Title: Water, Energy, and Cost: A Nexus Approach to Zero/Minimal Liquid Discharge Desalination Technologies

Margaret G. O'Connell,¹ Neha Rajendran,¹ Menachem Elimelech,² Jack Gilron,³ Jennifer B. Dunn^{1,*}

¹Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois 60208, United States

² Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06511, United States

³Zuckerberg Institute for Water Research, Ben-Gurion University of the Negev, Sde Boker 84990, Israel

*Corresponding author

<u>Abstract</u>

Desalination is increasingly essential to ensure water access as climate change and population growth stress fresh water supplies. Already in use in water-stressed regions around the world, desalination generates fresh water from salty sources, but forms a concentrated brine that requires disposal. There is a growing push for the adoption of zero/minimal liquid discharge (ZLD/MLD) technologies that recover additional water from this brine while reducing the liquid volumes requiring disposal. This analysis evaluates the cost, energy, and sustainability impacts of 7 overarching treatment trains with 75 different configurations. ZLD/MLD water recoveries are found to range from 32.6-98.6%, but with steep energy and cost tradeoffs that underscore the crucial role of ion-specific separations, heat integration, and clean energy sources. Ultimately, this analysis explores key tradeoffs between costs, energy, and water recovery, highlighting the increasingly tight connections at the central to the energy-water nexus and desalination.

There are few, if any, substances more fundamental to life than water. Whether for drinking, food, or hygiene, water's uses are core to quality of life. Still, billions continue to live without access to clean water, sanitation, and/or food.^{1–3} Aging infrastructure paired with a global population expected to reach nearly 10 billion by 2050 will continue to stress current water supplies.^{4,5} Climate change threatens the existence of this water in the first place, shrinking the cryosphere, increasing drought severity, and destabilizing the water cycle.⁶ These threats to water security tighten the energy-water nexus knot. There is no energy without water, and there is no water without energy. This relationship between water and energy is at the heart of desalination.

Desalination provides drinking and irrigation water from saline water bodies such as seawater and brackish groundwater. Water recoveries of approximately 40-50% and 70-90% are possible for seawater and brackish water desalination, respectively, with reverse osmosis acting as the predominant desalination technology.^{7,8} Currently, a global desalination capacity of approximately 34.81 billion m³/year generates 51.7 billion m³/year of brine, predominantly from seawater desalination.⁸ Typically, brine from desalination plants is disposed of by one of four processes.⁹ Surface water discharge (SD) is the most common but is not applicable for inland desalination plants.⁹ Deep-well injection (DWI) stores brine in underground geologic formations and can be feasible for inland plants.⁹ Strict geologic requirements and the potential for the concentrated brine to clog the injection apparatus limit DWI application.¹⁰ Desalination plants can send brine into the sewer system, but biological wastewater treatment systems generally cannot withstand such high levels of salinity.⁹ Finally, plants can dispose of brine in lined ponds.⁹ Eventually, the water evaporates, leaving salts behind that require disposal.¹¹ Areas with low solar insolation and limited land availability may not choose this technique which risks soil and groundwater contamination if liners fail.

Zero and minimal liquid discharge (ZLD/MLD) technologies shift this brine disposal paradigm. By increasing water recovery and reducing disposal volumes, ZLD/MLD transform brine from a harmful waste to a resource.¹² Yet this additional water recovery comes with cost, energy, and sustainability tradeoffs not yet fully understood. ZLD/MLD treatment trains broadly consist of a concentration step, a crystallization step, and a disposal step.¹³ Many previous analyses have assessed ZLD/MLD technologies, estimating costs and energy demands for a range of thermal and membrane-based operations.^{14–21} These analyses are important starting points, but

generally either focus on one technology, do not include both membrane and thermal technologies, do not include the entire treatment train through final disposal, or focus on only one water recovery case. What is missing is a holistic analysis of entire ZLD/MLD treatment trains that explores the relationship between water recovery, cost, energy, and sustainability effects.^{22,23} Analysis of the entire ZLD/MLD process uncovers dynamics that arise from the interactions between concentrator, crystallizer, and disposal steps not seen in optimization of any one step individually.

