DEVELOPMENT AND ASSESSMENT OF A NOVEL OSMOTIC HEAT ENGINE FOR ENERGY GENERATION FROM LOW-GRADE HEAT

by
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ABSTRACT

Development of clean energy technologies that maximize efficiency and minimize resource consumption is a necessary component for a clean and secure energy future. The osmotic heat engine (OHE) is a closed-loop, membrane based process that utilizes low-grade heat and salinity-gradient energy between two streams for electrical energy generation. The OHE couples pressure retarded osmosis (PRO), an osmotically driven membrane process, with membrane distillation (MD), a thermally driven membrane process. In PRO, water permeates via osmosis through a semi-permeable membrane from a low concentration feed stream into a higher concentration brine (draw solution). The permeate stream becomes pressurized on the high concentration side of the membrane and a mechanical device (e.g., turbine generator set) is used to convert the hydraulic pressure to electrical energy. The MD process utilizes low-grade heat to reconcentrate the diluted brine from the PRO process and to produce a deionized water stream; these streams are then resupplied to the PRO process in the OHE. High power-density (power generated per unit area of membrane) of the PRO membrane is essential to maximize the efficiency and minimize the capital and operating costs of the OHE. Likewise, high separation efficiency is needed in the MD process to effectively reconcentrate the diluted draw solution. Thus, robust PRO membranes that can support high pressure, have high water flux, low reverse salt flux, low structural parameter, and a good membrane support structure are essential. The MD process must also be able to withstand high operating temperatures (> 60 °C) and feed water concentrations, and have low pore wetting propensity. Additionally, the use of highly soluble ionic organic and inorganic draw solutions can increase PRO power densities while achieving high MD water fluxes, thus increasing efficiencies and decreasing costs of OHE. Therefore, the objective of this dissertation is to develop and demonstrate at the laboratory scale and through modeling work a novel, closed-loop, hybrid membrane-based system that converts low-grade heat to electrical energy. The performance of several membranes used for PRO and the effect of spacer configuration on membrane performance was evaluated. The performance of MD in concentrating hypersaline brines was evaluated and scale mitigation techniques were investigated to restore water flux and sustain the desalination process. Several ionic organic and inorganic draw solutions were evaluated as working fluids in the OHE, and their performance was assessed in terms of PRO power density and reverse salt diffusion, and MD separation and thermal
efficiency and membrane pore wetting. The experimental data was used to develop a system model that evaluates system efficiency, net power output, and costs. Modeling results were used to perform an environmental life-cycle assessment using GaBi, a life-cycle assessment software. Although, at its current state of technology, OHE electricity generation costs ($0.48 per kWh) are not competitive with conventional U.S. grid energy costs ($0.04 per kWh), system environmental impacts are an order of magnitude lower. Furthermore, with future improvements to membrane technology and OHE process performance, electricity generation costs for the OHE as an energy storage device ($0.12 per kWh) could be comparable to on-peak demand charges in Southern California ($0.15 per kWh), thus making the OHE an attractive energy storage device.
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<td>Osmotic heat engine</td>
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<td>PRO</td>
<td>Pressure retarded osmosis</td>
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<td>MD</td>
<td>Membrane distillation</td>
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<td>DCMD</td>
<td>Direct contact membrane distillation</td>
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<tr>
<td>LGH</td>
<td>Low-grade heat</td>
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<tr>
<td>RSF</td>
<td>Reverse solute flux</td>
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<td>ICP</td>
<td>Internal concentration polarization</td>
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<td>CCPP</td>
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CHAPTER 1
INTRODUCTION

The osmotic heat engine (OHE) is a closed-loop, membrane-based cycle that utilizes osmotic pressure gradients and thermal energy (i.e., low-grade heat) to produce electrical energy. This system couples pressure retarded osmosis (PRO), an osmotically driven membrane process, with membrane distillation (MD), a thermally driven membrane process. In PRO, water permeates through a semi-permeable membrane from a low-concentration stream into a high-concentration stream, subsequently generating a mixed stream and a hydraulic pressure build-up. The mixed stream is then expanded through a hydroturbine and converted into electric energy. MD utilizes low-grade heat to regenerate the mixed stream into a high-concentration and low-concentration stream, which are resupplied to the PRO process.

1.1 Problem statement and significance

Water and energy are interdependent and are increasingly in demand in both developed and developing countries, mainly due to population growth and economic expansion. Accordingly, it is essential to develop advanced technologies that maximize energy production, minimize emissions, reduce water consumption, and lessen reliance on fossil-based energy resources. In 2013, energy consumption surmounted energy production in the U.S. (where the remaining energy resources were imported), and only 11% of the energy produced in the U.S. was from renewables [1]. Renewable energy resources from water, or blue energy, are abundant and dependable [2, 3]; they include hydropower, geothermal, wave, tidal, algae biofuel, and salinity gradient energy. Furthermore, development of energy storage technologies with rapid response times is an important aspect for managing electricity usage during periods of peak demand.

Osmotic power, or salinity gradient power, harnesses the energy of mixing between high and low salinity streams. PRO is an osmotically driven membrane process that can facilitate conversion of the energy of mixing to mechanical energy, which can then be converted to electrical energy [4-6]. In PRO, water permeates via osmosis through a semi-permeable membrane from a low concentration feed stream into a high concentration draw solution, thus becoming pressurized and diluting the draw solution. For PRO to produce net energy, the hydraulic pressure of the draw solution is lower than the osmotic pressure difference between the
draw solution and the feed, and as a result, the net driving force for transport of water (permeate stream) is from the feed to the draw solution. The energy in the pressurized, diluted draw solution can then be converted into electrical energy via a turbine-generator set. Power density is an important performance parameter in PRO and it is defined as the amount of power generated (in watts) per unit membrane area used.

Proposed configurations of PRO include stand alone PRO for energy recovery from mixing of low concentration (e.g., river water) and high concentration waters (e.g., Dead Sea, Great Salt Lake, or seawater) [4-11], PRO coupled with RO for low-energy desalination [12, 13], and PRO hybridized with a thermal distillation process for energy generation from low-grade heat [14-17]. However, several limitations inhibit open-loop PRO process performance, including feed water pre-treatment, membrane fouling, and inconsistent solution chemistries and temperatures [9, 18, 19].

MD is a unique membrane process that can simultaneously concentrate hypersaline brines and produce high-quality, distilled water. MD is a thermally driven membrane process in which the driving force for mass transfer of water is the partial vapor pressure difference across a microporous hydrophobic membrane. Thus, compared to hydraulic pressure and electric field driven membrane processes, MD is potentially minimally affected by increased salt concentrations [20]. In direct contact MD (DCMD), a warm feed stream (e.g., brine) and a cooler fresh water stream (e.g., deionized water) are in direct contact with the active and support side of the membrane, respectively [20]. In DCMD, water evaporates from the feed stream at the feed-pore interface on the feed side of the membrane, water vapors diffuse through the membrane pores, and ultimately they condense into the distillate stream at the distillate-pore interface on the support side of the membrane.

The OHE is a novel hybrid, closed-loop membrane based system that couples MD with PRO to produce electrical energy from otherwise unutilized low-grade heat (Figure 1.1). In the OHE, MD utilizes low-grade heat to separate a saline stream into low concentration and high concentration streams. The two streams are then supplied to a PRO subsystem, where the salinity gradient between the streams is converted into mechanical energy, which is then converted to electrical energy via a turbine generator-set. The diluted draw solution from the PRO process is then separated again in the MD subsystem. Because of non-ideal conditions in the PRO membrane, reverse permeation of solutes from the draw solution into the feed stream occurs.
(referred to as reverse solute flux (RSF)). In the OHE, solutes will accumulate in the feed stream, reducing the osmotic driving force in PRO, and thus decreasing OHE net energy generation. Therefore, to maintain a high osmotic driving force in the OHE, a portion of the PRO feed stream has to be bled to the MD feed stream for recovery of solutes and control of PRO feed chemistry. The gross electrical power output ($W_t$) of the system is the product of the PRO power density, PRO membrane area, turbine efficiency, and generator efficiency. The OHE net power output is the difference between the gross electrical power output and pumping energy demands (i.e., pumping of the low concentration and high concentration streams in PRO and MD). The OHE system efficiency is the ratio of the net electrical power output to the heat input ($Q_{in}$).

![Figure 1.1. Schematic of the closed-loop OHE with bleeding of the low concentration PRO feed stream into the high concentration MD feed solution.](image)

The OHE has several major benefits over open-loop PRO. The closed-loop OHE allows for control of solution chemistries and temperatures. Because no impurities are introduced to the system, there is no need for chemical cleaning or membrane backwashing. Also, the OHE can use low-grade heat emitted from industrial processes, thereby increasing energy utilization. Industrial processes account for nearly 30% of the total U.S. energy demand, of which 20-50% of the energy consumed is lost as low-grade heat in the form of hot exhaust gases, cooling water, and heat lost from hot equipment surfaces and heated products [21]. Therefore, the OHE can be
co-located with existing power plants or other industrial processes emitting low-grade heat (i.e., traditional power plants, geothermal power plants, chemical processing plants, breweries). Lastly, the OHE has the potential for energy storage, which can be beneficial for supplementing peak power demands.

Figure 1.2. Schematic of the OHE for (a) energy storage after MD and (b) energy storage after PRO. In scenario A (energy storage after MD), the MD subsystem operates continuously over a 24-hour period and the PRO subsystem operates during periods of peak demand. In scenario B (energy storage after PRO), the MD and PRO subsystems operate continuously over a 24-hour period. The dilute draw solution is stored in an elevated storage tank and released through a hydroturbine during periods of peak demand.

The OHE is unique in that it has the capability to store energy until it is needed during periods of peak demands. The system can be used for energy storage in one of two ways: energy storage after MD (Figure 1.2 (a)) or energy storage after PRO (Figure 1.2 (b)). In the first scenario, the system is designed to have a small MD subsystem operating 24 hours a day, separating a diluted draw solution from the PRO process (stored in a separate tank) into high concentration and low concentration streams, which are held in separate storage tanks. When
energy is needed, a larger PRO subsystem is put into operation, utilizing the energy of mixing of the two streams to produce electricity. The diluted draw solution from the PRO subsystem is then sent back to the mixed stream storage tank (MD feed). In the second scenario, smaller PRO and MD subsystems operate continuously for 24 hours; however, the diluted draw solution from the PRO subsystem is stored in an elevated storage tank; thus, the system acts as an osmotic pump. Once there is a demand for excess power, the stream in the elevated tank is released through a hydroturbine, similar to a hydropower plant.

Although the closed-loop PRO system offers many benefits, several process barriers must be explored and addressed to promote development of the OHE. Primarily, both MD and PRO are relatively new membrane processes and their integration is not fully studied or understood. Currently, MD and PRO membranes are not available on a broad commercial scale; hydrophobic microfiltration membranes are commonly used for MD [22] and PRO forward osmosis (FO) membranes are used in all PRO investigations [23]. The membranes used for PRO must be mechanically stable at high operating pressures. Recent studies have shown that the mechanical stability of PRO membranes can be increased when unique membrane spacers are used [24, 25]; however, poor selection of spacers can lead to a membrane shadow effect (reduced permeation of water through the membrane) and increased channel pressure drops in PRO membrane modules. Therefore, both PRO and MD must be evaluated at the laboratory-scale to further investigate the performance of currently available membranes and to optimize operating conditions for use in the OHE. PRO and MD experimental results can then be used to validate a system model that assesses the performance of the synchronized processes and calculates the net power output and process efficiency. This model must also consider the techno-economic potential and life-cycle impacts of the OHE as a more holistic approach to assessing and comparing the OHE to competing renewable energy technologies.

1.2 Objective and scope of work

The main objective of this dissertation is to experimentally evaluate the performance of both PRO and MD for application in the OHE. The results will be used to develop and validate system models to assess the techno-economic feasibility and environmental impacts of the OHE. The research objectives of the dissertation are described below.
1. Assess the current state of commercially available FO membranes in terms of water flux, power density, reverse solute flux, and mechanical strength for application in PRO, and evaluate the use of unique spacer configurations in PRO and their effect on mass transfer, module pressure drop, and net positive energy generation.

2. Evaluate the performance of MD for reconcentrating hypersaline draw solutions and recovering distilled water for use in PRO, and investigate novel, chemical free scale mitigation techniques.

3. Evaluate ionic organic and inorganic draw solutions as working fluids in the OHE by assessing their performance in PRO (i.e., power densities and reverse solute diffusion) and MD (i.e., separation and thermal efficiency and potential for wetting).

4. Perform a techno-economic assessment of the OHE technology to market and its potential impact as a viable renewable energy generation and storage technology.

5. Perform a comparative life cycle assessment of the OHE process to competing technologies that convert low-grade heat to useful energy (e.g., Organic Rankine Cycle (ORC)).

The objectives of this research are met through the completion of five distinct studies. The focus of each study is on evaluating the performance of PRO and MD in the OHE as a potential technology for energy generation from low-grade heat.

1.3 Structure of dissertation

This dissertation investigates the closed-loop novel OHE as a potential clean energy generation and storage technology through experimental and modeling work, a techno-economic feasibility study, and an environmental life cycle assessment (LCA). This dissertation is comprised of five chapters. Chapter 2 is an experimental investigation of commercially available FO membranes and different spacers and spacer configuration for use in PRO and was submitted to the journal *Desalination* for the special issue on “Osmotic Power”. Chapter 3 is an experimental investigation on MD for concentration of hypersaline brines published in the *Journal of Membrane Science* and reprinted with copyright permission from Elsevier [26]. This chapter also resulted in a U.S. patent application [27]. The publication reproduction agreement granted by the publishing company and multiple author release agreement signed by all co-authors for this paper is provided in the appendix of this dissertation. Chapter 4 investigates the
performance of novel draw solutions in PRO and MD for use in the OHE. This chapter is currently under internal review for publication and will be submitted to the *Journal of Membrane Science*. Chapter 5 is a techno-economic assessment of the OHE as a continuous energy generation and storage device. This chapter is intended to be published in the journal *Energy and Environmental Science*. Chapter 6 is a comparative LCA evaluating the environmental impacts of the OHE and the ORC, a competing technology for energy generation from low-grade heat, and is intended to be published the journal *Energy*.

1.3.1 Experimental investigation of commercially available membranes and spacers for use in PRO

High PRO membrane power density is essential to maximize process efficiency and minimize the capital and operating costs of the OHE. Operating with high osmotic pressure draw solutions and at high hydraulic pressures can increase PRO power densities. Therefore, PRO membranes must be mechanically stable at high operating pressures, have high water flux (and hence power density), and low reverse solute flux. However, presently there are no commercially available membranes specific for PRO, so FO membranes are used. To date, little work has been done on comparing commercially available FO membranes for use in PRO. The use of unique membrane spacers can provide better support for the membrane against the high pressure and good flow passage in the membrane module. Furthermore, unique spacer configurations can increase mass transfer at the membrane interface, thus increasing power density. In addition to providing good mixing, membrane spacers must provide ample support to the membrane and adequate flow passage [25, 28-33]. Thus, further investigations on commercially available PRO membrane performance and spacer selection must be performed.

This chapter investigates the performance of different commercially available FO membranes for use in PRO. The effect of operating pressures, membrane spacers, and flow velocities were assessed for increased process performance. Of the commercial FO membranes tested, a thin film composite (TFC) membrane from Hydration Technology Innovations (HTI, Albany, OR) was found to be the most robust membrane and to have the highest selectivity. The use of unique spacers coupled with decreased draw solution cross-flow velocities was found to increase PRO process efficiency.
1.3.2 Evaluation of MD for concentration of hypersaline brines and novel operating techniques for scale mitigation

In the OHE, MD must be able to operate with highly concentrated feed solutions and withstand high operating temperatures so that high water fluxes can be obtained. Ideally, the MD feed solution in the OHE would be free of any scalants; however, due to natural impurities in salts, low solubility, scaling ions could be present in draw solutions and affect process performance. Scaling of sparingly soluble salts such as CaCO₃, CaSO₄, and silicates, has been identified as a cause of flux decline (e.g., via clogging of membrane pores) [34-41]. Scaling can alter membrane surface properties (i.e., hydrophobicity), change membrane pore structure, and ultimately decrease water flux. Furthermore, scaling can potentially lead to wetting of the membrane pores, which hinders water flux, lowers salt rejection, and impairs membrane integrity and performance. While membrane scaling has been extensively investigated in the literature [34-37, 42-48], effective scale mitigation techniques for maintaining and restoring water flux and salt rejection when desalinating saturated feed solutions are still lacking.

In Chapter 2, the performance of DCMD in simultaneously concentrating hypersaline brines and producing distilled water (supplied to PRO) was investigated, and operating conditions were improved to maximize water recovery and mitigate membrane scaling. DCMD was effective in concentrating hypersaline brines to greater than 350,000 mg/L (~6 M NaCl equivalent, operated at 50 °C). Operating DCMD at high feed temperatures (70 °C) compromised membrane performance (i.e., lowered salt rejection and water fluxes) because of membrane scaling and pore wetting. New scale mitigation techniques were developed to inhibit membrane scaling and wetting, thus sustaining high water fluxes and membrane performance. The new techniques are effective and simple to operate, and could be periodically employed for use in the OHE.

1.3.3 Assessment of alternative working fluid performance in the OHE

Highly soluble ionic organic and inorganic salts are expected to increase PRO power densities: thus, increasing OHE net power output. Although few studies have evaluated the potential of different draw solutions in PRO, the regeneration efficiency of these novel draw solutions with MD has not been investigated [49, 50]. Furthermore, the effect of RSF on OHE process performance has not been studied. In the OHE, the RSF is an indicator of the amount of
the PRO feed stream (low concentration stream) that needs to be drained or bled to the MD feed solution (high concentration stream) for desalination of the PRO feed stream and recovery of PRO draw solution solutes. The higher the portion of the PRO feed stream bled to the MD feed stream, the more MD membrane area required to reconcentrate the diluted draw solution from the PRO and the more pumping energy is needed to circulate the streams. Therefore, salts with high specific RSF can be unfavorable to OHE system costs.

In Chapter 3, the performance of eight organic ionic and inorganic draw solutions was experimentally investigated in PRO and MD. Their performance was assessed in terms of PRO power density and RSF, and MD water flux and thermal efficiency. Potential pore wetting of the MD membrane was also evaluated. Results indicate that several salts outperform NaCl (commonly used PRO draw solution) in terms of PRO power density and RSF, and in terms of MD water flux. Furthermore, there were no signs of MD membrane wetting, even at high feed concentrations. Results were used to perform an economic analysis and make future recommendations on the most suitable working fluid for the OHE.

1.3.4 Techno-economic assessment of the OHE for energy generation from low-grade heat

A key consideration when developing the OHE is to maximize net power output and minimize electricity generation costs. Although the OHE is in the early stages of development, prospective generation costs must be evaluated and compared with competing processes. The ORC is the benchmark technology, and the only commercially available technology that utilizes low-temperature, low-grade heat for electricity generation. Furthermore, the OHE market potential must be critically assessed.

The objective of Chapter 4 is to evaluate the technical and economic feasibility of the OHE as a continuous electricity generation and energy storage device. A system model was developed to evaluate system efficiency, net power output, and electricity generation costs. The system model integrates existing PRO and MD models and uses experimental data. A sensitivity analysis was performed to evaluate the influence of select model inputs, including MD operating temperatures and PRO power densities, on electricity costs. Results indicate that although OHE electricity costs ($0.48 per kWh) are not yet competitive with the ORC, further improvements to PRO membranes and MD modules would allow for the OHE to compete with existing energy generation and storage devices.
1.3.5 **Comparative environmental life cycle assessment of the OHE and ORC**

When coupled with conventional energy generation technologies, the OHE could increase process efficiencies and offer reduced emissions and environmental impacts. LCA is a tool employed to quantify environmental impacts associated with all stages of a system’s life (i.e., “cradle-to-grave”). LCA identifies key processes within a system that contribute to the largest environmental impacts. To take a more holistic approach in evaluating the OHE, a comparative LCA was performed.

The goal of Chapter 5 is to assess the environmental impacts of the OHE and compare them to the ORC and a conventional coal-fired power plant (CCPP) and natural gas-fired power plant (NGPP). Because the performance of the OHE is highly dependent on membrane performance, specifically PRO power density and MD water recovery, a sensitivity analysis on PRO membrane power density and MD operating temperatures was performed. The environmental impacts of the OHE were comparable to the ORC, and were an order of magnitude lower than CCPP and NGPP.

1.4 **References**


CHAPTER 2
ASSESSING THE CURRENT STATE OF COMMERCIALLY AVAILABLE MEMBRANES AND SPACERS FOR ENERGY PRODUCTION WITH PRO: AN EXPERIMENTAL INVESTIGATION
Submitted for potential publication in Desalination

Kerri L. Hickenbottom¹*, Johan Vanneste¹, Menachem Elimelech², and Tzahi Y. Cath¹*

2.1 Abstract
Pressure retarded osmosis (PRO) is an osmotically driven membrane process that utilizes the energy of mixing to generate electrical energy. High power density of the PRO membrane is essential to maximize process efficiency and minimize the capital and operating costs. Thus, robust PRO membranes that can support high pressure, have high water flux, low reverse salt flux, low structural parameter, and a good membrane support structure are essential. However, membranes specific for PRO are not commercially available, so forward osmosis (FO) membranes are used. Furthermore, little work has been done on comparing commercially available FO membranes for use in PRO. In this study, commercially available FO membranes were compared for use in PRO. The effect of operating pressures, membrane spacers, and flow velocities were assessed for increased process performance. Of the commercial FO membranes tested, a thin film composite (TFC) membrane from Hydration Technologies was found to be the most robust membrane and to have the highest selectivity. Compared to other spacer configurations, the use of unique feed channel spacer orientations was found to increase PRO power density by up to 46%, yielding a power density of 22.6 W m⁻² (3 M NaCl draw solution and 4.1 MPa of applied hydraulic pressure). However, membrane deformation was observed when operating pressures exceeded 3.5 MPa. The use of unique spacers coupled with decreased draw solution cross-flow velocities was found to increase PRO process efficiency.

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2.2 Introduction

Water and energy are interdependent and are increasingly in demand in both developed and developing countries, mainly due to population growth and economic expansion. Accordingly, it is essential to develop advanced technologies that maximize energy production, minimize emissions, reduce water consumption, and lessen reliance on fossil energy resources. In 2013, energy consumption exceeded energy production in the U.S. (where the remaining energy resources were imported), and only 11% of the energy produced in the U.S. was from renewables [1]. Renewable energy resources from water, or blue energy, are abundant and dependable [2, 3]; they include hydropower, geothermal, wave, tidal, algae biofuel, and salinity gradient energy.

Osmotic power, or salinity gradient power, harnesses the energy of mixing between high and low salinity streams. Pressure retarded osmosis (PRO) is an osmotically driven membrane process that can facilitate conversion of the energy of mixing to mechanical energy, which can further be converted to electrical energy [4-6]. In PRO, water permeates by osmosis through a semi-permeable membrane from a low concentration feed stream into a higher concentration brine (a.k.a. draw solution). The draw solution becomes diluted but is not allowed to spontaneously expand; thus, it is pressurized to a hydraulic pressure less than the osmotic pressure difference between the draw solution and feed. As a result, the net driving force for transport of water (permeate stream) remains in the direction of feed to the draw solution. The energy in the pressurized, diluted draw solution can then be converted into electrical energy via a turbine-generator set. Proposed configurations of PRO include stand alone PRO for energy recovery from mixing of low concentration (e.g., river water) and high concentration waters (e.g., Dead Sea, Great Salt Lake, or seawater) [4-11], PRO coupled with RO for low-energy desalination [12, 13], and PRO hybridized with a thermal distillation process for energy generation from low-grade heat [14-17].

The cost, selectivity, and robustness of PRO membranes have been identified as the main limitations for commercialization of osmotic power [10, 18]. Currently, commercial PRO membranes are not available; therefore, forward osmosis (FO) membranes are used in all PRO investigations [19]. Ideally, PRO membranes would demonstrate high water permeability and high selectivity. Membranes with high selectivity limit the transport and accumulation of draw
solution solutes in the feed solution, which would otherwise result in a lower driving force and lower energy recovery [20, 21].

Power density is an important performance parameter in PRO and it is defined as the amount of power generated (in watts) per unit membrane area used. In general, the maximum power density is determined by multiplying the water flux through the PRO membrane by the hydraulic pressure in the draw solution. Mathematically, the maximum power density for specific operating conditions occurs at an applied pressure equal to half of the osmotic pressure of the draw solution [22]. In order to achieve high PRO power density, internal and external concentration polarization (CP) [8, 18, 20, 21, 23-26]—two phenomena governing process performance in osmotically driven membrane processes—must be minimized. When water permeates from the low concentration feed to the high concentration draw solution, the draw solution at the draw solution-membrane interface becomes diluted and the osmotic pressure driving force across the membrane declines. This phenomenon is defined as external CP (ECP). Internal CP (ICP) in PRO is defined as the accumulation of salt in the membrane support structure, which also reduces the osmotic pressure driving force in PRO. Increased mixing and mass transfer at the feed and draw solution-membrane interfaces can reduce ECP. High cross-flow velocities and turbulence-enhancing spacers can be used to increase mixing; however, increasing flow velocities comes at the expense of increased pumping and pressure losses, which result in decreased net energy production.

High power density in PRO can also be generated by operating with high concentration draw solutions (i.e., high osmotic pressure) and thus high hydraulic pressures in the draw solution channels; therefore, PRO membranes must be mechanically stable at high operating pressures. Results from recent studies have shown increased mechanical stability of PRO membranes when feed-side tricot spacers (i.e., a densely woven mesh spacer typically used as a permeate carrier in reverse osmosis (RO) spiral wound membrane elements) are used [27, 28]. In addition to providing better support for the membrane against the high pressure in the draw solution channels, membrane spacers must provide good mixing and adequate flow passage, thus reducing energy loss induced by flow resistance in the PRO feed and draw solution flow channels (Figure 2.1) [28-34]. Poor selection of feed channel spacers can lead to increased feed channel pressure drops in PRO membrane modules and cause a membrane shadow effect (reduced effective membrane area and power density); both of which ultimately decrease net
power output. Therefore, additional research is needed to optimize PRO membrane performance and spacer selection.

**Figure 2.1.** Schematic of the PRO membrane flow cell with feed and draw solution spacers.

The main objectives of this study were to assess the performance of commercially available FO membranes for application in PRO and to evaluate key operating parameters for increased power density. Several commercial FO membranes were tested in PRO mode, and were evaluated in terms of water flux, reverse solute flux, power density, and mechanical integrity. Experiments were performed over prolonged periods of time to evaluate the effects of high operating pressures (up to 4.8 MPa (700 psi)) on membrane performance and mechanical stability. Finally, the use of unique spacer configurations and varying cross-flow velocities were evaluated in terms of their influence on PRO mass transfer, membrane cell pressure drop, and power densities.

**2.3 Materials and methods**

Four commercial FO membranes were tested in a bench-scale system for use in PRO. Different feed and draw solution spacer configurations and orientations and different flow rates were used to evaluate their effect on mass transfer and process performance, including salt flux and process efficiency.

**2.3.1 Membranes**

Commercial, semipermeable, flat-sheet FO membranes were acquired from Hydration Technology Innovation (HTI) (Albany, OR), Oasys Water (Boston, MA), and company X. Membranes from HTI, Oasys, and X are polyamide-based, thin-film composites (TFC), and one additional membrane from HTI is made of cellulose triacetate (CTA).
2.3.2 Determination of membrane properties

Membrane properties (Table 2.1) were experimentally determined using standard methods [35]. The HTI TFC and CTA membranes were pre-compacted with a 50 mM NaCl draw solution at 3.1 MPa (450 psi) until the flux stabilized. The Oasys and X TFC membranes were not pre-compacted because of their low operating pressures (1.0 MPa (150 psi)). The membrane water permeability (A) and salt permeability (B) were determined by performing experiments in a modified RO mode [34] using the PRO flow cell. The permeate stream (circulated in the PRO feed channel) was deionized water and the feed solution (circulated in the PRO draw solution channel) was 50 mM NaCl. The feed solution was pressurized at increasing pressure intervals of 690 kPa (100 psi) for high-pressure membranes (HTI TFC and CTA) and 340 kPa (50 psi) for low-pressure membranes (Oasys and X TFC). The mass transfer coefficient (k) was determined from the cell geometry, solution chemistries, spacer geometry, and operating flows [33]. Membrane burst pressure was found by closely monitoring the feed solution conductivity over each pressure interval, and the membrane was determined compromised when the feed solution conductivity sharply increased.

Table 2.1. Membrane water permeability (a), salt permeability (B), water/solute selectivity, structural parameter (S), and burst pressure for X, Oasys, and HTI membranes. The HTI TFC and CTA membranes were pre-compacted at 3.1 MPa.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>A, $10^{-2}$ L m$^{-2}$ hr$^{-1}$ kPa$^{-1}$</th>
<th>B, $10^{-2}$ L m$^{-2}$ hr$^{-1}$ kPa$^{-1}$</th>
<th>A/B</th>
<th>S, micron</th>
<th>Burst pressure, MPa (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>1.50</td>
<td>3.76</td>
<td>0.40</td>
<td>159</td>
<td>1.0 (150)</td>
</tr>
<tr>
<td>Oasys</td>
<td>1.94</td>
<td>1.99</td>
<td>0.97</td>
<td>274</td>
<td>1.0 (150)</td>
</tr>
<tr>
<td>HTI CTA</td>
<td>0.51</td>
<td>2.19</td>
<td>0.23</td>
<td>600</td>
<td>3.5 (500)</td>
</tr>
<tr>
<td>HTI TFC</td>
<td>1.63</td>
<td>1.42</td>
<td>1.15</td>
<td>295</td>
<td>4.8 (700)</td>
</tr>
</tbody>
</table>

2.3.3 Membrane cells

A stainless steel modified SEPA-CF II cell (GE Water & Process Technologies) was used in this study. The active surface area of the membrane in the cell is 139 cm$^2$, with a feed and draw solution flow channel depth of 1 mm. Viton O-rings were placed on the outer edge of the draw solution channel and outer perimeter of the cell to prevent leakage and cross contamination of the feed and draw solution streams. The feed and draw solution spacers were taped to the cell to prevent tearing of the membranes at the rims of the channels. Taping of the spacers decreased the effective membrane surface area to 124 cm$^2$. 
2.3.4 Feed and draw solution spacers

Tricot warp knit (Hornwood Inc., Lilesville, NC) and non-woven extruded mesh spacers were used in this investigation (Figure 2.2). The spacer properties are summarized in Table 2.2. The number of carrier channels per inch and thickness characterize tricot warp knit spacers.

![Figure 2.2](image-url) Picture of the (a) 35-channel tricot, (b) 20-channel tricot, and (c) extruded mesh spacer.

The extruded mesh spacers have square openings with a filament length of 3.24 mm. The spacer voidage was determined by a volumetric displacement method. A known amount of spacer area was submerged in deionized water. The voidage was determined by calculating the ratio of the volume of the free space in a spacer (through water displacement experiments) and the total spacer volume (known spacer area multiplied by total spacer thickness).

<table>
<thead>
<tr>
<th>Spacer name</th>
<th>Mesh Type</th>
<th>Thickness mm</th>
<th>Voidage %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-channel tricot</td>
<td>Warp knit</td>
<td>0.5</td>
<td>64</td>
</tr>
<tr>
<td>35-channel tricot</td>
<td>Warp knit</td>
<td>0.25</td>
<td>36</td>
</tr>
<tr>
<td>Diamond mesh</td>
<td>Extruded</td>
<td>0.68</td>
<td>86</td>
</tr>
</tbody>
</table>

Table 2.2. Spacer type, thickness, and voidage used in the experiments. The voidage was measured through a displacement method.

Two layers of spacers were used in both the feed and draw solution channels, except if otherwise stated (Figure 2.3). The draw solution spacer configurations investigated include two extruded mesh spacers, and an extruded mesh spacer with a 20-channel tricot spacer (nearest to membrane surface and parallel to the flow).
Two types of tricot spacers (20-channel and denser 35-channel) were used for feed channel spacers. Feed spacer orientations for the 20-channel tricot spacers are shown in Figure 2.4. The 35-channel tricot spacers were oriented with the channels parallel to the feed flow (similar to Figure 2.4a); four of these spacers were used to fill the feed channel. All tricot spacers were oriented with carrier channels facing away from the membrane.

![Figure 2.3](image)

**Figure 2.3.** Schematic of the spacer configuration in the PRO membrane flow cell.

![Figure 2.4](image)

**Figure 2.4.** Illustration of different feed spacer orientations for the 20-channel tricot spacers: (a) both channels oriented parallel to the flow, (b) one channel parallel and one channel at 90° to the flow, and (c) both channels positioned at 45° to the flow. The arrows indicate the direction of feed flow. The top spacer is in contact with the membrane and the bottom spacer is in contact with the flow cell.

### 2.3.5 Bench scale system

Bench scale experiments were performed to investigate water flux, reverse solute flux, power density, flow channel pressure drop, and PRO process efficiency. A supervisory control and data acquisition (SCADA) system (LabVIEW, National Instruments, Austin, TX; and LabJack, Lakewood, CO) was used to control and record pressures, flow rates, temperatures, and feed and draw solution concentrations.

A flow schematic of the test unit is illustrated in Figure 2.5. The thermally insulated feed and draw solution reservoirs were connected to a gear pump (Micropump, Vancouver, WA) and
a direct drive plunger pump (Cat Pumps, Minneapolis, MN), respectively, which circulated the two streams co-currently on the opposite sides of the membrane. In practice, the feed and draw solution would be circulated counter-currently; however, due to the small size of the test cell, operating in co-current mode has negligible effects on process performance. Echopod ultrasonic level sensors (FlowLine, Los Alamitos, CA) were installed on top of the draw solution, feed, and dosing solution reservoirs to monitor the levels of fluids, and thus calculate changes in volume in each reservoir. Pressure transducers (Omega Engineering, Stamford, CT) located at the inlets and outlets of the membrane cell monitored pressure drop in the feed and draw solution channels, and a proportional valve (Hass Manufacturing Co., Averill Park, NY) was used to control the hydraulic pressure in the draw solution flow channel in the membrane cell. Toroidal conductivity sensors (Sensorex, Garden Grove, CA), located at the membrane cell outlets, were used to monitor and facilitate the control of the feed and draw solution concentrations. A peristaltic pump (McMaster-Carr, Chicago, IL) was used to dose the draw solution with concentrated brine and maintain a constant draw solution concentration during the experiments. Stream temperatures were monitored with silicon crystal based sensors (LabJack, Lakewood, CO) and controlled with shell-and-tube heat exchangers, which were installed at the outlets of the membrane cell.

![Flow diagram of the bench scale PRO system used in the current study.](image)

**Figure 2.5.** Flow diagram of the bench scale PRO system used in the current study.
The feed and draw solution flow rates and temperatures were kept constant at 0.5 L min⁻¹ and 20 °C, respectively, and the draw solution hydraulic pressure was varied between 340 kPa (50 psi) and 4.8 MPa (700 psi). Changes in feed tank volume, feed solution conductivity, and membrane cell inlet and outlet pressures were used to calculate water flux, reverse solute flux, and feed channel pressure drop, respectively. Power density was calculated by multiplying the water flux by draw solution inlet pressure. The potential power generated in the PRO experiments was calculated by multiplying the power density by the membrane area. Specific reverse solute flux was determined through calculating the ratio between the reverse solute flux and water flux. PRO process efficiency was determined by calculating the ratio between the PRO power generated (power density × membrane area) and the sum of feed and draw solution pumping power (W_{pump,feed} + W_{pump,draw}). The pumping power for the feed solution was calculated by multiplying the feed solution flow rate and feed inlet pressure, then dividing by the pump efficiency (W_{pump} = Q × P ÷ η_{pump}). The pumping power for the draw solution was calculated by multiplying the draw solution flow rate, draw solution inlet pressure, and pressure exchanger (PX) efficiency, and dividing by the pump efficiency (W_{pump} = Q × P × (1 − η_{PX}) ÷ η_{pump}). A pump efficiency of 70% and a pressure exchanger efficiency of 95% were assumed.

2.3.6 Solution chemistry

Deionized water was used as the feed solution for all experiments. In PRO experiments, draw solutions of 1, 2, and 3 M NaCl (Certified ACS >99%, Fisher Scientific) were used. The feed solution conductivity was closely monitored throughout the experiments, and the feed solution was replaced once the conductivity reached 1,200 µS cm⁻¹ (equivalent to a concentration of 0.5 g L⁻¹ NaCl). OLI Stream Analyzer software (OLI Systems Inc., Cedar Knolls, NJ) was used to calculate solution diffusivities and osmotic pressure.

2.4 Results and discussion

Currently available commercial FO membranes were tested under real PRO conditions and their performance in terms of water flux, power density, reverse solute flux, and mechanical stability was evaluated. Unique spacer configurations under different cross-flow velocities were evaluated and their effect on mass transfer, pressure drop, and energy efficiency were quantified.
2.4.1 Evaluation of commercially available FO membranes for PRO

Power density and specific reverse solute flux as a function of hydraulic pressure for the four membranes are shown in Figure 2.6. The X, Oasys, and HTI TFC membranes all have similar power densities when tested at pressures lower than 1.0 MPa (150 psi) (Figure 2.6a). However, the X and Oasys TFC membranes are limited to operation at pressures of up to 1.0 MPa (~150 psi); reverse solute flux sharply increases and the membrane’s structural integrity becomes compromised at higher pressures. The HTI CTA and TFC membranes can withstand operation at pressures up to 3.5 MPa (~500 psi) and 4.8 MPa (~700 psi), respectively (Table 2.1). Operating the HTI TFC membrane at an applied hydraulic pressure of 2 MPa results in a membrane power density of 9 W m\(^{-2}\). The HTI CTA membrane was one of the least permeable membranes. Compared to the TFC membranes, the CTA membrane is thicker and has a denser skin layer [19] and a higher structural parameter (Table 2.1), which results in lower water fluxes and power densities.

The HTI TFC membrane had the lowest specific reverse solute flux (highest selectivity), followed by the HTI CTA, X, and Oasys membrane (Figure 2.6b). Although the HTI CTA membrane has a higher solute permeability compared to the Oasys membrane (Table 2.1), the membrane’s structural integrity remains intact at higher operating pressures (up to 3.5 MPa). For all membranes, the specific reverse solute flux increased and the selectivity decreased with increasing applied pressures. Decreased membrane selectivity results in increased feed solution concentrations and thus a decreased net driving force. Over time, the solute concentration in the feed stream will continue to increase and power density will decrease—specific reverse solute fluxes higher than 5 g L\(^{-1}\) reduce the effective driving force in PRO [22]. Additionally, solute accumulation in the feed stream is especially problematic in closed-loop PRO systems, such as in osmotic heat engines [14-17].

Although X and Oasys TFC membranes are limited to operating at low-pressure PRO applications (i.e., mixing of river water and seawater), it is important to note that these membranes are well suited for FO applications [36, 37]. Of the membranes investigated, the HTI TFC membrane demonstrated the highest mechanical strength, power density, and selectivity, and was used for the rest of the experiments.
Figure 2.6. (a) Power density and (b) specific reverse solute flux as a function of draw solution hydraulic pressure for the X, Oasys, and HTI TFC membranes and HTI CTA membrane. Experiments were conducted with stream temperatures of 20 °C, flow rates of 0.5 L min⁻¹, deionized water as the feed, and a 1 M NaCl draw solution. Two parallel 20-channel spacers were used in the feed channel and one 20-channel spacer with an extruded mesh spacer was used in the draw solution channel.

