced when the desalination plant is running at full capacity. Note that in this case, the PRO system is limited by wastewater availability, since the TBSDP is larger than the SCRWWTP. If the SCRWWTP is expanded or an additional wastewater plant is constructed nearby, then assuming the WW is not reused elsewhere, the amount of ROC recovered for PRO could be increased.

Note that this analysis assumes that operational costs include regular membrane replacement every 5–7 years and assumes that no additional staff would be hired to run this system. Furthermore, the price per square meter of membrane surface ($5.80 \text{ m}^{-2}$) is lower than current market prices for RO membranes (approximately $12.23 \text{ m}^{-2}$ for an 8040 sized TFC membrane purchased in bulk) and is based on projected costs for membranes in the next few decades (Naghiloo et al., 2015). Variations in membrane performance due to membrane fouling, staffing
requirements, and potential pretreatment requirements to mitigate fouling may significantly increase the length of the payback period. If fouling is properly mitigated, the operational costs and requirements of this system should be minimal, which would also prevent the need to hire additional operators.

Furthermore, this projection assumes that the system is installed with a rotary pressure exchanger, which would feed the pressurized diluted brine solution back into the RO system to produce more permeate water. Depending on how local restrictions for water reuse are interpreted for PRO-based energy recovery systems (since treated effluent from a wastewater treatment plant would technically be used as a feed water source), this may not be an option. If the system is installed with a Hydro turbine instead of the pressure exchanger, this would increase the payback period to 33 years due to the higher inefficiency of the system. In addition, this system assumes that internal pressure loss can be minimized to 0.4 bar by using a 1:3 ellipse type spacer. Variations in channel height and spacer geometry will impact internal pressure loss, with internal pressure loss potentially being as high as 1.4 bar if a 2:1 ellipse type spacer is used.

The system would have an estimated unit cost of $10,085 \( kW^{-1} \) installed capacity. Using cost data updated to November 2018 (EIA, 2013), PRO can be compared to other renewable energy sources. Under this configuration, PRO is more expensive than most renewable energy sources, which is primarily due to the high cost of building a transmission line from the SCRWWTP to the TBSDP. However, assuming that the cost of transmission can be negated, this would bring the unit cost down to $2516 \( kW^{-1} \). Even if the membrane cost were at current market rates for RO membranes ($12.23 \( m^{-2} \)), the price of constructing this PRO system without having to factor in transmission costs would still be significantly lower, at $3310 \( kW^{-1} \). This is similar to the cost of on-shore wind ($2417 \( kW^{-1} \)) and conventional hydroelectric ($3207 \( kW^{-1} \)), and less than the cost
of solar ($4231–$5535 kW$^{-1}$), biomass ($4494–$8935 kW$^{-1}$), nuclear ($6041$ kW$^{-1}$), geothermal ($4765–$6820 kW$^{-1}$), and waste-to-energy ($9080$ kW$^{-1}$). Therefore, it can be surmised that an ideal location for constructing a test PRO system would be somewhere where a seawater RO plant is co-located with a wastewater treatment plant, such as in Santa Barbara, California.

2.5.3 Sensitivity and Uncertainty Analysis

The results of a global sensitivity analysis can be demonstrated using total effect Sobol indices, which indicate the contribution that each parameter has to the total variance, and includes all variance caused by its interactions, of any order, with any other input parameter. These indices are shown for each salinity gradient in Table 2.2 and are generated for the net present value. Overall, all three scenarios were sensitive to three of the membrane parameters, specifically the water permeability, salt permeability, and structural parameter ($A$, $B$, $S$), which makes sense since these values determine the overall gross specific energy. The ROC-SW scenarios were more sensitive to the draw and feed concentrations ($c_D$ and $c_F$) than the other two scenarios, which is most likely due to the wider range of potential salinity gradients available when mixing RO concentrate and seawater. Energy price ($EP$) was a sensitive parameter in the ROC-WW and SW-WW scenarios, but it did not have much of an impact on the ROC-SW's net present value. This is most likely due to the combined effect of having low specific energies and high pretreatment costs for most ROC-SW scenarios, resulting in very few of the 6720 ROC-SW scenarios having a positive net present value. Furthermore, the ROC-WW scenarios were highly sensitive to the transmission pipe length and diameter, which makes sense, since these values are responsible for a large portion of both the economic and energetic cost of implementing a PRO system.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>ROC-WW</th>
<th>ROC-SW</th>
<th>SW-WW</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>0.002</td>
<td>0.096</td>
<td>0.003</td>
</tr>
<tr>
<td>$D$</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>$S$</td>
<td>0.088</td>
<td>0.498</td>
<td>0.106</td>
</tr>
<tr>
<td>$B$</td>
<td>0.172</td>
<td>1.008</td>
<td>0.230</td>
</tr>
<tr>
<td>$A$</td>
<td>0.031</td>
<td>0.111</td>
<td>0.134</td>
</tr>
<tr>
<td>$\eta_{Gen}$</td>
<td>0.008</td>
<td>0.097</td>
<td>0.033</td>
</tr>
<tr>
<td>$z_1$</td>
<td>0.008</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$z_2$</td>
<td>0.000</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$L$</td>
<td>0.276</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$d$</td>
<td>0.317</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$Q$</td>
<td>0.108</td>
<td>0.118</td>
<td>0.086</td>
</tr>
<tr>
<td>$c_D$</td>
<td>0.016</td>
<td>0.255</td>
<td>0.087</td>
</tr>
<tr>
<td>$c_F$</td>
<td>0.000</td>
<td>0.296</td>
<td>0.000</td>
</tr>
<tr>
<td>$EP$</td>
<td>0.217</td>
<td>0.011</td>
<td>0.420</td>
</tr>
<tr>
<td>$\Delta EP$</td>
<td>0.005</td>
<td>0.000</td>
<td>0.009</td>
</tr>
<tr>
<td>$R$</td>
<td>0.046</td>
<td>0.004</td>
<td>0.081</td>
</tr>
<tr>
<td>$OT$</td>
<td>0.043</td>
<td>0.003</td>
<td>0.079</td>
</tr>
<tr>
<td>$Cms$</td>
<td>0.002</td>
<td>0.045</td>
<td>0.049</td>
</tr>
<tr>
<td>$T$</td>
<td>0.008</td>
<td>0.082</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Analysis conducted on the net present value of the system. Values listed as 0.000 had a negligible impact, while values listed as N/A had no impact. Color scaling is per column. Note that the name and range of variation for each coefficient can be found in Table D.1.

Figure 2.9 showcases the trials from the sensitivity and uncertainty analysis that had a positive net specific energy. In this figure, the trends identified in the individual membrane performance scenarios (Figure 2.6) continue to hold. While very few of the ROC-SW scenarios have a positive net present value, several of the ROC-WW scenarios and SW-WW scenarios under favorable geographic (low transmission distances) and economic (high energy prices) conditions have a positive net present value. Furthermore, there exists a slight positive correlation across all three scenarios between increasing the net specific energy of the membrane and the net present value, with an $R^2$ of 0.51. This figure also shows that scenarios that use a counter-current flow configuration tend to have higher net specific energy values, which in turn translates to higher net present values under favorable geographic and economic conditions.
2.6 Conclusions

In this study, a model called Propmod was developed to predict the capital costs, potential payback period and base operational capacity of a PRO energy recovery system. The intended purpose of Propmod is for regional water utility planners to investigate the feasibility of implementing PRO-based energy recovery and brine management technologies in their water systems.

From the results of the sensitivity analysis, it can be safely assumed that it is unlikely that a ROC-SW system could be viable, and this is simply due to the low energy densities of the system. A SW-WW system is more possible, as favorable scenarios do have a positive net specific energy.
and payback periods with an interquartile range of 14 to 23 years. Overall, it is better to focus efforts on developing ROC-WW systems, since their higher specific energies allow for higher levels of energy recovery, and they also have shorter payback periods in the interquartile range of payback periods, at 7 to 19 years. What this means is that for a ROC-WW system to be implemented, it is crucial to evaluate not only the membrane characteristics but also the local economic and geographic conditions. Furthermore, it was found that under favorable conditions, the unit cost of this system is similar to the cost of other renewable energy systems, which means that PRO could be a competitive technology for energy recovery in desalination applications assuming the system can be built and operated as projected.

The primary limitation of this model is that it does not incorporate the effect of membrane fouling. While it has been assumed that fouling can be mitigated using pre-treatment, it is impossible to remove 100% of potential fouling agents, which means that the membranes will eventually foul. Future work will involve improving chemical processes in Propmod in order to better determine whether pretreatment is necessary, and what form of pretreatment is required by incorporating raw water quality parameters such as pH, dissolved minerals, carbon substrate (for biofouling), nutrients, and dissolved oxygen. By adding a more comprehensive water quality analysis as well as the long-term effect of fouling, model predictions will be more realistic and better suited for predicting overall system costs and performance. It is hoped that the continued development of both Propmod and enhanced understanding of both PRO and foulant prevention processes will help kickstart the implementation of PRO around the world.
Chapter 3: Potential Locations for the Implementation of Pressure Retarded Osmosis

Systems in the United States

3.1 Abstract

Currently, a significant challenge with seawater desalination is reducing the energy consumption of the process and the potential environmental impacts from brine disposal. In this paper, we developed a Python-based process model that simulates how a pressure-retarded osmosis system could function in preexisting seawater desalination systems. The advantages and limitations of implementing this technology are discussed in detail, and comparisons involving cost and environmental impact are made with other energy generation and brine management technologies. Overall, it was found that PRO would be most effective implemented in areas where seawater desalination plants and wastewater treatment plants are co-located, such as Santa Barbara, California, where a PRO system would have a net specific energy of 0.23 kWh m\(^{-3}\) with a unit cost of $3,119 kW\(^{-1}\) assuming there are no external pretreatment costs. PRO is also viable in areas with high electricity purchase prices, such as St. Thomas in the Virgin Islands, where the net specific energy would be 0.15 kWh m\(^{-3}\) with a payback period of 7 years, which is similar to what is expected for renewable energy projects.

2 Chapter 3 has been previously published as:
3.2 Introduction

Reverse osmosis (RO) is a treatment process widely implemented in desalination and advanced water reclamation facilities. Currently, a significant challenge with RO is reducing the energy consumption and environmental impacts of the process (Elimelech and Phillip, 2011). Elevated levels of energy consumption cause RO product water to be much more expensive than other conventional water sources and can prevent implementation of this crucial technology in areas that are under severe water stress, such as in Cape Town, South Africa (Oliver, 2017) and Orange County, California (Wisckol, 2018). While RO uses less energy than alternative desalination processes such as multi-effect distillation (MED) and multi-stage flash (MSF) (Ettouney et al., 2002), it is still a significant energy consumer, using 2.4 to 8.5 kWh m$^{-3}$ of product water (Yip et al., 2016). Furthermore, RO is also the principal technology implemented in seawater desalination facilities in the United States (combined capacity of 128 million m$^{3}$ yr$^{-1}$; (DOE, 2017)). Environmental impacts from RO primarily come from the emissions associated with energy input, especially if the energy is provided by thermoelectric power plants (Bruggen and Vandecasteele, 2002). Another primary environmental concern comes from RO concentrate disposal (Elimelech and Phillip, 2011). Depending on the temperature, salinity, and chemical input, RO concentrate disposal can negatively affect the oxygen content of the receiving water due to its salt content, and some RO discharge additionally contains biocides and anti-scaling additives (Sagle and Freeman, 2004).

These issues need to be addressed to make desalination a more effective technology for water strained regions. One option is to utilize the high osmotic pressure difference that exists when a highly concentrated solution, such as brine/RO concentrate (ROC), is placed on the opposite side of a semipermeable membrane from a solution with a low concentration of solutes,
such as freshwater or wastewater treatment plant (WWTP) effluent. This concentration difference creates an osmotic pressure, which causes water to flow through the membrane to alleviate this pressure. If an external hydraulic pressure is applied to the concentrated side that is lower than the osmotic pressure, then this will result in an excess of diluted and pressurized concentrate. This excess can then be divided into two streams and used for both power generation in a hydropower turbine and for pressurizing incoming concentrate using an in-line pressure exchanger (Skilhagen, 2010). This technology is known as pressure retarded osmosis (PRO) and offers a potential solution to the issues of high energy consumption and brine management in desalination that is non-intermittent, completely renewable, and carbon-free (Altaee et al., 2016; Altaee and Sharif, 2015; Saito et al., 2012). An illustration of how PRO varies from other osmotic processes can be seen in Figure 3.1.

Figure 3.1 Schematic representation of osmotic processes, where $p$ is hydraulic pressure, and $\pi$ is osmotic pressure.
However, PRO-based energy recovery does have its challenges, as energy is needed to transport and pretreat the solutions, as well as to backwash the system to mitigate membrane fouling. This necessitates a careful balance of energy expenditures and generation potential to maximize net energy recovery. In general, two source streams need to be paired to create a concentration gradient for osmotic power to be successfully generated: a feed solution (low concentration), and a draw solution (high concentration). For example, if freshwater (FW) is paired with salt water, then the theoretical maximum specific energy (SE) can be as high as $0.34 \text{ kWh m}^{-3}$ of mixed solution given a concentration gradient of 35 ppt of salt on the saline side and 0.001 ppt of salt on the freshwater side (Lin et al., 2014a). However, this is under an ideal situation and neglects practical conditions, such as membrane and hydraulic inefficiencies, variable mixing ratios, turbine inefficiencies, and pretreatment requirements for draw and feed solutions, which can drop this density substantially (Sarp et al., 2016). Consequently, it can be surmised that a higher salinity difference is needed to make the process feasible. This energy density can be increased by using a higher concentration gradient, such as that found between brine/RO concentrate (ROC) and tertiary WWTP effluent (WW) (Helfer and Lemckert, 2015). As the concentration gradient increases, so too does the theoretical maximum specific energy (Table 3.1).

<table>
<thead>
<tr>
<th>Draw Concentration ($M$)</th>
<th>Feed Concentration ($M$)</th>
<th>Salinity Gradient (Draw/Feed)</th>
<th>Maximum Theoretical Specific Energy ($kWh m^{-3}$ of mixed solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.015</td>
<td>SW/RW</td>
<td>0.256</td>
</tr>
<tr>
<td>1.2</td>
<td>0.015</td>
<td>ROC/WW</td>
<td>0.551</td>
</tr>
<tr>
<td>5.7</td>
<td>1.2</td>
<td>Dead Sea/ROC</td>
<td>1.110</td>
</tr>
<tr>
<td>4.6</td>
<td>0.015</td>
<td>Great Salt Lake/RW</td>
<td>2.260</td>
</tr>
</tbody>
</table>

*RW stands for river water, SW stands for saltwater, ROC stands for RO concentrate, WW stands for wastewater effluent. Values from (Lin et al., 2014a)

Aside from some localized high-salinity water bodies (the Dead Sea, the Great Salt Lake), the most common high-salinity gradient can be realized by combining ROC and wastewater effluent. Because of this, PRO is of significance in energy recovery and RO concentrate
management, with potential power densities (W) reportedly as high as 21.3 $W \, m^{-2}$ of membrane surface (Song et al., 2013). An illustration as to how a PRO system could be tied into an RO system can be seen in Figure 3.2. When ROC with a salinity of 77 ppt is paired with freshwater, the theoretical maximum specific energy increases to approximately 0.7 $kWh \, m^{-3}$ of mixed solution. This can make the process feasible as long as the overall treatment process technologies, including membrane type, pretreatment technique, and turbine selection are optimized to maximize net energy generation (Sarp et al., 2016). In addition, it also important to account for the main environmental impacts of the PRO process, which comes from the brine release, and the manufacturing and disposal stages for the PRO system components.

Figure 3.2  General process diagram for an RO/PRO system. The RO concentrate from the RO process first passes through a pressure exchanger to maintain system pressure for the RO system, which is typically on the order of 50 - 60 bar before then passing through an additional pressure exchanger and booster pump to get up to PRO system pressure, which would be around 15 - 20 bar. The draw solution then passes through the PRO membrane, where additional fluid enters from the feed side to also become pressurized before passing through both the turbine and the PRO pressure exchanger.
PRO is currently in its pilot phase, with several experimental plants throughout the world (Song et al. 2013). In this paper, we will discuss three existing investigations into how PRO has been implemented on a pilot scale, and then delve into three case studies that illustrate how PRO-based concentrate management and energy recovery technologies could be implemented for saltwater desalination plants in Florida, the U.S. Virgin Islands, and California.

3.2.1 Pre-existing PRO Plants

The first pilot PRO plant was the Statkraft plant in Tofte, Norway (Skilhagen, 2010). The plant was built in 2009 and used river water as a feed solution and saltwater as the draw solution. The hydraulic pressure was 12.5 bar, and a spiral wound membrane developed by Hydronautics was used starting in 2011. The plant was operated until it closed in 2013, primarily due to high operational costs that would make the power generated from a full-scale plant uncompetitive in the European power market. These high costs stemmed from pretreatment costs, low extractable work values, and inefficiencies in the hydraulic power generation system (Sarp et al., 2016; Yip et al., 2016). Projects that pair ROC with wastewater have been more successful, such as the Mega-ton Water System project in Japan, and the GMVP in South Korea. Both projects are currently in the pilot phase, with plans for eventual full-scale implementation (Kurihara et al., 2016; Kurihara and Hanakawa, 2013).

3.3 Model Description and Methods

Using the Python-based framework called Propmod that was developed in Chapter 2, PRO systems were simulated for three pre-existing saltwater desalination plants located across the United States. These plants were chosen to illustrate the variety of potential conditions where a PRO system could be implemented. How Propmod works is that it includes a sequence of modules to calculate membrane processes, feed water requirements, energy generation potential, and costs
To begin, Propmod first calculates the membrane flow fields. Once the flow fields are solved, then the membrane system is sized and priced. Next, the energy consumption and additional cost of transmission and pretreatment systems are added in if needed, and the net specific energy is calculated. If the net specific energy is greater than 0, then the power, total cost, unit cost ($ k\text{W}^{-1}$ of installed capacity), payback period, and net present value are calculated, and $\text{SysCon2}$ is set to 1 to represent a system with a net positive specific energy. If the net specific energy is less than or equal to zero, then $\text{SysCon2}$ is set to 0. This represents a system with a net negative specific energy, which means that that configuration would not be energetically feasible.

In these case studies, pretreatment energy expenditure will not be calculated, as it assumed that the quality of both source water streams is high enough where additional treatment is not needed. Note that this is contingent on the treatment quality of the WWTP plant and the desalination plant, and so may need to be amended after pilot-scale testing with the source water. Furthermore, the membrane that is used for these calculations is based on the one in (Achilli et al., 2014), which was chosen for its high performance in the areas of power density and permeate flow.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Input Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbine Efficiency*</td>
<td>$\eta_{\text{Turb}}$</td>
<td>85</td>
<td>%</td>
</tr>
<tr>
<td>Interest Rate</td>
<td>$R$</td>
<td>3</td>
<td>%</td>
</tr>
<tr>
<td>Cost per $m^2$ of Membrane</td>
<td>$C_{\text{ms}}$</td>
<td>12.23</td>
<td>$\text{$ m}^{-2}$</td>
</tr>
<tr>
<td>Mass Transfer Coefficient</td>
<td>$k$</td>
<td>99</td>
<td>$L \text{ m}^{-2} \text{ h}^{-1}$</td>
</tr>
<tr>
<td>Diffusion Coefficient</td>
<td>$D$</td>
<td>5.328E-6</td>
<td>$m^{-2} \text{ h}^{-1}$</td>
</tr>
<tr>
<td>Structural Parameter</td>
<td>$S$</td>
<td>310</td>
<td>$\text{Mm}$</td>
</tr>
<tr>
<td>Salt Permeability</td>
<td>$B$</td>
<td>0.09</td>
<td>$L \text{ m}^{-2} \text{ h}^{-1}$</td>
</tr>
<tr>
<td>Water Permeability</td>
<td>$A$</td>
<td>5.11</td>
<td>$L \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$</td>
</tr>
</tbody>
</table>

*Efficiency is 85% for a Pelton turbine.
Figure 3.3 Solution algorithm for Propmod. The presence of both transmission and pretreatment affects the overall net specific energy. SysCon2 is a variable that indicates whether a scenario has a net positive specific energy. If the net specific energy is less than 0, then placeholder values are used for values that require a positive net specific energy to calculate.

3.3.1 Tampa Bay Seawater Desalination Plant

The Tampa Bay Seawater Desalination Plant (TBSDP) is in Tampa, Florida, and is one of the largest desalination plants in the United States, providing up to 25 MGD (million gallons per day) ($1.10 \ m^3 \ s^{-1}$) of desalinated water to the region. The plant is essential during the dry season and ensures that the Tampa Bay area has a robust and continuous water supply. The plant began construction in 1997, and due to mismanagement and complications with the design, did not begin operation until 2007. The system is located next to the TECO (Tampa Electric Company) Big Bend Power Station, which captures 1.4 billion gallons a day of seawater for cooling purposes. The TBSDP then captures up to 44 MGD ($1.93 \ m^3 \ s^{-1}$) of that warm seawater when it exits the
power plant and treats the water through a five-stage treatment scheme consisting of coagulation, flocculation, sand filtration, dichotomous earth filtration, and cartridge filtration. The water then enters a RO treatment scheme which consists of a first pass and a partial second pass through the RO membranes. Finally, the effluent water is then stabilized before it is distributed to the Tampa Bay area. This process produces high-quality water that meets or exceeds all state and federal drinking water standards. When running at full capacity, the plant requires 11.67 MW of power to operate. On average, the plant consumes 3.43 kWh m$^3$ of product water, which ends up costing the plant 0.79 $\$ m^{-3}$ to produce the desalinated water. For context, in the Tampa Bay area, this production cost is 5 times as expensive as surface water and 10 times as expensive as groundwater. The wholesale water rate for Tampa Bay Water is $0.68 m^{-3}$ (Water, 2019) which is reflective of the mixed supply (desalinated water, surface water, and groundwater) that Tampa Bay water provides to its regional members. As for the rate to the customer, that varies per municipality. For example, in the City of Tampa, the residential water rate ranges from $0.76 m^{-3}$ to $2.85 m^{-3}$ depending on location within the city and water consumption (Tampa, 2019). The wastewater effluent would be transported from the nearby Howard F. Current Advanced Wastewater Treatment Plant (Figure 3.4), which currently releases 52 MGD (2.29 m$^3$ s$^{-1}$) into the Hillsborough Bay. The model inputs for the Tampa case can be seen in Table 3.3.
Figure 3.4 The distance between the Howard F. Curren Wastewater Treatment Plant (top) and the Tampa Bay Desalination Plant (bottom). It is assumed that the transmission pipe would be placed underneath the dotted pink line, and so the calculated transmission distance also includes five 90° turns and six 45° turns.