This analysis explores these tradeoffs through technoeconomic and life cycle analyses (TEA and LCA) of one baseline disposal operation and six ZLD/MLD treatment trains. These six ZLD/MLD treatment trains feature thermal and membrane-based concentrators operating across a swath of water recoveries, two pre-treatment options, four different crystallizer scenarios, and three disposal options evaluated over a range of costs and energy intensities. Altogether, 75 treatment train configurations comprising nearly two thousand individual levelized cost of water (LCOW) cases and approximately thirteen hundred specific energy consumption (SEC) cases are evaluated. Energy-water nexus implications are incorporated through life cycle greenhouse gas (GHG) emissions, energy consumption, and subsequent water consumption. Ultimately, this analysis provides a comprehensive assessment of the feasibility of ZLD/MLD operations and the tradeoffs at the core of unconventional water production.

Main Text

Holistic assessment of desalination treatment train options for zero and minimal liquid discharge

In this analysis, reverse osmosis desalination brine (principal RO brine) enters the ZLD/MLD processes with a total dissolved solids (TDS) concentration of 80.0 g/L at a flowrate of 41,000 m³/d (see Methods and Supporting Information (SI) Section 1).²⁴ One fundamental assumption underlies this work: additional water *must* be recovered from brine. Figure 1 illustrates the baseline disposal train (Train 0) and six ZLD/MLD treatment trains (Trains 1-6) assessed for this analysis. Mechanical vapor compression (MVC) is the thermal-based concentrator evaluated in Train 1, and low salt rejection reverse osmosis (LSRRO) is the membrane-based concentrator evaluated with different pre-treatment configurations in Trains 2-6. SI Section 4.2 provides a detailed description of LSRRO operation, but LSRRO generally builds on previous RO-adjusted operations such as high pressure RO (HPRO), osmotically assisted RO (OARO), and forward osmosis (FO) that work to overcome the pressure limitations of current RO membranes to recover

water from brine.^{9,25,26} LSRRO consists of an initial RO stage for water recovery, followed by subsequent stages of "impaired" RO that reduce the osmotic pressure difference and enable greater brine concentration.^{15,16} A three stage LSRRO system is modeled for this study.

Membrane operations such as LSRRO are prone to mineral scaling. Membrane scaling is a complex process whose effects on operation are difficult to capture in full-scale models. The addition of antiscalants that increase scalant solubility or the use of nanofiltration (NF) which can remove scale-forming divalent ions before LSRRO operation can reduce scaling impacts. Specifically, scaling reductions can extend membrane life, reduce cleaning requirements, and reduce energy requirements.^{27,28} A detailed analysis of these scaling impacts is beyond the scope of this analysis; however, antiscalants and NF are included as pre-treatment options to give an idea of their cost and energy requirements.

Unit operations are modeled with the National Alliance for Water Innovation's (NAWI) WaterTAP model, a Python-based model with optimization capabilities for numerous water technologies.^{16,29,30} The unit operations here are modeled to optimize the LCOW, calculating the overall process cost per m³ of usable water that is produced. See Methods and SI Sections 2-8 for modeling details. Note that the MVC unit modeled in Train 1 includes heat integration such that no external heating is necessary; thermal processes drive the separation with heat provided via condensation and heat exchange. SEC values for MVC reflect the electricity necessary for compression and pumping.



Figure 1: Treatment train types modeled for TEA and LCA. Train 0 is the baseline treatment train representing conventional disposal options. The use of RO in Train 0 fulfills the requirement that additional water be recovered. In Trains 3-6, NF produces a divalent-rich brine that is either sent to disposal (Trains 3-4) or blended with principal RO permeate to supply beneficial divalent ions (Trains 5-6). Italicized streams boxed in green indicate flows defined as "usable water" for the cost and energy calculations. Variations including no crystallizer and crystallizer operation at 50%, 70%, and 90% are considered, with dashed lines indicating treatment train alterations from crystallization use.