The performance of the HTI TFC membrane was evaluated with 1, 2, and 3 M NaCl draw solution concentrations (deionized water as the feed solution) with two parallel 20-channel tricot spacers in the feed channel and one 20-channel spacer and an extruded mesh spacer in the draw solution channel. Power density and specific reverse solute flux as a function of hydraulic pressure are shown in Figure 2.7. Experiments were performed with multiple membrane coupons to eliminate bias due to manufacturing defects. Power density increased with increasing driving force (draw solution concentration) and draw solution hydraulic pressure. The specific reverse solute flux also increased with increasing draw solution hydraulic pressure. However, the increased driving force (concentration difference) does not affect specific reverse solute flux in PRO. Similar to FO, the reverse solute selectivity is independent of the draw solution concentration and is solely determined by the active layer selectivity and inherent number of dissolved species in the draw solute [21]. The standard error between membrane coupons for power density and specific reverse solute flux increased with increasing draw solution hydraulic...
pressure, indicating that the membrane was losing its mechanical integrity and more prone to deformation at applied hydraulic pressures higher than 3.5 MPa (TMP of 3.3 MPa).

![Graph showing power density and specific reverse solute flux](image)

**Figure 2.7.** (a) power density and (b) specific reverse solute flux as a function of draw solution hydraulic pressure for the HTI TFC membrane at 1, 2, and 3 M NaCl draw solution concentrations. Two parallel 20-channel spacers were used in the feed channel and one 20-channel spacer with an extruded mesh spacer was used in the draw solution channel.

Although the HTI TFC membrane can be operated at 4.8 MPa (700 psi) with a 3 M NaCl draw solution, when operated over a prolonged period of time (Figure 2.8) the water flux steadily decreased and the specific reverse solute flux increased. The decrease in permeability and selectivity indicates that the membrane was deforming and losing its integrity at high operating pressures. Membrane deformation increases ICP, which subsequently lowers power density in PRO [28, 34]. Deformation of the HTI TFC membrane at high operating pressures (>3.5 MPa) is further confirmed by evaluating membrane characteristics (Figure 2.9), modeling results (Table 2.3), and SEM micrographs (Figure 2.10).
Figure 2.8. Water flux and normalized reverse solute flux as a function of elapsed time for the HTI TFC membrane operated at applied hydraulic pressure of 4.8 MPa (700 psi) (TMP of 4.5 MPa) and 3 M NaCl draw solution.

Theoretical maximum power densities for 1, 2, and 3 M NaCl draw solutions were modeled and compared to maximum experimental power densities (results from Figure 2.7) and are summarized in Table 2.3. The theoretical maximum power density was modeled using HTI TFC membrane characteristics (determined experimentally (Table 2.1)) and a previously established PRO model by Yip et al. [38]. For a 1 M NaCl draw solution, modeled and experimental power densities (9 and 8.3 W m\(^{-2}\), respectively) were in relatively good agreement. However, there is a large deviation between modeled and experimental power densities for the 2 and 3 M NaCl draw solutions. For the experiments performed with 2 and 3 M NaCl draw solution concentrations, the maximum experimental power density occurs when the applied pressure is at or greater than 3.5 MPa, which is when the HTI TFC membrane begins to lose its mechanical stability and selectivity. Once the membrane deforms, the membrane characteristics are no longer constant and the modeled values are not valid.
Table 2.3. Experimental and modeled power densities for the HTI TFC membrane operated with 1, 2, and 3 M NaCl draw solution concentrations and deionized water as the feed. The power density was modeled with A, B, and S values of $1.63 \times 10^{-2}$ L m$^{-2}$ hr$^{-1}$ kPa$^{-1}$, 1.42 L m$^{-2}$ hr$^{-1}$, and 295 micron, respectively.

<table>
<thead>
<tr>
<th>Draw solution concentration g L$^{-1}$ NaCl</th>
<th>Draw solution osmotic pressure MPa (psi)</th>
<th>Modeled Applied pressure MPa (psi)</th>
<th>Power density W m$^{-2}$</th>
<th>Experimental Applied pressure MPa (psi)</th>
<th>Power density W m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>58 (1 M)</td>
<td>4.8 (690)</td>
<td>2.4 (350)</td>
<td>9</td>
<td>2.1 (300)</td>
<td>8.3</td>
</tr>
<tr>
<td>117 (2 M)</td>
<td>10.5 (1,520)</td>
<td>5.25 (760)</td>
<td>26</td>
<td>3.5 (500)</td>
<td>11.5</td>
</tr>
<tr>
<td>175 (3 M)</td>
<td>17.4 (2,520)</td>
<td>8.7 (1,260)</td>
<td>44</td>
<td>4.1 (600)</td>
<td>15.5</td>
</tr>
</tbody>
</table>

The selectivity of the membranes compacted at 3.1 and 4.1 MPa is shown in Figure 2.9. Once operated at pressures greater than 3.5 MPa, the membrane properties change and the membrane becomes less selective. Examination of the membrane surface and cross-section with SEM imaging indicates that with increasing pressure, the finger-like structure of the support layer becomes more compressed and deformed (Figure 2.10).

![Figure 2.9](image_url)

**Figure 2.9.** Membrane water/solute selectivity (A/B) for the HTI TFC FO membrane after pre-compaction at 3.1 MPa (~450 psi) and 4.1 MPa (~600 psi).

Therefore, although the HTI TFC membrane can operate up to 4.8 MPa, the membrane becomes compromised above 3 MPa applied hydraulic pressure. At increased pressures, the membrane support layer becomes thinner, which increases the apparent tortuosity and decreases
the porosity. The overall increase in tortuosity and decrease in porosity results in an increased membrane structural parameter and decreased PRO power densities.

Figure 2.10. SEM micrographs of the HTI TFC virgin membrane (a) surface and (b) cross section; after compaction at 3.1 MPa (450 psi) (c) membrane surface and (d) cross section; and after compaction at 4.1 MPa (600 psi) (e) membrane surface and (f) cross section.
2.4.2 Spacer selection

Several spacer orientations were used to investigate their effect on mass transfer in PRO (Table 2.4). Feed channel spacer configurations and orientations include two 20-channel tricot spacers with both channels oriented parallel to the flow (configuration A), one channel parallel and one channel at 90° to the flow (configuration B), both channels positioned at 45° to the flow (configuration C), and four 35-channel tricot spacers with channels oriented parallel to the feed flow (configuration D). The draw solution spacer configurations include two extruded mesh spacers (configuration E) and one tricot spacer with one extruded mesh spacer (configuration F). It is important to note that because of the small size of the flow cell, recoveries were low (i.e., low efficiencies and energy recovery). Therefore, the PRO process efficiency is simply a qualitative measurement used to compare the performance of different spacer orientations.

<table>
<thead>
<tr>
<th>Spacers configuration</th>
<th>Channel</th>
<th>Spacers used</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Feed</td>
<td>Two 20-channel tricot</td>
<td>Parallel to feed flow</td>
</tr>
<tr>
<td>B</td>
<td>Feed</td>
<td>Two 20-channel tricot</td>
<td>90° to feed flow</td>
</tr>
<tr>
<td>C</td>
<td>Feed</td>
<td>Two 20-channel tricot</td>
<td>45° to feed flow</td>
</tr>
<tr>
<td>D</td>
<td>Feed</td>
<td>Four 35-channel tricot</td>
<td>Parallel to feed flow</td>
</tr>
<tr>
<td>E</td>
<td>Draw</td>
<td>Two extruded mesh spacers</td>
<td>90° to feed flow</td>
</tr>
<tr>
<td>F</td>
<td>Draw</td>
<td>One 20-channel tricot spacer and one extruded mesh spacer</td>
<td>Parallel to feed flow (tricot)</td>
</tr>
</tbody>
</table>

2.4.2.1 Effect of feed spacer on process performance

Power density, feed channel pressure drop, and process efficiency as a function of draw solution hydraulic pressure for different feed spacer configurations (spacerless draw solution channel) are shown in Figure 2.11. Feed spacer configuration C resulted in the highest PRO power density and process efficiency. Compared to configuration A, the feed channel pressure-drop for configuration C was reduced by 73%, thus increasing overall process efficiency. Spacer configuration A had a high feed channel pressure drop because the spacers most likely compressed—the ridges of the spacer near the membrane collapsed into the channels of the spacer beneath it. Although power density increased with increasing applied pressure, PRO
process efficiencies decreased due to increased feed channel pressure drop and increased energy demand for pumping.

![Graphs showing power density, feed channel pressure drop, and W_{pro}/W_{pump} as a function of draw solution pressure.](image)

**Figure 2.11.** (a) Power density, (b) feed channel pressure drop, and (c) \( W_{pro}/W_{pump} \) as a function of draw solution pressure for the HTI TFC FO membrane with different feed spacers and spacer orientations (Table 2.4) and a spacerless draw solution channel. Experiments were performed with 1 M NaCl draw solution, and feed and draw solution flow rates and temperatures were kept constant at 0.5 L min\(^{-1}\) and 20 °C, respectively.
The flow path in spacer configuration C most resembles what can be described as a “corkscrew” flow pattern (Figure 2.12). Changing the orientation of the feed spacers increased mass transfer at the feed membrane interface, thus decreasing concentration polarization at the membrane boundary layer in the draw solution channel. Da Costa et al. observed similar results for ultrafiltration; increasing the hydrodynamic angle of the spacer (i.e., direction that the fluid flows within the channel) greatly influences the hydrodynamics in spacer filled channels [39].

Although spacer configuration B has the largest hydrodynamic angle, power densities with this feed spacer configuration were not as high as the power densities for feed spacer configuration C. In spacer configuration B, the spacer adjacent to the membrane was oriented perpendicular to the feed flow and the spacer adjacent to the flow cell had its channels parallel to the feed flow. The feed stream most likely flowed preferentially in the path of least resistance (spacer parallel to flow), limiting mass transfer at the feed-membrane interface.

![Figure 2.12. Schematic of corkscrew flow for 45° feed spacer orientation.](image)

The motivation for using dense feed channel spacers (35-channel tricot) was to provide additional membrane support and reach higher membrane burst pressures. However, the dense tricot spacers did not result in higher burst pressures; it actually reduced the effective membrane area (increased shadow effect), limited mass transfer, and lowered power density. Furthermore, use of the dense spacers resulted in higher feed channel pressure drops and lower PRO process efficiencies.

2.4.2.2 Effect of draw solution spacer on process performance

Power density and process efficiency as a function of draw solution hydraulic pressure for different draw solution spacer configurations is shown in Figure 2.13. The best-case feed
spacer configuration (C) was used for these experiments. Compared to draw solution spacer configuration E, configuration F resulted in increased power densities (76% increase) and process efficiencies (2.5 times higher). Compared to the tricot spacer, the extruded mesh spacer has a higher voidage and thicker filaments, which result in increased turbulence [33]. Therefore, it is likely that the draw solution flows preferentially through the channels of the tricot spacer (path of least resistance), thus increasing mass transfer at the draw solution-membrane interface.

![Figure 2.13](image_url)

**Figure 2.13.** (a) Power density and (b) $W_{\text{pro}}/W_{\text{pump}}$ as a function of applied pressure for the HTI TFC membrane with different draw solution spacer configurations (E and F) and configuration F in the feed channel. Experiments were performed with 1 M NaCl draw solution, and feed and draw solution flow rates and temperatures were kept constant at 0.5 L min$^{-1}$ and 20 °C, respectively.

### 2.4.2.3 Best-case spacer configurations

Experiments were performed with the best-case feed and draw solution spacer configurations: configuration C in the feed channel and configuration F in the draw solution channel. Water flux and specific reverse solute flux as a function of draw solution hydraulic pressure is shown in Figure 2.14. The orange asterisks represent the maximum power densities from experimental results shown in Figure 2.7. Implementing this unique feed spacer orientation increased power densities from previous experiments by 28, 31, and 46 % for 1, 2, and 3 M NaCl.
Selection of spacers that increase process performance is impactful in future module design and system performance.

Although this unique feed spacer orientation was impactful in increasing power densities, power densities are still not as high as other reported values for HTI TFC membranes (60 W m$^{-2}$ operated with 3 M NaCl draw solution, cross flow velocity of 21.4 cm s$^{-1}$, and operating temperature of 25 ºC) [27]. In addition to increased flow velocities and elevated temperatures, the effective membrane area in the other study was six times smaller than the membrane area in this study (0.002 m$^2$ vs. 0.012 m$^2$) and experiments were performed over a shorter duration (35 minutes vs. two hours). Although larger membrane areas result in increased recoveries, effective membrane power densities are lowered. As water permeates from the low concentration feed stream into the higher concentration draw solution stream, the driving force and hence power densities decrease over the length of the module. Furthermore, operating membranes at high pressures over prolonged periods of time result in lower water fluxes (and hence power densities) and higher specific reverse solute fluxes, as illustrated in Figure 2.8.

**Figure 2.14.** (a) Power density and (b) specific reverse solute flux for the best-case spacer configuration (configuration C in the feed channel and configuration F in the draw solution channel) at 1, 2, and 3 M NaCl draw solution. The orange asterisks represent the maximum power densities from results shown in Figure 2.7 (configuration A in the feed channel and configuration F in the draw solution channel).
2.4.3 Flow conditions

Power density, feed pressure drop, and PRO process efficiency as a function of feed cross-flow velocity are shown in Figure 2.15, where each data series represents a different draw solution cross-flow velocity. Similar to other findings [12], power density increases with increasing feed cross-flow velocity. Compared to draw solution cross-flow velocities, increasing feed cross-flow velocity has a higher impact on membrane power densities, indicating that mass transfer in the feed stream is more critical to process performance. Increasing the feed flow velocity from 0.026 to 0.13 m s\(^{-1}\) resulted in a 48% increase in power density; however, when the draw solution velocity was increased from 0.026 to 0.13, power density increased by only 36%. Although increasing feed and draw solution cross-flow velocities result in increased power densities, PRO process efficiency is reduced due to increased energy demand for pumping.

![Figure 2.15](image)

**Figure 2.15.** (a) Power density and (b) \(W_{\text{pro}}/W_{\text{pump}}\) as a function of feed cross-flow velocity for the HTI TFC membrane operated with 1 M NaCl draw solution at 2.76 MPa (400 psi) hydraulic pressure, spacer configuration C in the feed channel, and spacer configuration F in the draw solution channel.

2.5 Conclusions

Several commercial FO membranes were investigated for use in PRO. The HTI TFC membrane was found to be the best membrane for PRO at this time. This membrane has the
highest selectivity and mechanical stability, which result in high PRO power densities. This study established that the HTI TFC membrane can withstand operating pressures of up to 3.5 MPa (500 psi) before significant membrane deformation occurs, which leads to higher ICP and decreased process performance. The specific reverse solute flux for the HTI TFC membrane was found to sharply increase at hydraulic pressures exceeding 2.0 MPa, which has significant impact in closed-loop PRO systems. Furthermore, membrane characteristics and performance change once the membrane is deformed and modeled results are no longer valid. The use of unique feed and draw solution spacers and orientations tested in this study enhanced mass transfer through the membrane, achieving a theoretical PRO power density of more than 22 W m$^{-2}$, which is a 46% improvement from other spacer orientations. Reducing both feed and draw solution flow rates resulted in four fold increase in overall PRO process efficiencies (4 to 16%). Furthermore, decreasing feed and draw solution flow rates resulted in lower parasitic pumping losses and decreased capital pumping costs. Although increased PRO power densities continue to be realized, PRO membrane development, module design, and pilot scale testing are essential for enabling PRO commercialization.

2.6 References


CHAPTER 3
SUSTAINABLE OPERATION OF MEMBRANE DISTILLATION FOR ENHANCEMENT OF MINERAL RECOVERY FROM HYPERSALINE SOLUTIONS

Modified from an article published in the *Journal of Membrane Science*¹

Kerri L. Hickenbottom²* and Tzahi Y. Cath²*

3.1 Abstract

Membrane distillation (MD) is an emerging desalination technology that has the ability to desalinate hypersaline brines, including those used in mineral production. MD can potentially replace evaporation ponds in conventional mineral production processes because of its small footprint and ability to utilize industrial low-grade heat. In the current study MD was investigated for sustained water recovery and concentration of hypersaline brines. Direct contact MD (DCMD) experiments were performed with water from the Great Salt Lake (>150,000 mg/L total dissolved solids) as the feed stream and deionized water as the distillate stream. DCMD was able to concentrate the feed solution to twice its original concentration, achieving close to complete inorganic salt rejection. During experiments water flux declined to 80% of its initial value (from 11 to 2 L m⁻² hr⁻¹). Real-time microscopy revealed that precipitation of salts on the membrane surface was the main contributor to the decline in water flux. The application of novel scale-mitigation techniques was highly effective in preventing scale formation on membrane surfaces, sustaining high water flux and salt rejection, and eliminating chemical consumption used for membrane cleaning. MD was compared to natural evaporation and was found to potentially replace 4,047 m² (one acre) of evaporation ponds with approximately 24 m² (259 ft²) of membrane area and to be nearly 170 times faster in concentrating hypersaline brines.

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3.2 Introduction

As population grows, an increased stress is placed on natural resources [1]; thus, there is a need for more holistic approaches to process intensification, in which process waste is considered a resource. For example, in desalination, brine is considered a byproduct and treated as a waste stream, whereas in mineral production, water is considered a byproduct and, as common practice, is evaporated to the atmosphere. Ironically, the waste stream of one process is the product of the other. Efficient utilization of brines and on-site energy resources could result in production of both water and high-value minerals for beneficial use, including potable water for urban areas and minerals for fertilizers or road deicing.

In mineral production, evaporation ponds are traditionally utilized for concentration of saline water and precipitation of minerals, which are then further processed in chemical plants. Evaporation ponds commonly use large areas, they are time and energy intensive, and when used, large volumes of valuable water are lost to the atmosphere [2]. In order to improve the efficiency of mineral recovery, replacement of evaporation ponds with desalination processes could minimize land use and increase water recovery from hypersaline streams.

Current engineered processes for desalination of brackish water and seawater include thermal distillation or membrane processes such as reverse osmosis (RO), nanofiltration (NF), and electrodialysis (ED). Conventional thermal distillation processes are capable of achieving high water recovery, but they are limited by high-energy consumption needed to heat the feed stream [3]. While RO, NF, and ED are commonly utilized membrane processes for desalination [2], when feed solutions are highly concentrated or approach supersaturation, these processes are limited by operating pressures (RO and NF) and applied voltage (ED), and in many cases membrane scaling [4].

Alternatively, membrane distillation (MD) is a novel and unique membrane process that can synergistically assist in mineral recovery and simultaneously produce pure water. MD is a thermally driven membrane process in which the driving force for mass transfer of water is the partial vapor pressure difference across a microporous hydrophobic membrane. Thus, compared to hydraulic pressure and electric field driven membrane processes, MD is potentially minimally affected by increased salt concentrations [5]. In direct contact MD (DCMD), a warm feed stream (e.g., brine) and a cooler fresh water stream (e.g., deionized water) are in direct contact with the active and support sides of the membrane, respectively [5]. In DCMD, water evaporates from the
feed solution at the feed-pore interface on the feed side of the membrane, water vapors then diffuse through the membrane pores, and ultimately they condense into the distillate stream at the distillate-pore interface on the support side of the membrane.

3.2.1 Factors affecting DCMD process performance

While MD is a unique process that can be utilized for desalination of hypersaline streams, several transport phenomena may limit water flux through the membrane. These include decrease in partial vapor pressure, heat and mass transfer resistance across the membrane, and concentration and temperature polarization (or loss in heat transfer) across the membrane [5, 6].

Heat and mass transfer dominate the vapor pressure driving force in MD. Because several phase changes occur during MD, the heat transfer resistances across the boundary layers of the membrane surface are often the rate-limiting step [5]. Although DCMD is considered one of the simpler configurations of MD, the conductive heat transfer across the membrane is greater than in other MD configurations [6, 7].

Heat transfer across the MD membrane gives rise to temperature polarization (TP) in which the temperature of the feed solution at the feed-membrane interface declines and the temperature of the distillate at the distillate-membrane interface increases. Mass transfer across the MD membrane gives rise to concentration polarization (CP) in which the vaporization of water from the feed stream through the MD membrane results in an increased solute concentration and thus a lower partial vapor pressure of the water at the feed-membrane interface. Similar to other membrane processes, CP can also induce membrane scaling, which further reduces process performance [8, 9].

Membrane scaling occurs when inorganic salts precipitate and accumulate on the membrane surface, thus blocking the pores for vapor to diffuse across the membrane and subsequently lowering water flux. Scaling of sparingly soluble salts such as CaCO₃, CaSO₄, and silicates has been identified as a cause of flux decline when recovering water from natural streams, including brines from desalination processes [10-17]. Two types of membrane scaling can occur: homogeneous and heterogeneous scaling. Homogeneous scaling occurs when crystals that form in the bulk solution precipitate on the membrane surface, and heterogeneous scaling occurs when salts crystallize directly on the membrane surface [18-20]. Scaling can alter membrane surface properties (i.e., hydrophobicity), change membrane pore structure, and
ultimately decrease process efficiency and potentially lead to wetting of the membrane pores [12, 13]. In MD it is essential that the porous membrane maintains its hydrophobicity to prevent membrane wetting, which will allow passage of water in a liquid phase through the membrane pores [5]. Pore wetting of the membrane hinders water flux, lowers salt rejection, and impairs membrane integrity (i.e., loss of hydrophobicity).

3.2.2 DCMD for concentration of supersaturated solutions in mineral production

Replacing traditional concentration methods with MD could produce high quality minerals and water, reduce land footprint of evaporation ponds, and eliminate the required pumping of water from pond to pond in mineral production sites. Recent studies have shown that MD consumes less energy than traditional thermal distillation such as multi-stage flash and multi-effect distillation, and can further concentrate brines from desalination processes such as RO, NF, and ED [10, 13, 15, 16, 21-23]. Furthermore, utilization of low-grade heat sources such as industrial heat emissions and solar energy can offset the overall energy consumption needed for MD [24-27].

Recent studies have coupled membrane processes with crystallizers to concentrate and recover minerals in hypersaline solutions [14, 22, 28-35]; however, none of these studies have effectively mitigated membrane scaling. While membrane scaling has been investigated [10-13, 23, 34, 36-40], effective scale mitigation techniques for maintaining and restoring water flux and salt rejection when desalinating saturated solutions are still lacking. In the current study, DCMD was applied to concentrate Great Salt Lake (GSL) water. The main objectives of the study were to evaluate the performance of DCMD in concentrating hypersaline brines from the GSL, and in doing so, optimize operating conditions to maximize water recovery and mitigate membrane scaling. Several unique methods were developed and tested to identify and mitigate membrane scaling. Finally, the replacement of evaporation ponds with DCMD was assessed as a means to intensify the mineral production process.

Experimental procedure

At the beginning of each experiment the feed reservoir was filled with 3 L of deionized water and the DS reservoir was filled with 1 L of premixed DS. The feed solution was dosed with 100 mg of ACS grade NaCl (approximately 33 mg L⁻¹) to guarantee that all feed samples were well within the detection limit of the analytical instruments used to measure individual ion
concentrations in the feed and DS. The pH of the DS was adjusted to 7 using hydrochloric acid (HCl) or sodium hydroxide (NaOH) prior to each experiment. The pH of the DS was measured periodically during testing and adjusted as necessary to maintain it at 7. The pH of the deionized water feed was measured before and after each DS experiment. The bench-scale system was operated for 30 min with the feed and DS continuously recirculated through the symmetric cross-flow membrane cell and heat exchangers to ensure that the system was operating at constant water flux and temperature (20 ºC) before the first samples were collected from the feed and DS reservoirs for analysis. The reservoirs were sampled again at the end of each experiment (90 min after the first sample); thus, each experiment was conducted for a total of 2 h.

Water flux was measured during all mixed salts DS experiments with DSs having osmotic pressures of 23 bar or 48 bar while water flux during single salt experiments, excluding NaCl, was only measured with DS having an osmotic pressure of 23 bar. The water flux for single salt DSs was not measured with DS having an osmotic pressure of 48 bar because the concentration of MgSO4 needed for the DS dosing solution (431 g L⁻¹) exceeded the solubility limit (255 g L⁻¹) under the experimental conditions, and because of the high viscosity and difficulty to dissolve some of the other salts tested. The NaCl and mixed salts DS experiments conducted with a DS having an osmotic pressure of 48 bar were repeated four times with different membrane coupons to validate the accuracy of the results. The integrity of the membrane was assessed at the beginning of each experiment using an NaCl DS to confirm that the water flux and RSF were in a reasonable range for the TFC membrane used for testing. Experiments were conducted only once at the osmotic pressure of 23 bar to evaluate if trends in mixed salts DS performance were similar to those observed for tests conducted at the higher osmotic pressure.

3.3 Materials and Methods

3.3.1 Membranes

Two hydrophobic microporous membranes were acquired from GE Water (Minnetonka, MN). The first membrane (TS22) is a composite membrane consisting of a thin polytetrafluoroethylene (PTFE) active layer and a polypropylene woven support layer. The overall thickness of the TS22 membrane is 175 micron, with an active layer thickness of 5-10 microns. The second membrane (PP22) is an isotropic membrane made of polypropylene (PP),
and is approximately 150 microns thick. Both membranes have a nominal pore size of 0.22 microns and a porosity of approximately 70% [41]. After experiments, the membranes were rinsed with deionized water and stored in a desiccator until analysis. A new membrane coupon was used for each set of experiments.

3.3.2 Membrane cells

Experiments were performed with acrylic membrane cells fitted to test flat sheet membranes. The cells were fabricated with symmetric flow channels on either side of the membrane, allowing for parallel flow of feed and distillate streams on the opposite sides of the membrane. Nitrile rubber gaskets were used to form flow channels, approximately 2 mm deep, on each side of the membrane. Turbulent enhancing spacers were placed in the flow channels to reduce temperature polarization effects, increase water flux [41], and ensure that the membrane lay flat and centered in the cell. Experiments were performed using a modified SEPA-CF cell with an effective membrane surface area of 139 cm$^2$. To prevent precipitation of salts on the membrane surface, the membrane cell was positioned horizontally with the feed side (active side) facing down. To observe real-time membrane scaling, an additional set of experiments was performed with a stereomicroscope (Stemi 2000, Carl Zeiss Microscope, Thornwood, NY) and a direct observation membrane cell that has a glass observation port (12.7 cm x 2.54 cm) and an effective membrane surface area of 89 cm$^2$. During these experiments, the feed side of the membrane was facing up.

3.3.3 Bench-scale system

Bench-scale experiments were performed to investigate water flux, salt rejection, and membrane scaling. A supervisory control and data acquisition (SCADA) system (LabVIEW, National Instruments, Austin, TX; and a LabJack UE-9 Pro, Lakewood, CO) was utilized to control the temperatures of the feed and distillate streams and collect data to calculate water flux and batch recovery.

A flow schematic of the test unit is illustrated in Figure 3.1. The thermally insulated feed and distillate reservoirs were connected to gear pumps (Micropump, Cole Parmer, Vernon Hills, IL) that circulate the feed and distillate streams co-currently on the opposite sides of the membrane. It is important to note that due to the small size of the membrane, operating in co-
current mode had negligible effects on process performance in this study. Thermocouples were installed at the inlets of the feed and distillate channels and connected to the SCADA system. The flow rate of the two streams was 1.6 L min\(^{-1}\) when using the modified SEPA-CF cell, and 0.6 L min\(^{-1}\) when using the direct observation cell. As feed water vaporized through the membrane and absorbed into the distillate stream, water overflowed from the distillate reservoir into a beaker positioned on an analytical balance (Model S-8001, Denver Instruments, Bohemia, NY), which was connected to the SCADA system. The overflow rate was used to calculate water flux through the membrane. The conductivity of the distillate reservoir was continuously measured (Waterproof pH/CON 300 Meter, Oakton Instruments, Vernon Hills, IL) and changes were used to calculate salt rejection and detect membrane wetting.

![Flow schematic of the DCMD bench scale system.](image)

**Figure 3.1.** Flow schematic of the DCMD bench scale system.

### 3.3.4 Preliminary pure water permeability experiments

A set of preliminary experiments was performed to evaluate the pure water permeability of the TS22 and PP22 membranes and to select experimental operating temperatures. In these experiments, deionized water was used as the feed and distillate streams. The temperature of the feed ranged from 30 to 70 °C in increments of 10 °C and the temperature of the distillate was 20 or 30 °C.
3.3.5 **Direct contact membrane distillation batch experiments**

Experiments were conducted in a batch mode, simultaneously concentrating the feed solution and producing purified water. The feed solution was representative water from the Bear River Bay (Salt Lake City, UT) on the eastern shore of the GSL and the distillate solution was deionized water. The raw GSL water was pre-filtered through a 0.5-micron cartridge filter to remove any suspended solids.

3.3.5.1 **Successive water flux and salt rejection experiments**

The performance of DCMD after multiple successive batch experiments was evaluated. These experiments utilized the PP22 and TS22 membranes. A high (40 °C) and low (20 °C) temperature difference across the membrane was chosen for these experiments. The temperature of the distillate stream was 30 °C and the temperature of the feed stream was either 50 or 70 °C. The experiments were performed until the water flux decreased to nearly 80% of its initial value, then the collected distillate was returned to the feed reservoir (diluting the feed solution to its original concentration), and the experiment resumed.

3.3.5.2 **Scale identification experiments**

3.3.5.2.1 **Optical microscope**

The onset of membrane scaling was observed with a stereo-microscope and the direct observation membrane cell. These experiments were performed with the PP22 membrane and 3 L of filtered GSL water as the feed. The feed and distillate temperatures were 50 and 30 °C, respectively. Images of membrane scaling were captured throughout the experiments (EOS Rebel XTi, Canon, Lake Success, NY).

3.3.5.2.2 **Isolation of sparingly soluble salts**

Experiments were carried out to evaluate the effect of sparingly soluble salts on the decline in water flux. To isolate the potential scalants, experiments were performed with a feed solution of 150 g/L NaCl (ACS grade) and with GSL water. The modified SEPA-CF cell, PP22 membrane, and 3 L of feed solution were used. The feed and distillate temperatures were 50 and 30 °C, respectively.
3.3.5.3 Extended scaling experiments

A set of experiments was performed to evaluate the onset of membrane scaling over a prolonged period of time. Each experiment was initiated with 10 L of filtered GSL water recirculating on the feed side, and process performance was evaluated over 125 hours. In these experiments, both the PP22 and TS22 membranes were tested and the feed and distillate temperatures were 50 and 30 °C, respectively. Each experiment was divided into 5-6 cycles. In each cycle, 1 L of distillate overflow was collected and removed from the system, then the distillate overflow (permeate) was continuously returned to the feed reservoir for approximately 12 hours. After the 12 hours, a new cycle started with withdrawal of another 1 L of distillate overflow. The cycles were repeated until the feed water was concentrated approximately 2.5 times relative to its original concentration.

3.3.6 Scale mitigation experiments

Three scaling mitigation techniques were investigated to prevent or remove membrane scaling and maintain membrane integrity. Batch experiments were performed with the modified SEPA-CF cell, PP22 membrane, and 8.5 L of filtered GSL feed water. The PP22 membrane was chosen because of its isentropic structure. The temperatures of the feed and distillate were 60 and 30 °C, respectively.

3.3.6.1 Mitigating rapid flux decline

In the first scale mitigation procedure, DCMD batch experiments were terminated before the water flux started to rapidly decline. After 12 hours of operation, or when 35-40% of the feed water was recovered, the collected distillate was returned to the feed reservoir, diluting the feed to its original concentration. Subsequently, the next batch experiment began. Eight successive batch experiments were performed without any membrane cleaning between cycles.

3.3.6.2 Flow reversal

Similar to the first technique, batch experiments were terminated before scaling occurred on the membrane surface, or after 35-40% of the feed water was recovered. Then, the feed side of the membrane was rinsed with approximately 200 mL of deionized water, and the feed and distillate channels of the membrane cell were exchanged: the feed side became the distillate side.
and the distillate side became the feed side. Subsequently, the next successive batch experiment began. This procedure was repeated six times.

### 3.3.6.3 Temperature reversal

Similar to the previous scale mitigation techniques, batch experiments were terminated before scaling occurred on the membrane surface, or after 35-40% of the feed water was recovered. Then, a colder GSL feed stream (15 °C) was circulated on the feed side of the membrane while the warmer distillate (30 °C) continued to be circulated on the distillate side of the membrane, thus reversing the direction of the driving force across the membrane. After 20 minutes, another batch concentration cycle started with a warmer feed (60 °C at 150,000 mg L⁻¹) and cooler distillate (30 °C) on their respective sides of the membrane. This procedure was repeated eight times. It is important to note that the colder feed stream could be taken directly from a colder source water; therefore, eliminating feed water cooling. In this case, the colder feed stream is taken directly from the GSL, which has an average temperature of 15 °C [42].

### 3.3.7 Solution chemistry and analytical methods

The GSL water was characterized using standard analytical methods. Water samples were prepared and analyzed for dissolved solids according to Standard Methods (APHA, 2005). Samples were diluted and filtered through a 0.45-micron filter and analyzed for anions with an ion chromatograph (Model ICS-90, Dionex, Sunnyvale, CA) and for cations with an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Optima 5300 DV, PerkinElmer Inc., Waltham, MA). The average total dissolved solids (TDS) concentration of the GSL water from the Bear River Bay was approximately 150,000 mg L⁻¹, most of which is sodium chloride (~84% w/w). A detailed ionic composition of the GSL water used in this study is summarized in Table 3.1. The feed solution chemistry was simulated with OLI Stream Analyzer™ (OLI Systems, Inc., Morris Plains, NJ) to determine the scaling tendencies at increasing temperatures (50-70 °C) and concentrations (150,000-500,000 mg L⁻¹).
Table 3.1. Ionic composition of the GSL water. All values are for the cartridge filtered GSL water.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration mg L⁻¹</th>
<th>Analyte</th>
<th>Concentration mg L⁻¹</th>
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</thead>
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<td>40.0</td>
<td>Si⁴⁺</td>
<td>9.16</td>
</tr>
<tr>
<td>Ba²⁺</td>
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<tr>
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<td>1.38</td>
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<td>Sr²⁺</td>
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<td>Cl⁻</td>
<td>81,600</td>
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<tr>
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<td>72</td>
</tr>
<tr>
<td>Mg²⁺</td>
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<td>NO₃⁻</td>
<td>13</td>
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<td>Mn²⁺</td>
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<tr>
<td>S²⁻*</td>
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*Sulfur not associated with SO₄²⁻*

3.3.8 Economic implications of DCMD utilization

The economic implication of using DCMD for concentration of GSL water was evaluated and compared to the use of evaporation ponds. The evaporative water loss for the Bear River Bay (approximately 1.4 m per year [42]) and the average DCMD water flux obtained from the temperature reversal experiments were standardized and used for comparison of the different concentration methods.

3.4 Results and discussion

3.4.1 Pure water permeability experiments

Water flux as a function of feed temperature for the two membranes is shown in Figure 3.2. Water flux increased exponentially with increasing of the temperature difference (or vapor pressure driving force) across the membrane. The water flux through the TS22 was consistently higher than the water flux through the PP22. This is because the PP22 is a thicker membrane with more tortuous pores that increase the resistance to vapor diffusion through the membrane pores, thus resulting in a lower permeability [41, 43]. Based on these results, a high temperature differential (ΔT = 40 °C) and low temperature differential (ΔT = 20 °C) were chosen for the successive batch concentration experiments; the temperature of the distillate stream was kept at 30 °C and the temperature of the feed stream was either 50 or 70 °C.
Figure 3.2. Water flux as a function of feed temperature for experiments performed with the TS22 and PP22 MD membrane. The distillate temperature ($T_d$) was either 20 or 30 ºC, the feed temperature was between 30 and 70 ºC, and the flow rates were kept constant at 1.6 L min$^{-1}$.

3.4.2 Direct contact membrane distillation batch experiments

3.4.2.1 Successive batch experiments: water flux and salt rejection

Water flux as a function of GSL water total solids concentration for experiments performed with the two membranes operated at $\Delta T$ of 40 and 20 ºC is shown in Figure 3.3. In all experiments the water flux gradually declined as the feed solution concentration increased, and thus the partial vapor pressure of water in the feed solution decreased. Thereafter, a sharp decline in water flux was observed in all the experiments.

Compared to the pure water permeability experiments, a lower initial water flux was observed during batch experiments performed with the GSL water. For example, in experiments performed with the PP22 and GSL feed solution, the initial water flux was 11% ($\Delta T$ of 20 ºC) and 20% ($\Delta T$ of 40 ºC) lower than that of the pure water permeability experiments performed with the same membrane and temperature differences. The experiments performed with the TS22 and GSL feed solution resulted in an initial water flux of 28% ($\Delta T$ of 20 ºC) and 38% ($\Delta T$ of 40 ºC) lower than in the pure water permeability experiments performed with the same membrane and temperature differences. The percent decrease in initial water flux for the experiments performed with the GSL feed water was lower for temperature difference of 20 ºC and for the PP22. The lower partial vapor pressure of water in the highly concentrated feed solution
(150,000 mg L$^{-1}$ total solids) was the main reason for a lower driving force across the membrane and the lower initial water flux. For example, Song et al. reported that solutions with salt concentrations of 10 and 20% reduced the partial vapor pressure by 6 and 20%, respectively [44].

Figure 3.3. Water flux as a function of total solids concentration for the successive batch experiments (runs) performed with (a) the TS22 membrane and (b) the PP22 membrane. Experiments were performed with filtered GSL water as feed and deionized water as distillate. The distillate temperature was 30 ºC and the feed temperature was either 50 (50/30) or 70 ºC (70/30). The flow rate was kept constant at 1.6 L min$^{-1}$.

At increased temperature differentials ($\Delta T$ of 40 ºC), a higher terminal GSL water concentration was achieved with the PP22. Although experiments conducted with the TS22 at a higher temperature difference ($\Delta T$ of 40 ºC) resulted in greater initial water fluxes compared to those with the PP22, the initial water flux decreased after each successive batch experiment. Several studies have reported that polarization effects are more severe at increased operating temperatures [8, 16, 23, 43, 45]; however, these effects are reduced when using membranes with low thermal conductivities [7, 25, 45]. Thus, it is likely that the lower thermal conductivity of the thicker PP22 mitigated the effects of temperature polarization when tested at increased
temperature differences across the membrane. Temperature polarization effects were more severe during experiments performed with the TS22 at increased temperature differences, which resulted in increased membrane scaling. Higher flux also results in higher heat fluxes, which subsequently decreases the temperature difference across the membrane and increases temperature polarization effects [8, 9, 16, 43].

Temperature polarization also affects the mechanisms of membrane scaling. Because the temperature is lower at the feed-membrane interface than in the bulk solution, the calcium species solubility is expected to increase, whereas NaCl solubility is expected to decrease. Additionally, increased water flux results in increased rates of scaling. Therefore, it is expected that the potential for scaling of NaCl will be higher for the TS22 membrane (higher flux) than the PP22 membrane.

Water flux and distillate conductivity as a function of time are shown in Figure 3.4 from data presented in Figure 3.3. The distillate conductivity for both sets of experiments performed at a ΔT of 20 ºC continuously decreased, indicating that the membrane rejected nearly 100% of all inorganic and non-volatile constituents. However, the distillate conductivity increased in both experiments operated at a higher temperature gradient. The distillate conductivity increased throughout the experiment performed with the PP22. In experiments performed with the TS22, the distillate conductivity started to increase towards the end of the experiment, indicating that the TS22 is less susceptible to wetting at higher operating temperatures. A previous study by Gryta et al. reported that operating at temperatures greater than 68 ºC may reduce the hydrophobicity of polypropylene membranes and lead to membrane wetting [36]. Saffarini et al. reported that PTFE membrane support layers showed no signs of degradation when exposed to high temperatures (<350 ºC); however, the potential for wetting of PTFE membranes does increases with increasing feed temperatures and salinities [46].