Table 3.3 Tampa case study model inputs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Input Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>WWTP Elevation</td>
<td>$z_1$</td>
<td>2.7</td>
<td>M</td>
</tr>
<tr>
<td>Desalination Plant Elevation</td>
<td>$z_2$</td>
<td>3.1</td>
<td>M</td>
</tr>
<tr>
<td>Transmission Pipe Length</td>
<td>$L$</td>
<td>23,500</td>
<td>M</td>
</tr>
<tr>
<td>Transmission Pipe Diameter</td>
<td>$d$</td>
<td>0.76</td>
<td>M</td>
</tr>
<tr>
<td>Draw Flow Rate</td>
<td>$Q$</td>
<td>0.83</td>
<td>$m^3 s^{-1}$</td>
</tr>
<tr>
<td>Draw Concentration</td>
<td>$c_D$</td>
<td>66</td>
<td>g kg$^{-1}$ [ppt]</td>
</tr>
<tr>
<td>Feed Concentration</td>
<td>$c_F$</td>
<td>0.04</td>
<td>g kg$^{-1}$ [ppt]</td>
</tr>
<tr>
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<td>$EP$</td>
<td>0.09</td>
<td>$$/kWh$^{-1}$</td>
</tr>
<tr>
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<td>% yr$^{-1}$</td>
</tr>
<tr>
<td>Water Temperature</td>
<td>$T$</td>
<td>27</td>
<td>°C</td>
</tr>
</tbody>
</table>
3.3.2 St. Thomas Seawater Desalination Plant

The St. Thomas Seawater Desalination Plant, also known as the Randolph E. Harley Seawater Desalination Plant, is located on St. Thomas, which is part of the U.S. Virgin Islands. The plant provides up to 3.3 MGD and is the primary water supply for a large part of the island, with the remaining supply provided by rainwater harvesting. The plant was originally constructed as a solar thermal desalination plant in 1992 but was retrofitted in 2013 by Seven Seas Water to become a reverse osmosis-based desalination plant. The system is located next to the Randolph E. Harley Power Station, which is the primary power plant for St. Thomas and relies on fuel oil. The plant operates at a 40% recovery ratio and generates up to 4 MGD of brine. The plant captures water from the nearby bay, and treats the water using a three-stage treatment train consisting of multi-media filtration, cartridge filtration, and reverse osmosis. After passing through the RO train, the water is post-treated and then distributed to both the natural gas plant to be used as boiler water, as well as to the lower elevation regions of St. Thomas. This treatment process uses 2.64–3.17 kWh m\(^{-3}\) (10–12 kWh/1000 gals) and is split into three individual trains that can each process 1.1 MGD. Currently, the plant disposes of its brine on the other side of the peninsula where the plant is located. If implemented with PRO, the nearest wastewater plant is the Red Point Wastewater Treatment Plant, which is located 2.6 km away by car (Figure 3.5). The Red Point wastewater plant was originally a treatment lagoon that was retrofitted by Veolia in 2004. Currently, the plant treats an average of 4 MGD, although it can treat up to 12 MGD. The model inputs for the St. Thomas case study can be seen in Table 3.4.
Figure 3.5 The distance between the Red Point Wastewater Plant (left) and the Randolph E. Harley Desalination Plant (right). It is assumed that the transmission pipe would be placed underneath the pink line and would include eight 90° turns and eight 45° turns.

Table 3.4 St. Thomas case study model inputs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Input Value</th>
<th>Unit</th>
</tr>
</thead>
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<tr>
<td>WWTP Elevation</td>
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<td>M</td>
</tr>
<tr>
<td>Desalination Plant Elevation*</td>
<td>$z_2$</td>
<td>59.7</td>
<td>M</td>
</tr>
<tr>
<td>Transmission Pipe Length</td>
<td>$L$</td>
<td>2600</td>
<td>M</td>
</tr>
<tr>
<td>Transmission Pipe Diameter</td>
<td>$d$</td>
<td>0.46</td>
<td>M</td>
</tr>
<tr>
<td>Draw Flow Rate</td>
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<td>m³ s⁻¹</td>
</tr>
<tr>
<td>Draw Concentration</td>
<td>$c_D$</td>
<td>59</td>
<td>g kg⁻¹ [ppt]</td>
</tr>
<tr>
<td>Feed Concentration</td>
<td>$c_F$</td>
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<td>g kg⁻¹ [ppt]</td>
</tr>
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<td>Energy Purchase Price</td>
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<td>$T$</td>
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<td>°C</td>
</tr>
</tbody>
</table>

Note: *The actual elevation of the Randolph E. Harley Desalination plant is 11 m. However, due to the hilly terrain of the Virgin Islands, the pipe would have to cross a hill to get to the plant, which is why the elevation of the hill (59.7 m) is used.
3.3.3 Santa Barbara Seawater Desalination Plant

The Santa Barbara Seawater Desalination Plant, also known as the Charles Meyer Seawater Desalination Plant, was originally constructed to augment the water supply of Santa Barbara, California in 1991 due to an ongoing drought. The plant was decommissioned after the drought due to its high operational costs and laid in standby mode until 2015 when the plant was reactivated at a cost of $71 million to help combat the California drought. Currently, the plant is responsible for 30% of Santa Barbara’s water supply, and produces 3 $MGD$ on average, with the potential to produce up to 10 $MGD$. The plant operates at a 50% recovery ratio and consequently, also produces 3–10 $MGD$ of brine. The plant captures water from an intake located 2500 feet offshore, where the water then enters a copper intake screen at a velocity of fewer than 0.5 $ft \ s^{-1}$ to prevent sea life from entering. The plant then uses a 3-stage treatment process, which consists of sand and gravel filtration followed by reverse osmosis, with a post-treatment re-mineralization stage. The brine from the plant is then mixed with the wastewater effluent from the nearby El Estero Wastewater Treatment plant and is discharged to the ocean at a point located 1.5 miles offshore (Figure 3.6). The El Estero plant treats anywhere from 8.92–4.25 $MGD$ of wastewater, with an average daily flow of 7.73 $MGD$. The model inputs for the Santa Barbara case study can be seen in Table 3.5.
Figure 3.6 The distance between the Charles Meyer Desalination Plant (top) and the El Estero Wastewater Treatment Plant (bottom). The pink line shows the existing connection.

Table 3.5  Santa Barbara case study model inputs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Input Value</th>
<th>Unit</th>
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<tr>
<td>Desalination Plant Elevation</td>
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<td>3.6</td>
<td>M</td>
</tr>
<tr>
<td>Transmission Pipe Length*</td>
<td>L</td>
<td>-</td>
<td>M</td>
</tr>
<tr>
<td>Transmission Pipe Diameter*</td>
<td>d</td>
<td>-</td>
<td>M</td>
</tr>
<tr>
<td>Draw Flow Rate</td>
<td>Q</td>
<td>0.13</td>
<td>m³ s⁻¹</td>
</tr>
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<td>Draw Concentration</td>
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<td>g kg⁻¹ [ppt]</td>
</tr>
<tr>
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<td>$ kWh⁻¹</td>
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<tr>
<td>Water Temperature</td>
<td>T</td>
<td>15</td>
<td>°C</td>
</tr>
</tbody>
</table>

*Note: Due to the preexisting connection and short transmission length, the energy and construction costs of transporting the brine to the wastewater plant will not be included.
3.4 Case Study Results and Comparison

Overall, in terms of net specific energy, all three scenarios had similar gross specific energies, at 0.26 \( \text{kWh m}^{-3} \) – 0.29 \( \text{kWh m}^{-3} \). However, when the additional energy losses from transmission and inefficiencies are subtracted, then the net specific energies decrease, as shown in Figure 3.7. The Santa Barbara case ends up having the highest net specific energy, since the desalination plant is co-located with the wastewater plant, which removes the energetic cost of transmission. In terms of percent energy recovered per m\(^3\) of drinking water permeate, the Tampa PRO plant would be the least efficient, only recovering 6%, which is due to the high recovery rate (57%) and transmission energy use at the Tampa plant. The St. Thomas and Santa Barbara plants could both recover 11% of the energy used for desalination, which is due to the lower recovery rate at St Thomas (40%) and the higher specific energy of the PRO stream in Santa Barbara.

![Figure 3.7 Net and gross levels of energy generation and consumption for the three case studies. Note that pretreatment was not considered in this study, and so none of the plants have losses stemming from pretreatment.](image)

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In terms of capital cost, the Tampa plant has the highest overall construction cost, at $20.1 million. This makes sense, given that the plant has the largest amount of brine flow, at 0.83 m$^3$s$^{-1}$. The next most expensive plant was the St. Thomas plant, at $2.52$ million, and the least expensive plant is the Santa Barbara plant, at $0.52$ million. Even in terms of unit cost (Figure 3.8), the Santa Barbara plant is the least expensive due to the cost savings stemming from the preexisting transmission line. The unit cost of installing PRO at the Santa Barbara plant is $3119.25$ per $kW$. Using cost data updated to November 2018 from (U.S. EIA, 2013), PRO can be compared to other renewable energy sources. Under this configuration, PRO is similar to the cost of on-shore wind ($2,417$ per $kW$) and conventional hydroelectric ($3,207$ per $kW$), and less than the cost of solar ($4,231$-$5,535$ per $kW$), biomass ($4,494$-$8,935$ per $kW$), nuclear ($6,041$ per $kW$), geothermal ($4,765$-$6,820$ per $kW$), and waste-to-energy ($9,080$ per $kW$). Furthermore, PRO also has the additional advantage of being non-intermittent, as it can recover energy whenever pressurized brine/ROC and wastewater effluent are generated.

Figure 3.8  Unit capital cost breakdown for each system. Note that since pretreatment was not considered, none of the systems had pretreatment costs included.
Over a 30-year period, the amount of energy cost savings produced by the plant in St. Thomas is the highest (Figure 3.9). This is primarily due to the high cost of electricity in St. Thomas, which is over 3x greater than the rates in Tampa and Santa Barbara. Because of this, purely from a cost savings perspective, the St. Thomas plant will generate the greatest amount of cost savings to the user over time. It can also be seen that the Tampa Bay plant will not have net positive savings over this period, and so it is not advised to implement PRO in Tampa using the wastewater effluent from the Howard F. Curren Wastewater Plant unless the underlying economic and mechanical factors change. In comparison, the St. Thomas plant has a payback period of 7 years, while the Santa Barbara plant has a payback period of 6 years, both of which are typical for renewable energy projects.

![Figure 3.9 Unit cost and savings for each potential PRO system.](image)

Overall, all three plants are net energy producers and dilute the concentrate, with effluent concentrations of 36.4 $ppt$ for the St Thomas case, 39.6 $ppt$ for the Tampa case, and 43.0 $ppt$ for the Santa Barbara case. If pretreatment were included on the feed side, it would decrease the net
specific energy available and increase the capital and operational costs. The impact of including both microfiltration and ultrafiltration as a pretreatment mechanism on unit cost and net specific energy for St. Thomas and Santa Barbara can be seen in Figures 3.10 and 3.11. Note that Tampa was not included in this analysis since it was already shown to not be economically feasible. Pretreatment energy consumption data were sourced from (EPRI, 2013), and unit cost data were sourced from (AWWA, 2008).

![Figure 3.10](image)

Figure 3.10  Net and gross levels of energy generation and consumption for the Santa Barbara (SB) and St. Thomas (ST) cases without pretreatment, and with microfiltration and ultrafiltration pretreatment on the feed side.

If the Santa Barbara system were to include pretreatment, the net specific energy would decrease from 0.23 \( kWh \ m^{-3} \) to 0.22 \( kWh \ m^{-3} \), the unit cost would increase from $3,119 \( kW^{-1} \) to $6,478 \( kW^{-1} \), and the payback period (which is essentially the break-even point between CAPEX, OPEX, and energy savings) would increase from 6 years to 14 years if microfiltration was used, and the values would change to 0.14 \( kWh \ m^{-3} \), $12,233 \( kW^{-1} \), and greater than 30 years if
ultrafiltration was used. If the St. Thomas system were to include pretreatment, the net specific energy would decrease from 0.16 to 0.15 $kWh \ m^{-3}$, the unit cost would increase from $12,534 \ kW^{-1}$ to $18,186 \ kW^{-1}$, and the payback period would increase from 7 years to 11 years if microfiltration was used, and the values would change to 0.07 $kWh \ m^{-3}$, $43,477 \ kW^{-1}$, and greater than 30 years if ultrafiltration was used.

One way to increase the viability of all three systems would be to use renewable energy credits, which are a financial instrument that allow power provider to transfer the “renewable” aspects of their power to the purchaser of the credits. These credits are typically allocated per $MWh$ of electricity generated, and are valued at prices ranging from $18 to $230 depending on the market and quantity requested (Partnership, 2018; PJM, 2021). These credits allow people who have

Figure 3.11  Unit capital cost breakdown for the Santa Barbara (SB) and St. Thomas (ST) cases without pretreatment, and with microfiltration and ultrafiltration pretreatment on the feed side.

One way to increase the viability of all three systems would be to use renewable energy credits, which are a financial instrument that allow power provider to transfer the “renewable” aspects of their power to the purchaser of the credits. These credits are typically allocated per $MWh$ of electricity generated, and are valued at prices ranging from $18 to $230 depending on the market and quantity requested (Partnership, 2018; PJM, 2021). These credits allow people who have
operations in areas where renewable energy is not available to still reduce their carbon footprints by financing the production of renewable energy in an area where it is more available.

To bring the payback period for the Tampa system down to 30 years, a credit valued at a minimum of $103 per $MWh would need to be used. This same credit, when applied to the St. Thomas and Santa Barbara systems would in turn decrease the payback periods to 5 years and 3 years respectively. In addition, if this $103 per $MWh credit were to be applied to the systems with ultrafiltration - which were both found to have a payback period of greater than 30 years initially - it would bring the payback periods down to 22 years for the St. Thomas system and 9 years for the Santa Barbara system. These potential reductions in payback period demonstrate the impact that external financial interventions can have when implementing emerging technologies such as PRO.

Currently, the primary limitation of this study is that the impact of membrane fouling and variations in operational performance efficiency are not included, which could be significant depending on the influent water quality for both the brine and the wastewater effluent streams. Future efforts in PRO research should focus on bench and pilot-scale testing using brine and wastewater effluent samples from the St. Thomas and Santa Barbara plants to determine each system’s resistance to corrosion and fouling. If it is found that these systems can be operated without extensive pretreatment, then these estimates should be accurate. If so, this would mean that the plants could implement PRO, which is a concentrate management and energy recovery technology that is non-intermittent, carbon-free, and, when applied correctly, at a price point similar to other forms of renewable energy.
Chapter 4: Optimizing Pressure Retarded Osmosis Spacer Geometries: An Experimental and CFD Modeling Study

4.1 Abstract

Existing desalination plants face the challenges of high energy costs and environmental impacts from brine disposal. Pressure retarded osmosis (PRO) is a membrane-based technology that could mitigate these issues by capturing the potential energy in the salinity gradient between brine and dilute (e.g., freshwater/wastewater) solutions. Currently, a major challenge facing PRO is concentration polarization (CP), which is the reduction of the salinity gradient caused by the buildup of solutes along both the brine side of the membrane surface (external) and within the membrane support structure (internal). CP can be reduced using membrane spacers, but they have the drawback of increasing the pressure drop along the length of the feed channel. Therefore, it is important to design a membrane spacer that can minimize the effects of both CP and the internal pressure drop.

In this study, we simulated the effect that membrane spacer geometries have on CP and the internal pressure drop via computational fluid dynamics (CFD) using the open-source software, OpenFOAM. Simulations were validated using experimental results for five physical spacer geometries on a bench-scale PRO system. The highest performing physical spacer geometry was a 47 mil (1.41 mm) thick parallel oriented spacer (47P), which was then improved upon through integrated CFD-based optimization using the open-source optimization toolkit, DAKOTA. Single-objective genetic algorithms were used to iteratively modify the spacer geometry by increasing the linearity of the thinner cross-strand and decreasing the linearity of the thicker parallel strand, which
created a more hexagonally shaped cross-section. This modification was able to increase overall system performance, which was represented by the ratio of the mass flux density of the feed permeate through the membrane to the pressure drop across the length of the feed channel, by 16.3%. This suggests that a membrane spacer with a parallel hexagonal configuration allows the fluid to flow with minimal internal pressure drop while still creating the necessary back-mixing from the membrane surface to the bulk fluid needed to promote mass transfer and reduce the impacts of CP. Implementing these improvements in spacer design would cause the feed pump to consume less energy, which would increase the net energy generation potential and overall sustainability of PRO systems.

4.2 Introduction

Pressure retarded osmosis (PRO) is an emerging technology that can convert the Gibbs free energy that exists in the salinity gradient between different water streams into usable hydraulic pressure. In this process, a dilute (feed) solution is separated from a pressurized highly concentrated (draw) solution using a semi-permeable membrane supported by a spacer matrix. This creates an osmotic gradient across the membrane, which causes the feed solution to permeate into the draw solution and creates an excess of pressurized concentrate that can then be diverted to a hydro turbine to create electricity. Previous studies have focused on identifying where this technology can be applied, with investigations in the areas of power generation using different water pairs such as river water and seawater (Skilhagen et al., 2008; Skilhagen, 2010), saltwater and desalination brine (Benjamin et al., 2020), and treated wastewater effluent and seawater desalination brine (Saito et al., 2012; Sakai et al., 2016). While the first two water pairs suffer from low energy densities, using wastewater treatment plant effluent and seawater desalination brine has been shown to have the most promise as long as the plants are co-located, as this pairing creates
the high salinity gradient needed for the process to work effectively with minimal energy losses (Benjamin et al., 2020). In addition, seawater desalination has issues stemming from high energy consumption and the creation of a concentrated brine waste stream (Elimelech and Phillip, 2011), both of which can be mitigated by PRO.

Two of the main issues that PRO faces are concentration polarization (CP) and an internal pressure drop that occurs across the length of the membrane channel (Bogler et al., 2017; Thelin et al., 2013; Yip and Elimelech, 2013). CP is caused by an increasing gradient of solutes towards the membrane surface that reduces the overall concentration gradient; this is a transport phenomenon and while it cannot be eliminated, it can be suppressed by promoting back-mixing from the membrane surface to the bulk of the fluid (F Li et al., 2002). Similarly, the pressure drop across the length of the membrane channel is caused by hydraulic resistance from both the membrane and the spacer matrix (Guillen and Hoek, 2009). The purpose of the spacer matrix is not only to separate different membrane layers but also to enhance mass transfer by reducing the extent of CP and promoting the formation of flow instabilities such as vortices and streamline distortions that can decrease the tendency for fouling to occur (Feron, 1991; Fimbres-Weihs and Wiley, 2007; Schwinge et al., 2003; Zhou et al., 2006). Therefore, the selection of a proper spacer geometry is crucial towards addressing the issues of CP and the internal pressure drop (Xie et al., 2019), as it is critical to understand the impacts that variations in spacer geometry can have on overall system performance. Prior studies on membrane spacer geometry have focused on designing new spacers that can increase mass transfer or reduce the internal pressure drop. However, these spacers usually improve flux and mitigate CP by increasing energy consumption (Fárková, 1991; F. Li et al., 2002; Li et al., 2005; Schock and Miquel, 1987; Subramani et al.,
2006), which is a product of insufficient knowledge regarding the complex internal hydraulic processes found in a membrane system.

Computational fluid dynamics (CFD) has been increasingly used in simulating membrane-based processes, as it can represent complex flow features in multiple dimensions at fine spatial resolutions (Schwinge et al., 2000). While there are several examples of CFD models for reverse osmosis in both 2D (Ahmad and Lau, 2006; Ma et al., 2004; Ma and Song, 2006; Schwinge et al., 2000; Subramani et al., 2006) and 3D (Iwatsu et al., 1989; Karode and Kumar, 2001; Kim et al., 1987; Li et al., 2005), there have only been a few studies describing the unique flow mechanics found in a PRO system (Aschmoneit and Hélix-Nielsen, 2021; Hayashi and Okumura, 2016; Wang et al., 2016). Previous PRO CFD studies have focused on modeling the effects of concentration polarization in hollow fiber modules (Hayashi and Okumura, 2016), comparing a semi-analytical model to a 2D CFD model (Wang et al., 2016), and creating a novel helically shaped geometry designed specifically for PRO (Aschmoneit and Hélix-Nielsen, 2021). However, none of the existing CFD models of PRO have been compared against physical experimental results, which is a crucial step in ensuring a model’s validity. In addition, there has not been a CFD study on understanding the influence that spacer geometry has on increasing mass transfer and reducing the internal pressure drop in PRO applications, or how optimization can be used to improve existing spacer designs.

Optimization is a useful tool for improving spacer designs and has been applied successfully for enhancing reverse osmosis (RO) spacer geometry (Haidari et al., 2018; F. Li et al., 2002; F Li et al., 2002). One such optimization method is the single-objective genetic algorithm (SOGA), which is a heuristic optimization algorithm based on principles found in genetics and natural selection (Ragsdale, 2011). This method allows for a guided optimization approach and is
especially useful for multivariate problems that would be computationally expensive to solve using other methods (Koch, 2015). While previous studies have used this approach for simplified 2D forward osmosis geometries (Koch, 2015), there is no study we know of that has used this optimization approach to improve the design of 3D PRO spacer geometries.

Therefore, to simulate and predict what effect feed spacer configurations have on PRO system performance, we developed a 3D CFD-based membrane model. This membrane-scale model resolves the local and transient conditions on the feed side of a PRO membrane for the feed permeate flow, the impact of spacer geometry on internal pressure drop, and the solute concentration. The model was used to simulate an 18.72 mm by 9.72 mm membrane section, and it was validated with a bench-scale PRO system using five physical membrane spacer geometries. The highest performing spacer geometry was then iteratively improved upon by using a SOGA, with an overall objective of determining what geometric guidelines should be followed to create membrane spacers that improve the overall hydraulic performance of PRO systems.

4.3 Materials and Methods

4.3.1 Experimental Description

4.3.1.1 Experimental Setup

Physical experiments were conducted on a custom-made bench-scale PRO unit (Figure 4.1) using FTSH2O flat sheet Cellulose Triacetate (CTA) membranes provided by Sterlitech. The membranes were 42.0 cm² in total area, with 33.6 cm² of that being actively exposed to the fluid. They were mounted with the active side facing the draw solution inside of a Sterlitech CF042D-FO membrane cell. The feed side of the membrane cell contained a 316 stainless steel pressure support plate and a membrane spacer, with the spacer geometry varied per trial. The draw solution was stored in a 5-gallon 316 stainless steel reservoir, while the feed solution was stored in a 7-
gallon polypropylene reservoir. The feed reservoir was placed on an Ohaus R71MD60 electrical balance. This balance has a maximum capacity of 60 kg with a resolution of 1 g and was used to measure the mass transfer of the feed water across the membrane. Each tank was instrumented with conductivity probes, with the feed tank having a Sensorex CS8300TC probe and the draw tank having a Sensorex TCS3020 probe. Both tanks were connected to a Polyscience MM71 chiller to maintain a constant temperature. A Cole-Parmer Masterflex gear pump was used to move the feed solution, while a Hydracell M-03S pump controlled by a Nidec M200 Unidrive variable frequency drive (VFD) was used for the draw solution. To prevent electromagnetic interference, the VFD was encased in a steel box and both the 3-phase power cable between the VFD and the motor and the conductivity sensor cables were wrapped in aluminum foil. Seametrics SPX flow meters were placed on each outlet of the membrane chamber to measure the flow rate. Turck pressure transducers were placed on each side of the membrane chamber to measure the hydraulic pressure difference, with a pressure relief valve and a bypass system placed on the draw inlet side as a safety measure. The instruments (excluding the scale) were connected to a breadboard with an EVO-In-Motion MEGO 24V power supply and fed into a Velocio Branch programmable logic controller (PLC). The PLC and the scale were then connected to a Lenovo ThinkPad X220 laptop, which recorded data every 15 seconds. Data were automatically backed up onto a cloud-based storage system (Box) to prevent data loss. The system was mounted on a steel cart to allow for portability and was designed so that the heavy equipment (water tanks, chiller, high-pressure pump) was mounted on the bottom level, while the more sensitive equipment (membrane, PLC, low-pressure pump, laptop) was on the top level.
Figure 4.1  Diagram of the laboratory-scale Pressure Retarded Osmosis (PRO) system. The letter C represents the conductivity meters, which are located inside of the draw and feed tanks. A version of this figure that includes a picture of the physical setup is included in Appendix E.1.