Zero and minimal liquid discharge train design faces tradeoffs among cost, energy, and land use

Figures 2a, 2b, and 2c present the LCOW, SEC, and evaporation pond land area requirements, respectively, for each treatment train configuration. Detailed analysis of each configuration can be found in SI Sections 2-8; the focus here is on the interactions between these variables that should drive ZLD/MLD treatment train design. Water recovery is perhaps the most critical variable to consider. Regions facing extreme water stress may have to prioritize water recovery above all else, and conventional RO technology (Train 0) achieves only up to 20.8 vol% recovery before exceeding RO membrane pressure limits.³¹ This low level of water recovery makes Train 0 inefficient across economic, energy, and land area considerations. ZLD/MLD technologies can achieve much higher recoveries; choices then center around crystallizer use. Trains 1-6 achieve recovery with the use of crystallization. In situations with expensive disposal requirements such as evaporation ponds, crystallization can both increase water recovery and even drive the overall LCOW down due to decreased liquid disposal requirements.

While beneficial from a water recovery perspective, there are key energy considerations associated with crystallization. Water recovery is driven entirely by concentrator operation when there is no crystallizer, but scenarios with crystallization recover water through a balance of concentrator and crystallizer recovery. The less water recovered by the concentrator, the more water is recovered as condensed steam during the crystallization process and vice versa. Each train therefore attains approximately the same water recovery independent of concentrator recovery when a crystallizer is utilized, with recoveries increasing as more brine is converted to steam to achieve higher crystallizer solid salt recoveries. Though a treatment train will achieve roughly the same recovery for a given crystallizer yield, there is variation in cost and energy requirements within treatment trains. LCOW variation is driven by different disposal method costs and by the greater cost of operating high recovery concentrators versus crystallization; LCOW is lower when recovery is driven by the crystallization process. The reverse trend is seen for energy; SEC generally decreases when recovery is driven by concentrator steps as opposed to crystallization. See Methods for additional crystallizer cost discussion and SI Sections 2-8 for discussion of exceptions that occur under severe concentrator operation cases. Essentially, crystallizer operation boosts water recovery and can improve economic efficiency when disposal is expensive, but comes with significant energy burdens.

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Yet water, costs, and energy are not the only considerations at play. Crystallization produces solid salt that requires disposal – a requirement otherwise not present in SD and DWI disposal cases. The higher the crystallizer yield, the more water is recovered, but the more solid salt is produced for SD and DWI cases. When evaporation ponds are the disposal option, the same amount of solid salt requires disposal independent of crystallizer operation; all TDS exiting the concentrator step is assumed to require disposal. Still, there are important crystallizer considerations in evaporation pond cases. If evaporation ponds are the only disposal option available, crystallization becomes almost imperative to reduce land requirements. Adding crystallization reduces pond area requirements from 566-2,190 acres to 34-1,479 acres, with pond area decreasing as crystallizer yield increases. Depending on space constraints, these land concerns may take priority over energy demand. Illustrated in Figure 3, evaporation ponds can be a primary LCOW driver depending on land costs.



Figure 2: a) LCOW b) SEC and c) evaporation pond area of Train 0 and Trains 1-6 under different crystallizer operation scenarios. Minimum and maximum cost cases are considered for each disposal method, and minimum and maximum energy cases are considered for SD (see Methods). Evaporation ponds are the most expensive disposal option, followed by DWI and then SD. DWI is the most energy intensive disposal option, followed by SD and then evaporation ponds.