When operated at a higher ΔT of 40 ºC, the water flux had more than tripled, increasing the overall water flux from 12.8 to 47 L m⁻² hr⁻¹ during experiments with the TS22 and from 12.3 to 40 L m⁻² hr⁻¹ during experiments with the PP22. Yet, while the process was accelerated at high temperature differences across the membrane, both salt rejection and initial water flux decreased after each successive batch experiment. When experiments were conducted at a ΔT of 20 ºC, the salt rejection of the membrane was high, the water flux after each successive batch run was restored, and the GSL water was concentrated to more than 300,000 mg L⁻¹ total solids.
Therefore, operating temperatures lower than 70 °C (50 and 60 °C) for the feed and 30 °C for the distillate (ΔT 20 °C) were chosen for the following experiments.

**Figure 3.4.** Water flux and distillate conductivity as a function of total solids concentration for (a) the TS22 membrane and (b) the PP22 membrane. Successive batch experiments were performed with filtered GSL feed water and deionized water as the distillate stream. The distillate temperature was kept at 30 °C and the feed temperature was either 50 (50/30) or 70 °C (70/30). The flow rate was kept constant at 1.6 L min⁻¹.

### 3.4.2.2 Membrane scaling investigation

To further investigate the onset of rapid flux decline, a set of experiments was performed with the aid of a stereomicroscope. Water flux and total solids concentration as a function of time are shown in Figure 3.5. The dashed lines in Figure 3.5 indicate when pictures of scaling on the membrane surface were taken. Images of the PP22 membrane surface were captured before and after the onset of rapid flux decline. Similar to results shown in Figure 3.3, the water flux begins to rapidly decline at a total solids concentration of approximately 300,000 mg L⁻¹.
Figure 3.5. Water flux and total solids concentration as a function of time for experiment conducted with the stereomicroscope. Feed and distillate temperatures were 50 and 30 °C, respectively, feed volume was 1.5 L, flow velocities were 0.8 L min⁻¹, and the PP22 membrane surface area was 89 cm². Labeled dashed lines correspond to images of the feed side of the membrane surface during the experiment performed with the stereomicroscope.

Images of the different stages of scale formation on the feed side of the membrane are also shown in Figure 3.5. The onset of membrane scaling is first visualized after 7.5 hours of operating time, or when the feed solution concentration approached 250,000 mg L⁻¹ total solids. Thereafter, crystals continued to precipitate on the membrane surface and the water flux continued to decline. After approximately 9.5 hours of operation, or at a bulk feed solution concentration of 300,000 mg L⁻¹ total solids, the membrane surface was mostly covered with salt resembling salt crystals [22, 47].

To further evaluate the effect of sparingly soluble salts on flux decline, results from experiments performed with pure NaCl as the feed solution were super-imposed on results from experiments performed with GSL water (Figure 3.5). Interestingly, similar to results from experiments with GSL water, the same sharp decline in water flux occurred during the experiments performed with the NaCl water, indicating that the onset of homogeneous precipitation of salts, mainly NaCl, correlates to the onset of rapid water flux decline.

Water flux was higher during experiments with NaCl feed than during experiments with GSL water. Also, compared to the experiments with the GSL water, the rapid decline in water flux is delayed in the experiments with NaCl feed. This can be explained by further evaluating
the complexity of the solution chemistry for the GSL water. Sparingly soluble salts and organic matter are present in the GSL water (Table 3.1). OLI modeling results revealed that at a bulk GSL water feed solution temperature of 50 °C, calcium species are the first to reach saturation (at 340,000 mg L$^{-1}$ TDS), followed by NaCl (at 400,000 mg L$^{-1}$ TDS). Curcio et al., found that divalent calcium ions in the presence of humic acid form complexes with the carboxyl functional groups and cause membrane scaling [17]. The calcium scaling then serves as nucleation cites for other species, such as NaCl [16]. Therefore, scaling of sparingly soluble salts and NaCl are the mechanisms of rapid water flux decline in GSL experiments.

**Figure 3.6.** Water flux and distillate conductivity as a function of (a) elapsed time and (b) total solids concentration in the feed for experiments with the PP22 and TS22 membranes using cartridge filtered GSL feed water. The temperature for the feed and distillate streams were 50 and 30 °C, respectively, and the stream flow rates were 1.6 L min$^{-1}$.

### 3.4.2.3 Extended scaling experiments

Water flux and distillate conductivity as a function of time and total solids concentration are shown in Figure 3.6a and 3.6b. Long-term batch experiments were performed in a unique operating mode to evaluate the effect of membrane scaling over time. The first part of the cycle
was performed to evaluate how water flux decreases as concentration increases. Similar to results obtained for the successive batch experiments (section 3.2.1), in both sets of experiments, the water flux gradually declined until the feed solution reached approximately 300,000 mg L\(^{-1}\) total solids. The second part of the cycle (recirculation step) was performed under constant conditions to evaluate membrane scaling over time and its effects on water flux. During the recirculation step, water flux continued to declined, further indicating that in addition to a reducing partial vapor pressure of the feed solution, nucleation of sparingly soluble salts on the membrane also contribute to the gradual decline in water flux.

### 3.4.3 Scaling mitigation techniques

Three unique operating techniques were investigated to mitigate membrane scaling. These include reduced operating length, reduced operating length with flow reversal, and reduced operating length with temperature reversal. The PP22 membrane was chosen for these experiments because of its isotropic structure. The operating temperatures were chosen because an accelerated operating time and increased feed concentration can be achieved without wetting the membrane and compromising its performance.

#### 3.4.3.1 Mitigating rapid flux decline

The first technique to prevent scale formation during successive batch experiments was to terminate the experiment before a rapid flux decline occurred. Water recovered from the feed and distillate conductivity as a function of elapsed time are shown in Figure 3.7. Each line represents a successive batch experiment, and the slope of each line divided by the membrane area (0.0139 m\(^2\)) is the average water flux (L m\(^{-2}\) hr\(^{-1}\)) during each batch experiment (labeled above each line). During the first five successive batch experiments the water recovery only minimally changed. However, during the 6\(^{th}\) batch, scaling on the membrane and wetting of some pores caused a rapid decline in water flux and a sharp increase in distillate conductivity. Following these results, two new operating techniques were tested to mitigate and reverse scaling of minerals on the membrane.
Figure 3.7. Water recovered and distillate conductivity as a function of elapsed time for the successive batch experiments (runs) performed with the PP22 membrane and filtered GSL feed water. The numbers at the top of each line represent the average water flux (L m$^{-2}$ hr$^{-1}$) for each batch run. The experiments were conducted with feed and distillate temperatures of 60 and 30 ºC, respectively.

3.4.3.2 Flow reversal

Water recovered (i.e., distillate collected) and distillate conductivity as a function of elapsed time are shown in Figure 3.8 and each line represents a successive batch experiment. In this scale mitigation technique, the feed and distillate flow channels were exchanged after each successive batch experiment. The average water flux (L m$^{-2}$ hr$^{-1}$) during each batch experiment is labeled above each line. The average water flux during all experiments was 19.5 L m$^{-2}$ hr$^{-1}$ with a standard deviation of 1.44 L m$^{-2}$ hr$^{-1}$, indicating that membrane scaling was minimal. Following the first experiment, the distillate conductivity increased. This increase in distillate conductivity was mostly due to residual salts in the distillate hydraulic loop from the previous cycle/experiment and/or dissolution of scalants that deposited on the membrane surface and in the membrane pores. The cause for the different trends in distillate conductivity on either side of the membrane is not well understood; however, it is likely that the slight difference in surface characteristics on the opposite sides of the membrane resulted in dissimilar scaling and wetting
patterns on the membrane. Additional research on membrane characteristics, nucleation kinetics, and scale formation could provide further insight to this trend.

**Figure 3.8.** Water recovered and distillate conductivity as a function of elapsed time for the successive batch experiments with alternating feed and distillate channels. The feed and distillate channels were alternated three times each. S1 and S2 denote the initial feed and distillate sides, respectively, whereas 1, 2, and 3 denote the first, second, and third alternations of the feed and distillate sides. The numbers at the top of each line represent the average water flux (L m\(^{-2}\) hr\(^{-1}\)) for each batch experiment. The experiments were performed with the PP22 membrane and filtered GSL feed water, and were conducted with feed and distillate stream temperatures of 60 and 30 °C, respectively, at 1.6 L min\(^{-1}\).

### 3.4.3.3 Temperature reversal

Water recovered and distillate conductivity as a function of elapsed time for the third scale mitigation technique are shown in Figure 3.9. The average water flux (L m\(^{-2}\) hr\(^{-1}\)) during each batch experiment is labeled above each line. In this technique, the temperature difference across the membrane was reversed for a period of time before a new batch experiment was performed.
Figure 3.9. Water recovered and distillate conductivity as a function of elapsed time for the successive batch experiments (runs) performed with the temperature reversal technique. The numbers at the top of each line represent the average water flux (L m\(^{-2}\) hr\(^{-1}\)) for each batch run. The experiments were performed with the PP22 membrane and filtered GSL feed water, and were conducted with feed and distillate stream temperatures of 60 and 30 °C, respectively, at 1.6 L min\(^{-1}\).

The average water flux during these experiments was 20.6 L m\(^{-2}\) hr\(^{-1}\) with a standard deviation of 0.95 L m\(^{-2}\) hr\(^{-1}\). The water flux slightly declined during the sixth experiment and the distillate conductivity slowly increased. Overall, the water flux and salt rejection were higher during this operating technique than the previous scale mitigation techniques, and the use of freshwater to flush the feed channel was eliminated. Flow and temperature reversal techniques proved to be very effective in maintaining water flux and mitigating membrane scaling. Compared to previous experiments performed without scale mitigation techniques, experiments performed with the flow and temperature reversal techniques resulted in sustained, high water fluxes throughout batch concentration experiments.

Also, these operating techniques were performed without the use of chemicals (i.e., antiscalants, acids, and bases) to remove scalants and energy to cool the feed water. Scale mitigation via temperature reversal achieved the greatest average water fluxes, rejected nearly
100% of non-volatiles for the first six batch concentration cycles, and was performed without additional water and energy inputs. Therefore, these scale mitigation techniques could prove to be very impactful in MD. A recent study by Kesieme et al. [48] reported that addition of a 0.5 micron filter before the feed channel inlet was effective in capturing sparingly soluble salts that would have otherwise precipitated on the membrane. Hybridization of the proposed scale mitigation techniques with a 0.5 micron filtration of the feed could further mitigate membrane scaling and wetting in MD.

3.4.4 Efficiency of MD over natural evaporation

When considering replacement of evaporation ponds with DCMD, two central considerations are the time and costs involved in concentrating brines. Production of high-value minerals will continue to increase with growing demands, and acquisition of land for additional ponds can be costly or in some cases impossible. Therefore, the efficiency of natural evaporation of the Bear River Bay was compared to MD.

The net annual evaporation rate for the Bay River Bay is 41 inches per year [42]. From a simple unit conversion, on average 2.85 mm of water is evaporated from the bay each day. From results obtained in this research, DCMD can concentrate GSL water at an average rate of 20 L m$^{-2}$ hr$^{-2}$ (Figure 3.9), and from a simple unit conversion, approximately 480 mm of high-quality distillate water can be recovered from GSL water each day using DCMD. Therefore, applying DCMD to mineral production not only recovers high quality water, but also accelerates the natural evaporation process in concentrating hypersaline solutions by approximately 170 times.

In terms of land use, one acre (4,047 m$^2$) of evaporation ponds could be replaced with 259 ft$^2$ (24 m$^2$) of flat sheet DCMD membrane. Several studies have shown that DCMD is an economically and environmentally competitive water treatment process to RO when low-grade heat is utilized [25, 48, 49]. A study by Al-Obaidani et al. estimated that operating DCMD with a heat recovery system could reduce water cost to $0.64$ m$^{-3}$ of water produced (~40 kWh m$^{-3}$), making DCMD a competitive membrane process to RO ($0.50$ m$^{-3}$ of water produced) [25]. A more recent study estimated that water production costs with DCMD could be further reduced to $0.57$ m$^{-3}$ when low-grade heat is utilized and carbon tax is applied [48]. Therefore, in addition to concentrating GSL water for mineral recovery, the high-quality water produced can be sold to further offset operating costs.
3.5 Conclusions

DCMD was effective in concentrating GSL water to greater than 350,000 mg L\(^{-1}\). Operating DCMD at high ΔT of 40 °C was not sustainable; the membrane performance was compromised because of membrane scaling and pore wetting. Consequently, operating DCMD in successive batch mode without the use of scale mitigation techniques resulted in decreased membrane performance (i.e., lowered salt rejection and water fluxes).

Flow reversal and temperature reversal are new operating techniques that proved very effective in sustaining high water fluxes and membrane performance. The scale mitigation techniques were effective in inhibiting homogeneous precipitation of salts and disrupting nucleation of sparingly soluble salts on the membrane surface. Of the three scale mitigation techniques, the temperature reversal technique was most effective in maintaining high water fluxes (>20 L m\(^{-2}\) hr\(^{-2}\)) and high salt rejection. The new techniques were simple to operate and very impactful in mitigating scaling. Furthermore, the need for antiscalants and other chemicals used for membrane cleaning was avoided.

Replacing natural evaporation ponds with DCMD can result in enhanced operations and reduced environmental footprints. Operating DCMD with low-grade heat recovered from the on-site chemical processing plant can drastically reduce MD operating costs, and high-quality water recovered from the GSL water can aid in offsetting operating costs.

3.6 References


CHAPTER 4
ASSESSMENT OF ALTERNATIVE DRAW SOLUTIONS FOR ENHANCED PERFORMANCE OF THE OSMOTIC HEAT ENGINE
Submitted for potential publication in the Journal of Membrane Science

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4.1 Abstract

Osmotic power harnesses the energy of mixing between high and low salinity streams. The osmotic heat engine (OHE) is a closed-loop, membrane-based power generation cycle that couples pressure retarded osmosis (PRO), an osmotically driven membrane process, with a thermal separation process. In this investigation, membrane distillation (MD), a thermally driven membrane process, was used. High power density in PRO is essential to minimize equipment costs and parasitic pumping losses. Likewise, high water flux is needed in MD to efficiently reconcentrate the diluted draw solution from the PRO process and minimize equipment costs. In this study, several ionic organic and inorganic draw solutions were evaluated as working fluids in the OHE. Their performance was assessed in terms of PRO power density and reverse solute diffusion, and MD water flux and thermal efficiency. Potential pore wetting of the MD membrane was also evaluated. The working fluids were also assessed in terms of their potential for equipment corrosion. Results indicate that sodium formate and CaCl₂ outperform NaCl (commonly used PRO draw solution) in terms of PRO power density and reverse solute diffusion, and that LiCl and CaCl₂ outperform NaCl in terms of MD water flux. Furthermore, there were no signs of MD membrane wetting, even at high feed concentrations. Results were used to perform an economic analysis and make future recommendations on the most suitable working fluid for the OHE. Of the select salts, CaCl₂, MgCl₂, sodium propionate, and LiCl resulted in the lowest OHE electricity generation costs and had the lowest potential for corrosion.

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4.2 Introduction

Pressure retarded osmosis (PRO) is an osmotically driven membrane process that harnesses the energy of mixing between high and low salinity streams to produce mechanical energy [1]. In PRO, water permeates via osmosis through a semi-permeable membrane from a low concentration feed stream into a high concentration draw solution, thus the permeate stream becomes pressurized and dilutes the draw solution. For PRO to produce net energy, the hydraulic pressure of the draw solution is lower than the osmotic pressure difference between the draw solution and the feed, and as a result, the net driving force for transport of water (permeate stream) is still from the feed to the draw solution. The energy in the pressurized, diluted draw solution can then be converted into electrical energy via a turbine-generator set. From its original concept, most studies investigated PRO in open-loop configurations (Figure 4.1a), including stand alone PRO for energy generation from mixing of low concentration (e.g., river water or wastewater) and high concentration waters (e.g., seawater, Dead Sea water, or Great Salt Lake water) [2-4] or coupled RO-PRO for low-energy desalination [5, 6]. However, several factors inhibit open loop PRO process performance and economics, including feed water pre-treatment, membrane fouling, and inconsistent solution chemistries and temperatures [7-9].

Another PRO configuration, also proposed by Loeb [10], is a closed-loop PRO system (Figure 4.1b). In this system, the diluted draw solution from the PRO process is regenerated with a thermal separation process (e.g., distillation column) that utilizes low-grade heat from natural or industrial processes. The thermal process produces a concentration draw solution and a deionized water stream, which are then used again in the PRO process. McGinnis et al. investigated this closed-loop configuration, naming it an Osmotic Heat Engine (OHE) [11]—in their first investigation they used a novel, thermolytic ammonia bicarbonate draw solution. Recently, another configuration of this system that couples PRO with membrane distillation (MD) was proposed (Figure 4.1c) [12]. The main benefit of this configuration is that compared to thermal distillation processes, MD can operate at lower temperatures and can potentially have lower capital costs [13].

MD is a thermally driven membrane process in which the driving force is the partial vapor pressure difference (temperature and concentration dependent) across the membrane. In direct contact MD (DCMD), a warm feed stream (e.g., concentrated brine) and a cooler distillate stream (e.g., fresh water) are separated by a microporous, hydrophobic membrane [14]. Water
evaporates from the feed stream at the feed-pore interface on the feed side of the membrane, diffuses through the membrane pores, and ultimately condenses into the distillate stream on the distillate side of the membrane. One of the main requirements of the MD process is that the membrane remains hydrophobic and no pore wetting occurs. Pore wetting of the MD membrane lowers rejection and process efficiency.

Figure 4.1. Basic configurations of PRO, including (a) open-loop PRO, (b) closed-loop PRO with thermal distillation for regeneration of the draw solution, and (c) closed-loop PRO with MD for reconcentration of the draw solution. $U$ is heat flow, $HC$ is high concentration, $LC$ is low concentration, $J_w$ is water flux, and $J_s$ is salt flux.

The closed-loop OHE has several major benefits over the open-loop PRO. The OHE allows for control of solution chemistries and temperatures. Because impurities are not introduced into the system, the potential for membrane fouling is reduced and the need for frequent chemical cleaning or membrane backwashing is eliminated. The OHE system can use low-grade heat emitted from industrial processes, which increases energy utilization—industrial processes account for nearly 30% of the total U.S. energy demand, of which 20-50% of the energy consumed is lost as waste heat in the form of hot exhaust gases, cooling water, and radiant heat from hot equipment surfaces and other heated products [15]. Therefore, the OHE can be co-located with existing power plants (e.g., traditional power plants or geothermal power plants).
plants) or other industrial processes emitting low-grade heat (e.g., chemical processing plants, cement plants, breweries, etc.).

Although the closed-loop PRO system offers many benefits, there are several barriers that hinder further development of the OHE. Primarily, both MD and PRO are relatively new membrane processes and their integration is not fully studied or understood. For example, high power density of the PRO membrane is essential to maximize process efficiency and minimize capital and operating costs of the OHE. Likewise, high separation efficiency and low potential for membrane wetting is needed in MD to reconcentrate the diluted draw solution from the PRO process. Several commercially available forward osmosis (FO) membranes have been investigated for use in PRO, and only a few of these membranes exhibited high water permeability, selectivity, and mechanical stability [16]. Because of non-ideal conditions in the PRO membrane, reverse permeation of solutes from the draw solution into the feed stream occurs (referred to as reverse solute flux (RSF)). As solute accumulates in the membrane support structure (referred to as internal concentration polarization (ICP)), the osmotic driving force in PRO is reduced [17] and can be detrimental to OHE performance. To maintain a high osmotic driving force in the OHE, a portion of the PRO feed stream has to be bled to the MD feed stream for recovery of solutes and control of PRO feed chemistry (Figure 4.1c). The additional loading on the MD process will increase the amount of membrane area, pumping energy, and electricity generation costs of the OHE.

Typically, NaCl is used as the standard draw solution in osmotically driven membrane processes [18]. Although NaCl is abundant and inexpensive, compared to other salts, it has higher RSF in osmotically driven membrane processes [19, 20]. Several studies have investigated the use of other inorganic and organic salts for use in FO [20-28]. McCutchoen et al. proposed a novel ammonia-carbon dioxide draw solution for use in FO [24, 25], which was later investigated in the OHE [11]. Although ammonium bicarbonate is highly soluble and has high osmotic pressures, high RSF of ammonia hinders efficient utilization of this draw solution [19]. Achilli et al. investigated the use of different inorganic draw solutions for use in FO-RO hybrid systems [19]. Their study established a protocol for selection of optimal draw solutions in FO and recognized that ICP strongly depends on draw solution diffusivity. These results were further confirmed by Zhao et al. [27]. Bowden et al. conducted a similar study with ionic inorganic and organic draw solutions in FO and found that organic salts with larger cations experience lower
RSF [19, 22]. More recently, studies have aimed at engineering new and mixed draw solutions [20, 21, 29]. Engineered draw solutions combine the effects of high water permeation and low RSF, which are two important performance parameters in both open and closed-loop osmotically driven membrane processes. The addition of small amounts of chemical surfactants in draw solutions has been investigated in order to decrease RSF and increase process performance [21]. However, the use of surfactants, alcohols, and other organic solutes that have low surface tension is not favourable in MD because it increases the potential for membrane wetting [30].

Highly soluble ionic organic and inorganic salts are expected to increase PRO power densities; however, the RSF in PRO and the water flux in MD of these highly concentrated draw solutions needs to be experimentally verified. Although few studies have evaluated the potential of different draw solutions in PRO, the regeneration efficiency of these draw solutions using MD has not been investigated [11, 31]. Therefore, the main objective of this study was to evaluate the performance of different ionic organic and inorganic salts in PRO and MD, and their potential as working fluids in the OHE. Experimental results were used to perform an economic analysis and make future recommendations on working fluids most suitable for the OHE. Results from this study can be useful for identifying ideal working fluids for other closed-loop membrane based processes such as closed-loop FO-MD.

4.3 Theory

Several transport phenomena govern water flux, solute flux, and power density in PRO. These include external concentration polarization (ECP), ICP, and RSF. Similarly, MD water flux is governed by several phenomena, including temperature and concentration polarization (TP and CP), heat and mass transfer resistances across the membrane, and membrane wetting.

4.3.1 PRO

The driving force for PRO is the osmotic pressure gradient between a low concentration feed and high concentration draw solution stream. In its simplest form, Eq. 1 is the general equation used to describe water flux ($J_w$) in PRO:

$$J_w = A(\Delta \pi - \Delta P) \quad (1)$$
where, \( A \) is the water permeability coefficient (membrane specific), \( \Delta \pi \) is the osmotic pressure difference across the membrane, and \( \Delta P \) is the hydraulic pressure difference across the membrane. However, several transport phenomena impede water flux in PRO, including ICP, ECP, and RSF (Figure 4.2). As water permeates from the low concentration feed to the high concentration draw solution, the draw solution at the draw solution-membrane interface becomes diluted and the osmotic pressure driving force across the membrane declines—this is referred to as ECP. Similarly, as solutes diffuse from the high concentration draw solution to the low concentration feed stream, they accumulate in the membrane porous support structure (described as ICP). ICP in PRO is more severe than ECP, which is considered negligible [3, 17, 32, 33].

**Figure 4.2.** Schematic of concentration profiles at the PRO membrane. \( J_w \) is water flux, \( J_s \) is salt flux, \( \Delta \pi \) is the osmotic pressure difference across the membrane, \( C_{DS,b} \) is the bulk draw solution concentration, \( C_{DS,m} \) is the draw solution concentration at the membrane, \( C_{F,b} \) is the bulk feed concentration, \( C_{F,m} \) is the feed concentration at the membrane, \( ECP_D \) is the dilutive external CP, and \( ICPC \) is the internal concentrative CP.

ICP and ECP describe the severity of polarization—they can be calculated from film theory [32, 34] (Eq. 2 and 3, respectively), and the closer the moduli are to unity, the lesser the degree of polarization:

\[
\frac{\pi_{F,m}}{\pi_{F,b}} = \exp \left( J_w \frac{S}{D} \right) \tag{2}
\]
where $S$ is the structural parameter (membrane specific and defined by support layer thickness times pore tortuosity, divided by support layer porosity), $D$ is the diffusion coefficient of the draw solution solute, and $k$ is the mass transport coefficient of the draw solution solute in the draw solution flow channel. Yip et al. further expanded the general equation for water flux to include the effects of ICP, ECP, and RSF on PRO water flux [35]:

$$J_w = A \frac{\pi_{DS,m} \exp\left(-\frac{J_w}{k}\right) - \pi_{F,b} \exp\left(\frac{J_w S}{D}\right)}{1 + \frac{B}{J_w} \exp\left(\frac{J_w S}{D}\right) - \exp\left(-\frac{J_w}{k}\right)} - \Delta P}$$

(4)

where $\pi_{DS,b}$ is the osmotic pressure of the bulk draw solution, $\pi_{F,b}$ is the osmotic pressure of the bulk feed stream, and $B$ is the salt permeability coefficient (membrane and solute specific). The mass transport coefficient is a function of channel geometry and draw solution viscosity, density, and solute diffusivity [3, 32, 36]:

$$k = \frac{Sh D}{d_h}$$

(5)

where $Sh$ is the Sherwood number and $d_h$ is the hydraulic diameter of the flow channel. For a spacer-filled channel, the flow regime becomes turbulent at relatively low Reynolds numbers ($Re < 50$) [36-38], and the following correlation can be used to calculate the Sherwood number [36]:

$$Sh = 0.2Re^{0.57}Sc^{0.40}$$

(6)

where $Sc$ is the Schmidt number. The Schmidt number is the ratio of the kinematic viscosity to the solute diffusivity ($Sc = \nu/D$). The methodology for calculating the Reynolds number for a spacer filled channel can be found elsewhere [36].

$A$, $B$, and $S$ are inherent properties specific to the membrane, and they can be determined experimentally [18]. The ratio of $S$ to $D$ is defined as the solute resistivity for diffusion within the
porous support layer \( (K = \frac{S}{D}) \) and is a measure of the effect of ICP on water flux—the smaller \( K \), the more severe the effects of ICP on water flux \([19, 32]\). The water permeability and salt permeability coefficients describe how well water and solutes permeate through the membrane, respectively. Therefore, membranes with high permeability and selectivity (aka perm-selectivity), and low structural parameter are desirable in osmotically driven membrane processes \([3, 32, 35, 39]\).

Power density in PRO is a measurement of the energy that can potentially be generated per membrane area, and can be determined experimentally by multiplying the water flux by the hydraulic pressure in the draw solution (Eq. 7):

\[
W = J_w \Delta P
\]  

Theoretically, the maximum power density in PRO (determined by differentiating Eq. 7 with respect to \( \Delta P \)) is reached when the applied pressure is half the osmotic pressure of the draw solution \([33]\). Non-ideal conditions in the PRO membrane and concentration difference across the membrane give rise to RSF, which can be calculated using Eq. 8 when expanded to include the effects of ICP and ECP:

\[
J_s = B \left\{ \frac{c_{DS,b} \exp \left( \frac{J_w}{k} \right) - c_{F,b} \exp \left( J_w \frac{S}{D} \right)}{1 + \frac{\beta}{J_w} \left[ \exp \left( J_w \frac{S}{D} \right) - \exp \left( -\frac{J_w}{k} \right) \right]} \right\}
\]  

4.3.2 MD

Water flux in MD is proportional to the partial vapor pressure (PVP) difference of the feed and distillate streams (\( \Delta P_v \)) at the membrane-liquid interfaces (Eq. 9):

\[
J = C \Delta P_v
\]  

The membrane permeation coefficient \( (C) \) is a function of the temperature, pressure, membrane material, and membrane structure (i.e., porosity, tortuosity, and thickness). In many cases, for a given membrane, the membrane permeation coefficient can be approximated as being constant \([14, 40]\). The PVP difference is dependent on the temperature and composition of
the solutions. Higher solution temperatures result in higher VP, while higher solution concentrations result in lower PVP.

Several phenomena limit MD water flux and process efficiency. These include mass transfer resistance and heat conductance of the membrane, concentration polarization, temperature polarization, and membrane wetting [14, 41, 42]. A schematic of the concentration and temperature profiles and heat and water flux in MD is illustrated in Figure 4.3.

Figure 4.3. Schematic of temperature and concentration profiles across the MD membrane. $Q$ is the heat flux, $\Delta T$ is the transmembrane temperature, $C_{F,b}$ is the bulk feed concentration, $C_{F,m}$ is the feed concentration at the membrane surface, $T_{F,b}$ is the bulk feed temperature, $T_{F,m}$ is the feed temperature at the membrane surface, $T_{D,b}$ is the bulk distillate temperature, and $T_{D,m}$ is the distillate temperature at the membrane surface.

In DCMD, the membrane acts as a heat transfer interface between the feed and distillate streams. The temperature at the feed membrane interface is lower than in the bulk feed solution and the temperature at the distillate membrane interface is higher than in the bulk distillate stream, thus reducing the driving force for mass transport through the MD membrane. This phenomenon is termed temperature polarization (TP) and is expressed in Eq. 10:

$$TP = \frac{T_{F,m} - T_{D,m}}{T_{F,b} - T_{D,b}}$$

(10)
where $T_{F,b}$ and $T_{D,b}$ are the feed and distillate temperatures of the bulk streams, respectively, and $T_{F,m}$ and $T_{D,m}$ are the feed and distillate temperatures at the membrane interface, respectively. Because of heat transfer resistance, especially conductive heat loss in DCMD, the TP ratio is less than 1. Likewise, as water evaporates at the feed membrane interface and water vapor diffuses through the membrane pores, the concentration at the feed membrane interface increases; like in PRO, this phenomenon is referred to as ECP. Both ECP and TP are affected by cross flow velocity and solution viscosity and density. Generally, the effects of ECP in MD of dilute streams are considered negligible [41]; however, it can substantially impact the performance of MD at high feed salt concentration.

Several phase changes occur during the MD process, and heat transfer resistances across the boundary layers are often the rate-limiting step [14]. Heat transfer resistances in MD occur at the feed–membrane interface (vapor transfer), distillate–membrane interface, and the membrane barrier itself (conductive heat transfer). Therefore, the total heat transfer across the membrane is the sum of the vapor transfer and conductive heat transfer. Thermal efficiency in MD is defined as the ratio of latent heat of vaporization to the total (latent and conduction) heat, and is used to describe heat losses in MD [43]:

$$\eta = \frac{J \Delta H_v}{J \Delta H_v + \frac{E_m}{\delta}(T_{f,m} - T_{p,m})} \quad (11)$$

The thermal efficiency can be determined experimentally by performing an energy balance on the distillate channel:

$$\eta = \frac{m_p h_{fg}}{(m_{d,in} + m_p)c_{p,d}T_{d, out} - m_{d,in}c_{p,d}T_{d, in}} \quad (12)$$

where, $m_p$ is the mass flow rate of the permeate stream, $h_{fg}$ is the latent heat of vaporization of water in the MD feed stream, $m_{d,in}$ is the mass flow rate of the influent distillate stream, $c_{p,d}$ is the average heat capacity of the distillate stream, and $T_{d,in}$ and $T_{d, out}$ are the inlet and outlet temperatures of the distillate stream, respectively. The energy balance is performed on the distillate channel because the heat losses to the environment from the distillate channel are lower than the heat losses from the feed channel.
Heat transfer efficiency in MD can be reduced by decreasing flow rates and operating with thicker membranes [41]; however, operating at high flow rates increases pumping demands, and the use of thicker membranes increases mass transfer resistance within the membrane [44, 45]. Pore wetting of the MD membrane lowers salt rejection, and impairs the integrity of the membrane (i.e., loss of hydrophobicity). To limit membrane wetting, the pressure at the feed-membrane interface must be less than the entry pressure at the membrane surface [14]; therefore, working fluids, namely organic solutes and alcohols, with low surface tensions must be avoided.

4.4 Materials and methods

PRO and MD bench-scale experiments were performed. Select salts were used as PRO draw solutions and MD feed solutions. A system model was developed to evaluate their suitability as working fluids in the OHE.

4.4.1 Membranes

A commercial, semipermeable, flat-sheet FO membrane was acquired from Hydration Technology Innovation (HTI) (Albany, OR) and a hydrophobic microporous membrane was acquired from 3M (St. Paul, MN). The FO membrane is a polyamide-based, thin-film composite (TFC) and was used for PRO. The 3M MD membrane is made of polypropylene (PP) and it has a nominal pore size of 0.2 microns.

4.4.2 Membrane cells

A modified, stainless steel SEPA-CF II cell (GE Water & Process Technologies, Trevose, PA) was used for the PRO experiments. The cell has an active membrane surface area of 139 cm², with a feed and draw solution flow channel depth of 1 mm. The cannel length and width were approximately 14 cm and 10 cm, respectively. The feed and draw solution spacers were taped to the cell to prevent tearing of the membranes at the edges of the channels. Taping of the spacers decreased the effective membrane surface area to 124 cm².

A similar modified SEPA-CF cell made of acrylic plastic was used for the MD experiments. Nitrile rubber gaskets were used to form flow channels, approximately 2 mm deep, on each side of the membrane. Turbulence enhancing spacers were placed in the flow channels to
reduce temperature polarization effects, increase water flux [46], and ensure that the membrane lay flat and centered in the cell.

4.4.3 Spacers

Tricot warp knit (Hornwood Inc., Lilesville, NC) and non-woven extruded mesh spacers were used in these experiments. The tricot spacers used have 20 carrier channels per inch (0.68 mm wide) and are 0.5 mm thick. Two types of extruded mesh spacers were used. The one used for PRO has an inner filament length and filament diameter of 2.5 and 0.5 mm, respectively, and the one used for MD has an inner filament length and filament diameter of 3.5 and 1.25 mm, respectively. Spacer configurations used in MD and PRO are illustrated in Figure 4.4. Two tricot spacers, positioned at 45° to the flow were used in the PRO feed channel, and one tricot spacer with one extruded mesh was used in the PRO draw solution channel. An extruded mesh spacer was used in the MD distillate and feed solution channels.

![Figure 4.4](image.png)

**Figure 4.4.** Spacer configurations for (a) MD and (b) PRO bench scale experiments. An extruded mesh spacer was used in the MD distillate and feed solution channels. Two tricot spacers, positioned at 45° to the flow were used in the PRO feed channel, and one tricot spacer with one extruded mesh was used in the PRO draw solution channel.

4.4.4 Bench scale systems

PRO and MD bench scale experiments were performed. Different working fluids were tested and their performance in PRO (water flux, RSF, and power density) and MD (water flux, thermal efficiency, and rejection) were investigated. A supervisory control and data acquisition (SCADA) system (LabVIEW, National Instruments, Austin, TX; and UE9-Pro, LabJack, Lakewood, CO) was used to control and record pressures, flow rates, temperatures, and feed and working fluid concentrations.
4.4.4.1 PRO bench scale system

A flow schematic of the PRO test unit is illustrated in Figure 4.5. The thermally insulted feed and draw solution reservoirs were connected to a gear pump (Micropump, Vancouver, WA) and a direct drive plunger pump (Cat Pumps, Minneapolis, MN), respectively, which circulated the two streams co-currently on the opposite sides of the membrane. In practice, the feed and draw solution would be circulated counter-currently; however, due to the small size of the test cell, operating in co-current mode has negligible effects on process performance. Echopod ultrasonic level sensors (FlowLine, Los Alamitos, CA) were installed on top of the feed and draw solution reservoirs to monitor the levels of fluids and calculate water flux. Pressure transducers (Omega Engineering, Stamford, CT) located at the inlets and outlets of the membrane cell monitored feed and draw solution channel pressure drops, and a proportional valve (Hass Manufacturing Co., Averill Park, NY) was used to control the hydraulic pressure in the draw solution flow channel. Toroidal conductivity sensors (Sensorex, Garden Grove, CA), located at the membrane cell outlets, were used to monitor and facilitate the control of the feed and draw solution concentrations. A peristaltic pump (McMaster-Carr, Chicago, IL) was used to dose the draw solution with concentrated brine and maintain constant draw solution concentrations during experiments. Stream temperatures were monitored with silicon crystal based sensors (LabJack, Lakewood, CO) and controlled with shell-and-tube heat exchangers.

The feed and draw solution flow rates and temperatures were kept constant at 0.5 L min\(^{-1}\) and 30 °C, respectively. Experiments were performed at draw solution hydraulic pressures of 2.1 MPa (300 psi). Changes in feed tank volume, feed stream conductivity, and membrane cell inlet and outlet pressures were used to calculate water flux, RSF, and feed channel pressure drop, respectively. Power density was calculated by multiplying the water flux by the draw solution inlet pressure. Specific RSF was determined by the ratio between the RSF and water flux (\(J_d/J_w\)). PRO experiments were conducted for 150 minutes (thirty minute stabilization period, two hour data collection period). The PRO feed stream conductivity was closely monitored throughout the experiments, and was replaced with a new batch of deionized water once the conductivity reached 1,200 µS cm\(^{-1}\) (500 mg L\(^{-1}\) NaCl). Feed and draw solution samples were collected for analysis at the beginning and end of the data collection period.
Although the HTI TFC membrane can operate at draw solution hydraulic pressures of up to 3.4 MPa (500 psi) before deformation [16], a lower draw solution pressure was chosen to obtain more accurate water flux readings. Integrity tests were performed before and after each experiment to ensure that the membrane was not damaged. Membrane integrity tests were performed with a 50 mM NaCl draw solution and deionized water as the feed. The feed and draw solution flow rates and temperatures were kept constant at 0.5 L min⁻¹ and 30 ºC, respectively. Water flux and RSF were closely monitored to ensure that the membrane performance remained the same.

![Flow diagram for the bench scale PRO system.](image)

**Figure 4.5.** Flow diagram for the bench scale PRO system.

### 4.4.4.2 MD Bench scale system

A flow schematic of the DCMD test unit is illustrated in Figure 4.6. The thermally insulated feed (draw solution) and distillate stream reservoirs were connected to gear pumps (Micropump, Vancouver, WA), which circulated the two streams counter-currently on the opposite sides of the membrane. The distillate reservoir was positioned on an analytical balance to monitor the change in weight of the distillate, and calculate water flux. A toroidal conductivity sensor and graphite electrode conductivity probe, located at the membrane cell outlets, were used to monitor and facilitate the control of the distillate and feed solution concentrations. Experiments were conducted at constant feed solution concentrations having osmotic pressure of 17.4 MPa. The feed solution concentration was maintained constant by manually dosing the concentrated feed solution reservoir with deionized water. Stream temperatures were monitored and controlled with shell-and-tube heat exchangers. Heating and cooling reservoirs (Fisher
Scientific, Pittsburg, PA) were used to maintain the distillate and feed solution at constant temperatures.

The distillate and feed solution flow rates were kept constant at 1.0 L min⁻¹, and the temperatures of the distillate and feed solution kept at 24±2 °C and 56±1.6 °C, respectively. Changes in distillate tank weight and conductivity were used to calculate water flux and salt rejection, respectively. MD experiments were performed for one hour (thirty minute stabilization period, 30 minute data collection period). Feed and distillate samples were collected for analysis at the beginning and end of the data collection period.

### 4.4.5 Desktop screening process and solution chemistry

Twenty-eight potential working fluids were initially screened for the OHE by evaluating their solubility in water, toxicity, osmotic pressure, and pH. OLI Stream analyzer software (OLI Systems, Inc, Morris Plains, NJ) was used to determine the osmotic pressure, PVP, diffusivities, viscosities, and pH of the select salts. Corrosion rates were determined with OLI studio Corrosion Analyzer (OLI Systems, Inc, Morris Plains, NJ). Solute diffusivities were calculated using a harmonic average of the diffusivity coefficients for the individual ions [47]. Salts that had osmotic pressures lower than 1 MPa at saturation were excluded. The remaining working fluid candidates were then evaluated in terms of their hazardous materials identification (HMIS) codes. Similar to other studies, salts with an HMIS level higher than 2 were excluded [19, 22]. Alcohols were also excluded (high potential for wetting of MD membrane). The membranes
used for PRO are stable at a pH range of 2 to 11 (specified by manufacture); therefore, solutions with pHs out of this range were not considered.