4.3.1.2 Experimental Procedure

Each experiment was conducted by following a modified version of the FO characterization procedure developed by Tiraferri et al. (Tiraferri et al., 2013), in which the hydraulic pressure on the draw side was kept at 16±0.5 bar to account for the difference in performance that occurs when a membrane is in PRO mode (Jungwon Kim et al., 2015). The tests were performed in four stages using different concentrations of draw solution (0.5 M, 0.7 M, 1.0 M, 1.3 M NaCl) with each stage lasting at least 1 hour and fifteen minutes (Sun et al., 2020). All experiments were carried out in a crossflow configuration using DI water on the feed side. Water temperature was maintained at 25±0.5 °C. Hydraulic pressure on the draw side was maintained at 16±0.5 bar, with the pump running at 16 Hz and an average flow rate of 3.78 L min⁻¹ (1 gal min⁻¹). The feed side pump was maintained at a level of at least 3/10 on the pump control dial. The feed-side effluent flow rate varied from 0.04 to 1.9 L min⁻¹ (0.01 to 0.5 gal min⁻¹) depending on which
spacer was used, with some of the spacers presenting a pressure barrier that required a higher feed flow rate to prevent backflow. Five polypropylene membrane spacer geometries provided by Sterlitech were evaluated (Figure 4.2); each test used a different membrane. The spacer number represents the general size of the spacer in mils (1 \textit{mil} = 0.03 \textit{mm}).

![Figure 4.2 The five different membrane spacers. Shown is the spacer ID.](image)

While each membrane spacer was made from the same material (polypropylene), there were differences across the membranes in terms of orientation, grid shape, particle size allowance (PSA), vertical symmetry, and void space. Orientation refers to whether the membranes were oriented in a diagonal (diamond) or parallel fashion. Grid shape refers to the grid geometry, either rectangular or square. PSA refers to the manufacturer’s recommended relative foulant PSA, which ranged from low to high. Vertical symmetry refers to whether there was a difference in shape between the top and bottom sides of the spacer. Finally, void space depends on the relative amount of volume that the fluid took up compared to the spacer in the fluid domain. The more space that the fluid could occupy, the greater the void space. This was measured using the simulated geometries developed in FreeCAD discussed in Section 4.3.2.3. These parameters are summarized
in Table 4.1. In addition, specific information about the dimensions of each spacer can be found in Table 4.2. Spacer dimensions were measured using a caliper and by analyzing scaled photographs in Adobe Acrobat Pro.

### Table 4.1 Membrane spacer characteristics

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</tr>
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<td>Void Space (%)</td>
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<td>70.8%</td>
<td>70.5%</td>
</tr>
</tbody>
</table>

\(^1\)PSA: Particle size allowance

### Table 4.2 Membrane spacer dimensions (in mm)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ID</th>
<th>17D-K</th>
<th>17D-N</th>
<th>31D</th>
<th>65D</th>
<th>47D/P-K</th>
<th>47D/P-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius Large</td>
<td>RL</td>
<td>0.32</td>
<td>0.40</td>
<td>0.33</td>
<td>0.56</td>
<td>0.86</td>
<td>0.70</td>
</tr>
<tr>
<td>Radius Small</td>
<td>RS</td>
<td>0.22</td>
<td>0.22</td>
<td>0.28</td>
<td>0.34</td>
<td>0.55</td>
<td>0.44</td>
</tr>
<tr>
<td>Length Large</td>
<td>LL</td>
<td>0.80</td>
<td>0.64</td>
<td>0.61</td>
<td>0.81</td>
<td>1.40</td>
<td>1.72</td>
</tr>
<tr>
<td>Length Slope</td>
<td>LSlp</td>
<td>0.37</td>
<td>0.20</td>
<td>0.36</td>
<td>0.81</td>
<td>1.80</td>
<td>0.44</td>
</tr>
<tr>
<td>Length Section</td>
<td>LSec</td>
<td>1.66</td>
<td>1.45</td>
<td>2.72</td>
<td>3.60</td>
<td>6.24</td>
<td>4.86</td>
</tr>
<tr>
<td>Thickness</td>
<td>T</td>
<td>0.66</td>
<td>0.66</td>
<td>0.79</td>
<td>1.87</td>
<td>1.19</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Note: D stands for diamond, P stands for parallel, K stands for thick, N stands for thin. A visual description of these dimensions is shown in Figure 4.4B

#### 4.3.1.3 Experimental Data Processing

During experimental runs, data were recorded every 15 seconds, giving a high-resolution picture of how the system performed over time. Each trial was conducted in four stages, with the salinity adjusted every hour and fifteen minutes. For each trial, the raw data from each sensor was collected and processed in a Python script to generate values for the mass flux density (mass transfer) of the feed permeate through the membrane (i.e. the water flux), \(J_w [L \cdot m^{-2} \cdot h^{-1}]\), the reverse solute flux, \(J_S [mMol \cdot m^{-2} \cdot h^{-1}]\), the feed concentration, \(c_F [mMol \cdot L^{-1}]\), and the draw concentration, \(c_D [mMol \cdot L^{-1}]\), for each stage. The feed and draw concentration were calculated by converting the conductivity measurements from the sensors from \([\mu S \cdot cm^{-1}]\) to \([mMol \cdot L^{-1}]\) using the conductivity.
to salinity conversion equation from (Fofonoff and Jr., 1983). The water flux and reverse salt flux were calculated as follows:

\[ J_w = \frac{V_{i-1} - V_i}{A_m \times \Delta t} \]  

\[ J_S = \frac{c_{F(i)}(V_i - J_w \times A_m \times \Delta t) - c_{F(i-1)} \times V_{i-1}}{A_m \times \Delta t} \]

where \( V \) [L] is the volume of fluid in the feed tank, \( \Delta t \) [hr] is the amount of time that has passed, and \( A_m \) [m²] is the membrane area. These values were calculated by taking a 30-minute section of relatively steady-state data from each stage, and then fitting the data for each stage using both linear regression and the Huber method (Huber and Ronchetti, 2009; Owen, 2006) to filter out background noise (especially in the feed conductivity readings). These values were then inserted into a modified version of the MATLAB script created by Tiraferri et al., (Tiraferri et al., 2013) which used an over-determined system of non-linear equations to calculate the water permeability coefficient \( A \) [L m⁻² h⁻¹ bar⁻¹]), solute permeability coefficient \( B \) [L m⁻² h⁻¹]), and the membrane structural parameter \( S \) [µm]) using least-squares minimization (Tiraferri et al., 2013). These calculated membrane characteristics were then used to estimate values for \( J_w \) and \( J_S \), which were compared to the processed values based on the measured data using the coefficient of determination, \( R^2 \). This process was then repeated several times for each trial. Once this was completed, the trials containing the highest \( R^2 \) were kept.

4.3.2 CFD Model Description

A three-dimensional CFD model was developed to understand the impact that spacer geometry has on the hydrodynamics of the feed side of the PRO membrane.
4.3.2.1 Governing Flow Equations

The flow on the feed side of the PRO membrane is assumed to be isothermal, laminar, incompressible (the density and pressure are not coupled), and Newtonian. The flow equations also assume that 1) the fluid density and the fluid viscosity are independent of the solute concentration, which is due to the low solute concentration, and the fact that only the feed side of the membrane was simulated, 2) that the effect of gravity is insignificant, and 3) that the solute diffusion coefficient $D \ [m^2 \ s^{-1}]$ is independent of the solute concentration. Note that assumption 3) is valid for NaCl since it was the only salt added to the system and is a compound whose diffusion coefficient does not show significant changes with concentration (Nimdeo et al., 2014). The equations governing the flow of the feed solution and solute concentration include the mass (the continuity equation) and momentum (the Navier-Stokes equations) conservation equations, (Equations (4.3) and (4.4), respectively) as well as the convection-diffusion transport equation (Equation (4.5)) (Haidari et al., 2018; Jungwon Kim et al., 2015; Moukalled et al., 2016):

$$\partial_t u_j = 0 \quad (4.3)$$

$$\partial_t u_i + u_j \partial_j u_i = -\frac{1}{\rho} \partial_i p + \nu \partial_{jj} u_i \quad (4.4)$$

$$\partial_t c = D \partial_{jj} c - u_j \partial_j c \quad (4.5)$$

where $\rho$ is density $[kg \ m^{-3}]$, $u_j$ is the velocity $[m \ s^{-1}]$, $p$ is the dynamic pressure $[m^2 \ s^{-2}]$, $\nu$ is the kinematic viscosity $[m^2 \ s]$, $D$ is the diffusion coefficient $[m^2 \ s]$, and $c$ is the solute concentration (in this case NaCl) $[g \ g^{-1}]$. Combined, these equations define the fluid transport model.

4.3.2.2 Boundary Conditions and Computational Domain

In terms of boundary conditions, each case had an inlet with prescribed fixed values for the velocity vector $U = (u_1, u_2, u_3)$ and zero normal gradient boundaries for $c$ and $p$, an outlet with a
fixed mean boundary for $p$ and zero normal gradient boundaries for $U$ and $c$, symmetry side planes, and a custom membrane boundary condition for the membrane surface (Figure 4.3). A custom boundary condition was needed for the membrane face due to the unique semi-porous structure of the membrane and its impacts on solute concentration and local velocity. All remaining faces had no-slip boundary conditions for $U$ (Figure 4.3) and zero normal gradient boundaries for $c$ and $p$ (Moukalled et al., 2016). All remaining faces had no-slip boundary conditions for $U$ (Figure 4.3) and zero normal gradient boundaries for $c$ and $p$ (Moukalled et al., 2016).

![Figure 4.3](image)

**Figure 4.3** The computational domain, shown for the 65D geometry. Note that only the feed side of the membrane is simulated, and is located below the top plane; the draw side of the membrane is not simulated and is located above the top plane. The bottom surface and the spacer walls have a no-slip boundary condition.

The membrane boundary was based on a modified version of the membrane boundary from the proFoam library developed by (Aschmoneit and Hélix-Nielsen, 2021). Changes were made to the PRO flux equation, the solute flux equation, and the solution algorithm. The reason why the flux equations were changed is that the initial form only included the effects of external concentration polarization, and assumed that the hydraulic pressure is equal to half of the osmotic
pressure difference. The modifications made to the code were to adjust the boundary condition so that it worked to solve for the feed side instead of the draw side of the membrane and to include the effects of internal concentration polarization, reverse salt transport, and external concentration polarization, as is commonly used in the literature (Benjamin et al., 2020; He et al., 2015). The membrane transport equation used was:

$$J_w[t_n] = A \left( \frac{\pi \cdot (c_D \cdot \exp(-J_w[t_n] \cdot K) - c_F[t_n] \cdot \exp(J_w[t_n] \cdot K))}{1 + B / J_w[t_n] \cdot (\exp(J_w[t_n] \cdot K) - \exp(-J_w[t_n] \cdot K))} - \Delta p \right)$$  \hspace{1cm} (4.6)

where $J_w$ [m s$^{-1}$] is the water flux across the membrane, $A$ [m s$^{-1}$ Pa$^{-1}$] is the water permeability of the active layer, $B$ [m s$^{-1}$] is the salt permeability of the active layer, $K$ [s m$^{-1}$] is the membrane diffusion resistivity, which is calculated as $S/D$, where $S$ is the membrane structural parameter [m] and $D$ is the diffusion coefficient [m$^2$ s$^{-1}$], $c_{D/F}$ [g g$^{-1}$] is the draw/feed solute concentration, $\pi$ [Pa] is the osmotic pressure coefficient, and $\Delta p$ [Pa] is the hydraulic pressure difference between the feed and the draw side of the membrane. All the values in this equation (except for $J_w$ and $c_F$) are fixed. Since this equation is implicit in $J_w$, a root-finding method known as Brent’s Method (Brent, 1974) was included in the boundary condition script and implemented in the solution algorithm. Solution of Equation (4.6) yielded the water flux boundary condition at the membrane side of the computational domain in Figure 4.1. Implementing Brent’s method also involved pre-compiling the boundary condition, as the initial boundary condition was implemented as a dynamic code script. Doing this sped up the simulation process since the code did not have to be recompiled every time a case was solved. The assumptions made with this model were that the salinity and pressure on the draw side remained constant and that the membrane could be treated as a flat surface located 40 $\mu$m from the top edge of the spacer.
The pressure \( p \) on the membrane boundary was modeled with a zero normal gradient boundary condition. The feed concentration \( (c_F) \) on the membrane surface was specified as a boundary condition in the CFD model. The feed concentration was obtained as follows. First, the diffusive salt flux across the membrane was calculated using Equation (4.7) (Aschmoneit and Hélix-Nielsen, 2021):

\[
J_S[t_n] = B \cdot \left\{ \frac{(c_D * \exp(-J_w[t_n] * K) - c_F[t_n] * \exp(J_w[t_n] * K))}{1 + B/J_w[t_n] * (\exp(J_w[t_n] * K) - \exp(-J_w[t_n] * K))} \right\}
\]  

(4.7)

where \( J_w \) has been computed from Equation (4.6). To solve for \( c_F \), at each cell along the membrane surface we evaluate \( J_S \) in Equation (4.7) over each of these cells, and then we write a temporally discrete salt mass balance (that includes advective and diffusive transport) was used for each of these cells:

\[
\frac{dc_F}{dt} V_{cell} \approx \frac{c_F[t_{n+1}] - c_F[t_n]}{\Delta t} V_{cell} = J_S[t_n] * A_{m,cell} - J_w[t_n] * c_F[t_n] * A_{m,cell}
\]

(4.8)

where \( t_{n+1} - t_n = \Delta t \). This equation was then rearranged to solve for the updated feed concentration along the membrane surface for a cell:

\[
c_F[t_{n+1}] = \frac{A_{m,cell} * \Delta t * (J_S[t_n] - J_w[t_n] * c_F[t_n])}{V_{cell}} + c_F[t_n]
\]

(4.9)

To ensure steady state of the simulation, the value of \( c_F \) was clipped at 0.0012 g g\(^{-1}\) because otherwise, the salt flux inherent in Equations (4.7) and (4.8) would result in a value of \( c_F \) that is constantly increasing over time.

4.3.2.3 Model Geometry and Numerical Methods

Five different types of membrane spacers were analyzed. Spacer dimensions were first measured using both a caliper and by analyzing scaled photographs in Adobe Acrobat Pro (Figure 4.4A). Each spacer geometry was then generated in FreeCAD 0.18, which is an open-source
computer-aided design software. In FreeCAD, a standardized experimental module size was used for each spacer geometry to ensure consistency across trials. This module was composed of a rectangular channel measuring 18.72 mm long by 9.72 mm wide, with the height varying depending on the thickness of the membrane spacer chosen. Characteristic dimensions for each of the five spacers are summarized in Table 4.2, with a visual description of what each dimension represents located in Figure 4.4B.

![Figure 4.4](image)

Figure 4.4 An illustration of the meshing process, shown using the 65D spacer. A) A photograph of the spacer. B) The dimensions of the 65D spacer. RL = Radius Large, RS = Radius Small, LL = Length Large, LSlp = Length Slope, LSec = Length Section, T = Thickness. A description of the dimensions for each spacer can be found in Table 4.2. C) The final mesh. D) The final mesh zoomed in to see the mesh refinement on the membrane surface.

The final mesh for the case using the 65D spacer can be seen in Figure 4.4C. The mesh was generated using SnappyHexMesh (a volume mesh generation tool for OpenFOAM (Greenshields, 2017)) with a standard mesh size of 50 µm. Mesh refinements were made on the top and bottom planes due to the proximity of the spacer (40 µm) on each side (Figure 4.4D). The
refinements had a relative element size of 0.5, and an edge refinement level of 0.250. The number of cells in each mesh ranged from 2.4 million (17D) to 4.4 million (65D). The geometry for all 5 of the spacer meshes can be seen side-by-side in Figure 4.5.

![Image of mesh geometries](image)

**Figure 4.5** The geometry for each membrane spacer is shown as modeled in FreeCAD.

The governing flow equations applied to the geometry and boundary conditions specified earlier were solved using a modified version of the SIMPLE (Semi-Implicit Method for Pressure Linked Equations) algorithm (Pantankar, 1980) developed by Aschmoneit and Helix-Nielsen (Aschmoneit and Hélix-Nielsen, 2021), with modifications made to simulate both water flow on the feed side and solute transport. This model is solved using the finite volume method and is based on the model developed by Wiley and Fletcher to study RO membrane flow processes, which has been successfully verified by comparison with well-accepted analytical and semi-analytical models (He et al., 2015; Moukalled et al., 2016). Simulations were conducted using the BlueCFD port of OpenFOAM 5.0 (Open-source Field Operations and Manipulations). OpenFOAM is a collection of C++ libraries, designed for solving nonlinear partial differential equations in continuum mechanics problems. This platform was chosen due to its robustness and customizability, as well as its ability to interact with FreeCAD using the CfdOF CFD workbench.
4.3.2.4 Validation Procedure

Simulations were validated through direct comparison with the experimental results using the water flux, $J_w$, and the pressure drop across the length of the feed channel, $\Delta p_d$. This was done by creating each spacer in FreeCAD, and then simulating flow through the spacers in OpenFOAM. To ensure consistency with the experiments, each spacer simulation kept the membrane transport coefficients ($A$, $B$, $S$), the pressure difference between the feed and draw side of the membrane, $\Delta p$, and the initial draw and feed concentrations consistent with the data from the experimental trials. To foster comparison across the CFD trials, the feed influent $Q$ was kept constant at 0.036 l min$^{-1}$ (0.01 gal min$^{-1}$), with the velocity varied depending on the individual spacer geometries. Each scenario was run for 80 seconds, the time by which all simulations had reached a relative steady state.

4.3.3 Optimization Technique

The optimization was conducted on the highest performing spacer design based on both the experimental and simulated results. The five different spacer types were compared using an objective function (Equation (4.10)):

$$f_o = \max \left( \frac{J_w}{J_{w,M}} \right) \left( \frac{\Delta p_d}{\Delta p_{d,M}} \right)$$

(4.9)

where $\Delta p_d$ is the pressure drop between the inlet and the outlet of the computational domain [bar (experimental), $m^2 s^{-2}$ (CFD)], $J_w$ is the water flux [$L m^{-2} hr$], and $\Delta p_{d,M}$ and $J_{w,M}$ are both normalizing coefficients that represent the maximum water flux and pressure drop in each set of values. This objective function was chosen since both the pressure drop across the length of the membrane channel and the degree of mass transfer across the membrane are impacted by hydraulic resistance from the spacer matrix (Guillen and Hoek, 2009). The spacer matrix creates this
resistance by interrupting the flow path of the fluid, which promotes flow instabilities such as vortices and streamline distortions that enhance mass transfer by reducing the extent of concentration polarization (Fimbres-Weihs and Wiley, 2007; Schwinge et al., 2003; Zhou et al., 2006). However, interrupting the flow path also increases the pressure barrier, thus it is important to find the optimal balance between promoting mass transfer across the membrane and increasing the required influent pressure on the feed-side.

The optimization scheme used was the genetic (or evolutionary) algorithm (GA) (Holland, 1992) because this heuristic algorithm can run through many potential spacer structural configurations in a near-optimal fashion without the computational burden of explicit calculation and storage (Abu-Lebdeh and Benekohal, 1999; Koch, 2015). Since there is only one objective, the algorithm used is the SOGA or single-objective genetic algorithm. The parameters varied were the length of the sloped section for both the thick (LSlp-K) and the thin strands (LSlp-N) as well as the radius of the thicker section of the thinner strand (RS-N). Definitions of these terms can be found in Table 4.2 and are visualized in Figure 4.4B. These parameters were chosen because they could be varied autonomously while keeping the geometry attributes (number of faces, boundary face IDs) fixed.

The SOGA optimization was conducted by coupling OpenFOAM, FreeCAD, and the open-source software DAKOTA (the Design Analysis Kit for Optimization and Terascale Applications), which is an optimization software developed by Sandia National Laboratory (Laboratories, 2020). The advantage of using DAKOTA is that it provides access to multiple iterative system analysis methods that can be linked to external simulation codes using its flexible, extensible interface. In this case, the algorithm was automated using a combination of batch files and python scripts. The inputs to the genetic algorithm (Table 4.3) were chosen to minimize the potential for computational
error while also limiting the total number of sample sets to prevent excessive computational runtime. For an explanation of the inputs please see the Dakota Reference Manual (Laboratories, 2020). A description of the solution algorithm is presented in Appendix E.2.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max function evaluations</td>
<td>400</td>
</tr>
<tr>
<td>Seed</td>
<td>10983</td>
</tr>
<tr>
<td>Population size</td>
<td>12</td>
</tr>
<tr>
<td>Initialization type</td>
<td>Unique random</td>
</tr>
<tr>
<td>Mutation type</td>
<td>Replace uniform</td>
</tr>
<tr>
<td>Mutation rate</td>
<td>0.2</td>
</tr>
<tr>
<td>Crossover type</td>
<td>Shuffle random</td>
</tr>
<tr>
<td>Number of offspring</td>
<td>2</td>
</tr>
<tr>
<td>Number of parents</td>
<td>3</td>
</tr>
<tr>
<td>Crossover rate</td>
<td>0.7</td>
</tr>
<tr>
<td>Replacement type</td>
<td>Elitist</td>
</tr>
<tr>
<td>Fitness type</td>
<td>Merit function</td>
</tr>
<tr>
<td>Constraint penalty</td>
<td>0.9</td>
</tr>
<tr>
<td>Convergence type</td>
<td>Best fitness tracker</td>
</tr>
<tr>
<td>Number of generations</td>
<td>102</td>
</tr>
<tr>
<td>Percent change</td>
<td>0.08</td>
</tr>
</tbody>
</table>

4.4 Results and Discussion

4.4.1 Experimental Results

Figure 4.6 shows the trends in conductivity, pressure, and flow rate for both the feed and draw side, as well as the mass of the water in the feed tank, using the data from the 31D trial (data from the remaining trials is presented in Appendix E.3). In terms of conductivity, as each experiment went on, the draw concentration increased in a stepwise fashion due to the experiments being run at four different salinities. The feed concentration steadily increased in each experiment, mainly because of reverse solute transport, which is made more apparent due to the skid being a
recirculation-based system. There is also noise in the feed conductivity, which was mainly due to electromagnetic interference from the VFD powering the draw pump.

Figure 4.6 Results from the 31D trial. Data shown is from when the draw pump is turned on to when it is turned off. A). The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank. Results from the remaining trials can be found in Appendix E.3.

In terms of pressure, there was a negligible difference between the inlet and outlet pressure on the draw side, which is what allowed for a constant value of $\Delta p$ to be used in Equation (4.6). This lack of pressure drop on the draw side was probably due to the absence of any membrane spacers on the draw side. This is made more apparent when comparing pressure drop rates on the draw side against the feed side, where the presence of membrane spacers consistently made the
effluent pressure on the feed side close to zero. The spacers also impacted the feed influent pressure, with the 17D, 31D, and 47D spacers having noticeable amounts of pressure drop (~7-7.3 bar), while the 65D spacer had a slight drop (~5 bar), and the 47P spacer had the lowest drop (~0.5 bar). These differences can be attributed to the differences in membrane spacer characteristics, with the higher void space of the 65D spacer allowing more relative volume for the fluid to travel through, which in turn decreased the pressure drop. Similarly, the unique parallel orientation of the 47P spacer created channels that allowed the fluid to flow relatively uninterrupted and prevented a pressure drop from occurring.