Unit operation cost and energy drivers

Figures 3a and 3b depict the LCOW and SEC contributions, respectively, of each unit operation under no crystallizer, 50%, 70%, and 90% crystallizer yield conditions. From the very first unit operation, design choices have implications that cascade throughout the treatment train. Pre-treatment methods do not contribute much to the LCOW or SEC themselves, but they do play a critical role in determining water recovery potential and disposal requirements. The use of NF instead of antiscalant addition limits how much volume actually makes it to the LSRRO step. Cases involving NF as a pre-treatment therefore only exceed the recovery of cases with antiscalant as a pre-treatment when the divalent-rich NF brine can be blended with the divalent-depleted principal RO permeate. Blending this brine also drives costs and energy demand down, both due to the increase in usable water that is the basis for LCOW and SEC calculations (see Discussion). In the absence of blending, however, faces composition limitations (see Discussion). In the absence of blending, the cost of treatment trains with large disposal requirements depends greatly on disposal cost assumptions and the volume of liquid requiring disposal, having greater impact under maximum cost assumptions and in Trains 1-4 where greater volumes are disposed of than in Trains 5 and 6.

Moving down the treatment train, in all cases concentrators play an important role in driving cost and energy requirements. The interplay between concentrator and crystallizer operation is further elucidated in Figure 3. For instance, it is evident that increasing LSRRO recovery decreases crystallizer energy demand by more than the corresponding increase in LSRRO energy demand, until the LSRRO reaches its more severe operating conditions. The increase in LSRRO recovery does increase LSRRO LCOW, but in cases without crystallization, can decrease disposal costs by an even greater amount, particularly for scenarios involving expensive DWI or evaporation ponds plus salt disposal.

Energy-water nexus

These interactions between pre-treatment, concentrator, crystallizer, and disposal steps shape the manner in which the energy-water nexus presents itself in ZLD/MLD processes. Figure 4 illustrates how costs and energy evolve with concentrator water recovery for scenarios involving no crystallizer and scenarios with 90% solid salt yield crystallization, covering the range of crystallization in this analysis. In Figure 2, there are instances where LCOW and SEC achieve

minimum values in certain scenarios; Figure 4 demonstrates that, unfortunately, minimum LCOW, minimum SEC, and maximum water recovery never overlap. For the variety of configurations modeled here, there will always be embedded tradeoffs.

There are several situation-dependent forms these tradeoffs take. In cases with no crystallizer, there are instances where minimum LCOW and minimum SEC do overlap, largely in Trains 2-6 scenarios with SD as the final disposal method and Trains 5-6 scenarios with DWI under minimum costing conditions. These are cases where disposal costs are low enough that they do not offset concentrator costs with increasing concentrator recovery; however, these minimum LCOW and SEC overlap cases happen when the trains are operating at minimum water recoveries. Train 1 almost achieves overlap at a water recovery that, while not the highest, is not the lowest due to the MVC's LCOW and SEC efficiency that initially improves with water recovery. Still, in cases with DWI under maximum costing conditions or evaporation pond use, a choice must be made: 1) achieve the highest water recovery, but with cost and energy penalties, 2) minimize cost, but with recovery and energy penalties, or 3) minimize energy, but with recovery and cost penalties.



Figure 3: a) LCOW and b) SEC by treatment train for cases involving a) no crystallizer b) 50% c) 70% and d) 90% solid salt yield crystallization. Increasing marker size relates to increasing concentrator recovery. All treatment trains use the same range of marker sizes.



In cases with 90% crystallizer yield, tradeoffs are present but somewhat mitigated. Governing all crystallizer scenarios is the tradeoff that higher recoveries are achieved but with higher energy requirements than no crystallizer scenarios. If the additional water is worth the additional energy, it is possible to minimize energy or cost without also sacrificing recovery. The aforementioned balance between concentrator- and crystallizer-driven water recovery means a concentrator-heavy scenario can minimize energy but with a cost penalty, or a crystallizer-heavy scenario can minimize costs but with an energy penalty. In either case, approximately the same amount of water is recovered. The more notable tradeoff remains the choice between higher water recoveries with crystallization compared to trains without crystallization, but with a substantial increase in energy demand.