From the initial list of salts, 18 ionic inorganic and organic salts were identified as possible working fluids; however, because the objective of the OHE is to produce energy, salts with high osmotic pressures must be used (high osmotic pressures produce higher power densities). Therefore, an additional screening criteria was applied: at saturation, salts must have osmotic pressures equal or higher than that of NaCl at saturation (~30 MPa). The additional screening criterion narrowed the list down to eight salts (Table 4.1). The salts were tested at concentrations equivalent to 17.4 MPa osmotic pressure (osmotic pressure of 3 M NaCl), and deionized water was used as the PRO feed and MD distillate. Specific salt costs are for certified ACS grade salts with purities higher than 99%, and were obtained from GFS Chemicals Inc. (Columbus, OH) and Univar USA, Inc. (City of Commerce, CA).

**Table 4.1.** Solubility, specific costs, and concentrations corresponding to 17.4 MPa osmotic pressure (equivalent osmotic pressure for 3 M NaCl) for eight potential OHE working fluids. Specific salt costs are bulk quotes from GFS Chemicals Inc., with the exception of Na(C2H5COO), which was referenced from Univar USA, Inc. The bulk salts are certified ACS grade, with purities > 99%.

<table>
<thead>
<tr>
<th>Working fluid</th>
<th>Solubility at 30 ºC g L⁻¹</th>
<th>Cost $ kg⁻¹</th>
<th>Concentration g L⁻¹</th>
<th>mol L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂</td>
<td>1,020</td>
<td>$9</td>
<td>175</td>
<td>1.6</td>
</tr>
<tr>
<td>HCOONa</td>
<td>655</td>
<td>$13</td>
<td>279</td>
<td>4.1</td>
</tr>
<tr>
<td>KBr</td>
<td>594</td>
<td>$20</td>
<td>381</td>
<td>3.2</td>
</tr>
<tr>
<td>LiBr</td>
<td>1,069</td>
<td>$48</td>
<td>191</td>
<td>2.2</td>
</tr>
<tr>
<td>LiCl</td>
<td>607</td>
<td>$56</td>
<td>108</td>
<td>2.6</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>751</td>
<td>$6</td>
<td>143</td>
<td>1.5</td>
</tr>
<tr>
<td>Na(C₂H₅COO)</td>
<td>1,000</td>
<td>$4</td>
<td>389</td>
<td>4.1</td>
</tr>
<tr>
<td>NaCl</td>
<td>318</td>
<td>$3</td>
<td>175</td>
<td>3.0</td>
</tr>
</tbody>
</table>

**4.4.6 Analytical procedure**

MD and PRO samples were prepared and analyzed for total dissolved solids concentration according to Standard Methods (APHA, 2005). Samples were diluted and analyzed for anions with an ion chromatograph (Model ICS-90, Dionex, Sunnyvale, CA) and for cations with an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Optima 5300 DV, PerkinElmer Inc., Waltham, MA). Total organic carbon for organic working fluids was analyzed using a carbon analyzer (Shimadzu, Kyoto, Japan).
4.4.7 System modeling and cost estimation

A series of mass and energy balances were used to determine system power outputs, system costs, and bleed ratios (salt specific). Bleed ratio is the fraction of the PRO feed stream (low concentration stream) that has to be diverted to the MD feed stream for recovery of salt and desalting of the PRO feed stream. The equations governing the cost and energy model are provided in the Appendix A. A schematic drawing of a full-scale OHE is illustrated in Figure 4.7.

![Figure 4.7. A schematic drawing of a full-scale OHE with the mass and energy flow symbols.](image)

Experimental results from PRO and MD bench scale experiments were used in the cost model, and include PRO water flux and RSF and MD water flux and rejection. Ideally, the PRO system would be operated at higher pressures and concentrations, allowing for higher power densities; however, it is expected that the relative ranking in terms of cost for different working fluids would be conserved at higher concentrations and pressures.

The parameters used in the model are summarized in Table 4.2. The MD recovery rate was referenced from literature [48]. At a feed and distillate temperature of 60 °C and 20 °C, respectively, the maximum theoretical recovery in MD was determined to be 6.3% [48], therefore, a recovery of 6% was chosen for the model. MD membrane wetting was assumed negligible, thus the low concentration inlet and outlet stream are deionized water. PRO
recoveries were referenced from FO manufacturer data [49]. The bleed ratio was determined by iterating until the inlet PRO feed concentration was 4 g L$^{-1}$. This PRO feed concentration was chosen because until this level it has minimal effect on the PRO driving force [3].

Table 4.2. Parameters used in the OHE energy and cost model. Specific membrane and module costs for PRO and MD were referenced from RO and MF manufacturing data, respectively. A 35% discount rate was applied to the quoted price to account for retail mark-up.

<table>
<thead>
<tr>
<th>System operating parameters</th>
<th>1,000 kW</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PRO operating inputs</strong></td>
<td></td>
</tr>
<tr>
<td>PRO water recovery</td>
<td>15%</td>
</tr>
<tr>
<td>Applied hydraulic pressure (DS)</td>
<td>2 (300) MPa (psi)</td>
</tr>
<tr>
<td>PRO module pressure drop</td>
<td>35 (5) kPa (psi)</td>
</tr>
<tr>
<td>Feed temperature</td>
<td>30 °C</td>
</tr>
<tr>
<td>Draw solution temperature</td>
<td>30 °C</td>
</tr>
<tr>
<td>Draw solution concentration</td>
<td>Salt specific g L$^{-1}$</td>
</tr>
<tr>
<td>Water flux</td>
<td>Salt specific L m$^{-2}$ hr$^{-1}$</td>
</tr>
<tr>
<td>Salt flux</td>
<td>Salt specific g m$^{-2}$ hr$^{-1}$</td>
</tr>
</tbody>
</table>

| **MD operating inputs**     |          |
| Water recovery               | 6%       |
| PRO module pressure drop     | 14 (2) kPa (psi) |
| Feed temperature             | 56 ± 2 °C |
| Distillate temperature       | 25 ± 1.5 °C |
| Feed concentration           | Salt specific g L$^{-1}$ |
| Water flux                   | Salt specific L m$^{-2}$ hr$^{-1}$ |
| Rejection                    | Salt specific % |

| **Specific costs**           |          |
| Specific PRO membrane element and vessel cost | 28 $ \text{m}^{-2}$ |
| Specific MD membrane element and vessel cost   | 38 $ \text{m}^{-2}$ |

| **Equipment efficiencies**   |          |
| ERD efficiency               | 95%      |
| Pump efficiency              | 70%      |

| **Design constraint**        |          |
| PRO feed concentration       | 4 g L$^{-1}$ or less |
4.5 Results and discussion

PRO and MD bench scale experiments were performed with select salts as OHE working fluids. Working fluid performance was evaluated in terms of PRO water flux, power density, and reverse solute flux, and MD water flux, thermal efficiency, and potential for wetting.

4.5.1 OLI modeling and working fluid selection

The maximum solubility and corresponding osmotic pressure of solution and PVP of water in solution for the initial screening of salts are shown in Figure 4.8. Although some of the salts are highly soluble, they do not have high osmotic pressures—in general, solutions that have high osmotic pressures, have low PVP of water in solution [52]. The relationships between osmotic pressure and PVP can be explained by the equations describing the osmotic pressure of solution (van’t Hoff equation) and PVP of water in solution (Raoult’s law), in which water is the solvent. The osmotic pressure of a solution is defined by a modified van’t Hoff equation and is a function of the ideal gas constant \((R)\), temperature of the solution \((T)\), activity of water \((\gamma_w)\), mole fraction of water \((\chi_w)\), and molar volume of water \((V)\) (Eq. 13):

\[
\Pi = \frac{-RT \ln (\gamma_w \chi_w)}{V_w} 
\]

The PVP of water in solution is defined by Raoult’s law and is a function of the vapor pressure of pure water \((P^*)\) (temperature dependent), the activity of water \((\gamma_w)\), and the mole fraction of water \((\chi_w)\) (Eq 14):

\[
P^* = P^0 \gamma_w \chi_w
\]

For example, when a given solution becomes more concentrated, the activity and mole fraction of water in the solution decreases, resulting in an increased osmotic pressure and decreased PVP. Therefore, working fluids that yield high PRO water fluxes most likely yield lower MD water fluxes.

Because the objective of the OHE is to produce energy, high PRO power densities must be obtained, and therefore, salts used in PRO must have high osmotic pressures. Following the initial screening, salts with osmotic pressures of 30 MPa at saturation (close to the osmotic
pressure of NaCl at saturation) or higher were chosen for investigation. These salts include potassium bromide (KBr), sodium chloride (NaCl), sodium formate (HCOONa), sodium propionate (Na(C₂H₅COO)), magnesium chloride (MgCl₂), calcium chloride (CaCl₂), lithium bromide (LiBr), and lithium chloride (LiCl). Of the select salts, NaCl is the least soluble and LiBr, CaCl₂, and Na(C₂H₅COO) are the most soluble.

**Figure 4.8.** The (a) maximum solubility (at 30 ºC) for the select salts and their corresponding (b) osmotic pressure (at 30 ºC) and PVP (at 60 ºC) at saturation.

Because the salts investigated in these experiments are at high concentrations, corrosion in the system is an important consideration. Corrosion can degrade pipes and turbo-machinery (e.g., pumps, turbines, heat exchangers, pressure exchangers) and reduce equipment lifetime. Furthermore, oxidized metals can deposit on the membranes and form scaling layers, thus decreasing PRO power density and possibly cause wetting of the MD membranes. Corrosion rates for the select salts at draw solution concentrations equivalent to 17.4 MPa of osmotic pressure with different metals (i.e., carbon steel, stainless steel 316, and stainless steel 304) are shown in Figure 4.9. Carbon steel was chosen because of its low cost. Stainless steel 304 and stainless steel 316 were chosen because of their resistance to corrosion. Titanium is another material with high resistance to corrosion; however, this metal is not available in the OLI Corrosion Analyzer database.
Figure 4.9. Corrosion rates and pH for select working fluids. Corrosion rates were calculated at draw solution concentrations equivalent to 17.4 MPa of osmotic pressure.

Stainless steel is a steel alloy enriched in chromium to increase oxidative corrosion resistance. Iron forms very brittle oxide films that easily detach and expose unoxidized metal. Conversely, chromium forms highly ductile oxide films that protect the underlying unoxidized metal. However, chloride ions are known to diffuse into the thin film of oxides and attack the underlying unpassivated steel [53]. Once this film is penetrated, pitting corrosion occurs [54]. Stainless steel 316 is enriched in molybdenum, which aids in decreasing chloride diffusion through the oxide layer. As a result, this alloy exhibits higher resistances to pitting corrosion.

Solution pH and chloride content are among the solution properties that most influence corrosion rates. For instance, LiBr has one of the lowest corrosion potentials, one of the lowest solution pH, and is absent of chloride. Overall, stainless steel 316 is one of the least corrosive materials for all salts, with the exception of HCOONa, which has one of the highest pHs and has the highest corrosion rate of all salts. HCOONa is also the only salt for which carbon steel is the least corrosive of the three materials. In general, carbon steel (absence of oxide film barrier) is most influenced by solution pH; the higher the pH of the solution, the higher the carbon steel corrosion rate; however, carbon steel is not sensitive to the chloride content of the working fluid. Conversely, the higher the chloride content in solution, the higher the corrosion rate for stainless steel 304. For example, stainless steel 304 had the highest corrosion rate for working fluids with chloride ions (i.e., NaCl, LiCl, CaCl₂, MgCl₂).
4.5.2 Experimental results: PRO

Water flux, power density, RSF, specific RSF, solute diffusivity coefficient ($D$), and permeability through the HTI TFC membrane ($B$) (calculated with Eq. 8) for the selected salts are shown in Figure 4.10. Although experiments were performed with the same osmotic pressure difference across the membrane (draw solution having osmotic pressure of 17.4 MPa), water flux ranged from 9.5 to 30 L m$^{-2}$ h$^{-1}$ and power density from 11.2 to 17.6 W m$^{-2}$. Of the investigated salts, HCOONa had the highest water flux and power density and Na(C$_2$H$_5$COO) had the lowest water flux and power density.

The difference in water flux and power density can be explained by the difference in ICP, ECP, and/or solute permeability. Several studies have concluded that ICP is more dominant than ECP, which is considered negligible [3, 17, 32, 33]. Because the same membrane was used for all experiments, the membrane structural parameter can be assumed constant [19], and therefore, the difference in solute diffusivity between the draw solutions dictates the severity of ICP [19]. As a result, the difference in water flux is due to the difference in solute diffusivity ($D$) and salt permeability ($B$).

Draw solution RSF ranged from 11.8 to 148 g m$^{-2}$ h$^{-1}$. Na(C$_2$H$_5$COO) and HCOONa had the lowest RSF and specific RSF. Similar to water flux, RSF (Eq. 8) is a function of ICP (related to $D$), ECP (related to $k$), and solute permeability; however, in contrast to water flux, a clear trend can be observed between RSF, specific RSF, and salt permeability. For example, KBr has one of the highest salt permeabilities and one of the highest RSF, whereas Na(C$_2$H$_5$COO) and HCOONa have the smallest salt permeability coefficients and the lowest RSF.

Salt permeability represents the diffusion of solutes in the membrane active layer and is dominated by the hydrated radius of the solute. From the Stokes-Einstein equation it can be derived that the hydrated radius of the solute is inversely proportional to its diffusivity [55]. Therefore, solute diffusivity is directly related to the hydrated radius of the solute and hence salt permeability. Achilli et al. also observed that ions with smaller hydration diameter, and thus higher diffusivity, exhibit higher RSF [19]. With the exception of the organic draw solutions, high diffusivities relate to high RSF. Similarly, solutes with ions of large hydration diameters relate to lower RSF. For example, KBr has the highest RSF, second highest diffusivity, and ions with two of the smallest hydration diameters (Table 4.3).
Figure 4.10. PRO (a) water flux, (b) power density, (c) reverse solute flux, and (d) specific reverse solute flux for select OHE working fluids. Solute diffusivity and permeability are also shown. PRO experiments operated at temperatures, flow rates, and applied hydraulic pressures (draw solution) of 30 ºC, 0.5 L min$^{-1}$, and 2 MPa (300 psi). The feed stream was deionized water and draw solution concentrations corresponded to osmotic pressures of 17.4 MPa (~2,500 psi). Thermodynamic properties and mass transfer coefficient for select draw solutions are also summarized in Table A1 of Appendix A.

However, the same trend between high diffusivity and high RSF does not apply to organic solutes. Organic compounds exhibit hydrophobic interactions with the carboxylic
functional groups in negatively charged polymeric membranes [56]. Therefore, other forces might play a role in retarding diffusive transport through the membrane.

Table 4.3. Hydrated diameters for different cations and anions [57, 58].

<table>
<thead>
<tr>
<th>Anion</th>
<th>Hydrated diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>0.30</td>
</tr>
<tr>
<td>C₂H₃COO⁻</td>
<td>0.50</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.30</td>
</tr>
<tr>
<td>HCOO⁻</td>
<td>0.35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cation</th>
<th>Hydrated diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>0.60</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.30</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.60</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.80</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Specific RSF values ranged from and 0.6 to 6 g L⁻¹. KBr, NaCl, and LiBr had the highest specific RSF and LiCl, MgCl₂, CaCl₂, Na(C₂H₅COO), and HCOONa had the lowest specific RSF. The specific RSF is a measurement of how much salt will need to be replenished in the draw solution, and in the OHE, it is an indicator of the bleed ratio (see section 3.7). Higher bleed ratio requires larger MD membrane area to reconcentrate the draw solution; therefore, salts with high specific RSF (i.e., KBr, NaCl, and LiBr) can be detrimental to OHE system costs and viability.

4.5.3 Experimental results: MD

Water flux, PVP of water in the MD bulk feed solution, and thermal efficiency for the MD experiments performed with the selected salts as the feed solutions are shown in Figure 4.11. The conductivity of the distillate stream (deionized water) decreased during the experiments, indicating that membranes rejected close to 100% of organic and inorganic feed solutes. The water flux for the different feed solutions ranged from 15 to 29 L m⁻² hr⁻¹, where LiCl had the highest water flux. For most salts (excluding LiCl, CaCl₂, and HCOONa) the water flux decreased with decreasing PVP of water in the feed. The viscosity, density, and heat capacity for the feed solutions at 56 ºC were evaluated (Table A2 in Appendix A); however, no clear trend could be drawn amongst the thermodynamic properties, PVP, and water flux.
Figure 4.11. MD (a) water flux and feed water PVP, and (b) thermal efficiency and distillate heat capacity. MD feed and distillate stream temperatures were 56±1.6 °C and 24±2 °C, respectively, and stream velocities were kept constant at 1 L min⁻¹. The distillate stream was deionized water and feed solution concentrations correspond to osmotic pressures of 17.4 MPa (~2,500 psi). The thermodynamic properties for the MD feed solutions at their respective concentrations are summarized in Table A2 of Appendix A.

The thermal efficiencies of the solutions ranged from 65 to 94%, with KBr having the highest thermal efficiency and Na(C₂H₅COO) having the lowest thermal efficiency. The thermal efficiency of the MD distillate stream decreased with decreasing water flux. Na(C₂H₅COO) had the lowest thermal efficiency, because of its high heat capacity and low water flux. Because thermal efficiency corresponds to the ratio of water flux to the total heat flux, it is an important parameter in the OHE. Working fluids with high thermal efficiencies are more effective in utilizing heat for their regeneration.

Although some of the investigated salts have desirable characteristics in PRO or MD (i.e., power density, specific RSF, water flux), they had undesirable characteristics in the other process. For example, HCOONa has the highest PRO power density and one of the lowest specific RSF; however, it had the lowest MD water flux. Na(C₂H₅COO) had a low PRO power density and low MD water flux, but had the lowest specific RSF. CaCl₂ on the other hand performed well in both PRO and MD — it had a high power density, low specific RSF, and high MD water flux. When evaluating individual experimental results, there is no obvious relation between performance in PRO and MD and it is difficult to draw a definitive conclusion about
which salt is best suited as an OHE working fluid. Therefore, a system model was developed and experimental results were used as inputs to evaluate system net power output and electricity generation costs for each of the working fluids.

4.5.4 Cost modeling results and working fluid selection

The system capital costs and net power output for the selected working fluids is shown in Figure 4.12. The total costs range from 5.9 to 10.1 million dollars and net electrical power outputs range from 150 to 450 kW (1 MW gross power). Salts with high RSF had high MD membrane costs and low net power outputs. This is due to the additional MD membrane area and pumping energy needed for recovering the salts from the PRO feed stream. For example, KBr has the highest RSF, the lowest net power output, and the highest system capital costs. The largest cost contributor to KBr is the additional MD membrane area needed to replenish the PRO draw solution, and additional pumping energy needed to replenish the draw solution substantially lowers system net power outputs. NaCl and LiBr also have two of the highest specific RSF, high additional MD membrane costs, and low net power outputs.

![Figure 4.12](image-url)

**Figure 4.12.** Capital costs and net power for a 1 MW OHE system for select working fluids using PRO and MD experimental data. PRO experiments were conducted at temperatures and applied hydraulic pressures of 30 °C and 2 MPa (300 psi), respectively. MD feed and distillate stream temperatures were 24 ± 2 °C and 56 ± 1.6 °C, respectively, and the cross flow velocities were kept constant at 1 L min⁻¹. Working fluid concentrations correspond to osmotic pressures of 17.4 MPa (~2,500 psi).
MD membrane cost is the largest contributor to system cost for all the salts tested. The costs for MD membranes (without bleeding of PRO feed) ranged from 2.4 to 4.4 million dollars and the costs for PRO membranes ranged from 1.6 to 2.5 million dollars—MD membrane total cost is nearly twice as high as total PRO membrane costs. Although water fluxes for MD and PRO were relatively similar (with the exception of HCOONa), the specific cost for MD membrane modules is nearly 36% higher than the costs for PRO membrane modules (Table 4.2). The total cost for MD membranes (i.e., membranes for working fluid regeneration and additional membranes for bleeding) is by far the greatest capital costs; therefore, when developing the OHE for commercial scale, attention must be given to optimizing the regeneration system. Selecting a working fluid with high MD water fluxes and low PRO specific RSF is paramount to realizing reduced capital costs for the regeneration system and subsequently the OHE.

The working fluid costs vary significantly among the different salts, ranging from $200,000 to $3.3 million dollars for a 1 MW (gross power) system. A system with LiBr as the working fluid has one of the highest specific salt costs (48 $ kg\(^{-1}\)) and the highest total working fluid cost. However, working fluids with high specific salt costs do not necessarily result in high system capital costs. For example, although LiCl has the highest specific salt cost (56 $ kg\(^{-1}\)), LiCl can generate higher osmotic pressures at lower concentrations; thus, less salt is needed. On the other hand, NaCl is one of the most abundant salts and has the lowest specific and total salt costs; however, a system with NaCl as the working fluid does not have the lowest capital costs because of the high RSF. While salt costs were not always the largest line-item for the continuous electricity generation OHE, these costs would be more significant if the system were used for energy storage.

The electricity generation costs for each of the working fluids is shown in Figure 4.13. KBr is the most expensive working fluid—it had the lowest net energy generation and second highest system costs. CaCl\(_2\) is the least expensive working fluid—it had one of the highest net energy productions and lowest system costs. CaCl\(_2\) had the second highest power density, one of the lowest specific RSF, and the second highest MD water flux. MgCl\(_2\), HCOONa, Na(C\(_2\)H\(_5\)COO), LiCl, and HCOONa have the lowest electricity generation costs ranging from 1.7 to $2.1 per kWh—these salts also had some of the lowest specific RSF and highest net energy production.
Figure 4.13. Electricity generation costs for a 1 MW OHE system for select working fluids using PRO and MD experimental data. PRO experiments operated at temperatures and applied hydraulic pressures of 30 ºC and 2 MPa (300 psi). MD feed and working fluid temperatures were 24 ± 2 ºC and 56 ± 1.6 ºC, respectively, and stream velocities were kept constant at 1 L min⁻¹. Working fluid concentrations correspond to osmotic pressures of 17.4 MPa (~2,500 psi).

Although electricity generation costs are a key consideration when evaluating the different working fluids, other performance criteria, including potential for system corrosion and thermal efficiency, must be considered. The performance criteria for each of the selected working fluids is summarized in Table 4.4. The relative performance of the working fluids for each of different criteria was assessed in terms of adequate (√) and inadequate (✗) rating. It can be conclude that working fluids with low RSF resulted in good net energy production and low electricity generation costs. The salt with the lowest electricity generation costs also had low specific salt costs and had good MD water fluxes. Although HCOONa had one of the lowest RSF, it has one of the highest corrosion potentials and lowest thermal efficiency. Salts with high corrosion rates have a higher potential for equipment degradation, which can result in increased capital costs. Likewise, working fluids with low thermal efficiencies will result in lowered system efficiencies. Of the working fluids evaluated, only CaCl₂ and MgCl₂ performed well in each category.
Table 4.4. Performance criteria for different working fluids

<table>
<thead>
<tr>
<th></th>
<th>PRO power density</th>
<th>RSF</th>
<th>MD water flux</th>
<th>MD thermal efficiency</th>
<th>Corrosion rate</th>
<th>Net energy</th>
<th>Specific salt cost</th>
<th>Electricity generation costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂</td>
<td>✓</td>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>MgCl₂</td>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Na(C₂H₅COO)</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>LiCl</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>HCOONa</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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</tr>
<tr>
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<td>x</td>
<td>✓</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
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</tr>
<tr>
<td>LiBr</td>
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<td>x</td>
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<tr>
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<td>✓</td>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

4.6 Conclusions

The performance of potential working fluids for the closed loop OHE was experimentally evaluated in both PRO and MD. HCOONa and CaCl₂ outperformed NaCl in terms of PRO power density and specific RSF, and LiCl and CaCl₂ outperformed NaCl in terms of MD water flux. Working fluids with low RSF lead to lower pumping energy and MD membrane area, which resulted in low capital costs, high net power generation, and low electricity generation costs. Of the select salts, CaCl₂, MgCl₂, sodium propionate, and LiCl resulted in the lowest OHE electricity generation costs and had the lowest potential for corrosion. CaCl₂ and MgCl₂, were the only two working fluids that performed well for each of the performance criteria (i.e., low specific salt costs and RSF, and high PRO power density, MD water flux, MD thermal efficiencies, and net power generation) — consequently, these salts had the two lowest electricity generation costs. Because several factors contribute to generation costs, an ideal salt would combine high power densities, low RSF, low salt costs, high MD water fluxes and thermal efficiencies, and low potential for equipment corrosion. Results from this study can also be impactful in identifying ideal working fluids for closed-loop FO-MD.

4.7 Symbols

\( A_m = \text{area} \ [m^2] \)
\( C = \text{concentration} \ [g \ L^{-1}] \)
\( HC = \text{high concentration} \)
\( J_s = \text{salt flux} \ [g \ m^{-2} \ h^{-1}] \)
\( J_w = \text{water flux} \ [L \ m^{-2} \ h^{-1}] \)
\( l = \text{module length} \ [m] \)
\( LC = \text{low concentration} \)
\( M = \text{mass} \ [kg] \)
\( N = \text{number of modules} \)
\[ P = \text{pressure} \ [kPa] \]
\[ PD = \text{power density} \ [W \ m^{-2}] \]
\[ Q = \text{flow} \ [L \ h^{-1}] \]
\[ r = \text{module radius} \ [m] \]
\[ R = \text{recovery} \ [%] \]
\[ S = \text{specific costs} \ [$^{-1}] \]
\[ U = \text{overall heat transfer coefficient} \ [kW] \]
\[ V = \text{volume} \ [m^3] \]
\[ W = \text{power} \ [kW] \]

\textbf{Subscripts}
\[ b = \text{bleed} \]
\[ d = \text{distillate} \]
\[ ds = \text{draw solution} \]
\[ h = \text{high concentration} \]
\[ i = \text{inlet} \]
\[ l = \text{low concentration} \]
\[ m = \text{membrane} \]
\[ MD = \text{membrane distillation} \]
\[ o = \text{outlet} \]
\[ p = \text{permeate} \]
\[ PRO = \text{pressure retarded osmosis} \]
\[ r = \text{recycle} \]
\[ t = \text{tank} \]
\[ tg = \text{turbine generator} \]

4.8 References


CHAPTER 5
TECHNO-ECONOMIC ASSESSMENT OF THE CLOSED LOOP OSMOTIC HEAT ENGINE FOR ENERGY GENERATION AND STORAGE

Manuscript being prepared for submission for potential publication in Desalination

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5.1 Abstract

Osmotic power harnesses the energy of mixing between high salinity and low salinity streams to generate useful energy. The closed loop osmotic heat engine (OHE) is a membrane-based cycle that couples pressure retarded osmosis (PRO), an osmotically driven membrane process, with membrane distillation (MD), a thermally driven membrane process. The OHE can also be designed to store energy that can be released as needed, for example during periods of peak electricity demand. The objective of this study is to evaluate the technical and economic feasibility of the OHE compared to alternative technologies, and to assess its potential as an energy storage system. Experimental data and previously established MD and PRO models were used to develop an OHE system model that calculates system efficiency, net power output, and electricity generation costs. A sensitivity analysis was performed to evaluate the influence of select model inputs on electricity costs, and the results indicate that PRO membrane power density has the highest impacts on electricity costs. Although OHE electricity generation cost of $0.48 per kWh is not competitive with conventional average U.S. grid electricity costs $0.04 per kWh, energy storage costs for the system could be competitive with other energy storage systems.

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5.2 Introduction

Increased energy efficiency of existing processes and widespread installation of alternative and renewable energy technologies can aid in reducing the consumption and dependence on fossil fuel. Conventional coal-fired power plants have an average efficiency of 32%, leaving a large percentage of waste heat to be recovered [1]. Industrial processes consume nearly 30% of the U.S. energy supply, and 20 to 50% of the energy consumed is lost in the form of low-grade heat (LGH) [2]. Existing technologies that can generate energy from LGH are operating at temperature higher than 90°C, thus representing significant opportunity for development and utilization of low-temperature (90°C), LGH recovery processes [2-5]. Furthermore, development and installation of renewable energy storage technologies is an important aspect for managing electricity usage during periods of peak demand. Recently, the California legislature passed a bill that mandates California public utilities to procure 1.3 GW of energy storage by 2020 [6].

The osmotic heat engine (OHE) is a closed-loop, membrane-based energy cycle that utilizes osmotic pressure and thermal energy (i.e., LGH) to produce electrical energy. This system couples pressure retarded osmosis (PRO), an osmotically driven membrane process, with membrane distillation (MD), a thermally driven membrane process. MD can utilize LGH to separate saline water into two streams: a low concentration deionized water and a high concentration brine. The two streams are then transferred into a PRO process, where the osmotic pressure difference between the streams is converted into mechanical energy that can be further converted into electrical energy via a turbine-generator set. The diluted brine from the PRO process is then regenerated in the MD process. The system net power output can be described as the difference between the work of the turbine and the sum of pumping energy and friction losses in the OHE system. The energy efficiency of the OHE system is the ratio of the net energy output to the LGH input.

In the past, PRO has been investigated mainly in open-loop applications, including energy generation from the mixing of river water or reclaimed water and high concentration streams such as seawater, Great Salt Lake Water, or Dead Sea water [7-17], and in low energy desalination [18-20]. However, in open-loop PRO, substantial pretreatment is needed to mitigate membrane fouling, and solution chemistry and temperatures are inconsistent [16, 17, 21]. Operating PRO in a closed-loop configuration such as the OHE (Figure 5.1) offers several
benefits over open-loop configurations. These include 1) control of solutions chemistry and temperature—high purity working fluids eliminate membrane fouling and scaling; thus, increasing membrane lifetime and reducing operating and maintenance costs associated with energy and chemicals for pretreatment, membrane cleaning, and membrane backwashing; 2) the OHE can be coupled with existing processes that emit LGH; 3) utilization of LGH emitted from industrial process can enhance process efficiencies and potentially decrease environmental emissions; and 4) the OHE can be used to store thermal energy in the regenerated concentrated brine and deionized water streams, making it a viable technology for energy storage.

![Figure 5.1. Schematic of the closed-loop osmotic heat engine. The blue arrows represents a portion of the PRO feed stream bled to the MD feed stream for recovery of solutes and control of PRO feed chemistry.](image)

The OHE can be configured as an energy storage device to provide electricity during periods of peak demand. Two configurations were identified where energy storage could be integrated in the process: energy storage after MD or energy storage after PRO. In the first scenario (Figure 5.2a), the system is designed to have a small MD subsystem operating 24 hours a day, and separating the diluted draw solution (stored in a separate tank) into a high concentration draw solution and deionized water stream, both held in separate storage tanks. When energy is needed, a larger PRO subsystem is put into operation, utilizing the energy of
mixing of the two streams to produce electricity. The mixed streams are then sent back to the mixed stream storage tank (MD feed). In the second scenario (Figure 5.2b), smaller-size PRO and MD subsystems operate continuously (24 hours per day); however, part of the mixed stream is stored in an elevated storage tank; thus, the system acts as an osmotic pump. Once there is a demand for excess power, the stream in the elevated tank is released through a hydroturbine, similar to a hydropower plant.

**Figure 5.2.** Schematic of the OHE for (a) energy storage after MD and (b) energy storage after PRO. In scenario A (energy storage after MD), the MD subsystem operates continuously over a 24-hour period and the PRO subsystem operates during periods of peak power demand. In scenario B (energy storage after PRO), the MD and PRO subsystems operate continuously, 24-hour per day. In scenario B the dilute draw solution is stored in an elevated storage tank and released through a hydroturbine during periods of peak power demand.

Although the closed-loop PRO process offers many benefits, several technical barriers must be addressed to promote the development of the OHE. Primarily, both MD and PRO are relatively new membrane processes and their integration is not fully optimized. PRO power density is an important performance parameter in the OHE and it is defined as the amount of
power generated (in watts) per unit PRO membrane area used. High PRO membrane power density is essential to maximize process efficiency and minimize the capital and operating costs of the OHE. Operating with high osmotic pressure draw solutions and at high hydraulic pressures can increase PRO power density; however, due to non-ideal conditions in the PRO membrane, reverse permeation of salts from the high concentration draw solution to the low concentration feed stream (referred to as reverse solute flux (RSF)) occurs, resulting in solute accumulation in the feed stream and a decline in the osmotic pressure driving force in the PRO process [22]. Therefore, to maintain a high osmotic pressure driving force in the OHE, a portion of the PRO feed stream has to be bled to the MD feed stream for recovery of solutes and control of PRO feed chemistry. The additional desalination loading on the MD process results in increased MD membrane area and pumping demands, which negatively impact the capital and O&M costs of the OHE. A recent study evaluated the thermodynamic efficiency of the OHE; however, this study did not evaluate electricity generation costs or consider practical limitations such as heat and mass transfer limitations in MD and PRO, energy demand for pumping, and equipment efficiency [23].

The key objectives when integrating MD and PRO into the OHE are to maximize net power output and minimize electricity generation costs. Although the OHE is in the early stages of development, prospective electricity generation costs must be at or below competing renewable energy technologies. The Organic Rankine Cycle (ORC) is the benchmark technology, and one of very few commercially available technologies that can utilize LGH for electricity generation. Therefore, the main objective of this study was to perform a techno-economic assessment of the OHE for continuous electricity generation and for energy storage. A system model was developed and the system net energy and efficiency were evaluated. Outputs from the system model were used to determine the capital and operation and maintenance (O&M) costs of the OHE. Results from the cost model were used to compare electricity costs to competing processes that utilize LGH for electricity generation (e.g., ORC).

5.3 Theory and modeling approach

Established PRO and MD models were integrated to develop an OHE system model. Model outputs were used to estimate electricity generation costs for the OHE as a continuous power generation system and as an energy storage device.
5.3.1 Pressure retarded osmosis

PRO is an osmotically driven membrane process that harnesses the chemical potential difference between two streams and converts it to mechanical energy. In PRO, a semi-permeable membrane separates a low concentration feed stream and a high concentration brine (draw solution). For PRO to generate energy, the osmotic pressure difference between the draw solution and feed stream must be higher than the hydraulic pressure of the draw solution, and as a result, the net driving force for transport of water (permeate stream) remains in the direction of the feed to the draw solution. The permeate stream becomes pressurized to the hydraulic pressure of the draw solution and the pressurized draw solution becomes diluted. The energy in the pressurized draw solution is then converted into electrical energy via a turbine-generator set. Eq. 1 is the general equation describing water flux ($J_w$) in PRO:

$$J_w = A(\Delta\pi - \Delta P)$$  \hspace{1cm} (1)

where, $A$ is the water permeability coefficient (membrane specific), $\Delta\pi$ is the osmotic pressure difference across the membrane active layer, and $\Delta P$ is the transmembrane hydraulic pressure. Similar to other osmotically driven processes, concentration polarization at the membrane surface and within the membrane support layer limit the driving force in PRO. Eq. 2 takes into account the effects of polarization on water flux [24]:

$$J_w = A \left\{ \frac{\pi_{D,b} \exp(-\frac{J_w S}{k}) - \pi_{F,b} \exp(\frac{J_w S}{B})}{1 + \frac{\pi_{F,b} \exp(\frac{J_w S}{B}) \exp(-\frac{J_w}{k})}{\pi_{D,b} \exp(-\frac{J_w S}{k})}} - \Delta P \right\}$$  \hspace{1cm} (2)

where $\pi_{D,b}$ is the osmotic pressure of the bulk draw solution, $\pi_{F,b}$ is the osmotic pressure of the bulk feed stream, $B$ is the salt permeability coefficient (membrane and solute specific), $S$ is the structural parameter (membrane specific), $D$ is the diffusion coefficient of the solute in the draw solution, and $k$ is the mass transport coefficient of the solute in the draw solution channel. $A$, $B$, and $S$ are inherent properties of the membrane and can be determined experimentally [25].

The power that can be generated per unit area of membrane (power density) equals the product of water flux through the PRO membrane and the transmembrane hydraulic pressure:
\[ W = J_\omega \Delta P \] (3)

The theoretical maximum power density can be derived mathematically from Eq. 3—it occurs when the hydraulic pressure is half the osmotic pressure of the draw solution [12].

Because PRO membranes are not ideal, reverse permeation of salts (i.e., RSF) from the draw solution into the feed stream occurs. Eq. 4 describes RSF, and it is expanded to include the effects of polarization:

\[ J_s = B \left\{ \frac{c_{D,b} \exp(-J_w \frac{S}{R}) - c_{F,b} \exp(J_w \frac{S}{R})}{1 + \frac{R}{J_w} \exp(J_w \frac{S}{R}) - \exp(-J_w \frac{S}{R})} \right\} \] (4)

RSF in PRO reduces the effective driving force and can diminish PRO process performance [26]. In the OHE, solutes that accumulate in the PRO feed stream reduces the osmotic pressure driving force between the two streams; therefore, to maintain a high osmotic driving force in PRO, a small portion of the PRO feed stream needs to be redirected to the MD feed stream to desalinate the PRO feed stream and replenish solutes in the PRO draw solution.

5.3.2 Membrane distillation

MD is a thermally driven membrane process in which the driving force for mass transfer of water is the partial vapor pressure difference across a microporous, hydrophobic membrane. In direct contact MD (DCMD), a warm feed stream (e.g., brine) and a cooler fresh water stream (e.g., deionized water) are in direct contact with opposite sides of the MD membrane [27]. Water evaporates from the feed stream at the feed-membrane interface on the feed side of the membrane, the vapors then diffuse through the membrane pores and subsequently condense into the distillate stream. The water flux in MD is a function of the partial vapor pressure difference of the distillate and feed streams (\(\Delta P_v\)) at the membrane interface (Eq. 5) [28]:

\[ J = C \frac{dP_v}{dT} (T_{f,m} - T_{d,m}) \] (5)
where $C$ is the MD membrane permeation coefficient, and $T_{f,m}$ and $T_{d,m}$ are the temperatures of the feed and distillate streams, respectively, at the membrane interface. The partial vapor pressure difference is a function of the temperature and composition of the solutions. Higher water temperatures result in higher vapor pressures, while higher solution concentrations result in lower partial vapor pressures of the solvent (water). The mechanisms for heat transfer in DCMD can be divided into three regions: convective heat transfer at the feed-membrane interface (often the rate-limiting step), and latent heat of vaporization and conductive heat transfer through the membrane [27, 29]. Because the MD membrane acts as a heat transfer interface between the feed and distillate streams, the temperature at the feed membrane interface is lower than in the bulk feed solution and the temperature at the distillate membrane interface is higher than in the bulk distillate stream. This phenomenon, known as temperature polarization (TP), reduces the driving force for mass transport through the MD membrane.

5.3.3 OHE system modeling approach

Mass and energy balance equations were used to determine system power outputs, system costs, and bleeding ratio (percent of the PRO flowrate drained to the MD feed stream). A diagram of the OHE modeling approach is shown in Figure 5.3 and the equations are summarized in Appendix B. The OHE is comprised of four sub-systems: power generation (PRO), working fluid regeneration (MD), hydraulic system (e.g., storage tanks, piping, working fluid, land, etc.), and control system (e.g., sensors, control valves, relays, etc.). Model inputs include system size, PRO membrane coefficients, working fluid concentration, PRO draw solution hydraulic pressure (aka. PRO operating pressure), MD membrane coefficients, and MD operating temperatures. The PRO and MD membrane coefficients are obtained from experimental data, while the other input parameters are user-defined. Using these inputs, the model determines the PRO system power density, MD water flux, membrane area, heating and cooling loads, heat exchangers area, pumping demands, pressure exchanger size, and turbine size. These output parameters are then used to calculate the net power, system efficiency, and system costs. The intent of the model is to evaluate at what operating conditions the OHE is economically viable; therefore, PRO and MD membrane elements were modeled as a black box, and module effects were not considered.
Model input parameters and assumptions are summarized in Table 5.1. The pump, turbine, generator, pressure exchanger, and heat exchanger efficiencies were sourced from manufacturers or process literature [30-38]. The base case OHE scenario is for a 2.5 MW (net power) system with a working fluid concentration of 3 M NaCl and PRO operating pressure of 3.4 MPa (~500 psi). The system size and lifetime is based on the average size and lifetime of commercially available ORC plants, which is the benchmark technology [5, 39]. The PRO draw solution hydraulic pressure was chosen because it is the maximum applied pressure that PRO membranes can currently withstand without compromising membrane integrity (i.e., water flux and solute rejection) [40]. NaCl is a draw solution commonly used in osmotically driven membrane processes [25] and was selected as the OHE working fluid. Thermodynamic properties of the working fluid were modeled with OLI Stream Analyzer software (OLI Systems, Inc., Morris Plains, NJ).