The effluent flow rate on the draw side remained relatively consistent across the trials at 3.79 l min⁻¹ (1 gal min⁻¹), while the flow on the feed side varied depending on the spacer type. Following a similar trend to the feed pressure, the feed effluent flow rate was minimal for the 17D, 31D, and 47D spacers, while the 65D and 47P spacers had higher flow rates. This difference is most likely due to the differences in spacer geometry mentioned before. Finally, the change in mass over time in the fluid tank represented the water flux, $J_w$. Across each trial, the value of $J_w$ increased in tandem with the salinity gradient.

Data from the fourth stage of each experiment were collected and used to compare the physical trials against each other (Table 4.4). The two quantities of interest were $J_w$, which measured the mass flux density of the feed permeate through the membrane (the water flux) and represents the membrane performance, and $\Delta p_d$, which measured the pressure drop across the length of the feed channel and represents the hydraulic performance. From these values, the 31D spacer had the highest water flux while the 47P spacer had an abnormally low pressure drop. This suggests that a trade-off exists between increasing hydraulic performance by using large parallel stranded spacers and improving membrane performance by using thinner diamond-latticed
spacers. However, there does seem to exist an optimal size for the diamond-latticed spacers, as the medium-sized 31D spacer had a higher $J_w$ than both the smaller 17D spacer and the larger 65D and 47D spacers. In addition, membrane deformation was observed in each trial, where the spacer pattern was imprinted on the membrane. In the 47D spacer, there was an additional deformation located along the feed inlet/draw outlet, where the membrane bulged towards the feed side. This additional deformation was not observed in the 47P trials, which suggests that the bulge may have been caused by the pressure drop inherent to the diagonally latticed spacers. This was most likely due to the high-pressure difference between the two solutions, which caused the membrane to be pressed against the feed spacer matrix (Giacalone et al., 2016). Images of the deformed membranes can be found in Appendix E.4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>17D</th>
<th>31D</th>
<th>65D</th>
<th>47D</th>
<th>47P</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta p_d$</td>
<td>7.233</td>
<td>7.226</td>
<td>4.985</td>
<td>7.195</td>
<td>0.450</td>
</tr>
<tr>
<td>$J_w$</td>
<td>14.58</td>
<td>19.79</td>
<td>10.27</td>
<td>10.41</td>
<td>11.96</td>
</tr>
<tr>
<td>$f_o$</td>
<td>0.74</td>
<td>1.00</td>
<td>0.75</td>
<td>0.53</td>
<td>9.72</td>
</tr>
</tbody>
</table>

$\Delta p_d$: Pressure drop across the length of the feed channel [bar], $J_w$: Water flux [$L m^{-2} h^{-1}$], $f_o$: objective function [-]

Finally, values of $c_F$, $c_D$, $J_w$, and $J_S$ were collected from each of the four stages in each trial and used to calculate the membrane performance parameters $A$, $B$, and $S$, which are shown in Table 4.5. The average $R^2$ value of the calculated values vs. the measured values based on the changes in the salinity gradient for $J_w$ was 0.953, while the average $R^2$ value for $J_S$ was 0.902. The difference between the two average $R^2$ values is most likely due to the high amount of noise in the conductivity signal on the feed side, despite being smoothed using either a linear fit method or the Huber method. However, both values are still above 0.9, which suggests a high degree of confidence. Interestingly, the values of $A$, $B$, and $S$ differed according to the chosen spacer, which suggests that spacer geometry has a direct impact on the degree of salt and fluid transport across the membrane.
Table 4.5  Summary of the calculated membrane characteristics from the bench-scale experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>17D-HF</th>
<th>31D-HF</th>
<th>65D-LF</th>
<th>47D-LF</th>
<th>47P-LF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>0.579</td>
<td>1.945</td>
<td>0.290</td>
<td>0.289</td>
<td>0.337</td>
</tr>
<tr>
<td>$B$</td>
<td>0.773</td>
<td>3.099</td>
<td>2.582</td>
<td>1.515</td>
<td>1.436</td>
</tr>
<tr>
<td>$S$</td>
<td>122.8</td>
<td>128.2</td>
<td>45.3</td>
<td>58.3</td>
<td>51.2</td>
</tr>
<tr>
<td>$R^2(J_w)$</td>
<td>0.972</td>
<td>0.999</td>
<td>0.901</td>
<td>0.952</td>
<td>0.939</td>
</tr>
<tr>
<td>$R^2(J_S)$</td>
<td>0.971</td>
<td>0.893</td>
<td>0.717</td>
<td>0.940</td>
<td>0.992</td>
</tr>
</tbody>
</table>

$A$: Water permeability coefficient [L m$^{-2}$ h$^{-1}$ bar$^{-1}$], $B$: Salt permeability coefficient [L m$^{-2}$ h$^{-1}$], $S$: Membrane structural parameter [$\mu$m]. LF means that a linear fit was used for calculating the water and salt fluxes. HF means that a Huber fit was used for calculating the fluxes. $R^2$ represents the correlation between the simulated values and the measured values based on the changes in the salinity gradient.

4.4.2 Model Comparison with Experimental Results

The OpenFOAM simulations were conducted solely for the feed side of the membrane, corresponding to the computational domain discussed earlier (Figure 4.3), as simulating both sides (the feed and the draw side) led to instability caused by the immense pressure difference between the two membrane sides, resulting in runaway solutions that never converged. The results of the simulations are summarized and compared with the physical experiments in Table 4.6. Overall, the simulations were able to closely match the trend in $J_w$ from the physical experiments, with the 65D spacer having the lowest $J_w$ and the 31D spacer having the highest $J_w$. There was a slight discrepancy in the $\Delta p_d$ trend, as each case followed the trend established in the physical experiments (from highest to lowest value: 17D, 31D, 47D, 65D, 47P) except for the 47D and 65D experiments, which had higher and lower $\Delta p_d$ values than expected. This divergence suggests that there may have been some discrepancies between factors such as the operating conditions in the physical trials, the influence on pressure caused by the differences in sampling positions, or the existence of some unknown mechanism that caused the value of $\Delta p_d$ to be so low in the simulated trials for the 65D spacer. This unknown mechanism could either be from experimental error (the $R^2$ for the $J_S$ value for the 65D trial was 0.713, which was much lower than the average $R^2$ of 0.901), or because only one side of the membrane was simulated, which could have impacted the...
simulated $\Delta p_d$ value. Furthermore, there was a difference between the physical and simulated trials in sampling positions for pressure, since the physical trials measured pressure using pressure meters outside of the membrane chamber while the simulations measured pressure at the simulation boundary.

Table 4.6  Physical vs simulated results

<table>
<thead>
<tr>
<th>Physical</th>
<th>17D</th>
<th>31D</th>
<th>65D</th>
<th>47D</th>
<th>47P</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta p_d$</td>
<td>7.233</td>
<td>7.226</td>
<td>4.985</td>
<td>7.195</td>
<td>0.450</td>
</tr>
<tr>
<td>$J_w$</td>
<td>14.58</td>
<td>19.79</td>
<td>10.27</td>
<td>10.41</td>
<td>11.96</td>
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<tr>
<td>$f_o$</td>
<td>0.74</td>
<td>1.00</td>
<td>0.75</td>
<td>0.53</td>
<td>9.72</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Simulated</th>
<th>17D</th>
<th>31D</th>
<th>65D</th>
<th>47D</th>
<th>47P</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta p_d^*$</td>
<td>0.226</td>
<td>0.061</td>
<td>0.005</td>
<td>0.309</td>
<td>0.026</td>
</tr>
<tr>
<td>$J_w$</td>
<td>13.26</td>
<td>18.01</td>
<td>9.23</td>
<td>9.73</td>
<td>10.91</td>
</tr>
<tr>
<td>$f_o$</td>
<td>1.01</td>
<td>5.06</td>
<td>34.81</td>
<td>0.54</td>
<td>7.10</td>
</tr>
</tbody>
</table>

$\Delta p_d$: Pressure drop across the length of the physical feed channel [bar], $\Delta p_d^*$: Pressure drop across the length of the simulated feed channel [$m^3 s^{-2}$], $J_w$: Water flux [$L m^{-2} h^{-1}$], $f_o$: objective function [-]

4.4.3 CFD Analysis

An analysis of the velocity flow fields (Figure 4.7) indicates that the spacers act as pressure barriers in all five trials, with the 47D spacer causing the greatest pressure drop, which in turn, gives it the greatest value of $\Delta p_d$ (0.309). This is most likely due to the large radius (RL/RS) of the 47D spacer’s thick strand and its diamond orientation. These two factors would cause the spacer to act as a large physical barrier, which in turn would cause the feed pump to work harder. This trend of diagonally oriented spacers acting as physical flow barriers continues for the 31D and 17D spacers but is not as prevalent in the 65D spacers, which is most likely due to the 65D spacer having a greater amount of void space (82.3%) than the other two spacers (31D: 78.6%, 17D: 62.4%), which provides a greater amount of alternative flow paths for the fluid to traverse the spacer matrix.
Figure 4.7  A plan view of pressure contours vs velocity flow fields for the five spacer comparison trials. The spacer geometry is colored with the pressure contour, while the computational domain is filled with the velocity streamlines. From top to bottom, the views are facing towards the inlet, the membrane (the view is from the bottom), and the outlet. Both graphics are on the same scale for pressure, $p \,[m^3 s^{-2}]$ and velocity, $U \,[m \, s^{-1}]$. For a high-resolution version of this figure, see the online edition.

While the 47P spacer has the same size strands as the 47D spacer, the parallel orientation of the spacer creates a field with thick strands running parallel to the main streamlines with thin strands interspersed throughout, which allows the fluid to travel freely with minimal energy losses. This contrasts with what happens with the 47D spacer, where the diagonal orientation creates complex flows as seen in the flow fields. In some areas, as the fluid traverses through the thin region between the spacer and the membrane/chamber wall, it creates regions of high velocity and subsequent pressure drops as the fluid expends energy to traverse the spacers. When looking at the other diagonally oriented spacers (65D, 31D, 17D), the pattern of obstruction is more uniform. This causes a smaller change in velocity and allows the streamline to spread out and become more distorted, which increases the total amount of contact time and area between the fluid and the membrane. This in turn creates the necessary back-mixing from the membrane surface to the bulk fluid needed to promote mass transfer and reduce the impacts of CP as the fluid weaves around
the spacer mesh. This explains why the 17D and 31D spacers had higher rates of $J_w$, since both spacers had a relatively uniform grid, having either a slightly rectangular geometry with similar thick and thin strands (17D) or a square geometry (31D), a “low foulant” PSA, and a thin channel height, which allowed for more interactions between the fluid and the membrane surface.

Figure 4.8 shows the salinity contours, which reveals that there are regions of high salinity along the surface of the membrane, most likely due to CP and reverse salt transport. The closer the spacer is to the membrane, the higher the localized salinity becomes, since there is less space for the fluid to remove the extra salt, which creates areas with a low amount of contact time relative to the total contact area. Overall, two trends emerge in terms of how the salinity and velocity fields interact. In areas with high localized velocity (e.g., low contact time) such as the top left corner of the 47D spacer, the fluid pushes the salt away from the streamlines, which causes a ripple effect emanating away from the streamline. In areas where the streamline spreads out and becomes distorted such as the bottom right corner of 47D, this effect reverses, where instead of pushing away the salt, the fluid instead picks up the salt. This is a result of the fluid and the salt having a longer contact time and a higher contact area in these areas. Both trends create ripples and wakes in the salinity contours along both the streamlines and the spacer matrix, which in turn impacts the degree of concentration polarization that may be experienced. The level of salinity drop/removal can be compared by looking at the percent increase in the average salinity over the 80 second period. From lowest to highest, the salinity increases are: 11.4% (65D), 19.2% (31D), 20.0% (47D), 31.6% (47P), 85.9% (17D). Looking at the percent increase of the average salinity versus the initial salinity, the trend seems to be that the spacers with a square geometry (65D and 31D) had lower degrees of salt drop than the rectangularly shaped geometries (47P, 47D, and 17D). This indicates that a relationship exists between salt transport and the formation of stagnation
points/streamline distortions caused by having a spacer with a square geometry. The 17D spacer seemed to have the highest local increase in salinity, which may be due to the low amount of void space and thickness of the spacer.

Figure 4.8 A plan view of pressure vs salinity contours for the five spacer comparison trials. The spacer geometry is colored with the pressure contour, while the computational domain is filled with the salinity contours. From top to bottom, the views are facing towards the inlet, the membrane (the view is from the bottom), and the outlet. Both graphics are on the same scale for pressure, \( p \) \( [m^3 s^{-2}] \) and salinity, \( c \) \( [g g^{-1}] \). For a high-resolution version of this figure, see the online edition.

Overall, the information presented here can be used in membrane module design, as a spacer with more void space and more linear channels for the fluid to travel across produces lower levels of pressure and salinity drop. However, there is also a compromise, as thicker spacers mean that less overall membrane surface area can be placed in a given volume, so it is important to consider the value of \( f_o \) when comparing different spacer geometries in membrane module design.

4.4.4 Optimized Spacer Geometry Configuration

The optimization was conducted on the 47P spacer because it had the lowest overall pressure drop in the experimental trials, one of the higher values of \( J_w \), an average degree of CP, and a relatively simple geometry, which facilitated automated meshing. Each simulation had a
mesh containing 2 to 3 million hexahedral cells and was generated, solved, and purged to preserve hard drive space. There were 365 simulations spread across 102 generations. The calculation took around 9 days on a Lenovo P330 ThinkStation with an Intel Xeon E-2226G CPU at 3.40 GHz and 32 GB of RAM running four simulations at a time. The difference in the spread of the output variable, \( f_o \) (the objective function – Equation (4.10), i.e., system performance), between the initial and final generation can be seen in Figure 4.9. In this figure, the initial generation (blue) had variables spread across the entire input range, with output values of \( f_o \) ranging from 4.30 (-39.4% performance) to 7.60 (+7.0% performance). The final generation (orange) shows that the model converged on a value for the length of the slope and the radius of the small section for the thin strand (LSlp-N and RS-N) and the simulations were within 8% (the cutoff threshold) for the length of the slope of the thick strand (LSlp-K). If the optimization was allowed to run longer, most likely the values would be even closer.

Figure 4.9  The results from the SOGA optimization. In this graph, each axis represents an input variable, with the size of the point indicative of the value of the objective function. Notice that the initial population has a wide range of decision variables and objective function values, while the final population clusters around a final set of values.
The optimized spacer geometry was able to improve system performance, which was measured by maximizing the ratio of mass transfer across the membrane surface to the pressure drop between the feed inlet and outlet, by 16.3% compared to the baseline scenario for the highest performing spacer geometry, which was the 47P spacer. The difference in geometry can be seen in Figure 4.10. From this figure, while RS-N stayed relatively constant, going from 0.440 \( \text{mm} \) to 0.441 \( \text{mm} \), both LSlp-K and LSlp-N were retracted, going from 1.80 \( \text{mm} \) to 1.49 \( \text{mm} \) and 0.44 \( \text{mm} \) to 0.09 \( \text{mm} \) respectively. This created a simpler, more hexagonal shape in the cross-section, which created a smoother flow field and decreased the pressure drop caused by the spacer matrix (Figure 4.11). The flow through the membrane remained consistent, at 10.91 \( L \text{ m}^2 \text{ hr}^{-1} \), which is due to the membrane transport parameters \((A, B, S)\) remaining the same throughout the optimization. In terms of the salinity contours, the increase in the linearity of the channel between the spacer strands caused by the retraction of LSlp-K and LSlp-N caused the salinity bulge around the edge of the spacer to become rounder and more continuous (Figure 4.12), which in turn allowed for the increased transport of salt away from the membrane, and decreased the average salinity by 2%, going from 2.92e-4 \( g \text{ g}^{-1} \) to 2.86e-4 \( g \text{ g}^{-1} \). These results suggest that spacer manufacturers should emphasize keeping the spacer strands more linear by and decreasing the length of the sloped section of the thin cross-strand (LSlp-N). This is because distortions to the streamline caused by differences in the thickness of the thin cross strand are what ultimately interrupt the flow paths and cause an enhanced pressure drop in the system. Making these improvements could ultimately improve the efficiency of PRO systems, as it would reduce the overall energy demand drawn by the feed pump by 16.3% since the feed pump does not have to work as hard, which increases the net energy generation potential.
Figure 4.10 Geometric comparison between A) the original 47P spacer and B) the optimized 47P spacer geometry. The image is oriented with the membrane on the top (facing towards the bottom plane).
Figure 4.11  A plan view of pressure vs velocity flow fields for A) original geometry compared with the B) optimized geometry. The spacer geometry is colored with the pressure contour, while the computational domain is filled with the velocity streamlines. From top to bottom, the views are facing towards the left side (assuming the inlet is the front), the membrane (the view is from the bottom), and the right side. Both graphics are on the same scale for pressure, $p [m^3 s^{-2}]$ and velocity, $U [m s^{-1}]$. For a high-resolution version of this figure, see the online edition.

Figure 4.12  A plan view of pressure vs the salinity contours for the A) original geometry compared with the B) optimized geometry. The spacer geometry is colored with the pressure contour, while the computational domain is filled with the salinity contours. From top to bottom, the views are facing towards the left side (assuming the inlet is the front), the membrane (the view is from the bottom), and the right side. Both graphics are on the same scale for pressure, $p [m^3 s^{-2}]$ and salinity, $c [g g^{-1}]$. For a high-resolution version of this figure, see the online edition.
4.5 Conclusions

This study investigated the impact that varying spacer geometry had on the performance of a pressure retarded osmosis system. A tradeoff was identified between having a decreased pressure drop in the feed side of the membrane versus increased salt and fluid transport across the membrane. A decreased pressure drop occurs with larger stranded parallel spacers, while an increased mass transfer rate occurred with medium-sized diagonally oriented spacers. Concentration polarization also seemed to be impacted by spacer geometry, with regularly distributed geometries having less CP. Future research is recommended to evaluate the performance of pressure-retarded osmosis systems, with an emphasis on membrane fouling and pretreatment. The study also showed the potential that single-objective genetic algorithms have in improving membrane spacer geometry and system performance as an optimized geometry improved overall performance (water flux/pressure drop) by 16.3%. This in turn means that if this spacer were to be applied, the feed pump would consume less energy, which would increase the net energy generation potential of the PRO system. In addition, this study has implications for not just the membrane community, but also the CFD and virtual prototyping communities. The developed algorithm integrates CAD, mesh generation, CFD, and optimization using 100% open-source software, so it is freely accessible to the design community. This also makes it easily transferrable to other cases and geometry, where it could be used to create digital twins (Molinaro et al., 2021) of existing objects for more effective designs.
Chapter 5: The Impact of Spacer Variation and Pretreatment Protocol on PRO Systems

Using Reverse Osmosis Concentrate and Reclaimed Tertiary Wastewater

5.1 Abstract

Existing seawater desalination plants face the challenges of high energy costs and environmental impacts from brine disposal. Pressure retarded osmosis (PRO) is a membrane-based technology that could mitigate these issues by capturing the potential energy in the salinity gradient between brine and dilute (e.g., freshwater/wastewater) solutions. Currently, a major challenge facing PRO is membrane fouling, which is the accumulation of unwanted substances on the membrane surface that reduce the potential surface area available for mass transfer. Membrane fouling can be reduced using pretreatment and by altering the available fluid flow paths using membrane spacers. However, pretreatment systems decrease the net energy generation potential from PRO, while membrane spacers impact both concentration polarization and the internal pressure drop in the membrane channel, both which have the effect of decreasing the net energy generation potential of a PRO system. Therefore, it is important to design a membrane spacer that can minimize the effects of both concentration polarization and the internal pressure drop.

In this study, we conducted a series of PRO fouling experiments to see how varying pretreatment and membrane spacer geometry on the feed side impacts the net energy density of a PRO system. This was done using synthetic tertiary treated wastewater (WW) and brine based on water collected from the Howard F. Curren Advanced Wastewater Treatment plant and the Tampa Bay Seawater Desalination Plant. The WW was dosed with Pseudomonas aeruginosa to promote biofouling in the system. Based on the results from an initial SEM-EDS membrane surface
analysis, ultraviolet disinfection (UV), Microfiltration, and the addition of Poly(L-aspartic acid sodium salt) - which is an antiscalant - were evaluated as candidate pretreatment protocols for the WW. The two spacer geometries tested were a parallel threaded large gridded spacer (47P) and a diamond threaded medium gridded spacer (31D). Results were compared using a series of water quality tests, energy consumption analysis, and by measuring the changes in water flux and power density over time. Overall, it was found that pretreating the water with UV combined with the 31D spacer was the most effective configuration, as it had both the lowest degradation in filtration effectiveness over time with 79.6% remaining effectiveness at 36.5 hours, as well as the highest net power generation potential. It was estimated that 12.53 kWh of energy would be generated with a specific energy of 0.24 kWh m$^{-3}$ of mixed solution using a size 4040 pressure vessel running at the optimal pressure level. This study has implications for the field of pressure-retarded osmosis, as it shows the potential that the technology has for effective energy recovery and brine management in seawater desalination systems.

5.2 Introduction

Pressure retarded osmosis (PRO) is an emerging membrane-based technology that has the potential to mitigate the issues of high energy consumption and concentrated brine management for seawater desalination systems that are co-located with wastewater treatment systems (Benjamin et al., 2020; Elimelech and Phillip, 2011). The process works by converting the Gibbs free energy that exists in the salinity gradient between different water streams into usable hydraulic pressure. In this process, a dilute (feed) solution is separated from a pressurized highly concentrated (draw) solution using a semi-permeable membrane supported by a spacer matrix. This creates an osmotic gradient across the membrane, which causes the feed solution to permeate
into the draw solution and creates an excess of pressurized concentrate that can then be diverted to a hydro turbine to create electricity.

The primary issues with pressure retarded osmosis are concentration polarization, which is the reduction in the overall salinity gradient caused by the buildup of solutes along the membrane surface, and membrane fouling, which is the accumulation of unwanted substances on the membrane surface that reduce the potential surface area available for mass transfer (Bogler et al., 2017; Thelin et al., 2013; Yip and Elimelech, 2013). Membrane fouling can be reduced using pretreatment and by altering the available fluid flow paths using membrane spacers. However, pretreatment systems decrease the net energy generation potential from PRO, while membrane spacers impact both concentration polarization and the internal pressure drop in the membrane channel, both which have the effect of decreasing the net energy generation potential of a PRO system. Therefore, it is important to select the pretreatment scheme and the membrane spacer that can maximize the net energy generation of a PRO system.

Membrane fouling reduces the permeability of the membrane and prevents water from flowing through the membrane matrix, but it can be controlled through pretreatment and process optimization schemes. It is important for fouling to be controlled, as it is one of the primary factors increasing overall energy generation costs to the point of making PRO economically unfeasible (Yip et al., 2016). When RO concentrate is mixed with tertiary WWTP effluent, fouling primarily occurs on the feed side of the membrane surface, as RO concentrate has lower concentrations of potential fouling agents, and the water flux through the membrane prevents foulants from accumulating on the draw side (Saito et al., 2012). Membrane fouling can be divided into four distinct categories: colloidal/particulate fouling, mineral scaling, organic fouling, and microbial fouling (biofouling) (Bogler et al., 2017; Sagle and Freeman, 2004). In general, membrane fouling
happens on both the membrane support layer, which is a polymeric matrix that adds stability to the membrane active surface under high pressures, as well as in the gaps inside of the spacer matrix (Bogler et al., 2017; Radu et al., 2010; Vrouwenvelder et al., 2010). Overall, the dominant mechanism is determined by foulant type and support layer pore size. The primary compounds of concern are suspended solids and colloidal suspensions, which can cause colloidal/particulate fouling; microbes such as *Pseudomonas aeruginosa* and *Pseudoalteromonas atlantica*, which can cause biofouling; natural organic matters, such as fulvic and humic acids, which can cause organic fouling; and cations and anions such as calcium, phosphate, sulfate, and silica, which can cause inorganic scaling (Bar-Zeev et al., 2015; Bogler et al., 2017; Han et al., 2016; Saito et al., 2012).