Figure 4: LCOW vs. SEC for treatment train scenarios involving a) no crystallizer and b) 90% solid salt yield. Increasing marker size relates to increasing concentrator recovery as in Figure 3.

Sustainability insights: Life-cycle energy, GHG, and water consumption implications

The GHG emissions accompanying the ZLD/MLD treatment trains must be considered; if ZLD/MLD treatments are increasingly necessary as climate change drives water scarcity, then ZLD/MLD treatments must minimize their own contributions to climate change. LCA is a tool that can estimate these contributions. For the ZLD/MLD treatment trains assessed here, we calculate life-cycle energy and water consumption and GHG emissions based on energy-, water-, and GHG-intensity factors from the Argonne National Laboratory's Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies Model (GREET)³² as detailed in Methods.

In calculating these metrics, we consider the energy, water, and GHG burdens associated with providing energy (electricity and natural gas), antiscalant, and HCl. When applicable, we also account for GHG burdens associated with transportation for salt disposal. Calculations are performed under two scenarios: 1) a wind-based electricity grid and 2) the U.S. electricity grid mix. Natural gas supplies the heat for crystallization in both scenarios. Figure 5 reports the life cycle energy results, illustrating that the feasibility of ZLD/MLD treatment trains is greatly impacted by the electricity supply. In the wind-based scenario, life-cycle SEC requirements range from 3.8-53 kWh/m³. A more substantial increase in energy requirements occurs in U.S. grid mix scenarios, with life-cycle SECs of 7.3-65 kWh/m³ usable water; meaning, the energy intensiveness of the electricity, heat, and chemicals consumed in ZLD/MLD trains can increase the SEC by approximately 37-115%.



Figure 5: Life cycle SEC for ZLD/MLD treatment trains under b & e) wind electricity scenarios and c & f) U.S. electricity mix scenarios compared to a & d) the energy required for the ZLD/MLD process with no life cycle considerations.

It is also critical to account for the GHG emissions and energy-water nexus implications of ZLD/MLD processes. Depicted in Figure 6a, GHG emissions are minimized under wind electricity scenarios when configurations do not include crystallization; an additional tradeoff therefore arises between higher water recoveries (achieved with crystallization) and minimal emissions (achieved without crystallization). In fact, how GHG emissions in wind versus U.S. grid electricity scenarios compare depends greatly on whether crystallization is present or not. Under both electricity scenarios, it is assumed that natural gas supplies heat for crystallization operations will emit more than treatment trains using wind electricity but with severe crystallization. Under wind and U.S. grid electricity scenarios, emissions range from 0.04-9.0 and 1.6-15 kg $CO_{2,eq}/m^3$ usable water, respectively, resulting in hundreds, thousands, or up to 190,000 metric tons of CO_{2e} per year at a single facility.

Generating the energy required to operate the ZLD/MLD treatment trains also consumes water. As illustrated in Figure 6b, this embedded water consumption is less than 1% of the water recovered via the ZLD/MLD trains in all cases when electricity is generated via a wind-based grid,

but can range from 0.77-6.0% consumption of the recovered water when a U.S. grid mix of electricity is employed. These GHG emissions and water consumption ramifications highlight the need for renewable-based energy generation. Cleaner electric grids and heat generation ensure that energy intensive processes such as ZLD/MLD treatment trains can maximize water production, minimize collateral water consumption, and minimize climate change ramifications.



Figure 6: a) GHG emissions and b) water consumption associated with the life cycle impacts of ZLD/MLD treatment trains under both wind-based and U.S. mix electricity grid scenarios.