![Input-output box diagram for the OHE cost analysis.](image)

**Figure 5.3.** Input-output box diagram for the OHE cost analysis. The user defines the OHE system size, working fluid concentration, PRO operating pressure, and system operating temperatures, and the model outputs system net power generation, efficiency, and costs (i.e., capital, operation and maintenance and electricity generation costs).

Because both MD and PRO are in early stages of development, and minimal work has been done on full-scale modules operated at high salinities, best available data was used. An average MD module recovery rate of 6% was sourced from the literature [41]. The MD module pressure drop was assumed to be 7 kPa (~1 psi), and a sensitivity analysis was performed to evaluate the impact of pressure drop on the OHE performance. A PRO module recovery of 15% and pressure drop of 14 kPa (~2 psi) were sourced from FO manufacturer data [42]. MD
membrane wetting was assumed to be negligible, and therefore the distillate stream of the MD process is consistently deionized water. The bleeding ratio was determined by changing the bleed flow rate until the inlet PRO feed concentration was $4 \text{ g L}^{-1} \text{ NaCl}$. This concentration was chosen because it has minimal effect on the PRO driving force [26]. A heat exchanger pressure drop of 7 kPa (1 psi) was assumed.

**Table 5.1.** Parameters used in the base case OHE energy and cost model. Specific membrane and module costs for PRO and MD were sourced from RO and MF manufacturing data, respectively. A 35% discount rate was applied to the quoted price to account for retail mark-up.

<table>
<thead>
<tr>
<th>System operating parameters</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System size</strong></td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Data and other assumptions</strong></td>
<td></td>
</tr>
<tr>
<td>Plant life</td>
<td>20 yr</td>
</tr>
<tr>
<td>Plant availability</td>
<td>90%</td>
</tr>
<tr>
<td>PRO membrane replacement</td>
<td>10%</td>
</tr>
<tr>
<td>MD membrane replacement</td>
<td>10%</td>
</tr>
<tr>
<td>Heat exchanger pressure drop</td>
<td>7 (~1)kPa (psi)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PRO operating inputs</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PRO water recovery</td>
<td>15%</td>
</tr>
<tr>
<td>Applied hydraulic pressure (DS)</td>
<td>3.4 (~500) MPa (psi)</td>
</tr>
<tr>
<td>PRO module pressure drop</td>
<td>14 (~2) kPa (psi)</td>
</tr>
<tr>
<td>Feed temperature</td>
<td>30°C</td>
</tr>
<tr>
<td>Draw solution temperature</td>
<td>30°C</td>
</tr>
<tr>
<td>Draw solution concentration</td>
<td>3 M NaCl</td>
</tr>
<tr>
<td>Draw solution osmotic pressure</td>
<td>18 (2,600) MPa (psi)</td>
</tr>
<tr>
<td>Membrane</td>
<td>HTI TFC</td>
</tr>
<tr>
<td>Membrane water permeability ($A$)</td>
<td>0.0249 L m$^{-2}$ h$^{-1}$ kPa$^{-1}$</td>
</tr>
<tr>
<td>Membrane solute permeability ($B$)</td>
<td>0.39 L m$^{-2}$ h$^{-1}$</td>
</tr>
<tr>
<td>Membrane structural parameter ($S$)</td>
<td>300 µm</td>
</tr>
<tr>
<td>Membrane mass transfer coefficient ($k$)</td>
<td>99 L m$^{-2}$ h$^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MD operating inputs</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Water recovery</td>
<td>6%</td>
</tr>
<tr>
<td>MD module pressure drop</td>
<td>7 (~1) kPa (psi)</td>
</tr>
<tr>
<td>Feed temperature</td>
<td>70°C</td>
</tr>
<tr>
<td>Distillate temperature</td>
<td>30°C</td>
</tr>
<tr>
<td>Draw solution concentration</td>
<td>3 M NaCl</td>
</tr>
<tr>
<td>MD membrane</td>
<td>3M 0.2 µm Polypropylene</td>
</tr>
<tr>
<td>MD membrane permeation coefficient ($C$)</td>
<td>5.21 kg m$^{-2}$ h$^{-1}$ kPa$^{-1}$</td>
</tr>
<tr>
<td>Temperature polarization coefficient</td>
<td>0.39</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Equipment efficiencies</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ERD efficiency</td>
<td>95%</td>
</tr>
<tr>
<td>Pump efficiency</td>
<td>70%</td>
</tr>
<tr>
<td>Turbine efficiency</td>
<td>90%</td>
</tr>
<tr>
<td>Generator efficiency</td>
<td>95%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Design constraint</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PRO feed concentration</td>
<td>4 g L$^{-1}$ or less</td>
</tr>
</tbody>
</table>
The PRO system was modeled using a thin-film composite (TFC), polyamide-based membrane from Hydration Technology Innovation (HTI) (Albany, OR). The membrane coefficients ($A$, $B$, and $S$) and mass transfer coefficient were sourced from the literature [44] and are specific to the draw solution and membrane. The MD system was modeled using results from testing with an MD membrane from 3M (St. Paul, MN). The membrane is made of polypropylene and has a nominal pore size of 0.2 microns. The MD membrane mass transfer coefficient ($C$) was determined experimentally using a method developed by Schofield et al. [28]. A temperature polarization coefficient [45] was applied to account for the decrease in water flux due to heat transfer losses in the MD process.

### 5.3.4 System costs

Specific costs and rate assumptions are summarized in Table 5.2. Specific costs were sourced from manufacturer data when possible, and from relevant literature. Costs were brought to present day values assuming an annual inflation rate of 3%, and a system discount rate of 8% was applied over the 20-year plant life. Because PRO and MD membranes are not yet commercial, membrane and module costs were sourced from commercially available RO and MF membrane and module costs [46, 47]—provided that hydrophobic, microfiltration membranes are used for MD and both RO and PRO membranes are thin-film composite polymer based membranes, this is not an unreasonable assumption. A 35% discount rate was applied to the quoted price to account for retail mark-up [48]. The cost of land was assumed to be 1.25 $ m^{-2}$. A 50% discount rate was applied to NaCl [49].

**Table 5.2.** Specific costs and rate assumptions used in the cost model. Specific costs were sourced from manufacture data and the literature. The cost for spare parts includes replacement costs for turbo-machinery, piping, valves, working fluid, etc.

<table>
<thead>
<tr>
<th>Specific costs and rate assumptions</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRO membrane element</td>
<td>11 $ m^{-2}$ [46]</td>
</tr>
<tr>
<td>PRO membrane vessel</td>
<td>17 $ m^{-2}$ [50]</td>
</tr>
<tr>
<td>MD membrane element</td>
<td>24 $ m^{-2}$ [47]</td>
</tr>
<tr>
<td>MD membrane vessel</td>
<td>14 $ m^{-2}$ [50]</td>
</tr>
<tr>
<td>DI water</td>
<td>5 $ m^{-3}$ Assumed</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.25 $ kg^{-1}$ [49]</td>
</tr>
<tr>
<td>Cost of land</td>
<td>1.24 $ m^{-2}$ [51]</td>
</tr>
<tr>
<td>Cost of labor</td>
<td>0.03 $ m^{-3}$ [35]</td>
</tr>
<tr>
<td>Cost of spares</td>
<td>0.03 $ m^{-3}$ [35]</td>
</tr>
<tr>
<td>Interest (discount) rate</td>
<td>8 %</td>
</tr>
<tr>
<td>Inflation rate</td>
<td>3 %</td>
</tr>
</tbody>
</table>

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Capital and O&M cost correlations were sourced from manufacturer data and literature and account for equipment economy of scale (Table 5.3). The costs of civil work, pumping, piping and valves, and the control system were sourced from membrane filtration and conventional water treatment literature [36, 52, 53]. The turbine was assumed to be a Francis turbine, the heat exchanger was assumed to be a stainless-steel plate-and-frame heat exchanger, and equipment costs were referenced from the literature [32, 54]. Pressure exchanger costs were obtained from ERI Inc. (San Leandro, CA). Because of the large system size and quantity of pressure exchangers needed, a 35% discount rate was applied to the quoted price to account for retail mark-up [48]. Storage tanks were assumed to be leg tanks for the continuous system and top and bottom-lined reservoirs for the systems with energy storage. Costs correlations were based on water distribution system costs [55].

Table 5.3. Capital and O&M cost correlations used in the OHE cost model. Capital and O&M costs were sourced from manufacturer data and relevant literature. Cost correlations were adjusted to reflect current value using a general annual inflation rate of 3%.

| Capital costs |  
|-------------------------------|------------------|
| Cost of civil work | $12,253 \times \Sigma A_m^{0.57}$ [36] |
| Turbine - generator set | $34,058 \times H^{0.274} \times W_{gross}^{0.66}$ [32] |
| Pressurized pump | $433 \times (1-\eta_{pp}) \times (Q_{i,h,pro} \times \Delta P_{pro} \times 0.024)^{0.39}$ [36] |
| Circulating pumps | $433 \times (Q \times \Delta P \times 0.024)^{0.39}$ [36] |
| Pressure exchanger | $146 \times (Q_{i,h,pro} \times 0.024)^{0.748}$ [34] |
| Membranes and modules | $A_m (S_e + S_v)$ [46, 47] |
| Heat exchangers | $300 \times (10.73 \times A_{hx})^{0.6907}$ [54] |
| Pipe fittings and valves | $9,233 \times \Sigma A_m^{0.42}$ [36] |
| Storage tanks | $(41 \times \ln(V_t) + 453) \times V_t$ [55] |
| DI Water | $V_{di} \times C_{di}$ - |
| NaCl | $M_s \times S_s$ - |
| Land | $FP_{ohc} \times S_{land}$ - |
| Control system | $2,252 \times \Sigma A_m^{0.66}$ [36] |
| Amortization factor | $i \times (1+i)^n \div ((1+i)^n-1)$ - |
| Indirect capital costs | $\Sigma direct capital costs \times 0.1$ [35] |
| Annual fixed charges | Indirect capital cost \times a \div (W_{net} \times PA \times 365 \times 24)$ [35] |

| Operation and maintenance (O&M) costs |  
|-------------------------------|------------------|
| Membrane replacement ($\$ yr^{-1}$) | $\lambda \times A_m \times C_e$ - |
| Cost of labor and spares ($\$ yr^{-1}$) | $(S_{labo} + S_{spares}) \times Q_{p,pro} \times 365 \times PA$ [35] |
| Total annual O&M costs ($\$ kWH^{-1}$) | $\Sigma membrane replacement + labor costs$ [35] |
| Annual O&M charges ($\$ kWH^{-1}$) | total annual O&M charges \div (W_{net} \times PA \times 365 \times 24)$ - |
| Total cost ($\$ kWH^{-1}$) | annual fixed charges + annual O&M charges - |
5.4 Results and discussion

A system model was used to evaluate OHE net energy generation, efficiency, footprint, and electricity generation costs. The OHE was investigated for continuous electricity generation and for energy storage. Two energy storage scenarios were evaluated: energy storage after MD and energy storage after PRO. Sensitivity analyses simulations were performed and ideal scenarios were evaluated.

5.4.1 System costs

The model outputs for the base-case, continuous generation OHE are summarized in Table 5.4. For an OHE system producing 2.5 MW of net power (4.9 MW gross power), the capital and O&M costs are $57.3 million and 3.6 million $ yr\(^{-1}\), respectively, and the electricity generation costs are $0.48 per kWh. At its current state, electricity generation costs for the OHE are not competitive with electricity generation costs for U.S. grid energy (averaging $0.04 per kWh [56]) or ORC ($0.08–0.13 per kWh [57]). OHE electricity generation costs can be reduced by decreasing capital and O&M costs, and by reducing energy demand for pumping in the system.

Table 5.4. Model results for 2.5 MW OHE continuous energy generation base case scenario with a 3 M NaCl solution and PRO draw solution hydraulic pressure of 3.4 MPa (~500 psi). Other values used for the base case scenario are summarized in Table 5.1.

<table>
<thead>
<tr>
<th>Model input/output</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>System size (gross power)</td>
<td>4.9</td>
<td>MW</td>
</tr>
<tr>
<td>System size (net power)</td>
<td>2.5</td>
<td>MW</td>
</tr>
<tr>
<td>MD pumping losses</td>
<td>1,040</td>
<td>kW</td>
</tr>
<tr>
<td>PRO pumping losses</td>
<td>625</td>
<td>kW</td>
</tr>
<tr>
<td>Process efficiency</td>
<td>0.1</td>
<td>%</td>
</tr>
<tr>
<td>System footprint</td>
<td>920 (0.23)</td>
<td>m(^2) (acres)</td>
</tr>
<tr>
<td>Membrane area</td>
<td>904</td>
<td>m(^2)</td>
</tr>
<tr>
<td>Other</td>
<td>16</td>
<td>m(^2)</td>
</tr>
<tr>
<td>PRO power density</td>
<td>45</td>
<td>W m(^{-2})</td>
</tr>
<tr>
<td>PRO water flux</td>
<td>25</td>
<td>L m(^{-2}) h(^{-1})</td>
</tr>
<tr>
<td>PRO RSF</td>
<td>25</td>
<td>g m(^{-2}) h(^{-1})</td>
</tr>
<tr>
<td>MD water flux</td>
<td>27</td>
<td>L m(^{-2}) h(^{-1})</td>
</tr>
<tr>
<td>Capital costs</td>
<td>57.3</td>
<td>million $</td>
</tr>
<tr>
<td>O&amp;M costs</td>
<td>3.6</td>
<td>million $ yr(^{-1})</td>
</tr>
<tr>
<td>Electricity generation costs</td>
<td>0.48</td>
<td>$ kWh(^{-1})</td>
</tr>
</tbody>
</table>
The OHE system footprint is approximately 920 m² (0.23 acres), which compared to an ORC system with the same capacity (120 m² system footprint), has a much larger footprint [39]. PRO and MD membrane area consume the majority of the OHE footprint, but the membrane footprint can be reduced by increasing PRO power density or MD water flux. Operating with high osmotic pressure draw solutions and at higher hydraulic draw solution pressures can increase PRO power density. MD water fluxes can be improved by increasing the partial vapor pressure difference between the feed and distillate streams (i.e., operating at higher feed solution temperatures or lower distillate stream temperatures).

The system efficiency is less than 1%, which is approximately 4% of the theoretical efficiency. The theoretical efficiency was estimated to be 2.5% with MD feed and distillate temperatures of 60 °C and 20 °C, respectively, and does not include non-idealities associated with heat and mass transfer in PRO and MD, turbo-machinery inefficiencies, or pumping energy demand [23]. Thus, system efficiency can also be improved by increasing net power outputs, PRO power density, and MD water recovery (i.e., higher water flux).

The net power is nearly 50% of the gross power because of the pumping energy needed to circulate the working fluids in the system. Pumping energy can be reduced by increasing PRO and MD recoveries. Studies have shown that although power density decreases with increasing recovery, the specific energy is increased [18, 58]. MD recovery can be improved by integrating an internal heat exchanger in the MD module [59]. Because the MD membrane acts as a heat transfer mechanism, the temperature of the feed stream, and thus the driving force for water flux, rapidly decreases along the length of the module. Therefore, the integrated heat exchanger–MD module design can maintain the high temperature of MD feed stream and increase MD recovery.

The capital and O&M costs for the various components of the OHE are shown in Figure 5.4. The largest contributor to capital costs is civil work and the largest contributor to O&M costs are labor and equipment spare parts. The costs for civil work and labor and equipment spare parts are a function of membrane area. The working fluid regeneration subsystem (MD) has the highest capital and O&M costs. Compared to the PRO subsystem, the water flux for MD is lower; thus, a larger MD system is needed to accommodate regeneration of the diluted draw solution from the PRO. Additionally, recovery of solutes from the PRO feed stream increases the area of MD membrane needed. MD membranes are the largest cost component for the MD subsystem and account for 14% of the total capital costs; therefore, minimizing MD membrane
area is critical to reducing electricity generation costs. The MD membrane area can be decreased by increasing MD water flux, which subsequently decreases OHE capital, O&M, and thus electricity generation costs.

The additional capital and O&M costs for bleeding of the PRO feed to the MD system are 16 and 6%, respectively, and an additional 100 kW of pumping power is needed for purging of the PRO feed. Selecting a working fluid with lower RSF could decrease the additional costs and pumping power associated with purging of the PRO feed. We evaluated different working fluids for use in the closed-loop OHE and concluded that electricity generation costs can be considerably reduced when choosing working fluids with low RSF (see Chapter 4).

![Figure 5.4](attachment:image.png)

**Figure 5.4.** (a) Capital and (b) O&M costs for the base case, 2.5 MW OHE with a 3 M NaCl draw solution and PRO draw solution hydraulic pressure of 3.4 MPa (~500 psi). Other values used for the base case scenario are summarized in Table 5.1.

### 5.4.1.1 OHE sensitivity analysis

A sensitivity analysis was performed to evaluate the effects of different operating parameters on system electricity generation costs. Ranges of select cost model parameters used in the sensitivity analysis are summarized in Table 5.5. These include OHE system size, PRO operating pressures, PRO and MD recoveries, MD operating temperatures, and MD module pressure drop. The draw solution used in the sensitivity analysis is a 3 M NaCl solution, and it is important to note that the heat exchangers were designed with an approach temperature of 10 °C;
thus, the LGH temperature is 10 °C higher than the MD feed temperature. Likewise, the cooling temperature is 10 °C lower than the distillate temperature.

OHE electricity generation costs and system efficiencies for the select ranges of parameters are shown in Figure 5.5. Increasing MD and PRO recoveries decreases pumping energy demand, subsequently decreasing electricity generation costs and increasing process efficiency. Increasing PRO recoveries from 15 to 40% decreases electricity costs by 20% (from $0.48 to 0.38 per kWh) and increases system efficiency by 32% (from 0.1 to 0.13%). Likewise, increasing MD water recovery from 6 to 30% decreased electricity costs by 25% (from $0.48 to 0.36 per kWh) and resulted in a six fold increase in process efficiency (0.1 to 0.6%).

Table 5.5. OHE base case values and sensitivity ranges for select operating parameters. Sensitivity analysis was performed by varying one of the select operating parameter while the other base case parameters were kept constant.

<table>
<thead>
<tr>
<th>OHE Sensitivities</th>
<th>Base case</th>
<th>Range for sensitivity analysis</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>System size (net power)</td>
<td>2.5</td>
<td>100 – 0.25</td>
<td>MW</td>
</tr>
<tr>
<td>PRO operating pressures</td>
<td>3.4 (500)</td>
<td>2.1–9 (300 – 1,300)</td>
<td>MPa (psi)</td>
</tr>
<tr>
<td>PRO recoveries</td>
<td>15</td>
<td>10 – 80</td>
<td>%</td>
</tr>
<tr>
<td>MD feed (LGH) temperature</td>
<td>70 (80)</td>
<td>90 – 50 (100 – 60)</td>
<td>°C</td>
</tr>
<tr>
<td>MD distillate (cooling) temperature</td>
<td>30 (20)</td>
<td>15 – 30 (5 – 20)</td>
<td>°C</td>
</tr>
<tr>
<td>MD recoveries</td>
<td>6</td>
<td>6 – 80</td>
<td>%</td>
</tr>
<tr>
<td>MD module pressure drop</td>
<td>7</td>
<td>3 – 34</td>
<td>kPa</td>
</tr>
</tbody>
</table>

Increasing PRO power density by increasing draw solution hydraulic pressures resulted in increased system efficiency and decreased electricity generation costs. The osmotic pressure of a 3 M NaCl draw solution is approximately 18 MPa; therefore, the theoretical maximum PRO power density occurs at a draw solution hydraulic pressure of ~9 MPa (1,300 psi). Increasing PRO operating pressures from 3.4 to 9 MPa decreased electricity generation costs by 55 % (from $0.48 to 0.21 per kWh) and tripled system efficiency (0.1 to 0.3%). As the hydraulic pressure of the draw solution increases, the power density increases, and less membrane area and pumping energy are needed. One caveat of operating at higher hydraulic pressures is that RSF increases; therefore, additional purging of the PRO feed stream to the MD feed stream (pumping losses and membrane area) is needed. However, the benefit of operating at higher hydraulic pressures outweighs the drawback of increased PRO feed stream purging. Current commercially available membranes used for PRO are not specific to this process and are compromised when operated at
hydraulic pressures higher than 3.4 MPa [58]—nevertheless, the development of high pressure PRO membranes should be achievable. For example, seawater RO membranes which are also thin-film composite polymeric membranes typically operate at close to 7 MPa [60]; therefore, continued research and development of high pressure PRO membranes is needed.

**Figure 5.5.** Results for select OHE sensitivity analysis. Electricity generation cost and system efficiency as a function of (a) MD recovery, (b) PRO recovery, (c) PRO hydraulic pressure, (d) MD pressure drop, and (e) MD feed and distillate temperatures; and (F) electricity generation cost, system footprint, and LGH required as a function of OHE system size.

MD module pressure drops can be detrimental to electricity generation costs and system efficiencies. Increased MD module pressure drops results in increased MD pumping energy and decreased net power outputs. Increasing MD module pressure drops from 7 to 14 kPa, results in a 21% increase in electricity generation costs (from $0.48 to 0.58 per kWh) and an 18% decrease in system efficiency (from 0.1 to 0.08%). Pressure drops as high as 70 kPa have been reported.
for MD spiral wound modules [61]; therefore, development of MD membrane modules that reduce pressure losses is critical for OHE process development.

Electricity generation decreases with increasing MD feed temperatures. Although the MD driving force is improved with decreased distillate temperatures, there is little effect on generation costs. According to Raoult’s law, the partial vapor pressure of a solution exponentially increases with temperature; therefore, compared to operating at lower distillate temperatures, operating at higher feed temperatures results in a higher MD driving force and higher water fluxes. Interestingly, operating with higher feed temperatures decreases system efficiency. Although MD water fluxes are increased at high feed temperatures, more heating is required, which results in decreased process efficiencies.

Electricity generation costs decrease with increasing system size. Electricity generation costs for systems smaller than 2.5 MW are not economical. Increasing the system size from 2.5 to 25 MW decreased electricity generation costs by nearly 30% (from $0.48 to 0.34 per kWh); however, larger systems require additional LGH and have a larger footprint.

5.4.1.2 OHE best case scenario

A best case scenario for the continuous energy generation OHE was performed and compared to the base-case scenario (Table 5.6). The ideal scenario evaluates OHE process performance and electricity generation costs assuming that future improvements are made to PRO and MD membranes and modules, and OHE operation conditions. In the best scenario, the OHE system size was increased to 25 MW (net power) and the PRO and MD recoveries were increased to 40% and 30%, respectively.

Because the OHE is a closed system, the potential for membrane fouling is reduced and the membranes can be replaced less frequently [43]; therefore, membrane replacement rate was decreased from 10% to 5% per year. The same working fluid and concentration (3 M NaCl) was used, but the hydraulic pressure of the PRO draw solution was increased from 3.4 to 7.6 MPa. The increased draw solution hydraulic pressure resulted in a 70% increase in PRO power density (from 45 to 76 W m$^{-2}$). Increasing the driving force (temperature difference) in MD resulted in a 40% increase in water flux (from 27 to 38 L m$^{-2}$ h$^{-1}$). If the parameters summarized in Table 5.6 were obtainable, electricity prices for this scenario would drop from $0.48 to 0.10 per kWh.
Table 5.6. Base and ideal case values for the OHE continuous generation system. The base case scenario evaluates OHE at the current state of technology and the ideal scenario evaluates OHE process performance and electricity generation costs assuming that future improvements are made to PRO and MD membranes and modules, and OHE operation conditions.

<table>
<thead>
<tr>
<th>Var</th>
<th>Base</th>
<th>Ideal</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>System size (net power)</td>
<td>2.5</td>
<td>25</td>
<td>MW</td>
</tr>
<tr>
<td>PRO operating pressure</td>
<td>3.4</td>
<td>7.6</td>
<td>MPa</td>
</tr>
<tr>
<td>PRO power density</td>
<td>45</td>
<td>76</td>
<td>W m⁻²</td>
</tr>
<tr>
<td>PRO recoveries</td>
<td>15</td>
<td>40</td>
<td>%</td>
</tr>
<tr>
<td>MD feed (LGH) temperature</td>
<td>70</td>
<td>85</td>
<td>°C</td>
</tr>
<tr>
<td>PRO recoveries</td>
<td>15</td>
<td>40</td>
<td>%</td>
</tr>
<tr>
<td>MD distillate (cooling) temperature</td>
<td>30</td>
<td>15</td>
<td>°C</td>
</tr>
<tr>
<td>MD recoveries</td>
<td>6</td>
<td>30</td>
<td>%</td>
</tr>
<tr>
<td>MD water flux</td>
<td>27</td>
<td>38</td>
<td>L m⁻² h⁻¹</td>
</tr>
<tr>
<td>Membrane replacement</td>
<td>10</td>
<td>5</td>
<td>% yr⁻¹</td>
</tr>
<tr>
<td>System efficiency</td>
<td>0.1</td>
<td>0.8</td>
<td>%</td>
</tr>
<tr>
<td>Electricity generation costs</td>
<td>0.48</td>
<td>0.10</td>
<td>$ kWh⁻¹</td>
</tr>
</tbody>
</table>

5.4.2 OHE with energy storage scenarios

The cost model was modified to evaluate the OHE as a potential energy storage device. Two scenarios were considered: energy storage after MD (scenario A), and elevated energy storage after PRO (scenario B). The operating conditions and select model outputs for the energy storage scenarios are summarized in Table 5.7.

Table 5.7. Cost model inputs and select outputs for energy storage after MD (scenario A) and elevated energy storage after PRO (scenario B).

<table>
<thead>
<tr>
<th>Variable</th>
<th>Storage after MD</th>
<th>Storage after PRO</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant size (net power)</td>
<td>2.5</td>
<td>2.5</td>
<td>MW</td>
</tr>
<tr>
<td>System efficiency</td>
<td>0.3</td>
<td>0.4</td>
<td>%</td>
</tr>
<tr>
<td>LGH required</td>
<td>660</td>
<td>550</td>
<td>MW</td>
</tr>
<tr>
<td>PRO membrane permeation rate</td>
<td>73,300</td>
<td>24,400</td>
<td>m³ day⁻¹</td>
</tr>
<tr>
<td>MD membrane permeation rate</td>
<td>33,000</td>
<td>27,000</td>
<td>m³ day⁻¹</td>
</tr>
<tr>
<td>PRO power density</td>
<td>45</td>
<td>45</td>
<td>W m⁻²</td>
</tr>
<tr>
<td>PRO water flux</td>
<td>47</td>
<td>47</td>
<td>L m⁻² h⁻¹</td>
</tr>
<tr>
<td>PRO solute flux</td>
<td>25</td>
<td>25</td>
<td>g m⁻² h⁻¹</td>
</tr>
<tr>
<td>MD water flux</td>
<td>27</td>
<td>27</td>
<td>L m⁻² h⁻¹</td>
</tr>
<tr>
<td>MD brine inlet temperature</td>
<td>70</td>
<td>70</td>
<td>°C</td>
</tr>
<tr>
<td>MD DI inlet temperature</td>
<td>30</td>
<td>30</td>
<td>°C</td>
</tr>
<tr>
<td>PRO membrane area</td>
<td>64,500</td>
<td>21,500</td>
<td>m²</td>
</tr>
<tr>
<td>MD membrane area</td>
<td>51,000</td>
<td>42,000</td>
<td>m²</td>
</tr>
<tr>
<td>System footprint</td>
<td>42,400 (10)</td>
<td>21,000 (5)</td>
<td>m² (acre)</td>
</tr>
<tr>
<td>Specific energy</td>
<td>2</td>
<td>3</td>
<td>kJ kg⁻¹</td>
</tr>
<tr>
<td>Height of storage reservoir</td>
<td>-</td>
<td>320</td>
<td>m</td>
</tr>
<tr>
<td>System costs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electricity generation costs</td>
<td>0.85</td>
<td>0.45</td>
<td>$ kWh⁻¹</td>
</tr>
<tr>
<td>Energy storage costs</td>
<td>15,400</td>
<td>8,750</td>
<td>$ kW⁻¹</td>
</tr>
</tbody>
</table>
The base case scenario for both systems is for a 2.5 MW (net power) system. The working fluid concentration was 3 M NaCl and the PRO operating pressure was 3.4 MPa (500 psi). Both systems were assumed to generate electricity over an 8-hour peak demand period. The specific energy storage costs were calculated by normalizing the total system capital costs to the gross power output. Because the energy storage systems are not continuously generating power, grid electricity was used to power the pumps. The pumping energy was included in the system O&M costs, and the electricity rate used was based on the U.S. average ($0.04 per kWh [56]). The specific energy is the ratio of the energy produced during the peak demand period to the amount of energy stored in the unmixed streams.

Figure 5.6. Energy storage cost breakdown for energy storage after MD (scenario A) and energy storage after PRO (scenario B).

The capital costs for scenario A and B are $15,400 and $8,750 per kW for energy storage, respectively. The costs for scenario B are lower than the costs for scenario A because of the smaller power generation subsystem (PRO)—the PRO system in scenario A is larger than the PRO system in scenario B because it only operates for 8-hour a day (note that both systems produce the same amount of net power). The regeneration system for scenario A is also slightly larger because additional membrane area is needed to recover the solutes from the PRO feed stream. Because of the larger MD and PRO subsystems in scenario A, additional civil work and a
larger control system are needed compared to scenario B. The hydraulic system costs are the largest cost for both systems because of the large energy storage reservoirs. Because the storage reservoirs for scenario A are larger than for scenario B, the hydraulic system costs are also larger. Overall, electricity generation costs for scenario B are lower than scenario A; however, scenario B is limited to areas with unique topography and elevation gains.

5.4.2.1 OHE storage sensitivity analysis and best case

A sensitivity analysis was performed on the elevation of the storage reservoir for scenario B (energy storage after PRO). The specific energy storage costs, system footprint, and PRO operating pressure as a function of storage reservoir elevation is shown in Figure 5.8. The elevation of the storage reservoir determines the hydraulic pressure of the PRO draw solution; therefore, the hydraulic pressure of the PRO draw solution increases with increasing base elevation of the storage reservoir. Subsequently, PRO power density increases and system footprint and specific energy storage costs decrease. Increasing the storage reservoir elevation from 320 m (base case) to 800 m (8.6 MPa) decreases energy storage costs by 41% and decreases system footprint by 60%.

![Figure 5.7](image)

**Figure 5.7.** Energy storage costs, system footprint, and PRO operating pressure (draw solution hydraulic pressure) as a function of storage reservoir elevation for energy storage after PRO (scenario B).
An ideal case scenario for energy storage after MD and PRO was evaluated. The operating parameters for the ideal case storage scenario are the same as the ideal case parameters used in the continuous generation scenario (Table 5.6).

![Graphs showing energy storage costs and system footprint as a function of net power for different scenarios.](image)

**Figure 5.8.** Energy storage costs and system footprint as a function of net power for (a) energy storage after MD and (b) energy storage after PRO; and electricity generation costs and LGH required as a function of net power for (c) energy storage after MD and (d) energy storage after PRO. The asterisks indicate the storage costs for the base case scenarios.
Energy storage costs, electricity generation costs, system footprint, and LGH required as a function of net power output for the ideal storage scenarios are shown in Figure 5.8. The asterisk denotes the base case energy storage costs. Similar to the continuous energy generation scenario, system costs are highly dependent on system size. For the ideal scenarios, the energy storage costs for a 2.5 MW (net power) system were $9,000 per kW for energy storage after MD and $15,000 per kW for energy storage after PRO. The electricity generation costs for the ideal scenarios become competitive to grid on-peak electricity costs as system size increases. Wholesale on-peak electricity price in Southern California is $0.15 per kWh [62], and peak demand loads are projected to increase by nearly 10% by the year 2022 [63].

5.4.3 Market potential evaluation

The best and ideal case continuous power generation OHE were compared to several competing technologies for energy generation from LGH. The performance characteristics and select operating ranges for competing technologies that utilize LGH for energy generation are summarized in Table 5.8. Because all LGH is not the quality, the type of LGH is categorized based on temperature: low-temperature LGH is less than 230 °C, medium-temperature LGH is between 230–650 °C, and high-temperature LGH is more than 650 °C [2].

<table>
<thead>
<tr>
<th>Operating temperature*</th>
<th>Osmotic Heat Engine</th>
<th>Organic Rankine Cycle</th>
<th>Piezoelectric Generation</th>
<th>Steam Rankine Cycle</th>
<th>Thermoelectric Generation</th>
<th>Thermophotovoltaic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage of development</td>
<td>Early</td>
<td>Mature</td>
<td>Early</td>
<td>Mature</td>
<td>Early</td>
<td>Early</td>
</tr>
<tr>
<td>Capital costs, $ kW⁻¹</td>
<td>3,500 – 11,800</td>
<td>1,500 – 3,500</td>
<td>10,000,000</td>
<td>1,100 – 1,400</td>
<td>20,000 – 30,000</td>
<td>N/A</td>
</tr>
<tr>
<td>Carnot efficiency, %</td>
<td>7.5 - 30</td>
<td>1-10</td>
<td>30-40</td>
<td>2-15</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>LGH temperature range, °C</td>
<td>40-80</td>
<td>100+</td>
<td>100-150</td>
<td>340-370</td>
<td>&gt;350</td>
<td>1,261</td>
</tr>
<tr>
<td>Energy storage capability</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes (thermal)</td>
</tr>
</tbody>
</table>

*Referenced LGH temperature ranges: low = <230 °C, medium = 230–650 °C, high = >650 °C
The capital costs for the OHE are based on gross power outputs and represent the capital costs range for the base case (low range) and ideal case (high range) continuous power generation OHE. Compared to other technologies in the early stage of development (i.e., thermal photovoltaic, piezoelectric generation, and thermoelectric generation), OHE costs are more competitive. ORC is the only commercially available technology that operates at low-to-medium temperature ranges. Although OHE capital costs are not yet competitive with ORC, the OHE has the potential for energy storage. Additionally, compared to ORC, OHE working fluids are non-flammable, non-toxic, and non fossil fuel based.

Electricity generation costs for renewable- and fossil fuel-based energy generation technologies are compared in Figure 5.9. The generation costs of the ideal case continuous generation OHE scenario ($0.10 per kWh) are comparable to the ORC and other renewable energy technology costs. Compared to wind and solar, the OHE can be considered a more reliable source of renewable energy if co-located with industrial processes that provides a constant source of LGH.

![Electricity generation costs for the OHE and competing energy technologies.](image)

**Figure 5.9.** Electricity generation costs for the OHE and competing energy technologies.

The electricity generation costs for the base and best case energy storage scenarios were compared to electricity generation costs for competing technologies (Figure 5.10). The values
represent the average energy storage costs and the error bars represent the range of reported values [64]. The range of reported values for the OHE are based on system size. Of the proposed storage technologies, pumped hydro, flywheels, compressed air, and sodium sulfur batteries are the more commercially available storage technologies. Currently, 95% of the U.S. energy storage capacity is pumped hydro [64]. At its current state of technology, the OHE as an energy storage device is not competitive; however, with future improvements to membranes and module design, the OHE could be more competitive with other energy storage technologies.

Figure 5.10. Capital costs for competing energy storage technologies [64]. The OHE is represented in green, commercially available technologies (i.e., compressed air energy storage, flywheel, and pumped hydro) are represented in gray, and battery technologies are represented in gray. The hybrid capacitor is a hybrid lead acid and double-layer capacitor.

To further evaluate the potential viability OHE to market, the strengths, weaknesses, opportunities, and threats of the OHE at its current stage of development were considered (Table 5.9). In addition to utilizing low-temperature, LGH and the use of non-toxic working fluids, the OHE could potentially be separated and the MD system can be used for generation of high quality distillate water.
Table 5.9. The strengths, weaknesses, opportunities, and threats for the OHE at its current stage of development.

<table>
<thead>
<tr>
<th>Strengths</th>
<th>Weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Working fluid is non flammable, non-toxic, non-fossil fuel based</td>
<td>• PRO and MD membranes and modules are in early stages of development</td>
</tr>
<tr>
<td>• Low temperature operation (LGH temperature 60 °C +)</td>
<td>• Space requirement for energy storage</td>
</tr>
<tr>
<td>• System can be used as an energy storage device</td>
<td>• High pumping losses</td>
</tr>
<tr>
<td>• Potential to bifurcate system</td>
<td>• PRO reverse solute flux</td>
</tr>
<tr>
<td>• Modular system</td>
<td>• Low efficiencies</td>
</tr>
<tr>
<td>• Modular system</td>
<td>• System complexity</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Opportunities</th>
<th>Threats</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Development of next generation PRO and MD membranes and modules</td>
<td>• Commercialization of PRO and MD membrane technologies</td>
</tr>
<tr>
<td>• Tax incentives and subsidies for renewable energy technologies</td>
<td>• Competing technologies for energy storage and LGH to electricity conversion</td>
</tr>
<tr>
<td>• Increased demand for renewable energy technologies</td>
<td>• Accessibility to cooling and LGH source</td>
</tr>
<tr>
<td>• Low-temperature, LGH market</td>
<td></td>
</tr>
</tbody>
</table>

The main weakness of the OHE is the cost of electricity generation; at its current state of technology, electricity generation costs are not competitive ($0.48 per kWh). The OHE is also very sensitive to scale, which limits the number of potential markets. For example, systems smaller than 2.5 MW (~65 MW of LGH) are not economically favorable. The primary threat to commercialization of the OHE is the development of alternative technologies that can more efficiently convert LGH to electricity.

The Department of Energy identified four major challenges confronting potential energy storage devices. These include the reliability of the energy sources, accessibility (or ramp-up time) of the stored energy, grid integration, and equitable regulatory environments [65, 66]. The ramp-up and ramp-down times for the OHE are expected to be similar to those of RO, whose ramp-up rate is 10 psi per second [67]. In terms of reliability of energy resources, the OHE can be coupled with conventional and geothermal power plants, which continuously emit low-grade heat.

5.5 Conclusions

Results from this study confirm that at the current state of technology, the OHE as a continuously operating energy generation system is not competitive with average U.S. grid electricity prices or with competing renewable energy processes that utilize LGH for energy
generation (e.g., ORC). However, higher MD water fluxes and PRO draw solution hydraulic pressure substantially decrease OHE system costs, and with future improvements to MD and PRO membranes and modules, OHE electricity generation costs could reach $0.10 per kWh, which is comparable to ORC electricity generation costs ($0.13–0.08 per kWh). Moreover, the OHE can use a wide variety of working fluids that are less toxic and safer (non-flammable) than those typically used in the ORC process.

With future improvements to membrane technologies, the OHE could be a competitive energy storage device: electricity generation costs for the storage scenarios could reach $0.12 per kWh, which are comparable to on-peak wholesale electricity prices in California ($0.15 per kWh). Energy storage after PRO was more competitive than energy storage after MD due to the lower PRO system size; however, energy storage after PRO is limited to high elevation areas. The results of the TEA suggest that the most attractive target markets for OHE will have four attributes: (i) high electricity generation costs, (ii) adequate LGH supplies; (iii) significant peak demand challenges, and (iv) incentives for increasing grid storage capacities.