Biofouling and organic fouling have been shown to be the two most problematic types of foulants, as scaling can be controlled through the use of acids and scalant inhibitors such as EDTA, HEDP, and Poly(L-aspartic acid sodium salt), and colloidal/particulate fouling can be controlled using filtration-based pretreatment (Han et al., 2016; Picioreanu et al., 2009). Biofouling is caused by the growth of biomass on both the membrane and spacer surface and occurs under two different pathways that can both occur simultaneously. The first pathway is the deposition of cells and organic matter due to the permeate water flux through the membrane, and the second pathway is from cell growth on the membrane surface (Bogler et al., 2017). Once established, bacteria create a biofilm, which begins by first creating a “conditioning film” that other bacteria can then attach to via van der Walls, hydrogen bonding, and hydrophobic interactions. Eventually, the initial colonies of bacteria excrete extracellular polymeric substances, which reinforces the bacterial communities and creates a functional biofilm (Song et al., 2013). While bio and organic fouling can be controlled using osmotic backwashing (Bar-Zeev et al., 2015), pressure-aided osmotic backwashing (Bar-Zeev et al., 2015), and chemical treatment (Han et al., 2016) none of these
methods have been found to be 100% effective (Bogler et al., 2017). PRO is especially susceptible to fouling since the support layer faces the feed side, which allows bacteria to propagate inside of the porous structure of the support layer and cause severe ICP (Bogler et al., 2017). Reducing fouling will make membranes more cost-effective by extending their operational lifetime and lowering their energy requirements (Bogler et al., 2017).

Previous research on membrane fouling in PRO has primarily focused on characterizing and controlling foulant propagation rates. In this area, there have been studies on controlling inorganic fouling and gypsum scaling when using DI water and NaCl (Zhang et al., 2014), characterizing fouling rates with various river water and seawater solutions (Abbasi-Garravand et al., 2018), investigating the effect of hydraulic pressure and pH on organic fouling when using synthetic ROC and wastewater effluent (Jihye Kim et al., 2015b), and investigating the impact of biofouling on membrane performance when using synthetic ROC and wastewater effluent (Bar-Zeev et al., 2015). In particular, the paper by Bar-Zeev et al. (2015) indicated that spacer blockage has a significant impact on foulant propagation rates, and that studies need to be done to quantify the appropriate combination of feed pretreatment and spacer orientation necessary to minimize membrane fouling.

To address these issues, we conducted a series of PRO fouling experiments to investigate how varying pretreatment and membrane spacer geometry on the feed side impacts the net specific energy of a PRO system. This was done using synthetic tertiary treated wastewater (SWW) and brine based on water collected from the Howard F. Curren Advanced Wastewater Treatment plant and the Tampa Bay Seawater Desalination Plant. The membranes were then analyzed using SEM-EDS to characterize the different foulants on the membrane surface and select the appropriate pretreatments. The SWW was dosed with *Pseudomonas aeruginosa* to promote biofouling in the
system. The water on the feed side was pretreated using combinations of ultraviolet disinfection (UV), Microfiltration, and the addition of Poly(L-aspartic acid sodium salt), which is an antiscalant. The two spacer geometries tested were a parallel threaded large gridded spacer (47P) and a diamond threaded medium gridded spacer (31D). Results were compared using a series of water quality tests, energy consumption analysis, and by measuring the changes in water flux and power density over time, with an overall objective of finding the configuration with the highest net specific energy.

5.3 Materials and Methods

5.3.1 Solution Preparation and Bacterial Strain

5.3.1.1 Sample Collection

Fourteen-gallon (53 L) samples were collected for both the draw (ROC) and feed (treated wastewater effluent, WW) solutions to create synthetic ROC and WW recipes for the experiments. The feed solution was collected at the Howard F. Curren Advanced Wastewater Plant (HCWWTP) in Tampa, FL. The water was taken from the end of the secondary treatment stage and before the disinfection stage. The water sample was taken from this point because the plant uses chlorine for disinfection, which is best to avoid when using PRO membranes to avoid destruction by chlorine attack (Gohil and Suresh, 2017). The draw solution was collected from the Tampa Bay Seawater Desalination Plant (TBSDP) at their ROC sampling tap. Both samples were collected on the same day and transported over ice to the Environmental Engineering Laboratory at the University of South Florida, where they were then analyzed and stored. The water quality parameter and analysis methods of the samples collected are shown Appendix F.1.
5.3.1.2 Synthetic Solution Preparation

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</tr>
</tbody>
</table>

Synthetic versions of the draw and feed solutions were created to ensure consistency across the different trials. The synthetic reverse osmosis concentrate (SROC) was created using Instant Ocean Sea Salt dosed at of 70.97 g L⁻¹, with each experiment using 8 L of SROC. Instant Ocean Sea Salt was chosen since it closely matches the ion balance of ocean water, and has been used before as a model SROC solution (Bar-Zeev et al., 2015). The synthetic wastewater effluent (SWW) was created by first starting with previously published SWW recipes as a base (Bar-Zeev et al., 2015; Uslu et al., 2016). These recipes were modified using historic wastewater effluent reports from the HCWWTP (FDEP, 2009; McCormick et al., 2018), the latest effluent sample report from the HCWWTP, and the results from the in-house analysis. Individual concentrations from each source were tabulated, and the recipe was constructed to be in line with each set of parameters (Table 5.1). The SWW solution was prepared by making 1 L of 20x stock concentrate,
and diluting it into 20 L of solution. 10 L of SWW was used in each experiment, so each bottle of SWW concentrate was enough for two experiments.

5.3.1.3 Bacterial Strain

To induce biofouling, the SWW was dosed with 1.5 mL of a nutrient broth composed of 62.5% peptones and 37.5% beef extract containing a culture of *Pseudomonas aeruginosa*, an encapsulated, gram-negative, strict aerobic, rod-shaped bacterium, which is highly effective at creating biofilms and has been used in previous osmotic membrane studies (Bar-Zeev et al., 2015; Kwan et al., 2015; Xie et al., 2015). The culture was kept in the exponential growth phase by placing the culture on a mechanical shaker at 60 rpm under a constant temperature of 35°C. The culture was maintained by replacing half of the broth with fresh nutrient broth every two weeks to ensure that it stayed in the exponential growth phase. Both the bacterial culture and the broth were provided by Carolina Laboratory Supplies.

5.3.2 Water Quality Testing

Both the SROC and SWW solutions were analyzed for pH, conductivity, dissolved oxygen (DO), turbidity, hardness, and chemical oxygen demand (COD) before and after each experiment. In addition, the SWW was analyzed after it was pretreated to determine the effect of pretreatment on the water, for a total of five samples for each experiment. pH, conductivity and DO were analyzed using a Thermo Scientific Orion 5-Star Benchtop Multimeter, turbidity was analyzed using a HACH 2100Q Portable Turbidimeter, hardness was analyzed using CHEMetrics 100–1000 ppm EDTA Total Hardness Titrets, and COD was analyzed using CHEMetrics LR (0–150 mg L⁻¹) COD vials. The SWW samples were also analyzed for the presence of *Pseudomonas aeruginosa* using the IDEXX Pseudalert* test to determine the bacterial count, BC. The Pseudalert* test was performed on the raw sample, after pretreatment, and after the experiment was concluded.
5.3.3 SEM and EDS Analysis

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to further understand the impacts of fouling on the PRO membrane used with the ROC - WW configuration to determine the appropriate pretreatment technology. Membrane samples were photographed and then cut in half so that an image could be taken for both the draw and feed side of the membrane immediately after each experiment was concluded, with the samples then placed into a Thermo Scientific Nalgene 5312 Nucerite Desiccator for at least 24 hours to dry before they were placed into the SEM. An FEI Quanta 200 3D Dual Beam SEM/FIB outfitted with a IXRF SEM/EDS system was used for this analysis, which was housed in the USF Nanotechnology Research & Education Center (NREC). SEM images were taken in low-vacuum mode using the Large Field Detector (LFD), at 15 - 17 mm working distance, 0.53 Torr pressure, 0.35 nA current, and 30.00 kV to prevent the accumulation/buildup of static charge due to the non-conductive nature of the membrane samples. Images used for EDS analysis were taken in high vacuum mode using the Everhart Thornley detector (ETD), which was necessary since the introduction of water vapor that occurs in low vacuum mode causes interference with the X-rays used for EDS analysis. These images were taken at 15 - 17 mm working distance, 4E-6 - 5E-6 Torr pressure, 0.35 nA current, and 30.00 kV to prevent beam interference.

5.3.4 Pretreatment Technologies

Ultraviolet (UV) disinfection, microfiltration (MF), and the addition of an antiscalant (AS) were tested both individually and in tandem as potential pretreatment technologies. When combined, the treatment order was microfiltration, followed by UV disinfection, followed by adding the antiscalant.
UV disinfection was done using a Katadyn Steripen Ultra. The water was disinfected 1 L at a time in 90 second intervals, and then added to the feed reservoir. Once all the water was added to the feed reservoir, another UV disinfection cycle was conducted inside of the reservoir to remove any residual bacteria. Microfiltration was done using a Katadyn BeFree 3.0L water filter system, which contained an EZ-Clean Membrane™, which is a 0.1-micron hollow fiber membrane microfilter. The water was filtered in 3 L intervals, and then added to the feed reservoir. The microfiltration system was cleaned between trials using dilute sodium hypochlorite as per the manufacturer’s recommendations.

The antiscalant used was Poly(L-aspartic acid sodium salt) (CAS# 34345-47-6, x = 30 repeating units, MW = 4,100 Da), which was provided by Alamanda Polymers. This antiscalant was chosen because it is biodegradable, phosphorus free, and has been shown to have some success as a membrane antiscalant in previous studies (Pramanik et al., 2017; Yang et al., 2010a, 2010b). It works by forming molecular chains of water-soluble Ca²⁺ complexes, which increase the average particle size and minimizes the area that the particles would cover on the membrane (Pramanik et al., 2017). Before being added, the antiscalant was sonicated using a Fisher Scientific FS20 sonicator for ten minutes and then dosed into the feed tank at 1 mg L⁻¹. Between trials, it was stored in a freezer under nitrogen gas to prevent the antiscalant’s polymers from degrading.

5.3.5 PRO Unit

The PRO system used was the same as described in Chapter 4. Modifications were made to the system by replacing some of the tubing, removing the RO bypass valve, and placing black electrical tape over the feed-side tubing to prevent algal propagation. In addition, BALDR electrical meters were attached to the outlets of the feed pump and the draw pump to measure electrical consumption. The membranes used were FTSH2O flat sheet Cellulose Triacetate (CTA)
membranes provided by Sterlitech. The membranes were 42.0 cm² in total area, with 33.6 cm² of that being actively exposed to the fluid. They were mounted with the active side facing the draw solution.

5.3.6 Experimental Procedure

Nineteen different experiments were conducted in total, with variations made to the spacer type, pretreatment type, and water type, as summarized in Table 5.2. The two different spacers used were the 47P and 31D spacers, as described in Chapter 4. All experiments were carried out in a crossflow configuration. Water temperature was maintained at 25±0.5 °C. Hydraulic pressure on the draw side was maintained at 8±0.5 bar, with the draw pump running at 16 Hz and an average flow rate of 3.78 L min⁻¹ (1 gal min⁻¹). The feed side pump was maintained at a level of 3/10 on the pump control dial. The feed-side effluent flow rate varied from 1.36 - 0.53 L min⁻¹ (0.36 - 0.14 gal min⁻¹) for the 31D spacer, and 3.94 - 1.25 L min⁻¹ (1.04 - 0.33 gal min⁻¹) for the 47P spacer. The reason for the difference is due to the increased hydraulic barrier created by the 31D spacer, as described in Chapter 4. The first three experiments compared the performance of the SWW and SROC to the WW and ROC, and were done at a lower hydraulic pressure of 2–3 bar due to issues with the draw pump at the time. Each experiment began by first soaking the PRO membrane in DI water for an hour to activate the membrane, followed by being compacted for 1 hour using 4 L of DI water in each tank under 8±0.5 bar of pressure. After that, the DI water was drained from each tank, and 10 L of WW/SWW was placed in the feed tank, and 8 L of ROC/SROC was placed into the draw tank. The experiment would then run for a minimum of 36.5 hours, with measurements recorded every fifteen seconds.
Table 5.2  Experimental configurations

<table>
<thead>
<tr>
<th>Test #</th>
<th>Draw Solution</th>
<th>Feed Solution</th>
<th>Spacer</th>
<th>UV</th>
<th>MF</th>
<th>AS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SROC</td>
<td>WW</td>
<td>31D</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>ROC</td>
<td>WW</td>
<td>31D</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>ROC</td>
<td>SWW</td>
<td>31D</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>SROC</td>
<td>SWW</td>
<td>31D</td>
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</tr>
<tr>
<td>5</td>
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<td>SWW</td>
<td>47P</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>SROC</td>
<td>SWW</td>
<td>31D</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>SROC</td>
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<td>47P</td>
<td>X</td>
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<tr>
<td>8</td>
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<td>SWW</td>
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<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
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<td>SROC</td>
<td>SWW</td>
<td>47P</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

*S stands for synthetic, ROC stands for reverse osmosis concentrate, WW stands for treated wastewater effluent, UV stands for ultraviolet disinfection, MF stands for microfiltration, and AS stands for adding poly(L-aspartic acid sodium salt) as an antiscalant.

5.3.6.1 Cleaning Procedure

Once an experiment was completed, both tanks were sampled and then drained, and the experimental membrane was removed, photographed, and cut up and placed into a desiccator for future SEM analysis. Next, one of two “cleaning membranes” was placed into the membrane chamber, with each spacer type (47P and 31D) using a different membrane. 6 L of DI water was then placed into each tank, with the $pH$ increased to 8 using sodium hydroxide (NaOH). After that, the system ran at 4 bars of pressure at 35±0.5 °C for 40 minutes, followed by 10 minutes of dormancy to allow the cleaning solution to soak, and an additional 10 minutes of pressurized flow to complete the base treatment. Next, the system was spiked with hydrochloric acid (HCL) to decrease the $pH$ to 2, and a similar process was conducted (40 minutes of circulation, 10 minutes of soaking, 10 minutes of recirculation) to do an acid treatment. Finally, the system was drained, and then flushed with 4 L of DI water in each tank for 30 minutes to flush out any residual salt/acid.
This cleaning process conducted under the recommendation of the providers of the PRO membrane used (Sterlitech).

5.3.7 System Performance Analysis

For each trial, the raw data from each sensor was collected and processed in a Python script to generate values for the mass flux density (mass transfer) of the feed permeate through the membrane (i.e. the water flux), \( J_w \ [L \ m^{-2} \ h^{-1}] \), the reverse solute flux, \( J_S \ [mMol \ m^{-2} \ h^{-1}] \), the feed concentration, \( c_F \ [mMol \ L^{-1}] \), and the draw concentration, \( c_D \ [mMol \ L^{-1}] \), for each stage. The feed and draw concentration were calculated by converting the conductivity measurements from the sensors from \([\mu s \ cm^{-1}]\) to \([mMol \ L^{-1}]\) using the conductivity to salinity conversion equation from Fofonoff and Millard (Fofonoff and Millard, 1983). The water flux and reverse salt flux were calculated as follows:

\[
J_w = \frac{V_{i-1} - V_i}{A_m \cdot \Delta t} \tag{5.1}
\]

\[
J_S = \frac{c_F(i)(V_i - J_w \cdot A_m \cdot \Delta t) - c_F(i-1) \cdot V_{i-1}}{A_m \cdot \Delta t} \tag{5.2}
\]

where \( V \ [L] \) is the volume of fluid in the feed tank, \( \Delta t \ [hr] \) is the amount of time that has passed, and \( A_m \ [m^2] \) is the membrane area. Due to noise in the feed conductivity sensor caused by interference from the electro-magnetic field generated by the draw pump, the data for \( c_F \) was smoothed using the Huber method (Huber and Ronchetti, 2009; Owen, 2006) using an epsilon of 1.35.

Once these values were calculated, they were then inserted into a modified version of the MATLAB script created by (Tiraferri et al., 2013) that was used in Chapter 4, which used an over-determined system of non-linear equations to calculate the water permeability coefficient \( (A \ [L \ m^{-2} \ h^{-1} \ bar^{-1}]) \), solute permeability coefficient \( (B \ [L \ m^{-2} \ h^{-1}]) \), and the membrane structural
parameter \((S \,[\mu m])\) using least-squares minimization (Tiraferri et al., 2013). These coefficients were then averaged for each spacer type, and then used to calculate \(J_{\text{w-calc}}\) (Equation 5.3), which represents the water flux that would have occurred if there was no fouling.

\[
J_{w-calc(i)} = A \left\{ \frac{\pi \cdot (c_{D(i)} \cdot \exp(-J_{w(i)} \cdot K) - c_{F(i)} \cdot \exp(J_{w(i)} \cdot K))}{1 + B / J_{w(i)} \cdot (\exp(J_{w(i)} \cdot K) - \exp(-J_{w(i)} \cdot K))} - \Delta p_{(i)} \right\}
\]  

(5.3)

In this equation, \(K \,[m^2 \, hr^{-1}]\) is the membrane diffusion resistivity, which is calculated as \(S/D\), where \(S\) is the membrane structural parameter \([m]\) and \(D\) is the diffusion coefficient \([m^2 \, hr^{-1}]\), \(c_{D,F} \,[g \, g^{-1}]\) is the draw/feed solute concentration, \(\pi \,[\text{bar}]\) is the osmotic pressure coefficient, and \(\Delta p \,[\text{bar}]\) is the hydraulic pressure difference between the feed and the draw side of the membrane. This value was calculated to remove the impact from the change in the salinity gradient over time that occurs in a recirculating PRO system.

This calculated value was then used to calculate an adjusted value of \(J_w\), \(J_{w-adj}\), using Equation 5.4:

\[
J_{w-adj(i)} = J_{w(i)} + (J_{w-calc(0)} - J_{w-calc(i)})
\]  

(5.4)

This value was then fitted with the exponential function \(m \cdot e^{-kf \cdot t} + b\) using the non-linear least squares minimization method through the scipy.optimize.curve_fit protocol (Community, 2021), where \(t\) represents time, and \(m \, [-], \, kf \, [hr^{-1}]\), and \(b \, [-]\) are calculated coefficients. These fitted curves were then used to compare the effectiveness of the different pretreatment protocols.

### 5.3.7.1 Net Energy Calculation

Once the fouling curves were generated for each pretreatment, they were then used to calculate the gross energy production, \(E_{\text{gross}}\):
\[ E_{\text{gross}} = W_{\text{adj,max}} \cdot A_{m, PV} \cdot \int_{0}^{t} (m \cdot e^{-k_f \cdot t} + b) \, dt \]  

(5.5)

where \( W_{\text{adj,max}} \) is the adjusted maximum power density achieved while the system was running, \( A_{m, PV} \) is the membrane area of 7 Toray TMH10A membrane elements, which are 4040-sized elements that have an individual membrane area of 10.44 \( m^2 \) and were used to represent the total area in a single pressure vessel, and the integral represents the fouling decay curve. The reason why the area of a full-size pressure vessel was used is because an individual membrane coupon does not have a net positive power production due to the coupon’s small size. It is important to calculate the net power production, as it gives a more accurate estimate of the energy recovery potential of the technology when applied at full scale.

The net energy production, \( E_{\text{net}} \) [\( kW \)], was calculated using the following equation:

\[ E_{\text{net}} = E_{\text{gross}} \cdot \eta_{\text{gen}} - (P_{\text{PT}} - P_{D} - P_{F}) \cdot t \]  

(5.6)

where \( \eta_{\text{gen}} \) is the efficiency of the turbine used (95\%), \( P_{\text{PT}} \) [\( kW \)] is the power consumed by pretreatment, and \( P_{D} \) and \( P_{F} \) are the average amount of power used by the draw and feed pumps, respectively, as measured by the BALDR energy meters in kW. All values were calculated at \( t = 36.5 \) hours, as that was the standardized time used to compare across the different experimental configurations. \( P_{\text{PT}} \) was calculated as follows:

\[ P_{\text{PT}} = SE_{\text{PT}} \cdot (Q_{F, \text{out}} + J_{w,adj} \cdot A_{m, PV}) \]  

(5.7)

where \( SE_{\text{PT}} \) is the specific energy in \( kWh \, m^{-3} \) for the pretreatment used in each scenario. \( Q_{F, \text{out}} \) represents the flow rate captured by the feed effluent flow meter in \( m^3 \, hr^{-1} \), and \( J_{w,adj} \cdot A_{m, PV} \) represents the total flow that passed through the membrane, which together represent the feed influent flow rate that would need to be pretreated, \( Q_{F, \text{in}} \). The values for \( SE_{\text{PT}} \) were from (EPRI, 2013), and are 0.016 \( kWh \, m^{-3} \) for UV, 0.026 \( kWh \, m^{-3} \) for MF, and 0.017 \( kWh \, m^{-3} \) for AS, with
the value for AS calculated using the specific energy for chemical feed systems. Once $E_{\text{net}}$ was calculated, it was then used to find the net specific energy per $m^3$ of mixed solution, $SE_{\text{net}}$. This was only calculated for the highest performing pretreatment, and was done to have a normalized net energy value that could be compared against other PRO process train designs, as done in Chapters 2 and 3. $SE_{\text{net}}$ was calculated as:

$$SE_{\text{net}} = E_{\text{net}} / \left( t \times (Q_{\text{D,in}} + Q_{\text{F,in}}) \right)$$  \hspace{1cm} (5.8)

where $Q_{\text{D,in}}$ was the draw influent flow rate.

### 5.4 Results and Discussion

#### 5.4.1 Synthetic Solution Comparison

The first four trials were conducted to compare the synthetic solutions to the collected samples. The time-series results from the four trials can be seen in Appendix F.2. The average initial value for the $pH$, salinity ($c$), dissolved oxygen concentration ($DO$), chemical oxygen demand ($COD$), hardness, and turbidity for both the real and synthetic versions of the ROC and WW can be found in Table 5.3. Overall, the values matched quite well for $pH$ and $c$ for both the ROC and WW, as well as for $COD$ in the WW solutions and hardness and turbidity for the ROC solutions. $DO$ was most likely higher for both real solutions due to the additional aeration from being transported through both the plant and to campus compared to the synthetic versions. The $COD$ was most likely higher for the synthetic ROC due to differences in sample preparation, where the $COD$ for the real ROC was measured by adding Mercuric Sulfate to compensate for chlorine interference to the test, while the synthetic ROC used a different type of test kit that mitigated the impacts from chloride interference by diluting the water to make the chloride concentration within the recommended limit. The method was changed to limit the formation of hazardous waste from the Mercuric Sulfate. Finally, there were differences in the hardness and turbidity between the real
and synthetic wastewater, which were due to the hardness of the real solution being higher than the historical average that the synthetic solution represents, while the turbidity was most likely higher in the wastewater due to the presence of a multitude of colored organic compounds and coagulants that could not be included in the synthetic formulation.

Table 5.3  Real (R) vs synthetic (S) average initial water quality

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>c</th>
<th>DO</th>
<th>COD</th>
<th>Hd</th>
<th>Tr</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>7.55</td>
<td>0.89</td>
<td>11.00</td>
<td>24.44</td>
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<td>0.61</td>
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<td>6.55</td>
</tr>
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<td>ROC</td>
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<td>c</td>
<td>DO</td>
<td>COD</td>
<td>Hd</td>
<td>Tr</td>
</tr>
<tr>
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<td>122.56</td>
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<td>1.30</td>
</tr>
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<td>46.78</td>
<td>6.47</td>
<td>796.26</td>
<td>10800</td>
<td>1.75</td>
</tr>
</tbody>
</table>

$c$: salinity [ppt], $DO$: dissolved oxygen [$mg L^{-1}$], $COD$: chemical oxygen demand [$mg L^{-1}$], $Hd$: hardness [$mg L^{-1} CaCO_3$], $Tr$: turbidity [NTU].