5.6 Symbols

\[ A_m = \text{membrane area \ [m}^2\text{]} \]
\[ A_{hx} = \text{heat exchanger area \ [m}^2\text{]} \]
\[ a = \text{amortization factor} \]
\[ C = \text{concentration \ [g L}^{-1}\text{]} \]
\[ FP = \text{footprint \ [m}^2\text{]} \]
\[ HC = \text{high concentration} \]
\[ H = \text{pressure head \ [m]} \]
\[ i = \text{inflation rate \ [%]} \]
\[ J_s = \text{salt flux \ [g m}^{-2}\text{h}^{-1}\text{]} \]
\[ J_{w,\text{MD}} = \text{MD water flux \ [L m}^{-2}\text{h}^{-1}\text{]} \]
\[ J_{w,\text{PRO}} = \text{PRO water flux \ [L m}^{-2}\text{h}^{-1}\text{]} \]
\[ l = \text{module length \ [m]} \]
\[ LC = \text{low concentration} \]
\[ M = \text{mass \ [kg]} \]
\[ n = \text{plant lifetime \ [yr]} \]
\[ N = \text{number of modules} \]
\[ OHE = \text{Osmotic heat engine} \]
\[ P = \text{pressure \ [kPa]} \]
\[ PA = \text{plant availability \ [%]} \]
\[ PD = \text{power density \ [W m}^{-2}\text{]} \]
\[ Q = \text{flow \ [L h}^{-1}\text{]} \]
\[ r = \text{module radius \ [m]} \]
\( R = \text{recovery} \ [%\] \)
\( S = \text{specific costs} \ [\$ \cdot \text{^{-1}}] \)
\( U = \text{overall heat transfer coefficient} \ [\text{kW}] \)
\( V = \text{volume} \ [\text{m}^3] \)
\( W = \text{power} \ [\text{kW}] \)
\( \eta = \text{efficiency} \ [%\] \)
\( \lambda = \text{membrane replacement rate} \)

**Subscripts**
- \( b = \text{bleed} \)
- \( e = \text{element} \)
- \( f/d = \text{feed or d} \)
- \( h = \text{high concentration} \)
- \( hx = \text{heat exchanger} \)
- \( i = \text{inlet} \)
- \( l = \text{low concentration} \)
- \( m = \text{membrane} \)
- \( MD = \text{membrane distillation} \)
- \( o = \text{outlet} \)
- \( p = \text{permeate} \)
- \( PRO = \text{pressure retarded osmosis} \)
- \( px = \text{pressure exchanger} \)
- \( r = \text{recycle} \)
- \( t = \text{tank} \)
- \( tg = \text{turbine generator} \)
- \( v = \text{vessel} \)

5.7 References


[33] Seawater RO membranes, in, Freshwater Systems.


CHAPTER 6
COMPARATIVE LIFE CYCLE ASSESSMENT OF A NOVEL OSMOTIC HEAT ENGINE AND AN ORGANIC RANKINE CYCLE FOR ENERGY PRODUCTION FROM LOW-GRADE HEAT
Prepared for submission for potential publication in Desalination

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6.1 Abstract
A comparative life cycle assessment (LCA) was performed to evaluate the environmental impacts of an osmotic heat engine (OHE) and an organic rankine cycle (ORC) for electrical energy generation from low-grade heat. The OHE is a novel membrane based process that couples pressure retarded osmosis (an energy generating process) and membrane distillation (the working fluid regeneration process), and the ORC is an established thermal energy cycle. The environmental impacts for the construction and operation stages of the OHE were higher than the ORC; however, the global warming, ozone depletion, smog, and ecotoxicity impacts for the OHE disposal stage was less than the ORC. The OHE environmental impacts can be reduced by 80% with future improvements to PRO membrane and membrane module performance. Additionally, the OHE could be a viable energy production process that can increase energy efficiency and reduce CO₂ emissions from coal and natural gas power plants by 18.4 and 10.7 million kg of CO₂ per year, respectively.

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6.2 Introduction

Development of renewable energy production technologies that maximize efficiency and minimize resource consumption is necessary for protecting the environment and securing energy for future generations. Fossil fuel-based energy has been identified as the main source of anthropogenic greenhouse gas emissions [1, 2]; CO$_2$, NO$_x$, and hydrocarbon emissions can be reduced by implementing low carbon energy technologies and increasing energy efficiency in existing power plants and industrial processes [3]. Thermal inefficiencies in conventional power plants and industrial processes exist in the form of low-grade heat (LGH)—an abundant, and largely underutilized energy source [4]. Several technologies have been developed and investigated for utilization of LGH; however, the Organic Rankine Cycle (ORC) is one of the only commercially available technologies that can utilize LGH to generate electrical energy [4, 5]. The ORC is similar to a steam cycle, but in place of water, an organic working fluid is used. The benefits of using an organic working fluid include lowered risk of condensation in the expander and lower critical temperatures; however, organic working fluids are typically toxic, less chemically stable, flammable, and can have high global warming and ozone depletion emissions [6-11]. Additionally, the ORC is limited to operating at temperatures higher than 90 °C [6, 7].

The osmotic heat engine (OHE) is a hybrid, closed-loop membrane-based system that utilizes low-temperature (50 °C+), LGH and salinity gradient energy to produce electrical energy (Figure 6.1) [12, 13]. In the OHE, membrane distillation (MD), a thermally driven membrane process, is coupled with pressure retarded osmosis (PRO), an osmotically driven membrane process. In PRO, water permeates via osmosis through a semi-permeable membrane from a low concentration feed stream into a higher concentration brine (draw solution). The permeate stream becomes pressurized on the high concentration side of the membrane and a mechanical device (e.g., turbine generator set) is used to convert the hydraulic pressure to useful electric energy. Utilizing LGH from power generation or industrial processes, the diluted brine from the PRO process is separated with the MD process into concentrated draw solution and distilled water, which are then resupplied to the PRO process in the OHE. PRO power density (measured in Watts per m$^2$) is an important performance parameter in PRO and the OHE, and is defined as the product of the PRO water flux (membrane permeation rate per unit area of membrane) and the transmembrane hydraulic pressure.
The primary benefits of the OHE over the ORC include: 1) lower operating temperatures, 2) lower emission working fluids, and 3) potential for energy storage during periods of peak demand. Compared to the ORC, the OHE can operate at temperatures as low as 50 ºC, thus reaching broader markets. Additionally, the OHE can utilize non-toxic, non-flammable, chemically stable, non-fossil-fuel based, inorganic working fluids, which could make the OHE more competitive technology over the ORC.

To fully understand the benefits of the OHE over the ORC, the environmental impacts of the two processes should be evaluated. Life cycle assessment (LCA) is a useful tool that can be employed to quantify environmental impacts associated with all stages of a system's life (i.e., “cradle-to-grave”). LCA is a systematic approach that accounts for resource use and environmental emissions associated with material and energy flows consumed during the construction, operation, and disposal stages of a product or process [14, 15]. LCAs are commonly used to identify key stages and process components that contribute the largest
environmental impacts within a product or process, and to compare environmental impacts of similar products [15-19]. Results from LCAs can be used to make necessary operating, manufacturing, and supply-chain decisions.

Thus, the main objectives of this LCA are to compare the environmental impacts of the OHE and ORC, and evaluate how OHE life-cycle environmental impacts can be reduced. The overall performance of the OHE is highly dependent on MD and PRO process performance (see Chapter 5); therefore, sensitivity analyses were performed on PRO membrane power density and MD operating temperature. The sensitivity analysis was also extended to include an evaluation of an ideal case scenario OHE. The results from the life cycle impact assessment (LCIA) for the ideal case scenario OHE were compared to the ORC (benchmark technology), and CO₂ emissions were compared to a conventional coal power plant (CCPP) and natural gas power plant (NGPP). Ultimately, this information can aid in identifying and recommending potential improvements to the design and operation of OHEs.

6.3 Methodology

The life-cycle environmental impacts of the OHE and ORC for utilization of LGH for energy production were evaluated. The LCA considers material use for system construction and operation, and disposal of consumed materials over the system’s life. The framework for this LCA is described by the International Standards Organization [20], and in place of an external reviewer, two LCA experts contributed to this study.

6.3.1 Goal and scope

The goals of the study are to 1) perform an environmental LCA on the OHE, 2) identify OHE subsystems and equipment that have the largest contribution to life-cycle impacts, 3) assess how OHE impacts can be reduced, and 4) compare the life-cycle impacts of the OHE to those of ORC (a competing technology for energy production from LGH). The scope of this study extends to include material requirements for the construction, operation, and disposal (system consumables only) life-cycle stages of the OHE and ORC. The material and energy process flows and system boundaries are shown in Figure 6.2 for a 20-year system lifetime [21].
Figure 6.2. Study boundaries for the (a) OHE and (b) ORC. Materials and energy flows for system construction, operation, and disposal are considered in the LCA. The systems were evaluated over a 20-year lifetime, and with the same net power outputs and LGH and cooling temperatures.

Energy requirements for construction, transportation, and installation were excluded due to their small percentage of the total environmental load [17]. Because the pumping energy is supplied by the systems, external energy inputs for the operating stage are not included in the
study. The system boundaries reflect the final goal of this LCA study (i.e., to perform a comparative analysis of the environmental impacts of the two systems); therefore, OHE and ORC material and energy flows that are considered similar were not included in the system boundaries (e.g., control systems, land use, sourcing and discharge of LGH and cooling water). Although the OHE system footprint is much larger than the OHE system footprint (920 m$^2$ vs. 120 m$^2$) [12, 22], relative to the large environmental impacts of the turbo-machinery and other equipment needed, the additional environmental impacts associated with land use were considered negligible [10]. While sourcing and discharge of the LGH and cooling sources (used to heat and cool the ORC or OHE working fluid) can be harmful to aquatic life [23], the associated environmental impacts were considered similar for both systems and were not included in the analysis. The material outputs for the disposal stages of the OHE and ORC include membrane waste and working fluid disposal, respectively; however, the end-of-life for the turbo-machinery of the OHE and ORC (i.e., pumps, boiler, condenser, turbines, etc.) was not considered.

The systems were designed to produce 2.5 MW of net energy, which is the average size of a small scale commercially available ORCs [11, 22, 24], and to utilize the same heating and cooling source temperatures. The functional unit is one kWh of gross electrical energy produced; in other words, the environmental impacts were normalized to the gross electrical energy output.

6.3.2 Life cycle inventory

The life cycle inventory was completed in three phases. These include 1) design of the OHE and ORC at the target system size, 2) collection and scaling of data, and 3) inventory input to GaBi software (PE International, Seattle, WA). OHE equipment inventory and subsystem sizes were determined using a previously established system model (see Chapter 5). The OHE subsystems include: power generation (PRO), working fluid regeneration (MD), hydraulic system (i.e., storage tanks, piping, working fluid, land, etc.), and control system (i.e., sensors, control valves, relays, etc.). Base case and ideal case scenarios were considered for the OHE. The base case scenario describes the OHE at the current state of technology, and the ideal case scenario describes the OHE with future improvements to the technology. OHE and ORC design conditions are summarized in Table 6.1.
When possible, primary data were gathered and obtained from manufacturers and experimental results. Otherwise, secondary data were obtained from literature. The equipment inventories for the OHE and ORC are summarized in Table C1 in Appendix C. OHE material weights for the turbine, pump, and heat exchangers were obtained from Bai [9]. The OHE working fluid is a 3 M NaCl solution, a commonly used draw solution in osmotically driven membrane processes [25]. A recent study identified several OHE working fluids (i.e., LiCl, CaCl$_2$, MgCl$_2$) that outperform NaCl (see Chapter 4); however, these salts are not found in the GaBi database, and building a life cycle inventory for these salts is outside the scope of this study. Because the OHE is a closed loop-system and an inorganic working fluid is used (no degradation), the working fluid lifetime was assumed to be the same as the system lifetime and working fluid replacement was assumed at a rate of 0.5% per year to account for leaks and maintenance. Disposal was not considered because the “used” working fluid does not degrade and can be reused in the system. The PRO and MD membrane replacement rate is 10% per year [26], and the membranes are disposed of in a landfill [16, 17, 27, 28]. Sensitivity analyses were performed on PRO power density and MD operating temperature. It is important to note that the heat exchangers were designed with an approach temperature of 10 ºC; therefore, the LGH temperature is 10 ºC higher than the MD feed temperature and the cooling stream temperature is 10 ºC lower than the MD distillate stream temperature.

Table 6.1. Design conditions for the ORC and OHE. The base case OHE is designed with PRO and MD module water recoveries of 15 and 6%, respectively. The ideal case OHE scenario evaluates OHE process performance and electricity generation costs assuming that future improvements are made to PRO and MD membranes and modules and to OHE operation conditions, and that the system is designed with PRO and MD process recovery of 40 and 30%, respectively, higher PRO hydraulic pressures, and higher MD temperature difference.

<table>
<thead>
<tr>
<th>System operating condition</th>
<th>ORC</th>
<th>OHE – Base case</th>
<th>OHE – Ideal case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross electric power output, MW</td>
<td>3</td>
<td>4.9</td>
<td>3.1</td>
</tr>
<tr>
<td>Net electric power output, MW</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Design life, years</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>LGH temperature, ºC</td>
<td>85</td>
<td>85</td>
<td>100</td>
</tr>
<tr>
<td>Cooling temperature, ºC</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>PRO draw solution hydraulic pressure, MPa</td>
<td>N/A</td>
<td>3.4</td>
<td>7.6</td>
</tr>
<tr>
<td>Membrane replacement, % yr$^{-1}$</td>
<td>N/A</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td>Plant life, yr</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Plant availability %</td>
<td>90%</td>
<td>90%</td>
<td>90%</td>
</tr>
<tr>
<td>Working fluid</td>
<td>Pentane</td>
<td>3 M NaCl</td>
<td>3 M NaCl</td>
</tr>
<tr>
<td>Working fluid replacement, % yr$^{-1}$</td>
<td>10%</td>
<td>0.5%</td>
<td>0.5%</td>
</tr>
</tbody>
</table>
The ORC equipment inventory, equipment sizes, and material weights were modeled after a 250 kW (gross power) commercially available ORC [9]. The equipment sizes for the 2.5 MW ORC were scaled linearly with process size [21, 29]. The ORC working fluid used in this analysis is pentane. Compared to other working fluids (i.e., R 114, R245fa, R123, etc.), pentane has lower environmental impacts [8-10]. Because the ORC working fluid is organic and will degrade over time, the working fluid is assumed to be replaced at a rate of 10% per year due to system maintenance and repair for the ORC [9], and incineration is used as the disposal method. The material weight for the pumps, turbines, and heat exchangers (ORC boiler or evaporator and condenser) were adjusted using a series of scaling laws [29]. The adjustment for material weights follow a similar law to cost scaling laws:

\[
\frac{m_j}{m_{j,\text{ref}}} = \left( \frac{F_j}{F_{j,\text{ref}}} \right)^{k_{j,m}}
\]

where \(m_j\) is the mass to be calculated for material \(j\), \(m_{j,\text{ref}}\) is the reference mass for material \(j\), \(F_j\) is the functional parameter for equipment \(j\), \(F_{j,\text{ref}}\) is the reference functional parameter for equipment \(j\), and \(k_{j,m}\) is the scaling exponent, which is specific to the equipment (i.e., pump, boiler, heat exchanger, etc.). The functional parameter for the process equipment is based on equipment size (MW). The scaling exponents for process equipment were determined from reference datasets, whose methodology can be found elsewhere [29]. The scaling exponent is 1.0 for the pump and cooling heat exchanger (condenser) and 0.8 for the heating heat exchanger (boiler). The scaling exponent for ORC condenser was assumed to be the same as the heat exchanger, and the scaling exponent for a turbine was assumed to be the same as a pump.

The pressure exchanger is a PX-300 from Energy Recovery, Inc. (San Leandro, CA); its material and material weights were obtained from the manufacturer [30]. The holding reservoirs for the OHE were assumed to be vertical storage tanks with a 20-year lifetime, and the materials type and weight were obtained from manufacture data [31]. The PRO membrane is a thin-film composite membrane, and the membrane materials are obtained from the literature [32]. The MD membrane is a polypropylene membrane. PRO and MD membrane spacers were obtained from the literature [33]. The specific weight of the MD membrane and membrane spacers were determined by weighing a known area of representative sample. Membrane vessel material and material weights were obtained from a previous LCA study on membrane processes [16].
6.3.3 Life Cycle Impact Assessment

To identify environmental releases associated with the system material and energy flows, GaBi Product Sustainability Software (version 6), and GaBi library databases were used (Table C1 and S2 in Appendix C). The GaBi databases include over 7,000 life-cycle inventory profiles based on primary industry data [34]. TRACI version 2.1 was chosen as the impact assessment method within GaBi 6.0. TRACI is a midpoint oriented assessment model developed by the U.S. EPA, and reflects U.S. context [35]. A study by Zhou et al. evaluated the different impact assessment methods and their effects on the environmental impacts of desalination processes, and concluded that there are small discrepancies among the different impact assessment methods at the global level [36]. The impact categories and their respective units summarized in Table 6.2 include ozone depletion, global warming potential, acidification, eutrophication, human toxicity, ecotoxicity, and fossil fuel depletion.

Table 6.2. TRACI impact categories and their respective units per functional unit (kWh). The impact categories can be grouped into three general impact categories: ecosystem, human health, and resource depletion.

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Unit per functional unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecosystem</td>
<td></td>
</tr>
<tr>
<td>Ozone depletion</td>
<td>Trichlorofluoromethane (CFC-11) equivalent per kWh</td>
</tr>
<tr>
<td>Global warming</td>
<td>Carbon dioxide (CO₂) equivalent per kWh</td>
</tr>
<tr>
<td>Smog formation</td>
<td>Nitrogen oxides (NOₓ) equivalent per kWh</td>
</tr>
<tr>
<td>Acidification</td>
<td>Hydrogen ion (H⁺) equivalent per kWh</td>
</tr>
<tr>
<td>Eutrophication</td>
<td>Nitrogen (N) equivalent per kWh</td>
</tr>
<tr>
<td>Human health</td>
<td></td>
</tr>
<tr>
<td>Human health cancer</td>
<td>Comparative toxic units for humans (CTUh) per kWh</td>
</tr>
<tr>
<td>Human health non-cancer</td>
<td>Comparative toxic units for humans (CTUh) per kWh</td>
</tr>
<tr>
<td>Human health particulates</td>
<td>Fine particulate matter (PM 2.5) equivalent per kWh</td>
</tr>
<tr>
<td>Ecotoxicity</td>
<td>Comparative toxic units for ecotoxicity (CTUe) per kWh</td>
</tr>
<tr>
<td>Resource depletion</td>
<td>Fossil fuel depletion</td>
</tr>
<tr>
<td></td>
<td>Joules (J) surplus energy per kWh</td>
</tr>
</tbody>
</table>

6.4 Results and discussion

The environmental impacts for the OHE at its current state of technology (base case scenario) were evaluated. Sensitivity analyses on PRO operating pressures (associated with PRO power density) and MD operating temperatures (associated with MD water fluxes) were performed. Results from the sensitivity analyses were used to perform an LCIA for an ideal case scenario OHE. The life-cycle impacts of the OHE ideal case scenario were then compared to the life-cycle impacts of an ORC, CCPP, and NGPP.
6.4.1 Base case scenario OHE

The categorized impacts and percent impact contribution for the OHE subsystems for the base case scenario are shown in Figures 6.3 and 6.4 and summarized in Table 6.3. The working fluid regeneration subsystem (MD) followed by the power generation subsystem (PRO) have the largest contributions for each impact category, and the hydraulic subsystem has the lowest environmental impacts for the OHE (Figure 6.3). The largest impact for the hydraulic subsystem is for the working fluid solute (i.e., NaCl), followed by the combined impacts for the storage reservoirs (Figure 6.4c).

**Figure 6.3.** Life-cycle (a) categorized impacts in logarithmic scale and (b) percent impact contribution for the base case, 2.5 MW OHE. The impacts are normalized to the gross power output (4.9 MW) and the units for the impact categories are: acidification, mg SO$_2$ Eq. kWh$^{-1}$; ecotoxicity, $10^{-3}$ CTUe kWh$^{-1}$; eutrophication, mg N Eq. kWh$^{-1}$; global warming, g CO$_2$ Eq. kWh$^{-1}$; particulate matter, mg PM 2.5 Eq. kWh$^{-1}$; cancer $10^{-9}$ CTUh kWh$^{-1}$; non-cancer $10^{-9}$ CTUh kWh$^{-1}$; ozone depletion $10^{-6}$ mg CFC 11 Eq. kWh$^{-1}$; fossil fuels kJ kWh$^{-1}$; smog g O$_3$ Eq. kWh$^{-1}$.

PRO membrane elements contribute the largest impacts (with the exception of ozone depletion) for the power generation subsystem, and the heat exchangers contribute the largest impacts for the working fluid regeneration subsystem (Figure 6.4a and 6.4b).
Figure 6.4. Impact contribution for the base case scenario OHE subsystems, which include (a) power generation (PRO), (b) working fluid regeneration (MD), and (c) hydraulic system. The heat exchangers are denoted by HX. The base case scenario was evaluate at 2.5 MW net power with a LGH and cooling temperature of 85 and 5 °C, respectively, and with a PRO draw solution hydraulic pressure of 3.4 MPa (~500 psi).

The heat exchangers are the largest sized equipment, have the largest material weight, and contribute the largest impacts for the OHE; therefore, it can be concluded that the material
use in the construction stage has the highest environmental impacts for the OHE. Liu et al. also concluded that compared to the other life-cycle stages (i.e., operation and disposal) the environmental impacts associated with the material inputs for the construction stage contributed to the largest environmental impacts for an ORC [10].

Table 6.3. Environmental impacts for the base case scenario 2.5 MW OHE and subsystems. The working fluid is a 3 M NaCl solution and the PRO draw solution hydraulic pressure was 3.4 MPa (~ 500 psi). The MD feed solution and distillate stream temperatures were kept constant at 75 and 15 ºC, respectively.

<table>
<thead>
<tr>
<th>Impact Category</th>
<th>Total</th>
<th>Generation (PRO)</th>
<th>Regeneration (MD)</th>
<th>Hydraulic system</th>
<th>Disposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidification (mg SO₂-Eq. kWh⁻¹)</td>
<td>150</td>
<td>12</td>
<td>138</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>Ecotoxicity (10⁻³ CTUe kWh⁻¹)</td>
<td>35.8</td>
<td>0.6</td>
<td>35</td>
<td>1.2x10⁻³</td>
<td>1.6x10⁻²</td>
</tr>
<tr>
<td>Eutrophication (mg N-Eq. kWh⁻¹)</td>
<td>6.0</td>
<td>1.0</td>
<td>5</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Global warming (g CO₂-Eq. kWh⁻¹)</td>
<td>35.3</td>
<td>5.5</td>
<td>29.8</td>
<td>7x10⁻³</td>
<td>5.6x10⁻²</td>
</tr>
<tr>
<td>Particulate matter (mg PM 2.5-Eq. kWh⁻¹)</td>
<td>32</td>
<td>1.7</td>
<td>30</td>
<td>0.01</td>
<td>0.2</td>
</tr>
<tr>
<td>Cancer (10⁻⁹ CTUh kWh⁻¹)</td>
<td>0.12</td>
<td>3.5x10⁻²</td>
<td>8.6x10⁻²</td>
<td>6.6x10⁻⁶</td>
<td>2.8x10⁻⁴</td>
</tr>
<tr>
<td>Non-cancer (10⁻⁹ CTUh kWh⁻¹)</td>
<td>14.5</td>
<td>4.1</td>
<td>10</td>
<td>9.4x10⁻⁴</td>
<td>3.9x10⁻²</td>
</tr>
<tr>
<td>Ozone depletion (10⁻⁶ mg CFC 11-Eq. kWh⁻¹)</td>
<td>55.4</td>
<td>3.4</td>
<td>51.7</td>
<td>5.0x10⁻⁴</td>
<td>1.3x10⁻³</td>
</tr>
<tr>
<td>Fossil fuels (kJ kWh⁻¹)</td>
<td>34.4</td>
<td>12</td>
<td>22.3</td>
<td>0.02</td>
<td>0.11</td>
</tr>
<tr>
<td>Smog (g O₃-Eq. kWh⁻¹)</td>
<td>1.7</td>
<td>0.2</td>
<td>1.5</td>
<td>0.001</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Disposal of PRO and MD membranes has the third largest impacts for each of the impact categories, and has a high eutrophication potential (Figure 6.3b). Although membranes are typically disposed of in landfills or incinerated, a study by Lawler et al. investigated the potential for reuse and recycling of used RO membranes in other applications such as reuse in NF or UF processes or recycled for use as geotextiles [37]. Because PRO membranes are made of similar material and exhibit similar membrane properties to RO membranes [38], reuse of PRO membranes could reduce OHE emissions.
6.4.2 OHE sensitivity analysis

A recent study determined that increased PRO power density and MD water flux have the largest impact on OHE system performance and costs; increasing PRO power density and MD water flux resulted in decreased membrane area and equipment size [12]. Therefore, sensitivity analyses on PRO operating pressures (associated with power density) and MD operating temperatures (associated with MD water flux) were performed. Increased PRO power density can be realized by operating at higher draw solution hydraulic pressures. The theoretical maximum power density for a given draw solution occurs when the hydraulic pressure of the draw solution is half the osmotic pressure of the draw solution [39, 40], and for a 3 M NaCl solution, the maximum theoretical power density occurs at 8.7 MPa [41]. Therefore, the PRO power density sensitivity was performed for draw solution hydraulic pressures of 2.1, 3.4, 5.2, and 8.6 kPa. Operating with higher feed solution temperatures and lower distillate stream temperatures increases MD water fluxes (temperature dependent); therefore, the MD water flux sensitivity was performed by varying MD feed solution and distillate stream temperatures.

6.4.2.1 PRO power density sensitivity

The effects of PRO draw solution hydraulic pressure, and thus PRO power density, on OHE environmental impacts were investigated. In this sensitivity analysis the OHE system size (2.5 MW), MD operating temperatures (feed solution and distillate temperature of 75 °C and 15 °C, respectively), and the working fluid concentration (3 M NaCl) were kept constant, while the PRO draw solution hydraulic pressure was varied. The corresponding power density for draw solution hydraulic pressures of 2.1, 3.4, 5.2, and 8.6 MPa were 29, 45, 62, and 78 W m\(^{-2}\), respectively.

The environmental impacts as a function of PRO draw solution hydraulic pressure are shown in Figure 6.5, and the equipment sizes are summarized in Table 6.4. Increasing PRO draw solution hydraulic pressures results in increased PRO power density and decreased membrane permeation rates (in the direction from the feed to the draw solution), which results in an overall decrease in OHE system size.
Increasing PRO power density results in decreased PRO membrane area and equipment sizes (i.e., pressure exchanger, turbine, and pumps); thus, the power generation subsystem life cycle impacts are decreased. Because the working fluid regeneration and hydraulic subsystems are sized based on the permeation rate of the PRO membranes (see Chapter 5), the equipment size, MD membrane area, and life-cycle impacts for these subsystems are reduced. Therefore, increasing PRO power density results in decreased life-cycle impacts for membrane disposal and for all subsystems. For example, increasing PRO draw solution hydraulic pressures from 3.4
MPa (base case) to 8.6 MPa reduces OHE global warming impacts by more than 50%. All impact categories exhibit the same trend (i.e., decreased impacts with increased PRO hydraulic pressure) because life-cycle impacts scale linearly with equipment size [29].

**Table 6.4.** PRO draw solution hydraulic pressure sensitivity for a 2.5 MW (net power) OHE with a 3 M NaCl working fluid. The MD feed solution and distillate stream temperatures were kept constant at 75 and 15 °C, respectively, and the PRO draw solution hydraulic pressure was varied.

<table>
<thead>
<tr>
<th>Sensitivity</th>
<th>PRO operating pressure</th>
<th>PRO power density</th>
<th>PRO water flux</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.6 (1,250)</td>
<td>5.2 (750)</td>
<td>3.4 (500)</td>
</tr>
<tr>
<td></td>
<td>2.1 (300)</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>kPa (psi)</td>
<td>W m⁻²</td>
<td>L m⁻² h⁻¹</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>62</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>System Size</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gross power</td>
<td>3.6</td>
<td>4.1</td>
<td>4.9</td>
</tr>
<tr>
<td>Net power</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Generation (PRO)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbine</td>
<td>3.2</td>
<td>3.6</td>
<td>4.4</td>
</tr>
<tr>
<td>Pressure exchanger</td>
<td>0.3</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>PRO pump - draw solution side</td>
<td>171</td>
<td>193</td>
<td>232</td>
</tr>
<tr>
<td>PRO pump - feed side</td>
<td>53</td>
<td>177</td>
<td>393</td>
</tr>
<tr>
<td>PRO membrane area</td>
<td>46</td>
<td>66</td>
<td>107</td>
</tr>
<tr>
<td>PRO membrane elements and vessels</td>
<td>471</td>
<td>671</td>
<td>1,096</td>
</tr>
<tr>
<td>Regeneration (MD)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat exchanger - cooling</td>
<td>1,777</td>
<td>3,055</td>
<td>5,332</td>
</tr>
<tr>
<td>Heat exchanger - intermittent cooling</td>
<td>11</td>
<td>20</td>
<td>37</td>
</tr>
<tr>
<td>Heat exchanger - heating</td>
<td>1,556</td>
<td>2,675</td>
<td>4,667</td>
</tr>
<tr>
<td>MD pump - distillate side</td>
<td>104</td>
<td>167</td>
<td>284</td>
</tr>
<tr>
<td>MD pump - feed solution side</td>
<td>104</td>
<td>167</td>
<td>284</td>
</tr>
<tr>
<td>Membrane area</td>
<td>60</td>
<td>104</td>
<td>181</td>
</tr>
<tr>
<td>MD membrane elements and vessels</td>
<td>233</td>
<td>401</td>
<td>699</td>
</tr>
<tr>
<td>Hyrdraulic system</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DI water</td>
<td>114</td>
<td>192</td>
<td>333</td>
</tr>
<tr>
<td>NaCl</td>
<td>11</td>
<td>19</td>
<td>32</td>
</tr>
<tr>
<td>PRO feed tank</td>
<td>4</td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td>MD distillate tank</td>
<td>6</td>
<td>11</td>
<td>20</td>
</tr>
<tr>
<td>Mixed tank</td>
<td>4</td>
<td>7</td>
<td>12</td>
</tr>
</tbody>
</table>

**6.4.2.2 MD temperature sensitivity**

The effect of system operating temperatures, and hence MD water fluxes, on OHE environmental impacts was investigated. In this sensitivity analysis, OHE system size (2.5 MW), PRO draw solution hydraulic pressure (3.4 MPa), and working fluid concentration (3 M NaCl) were kept constant, while the MD feed and distillate temperatures were varied. The environmental impacts as a function of MD feed temperature, where the trend lines represent the different distillate stream temperatures, are shown in Figure 6.6, and the equipment sizes and MD water fluxes are summarized in Table 6.5. Unlike the sensitivity analysis for PRO power
density (i.e., draw solution hydraulic pressure), the sensitivity analysis for MD operating temperatures only affects the working fluid regeneration subsystem; therefore, compared to the PRO power density sensitivity analysis, the effects of increased MD water flux on OHE life-cycle impacts are expected to be milder.

Figure 6.6. Environmental impacts for the MD operating temperature sensitivity analysis. The x-axis is MD feed temperature in °C for all plots. Analysis was performed for distillate temperature of 15 °C and 30 °C. The impact categories and their respective units include, (a) fossil fuels, kJ kWh⁻¹; (b) cancer, 1₀⁻⁹ CTUh kWh⁻¹; (c) non-cancer, 1₀⁻⁹ CTUh kWh⁻¹; (d) ecotoxicity, 1₀⁻³ CTUe kWh⁻¹; (e) global warming, g CO₂ Eq. kWh⁻¹; (f) eutrophication, mg N Eq. kWh⁻¹; (g) particulate matter, mg PM 2.5 Eq. kWh⁻¹; (h) ozone depletion, 1₀⁻⁶ mg CFC 11 Eq. kWh⁻¹; (i) acidification, mg SO₂ Eq. kWh⁻¹; and (j) smog, g O₃ Eq. kWh⁻¹.

Although increasing the temperature difference in MD (increased feed solution temperature and decreased distillate stream temperature) results in increased driving forces and
thus increased MD water flux, the environmental impacts for the OHE system increase. This can be attributed to the additional heat exchanger area needed for the additional heat transfer. For example, by increasing the MD feed solution temperature from 75 °C (base case) to 90 °C and decreasing the MD distillate stream temperature from 30 °C to 15 °C (base case), the global warming impacts increase by more than 63%.

Interestingly, though increasing the MD driving force results in increased environmental impacts, a separate study found that system electricity generation costs decrease with increasing MD flux (i.e., less membrane area is needed for higher water fluxes) (see Chapter 5). Therefore, when considering environmental impacts, it is important to reduce heat exchanger area; however, this comes at the expense of less favorable electricity generation costs.

Table 6.5. MD operating temperature sensitivity for a 2.5 MW (net power) OHE with a 3 M NaCl working fluid. The PRO draw solution operating pressure was kept constant at 3.4 MPa and PRO stream temperatures are 30 °C and the MD feed solution and distillate stream temperatures were varied.

<table>
<thead>
<tr>
<th></th>
<th>Sensitivity</th>
<th>MD feed stream/LGH temperature</th>
<th>MD distillate/Cooling water temperature</th>
<th>MD water flux</th>
<th>Regeneration (MD)</th>
<th>Hydraulic system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50/60</td>
<td>75/85</td>
<td>90/100</td>
<td>50/60</td>
<td>75/85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30/20</td>
<td>30/20</td>
<td>30/20</td>
<td>30/20</td>
<td></td>
</tr>
<tr>
<td>Heat exchanger - cooling</td>
<td>2,694</td>
<td>5,332</td>
<td>6,875</td>
<td>1,080</td>
<td>3,742</td>
<td>5,302</td>
</tr>
<tr>
<td>Heat exchanger - intermittent cooling</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Heat exchanger - heating</td>
<td>2,425</td>
<td>4,667</td>
<td>5,931</td>
<td>947</td>
<td>3,186</td>
<td>4,448</td>
</tr>
<tr>
<td>MD pump - distillate side</td>
<td>284</td>
<td>284</td>
<td>284</td>
<td>284</td>
<td>284</td>
<td>284</td>
</tr>
<tr>
<td>MD pump - feed solution side</td>
<td>284</td>
<td>284</td>
<td>284</td>
<td>284</td>
<td>284</td>
<td>284</td>
</tr>
<tr>
<td>Membrane area</td>
<td>310</td>
<td>181</td>
<td>139</td>
<td>338</td>
<td>188</td>
<td>143</td>
</tr>
<tr>
<td>MD membrane elements and vessels</td>
<td>1,199</td>
<td>699</td>
<td>538</td>
<td>1,304</td>
<td>726</td>
<td>551</td>
</tr>
<tr>
<td>DI water</td>
<td>461</td>
<td>333</td>
<td>292</td>
<td>488</td>
<td>340</td>
<td>295</td>
</tr>
<tr>
<td>NaCl</td>
<td>44</td>
<td>32</td>
<td>28</td>
<td>47</td>
<td>32</td>
<td>28</td>
</tr>
<tr>
<td>PRO feed tank</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>MD distillate tank</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Mixed tank</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>

6.4.3 OHE ideal case scenario

Results from the sensitivity analysis were used to perform an ideal case scenario analysis on the OHE. Chapter 5 concluded that increasing PRO and MD water recovery, PRO power density, and MD water flux, could substantially decrease OHE equipment size, PRO and MD membrane area, and OHE electricity generation costs. Therefore, similar to Chapter 5, an ideal
case scenario was performed to evaluate the OHE environmental impacts if future system improvements were made.

![Categorized impacts per kWh](image.png)

**Figure 6.7.** Life-cycle (a) categorized impacts in logarithmic scale for the base and ideal case OHE and (b) percent impact contribution for the ideal case OHE. Both the ideal and the base case OHE produce 2.5 MW net power; however the PRO draw solution hydraulic pressure was increased from 3.4 to 7.6 MPa, respectively, and the MD and PRO process water recoveries were increased from 6 and 15% to 30 and 40%, respectively. The impacts are normalized to the gross power output (4.9 MW) and the units for the impact categories are: acidification, mg SO\textsubscript{2} Eq. kWh\textsuperscript{-1}; ecotoxicity, 10\textsuperscript{-3} CTUe kWh\textsuperscript{-1}; eutrophication, mg N Eq. kWh\textsuperscript{-1}; global warming, g CO\textsubscript{2} Eq. kWh\textsuperscript{-1}; particulate matter, mg PM 2.5 Eq. kWh\textsuperscript{-1}; cancer, 10\textsuperscript{-9} CTUh kWh\textsuperscript{-1}; non-cancer, 10\textsuperscript{-9} CTUh kWh\textsuperscript{-1}; ozone depletion, 10\textsuperscript{-6} mg CFC 11 Eq. kWh\textsuperscript{-1}; fossil fuels, kJ kWh\textsuperscript{-1}; smog, g O\textsubscript{3} Eq. kWh\textsuperscript{-1}.

Because OHE environmental impacts are directly related to equipment size, the intent of the ideal case scenario is to evaluate the OHE with operating parameters in which equipment size, and thus environmental impacts are reduced. Results from the sensitivity analysis performed in section 6.4.2.1 indicated that increasing PRO power density has a global effect on OHE system performance and environmental impacts. Therefore, in the ideal case scenario, the PRO draw solution hydraulic pressure was increased from 3.4 (base case) to 7.6 kPa, thus increasing PRO power density from 45 (base case) to 76 kPa. Chapter 5 also concluded that increasing PRO and MD water recovery reduces equipment size and OHE electricity generation.
costs; therefore, in the ideal case scenario, MD water recovery was increased from 6 % (base case) to 30 % and PRO water recovery was increased from 15 % (base case) to 40 %, respectively. Because environmental impacts increase with increasing MD operating temperatures, the MD operating temperatures for the ideal case scenario are the same as the base case scenario.

Table 6.6. Environmental impacts for a 2.5 MW OHE evaluated at the ideal case scenario. The the PRO draw solution hydraulic pressure was is 7.6 MPa, and the MD and PRO process water recoveries were are 30 and 40%, respectively. The MD feed solution and distillate stream temperatures are 75 and 15 30 ºC, respectively, and the PRO stream temperatures are 30 ºC.

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>Generation (PRO)</th>
<th>Regeneration (MD)</th>
<th>Hydraulic system</th>
<th>Disposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidification (mg SO2-Eq. kWh⁻¹)</td>
<td>24</td>
<td>8</td>
<td>16</td>
<td>0.02</td>
<td>0.5</td>
</tr>
<tr>
<td>Ecotoxicity (10⁻³ CTUe kWh⁻¹)</td>
<td>4.3</td>
<td>0.38</td>
<td>3.9</td>
<td>5×10⁻⁴</td>
<td>9×10⁻³</td>
</tr>
<tr>
<td>Eutrophication (mg N-Eq. kWh⁻¹)</td>
<td>1.3</td>
<td>0.6</td>
<td>0.6</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Global warming (g CO₂-Eq. kWh⁻¹)</td>
<td>7.1</td>
<td>3.5</td>
<td>3.55</td>
<td>3×10⁻³</td>
<td>3.1×10⁻²</td>
</tr>
<tr>
<td>Particulate matter (mg PM 2.5-Eq. kWh⁻¹)</td>
<td>4.6</td>
<td>1.1</td>
<td>3.4</td>
<td>0.002</td>
<td>0.1</td>
</tr>
<tr>
<td>Cancer (10⁻⁹ CTUh kWh⁻¹)</td>
<td>3.1×10⁻²</td>
<td>2.1×10⁻²</td>
<td>9.7×10⁻³</td>
<td>2.7×10⁻⁶</td>
<td>1.6×10⁻⁴</td>
</tr>
<tr>
<td>Non-cancer (10⁻⁹ CTUh kWh⁻¹)</td>
<td>3.7</td>
<td>2.5</td>
<td>1.16</td>
<td>3.9×10⁻⁴</td>
<td>2.1×10⁻²</td>
</tr>
<tr>
<td>Ozone depletion (10⁻⁶ mg CFC 11-Eq. kWh⁻¹)</td>
<td>9.0</td>
<td>3.2</td>
<td>5.8</td>
<td>2.0×10⁻⁴</td>
<td>7.4×10⁻⁴</td>
</tr>
<tr>
<td>Fossil fuels (kJ kWh⁻¹)</td>
<td>10.6</td>
<td>7.25</td>
<td>3.3</td>
<td>8×10⁻³</td>
<td>6×10⁻²</td>
</tr>
<tr>
<td>Smog (g O₃-Eq. kWh⁻¹)</td>
<td>0.3</td>
<td>0.12</td>
<td>0.18</td>
<td>1×10⁻³</td>
<td>4×10⁻³</td>
</tr>
</tbody>
</table>

The categorized impacts for the base and ideal case OHE, and the percent impact contribution for the ideal case OHE are shown in Figure 6.7. The categorized impacts for the total ideal case OHE system and subsystems are summarized in Table 6.6. Compared to the base case OHE, the life-cycle impacts for the ideal case OHE decrease by approximately 80% for each of the impact categories. The life-cycle impacts associated with the working fluid regeneration subsystem (MD) are significantly reduced, mainly because of the decreased heat exchanger area; the heat exchanger size for the ideal case scenario (324 MW) reduced by an order of magnitude compared to the base case scenario (4.7 GW). Because of the overall low OHE efficiency, the heat exchanger size is ratio of the OHE gross power output to the system.
efficiency. Also, compared to the base case scenario, the size of the turbine in the ideal scenario decreased by nearly 40% (2.8 MW compared to 4.4 MW). The large reduction in environmental impacts between the base and the ideal case scenario emphasizes the importance of operating the OHE with high PRO power density and at increased PRO and MD WATER recoveries.

6.4.4 Comparison of OHE to competitive technologies

The life-cycle categorized impacts for the ideal and base case OHE, and for the ORC are shown in Figure 6.8. All systems produce a net power output of 2.5 MW and were designed to utilize the same LGH source. The categorized impacts and percent contribution for the ORC equipment is shown in Figure C1 and summarized in Table C3 in Appendix C. The environmental impacts for the ORC are in agreement with those reported in the literature [10]. The ORC clearly outperforms the base and ideal case OHE for all impact categories. In general, the ORC requires less equipment than the OHE (4 compared to 14), and the equipment size and weight (i.e., pump, boiler, condenser, and turbine) for the ORC is much less than the equipment size and weight for the OHE. Because the ORC utilizes an organic working fluid, with a lower boiling point than water, the overall system size is smaller [6]. Nevertheless, compared to the ideal case OHE, the life-cycle impacts for four of the ten impact categories are larger for the ORC disposal scenario (incineration of working fluid); these include ecotoxicity, global warming, ozone depletion, and smog. Although the disposal scenario for the OHE and ORC are different, disposal of membranes to landfill is considered to have higher environmental impacts compared to membrane disposal via incineration [42].

Although the life-cycle impacts for the OHE are higher than the ORC, the impacts may be lower than conventional power. Average CO₂ emissions from generating electricity with CCPP and NGPP are 940 and 550 g CO₂ kWh⁻¹, respectively [3]; yet, average CO₂ emissions for the base and ideal case OHE are 35 and 7 g CO₂ kWh⁻¹, respectively. Therefore, coupling the OHE with CCPP and NGPP could increase process efficiency and decrease CO₂ emissions. For example, if 4.7 GW of LGH was available at CCPP or NGPP and a 2.5 MW OHE at its current state of technology (base case) was installed with a 90% plant availability, CO₂ emissions would be reduced by 19.9 million kg yr⁻¹ for a CCPP and 11.3 million kg yr⁻¹ for a NGPP. Similarly, if 325 MW of LGH was available at CCPP or NGPP and a 2.5 MW OHE with future technological
improvements (ideal case) was installed with a 90% plant availability, CO$_2$ emissions would be reduced by 20.5 million kg yr$^{-1}$ for a CCPP and 11.9 million kg yr$^{-1}$ for a NGPP.

![Graph showing life-cycle categorized impacts for OHE and ORC]

**Figure 6.8.** Life-cycle categorized impacts for the base and ideal case OHE and the ORC. The impacts are normalized to the gross power output (4.9 MW) and the units for the impact categories are: acidification, mg SO$_2$ Eq. kWh$^{-1}$; ecotoxicity, 10$^{-3}$ CTUe kWh$^{-1}$; eutrophication, mg N Eq. kWh$^{-1}$; global warming, g CO$_2$ Eq. kWh$^{-1}$; particulate matter, mg PM 2.5 Eq. kWh$^{-1}$; cancer, 10$^{-9}$ CTUh kWh$^{-1}$; non-cancer, 10$^{-9}$ CTUh kWh$^{-1}$; ozone depletion, 10$^{-6}$ mg CFC 11 Eq. kWh$^{-1}$; fossil fuels, kJ kWh$^{-1}$; smog, g O$_3$ Eq. kWh$^{-1}$.

### 6.5 Conclusions

Results from the LCA indicate that life-cycle impacts for the OHE are higher than the ORC. The process stage with the largest contributions to the LCIA was determined to be the construction stage. The working fluid regeneration (MD) subsystem was determined to have the highest impact contribution to the OHE LCIA. Increasing PRO membrane power density and increasing MD and PRO water recoveries was found to reduce OHE life-cycle impacts by approximately 80%. Results from the ideal case scenario indicate that with future improvements to PRO power density and module water recovery, the life-cycle impacts for four of the ten impact categories (including global warming, ozone depletion, and smog) for the OHE disposal stage are lower than the ORC disposal stage. Furthermore, utilizing the OHE for energy recovery

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from CCPP and NGPP could reduce CO$_2$ emissions by 18.4 million kg yr$^{-1}$ and 10.7 million kg yr$^{-1}$, respectively.

Although the ORC outperforms the OHE in terms of environmental impacts and economics [12], it is important to note that the ORC is a mature technology that has been optimized for performance. The OHE is a novel technology in the initial stages of development and neither MD or PRO are available on a broad commercial scale; therefore, there is much room for future technological improvement and process optimization. Continued development of membrane and module design and working fluid selection is needed. In particular, much effort should focus on increasing PRO power density. Our recent study investigating the use of novel working fluids for the use in the OHE (Chapter 5) concluded that HCOONa and CaCl$_2$ can yield higher power densities than NaCl. Further work should assess the environmental impacts of the OHE with these novel draw solutions. Furthermore, compared to the ORC, this technology has the potential to operate with a wider range of LGH streams and can be used for energy storage, which can be impactful in further reducing carbon emissions.

6.6 References


CHAPTER 7
CONCLUSIONS

The performance of the OHE as a viable energy generation and storage technology was evaluated through experimental and modeling work. At the current state of technology, OHE electricity generation costs are higher than those of competing renewable energy and energy storage technologies. Increased PRO membrane power density was identified as a critical performance parameter for decreasing OHE electricity generation costs. The use of high osmotic pressure working fluids and robust PRO membranes facilitated high PRO power densities. Further development of highly permeable and selective PRO membranes that are mechanically stable at increased pressures is necessary for further development of the OHE. Furthermore, working fluids that were efficiently separated with MD can increase OHE performance and decrease electricity generation costs. In addition to improved membranes and working fluids, further development of PRO and MD membrane modules and testing of pilot scale systems are essential for enabling commercialization of the OHE. With future improvements to PRO and MD membranes and system operational performance, the OHE could become a competitive renewable energy and storage technology. Furthermore, compared to conventional coal and natural gas power plants, the OHE could offer reduced life cycle impacts and CO₂ emissions.

7.1 Research synopsis

This dissertation is a collection of five studies that systematically investigates the performance, through lab-scale experiments and modelling, of the closed-loop, membrane-based OHE for electrical energy generation and storage from low-grade heat. The studies investigate: (1) the performance of commercially available membranes and spacer configurations in PRO, (2) DCMD for concentration of hypersaline brines and novel scale mitigation techniques, (3) the performance of ionic organic and inorganic working fluids in for use in the OHE, (4) the technical and economic performance of the OHE for energy generation and storage, and (5) a the environmental life cycle impacts for the OHE compared to the ORC, CCPP, and NGPP.

7.2 Summary of PRO membrane and spacer assessment

Several commercial FO membranes were investigated for use in PRO. The HTI TFC membrane was found to be the best membrane for PRO at this time. This membrane has the
highest selectivity and mechanical stability, which result in high PRO power densities. This study established that the HTI TFC membrane can withstand operating pressures of up to 3.5 MPa (500 psi) before significant membrane deformation occurs, which leads to higher ICP and decreased process performance. The specific reverse solute flux for the HTI TFC membrane was found to sharply increase at hydraulic pressures exceeding 2.0 MPa, which has significant impact in closed-loop PRO systems. Furthermore, membrane characteristics and performance change once the membrane is deformed and modeled results are no longer valid. The use of unique feed and draw solution spacers and orientations tested in this study enhanced mass transfer through the membrane, achieving a theoretical PRO power density of more than 22 W m$^{-2}$, which is a 46% improvement from other spacer orientations. Reducing both feed and draw solution flow rates resulted in four fold increase in overall PRO process efficiencies (4 to 16%). Furthermore, decreasing feed and draw solution flow rates resulted in lower parasitic pumping losses and decreased capital pumping costs. Although increased PRO power densities continue to be realized, PRO membrane development, module design, and pilot scale testing are essential for enabling PRO commercialization.

### 7.3 Summary of MD for concentration of hypersaline brines

DCMD was effective in concentrating hypersaline water to greater than 350,000 mg L$^{-1}$. Operating DCMD at feed solution and distillate stream temperatures of 70 and 30 °C was not sustainable; the membrane performance was compromised because of membrane scaling and pore wetting. Consequently, operating DCMD in successive batch mode without the use of scale mitigation techniques resulted in decreased membrane performance (i.e., lowered salt rejection and water fluxes). Novel scale mitigation techniques were developed to mitigate membrane scaling and sustain high water fluxes. Of the three scale mitigation techniques, the temperature reversal technique was most effective in maintaining high water fluxes (>20 L m$^{-2}$ hr$^{-2}$) and high salt rejection. The new techniques were simple to operate and very impactful in mitigating scaling. Furthermore, the need for antiscalants and other chemicals used for membrane cleaning was avoided.
7.4 Summary of OHE working fluid selection

The performance of potential working fluids for the closed loop OHE was experimentally evaluated in both PRO and MD. HCOONa and CaCl$_2$ outperformed NaCl in terms of PRO power density and specific RSF, and LiCl and CaCl$_2$ outperformed NaCl in terms of MD water flux. Working fluids with low RSF lead to lower pumping energy and MD membrane area, which resulted in low capital costs, high net power generation, and low electricity generation costs. Of the select salts, CaCl$_2$, MgCl$_2$, sodium propionate, and LiCl resulted in the lowest OHE electricity generation costs and had the lowest potential for corrosion. CaCl$_2$ and MgCl$_2$, were the only two working fluids that performed well for each of the performance criteria (i.e., low specific salt costs and RSF, and high PRO power density, MD water flux, MD thermal efficiencies, and net power generation) — consequently, these salts had the two lowest electricity generation costs. Because several factors contribute to generation costs, an ideal salt would combine high power densities, low RSF, low salt costs, high MD water fluxes and thermal efficiencies, and low potential for equipment corrosion.

7.5 Summary of techno-economic assessment of the OHE

Results from this study confirm that at the current state of technology, the OHE as a continuously operating energy generation system is not competitive with average U.S. grid electricity prices or with competing renewable energy processes that utilize LGH for energy generation (e.g., ORC). However, higher MD water fluxes and PRO draw solution hydraulic pressure substantially decrease OHE system costs, and with future improvements to MD and PRO membranes and modules, OHE electricity generation costs could reach $0.10 per kWh, which is comparable to ORC electricity generation costs ($0.13–0.08 per kWh). Moreover, the OHE can use a wide variety of working fluids that are less toxic and safer (non-flammable) than those typically used in the ORC process. Furthermore, with future improvements to membrane technologies, the OHE could be a competitive energy storage device: electricity generation costs for the storage scenarios could reach $0.12 per kWh, which are comparable to on-peak wholesale electricity prices in California ($0.15 per kWh). Energy storage after PRO was more competitive than energy storage after MD due to the lower PRO system size; however, energy storage after PRO is limited to areas with elevation gains. The results of the TEA suggest that the most attractive target markets for OHE will have four attributes: (i) high electricity generation costs,
(ii) adequate LGH supplies; (iii) significant peak demand challenges, and (iV) incentives for increasing grid storage capacities.

7.6 Summary of environmental LCA for the OHE compared to the ORC

Results from the LCA indicate that the life-cycle impacts for the OHE are larger than the ORC. The process stage with the largest contributions to the LCIA was determined to be the construction stage. The major contributor to the OHE LCIA results is the working fluid regeneration (MD) subsystem. Increasing PRO membrane power density and increasing MD and PRO recoveries was found to substantially reduce OHE life-cycle impacts. Results from the ideal case scenario indicate that with future improvements to PRO power density and module recovery, the life-cycle impacts for the OHE disposal stage are lower than the ORC disposal stage. Furthermore, utilizing the OHE for energy recovery from CCPP and NGPP could reduce CO$_2$ emissions by 20.5 million kg yr$^{-1}$ and 11.9 million kg yr$^{-1}$, respectfully. Considering that the OHE is a novel membrane based technology in the early stages of development, much improvement can be made to system design and operation performance. Furthermore, compared to the ORC, this technology has the potential to operate with a wider range of LGH streams and can be used for energy storage, which can be impactful in further reducing carbon emissions.
APPENDIX A
SUPPORTING INFORMATION FOR: ASSESSMENT OF ALTERNATIVE DRAW SOLUTIONS FOR ENHANCED PERFORMANCE OF THE OSMOTIC HEAT ENGINE

Submitted for potential publication in the Journal of Membrane Science

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System modeling and costing
A series of mass and energy balances were used to determine OHE net power outputs, system generation costs, and bleed ratios (salt specific) (Fig. S1).

Figure A1. A schematic drawing of a full-scale OHE.
Mass balances on the PRO side were determined by first calculating the PRO membrane area \( A_{m,pro} \), which is the ratio of the gross power to PRO power density (salt specific).

\[
A_{m,pro} = \frac{W_{gross}}{PD_{PRO}}
\]  

(1)

The permeate flow rate in PRO \( (Q_{p,pro}) \) was calculated by multiplying the PRO water flux by the PRO membrane area,

\[
Q_{p,pro} = J_{w,pro} \times A_{m,pro}
\]  

(2)

The flow rate of the low concentration inlet stream \( (Q_{i,l,pro}) \) was determined from the PRO permeation rate and assumed recovery. The flow rate of the low concentration inlet stream can also be expressed as the sum of the inlet bleed flow \( (Q_{b,i}) \) and the low concentration return flow \( (Q_{r,l,pro}) \).

\[
Q_{i,l,pro} = Q_{b,i} + Q_{r,l,pro} = \frac{Q_{p,pro}}{R_{pro}}
\]  

(3)

The flow rate of the high concentration inlet stream \( (Q_{i,h,pro}) \) was assumed to be 10% of the flow rate of the low concentration stream (referenced from manufacturer data [1]).

\[
Q_{i,h,pro} = 0.1 \times Q_{i,l,pro}
\]  

(4)

The flow rates of the low concentration and high concentration outlet streams \( (Q_{o,l,pro} \) and \( Q_{o,h,pro} \) \) were determined from the PRO permeation rate \( (Q_{p,pro}) \) and the respective flow rates of the low concentration and high concentration inlet streams \( (Q_{i,l,pro} \) and \( Q_{i,h,pro} \) ).

\[
Q_{o,l,pro} = Q_{i,l,pro} - Q_{p,pro}
\]  

(5)

\[
Q_{o,h,pro} = Q_{i,h,pro} + Q_{p,pro}
\]  

(6)
The portion of the PRO feed stream bled to the low concentration inlet stream in MD (defined as the bleed ratio) was determined by iterating the inlet feed concentration in PRO until the set feed concentration of 4 g/L was reached. The bleed flow rate \( Q_{o,b} \) was calculated by taking the product of the bleed ratio and flow rate of the low concentration outlet stream in PRO.

\[
Q_{o,b} = R_b \times Q_{o,l,pro}
\]  

(7)

The flow rate of the low concentration recycle stream \( Q_{r,l,pro} \) was found by subtracting the portion of low concentration stream bled into the MD feed stream \( Q_{b,o} \) from the flow rate of the low concentration outlet stream \( Q_{o,l,pro} \).

\[
Q_{r,l,pro} = Q_{o,l,pro} - Q_{b,o}
\]  

(8)

The concentration of the low concentration and high concentration outlet streams in PRO were calculated by performing a mass balance over the feed and draw solution channel inlet and outlets (Eq. 9 and 10).

\[
C_{o,l,pro} = C_{o,b} = \frac{[C_{l,pro} \times Q_{l,pro} + (J_s \times A_{m,pro})]}{Q_{o,l,pro}}
\]  

(9)

\[
C_{o,h,pro} = \frac{[C_{l,h,pro} \times Q_{l,h,pro} - (J_s \times A_{m,pro})]}{Q_{o,h,pro}}
\]  

(10)

Mass balances on the MD side were determined by first setting the MD permeation rate equal \( (Q_{p,md}) \) to the sum of the PRO permeation rate \( (Q_{p,pro}) \) and bleed rate \( (Q_{o,b}) \).

\[
Q_{p,md} = Q_{p,pro} + Q_{o,b}
\]  

(11)

The MD membrane area \( (A_{m,md}) \) was determined by taking the ratio of the MD permeation rate and the MD water flux (specific to each salt).

\[
A_{m,md} = \frac{Q_{p,md}}{J_{w,md}}
\]  

(12)
The flow rates of the low concentration (distillate) and high concentration (feed solution) inlet streams \((Q_{i,l,md} \text{ and } Q_{i,h,md})\) were set equal, and were determined by dividing the MD permeation rate by the MD recovery rate.

\[
Q_{i,l,md} = Q_{i,h,md} = Q_{o,h,t} = \frac{Q_{p,md}}{R_{md}} \tag{13}
\]

The flow rates of the high concentration and low concentration outlet streams in MD \((Q_{o,h,md} \text{ and } Q_{o,l,md})\) were determined from the MD permeation rate \((Q_{p,md})\) and flow rates of the high concentration and low concentration inlet streams \((Q_{i,h,md} \text{ and } Q_{i,l,md})\).

\[
Q_{o,h,md} = Q_{i,h,md} - Q_{p,md} \tag{14}
\]

\[
Q_{o,l,md} = Q_{i,l,md} + Q_{p,md} \tag{15}
\]

MD membrane wetting was assumed negligible, therefore, the concentration of the low concentration inlet and outlet streams, and the stream bled back into the PRO feed stream \((Q_{i,l,pro})\) are deionized water. The high concentration inlet stream concentration in MD \((C_{i,h,md})\) was determined by performing a mass balance over the high concentration buffer tank.

\[
C_{i,h,md} = C_{o,h,t} = \left[\frac{(Q_{i,h,t} \times C_{i,h,t}) + (Q_{o,b} \times C_{o,b}) + (C_{o,h,pro} \times Q_{o,h,pro})}{Q_{o,h,t}}\right] \tag{16}
\]

The outlet concentration of the high concentration stream \((C_{o,h,md})\) was determined by performing a mass balance over the high concentration channel of the MD module.

\[
C_{o,h,md} = \left(\frac{Q_{i,h,md} \times C_{i,h,md}}{Q_{o,h,md}}\right) \tag{17}
\]

Finally, the inlet concentration of the high concentration stream in PRO was set equal to the outlet concentration of the high concentration stream in MD.
The net energy was calculated by subtracting the MD and PRO pumping energy from the gross energy (model input).

\[ W_{\text{net}} = W_{\text{gross}} - W_{\text{md}} - W_{\text{pro}} \] (18)

The pumping energy in MD and PRO is the sum of the pumping energy required for the low concentration and high concentration streams.

\[ W_{\text{md}} = W_{h, \text{md}} + W_{l, \text{md}} \] (19)

\[ W_{\text{pro}} = W_{h, \text{pro}} + W_{l, \text{pro}} \] (20)

The pumping energy for the low concentration MD and PRO streams and high concentration MD stream were calculated by taking the product of the flow rate and the inlet pressure (equivalent to the module pressure drop) divided by the pumping efficiency.

\[ W_{\text{md/pro}} = \frac{Q_l \times P_l}{\eta_{\text{pump}}} \] (21)

The pumping energy for the high concentration PRO stream was calculated by taking the product of the flow rate, applied hydraulic pressure, one minus the pressure exchanger efficiency, divided by the pumping efficiency

\[ W_{h, \text{pro}} = \frac{Q_{h, \text{pro}} \times P_{h, \text{pro}} \times (1-\eta_{\text{px}})}{\eta_p} \] (22)

The costs considered in this model were PRO and MD membrane and module costs and salt costs, which are assumed to be the dominant system costs. The number of PRO and MD modules needed \((N_{m, \text{pro}} or N_{m, \text{md}})\) was calculated by dividing the total membrane area \((A_{m, \text{pro}} or A_{m, \text{md}})\) by the specific membrane module area \((A_{sm, \text{pro}} or A_{sm, \text{md}})\).
The mass of salt needed in the system was calculated by multiplying the total volume of the high concentration working fluid and working fluid concentration (specific per salt).

\[ M_{salt} = V_h \times C_{i,h,pro} \]  \hspace{1cm} (24)

\[ V_h = V_{h,pro} + V_{h,md} \]  \hspace{1cm} (25)

The volume of high concentration working fluid for MD and PRO was estimated by taking half the dead volume of the module multiplied by the total number of modules plus the dead volume in the pipes (assumed to be 20% of the working fluid dead volume in the module)

\[ V_{h,pro/md} = N_{m,pro/md} \times V_{m,pro/md} \times (1 + 0.2) \]  \hspace{1cm} (26)

\[ V_{m,pro/md} = \frac{\pi \times r^2 \times l}{2} \]  \hspace{1cm} (27)

The total salt cost was determined by taking the product of the total mass of salt and specific salt costs.

\[ Cost_{salt} = M_{salt} \times S_{salt} \]  \hspace{1cm} (28)

The total cost for the membrane modules is the sum of MD and PRO module costs, where the module cost is the product of the total membrane area and specific membrane and module costs.

\[ Cost_m = Cost_{m,pro} + Cost_{m,md} \]  \hspace{1cm} (29)

\[ Cost_{m,pro/md} = A_{m,pro/md} \times S_{m,pro/md} \]  \hspace{1cm} (30)
Table A1. Thermodynamic properties and mass transfer coefficient for PRO select draw solutions at 30 °C.

<table>
<thead>
<tr>
<th></th>
<th>Concentration</th>
<th>Diffusivity</th>
<th>Viscosity</th>
<th>Density</th>
<th>Mass transfer coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g L⁻¹</td>
<td>M</td>
<td>10⁻⁹ m² s⁻¹</td>
<td>10⁻³ Pa-s</td>
<td>kg L⁻¹</td>
</tr>
<tr>
<td>HCOONa</td>
<td>279</td>
<td>4.1</td>
<td>1.5</td>
<td>1.4</td>
<td>1.13</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>175</td>
<td>1.6</td>
<td>1.2</td>
<td>1.3</td>
<td>1.14</td>
</tr>
<tr>
<td>KBr</td>
<td>381</td>
<td>3.2</td>
<td>2.3</td>
<td>0.8</td>
<td>1.23</td>
</tr>
<tr>
<td>NaCl</td>
<td>175</td>
<td>3.0</td>
<td>1.3</td>
<td>1.1</td>
<td>1.11</td>
</tr>
<tr>
<td>LiBr</td>
<td>191</td>
<td>2.2</td>
<td>1.3</td>
<td>1.0</td>
<td>1.13</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>143</td>
<td>1.5</td>
<td>0.9</td>
<td>1.4</td>
<td>1.11</td>
</tr>
<tr>
<td>LiCl</td>
<td>108</td>
<td>2.6</td>
<td>1.2</td>
<td>1.1</td>
<td>1.06</td>
</tr>
<tr>
<td>Na(C₂H₅COO)</td>
<td>389</td>
<td>4.1</td>
<td>2.9</td>
<td>0.9</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Table A2. Thermodynamic properties for the MD feed solution at 56 °C.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration</th>
<th>Heat capacity (feed)</th>
<th>Viscosity (feed)</th>
<th>Density (feed)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/L</td>
<td>M</td>
<td>(10⁻³) J/kg K</td>
<td>(10⁻³) Pa-s</td>
</tr>
<tr>
<td>LiCl</td>
<td>108</td>
<td>2.6</td>
<td>3.7</td>
<td>7.3</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>183</td>
<td>1.7</td>
<td>3.4</td>
<td>8.3</td>
</tr>
<tr>
<td>NaCl</td>
<td>175</td>
<td>3.0</td>
<td>3.4</td>
<td>6.9</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>143</td>
<td>1.5</td>
<td>3.4</td>
<td>8.7</td>
</tr>
<tr>
<td>KBr</td>
<td>381</td>
<td>3.2</td>
<td>2.7</td>
<td>5.5</td>
</tr>
<tr>
<td>LiBr</td>
<td>191</td>
<td>2.2</td>
<td>3.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Na(C₂H₅COO)</td>
<td>389</td>
<td>4.1</td>
<td>3.9</td>
<td>5.9</td>
</tr>
<tr>
<td>HCOONa</td>
<td>279</td>
<td>4.1</td>
<td>3.4</td>
<td>8.7</td>
</tr>
</tbody>
</table>

References

System modeling and costing

Continuous energy generation system

OHE system size is based on a net power output of 2.5 MW. The net power is generator power minus the pumping losses:

\[ W_{\text{net}} = W_{\text{gen}} - (W_{\text{pro}} + W_{\text{md}}) \]  

(1)

where, the generator power \((W_{\text{gen}})\) is the product of the work of the turbine \((W_t)\) and the generator efficiency

\[ W_{\text{gen}} = W_t \times \eta_{\text{gen}} \]  

(2)

The work of the turbine is the product of the gross power and turbine efficiency

\[ W_t = W_{\text{gross}} \times \eta_t \]  

(3)

The gross power was iterated until the desired net power was reached.
The pumping energy for MD and PRO \((W_{md} \text{ or } W_{pro})\) were calculated by taking the product of the flow rate and the inlet pressure (equivalent to the module pressure drop) divided by the pumping efficiency.

\[
W_{md/pro} = \frac{Q_i \times P_i}{\eta_{pump}}
\]  

(4)

The pumping energy for the high concentration PRO stream was calculated by taking the product of the flow rate, applied hydraulic pressure, and pressure exchanger efficiency, divided by the pumping efficiency

\[
W_{h,pro} = \frac{Q_{h,pro} \times P_{h,pro} \times (1-\eta_{px})}{\eta_p}
\]  

(5)

From the system gross power output and the PRO power density, the PRO membrane area can be determined:

\[
A_{m,pro} = \frac{W_{gross}}{PDP_{pro}}
\]  

(6)

For the continuous generation system, the permeate flow rate in PRO \((Q_{p,pro})\) was calculated by multiplying the PRO water flux by PRO membrane area,

\[
Q_{p,pro} = J_{w,pro} \times A_{m,pro}
\]  

(7)

From the PRO permeate flow rate and assumed recovery, the feed flow rate (low concentration stream) \((Q_{i,l,pro})\) can be determined:

\[
Q_{i,l,pro} = \frac{Q_{p,pro}}{R_{pro}}
\]  

(10)

MD and PRO recoveries were assumed based on previous modeling and pilot scale values found in the literature [1, 2]. The portion of PRO feed stream bled to the low concentration inlet stream in MD (defined as the bleed ratio) was determined by performing a series of mass and flow
balances on the system and iterating the inlet feed concentration in PRO until the established feed concentration of 4 g L\(^{-1}\) was met. Detailed methods are found in [3].

The PRO draw solution (high concentration stream) flow rate \(Q_{i,h,\text{pro}}\) was assumed to be 1/10 of the flow rate of the low concentration stream (referenced from manufacturer data [2]). The module pressure drop is proportional to flow and was referenced from manufacturer data and kept below 20 psi (maximum pressure drop specified by the manufacture) [2].

The MD membrane permeate rate is equal to the PRO permeation rate plus the flow rate of the feed stream being bled from the PRO feed solution.

\[
Q_{p,md} = Q_{p,\text{pro}} + Q_b
\]  

(8)

The MD membrane area was determined by taking the ratio of the membrane permeation rate to MD water flux:

\[
A_{m,md} = \frac{Q_{p,md}}{I_{w,md}}
\]  

(9)

The feed and distillate flow rates in MD were assumed equal and were determined by taking the ratio of the MD permeation rate to the MD recovery ratio.

\[
Q_{f/d,md} = \frac{Q_{p,md}}{R_{md}}
\]  

(10)

Because of the lack of available data on spiral wound MD membrane modules, the feed outlet temperature was assumed to be 10 °C higher than the distillate inlet temperature and the distillate outlet temperature was assumed to be 10 °C lower than the feed inlet temperature. The module pressure drop in MD was assumed to be 7 kPa (1 psi).

The heat exchanger area was modeled using a log mean temperature difference approach.

\[
U = u \times A_{hx} \times LMTD
\]  

(11)
where, $U$ is the heating duty, $u$ is the heat transfer coefficient, $A_{hx}$ is the required heat exchanger area, and LMTD is the log-mean temperature difference. A global heat transfer coefficient of 7,000 W/m$^2$-K was determined with APSEN plus Software (ASPENTech, Bedford, MA) for a counter-current, plate-and-frame heat exchanger. Pinch temperatures of 10 °C was assumed. The required heating and cooling duty was determined by performing an energy balance on the working fluid side of the heat exchanger,

$$U = \dot{m} \times c_p \times \Delta T$$

(12)

The same equation was applied to the process heating and cooling side of the heat exchanger to find the process heating and cooling outlet temperatures. The flow rate of the process heating or cooling stream was assumed to be the same as the flow rate of the working fluid stream.

From the heat exchanger inlet and outlet stream temperatures, the log-mean temperature difference was determined,

$$LMTD = \frac{\Delta T_A - \Delta T_B}{\ln\left(\frac{\Delta T_A}{\Delta T_B}\right)}$$

(13)

where $\Delta T_A$ and $\Delta T_B$ denote the temperature difference at the inlet and outlet of the heat exchanger.

The system footprint is the sum of the area needed for the PRO and MD elements and the storage tanks (mixed, MD distillate, and PRO feed). PRO and MD membrane element area was found by assuming a module configuration of 7 elements per vessel and 12 stacked rows of modules. Each vessel was assumed to have a footprint of 2.84 m$^2$ (7 m x 0.4 m), with 100% spacing between modules. The tanks were assumed to be cylindrical, and have a height of 6 m. The footprint of the tanks was found by assuming tank volumes equal to 1/10,000 of the PRO feed flow and 1/100,000 of the MD distillate flow. The mixed tank volume is the sum of the PRO feed and MD distillate tank. The total amount of water and salt needed for the system was calculated from the dead volume in the membrane modules and in the storage tanks.
**Energy storage**

A system gross power output of 2.5 MW was assumed. Because the storage systems are operating when the OHE is not producing energy, the cost for pumping energy was integrated into the system O&M costs and the net power production is the same as the gross power production. The PRO membrane area was calculated the same as in the continuous generation system. From the gross power and the hydrostatic pressure, the flow rate through the turbine was calculated.

\[
Q_t = W_{\text{gross}} \times P_{\text{hs}}
\]  

(14)

The hydrostatic pressure is the same as the applied hydraulic pressure of the draw solution.

The membrane permeation rate was calculated from the turbine flow rate, peak demand frequency and duration, and subsystem operating time:

\[
Q_p = \frac{Q_t \times \text{frequency}_{pd} \times \text{duration}_{pd}}{\text{System operating time}}
\]  

(15)

The PRO feed flow rate, pumping energy, generation and electrical power, MD permeation rate, membrane area, pumping energy and heat exchanger sizing were calculated similar to the continuous generation system.

For the energy storage scenario, the storage tank volumes were calculated by multiplying the PRO permeation rate by the peak demand frequency and duration. The normalized hydraulic system costs were calculated by taking the ratio of the total capital hydraulic system cost to the gross electrical power. The normalized storage system costs were calculated similarly (ratio of total capital costs to the gross electrical power). The specific energy in the storage system is the ratio of the gross power to the PRO permeation rate.
References


APPENDIX C
SUPPORTING INFORMATION FOR: COMPARATIVE LIFE CYCLE ASSESSMENT
OF A NOVEL OSMOTIC HEAT ENGINE AND AN ORGANIC RANKINE CYCLE
FOR ENERGY PRODUCTION FROM LOW-GRADE HEAT
Prepared for submission for potential publication in Desalination

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Table C1. Summary of equipment sizes and material weights for the base case scenario 2.5 MW OHE for the base and ideal case scenario.

<table>
<thead>
<tr>
<th>Equipment/material</th>
<th>Base</th>
<th>Ideal</th>
<th>Units</th>
<th>GaBi flows/notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Generation system (PRO)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbine</td>
<td>4,385</td>
<td>2,757</td>
<td>kW</td>
<td></td>
</tr>
<tr>
<td>Reinforcing Steel</td>
<td>45,533</td>
<td>28,633</td>
<td>kg</td>
<td>Steel part [Metal parts]</td>
</tr>
<tr>
<td>Steel, low-alloyed</td>
<td>75,000</td>
<td>47,163</td>
<td>kg</td>
<td>Steel part [Metal parts]</td>
</tr>
<tr>
<td>Chromium steel 18/8</td>
<td>16,347</td>
<td>10,280</td>
<td>kg</td>
<td>Steel part [Metal parts]</td>
</tr>
<tr>
<td>Copper</td>
<td>4,420</td>
<td>2,779</td>
<td>kg</td>
<td>Copper [Metals]</td>
</tr>
<tr>
<td>Aluminum</td>
<td>2,508</td>
<td>1,577</td>
<td>kg</td>
<td>Aluminum part [Metal parts]</td>
</tr>
<tr>
<td>Iron-nickel-chromium alloy</td>
<td>1,333</td>
<td>838</td>
<td>kg</td>
<td>Cast iron part [Metal parts]</td>
</tr>
<tr>
<td>Polyethylene, HDPE, granulate</td>
<td>1,105</td>
<td>695</td>
<td>kg</td>
<td>Polyethylene high density part (HDPE/PE-HD) [Plastic parts]</td>
</tr>
<tr>
<td>Pressure exchangers (PX)</td>
<td>81,406</td>
<td>8,726</td>
<td>m³ day⁻¹</td>
<td>Total flowrate through PX</td>
</tr>
<tr>
<td>Fiberglass</td>
<td>685</td>
<td>73</td>
<td>kg</td>
<td>Glass fiber mesh (thermal insulation system) [Minerals]</td>
</tr>
<tr>
<td>Epoxy Resin</td>
<td>685</td>
<td>73</td>
<td>kg</td>
<td>Epoxy resin [Plastics]</td>
</tr>
<tr>
<td>Alumina Ceramic</td>
<td>1,315</td>
<td>141</td>
<td>kg</td>
<td>Ceramic [Minerals]</td>
</tr>
<tr>
<td>Aluminum</td>
<td>299</td>
<td>32</td>
<td>kg</td>
<td>Aluminum [Metals]</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>967</td>
<td>104</td>
<td>kg</td>
<td>Stainless Steel Hot Rolled Sheet (ELCD) [Metals]</td>
</tr>
<tr>
<td>Titanium</td>
<td>45</td>
<td>5</td>
<td>kg</td>
<td>Ferro silicon mix [Materials]¹</td>
</tr>
<tr>
<td><strong>PRO pump - draw solution side</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel hot rolled coil</td>
<td>232</td>
<td>55</td>
<td>kW</td>
<td>Stainless steel hot rolled coil, annealed and pickled [Metals]</td>
</tr>
<tr>
<td>Copper</td>
<td>85</td>
<td>20</td>
<td>kg</td>
<td>Copper [Metals]</td>
</tr>
<tr>
<td><strong>PRO pump - feed side</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel hot rolled coil</td>
<td>393</td>
<td>3</td>
<td>kW</td>
<td>Stainless steel hot rolled coil, annealed and pickled [Metals]</td>
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<tr>
<td>Copper</td>
<td>144</td>
<td>1</td>
<td>kg</td>
<td>Copper [Metals]</td>
</tr>
<tr>
<td>PRO membrane element</td>
<td>Membrane</td>
<td>107,413</td>
<td>40,554</td>
<td>m²</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------</td>
<td>---------</td>
<td>--------</td>
<td>-----</td>
</tr>
<tr>
<td>Poly(ether sulfone)</td>
<td>10,741</td>
<td>4,055</td>
<td>kg</td>
<td>Polyphenylene ether part (PPE) [Plastic parts]</td>
</tr>
<tr>
<td>N-methyl-2-pyrrolidone</td>
<td>213,195</td>
<td>80,491</td>
<td>kg</td>
<td>RER: N-methyl-2-pyrrolidone, at plant [organics]</td>
</tr>
<tr>
<td>diamine mono-piperazine</td>
<td>85,930</td>
<td>32,443</td>
<td>kg</td>
<td>Ethylenediamine [Organic intermediate products]</td>
</tr>
<tr>
<td>trimesoychloride</td>
<td>107,413</td>
<td>40,554</td>
<td>kg</td>
<td>Phosphorus trichloride [Inorganic intermediate products]</td>
</tr>
<tr>
<td>Hexane</td>
<td>214,826</td>
<td>81,107</td>
<td>kg</td>
<td>Hexane (n-hexane) [Organic intermediate products]</td>
</tr>
<tr>
<td>Spacer</td>
<td>107,413</td>
<td>40,554</td>
<td>m²</td>
<td>Total spacer area including replacement spacers</td>
</tr>
<tr>
<td>Polyester extruded mesh (draw side)</td>
<td>29,340</td>
<td>11,077</td>
<td>kg</td>
<td>Copolyester (aliphatic) [Plastics]</td>
</tr>
<tr>
<td>Polyester tricot (feed side)</td>
<td>78,507</td>
<td>29,640</td>
<td>kg</td>
<td>Copolyester (aliphatic) [Plastics]</td>
</tr>
<tr>
<td>PRO membrane vessel</td>
<td>Fiberglass (shell)</td>
<td>1,297</td>
<td>490</td>
<td>kg</td>
</tr>
<tr>
<td>Epoxy Resin (shell)</td>
<td>1,297</td>
<td>490</td>
<td>kg</td>
<td>Epoxy resin [Plastics]</td>
</tr>
<tr>
<td>PVC (shell)</td>
<td>647</td>
<td>244</td>
<td>kg</td>
<td>Polyvinylchloride injection molding part (PVC) [Plastic parts]</td>
</tr>
<tr>
<td>PVC (end caps)</td>
<td>199</td>
<td>75</td>
<td>kg</td>
<td>Polyvinylchloride injection molding part (PVC) [Plastic parts]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Regeneration system (MD)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Heat exchanger - cooling</strong></td>
</tr>
<tr>
<td>Steel, low-alloyed</td>
</tr>
<tr>
<td>Chromium</td>
</tr>
<tr>
<td>Nickel, 99.5%</td>
</tr>
<tr>
<td><strong>Heat exchanger - intermittent cooling</strong></td>
</tr>
<tr>
<td>Steel, low-alloyed</td>
</tr>
<tr>
<td>Chromium</td>
</tr>
<tr>
<td>Nickel, 99.5%</td>
</tr>
<tr>
<td><strong>Heat exchanger - heating</strong></td>
</tr>
<tr>
<td>Copper tube</td>
</tr>
<tr>
<td>Nickel, 99.5%</td>
</tr>
<tr>
<td>Iron and steel</td>
</tr>
<tr>
<td><strong>MD pump - distillate side</strong></td>
</tr>
<tr>
<td>Stainless steel hot rolled coil</td>
</tr>
<tr>
<td>Copper</td>
</tr>
<tr>
<td><strong>MD pump - feed solution side</strong></td>
</tr>
<tr>
<td>Stainless steel hot rolled coil</td>
</tr>
<tr>
<td>Copper</td>
</tr>
<tr>
<td><strong>MD membrane element</strong></td>
</tr>
<tr>
<td>Polypropylene</td>
</tr>
<tr>
<td>Spacer</td>
</tr>
</tbody>
</table>
### Table C2. Summary of equipment sizes and material weights for the 2.5 MW ORC.