The normalized adjusted trends in water flux and the differences in operating pressure for the four comparison trials can be seen in Figure 5.1. Both the real and synthetic versions exhibited similar levels of exponential decay in the water flux over the course of the experiment even after being adjusted to remove the impact from variations in the salinity gradient over time, which indicates that both real and synthetic solutions were subject to membrane fouling. The two closest curves were the ROC-WW and SROC-WW trials, which were ran at similar pressure levels. The reason why the pressure level was changed over the course of the comparison trials was because the draw-side pump needing to be repaired before the trials began, which led to the pump being ran at a lower pressure level until it was deemed safe to operate at higher pressures. Despite these variations in pressure, the level of similarity in the flux decay over time and the water quality was deemed sufficient to warrant using the synthetic solutions in place of the real solution for the spacer and pretreatment comparisons.
Figure 5.1  Time-series data comparison between the synthetic and real ROC and WW solutions. ROC stands for reverse osmosis concentrate; WW stands for tertiary wastewater effluent. The top graph shows the differences in the normalized adjusted water flux data, where \( J_{w,n\text{-adj}} = J_{w\text{-adj}} / J_{w\text{-adj,max}} \) while the bottom graph shows the differences in the hydraulic pressure difference, \( \Delta p \), across the four trials.

5.4.2 Foulant Characterization Using SEM-EDS

Images were captured using SEM-EDS to analyze for the presence of membrane foulants on both the draw side and feed side of the PRO membranes for the ROC-WW trial. These images were used to determine what type of fouling would be most likely to occur and were used in the pretreatment selection process. The images presented below are from an initial trial that was not included in the later analysis. In this trial, the draw pump was having issues with cavitation in the inlet manifold due to a faulty inlet valve, which caused the pressure to rapidly fluctuate between 8
and 16 bars throughout the experiment. As such, the images also illustrate how a membrane performs under rapidly changing pressure levels. Unfortunately, SEM-EDS images could not be captured for the data from the experimental trials due to the SEM-EDS being under repair while the experiments were being conducted.

5.4.2.1 Draw Side Analysis

The experiments were conducted in the AS-DS configuration, where the active side of the membrane was facing the draw side. Images were taken in low-vacuum mode using the large field detector to mitigate the impact from the charge effect, since the membrane was not electrically conductive. This can be seen in Figure 5.2, which shows the draw side of the membrane from the ROC-WW trial at A) 200x, B) 800x and C) 3000x magnification on a scaled section of the membrane surface, as well as the D) 800x magnified section that was used for the EDS analysis. Overall, there was some minor scaling, with concentrations of Al, Si, P, S, Cl, K, Ca, Cr, and Fe detected. Si, P, S, Cl, K, Ca are all commonly found in seawater. Al was probably introduced into the system through corrosion of the protective wrapping around the conductivity meter cable, and Cr and Fe were probably introduced through pipe corrosion. The EDS spectrographic breakdown and elemental maps can be seen below in Figure 5.3. Note that the image in the EDS mapping is the same as the one in Figure 5.2D, it is just at a higher magnification (1600x) and has been slightly degraded because of the 30.00 kV electron beam bombarding the membrane surface.
Figure 5.2 SEM images of the draw side of the initial ROC-WW trial. ROC stands for reverse osmosis concentrate; WW stands for tertiary wastewater effluent. A) Membrane scaling at 200x magnification. B) Membrane scaling at 800x magnification. C) Membrane scaling at 3000x magnification. D) The section of the membrane that was probed using EDS at 800x magnification.
Figure 5.3 EDS images of the draw side of the initial ROC-WW trial. ROC stands for reverse osmosis concentrate; WW stands for tertiary wastewater effluent. The top portion of the figure shows the spectroscopic readout, the bottom portion shows the elemental maps of the section. Image taken at 1600x magnification.
5.4.2.2 Feed Side Analysis

While the draw side images showcase the active side of the membrane, the feed side shows the membrane support layer. Like the draw side, detailed images were taken in low-vacuum mode using the LFD, and EDS images were taken in high-vacuum mode with the ETD. The detailed images of the feed side can be seen in Figure 5.4, which shows some of the damage that operating at high levels of fluctuating pressure does to the membrane at A) 200x and B) resolution, as well as C) some of the biofouling that was detected at 4000x resolution, and D) some of the membrane scaling images that were further analyzed with EDS. Overall, there was some minor scaling, with concentrations of Al, Si, S, Cl, Ca, Fe, Cu, Zn, and Mo detected. Si, S, Cl, Ca, Fe, Cu, Zn, and Mo are all commonly found in wastewater effluent. Al was probably introduced into the system through corrosion of the protective wrapping around the conductivity meter cable. The EDS spectrographic breakdown and elemental maps can be seen below in Figure 5.5. The presence of both scaling and biofouling in the system is what was used to choose the three pretreatment options, as UV disinfection would prevent bacteria from multiplying and covering up the membrane surface, microfiltration would physically remove organic and biological materials that could cause bio and organic fouling as well as some larger colloidal particles, and adding the Poly(L-aspartic acid sodium salt) antiscalant would reduce the impacts of membrane scaling.
Figure 5.4 SEM images of the feed side of the initial ROC-WW trial. ROC stands for reverse osmosis concentrate; WW stands for tertiary wastewater effluent. A) the membrane surface at 200x magnification. B) The membrane surface at 800x magnification, showing some of the damage caused by rapid pressure fluctuations. C) A cellular organism that causes biofouling captured at 4000x magnification. D) The section of the membrane covered with scale that was probed using EDS at 1500x magnification.
Figure 5.5  EDS images of the feed side of the initial ROC-WW trial. ROC stands for reverse osmosis concentrate; WW stands for tertiary wastewater effluent. The top portion of the figure shows the spectroscopic readout, the bottom portion shows the elemental maps of the section. Image taken at 1500x magnification.

5.4.3 Water Quality Analysis

The water quality parameters of interest were $pH$, $c$, $DO$, $COD$, hardness, turbidity, and bacterial count ($BC$). Table 5.4 shows each the average value of each parameter for the raw synthetic ROC and WW both before and after the experiments. The $pH$ typically decreased slightly...
for the SWW and increased slightly for the SROC, but not enough to make a significant impact. The salinity, $c$, hardness, and turbidity increased for the SWW and decreased for the SROC because of reverse salt transport. The DO had a slight increase for both sides, which was most likely due to the water being aerated by moving through the system. The COD decreased for the SWW, which means that the combination of pretreatment and recirculation through the PRO membrane allowed the organic content in the water to decrease over time. The range of variation for the COD concentrations for the pre and post stage of the SROC were overlapping, which means that for the SROC, there was not a significant impact on COD levels over time. Finally, the bacterial count decreased as the experiment went on, which is most likely because of the MF and UV pretreatments.

Table 5.4  Average synthetic water quality

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>c</th>
<th>DO</th>
<th>COD</th>
<th>Hd</th>
<th>Tr</th>
<th>BC</th>
</tr>
</thead>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre</td>
<td>8.04±0.19</td>
<td>0.53±0.08</td>
<td>7.35±3.42</td>
<td>49.8±28.8</td>
<td>217±74</td>
<td>2.63±3.08</td>
<td>42.84±17.52</td>
</tr>
<tr>
<td>Post</td>
<td>7.70±0.39</td>
<td>1.12±0.31</td>
<td>7.94±3.91</td>
<td>8.8±6.6</td>
<td>275±100</td>
<td>3.98±5.53</td>
<td>6.96±7.63</td>
</tr>
<tr>
<td>SROC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre</td>
<td>7.98±0.16</td>
<td>50.40±2.75</td>
<td>7.12±3.48</td>
<td>553.3±454.9</td>
<td>10042±1600</td>
<td>2.45±3.14</td>
<td>N.M.</td>
</tr>
<tr>
<td>Post</td>
<td>8.09±0.16</td>
<td>42.65±2.76</td>
<td>7.52±3.15</td>
<td>624.8±708.1</td>
<td>8692±1461</td>
<td>0.35±0.50</td>
<td>N.M.</td>
</tr>
</tbody>
</table>

$c$: salinity [ppt], $DO$: dissolved oxygen [mg L$^{-1}$], $COD$: chemical oxygen demand [mg L$^{-1}$], $Hd$: hardness [mg L$^{-1}$ CaCO$_3$], $Tr$: turbidity [NTU], $BC$: bacterial count [MPN], N.M. means not measured.

One noticeable result was the trend in the dissolved oxygen over time, where the $DO$ increased for both the initial SROC and SWW for some of the trials before returning to the normal range (Figure 5.6). It is important to note that the $pH$, $c$, and $DO$ were all measured by the same instrument, which means that if there was any issue with the instrument, it would show up on the reading for all three parameters. Because of this, most likely what happened was that there was some form of contamination in the DI water system that served the facility. This was later confirmed after speaking with one of the building technicians, who mentioned that they recently had to replace one of the tanks in the DI water system. The trial where the $DO$ returned to normal
was conducted the day after the DI system was repaired, which means that was the most likely cause in the \( DO \) variation.

Figure 5.6  The trend in initial water quality over time. The x-axis represents the experiments in the order they were conducted. Shown are the normalized trends for \( pH \), \( DO \), and \( c \) for the initial SROC and SWW. The increase in \( DO \) for both the SROC and SWW for a few weeks indicates that there was an issue with the quality of the DI water that was used to create both solutions.

The effectiveness of each set of pretreatment protocols on the overall wastewater quality for \( pH \), hardness, and \( c \) can be seen in Figure 5.7, and can be seen for \( DO \), \( COD \), turbidity, and \( BC \) in Figure 5.8. The \( pH \) was consistent across each of the pretreatments, which makes sense given that none of the pretreatments specifically targeted \( pH \). There was some slight variation in hardness and \( c \) across the pretreatments, with the general trend being that the pretreated water had around the same value as the original water, with the post-experimental water having a higher hardness and \( c \) because of reverse salt transport.
Figure 5.7  The SWW water quality parameters for A) pH; B) hardness ($H_d$); and C) salinity ($c$). PR means the initial bulk SWW water quality, PT means the bulk SWW water quality after being pretreated, and PO means the bulk SWW water quality after the experiment ran. The values are averaged across the two spacer trials for each pretreatment protocol.

Figure 5.8 The SWW water quality parameters for A) dissolved oxygen (DO); B) chemical oxygen demand ($COD$), C) turbidity ($Tr$), and D) bacterial count ($BC$). PR means the initial bulk SWW water quality, PT means the bulk SWW water quality after being pretreated, and PO means the bulk SWW water quality after the experiment ran. The values are averaged across the two spacer trials for each pretreatment protocol.
In terms of DO, the MF-AS and UV-AS trials had higher values than the other trials, which was primarily due to the disparity in the initial DO concentration that occurred during those trials. The remaining pretreatments typically increased the DO concentration due to both the increased amount of aeration introduced during the pretreatment process combined with the increased amount of available oxygen caused by the decreased bacterial counts of *Pseudomonas aeruginosa*, which is an aerobic bacterium.

The COD went down when the pretreatment involved either UV or MF, which makes sense given that UV deactivates the bacteria and prevents them from replicating, while MF physically removes the bacteria from solution. This physical removal phenomenon is most likely why the water samples after the experiment was completed typically had a lower COD, since a large portion of the organic matter would become attached to either the membrane surface or the walls of the pipes. Over the course of the experiments, it was observed that the tubes would become covered with a black film of an algae-like substance. The tubes were coated with black electrical tape to prevent the algal growth from continuing, but they most likely created a surface that was attractive to organic matter. The antiscalant trials had a slight increase in COD after treatment due to the lack of physical separation involved, but they still had a reduced COD after the experiments were complete.

The turbidity of the water typically decreased after pretreatment except for the AS and UV-AS trials, which had an increase in turbidity most likely due to the addition of the antiscalant, which forms molecular chains of water-soluble Ca$^{2+}$ complexes, which in turn would increase the turbidity due to the larger size of the suspended compounds (Pramanik et al., 2017). The turbidity typically increased over the course of the experiment due to the increased salinity, with a significant increase in the turbidity in the MF-AS trial.
The bacterial count decreased in the trials with the MF and UV pretreatments because of deactivation and physical separation. There was not a significant decrease in the antiscalant trial since the antiscalant did not target the bacteria. In addition, the bacterial count typically increased slightly over the course of the experiment, especially in the antiscalant trials, where the antiscalant may have acted as a carbon source for the bacteria due to its biodegradability. This increase was especially pronounced since the water was recirculating and so any surviving bacteria would be able to reproduce in the system. It is hypothesized that this would not be the case if this was a pass-through system since the water would not act as a breeding ground for the bacteria.

5.4.4 System Performance Analysis

5.4.4.1 Salinity Correction

To create a fairer comparison, it was important to adjust the water flux data to remove the impact of the decrease in salinity gradient over time. This was done by first taking the raw experimental data and trimming it, so it only included the data from the active experiment, since the instruments also recorded the membrane compaction and system cleaning. The data readout from the 31D - SROC - SWW - No PT trial can be seen in Figure 5.9. Note that the data from the remaining trials can be seen in Appendix F.3.

The next step in processing the performance data was to correct the raw $c_F$ reading, which had a high degree of noise due to external interference from the electromagnetic field created by the VFD powering the draw pump. The two potential correction methods were the Huber method, and linear regression, shown in Figure 5.10. The Huber method was chosen over linear regression since it created a smoother profile. After the $c_F$ data was smoothed, the water flux, $J_w$, salt flux, $J_S$, internal pressure buildup on the draw and feed side ($\Delta p_D$ and $\Delta p_F$), and power density, $W$, were calculated for a 36.5-hour period, as shown in Figure 5.11.
Figure 5.9  Results from the 31D - SROC - SWW - No PT trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.

Figure 5.10  Correcting the $c_F$ curve using both the Huber method and linear regression. Data was split into ten-minute intervals and then averaged out over a three-hour interval. The data was then fitted over the interval, and the first ten minutes for each interval was used in the final analysis.
Figure 5.11 Calculated values for the 31D - SROC - SWW - No PT trial. A) The salinity values on the draw and feed sides. B) The hydraulic pressure difference $\Delta p$, the internal pressure loss on the draw and feed side, and the reverse salt flux, $J_s$. C) The water flux $J_w$, as well as the power density $W$.

The first four water flux, hydraulic pressure difference, salt flux, and draw and feed concentration values were then used to calculate the membrane transport parameters, $A$, $B$, and $S$, and then averaged for each spacer type. The values of $A$, $B$, and $S$ for the 31D spacer were 4.010 $L\ m^{-2}\ hr^{-1}\ bar^{-1}$, 1.988 $L\ m^{-2}\ hr^{-1}$, and 128.2 $\mu m$, while the values for the 47P spacer were 3.558 $L\ m^{-2}\ hr^{-1}\ bar^{-1}$, 2.654 $L\ m^{-2}\ hr^{-1}$, and 480.8 $\mu m$. These values were then used to calculate $J_{w\text{-calc}}$, which is the decay in water flux over time due to the change in salinity gradient. $J_{w\text{-calc}}$ was then used to adjust the water flux and fitted with an exponential function, as shown in Figure 5.12.
Figure 5.12 Adjusting the value of $J_{w-calc}$ to account for the salinity gradient reduction. This graph shows the normalized values of $J_w$, $J_{w-calc}$, $J_{w-adj}$, and the fitted exponential decay curve, $J_{w-fit}$.

### 5.4.4.2 Hydraulic Comparison

The main difference in performance between the two spacer types can be visualized using the adjusted $J_w$ and $\Delta p_F$ values, as shown in Figure 5.13, which shows both the mean value and range of variation for each spacer type. Note that a version of this graph that is broken down by the individual trials can be seen in Appendix F.4. The 31D spacer typically had a higher water flux than the 47P spacers, with an average initial $J_{w-adj}$ of 15.23 $L \ m^{-2} \ hr^{-1}$, compared to the 47P’s average initial $J_{w-adj}$ of 11.10 $L \ m^{-2} \ hr^{-1}$. In contrast, the 47P spacer had a much lower internal pressure drop, with an average initial $\Delta p_F$ of 4.90 bar compared to the 31D spacer, which had an average initial $\Delta p_F$ of 0.48 bar. This indicates that the 47P spacer provided less resistance to flow due to its parallel orientation and larger profile, which also translated to a lower average feed pump power consumption, $P_F$, of 14.52 $W$ vs the 31D spacer, which had an average $P_F$ of 43.76 $W$. 
Figure 5.13 The range of variation for A) $J_{w,adj}$ and B) $\Delta p_F$ for the 31D and 47P spacers. The dashed line represents the mean value, and the colored field represents the range of variation between the maximum and minimum values.

5.4.4.3 Pretreatment Effectiveness Comparison

Using the normalized $J_{w,fit}$ curves (the fouling curves), the impact that each pretreatment had on membrane fouling could be observed (Figure 5.14). The coefficients for each fouling curve, as well as the $R^2$ values and the filtration effectiveness, $E_f$, which is the value that each curve had at $t = 36.5$ hours, are collected in Table 5.5, ordered from most effective on the top to least effective on the bottom. In general, the curves had a high degree of confidence, with an average $R^2$ of 0.924.
While none of the treatments were able to mitigate fouling completely, the most effective treatment/spacer combination, which was the 31D-UV combination, was able to maintain a 79.6% effectiveness. This contrasts with the 47P-MF-AS combination, which was the least effective treatment/spacer combination with a final $E_f$ of 57.6%.

![Graph A) $J_{w,n - nt}$ - 31D](image1.png)

![Graph B) $J_{w,n - nt}$ - 47P](image2.png)

Figure 5.14 The fitted $J_{w,n}$ curves for the 31D and 47P spacers. A) The 31D curves are individually plotted, with the range of variation for the 47P spacers underlaid in gray. B) The 47P curves are individually plotted, with the range of variation for the 31D spacers underlaid in gray.
### Table 5.5 Pretreatment coefficients

<table>
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<tr>
<th>Test ID</th>
<th>$m$</th>
<th>$k_f$</th>
<th>$b$</th>
<th>$R^2$</th>
<th>$Ef$</th>
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<tbody>
<tr>
<td>31D - UV</td>
<td>0.212</td>
<td>0.055</td>
<td>0.768</td>
<td>0.785</td>
<td>79.6%</td>
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<tr>
<td>31D - MF - UV - AS</td>
<td>0.304</td>
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<td>0.891</td>
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<tr>
<td>31D - AS</td>
<td>0.329</td>
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<td>0.719</td>
<td>0.956</td>
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<tr>
<td>31D - No PT</td>
<td>0.320</td>
<td>0.105</td>
<td>0.675</td>
<td>0.969</td>
<td>72.1%</td>
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<tr>
<td>31D - MF</td>
<td>0.356</td>
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<td>0.651</td>
<td>0.935</td>
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<td>47P - AS</td>
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<td>0.658</td>
<td>0.917</td>
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<td>47P - MF - UV</td>
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<td>0.110</td>
<td>0.651</td>
<td>0.977</td>
<td>65.8%</td>
</tr>
<tr>
<td>31D - UV - AS</td>
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<td>0.648</td>
<td>0.946</td>
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<td>47P - MF - UV - AS</td>
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<td>0.188</td>
<td>0.625</td>
<td>0.927</td>
<td>62.8%</td>
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<tr>
<td>47P - UV - AS</td>
<td>0.443</td>
<td>0.274</td>
<td>0.614</td>
<td>0.913</td>
<td>62.5%</td>
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<td>47P - MF</td>
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<td>0.560</td>
<td>0.992</td>
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<tr>
<td>47P - MF - AS</td>
<td>0.623</td>
<td>0.108</td>
<td>0.403</td>
<td>0.954</td>
<td>57.6%</td>
</tr>
</tbody>
</table>

$k_f$: [hr$^{-1}$], $Ef$: pretreatment effectiveness [%], $m$, $b$, $R^2$ [-]. Values arranged from greatest (top) to least (bottom) $Ef$.

In general, the 31D spacers trials were able to maintain a higher normalized water flux over time than the 47P spacers, with an average $Ef$ of 68.4% at 36.5 hours versus the $Ef$ for the 47P spacers, which was 59.9%. This is due to the difference in geometry, with the 31D spacer creating a more complex flow profile as shown in Chapter 4, Figure 4.7, that prevented foulants from adhering to the membrane. In addition, the 31D spacer was classified as a “low-foulant” spacer by the manufacturer, while the 47P spacer was classified as a “medium-foulant” spacer, which is backed up by the data from this experiment. While the UV treatment was the most effective with the 31D spacer, it was one of the least effective treatments with the 47P spacer. This was probably since the power went out in the middle of the 47P-UV trial, which caused a change in the overall operating conditions. In addition, the trials with multiple stages of pretreatment did not always perform better than the trials with individual pretreatments, which indicates that adding the extra
pretreatment does not guarantee that the system will perform better. Note that there is a slight
caveat to this due to the variations in initial water quality impacting some of the trials, but the trend
still holds for the trials that had similar initial quality levels.

5.4.4.4 Net Energy Comparison

When choosing the most effective pretreatment/spacer combination, it is crucial to evaluate
different options based on their net energy recovery potential using the net power, which are
summarized in Table 5.6. Overall, the test that had the highest net energy, $E_{net}$, was the 31D - UV
trial, with an $E_{net}$ of 1.64 kWh at 36.5 hours. This would give a net specific energy, $S_{E_{net}}$, of 0.04
kWh m$^{-3}$ mixed solution ($Q_{D,in} + Q_{F,in}$), where $Q_{D,in}$ was 0.24 m$^3$ hr$^{-1}$ (1.06 gal min$^{-1}$), as measured
by the draw flow meter. Note that while the 31D - UV trial had the highest net power, it did not
have the highest gross power or the highest $W_{max}$, which belonged to the 31D MF- UV trial and
the 31D - UV - AS trial respectively. This disparity illustrates the importance of finding how the
system behaves under different forms of pretreatment, as the configuration with the highest $W_{max}$
value did not have the highest $E_{gross}$ due to it having a lower final efficiency value of 65.7%
compared to the final efficiency of the 31D - UV trial at 79.6%. These values are reflective of
individual trials using the same influent water quality standard. Pretreatment effectiveness may
vary depending on changes in initial water quality, which will be tackled in future work. In
addition, it is possible to increase the energy density by operating the system at a higher pressure.

The membrane transport coefficients for the 31D system from Chapter 4, where $A = 1.945$, $L m^{-2} hr^{-1} bar^{-1}$, $B = 3.099 L m^{-2} hr^{-1}$, and $S = 128.2 \mu m$, can be plugged into Equation 5.3 to
find the maximum possible $W$, which was used to find the theoretical optimal operating pressure.
These values were used since they had a higher degree of accuracy for operating at the optimum
pressure than the ones used for the curve fitting, since they were calculated at a higher pressure.
level (16 bar vs 8 bar) using multiple salinity gradients. If the system were able to run at the same level of pretreatment effectiveness (79.6%) at the theoretical optimum pressure, then the optimum \( W_{\text{max}} \) would be 8.75 \( W \ m^{-2} \), the \( J_w \) would be 15.99 \( L \ m^{-2} \ hr^{-1} \) leading to a \( Q_{F-in} \) of 1.18 \( m^3 \ hr^{-1} \), and the \( \Delta p \) would be 19.7 \( \text{bar} \). This would lead to a gross energy production of 20.04 kWh at 36.5 hours, creating a net energy production of 12.53 kWh, a 664% increase. This assumes that the pumps perform at a similar rate of energy consumption, and that the membrane can perform at the projected efficiency. The specific energy would also be increased, going from 0.04 kWh m\(^{-3}\) to 0.24 kWh m\(^{-3}\), a 500% increase. Due to these immense increases, it is imperative that systems be operated at the optimal operating pressure to maximize potential energy generation ability.

### Table 5.6 Full scale net energy projections

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<tr>
<th>Test ID</th>
<th>( P_F )</th>
<th>( P_D )</th>
<th>( P_{PT} )</th>
<th>( W_{\text{max}} )</th>
<th>( Q_{F-in} )</th>
<th>( E_{\text{gross}} )</th>
<th>( E_{\text{net}} )</th>
</tr>
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<td>43.76</td>
<td>115.78</td>
<td>15.74</td>
<td>3.69</td>
<td>0.98</td>
<td>8.46</td>
<td>1.64</td>
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<tr>
<td>31D - MF - UV</td>
<td>38.53</td>
<td>117.73</td>
<td>44.51</td>
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<td>1.06</td>
<td>9.38</td>
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<td>40.47</td>
<td>118.92</td>
<td>16.56</td>
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<td>8.34</td>
<td>1.50</td>
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<tr>
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<td>1.07</td>
<td>8.83</td>
<td>1.13</td>
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<td>7.07</td>
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<td>0.62</td>
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<td>2.72</td>
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<td>115.63</td>
<td>36.44</td>
<td>2.72</td>
<td>0.87</td>
<td>5.34</td>
<td>-1.13</td>
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<td>0.71</td>
<td>4.76</td>
<td>-1.31</td>
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<td>113.22</td>
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<td>0.70</td>
<td>5.45</td>
<td>-1.68</td>
</tr>
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<td>14.15</td>
<td>119.50</td>
<td>42.62</td>
<td>2.62</td>
<td>0.72</td>
<td>4.81</td>
<td>-1.86</td>
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<tr>
<td>47P - MF - AS</td>
<td>15.86</td>
<td>117.67</td>
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<td>2.03</td>
<td>0.52</td>
<td>3.02</td>
<td>-2.81</td>
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<tr>
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<td>38.60</td>
<td>2.19</td>
<td>0.65</td>
<td>4.81</td>
<td>-3.02</td>
</tr>
</tbody>
</table>

\( P_F \): feed pump power consumption [W], \( P_D \): draw pump power consumption [W], \( P_{PT} \): pretreatment power consumption [W], \( W_{\text{max}} \): maximum energy density [W m\(^{-2}\)], \( Q_{F-in} \): feed influent flow rate [m\(^3\) hr\(^{-1}\)], \( E_{\text{gross}} \): gross energy production [kWh], \( E_{\text{net}} \): net energy production [kWh]. Note: Values colored from best (green) to worst (red). \( E_{\text{gross}} \) and \( E_{\text{net}} \) calculated at \( t = 36.5 \) hours.
5.5 Conclusions

This study investigated the impact that varying pretreatment protocols and the membrane spacer geometry on the feed side has on the net power of a PRO system. Overall, it was found that pretreating the water with UV combined with the 31D spacer was the most effective configuration, as it had both the lowest degradation in filtration effectiveness over time with 79.6% remaining effectiveness at 36.5 hours, as well as the highest net power generation potential, able to create an estimated 1.64 kWh of energy with a specific energy of 0.04 kWh m$^3$ mixed solution using a 4040-pressure vessel with 7 membrane elements with a $Q_{F-in}$ of 0.98 m$^3$ hr$^{-1}$. If this configuration were to be ran at ideal pressure levels, the projected power generation potential increases to 12.53 kWh over a 36.5-hour period, with a $Q_{F-in}$ of 1.18 m$^3$ hr$^{-1}$ and a specific energy of 0.24 kWh m$^{-3}$ of mixed solution. This is similar in magnitude to the maximum specific energy level predicted in Chapter 2, which was 0.25 kWh m$^{-3}$. This also indicates that with proper pretreatment and operational conditions, a PRO system can perform at high enough efficiency to match the performance of a large ($Q_{F-in} = 733.89$ m$^3$ hr$^{-1}$) PRO system with a high transmission cost and no fouling decay included, as shown in Chapter 2, or a medium-sized ($Q_{F-in} = 335.39$ m$^3$ hr$^{-1}$) PRO system with minimal transmission costs and no fouling decay included, as shown in Chapter 3.

While the 31D-UV configuration had the highest net power, the 31D-MF-UV trial had the greatest gross power, which demonstrates the importance of finding the net power generation rate when designing an energy recovery system. In addition, these projections are based on single trials, using one set of synthetic wastewater and RO concentrate water qualities operating at the same operating pressure, so the system may perform at a higher or lower operational efficiency under different conditions even with the same pretreatment. In addition, variations in the initial quality of the DI water used showed the importance of doing continuous checks for water quality on both
the influent and effluent side, as well as having different pretreatment options available in areas where water quality varies. It is recommended that future work focuses on varying the influent water quality and performing duplicate studies at different operating pressures to see if the trends identified in this study hold up. In addition, it is also recommended that longer term studies be conducted, to see how a PRO system performs over a long period of time under multiple backwashing cycles. Finally, this study has implications for the field of pressure-retarded osmosis, as it shows the potential that the technology has for effective energy recovery and brine management in seawater desalination systems.
Chapter 6: Conclusions

6.1 Summary

This dissertation focused on conducting a comprehensive assessment on how pressure-retarded osmosis could potentially be implemented in seawater desalination systems as an energy recovery and brine management system. The primary metric used was the net specific energy, which indicated how much energy recovery potential a PRO configuration had. Analysis were conducted on choosing the correct salinity gradient and process configuration to maximize energy recovery potential, finding the necessary geographic and economic conditions, determining the impact that feed spacer geometry has on internal hydraulics, and determining the impact that influent water quality, spacer geometry, and pretreatment has on the net specific energy level. Overall, the results from this study suggest that there is potential for PRO to be an economically viable form of energy recovery and brine management for seawater desalination. To maximize performance, PRO should be implemented using a pressure and foulant resistant integrated membrane/spacer pairing combined with source streams that require minimal pretreatment in regions where seawater desalination plants are co-located with wastewater plants and/or have high energy prices.

6.2 Key Findings

This dissertation was centered around the main question of “Under what cases is PRO a viable form of energy recovery and brine management for desalination?”, which in turn was divided into four research questions, which were elaborated on in Chapters 2 - 5. Presented below are the questions and answers.
1. How can system characteristics such as salinity gradient and membrane type be configured to optimize a PRO system in terms of baseline net specific energy and economic performance?

In Chapter 2, it was found that it is unlikely that a ROC-SW system could be viable due to the low energy densities of the system. A SW-WW system was found to be more possible, as favorable scenarios do have a positive net specific energy and payback periods with an interquartile range of 14 to 23 years. Overall, it is recommended to focus future efforts on developing ROC-WW systems, since their higher specific energies allow for higher levels of energy recovery, and they were found to have shorter payback periods in the interquartile range of payback periods, at 7 to 19 years. What this means is that for a ROC-WW system to be implemented, it is crucial to evaluate not only the membrane characteristics but also the local geographic and economic conditions. Furthermore, it was found that under favorable conditions, the unit cost of this system is similar to the cost of other renewable energy systems, which means that PRO could be a competitive technology for energy recovery in desalination applications assuming the system could be built and operated as projected.

2. What impact do local geography and economic conditions have on the viability of a PRO system?

In Chapter 3, three preexisting seawater desalination plants were identified as candidates for PRO implementation. The first site, which was Tampa Bay, was found to be unviable due to the plant being too far from any available low-salinity stream that could be used on the feed side. It was found that PRO would be most effectively implemented in areas where seawater desalination plants and wastewater treatment plants are co-located, such as Santa Barbara, California, where a PRO system would have a net specific energy of 0.23 kWh m\(^{-3}\) with a unit cost
of $3,119 \text{ kW}^{-1}$ assuming there are no external pretreatment costs. PRO was also found to be viable in areas with high electricity purchase prices, such as St. Thomas in the Virgin Islands, where the net specific energy would be $0.15 \text{ kWh m}^{-3}$ with a payback period of 7 years, which is similar to what is expected for renewable energy projects. In addition, it was found that while adding additional forms of pretreatment adds an additional capital cost, these costs can be offset using renewable energy credits. These projections indicate that both sites warrant further analysis, and that pretreatment protocols for these systems should be developed to see how effectively a PRO system could perform using the available water sources.

3. What effect does membrane spacer geometry have on PRO membrane hydraulic performance, and how can it be improved?

In Chapter 4, a tradeoff was identified between reducing pressure drop in the feed side of the membrane versus increasing salt and fluid transport across the membrane. A decreased pressure drop occurs with larger stranded parallel spacers, while an increased mass transfer rate occurred with medium-sized diagonally oriented spacers. Concentration polarization also seemed to be impacted by spacer geometry, with regularly distributed geometries having less CP. It was recommended that spacer manufacturers should emphasize keeping the spacer strands more linear by decreasing the length of the sloped section of the thin cross-strand. This is because distortions to the streamline caused by differences in the thickness of the thin cross strand are what ultimately interrupt the flow paths and cause an enhanced pressure drop in the system. These improvements could ultimately improve the efficiency of PRO systems, as it would reduce the overall energy demand drawn by the feed pump, which in turn increases the net energy generation potential.

4. What effect does membrane spacer geometry and pretreatment have on bio and organic fouling rates and the net energy density of the system?
In Chapter 5, it was found that pretreating the water with UV combined with the 31D spacer was the most effective configuration, as it had both the lowest degradation in filtration effectiveness over time with 79.6% remaining effectiveness at 36.5 hours, as well as the highest net power generation potential. If this configuration were to be run at ideal pressure levels, the projected power generation potential increases to 12.53 kWh over a 36.5-hour period, with a feed influent flow rate \(Q_{F-in}\) of 1.18 \(m^3\ hr^{-1}\) and a specific energy of 0.24 \(kWh\ m^{-3}\) of mixed solution, which is similar in magnitude to the maximum specific energy level predicted in Chapter 2, which was 0.25 \(kWh\ m^{-3}\). This also indicates that with proper pretreatment and operational conditions, a PRO system can perform at high enough efficiency to match the performance of a large \(Q_{F-in} = 733.89\ m^3\ hr^{-1}\) PRO system with a high transmission cost and no fouling decay included, or a medium-sized \(Q_{F-in} = 335.39\ m^3\ hr^{-1}\) PRO system with minimal transmission costs and no fouling decay included. In addition, the fact that the large system with additional energetic costs due to transmission performs at a similar net specific energy level to the medium sized system with no transmission expenditures demonstrates the increased efficiency that can be gained by operating a larger-scaled system.

Finally, the answer to the main question, which was “Under what cases is PRO a viable form of energy recovery and brine management for desalination?”, is that PRO has the potential to be an economically viable form of energy recovery and brine management for seawater desalination. This is as long as it is implemented using a pressure and foulant resistant integrated membrane/spacer pairing combined with source streams that require minimal pretreatment in regions where seawater desalination plants are co-located with wastewater plants and/or have high energy prices.
6.3 Scientific Contributions

The scientific contributions from this dissertation can be broken down into three main categories: Publications/presentations, software, and hardware.

In terms of publications, Chapter 2 was published in the journal *Desalination*, while Chapter 3 was published in the Conference Proceedings for the 2019 International Water Conference. Chapter 4 has been submitted for publication in the *Journal of Membrane Science*, and Chapter 5 is in preparation for publication. In addition, the material from this dissertation will also be published and presented in a report to the Bureau of Reclamation’s Desalination and Water Purification Research Program, as part of Cooperative Agreement Number R19AC00100. The work from this dissertation has been presented at the following venues: as an oral presentation at the 18th Annual Meeting of the American Ecological Engineering Society in Houston TX; as a poster at the 2018 AEESP Distinguished Lectureship Workshop in Tampa, FL; as an oral presentation at the 2019 McKnight Mid-Year Research and Writing Conference in Tampa, FL; as an oral presentation at the 2019 AEESP Research and Education Conference at ASU in Tempe, AZ; as an invited oral presentation at the 2019 International Water Conference in Orlando, FL; as a poster presentation at the 2019 AEESP Distinguished Lectureship Workshop in Gainesville, FL; as a virtual oral presentation at the 2020 International Congress on Membranes and Membrane Processes; as a virtual poster presentation at the 2021 USF Graduate Research Symposium where it won first place; as a poster presentation at the 2021 GEM Annual Board Meeting and Conference in Houston Texas where it won third place; and it will be presented virtually as an oral presentation at the 2021 International Conference on Desalination using Membrane Technology.

In terms of software contributions, Propmod, which is the model used in Chapters 2 and 3 is available for download for free from GitHub at [https://github.com/drizdar/Propmod](https://github.com/drizdar/Propmod). In addition,
the custom OpenFOAM PRO membrane boundary conditions and solver used in Chapter 4 are available for download at https://github.com/drizdar/proFoam, and the DAKOTA optimization algorithm used in Chapter 4 and an OpenFOAM example case are also available for download at https://github.com/drizdar/OpenFOAM-GA-Optimizer. All software packages were built using 100% Open-Source software and are licensed under an MIT License. In addition, scripting files used in recording and post-processing the data generated by the PRO skid are available internally on Box for future USF students to use.

Finally, the main hardware/physical contribution from this dissertation was the PRO skid itself, which is located in the IDR107 Lab at USF. The skid is designed to test PRO, RO, and FO processes, and can run processes at constant temperature and flow conditions at up to 68.9 bar (1000 psi) of pressure on the draw side (note that the max the system has currently been ran at is 16 bars). The skid is fully equipped with sensors, and can log salinity, pressure on both the membrane inlet and outlet, and the outlet flow rate for both the draw and feed side of the membrane. In addition, there is a scale on the feed side that can track the change in mass over time, which can be used to track the mass flow rate of the system, with the sensors currently configured to log data every fifteen seconds. The system is described in full in the methods sections of Chapters 4 and 5.

6.4 Recommendations and Future Work

Based on the results from this dissertation, there are three main thrusts that the future work can be divided into: conducting additional physical experiments, integrating fouling processes and additional water quality variables into the predictive models, and conducting more in-depth comparative analyses against alternative brine management and energy recovery technologies.
On the experimental side, it is recommended that future experimental work focus on performing duplicate studies at different operating pressures to see how PRO membranes perform under varying pressure loads, and how the system performs at the optimal point identified in Chapter 5. It is also recommended that long-term operational studies be conducted to see how a PRO system performs over a long period of time under multiple backwashing cycles. In addition, it is recommended that future efforts focus on bench and pilot-scale testing using brine and wastewater effluent samples from the St. Thomas and Santa Barbara plants to gain additional data on how the various pretreatments perform with variations in influent water quality, as well as to see how a PRO system would perform in those two locations. If it is found that these systems can be operated without extensive pretreatment, then the estimates presented in Chapter 3 should be accurate, which would open the door towards eventual implementation of a full-scale PRO system.

On the modeling side, future work should involve improving the chemical processes in both Propmod and the CFD model to better determine whether pretreatment is necessary, and what form of pretreatment is required by incorporating raw water quality parameters such as pH, dissolved minerals, carbon substrate (for biofouling), nutrients, and dissolved oxygen. By adding a more comprehensive water quality analysis as well as the long-term effect of fouling, model predictions will be more realistic and better suited for predicting overall system costs and performance. It is hoped that the continued development of both Propmod and enhanced understanding of both PRO and foulant prevention processes will help kickstart the implementation of PRO around the world.

On the technical analysis side, a more comprehensive technical comparison with other forms of brine management and energy recovery are needed in order to better recommend potential locations for PRO implementation. While PRO was compared with other renewable energy
technologies in terms of $\dfrac{kWh}{\text{m}^2}$, these comparisons were made using generalized costs for the United States, which may vary depending on local factors such as resource and land availability. In addition, PRO needs to be compared with other brine management technologies and end of use options to ensure it is the best usage case for the concentrated brine. The other options it could be compared against include deep-well injection, wide-spread dispersion using pressurized dispersion nozzles in receiving water bodies, being converted to acid and base products using bipolar membrane electrodialysis or being mined for scarce metals using thermal evaporation (Jones et al., 2018). These additional experiments and analyses can inform a geospatial analysis to identify locations around the world where PRO would be suitable from a technical, economic, and environmental impact perspective. Thereafter, pilot-scale studies using a pass-through system are recommended at feasible locations for the eventual transition to a full-scale implementation of PRO to ultimately augment the performance of seawater desalination systems.


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Appendix A: Terminology Guide

A.1 Nomenclature

A  
water permeability coefficient \([L \ m^{-2} \ hr^{-1} \ bar^{-1}]\)

\(A_m\)  
membrane area \([m^2]\)

\(Alk\)  
alkalinity \([mg \ L^{-1} \ CaCO_3]\)

\(b\)  
fitted pretreatment decay coefficient \([-\] \]

\(B\)  
salt permeability coefficient \([L \ m^{-2} \ hr^{-1}]\)

BC  
bacterial count [MPN - most probable number]

c  
solute concentration \([g \ kg^{-1}]\)

\(Cms\)  
cost per m\(^2\) of membrane \([\$ \ m^{-2}]\)

\(COD\)  
chemical oxygen demand \([mg \ L^{-1}]\)

d  
transmission pipe diameter \([m]\)

\(d_h\)  
hydraulic diameter \([m]\)

\(D\)  
diffusion constant \([m^2 \ s^{-1}]\)

\(DO\)  
dissolved oxygen \([mg \ L^{-1}]\)

\(E\)  
energy recovered by the system per year \([MWh \ yr^{-1}]\)

\(Ef\)  
pretreatment effectiveness \([\%]\)

\(EP\)  
energy price \([\$ \ kWh^{-1}]\)

\(ERP\)  
energy recovery percentage \([\%]\)

\(f\)  
Colebrook friction factor \([-\] \]

\(f_o\)  
objective function \([-\] \]
\(g\) acceleration due to gravity \([m \ s^{-1}]\)

\(h\) height \([m]\)

\(H\) pump head \([m]\)

\(Hd\) Hardness \([mg \ L^{-1} \text{CaCO}_3]\)

\(i\) Van’t Hoff factor \([-\]\)

\(J_S\) reverse solute flux \([g \ L \ m^{-2} \ hr^{-1} \text{kg}^{-1} \text{or} \ mMol \ m^{-2} \ hr^{-1}]\)

\(J_w\) water flux \([L \ m^{-2} \ hr^{-1}]\)

\(k\) mass transfer coefficient \([L \ m^{-2} \ hr^{-1}]\)

\(kf\) fitted pretreatment decay coefficient \([hr^{-1}]\)

\(K\) diffusion resistivity \([hr \ m^{-1}]\)

\(L\) transmission pipe length \([m]\)

\(m\) fitted pretreatment decay coefficient \([-\]\)

\(M\) molecular weight \([mol \ L^{-1}]\)

\(OT\) Annual plant operation time \([\% \ yr^{-1}]\)

\(p\) hydraulic pressure \([bar]\)

\(\Delta p_d\) pressure drop \([bar]\)

\(pH\) potential/power of hydrogen \([-\]\)

\(P\) power \([kW \text{or} \ MW]\)

\(Q\) flow rate \([m^3 \ s^{-1} \text{or} \ L \ hr^{-1}]\)

\(r\) interest rate \([\%]\)

\(R\) ideal gas constant \([kWh \ mol^{-1} \ k^{-1}]\)

\(R^2\) coefficient of determination \([-\]\)

\(s\) discrete membrane element \([m^2]\)
$S$  membrane structural parameter [$\mu m$]

$SE$  specific energy [$kWh m^{-3}$]

$t$  time [$hr$]

$T$  water temperature [$K$]

$Tr$  turbidity [$NTU$ - Nephelometric Turbidity Unit]

$U$  velocity [$m s^{-1}$]

$V$  volume [$L$]

$V_{SP}$  present value of energy cost savings [$S$]

$V_{NP}$  net present value of energy cost savings [$S$]

$w$  width [$m$]

$W$  power density [$W m^{-2}$]

$x$  discrete membrane element [$m$]

$z$  elevation [$m$]

$\lambda$  friction coefficient [–]

$\eta$  hydraulic efficiency [%]

$\nu$  kinematic viscosity [$m^2 s$]

$\pi$  osmotic pressure coefficient [bar]

$\rho$  density [$kg L^{-1}$ or $kg m^{-1}$]

**A.2 Subscripts**

$adj$  adjusted for the change in salinity gradient

$calc$  calculated

$Circ$  represents the circulation component

$D$  draw-side
eff effluent

elem represents an individual membrane element

F feed-side

gross represents gross quantities

Gen represents the turbine generation component

in influent

max maximum

memb represents the PRO membrane component

M mixed (draw side + feed side)

n normalized

net represents net quantities

o observed values

Perm RO permeate

PV represents an individual membrane pressure vessel

PT represent the pretreatment component

s simulated values

skid represents an individual membrane skid

Tot represents the entire system

Tra represents the transmission component

A.3 Abbreviations

AS antiscalant

CP concentration polarization

CFD computational fluid dynamics
CTA  cellulose tri-acetate
ECP  external concentration polarization
EDS  energy dispersive spectroscopy
ETD  Everhart Thornley Detector
HCWWTP  Howard F. Curren Wastewater Treatment Plant
ICP  internal concentration polarization
LL  Length Large
LFD  Large Field Detector
LSec  Length Section
LSlp  Length Slope
MF  microfiltration
MGD  million gallons daily
PLC  programmable logic controller
PSA  particle size allowance
PRO  pressure retarded osmosis
RL  Radius Large
RO  reverse osmosis
ROC  reverse osmosis concentrate
RS  Radius Small
SCRWWTP  South County Regional Wastewater Treatment Plant
SEM  scanning electron microscopy
SOGA  single objective genetic algorithm
SROC  synthetic reverse osmosis concentrate
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<td>SW</td>
<td>seawater</td>
</tr>
<tr>
<td>SWW</td>
<td>synthetic wastewater treatment plant effluent</td>
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<td>T</td>
<td>Thickness</td>
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<td>TBSDP</td>
<td>Tampa Bay Seawater Desalination Plant</td>
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<td>TFC</td>
<td>thin film composite</td>
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<td>TSS</td>
<td>total suspended solids</td>
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<td>UV</td>
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</tr>
<tr>
<td>VFD</td>
<td>variable frequency drive</td>
</tr>
<tr>
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<td>wastewater treatment plant effluent</td>
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<td>wastewater treatment plant</td>
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Appendix B: Software Availability

Propmod, which is the model used in Chapters 2 and 3, was coded in Python 3.7 and is licensed under an MIT License. It is available for download for free from GitHub at https://github.com/drizdar/Propmod.

The custom OpenFOAM PRO membrane boundary conditions and solver used in Chapter 4 are available for download at: https://github.com/drizdar/proFoam. The DAKOTA optimization algorithm used in Chapter 4 and an OpenFOAM example case are available for download at: https://github.com/drizdar/OpenFOAM-GA-Optimizer. Both software packages are licensed under an MIT License.
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A techno-economic process model for pressure retarded osmosis based energy recovery in desalination plants
Author: Joshua Benjamin, Mauricio E. Arias, Qiong Zhang
Publication: Desalination
Publisher: Elsevier
Date: 15 February 2020
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Appendix D: Supplementary Material for Chapter 2

D.1 Membrane Solution Algorithm and Input Data

Due to the non-linear nature of these equations, a multi-faceted approach was used to solve for counter-current flow configurations, which can be visualized in Figure D.1.