<table>
<thead>
<tr>
<th>Equipment/material</th>
<th>Quantity</th>
<th>Units</th>
<th>GaBi flows/notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Turbine</strong></td>
<td>2,976</td>
<td>kW</td>
<td></td>
</tr>
<tr>
<td>Reinforcing Steel</td>
<td>30,905</td>
<td>kg</td>
<td>Steel part [Metal parts]</td>
</tr>
<tr>
<td>Steel, low-alloyed</td>
<td>50,905</td>
<td>kg</td>
<td>Steel part [Metal parts]</td>
</tr>
<tr>
<td>Chromium steel 18/8</td>
<td>11,095</td>
<td>kg</td>
<td>Steel part [Metal parts]</td>
</tr>
<tr>
<td>Copper</td>
<td>3,000</td>
<td>kg</td>
<td>Copper [Metals]</td>
</tr>
<tr>
<td>Aluminum</td>
<td>1,702</td>
<td>kg</td>
<td>Aluminum part [Metal parts]</td>
</tr>
<tr>
<td>Iron-nickel-chromium alloy</td>
<td>905</td>
<td>kg</td>
<td>Cast iron part [Metal parts]</td>
</tr>
<tr>
<td>Polyethylene, HDPE, granulate</td>
<td>750</td>
<td>kg</td>
<td>Polyethylene high density part [Plastic parts]</td>
</tr>
</tbody>
</table>

| **Condenser**                       | 28,095   | kW    |                                                      |
| Steel, low-alloyed                  | 13,595   | kg    | Steel part [Metal parts]                             |
| Chromium                            | 3,500    | kg    | Chromium [Metals]                                   |
| Nickel, 99.5%                       | 1,940    | kg    | Nickel (99.95%; electrolyte nickel) [Metals]        |

| **Evaporator**                      | 30,714   | kW    |                                                      |
| Copper tube                         | 6,113    | kg    | Copper pipes [Metal parts]                           |
| Nickel, 99.5%                       | 698      | kg    | Nickel (99.95%; electrolyte nickel) [Metals]        |
| Iron and steel                      | 98       | kg    | Steel part [Metal parts]                             |

*Assumed that titanium behaves chemically similar to silicon, and therefore has similar impacts for production*

**Total mass of PRO and MD elements (spacers and membranes) disposed of**
<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump</td>
<td>476 kW</td>
<td>Stainless steel hot rolled coil, annealed and pickled [Metals]</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>524 kg</td>
<td>hot rolled coil</td>
</tr>
<tr>
<td>Copper</td>
<td>175 kg</td>
<td>Stainless steel hot rolled coil, annealed and pickled [Metals]</td>
</tr>
<tr>
<td>Working fluid</td>
<td>Pentane</td>
<td>33,143 kg RER: Pentane Plastics Europe</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Working fluid</th>
<th>Quantity</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disposal</td>
<td>Incineration</td>
<td>33,143 kg US: Municipal Solid Waste Incineration PE</td>
</tr>
</tbody>
</table>

**Figure C1.** Life cycle (a) categorized impacts in logarithmic scale and (b) percent impact contribution for the 2.5 MW ORC. The impacts are normalized to the gross power output (4.9 MW) and the units for the impact categories are: acidification, mg SO₂ Eq. kWh⁻¹; ecotoxicity, 10⁻³ CTUe kWh⁻¹; eutrophication, mg N Eq. kWh⁻¹; global warming, g CO₂ Eq. kWh⁻¹; particulate matter, mg PM 2.5 Eq. kWh⁻¹; cancer 10⁻⁸ CTUh kWh⁻¹; non-cancer 10⁻⁹ CTUh kWh⁻¹; ozone depletion 10⁻⁶ mg CFC 11 Eq. kWh⁻¹; fossil fuels kJ kWh⁻¹; smog g O₃ Eq. kWh⁻¹.
Table C3. Environmental impacts for the 2.5 MW ORC. The ORC utilizes a LHG and cooling source of 85 and 5°C, respectively and material sizes and weight were adapted from Bui et al. [1].

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>Turbine</th>
<th>Condenser</th>
<th>Evaporator</th>
<th>Pump</th>
<th>Working fluid</th>
<th>Disposal</th>
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</thead>
<tbody>
<tr>
<td>Acidification (mg SO₂-Eq. kWh⁻¹)</td>
<td>3</td>
<td>1</td>
<td>0.7</td>
<td>0.3</td>
<td>0.0</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Ecotoxicity (10⁻³ CTUe kWh⁻¹)</td>
<td>361</td>
<td>100</td>
<td>50</td>
<td>193</td>
<td>5</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>Eutrophication (mg N-Eq. kWh⁻¹)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Global warming (g CO₂-Eq. kWh⁻¹)</td>
<td>990</td>
<td>510</td>
<td>160</td>
<td>65</td>
<td>5</td>
<td>78</td>
<td>172</td>
</tr>
<tr>
<td>Particulate matter (mg PM 2.5-Eq. kWh⁻¹)</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td>0.11</td>
<td>0.0</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Cancer (10⁻⁹ CTUh kWh⁻¹)</td>
<td>9.9×10⁻⁷</td>
<td>2.1×10⁻⁷</td>
<td>4.1×10⁻⁷</td>
<td>2.4×10⁻⁷</td>
<td>7.9×10⁻⁹</td>
<td>2.8×10⁻¹⁰</td>
<td>1.1×10⁻⁷</td>
</tr>
<tr>
<td>Non-cancer (10⁻⁹ CTUh kWh⁻¹)</td>
<td>1.5×10⁻⁴</td>
<td>6.0×10⁻⁵</td>
<td>7.5×10⁻⁶</td>
<td>6.3×10⁻⁵</td>
<td>1.8×10⁻⁶</td>
<td>3.4×10⁻⁸</td>
<td>1.4×10⁻⁵</td>
</tr>
<tr>
<td>Ozone depletion (10⁻⁶ mg CFC 11-Eq. kWh⁻¹)</td>
<td>3.7×10⁻⁶</td>
<td>3.3×10⁻⁶</td>
<td>4.2×10⁻⁷</td>
<td>1.4×10⁻⁸</td>
<td>1.9×10⁻¹⁰</td>
<td>0</td>
<td>1.7×10⁻⁹</td>
</tr>
<tr>
<td>Fossil fuels (kJ kWh⁻¹)</td>
<td>1,131</td>
<td>160</td>
<td>63</td>
<td>80</td>
<td>4</td>
<td>800</td>
<td>24</td>
</tr>
<tr>
<td>Smog (g O₃-Eq. kWh⁻¹)</td>
<td>37</td>
<td>17</td>
<td>8</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>

References

APPENDIX D

MULTIPLE AUTHOR RELEASE FORMS FOR DOCTORAL DISSERTATION
MULTIPLE AUTHOR RELEASE FOR DOCTORAL DISSERTATION

SUSTAINABLE OPERATION OF MEMBRANE DISTILLATION FOR
ENHANCEMENT OF MINERAL RECOVERY FROM HYPERSALINE SOLUTIONS
Modified from a paper published in Journal of Membrane Science¹

Kerri L. Hickenbottom²* and Tzahi Y. Cath²*

Kerri L. Hickenbottom has my permission to include the above-mentioned publication, of which I was a co-author, in his doctoral dissertation submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Civil and Environmental Engineering).

______________________________                                                       ____________________
Tzahi Y. Cath                                                                                                                 Date Signed

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APPENDIX E
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Sustainable operation of membrane distillation for enhancement of mineral recovery from hypersaline solutions

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ABSTRACT

Membrane distillation (MD) is a nascent emerging desalination technology that has the ability to desalinate hypersaline brines, including those used in mineral production. MD can potentially replace evaporation ponds in conventional mineral production processes because of its small footprint and ability to utilize industrial low-grade heat. In the current study MD was investigated for sustained water recovery and concentration of hypersaline brines. Direct contact MD (DCMD) experiments were performed with water from the Great Salt Lake (> 150,000 mg/L total dissolved solids) as the feed stream and deionized water as the distillate stream. DCMD was able to concentrate the feed solution to twice its original concentration, achieving close to complete inorganic salt rejection. During experiments water flux declined to 80% of its initial value (from 11 to 2.1 m⁻² h⁻¹). Real-time microscopy revealed that precipitation of salts on the membrane surface was the main contributor to the decline in water flux. The application of novel scale-mitigation techniques was highly effective in preventing scale formation on membrane surfaces, sustaining high water flux and salt rejection, and eliminating chemical consumption used for membrane cleaning. MD was compared to natural evaporation and was found to potentially replace 40.47 m⁻² (1 acre) of evaporation ponds with approximately 24 m² (259 ft²) of membrane area and to be nearly 770 times faster in concentrating hypersaline brines.

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1. Introduction

As population grows, an increased stress is placed on natural resources [1]; thus, there is a need for more holistic approaches to process intensification, in which process waste is considered a resource. For example, in desalination, brine is considered a byproduct and treated as a waste stream, whereas in mineral production water is considered a byproduct and, as common practice, is evaporated to the atmosphere. Ironically, the waste stream of one process is the product of the other. Efficient utilization of brines and on-site energy resources could result in production of both water and high-value minerals for beneficial use, including potable water for urban areas and minerals for fertilizers or road deicing.

In mineral production, evaporation ponds are traditionally utilized for concentration of saline water and precipitation of minerals, which are then further processed in chemical plants. Evaporation ponds commonly use large areas, they are time and energy intensive, and when used, large volumes of valuable water are lost to the atmosphere [2]. In order to improve the efficiency of mineral recovery, replacement of evaporation ponds with desalination processes could minimize land use and increase water recovery from hypersaline streams.

Current engineered processes for desalination of brackish water and seawater include thermal distillation or membrane processes such as reverse osmosis (RO), nanofiltration (NF), and electrodialysis (ED). Conventional thermal distillation processes are capable of achieving high water recovery, but they are limited by high-energy consumption needed to heat the feed stream [3]. While RO, NF, and ED are commonly utilized membrane processes for desalination [2], when feed solutions are highly concentrated or approach saturation, these processes are limited by operating pressures (RO and NF) or applied voltage (ED), and in many cases membrane scaling [4].

Alternatively, membrane distillation (MD) is a novel and unique membrane process that can synergistically assist in mineral recovery and simultaneously produce pure water. MD is a thermally driven membrane process in which the driving force for mass transfer of water is the partial vapor pressure difference across a microporous hydrophobic membrane. Thus, compared to hydraulic pressure and electric field driven membrane processes, MD is minimally affected by increased salt concentrations [5]. In direct contact MD (DCMD), a warm feed stream (e.g., brine) and a cooler fresh water stream (e.g., deionized water) are in direct contact with the active and support sides of the membrane, respectively [5]. In DCMD, water evaporates from the feed solution...
at the feed-pore interface on the feed side of the membrane, water vapors then diffuse through the membrane pores, and ultimately condense into the distillate stream at the distillate-pore interface on the support side of the membrane.

1.1. Factors affecting DCMD process performance

While MD is a unique process that can be utilized for desalination of hypersaline streams, several transport phenomena may limit water flux through the membrane. These include decrease in partial vapor pressure, heat and mass transfer resistance across the membrane, and concentration and temperature polarization (or loss in heat transfer) across the membrane [5,6].

Heat and mass transfer dominate the vapor pressure driving force in MD. Because several phase changes occur during MD, the heat transfer resistances across the boundary layers of the membrane surface are often the rate-limiting step [5]. Although DCMD is considered one of the simpler configurations of MD, the conductive heat transfer across the membrane is greater than in other MD configurations [67].

Heat transfer across the MD membrane gives rise to temperature polarization (TP) in which the temperature of the feed solution at the feed-membrane interface declines and the temperature of the distillate at the distillate-membrane interface increases. Mass transfer across the MD membrane gives rise to concentration polarization (CP) and/or electrical conductivity polarization (CP) in which the vaporization of water from the feed stream through the MD membrane results in an increased solute concentration and thus a lower partial vapor pressure of water at the feed-membrane interface. Similar to other membrane processes, CP can also induce membrane scaling, which further reduces process performance [8,9].

Membrane scaling occurs when inorganic salts precipitate and accumulate on the membrane surface, thus blocking the pores for vapor to diffuse across the membrane and subsequently lowering water flux. Scaling of sparingly soluble salts such as CaSO₄, CaCO₃, and silicas has been identified as a cause of flux decline when recovering water from natural streams, including brines from desalination processes [10–17]. Two types of membrane scaling can occur: homogeneous and heterogeneous scaling. Homogeneous scaling occurs when crystals that form in the bulk solution precipitate on the membrane surface, and heterogeneous scaling occurs when salts crystallize directly on the membrane surface [18–20]. Scaling can alter membrane surface properties, i.e., hydrophobicity, change membrane pore structure, and ultimately decrease process efficiency and potentially lead to wetting of the membrane pores [12,13]. In MD it is essential that the porous membrane maintains its hydrophobicity to prevent membrane wetting, which will allow passage of water in a liquid phase through the membrane pores [5]. Pore wetting of the membrane hinders water flux, lowers salt rejection, and further impairs membrane integrity (i.e., loss of hydrophobicity).

1.2. DCMD for concentration of supersaturated solutions in mineral production

Replacing traditional concentration methods with MD could produce high quality minerals and water, reduce land footprint of evaporation ponds, and eliminate the required pumping of water from pond to pond in mineral production sites. Recent studies have shown that MD consumes less energy than traditional thermal distillation such as multi-stage flash and multi-effect distillation, and can further concentrate brines from desalination processes such as RO, NF, and ED [10,13,15,16,21–23]. Furthermore, utilization of low-grade heat sources such as industrial heat emissions and solar energy can offset the overall energy consumption needed for MD [24–27].

Recent studies have coupled membrane processes with crystallizers to concentrate and recover minerals in hypersaline solutions [14,22,28–35]; however, none of these studies have effectively mitigated membrane scaling. While membrane scaling has been investigated [10–13,23,34,36–40], effective scale mitigation techniques for maintaining and restoring water flux and salt rejection when desalinating saturated solutions are still lacking. In the current study, DCMD was applied to concentrate Great Salt Lake (GSL) water. The main objectives of the study were to evaluate the performance of DCMD in concentrating hypersaline brines from the GSL, and in doing so, optimize operating conditions to maximize water recovery and mitigate membrane scaling. Several unique methods were developed and tested to identify and mitigate membrane scaling. Finally, the replacement of evaporation ponds with DCMD was assessed as a means to intensify the mineral production process.

2. Materials and methods

2.1. Membranes

Two hydrophobic microporous membranes were acquired from GE Water (Minnetonka, MN). The first membrane (TS22) is a composite membrane consisting of a thin polytetrafluoroethylene (PTFE) active layer and a polypropylene woven support layer. The overall thickness of the TS22 membrane is 175 μm, with an active layer thickness of 5–10 μm. The second membrane (PP22) is an isotropic membrane made of polypropylene (PP), and is approximately 150 μm thick. Both membranes have a nominal pore size of 0.22 μm and a porosity of approximately 70% [41]. After experiments, the membranes were rinsed with deionized water and stored in a desiccator until analysis. A new membrane coupon was used for each set of experiments.

2.2. Membrane cells

Experiments were performed with acrylic membrane cells fitted to test flat sheet membranes. The cells were fabricated with symmetric flow channels on either side of the membrane, allowing for parallel flow of feed and distillate streams on the opposite sides of the membrane. Nitrile rubber gaskets were used to form flow channels, approximately 2 mm deep, on each side of the membrane. Turbulent enhancing spacers were placed in the flow channels to reduce temperature polarization effects, increase water flux, and ensure that the membrane lay flat and centered in the cell [41]. Experiments were performed using a modified SEPAC-DF cell with an effective membrane surface area of 130 cm². To prevent precipitation of salts on the membrane surface, the membrane cell was positioned horizontally with the feed side (active side) facing down. To observe real-time membrane scaling, an additional set of experiments was performed with a stereomicroscope (Semi 2000, Carl Zeiss Microscope, Thornwood, NY) and a direct observation microscope cell that has a glass observation port (127 cm x 254 cm) and an effective membrane surface area of 89 cm². During these experiments, the feed side of the membrane was facing up.

2.3. Bench-scale system

Bench-scale experiments were performed to investigate water flux, salt rejection, and membrane scaling. A supervisory control and data acquisition (SCADA) system (LabVIEW, National Instruments, Austin, TX; and a LabJack UE-9 Pro, Lakewood, CO) was utilized to control the temperatures of the feed and distillate streams and collect data to calculate water flux and batch recovery.
A flow schematic of the test unit is illustrated in Fig. 1. The thermally insulated feed and distillate reservoirs were connected to gear pumps (Micropump, Cole Parmer, Vernon Hills, IL) that circulated the feed and distillate streams co-currently on the opposite sides of the membrane. It is important to note that due to the small size of the membrane, operating in co-current mode had negligible effects on process performance in this study. Thermocouples were installed at the inlets of the feed and distillate channels and connected to the SCADA system. The flow rate of the two streams was 1.6 L.min⁻¹ when using the modified SEPA-CF cell, and 0.6 L.min⁻¹ when using the direct observation cell. As feed water evaporates through the membrane and absorbs into the distillate stream, water overflowed from the distillate reservoir into a beaker positioned on an analytical balance (Model S-8001, Denver Instruments, Bohemia, NY), which was connected to the SCADA system. The overflow rate was used to calculate water flux through the membrane. The conductivity of the distillate reservoir was continuously measured (Waterproof pH/CON 300m, Oakton Instruments, Vernon Hills, IL) and changes in conductivity were used to calculate salt rejection and detect membrane wetting.

2.4. Preliminary pure water permeability experiments

A set of preliminary experiments was performed to evaluate the pure water permeability of the TS22 and PP22 membranes and to select experimental operating temperatures. In these experiments, deionized water was used as the feed and distillate streams. The temperature of the feed ranged from 30 to 70 °C in increments of 10 °C and the temperature of the distillate was 20 or 30 °C.

2.5. Direct contact membrane distillation batch experiments

Experiments were conducted in a batch mode, simultaneously concentrating the feed solution and producing permeate. The feed solution was representative water from the Bear River Bay (Great Salt Lake, UT) on the eastern shore of the GSL and the distillate solution was deionized water. The raw GSL water was pre-filtered through a 0.5-μm cartridge filter to remove any suspended solids.

2.5.1. Successive water flux and salt rejection experiments

The performance of DCMO after multiple successive batch experiments was evaluated. These experiments utilized the PP22 and TS22 membranes. A high (40 °C) and low (20 °C) temperature difference across the membrane was chosen for these experiments. The temperature of the distillate stream was 30 °C and the temperature of the feed stream was either 50 or 70 °C. The experiments were performed until the water flux decreased to nearly 80% of its initial value, then the collected distillate was returned to the feed reservoir (diluting the feed solution to its original concentration), and the experiment resumed.

2.5.2. Scale identification experiments

2.5.2.1. Optical microscope. The onset of membrane scaling was observed with a stereo-microscope and the direct observation membrane cell. These experiments were performed with the PP22 membrane and 3 L of filtered GSL water as the feed. The feed and distillate temperatures were 50 and 30 °C, respectively. Images of membrane scaling were captured throughout the experiments (EOS Rebel XT, Canon, Lake Success, NY).

2.5.2.2 Isolation of sparingly soluble salts. Experiments were carried out to evaluate the effect of sparingly soluble salts on the decline in water flux. To isolate the potential scalants, experiments were performed with a feed solution of 150 gL⁻¹ NaCl (ACS grade). The modified SEPA-CF cell, PP22 membrane, and 3 L of feed solution were used. The feed and distillate temperatures were 50 and 30 °C, respectively.

2.5.3. Extended scaling experiments

A set of experiments was performed to evaluate the onset of membrane scaling over a prolonged period of time. Each experiment was initiated with 10 L of filtered GSL water recirculating on the feed side, and process performance was evaluated over 125 h. In these experiments, both the PP22 and TS22 membranes were tested and the feed and distillate temperatures were 50 and 30 °C, respectively. Each experiment was divided into 5-6 cycles. In each cycle, 1 L of distillate overflow was collected and removed from the system, then the distillate overflow (permeate) was continuously returned to the feed reservoir for approximately 12 h. After the 12 hour period, a new cycle started and another 1 L of distillate overflow was removed from the system. The cycles were repeated until the feed water was concentrated approximately 2.5 times relative to its original concentration.

2.6. Scale mitigation experiments

Three scaling mitigation techniques were investigated to prevent or remove membrane scaling and maintain membrane integrity. Batch experiments were performed with the modified SEPA-CF cell, PP22 membrane, and 8.5 L of filtered GSL feed water. The PP22 membrane was chosen because of its isotropic structure. The temperatures of the feed and distillate were 60 and 30 °C, respectively.

2.6.1. Mitigating rapid flux decline

In the first scale mitigation procedure, DCMO batch experiments were terminated before the water flux started to rapidly decline. After 12 h of operation, or when 35-40% of the feed water was recovered, the collected distillate was returned to the feed reservoir, diluting the feed to its original concentration. Subsequently, the next batch experiment began. Eight successive batch experiments were performed without membrane cleaning between cycles.

2.6.2. Flow reversal

Similar to the first technique, batch experiments were terminated before scaling occurred on the membrane surface, or after 35-40% of the feed water was recovered. Then, the feed side of the membrane was rinsed with approximately 200 mL of deionized water, and the feed and distillate channels of the membrane cell were exchanged: the feed side became the distillate side and the distillate side became the feed side. Subsequently, the next successive batch experiment began. This procedure was repeated six times.
2.6.3 Temperature reversal

Similar to the previous scale mitigation techniques, batch experiments were terminated before scaling occurred on the membrane surface, or after 35-40% of the feed water was recovered. Then, a colder GSL feed stream (15°C) was circulated on the feed side of the membrane while the warmer distillate (30°C) continued to be circulated on the distillate side of the membrane, thus reversing the direction of the driving force across the membrane. After 20 minutes, another batch concentration cycle started with a warmer feed (60°C at 150,000 mg/L) and cooler distillate (30°C) on their respective sides of the membrane. This procedure was repeated eight times. It is important to note that the colder feed stream could be taken directly from a colder source water; therefore, eliminating feed water cooling. In this case, the colder feed stream could be taken directly from the GSL, which has an average temperature of 15°C [41].

2.7. Solution chemistry and analytical methods

The GSL water was characterized using standard analytical methods. Water samples were prepared and analyzed for dissolved solids according to Standard Methods (APHA, 2005). Samples were diluted and filtered through a 0.45-μm filter and analyzed for anions with an ion chromatograph (Model ICS-90, Dionex, Sunnyvale, CA) and for cations with an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Optima 5300 DV, PerkinElmer Inc., Waltham, MA). The average total dissolved solids (TDS) concentration of the GSL water from the Bear River Bay was approximately 150,000 mg/L, most of which is sodium chloride (~84% w/w). A detailed ionic composition of the GSL water used in this study is summarized in Table 1. The feed solution chemistry was simulated with OLISim Analyzer™ (OLI Systems, Inc., Morris Plains, NJ) to determine the scaling tendencies at increasing temperatures (50-70°C) and concentrations (150,000-500,000 mg/L).

2.8. Economic implications of DCM utilization

The economic implication of using DCM for concentration of GSL water was evaluated and compared to the use of evaporation ponds. The evaporative water loss for the Bear River Bay (approximately 1.4 m per year [42]) and the average DCM water flux obtained from the temperature reversal experiments were standardized and used for comparison of the different concentration methods.

3. Results and discussion

3.1. Pure water permeability experiments

Water flux as a function of feed temperature for the two membranes is shown in Fig. 2. Water flux increased exponentially with increasing temperature difference (or vapor pressure driving force) across the membrane. The water flux through the TS22 was consistently higher than the water flux through the PP22. This is because the PP22 is a thicker membrane with more tortuous pores that increase the resistance to vapor diffusion through the membrane pores, thus resulting in a lower permeability [41,43]. Based on these results, a high temperature differential (ΔT = 40°C) and low temperature differential (ΔT = 20°C) were chosen for the successive batch concentration experiments; the temperature of the distillate stream was kept at 30°C and the temperature of the feed stream was either 50 or 70°C.

3.2. Direct contact membrane distillation batch experiments

3.2.1. Successive batch experiments: water flux and salt rejection

Water flux as a function of GSL water total solids concentration for experiments performed with the two membranes operated at a ΔT of 40 and 20°C is shown in Fig. 3. In all experiments the water flux gradually declined as the feed solution concentration increased, and thus the partial vapor pressure of water in the feed solution decreased. Therefore, a sharp decline in water flux was observed in all the experiments.

Compared to the pure water permeability experiments, a lower initial water flux was observed during batch experiments performed with the GSL water. For example, in experiments performed with the PP22 and GSL feed solution, the initial water flux was 11% (ΔT of 20°C) and 20% (ΔT of 40°C) lower than that of the pure water permeability experiments performed with the same membrane and the same temperature differences. The experiments performed with the TS22 and GSL feed solution resulted in an initial water flux of 28% (ΔT of 20°C) and 38% (ΔT of 40°C) lower than in the pure water permeability experiments performed with the same membrane and temperature differences. The percent decrease in initial water flux for the experiments performed with the GSL feed water was lower for temperature difference of 20°C and for the PP22. The lower partial vapor pressure of water in the highly concentrated feed solution (150,000 mg/L total solids) was the main reason for a lower driving force across the membrane and the lower initial water flux. For example, Song et al. reported that solutions with salt concentrations of 10% and 20% reduced the partial vapor pressure by 6% and 20%, respectively [44].

As increased temperature differentials (ΔT of 40°C), a higher terminal GSL water concentration was achieved with the PP22. Although experiments conducted with the TS22 at a higher temperature difference (ΔT of 40°C) resulted in greater initial water fluxes compared to those with the PP22, the initial water flux decreased after each successive batch experiment. Several studies have reported that polarization effects are more severe at increased operating temperatures [8,16,23,43,45]; however, these effects are reduced when using membranes with low thermal conductivities [7,25,45]. Thus, it is likely that the lower thermal conductivity of the thicker PP22 mitigated the effects of temperature polarization when tested at increased temperature differences across the membrane. Temperature polarization effects were more severe during experiments performed with the TS22 at increased temperature differences, which resulted in increased membrane scaling. Higher flux also results in
Fig. 2. Water flux as a function of feed temperature for experiments performed with the TS22 and PP22 MD membrane. The distillate temperature (T_d) was either (a) 20 or (b) 30 °C; the feed temperature was between 30 and 70 °C, and the flow rates were kept constant at 1.61 min⁻¹.

Fig. 3. Water flux as a function of total solids concentration for the successive batch experiments (runs) performed with (a) the TS22 membrane and (b) the PP22 membrane. Experiments were performed with filtered GW water as feed and deionized water as distillate. The distillate temperature was 30 °C and the feed temperature was either 50 (50/30) or 70 °C (70/30). The flow rate was kept constant at 1.61 min⁻¹.

higher heat fluxes, which subsequently decreases the temperature difference across the membrane and increases temperature polarization effects [8,9,16,43].

Temperature polarization also affects the mechanisms of membrane scaling. Because the temperature is lower at the feed-membrane interface than in the bulk solution, the calcium species solubility is expected to increase, whereas NaCl solubility is expected to decrease. Additionally, increased water flux results in increased rates of scaling. Therefore, it is expected that the potential for scaling of NaCl will be higher for the TS22 membrane (higher flux) than the PP22 membrane.

Water flux and distillate conductivity as a function of time are shown in Fig. 4 from data presented in Fig. 3. The distillate conductivity for both sets of experiments performed at a ΔT of 20 °C continuously decreased, indicating that the membrane rejected nearly 100% of all inorganic and non-volatile constituents. However, the distillate conductivity increased in both experiments operated at a higher temperature gradient. The distillate
conductivity increased throughout the experiment performed with the PP22. In experiments performed with the TS22, the distillate conductivity started to increase only towards the end of the experiment, indicating that the TS22 is less susceptible to wetting at higher operating temperatures. A previous study by Gryta et al. reported that operating at temperatures greater than 68 °C may reduce the hydrophobicity of polypropylene membranes and lead to membrane wetting [36]. Safarzadeh et al. reported that PTFE membrane support layers showed no signs of degradation when exposed to high temperatures (< 350 °C); however, the potential for wetting of PTFE membranes does increase with increasing feed temperatures and salinities [46].

When operated at a higher AT of 40 °C, the water flux had more than tripled, increasing the overall water flux from 12.8 to 47 Lm⁻²h⁻¹ during experiments with the TS22 and from 12.3 to 40 Lm⁻²h⁻¹ during experiments with the PP22. Yet, while the process was accelerated at high temperature differences across the membrane, both salt rejection and initial water flux decreased after each successive batch experiment. When experiments were conducted at a AT of 20 °C, the salt rejection of the membrane was high, the water flux after each successive batch run was restored, and the GSL water was concentrated to more than 300,000 mg/L total solids. Therefore, operating temperatures lower than 70 °C (50 and 60 °C) for the feed and 30 °C for the distillate were chosen for the following experiments.

3.2.2 Membrane scaling investigation

To further investigate the onset of rapid flux decline, a set of experiments was performed in conjunction with stereomicroscope observation. Water flux and total solids concentration as a function of time are shown in Fig. 5. The dashed lines in Fig. 5 indicate when pictures of scaling on the membrane surface were taken. Images of the PP22 membrane surface were captured before and after the onset of rapid flux decline. Similar to results shown in Fig. 3, the water flux begins to rapidly decline at a total solids concentration of approximately 300,000 mg/L.

Images of the different stages of scale formation on the feed side of the membrane are also shown in Fig. 5. The onset of membrane scaling is first visualized after 7.5 h of operating time, or when the feed solution concentration approached 250,000 mg/L total solids. Thereafter, crystals continued to precipitate on the membrane surface and the water flux continued to decline. After approximately 9.5 h of operation, or at a bulk feed solution concentration of 300,000 mg/L total solids, the membrane surface was mostly covered with salt resembling NaCl crystals [22,37].

To further evaluate the effect of sparingly soluble salts on flux decline, results from experiments performed with pure NaCl as the feed solution were super-imposed on results from experiments performed with GSL water (Fig. 5). Interestingly, similar to results from experiments with GSL water, the same sharp decline in water flux occurred during the experiments performed with the NaCl water, indicating that the onset of homogeneous precipitation of salts, mainly NaCl, correlates to the onset of rapid water flux decline.

Water flux was higher during experiments with NaCl feed than during experiments with GSL water. Also, compared to the experiments with the GSL water, the rapid decline in water flux is delayed in the experiments with NaCl feed. This can be explained by further evaluating the complexity of the solution chemistry for the GSL water. Sparingly soluble salts and organic matter are present in the GSL water (Table 1). OLI modeling results revealed that at a bulk GSL water feed solution temperature of 50 °C, calcium species are the first to reach saturation (at 340,000 mg/L TDS), followed by NaCl (at 400,000 mg/L TDS). Garcia et al. found that divalent calcium ions in the presence of humic acid form complexes with the carboxyl functional groups and cause membrane scaling [17]. The calcium scaling then serves as nucleation sites for other species, such as NaCl [16]. Therefore, scaling of sparingly soluble salts and NaCl were both the cause of rapid water flux decline during the experiments with GSL feed water.

3.2.3 Extended scaling experiments

Water flux and distillate conductivity as a function of time and feed total solids concentration are shown in Fig. 6a and b. Long-
term batch experiments were performed in a unique operating mode to evaluate the effect of membrane scaling over time. The first part of the cycle was performed to evaluate how water flux decreases as concentration increases. Similar to results obtained for the successive batch experiments (Section 3.2.1), in both sets of experiments, the water flux gradually declined until the feed solution reached approximately 300,000 mg/L total solids. The second part of the cycle (recirculation step) was performed under constant conditions to evaluate membrane scaling over time and its effects on water flux. During the recirculation step, water flux continued to declined, further indicating that in addition to a reducing partial vapor pressure of the feed solution, nucleation of sparingly soluble salts on the membrane also contribute to the gradual decline in water flux.

### 3.3 Scaling mitigation techniques

Three unique operating techniques were investigated to mitigate membrane scaling. These include reduced operating time interval, reduced operating time interval with flow reversal, and reduced operating time interval with temperature reversal. The PP22 membrane was chosen for these experiments because of its isotropic structure. The operating temperatures were chosen because an accelerated operating time and increased feed concentration can be
achieved without wetting the membrane and compromising its performance.

3.3.1 Mitigating rapid flux decline

The first technique to prevent scale formation during successive batch experiments was to terminate the experiment before a rapid flux decline occurred. Water volume recovered from the feed and distillate conductivity as a function of elapsed time are shown in Fig. 7. Each line represents a successive batch experiment, and the slope of each line divided by the membrane area (0.0139 m²) is the average water flux (in L m⁻² h⁻¹) during each batch experiment (labeled above each line). During the first five successive batch experiments the water recovery only minimally changed. However, during the 6th batch, scaling on the membrane and wetting of some pores caused a rapid decline in water flux and a sharp increase in distillate conductivity. Following these results, two new operating techniques were tested to mitigate and reverse scaling of minerals on the membrane.

3.3.2 Flow reversal

Water volume recovered (i.e., distillate collected) and distillate conductivity as a function of elapsed time are shown in Fig. 8 and each line represents a successive batch experiment. In this scale mitigation technique, the feed and distillate flow channels were exchanged after each successive batch experiment. The average water flux (in L m⁻² h⁻¹) during each batch experiment is labeled above each line. The average water flux during all experiments was 19.51 m⁻² h⁻¹ with a standard deviation of 14.41 m⁻² h⁻¹, indicating that membrane scaling was minimal. Following the first experiment, the distillate conductivity increased. This increase in distillate conductivity was mostly due to residual salts in the distillate hydraulic loop from the previous cycle experiments and dissolution of scalants that deposit on the membrane surface and in the membrane pores. The cause for the different trends in distillate conductivity on either side of the membrane is not well understood; however, it is likely that the slight difference in surface characteristics on the opposite sides of the membrane resulted in dissimilar scaling and wetting patterns on the membrane. Additional research on membrane characteristics, nucleation kinetics, and scale formation could provide further insight into this trend.

3.3.3 Temperature reversal

Water volume recovered and distillate conductivity as a function of elapsed time for the third scale mitigation technique are shown in Fig. 9. The average water flux (in L m⁻² h⁻¹) during each batch experiment is labeled above each line. In this technique, the temperature difference across the membrane was reversed for a period of time before a new batch experiment was performed.

The average water flux during these experiments was 20.61 m⁻² h⁻¹ with a standard deviation of 0.95 m⁻² h⁻¹. The water flux slightly declined during the sixth experiment and the distillate conductivity slowly increased. Overall, the water flux and salt rejection were higher during this operating technique than the previous scale mitigation techniques, and the use of freshwater to flush the feed channel was eliminated.

Flow and temperature reversal techniques proved to be very effective in maintaining water flux and mitigating membrane scaling. Compared to previous experiments performed without scale mitigation techniques, experiments performed with the flow and temperature reversal techniques resulted in sustained, high water fluxes throughout batch concentration experiments. Also, these operating techniques were performed without the use of chemicals (i.e., antiscalants, acids, and bases) to remove scalants, and without additional energy to cool the feed water. Scale mitigation via temperature reversal achieved the greatest average water fluxes, rejected nearly 100% of non-volatiles for the first six batch concentration cycles, and was performed without additional water and energy inputs. Therefore, this scale mitigation technique could prove to be very impactful in MD. A recent study by Keselme
et al. [48] reported that addition of a 0.5 μm filter before the feed channel inlet was effective in capturing precipitated salts that would have otherwise deposited on the membrane. Hybridization of the proposed scale mitigation techniques with a 0.5 μm filtration of the feed could further reduce membrane scaling and wetting in MD.

3.4. Efficiency of MD over natural evaporation

When considering replacement of evaporation ponds with DCMED, two central considerations are the time and costs involved in concentrating brines. Production of high-value minerals will continue to increase with growing demands, and acquisition of land for additional ponds can be costly or in some cases impossible. Therefore, the efficiency of natural evaporation of the Bear River Bay was compared to MD.

The net annual evaporation rate at the Bear River Bay is 1040 mm (41 in.) per year [42]. From a single unit conversion, on average 2.85 mm of water is evaporated from the bay each day. From results obtained in this research, DCMED can concentrate GSL water at an average rate of 201. m⁻² h⁻¹ (Fig. 9), and from a simple unit conversion, approximately 480 mm of high-quality distillate water can be recovered from GSL water each day using a DCMED membrane of the same area. Therefore, applying DCMED to mineral production not only recovers high-quality water, but also accelerates the natural evaporation process by concentrating hypersaline solutions by approximately 170 times.

In terms of land use, one acre (4047 m²) of evaporation ponds could be replaced with approximately 259 ft² (24 m²) of flat sheet DCMED membrane. Several studies have shown that DCMED is an economically and environmentally competitive water treatment process to RO when low-grade heat is utilized [25,48,49]. A study by Al-Obaidani et al. estimated that operating DCMED with a heat recovery system could reduce water cost to $0.64 m⁻³ of water produced (≈$0.004 kWh/m²), making DCMED a competitive membrane process to RO ($0.50 m⁻³ of water produced) [25]. A more recent study estimated that water production costs with DCMED could be further reduced to $0.57 m⁻³ when low-grade heat is utilized and carbon tax is applied [48]. Therefore, in addition to concentrating GSL water for mineral recovery, the high-quality water produced can be sold to further offset operating costs.

4. Conclusions

DCMED was effective in concentrating GSL water to greater than 350,000 mg L⁻¹. Operating DCMED at high T of 40 °C was not sustainable; the membrane performance was compromised because of membrane scaling and pore wetting. Consequently, operating DCMED in successive batch mode without the use of scale mitigation techniques resulted in decreased membrane performance (i.e., lowered salt rejection and water fluxes).

Flow reversal and temperature reversal are new operating techniques that proved very effective in sustaining high water fluxes and membrane performance [50]. The scale mitigation techniques were effective in inhibiting homogeneous precipitation of salts and disrupting nucleation of sparingly soluble salts on the membrane surface. Of the three scale mitigation techniques, the temperature reversal technique was most effective in maintaining high water fluxes (≥20 L m⁻² h⁻¹) and high salt rejection. The new techniques were simple to operate and very impactful in mitigating scaling. Furthermore, the need for antiscalants and other chemicals used for membrane cleaning was avoided.

Replacing natural evaporation ponds with DCMED can result in enhanced operations and reduced environmental footprints. Operating DCMED with low-grade heat recovered from the on-site chemical processing plant can drastically reduce MD operating costs, and high-quality water recovered from the GSL water can aid in offsetting operating costs.

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