Figure D.1 Solution algorithm for solving the membrane flow fields. The algorithm begins by solving an optimized co-current flow field, which attempts to exhaust the overall salinity potential salinity gradient by varying the feed solution flow. Once the co-current field is solved, the algorithm then uses the flow rates from the co-current field to solve the counter-current field. If the counter-current field encounters a flow reversal during the solution process, then the co-current solution is used and $SysCon$ is set to 0. If the counter-current field can be successfully solved, then $SysCon$ is set to 1.
The first step was to solve Equations 2.1A-D (the co-current flow fields), and then use them as inputs into the counter-current flow fields (reverse the polarity of Equation 2.1B and 2.1D). If the starting value for $J_S$ was greater than the starting value for $J_w$, than the results from the co-current trial were accepted, since having a $J_S$ greater than $J_w$ would lead to an error when calculating the countercurrent equations. This is because of the non-linear nature of the $J_w$ equation, which necessitates using a root-finding method in order to converge at an appropriate solution. Since $J_w$ was solved for using the Brent Method (Brent, 1974), the final value of $J_w$ must be greater than 0 for the algorithm to converge. Furthermore, if the water flux approached zero in the counter-current configuration before the entire solution could be solved, then it was assumed that there would be a flow-reversal in the chamber and the results from the counter-current trials were voided and the co-current results were accepted. Trials that had a flow reversal can be identified using the $SysCon$ variable, where a $SysCon$ value of 0 means that there was a flow reversal within the counter-current configuration, and so the solution for the co-current configuration was used instead. This was done using check functions (is $cF$ ever <-0.05 and is $cF[end]$ within 10% of $cFchk$ and is $QF[end]$ within 50% of $QFchk$) which were calibrated to revert to the co-current solution if the value of $J_w$ was approaching 0.
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<td>5.364E-6</td>
<td>3.32E-4</td>
<td>0.77</td>
<td>4.08</td>
<td>TFC</td>
<td>Y_11_5</td>
</tr>
<tr>
<td>(Yip et al., 2011)</td>
<td>138.6</td>
<td>5.364E-6</td>
<td>3.16E-4</td>
<td>0.61</td>
<td>3.16</td>
<td>TFC</td>
<td>Y_11_6</td>
</tr>
<tr>
<td>(Yip et al., 2011)</td>
<td>138.6</td>
<td>5.364E-6</td>
<td>3.27E-4</td>
<td>5.45</td>
<td>7.55</td>
<td>TFC</td>
<td>Y_11_7</td>
</tr>
<tr>
<td>(Yip et al., 2011)</td>
<td>138.6</td>
<td>5.364E-6</td>
<td>3.36E-4</td>
<td>4.12</td>
<td>7.35</td>
<td>TFC</td>
<td>Y_11_8</td>
</tr>
<tr>
<td>(Yip et al., 2011)</td>
<td>138.6</td>
<td>5.364E-6</td>
<td>4.16E-4</td>
<td>3.86</td>
<td>7.76</td>
<td>TFC</td>
<td>Y_11_9</td>
</tr>
<tr>
<td>(Chou et al., 2012)</td>
<td>12.2</td>
<td>5.328E-6</td>
<td>4.60E-4</td>
<td>0.14</td>
<td>3.32</td>
<td>TFC</td>
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</tr>
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<td>(She et al., 2012)</td>
<td>12.06</td>
<td>5.796E-6</td>
<td>4.80E-4</td>
<td>0.63</td>
<td>0.749</td>
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<tr>
<td>(She et al., 2012)</td>
<td>4.21</td>
<td>5.796E-6</td>
<td>1.38E-3</td>
<td>0.07</td>
<td>0.436</td>
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<td>(She et al., 2012)</td>
<td>9.83</td>
<td>5.796E-6</td>
<td>5.90E-4</td>
<td>0.28</td>
<td>0.367</td>
<td>CTA</td>
<td>S_12_3</td>
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<tr>
<td>(Chou et al., 2013)</td>
<td>8.73</td>
<td>5.328E-6</td>
<td>6.10E-4</td>
<td>0.24</td>
<td>1.52</td>
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<td>C_13_1</td>
</tr>
<tr>
<td>(Han et al., 2013)</td>
<td>76.7*</td>
<td>5.210E-6</td>
<td>9.87E-4</td>
<td>0.13</td>
<td>1.40</td>
<td>TFC</td>
<td>H_13_1</td>
</tr>
<tr>
<td>(Han et al., 2013)</td>
<td>76.7*</td>
<td>5.321E-6</td>
<td>7.45E-4</td>
<td>0.41</td>
<td>1.70</td>
<td>TFC</td>
<td>H_13_2</td>
</tr>
<tr>
<td>(Han et al., 2013)</td>
<td>76.7*</td>
<td>5.331E-5</td>
<td>7.76E-4</td>
<td>0.48</td>
<td>1.90</td>
<td>TFC</td>
<td>H_13_3</td>
</tr>
<tr>
<td>(Song et al., 2013)</td>
<td>76.7</td>
<td>5.328E-6</td>
<td>1.49E-4</td>
<td>0.28</td>
<td>1.23</td>
<td>TFC</td>
<td>S_13_1</td>
</tr>
<tr>
<td>(Song et al., 2013)</td>
<td>76.7</td>
<td>5.328E-6</td>
<td>1.35E-4</td>
<td>1.19</td>
<td>3.82</td>
<td>TFC</td>
<td>S_13_2</td>
</tr>
<tr>
<td>(Song et al., 2013)</td>
<td>76.7</td>
<td>5.328E-6</td>
<td>1.40E-4</td>
<td>3.86</td>
<td>5.31</td>
<td>TFC</td>
<td>S_13_3</td>
</tr>
<tr>
<td>(Achilli et al., 2014)</td>
<td>99*</td>
<td>5.328E-6*</td>
<td>3.10E-4</td>
<td>0.09</td>
<td>5.11</td>
<td>TFC</td>
<td>A_14_1</td>
</tr>
<tr>
<td>(Straub et al., 2014b)</td>
<td>99</td>
<td>5.328E-6</td>
<td>5.64E-4</td>
<td>0.39</td>
<td>2.49</td>
<td>TFC</td>
<td>S_14_1</td>
</tr>
<tr>
<td>(Altaee et al., 2016)</td>
<td>306</td>
<td>6.250E-6</td>
<td>8.00E-4</td>
<td>0.40</td>
<td>0.67</td>
<td>CTA</td>
<td>A_16_1</td>
</tr>
</tbody>
</table>

Note: values with an * are estimated by copying from another membrane with similar properties. CTA is cellulose triacetate, while TFC is polyamide thin-film composite.
D.2 Hydraulic Equations

To calculate the energy used in transporting the WWTP effluent, the energy equation is used:

\[ H = (z_2 - z_1) + \left( f \left( \frac{L}{d} \right) + k_{L,tot} \right) \left( \frac{V^2}{2g} \right) + \frac{p_{base}}{\rho g} \]  \hspace{1cm} (D.1)

where \( H \) [m] is the amount of pump head necessary, \( z_1 \) and \( z_2 \) are the elevations of the WWTP and the desalination plant [m], \( f \) is the friction factor, \( L \) is the pipe length [m], \( d \) is the pipe diameter [m], \( k_{L,tot} \) is the sum of the loss coefficients, \( V \) is the velocity \([m \, s^{-1}]\), \( g \) is the acceleration due to gravity \([m \, s^{-2}]\), \( \rho \) is density \([kg \, m^{-3}]\), and \( p_{base} \) is the minimum system pressure \([Pa]\). For this case, it is assumed that \( V = Q \ell / A_{pipe} \), and that it remains constant on both sides. The \( k_L \) coefficients are tabulated in Propmod and are sourced from (Young et al., 2012). The friction factor \( f \) can be solved for using the Colebrook equation:

\[ \frac{1}{\sqrt{f}} = -2 \log \left( \frac{k_s / d}{3.7 \times 1000} + \frac{2.51}{Re \sqrt{f}} \right) \] \hspace{1cm} (D.2)

where \( Re \) is the Reynold’s number, and \( k_s \) is the pipe roughness coefficient [m]. Values of \( k_s \) are coded into Propmod and were collected from various sources (Chadwick and Morfett, 1998; Young et al., 2012).

D.3 Validation Equations

Below are the equations used for model validation. In the first three equations (D.3, D.4, and D.5) \( W \) is the tested value (power density – note that since \( W = \Delta p \ast J_w \), for similar \( \Delta p \)'s \( W \) and \( J_w \) will have the same variance), \( n \) is the number of values compared, the subscript o is for observed values, and the subscript s is for simulated values. \( NS \) values (Equation D.3) range from negative infinity to 1, with values from 0 to 1 deemed to be acceptable.
\[ NS = 1 - \frac{\sum_i(W_o - W_z)_i^2}{\sum_i(W_o - \bar{W}_o)^2} \] (D.3)

RSR values (Equation D.4) range from 0 to larger positive values, with values closer to zero being better.

\[ RSR = \sqrt{\frac{\sum_{i=1}^{n}(W_o - W_z)_i^2}{\sum_{i=1}^{n}(W_o - \bar{W}_o)^2}} \] (D.4)

MSE values (Equation D.5) range from 0 to infinity, with lower values being better, and a value of 0 representing a perfect fit.

\[ MSE = \frac{1}{n} \sum_{i=1}^{n} (W_o - W_z)_i^2 \] (D.5)

The thermodynamic maximum for the reversible processes is:

\[ SE_{Max,RP} = \left[ \exp \left( \frac{c_D \ln(c_D) - c_F \ln(c_F)}{c_D - c_F} - 1 \right) - \frac{c_D c_F}{c_D - c_F} (\ln(c_D) - \ln(c_F)) \right] iRT \] (D.6)

where \( i \) is the Van’t Hoff factor for NaCl, \( T \) is temperature [K], and \( R \) is the ideal gas constant [kWh mol\(^{-1}\) K\(^{-1}\)]. For a co-current configuration, the maximum specific energy is:

\[ SE_{Max,CoCur} = \left[ \frac{(\sqrt{c_D} - \sqrt{c_F})^2}{4} \right] iRT \] (D.7)

Likewise, for a counter-current configuration, the maximum specific energy is:

\[ SE_{Max,CntCur} = \left[ \frac{1 (c_D - c_F)^2}{4 (c_D + c_F)} \right] iRT \] (D.8)

In the previous three equations, \( c_D \) and \( c_F \) represented initial concentrations with units of [mol m\(^{-3}\)]. To convert \( c_D \) and \( c_F \) from [g kg\(^{-1}\)] to [mol m\(^{-3}\)], they were multiplied by the density of saltwater, which was calculated using the method from (Millero and Poisson, 1981), and then divided by the molar mass of NaCl.
## D.4 Sensitivity Analysis Inputs

Table D.2  Range of variation for model parameters in sensitivity and uncertainty analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Range of Values</th>
<th>Unit</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Transfer Coefficient</td>
<td>( k )</td>
<td>76.7–138.6</td>
<td>( \text{L} \text{m}^{-2} \text{h}^{-1} )</td>
<td>(Song et al., 2013; Yip et al., 2011)</td>
</tr>
<tr>
<td>Diffusion Constant</td>
<td>( D )</td>
<td>5.210E-6–5.364E-6</td>
<td>( \text{m}^2 \text{h}^{-1} )</td>
<td>(Han et al., 2013; Yip et al., 2011)</td>
</tr>
<tr>
<td>Structural Parameter</td>
<td>( S )</td>
<td>1.49E-4–9.87E-4</td>
<td>( \text{m} )</td>
<td>(Han et al., 2013; Song et al., 2013)</td>
</tr>
<tr>
<td>Salt Permeability</td>
<td>( B )</td>
<td>0.08–0.88</td>
<td>( \text{L} \text{m}^{-2} \text{h}^{-1} )</td>
<td>(Yip et al., 2011)</td>
</tr>
<tr>
<td>Water Permeability</td>
<td>( A )</td>
<td>1.23–5.81</td>
<td>( \text{L} \text{m}^{-2} \text{h}^{-1} )</td>
<td>(Achilli et al., 2014; Song et al., 2013)</td>
</tr>
<tr>
<td>Turbine Efficiency</td>
<td>( \eta_{\text{Geo}} )</td>
<td>85–99</td>
<td>%</td>
<td>(Feinberg et al., 2015; Stover, 2005)</td>
</tr>
<tr>
<td>WWTP Elevation</td>
<td>( z_1 )</td>
<td>2–20</td>
<td>( \text{m} )</td>
<td>(USGS, 2019)</td>
</tr>
<tr>
<td>Desalination Plant Elevation</td>
<td>( z_2 )</td>
<td>0–4</td>
<td>( \text{m} )</td>
<td>(USGS, 2019)</td>
</tr>
<tr>
<td>Transmission Pipe Length</td>
<td>( L )</td>
<td>0–23,500</td>
<td>( \text{m} )</td>
<td>(USGS, 2019)</td>
</tr>
<tr>
<td>Transmission Pipe Diameter</td>
<td>( d )</td>
<td>0.1–1</td>
<td>( \text{m} )</td>
<td>(Quiroga et al., 2007)</td>
</tr>
<tr>
<td>Draw Flow Rate*</td>
<td>( Q )</td>
<td>0.20–0.83</td>
<td>( \text{m}^3 \text{s}^{-1} )</td>
<td>(EPRI, 2013)</td>
</tr>
<tr>
<td>Draw Concentration*</td>
<td>( c_D )</td>
<td>60–72</td>
<td>( \text{g kg}^{-1} ) [ppt]</td>
<td>(EPRI, 2013)</td>
</tr>
<tr>
<td>Feed Concentration*</td>
<td>( c_F )</td>
<td>0.02–0.06</td>
<td>( \text{g kg}^{-1} ) [ppt]</td>
<td>(FDEP, 2013; Kurihara and Hanakawa, 2013)</td>
</tr>
<tr>
<td>Energy Purchase Price</td>
<td>( EP )</td>
<td>0.08–0.34</td>
<td>( $ \text{ kWh}^{-1} )</td>
<td>(EPRI, 2013)</td>
</tr>
<tr>
<td>Annual Energy Price Change</td>
<td>( \Delta EP )</td>
<td>0.003–0.015</td>
<td>( $ )</td>
<td>(EPRI, 2013)</td>
</tr>
<tr>
<td>Interest Rate</td>
<td>( r )</td>
<td>1–5</td>
<td>%</td>
<td>(EPRI, 2013)</td>
</tr>
<tr>
<td>Annual RO Plant Operation Time</td>
<td>( OT )</td>
<td>60–100</td>
<td>% \text{yr}^{-1}</td>
<td>(EPRI, 2013)</td>
</tr>
<tr>
<td>Cost per m$^2$ of membrane</td>
<td>( C_{\text{ms}} )</td>
<td>5.80–14.18</td>
<td>( $ \text{ m}^{-2} )</td>
<td>(Helfer and Lemckert, 2015; Naghiloo et al., 2015)</td>
</tr>
<tr>
<td>Water Temperature</td>
<td>( T )</td>
<td>14.5–31.6</td>
<td>( ^\circ \text{C} )</td>
<td>(TBEP, 2019)</td>
</tr>
</tbody>
</table>

Note: *These ranges are for the ROC-WW scenarios. For the ROC-SW scenarios, \( c_D = 60–72 \) ppt and \( c_F = 27–35 \) ppt. For the SW-WW Scenarios, \( c_D = 27–35 \) ppt, and \( c_F = 0.02–0.06 \) ppt. **This range is for the ROC-WW and ROC-SW scenarios. For the SW-WW scenario, \( Q = 0.6–2.29 \text{ m}^3 \text{s}^{-1} \) to account for the larger range of flow from a WWTP.
Appendix E: Supplementary Material for Chapter 4

E.1 Physical Setup Graphic

Figure E.1  A) Diagram of the laboratory-scale Pressure Retarded Osmosis (PRO) system. The letter C represents the conductivity meters, which are located inside of the draw and feed tanks. The lower-case letters correspond to the individual instruments on the system pictured in B).
E.2 SOGA Solution Algorithm

The overall solution algorithm can be seen in Figure E2. GA first starts with a given population composed of a set of chromosomes (numeric vectors) that represent different potential case geometries with each membrane spacer measurement (a numeric value) inside of a chromosome represented as a gene (Ragsdale, 2011). Within the population, each case is then solved by first generating a mesh and then solving the CFD equations, and then chromosomes from each case are assigned a fitness value that pertains to the objective function, $f_o$. Next, the GA creates new chromosomes using crossover and mutation (C&M), with crossover being the probabilistic exchange of genes between chromosomes and mutation being the random replacement of genes within a chromosome and solves for the C&M population. Afterward, the solutions with the highest fitness value are selected from both the initial population and the C&M population and brought to the next generation, embodying the principle of “survival of the fittest”. This process repeats until either a set number of generations passes (in this case, 102), or the percent change/tolerance threshold (8%) is met based on the objective function.

Figure E.2 A description of the algorithm used for the optimization trials.
E.3 Experimental Time-series Graphs

Shown are the experimental time-series graphs for the 17D, 65D, 47P, and 47D spacers.

Figure E.3 Results from the 17D trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure E.4 Results from the 65D trial. Data shown is from when the draw pump is turned on to when it is turned off. There was a data gap in the beginning, which is why the initial spike in the draw flow is not fully shown. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure E.5  Results from the 47D trial. Data shown is from when the draw pump is turned on to when it is turned off. A). The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure E.6  Results from the 47P trial. Data shown is from when the draw pump is turned on to 2 hours into the 4th stage (this trial was run for 1 day and two hours to see how the system performs over extended periods. For the sake of comparison, the additional data was cut off). A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
E.4 Membrane Deformation Images

Figure E.7 The five used membranes, with the spacer patterns imprinted on the membrane surfaces. Images taken from the draw side, with the draw outlet/feed inlet located on the bottom. Note the additional deformation (the bulge) located on the bottom of the membrane used with the 47D spacer.
Appendix F: Supplementary Material for Chapter 5

F.1 Sample Collection Results

Table F.1 shows the water quality parameter and analysis methods of the samples collected. The ROC was collected from the Tampa Bay Seawater Desalination Plant, while the WW was collected at the Howard F. Curren Advanced Wastewater Plant, both in the Tampa Bay area.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>ROC</th>
<th>WW</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH [-]</td>
<td>7.75</td>
<td>7.61</td>
<td>Probe</td>
</tr>
<tr>
<td>$T \ [^\circ C]$</td>
<td>22</td>
<td>22</td>
<td>Probe</td>
</tr>
<tr>
<td>$c \ [\mu S \ cm^{-1}]$</td>
<td>73,300</td>
<td>1843</td>
<td>Probe</td>
</tr>
<tr>
<td>$c \ [ppt]$</td>
<td>54.14</td>
<td>1.00</td>
<td>Calculated</td>
</tr>
<tr>
<td>Na$^+$ [ppm]</td>
<td>25789.2</td>
<td>347.3</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>K$^+$ [ppm]</td>
<td>969.1</td>
<td>18.17</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>Ca$^{2+}$ [ppm]</td>
<td>1835.8</td>
<td>421.8</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>Mg$^{2+}$ [ppm]</td>
<td>3930.4</td>
<td>43.3</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>Cl$^-$ [ppm]</td>
<td>49614.2</td>
<td>173.6</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>NO$_2^-$ [ppm]</td>
<td>N.D.</td>
<td>0.1</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>NO$_3^-$ [ppm]</td>
<td>3.1</td>
<td>0.3</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>PO$_4^{3-}$ [ppm]</td>
<td>98.8</td>
<td>0.4</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>SO$_4^{2-}$ [ppm]</td>
<td>6459.5</td>
<td>439.3</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>Alk [mg L$^{-1}$ CaCO$_3$]</td>
<td>N.M.</td>
<td>203.2</td>
<td>Titration</td>
</tr>
<tr>
<td>Tr [NTU]</td>
<td>0.2</td>
<td>1.03</td>
<td>Turbidimeter</td>
</tr>
<tr>
<td>TSS [mg L$^{-1}$]</td>
<td>53.1</td>
<td>1.84</td>
<td>Gravity method</td>
</tr>
<tr>
<td>Total Cl$^-$ [mg L$^{-1}$]</td>
<td>N.M.</td>
<td>0.30</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>COD [mg L$^{-1}$]</td>
<td>67.92</td>
<td>13.02</td>
<td>Spectrophotometry</td>
</tr>
</tbody>
</table>

Alk stands for alkalinity. Tr stands for turbidity. TSS stands for total suspended solids. N.D. means not detected. N.M. means not measured. For ion chromatography, the ROC (reverse osmosis concentrate) was diluted using a 1:100 dilution ratio, while the WW (tertiary treated wastewater) was diluted using a 1:10 dilution ratio.
F.2 Simulated vs Physical Time-series Graphs

Presented below are the experimental time-series graphs for the remaining simulated vs physical comparison trials in the order in which the experiments were conducted.

Figure F.1 Results from the 31D - SROC - WW trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.2  Results from the 31D - ROC - WW trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.3  Results from the 31D - ROC - SWW trial. Data shown is from when the draw pump is turned on to when it is turned off. Note that the PLC became disconnected in the middle of the trial, which caused a data gap that was filled in using linear interpolation. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
F.3 Experimental Time-series Graphs

Presented below are the experimental time-series graphs for the remaining pretreatment trials in the order in which the experiments were conducted.

Figure F.4 Results from the 47P – No PT trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.5 Results from the 31D - UV trial. Data shown is from when the draw pump is turned on to when it is turned off. Note that the PC restarted itself at the beginning of the trial, which caused a data gap that was filled in using linear interpolation. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.6  Results from the 47P - UV trial. Data shown is from when the draw pump is turned on to when it is turned off. Note that the power in the building went out in the middle of the trial, which created a slight bump in the data since the system had to be restarted. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.7 Results from the 31D - MF trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.8  Results from the 47P - MF trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.9  Results from the 31D - MF - UV trial. Data shown is from when the draw pump is turned on to when it is turned off. Note that the draw and flow meters both became clogged, which caused the PLC’s to eventually short and continuously record the same data point until they could be manually restarted. The flow meters were then deconstructed and cleaned before the next trial started. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.10 Results from the 31D - AS trial. Data shown is from when the draw pump is turned on to when it is turned off. Note that the PC restarted itself at the beginning of the trial, which caused a data gap that was filled in using linear interpolation. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.11  Results from the 31D - UV - AS trial. Data shown is from when the draw pump is turned on to when it is turned off. Note that the PLC became disconnected in the middle of the trial, which caused a data gap that was filled in using linear interpolation. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.12  Results from the 47P - AS trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.13 Results from the 47P - MF - UV - AS trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.14  Results from the 47P - UV - AS trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.15 Results from the 31D - MF - AS trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.16 Results from the 47P - MF - AS trial. Data shown is from when the draw pump is turned on to when it is turned off. Note that the PLC became disconnected in the middle of the trial, which caused a data gap that was filled in using linear interpolation. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.17 Results from the 31D - MF - UV - AS trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
Figure F.18 Results from the 47P - MF - UV trial. Data shown is from when the draw pump is turned on to when it is turned off. A) The conductivity values on the draw and feed sides. B) The pressure values on the draw and feed inlet and outlet. C) The draw and feed pump flow rates after the membrane outlet, as well as the mass of the water in the feed tank.
F.4 Individual Adjusted Water Flux and Internal Pressure Drop Trends

Figure F.19 The individual trends for A) $J_{w\text{-adj}}$ and B) $\Delta p_F$ for the 31D and 47P spacers. The solid lines represent the 31D spacers and the dashed lines represent the 47P spacers. The curves are colored based on the individual pretreatments.