Discussion

While there are limitations to this analysis, the wide variety of treatment train configurations provides much needed insights regarding ZLD/MLD processes. Moreover, our results align with those of previous studies that found the LCOWs and SECs of NF to be approximately 0.3-0.6 \$/m³ and 0.5-1.0 kWh/m³,³³ LSRRO to be approximately 1-4 \$/m³ and 3-20 kWh/m³,^{15,16} MVC to be approximately 0.8-10 \$/m³ and on the order of 10s of kWh/m³,^{34,35} and crystallization to be <1 \$/m³ and approximately 25-66 kWh/m^{3.21,34} The exact values vary across configuration, flow rate, salinity, and other case-specific operating conditions. Given the case-specific nature of these processes, the LCOWs and SECs presented here should be taken less for their exact value and more for their overall tradeoffs that provide lessons across use cases. These tradeoffs indicate that it is critical to improve a) the accuracy of heat recovery potential in crystallization and b) ion-specific separation process modeling. Such improvements are continuously being made to modeling software such as WaterTAP; as full-scale unit operation modeling capabilities progress, heat integration along with fouling considerations and other ionspecific phenomena can be better incorporated. For now, the primary ion-specific modeling took place for NF units, where divalent and monovalent selectivity plays a key role in blending opportunities,³⁶⁻³⁸ and assumptions around crystallization heat recovery are made based on a combination of modeling and literature data (Methods and SI Section 3.2).³⁹

The divalent ions concentrated in NF brine are prone to scaling LSRRO membranes, but are important for drinking and irrigation water applications. Blending this divalent-rich stream with the divalent-depleted principal RO permeate reduces the need for desalination plants to add divalent ions like calcium back into the product water.^{37,38,40} In reality, operations will likely blend somewhere between none (Trains 3 and 4) and all (Train 5 and 6) of the NF brine, so these trains operate as bounding cases. The level of blending plays a key role in cost, energy, and water recovery potential. Trains 5 and 6 achieve high recoveries for relatively low cost and energy demand, but this level of blending may be unrealistic with NF pre-treatment. For instance, even the most chloride-tolerant crops can only withstand roughly 2.8 kg Cl⁻/m³ before yield losses occur,⁴¹ and the blended NF brines from Trains 5 and 6 reach chloride levels of approximately 11 and 15 kg Cl⁻/m³, respectively (see Methods for additional discussion). This analysis does not account for downstream processing necessary to remove this chloride, but also does not account for the cost savings from removing divalent salt addition steps. Whether from the growing need

for ZLD/MLD, the push for minerals recovery from desalination brine,⁴² or other ion-specific needs, future studies should explore exactly how such ion-specific separations and blending may look in greater detail. Emerging technologies such as monovalent selective electrodialysis and capacitive deionization currently lack industrial-scale use, but may prove capable of achieving high-blending scenarios.⁴³

Limitations considered, this analysis provides insights on the challenges and tradeoffs at the center of ZLD/MLD treatment trains. Pre-treatments can reduce scaling in membrane-based operations, but can generate additional brines that require handling. In scenarios without a crystallizer, MVC achieves higher water recoveries than several of the LSRRO-based processes, but often at a greater cost and with greater energy demand. Crystallization increases water recovery and decreases evaporation pond land area, but with a steep increase in energy consumption and greater solid salts for disposal. Future efforts may find that crystallization leads to greater cost tradeoffs as well (see Methods). Such tradeoffs necessitate careful ZLD/MLD process design based on the treatment train's specific operating conditions.

In many cases, treatment train design should begin with the end. Final disposal method must be one of the first considerations: SD typically requires a large, saline waterbody; DWI requires specific underground geologic formations; evaporation ponds require large tracts of land in regions with high solar irradiance. After selecting the disposal method, choices can be made regarding crystallizer use, concentrator type, and pre-treatment requirements. Each of these choices revolves around the demand for water, the pressure to reduce brine discharge, and subsequent cost and energy ramifications. Be it materials, land, or energy supply, enhanced water security from ZLD/MLD treatment trains cannot happen without the large-scale physical and financial infrastructure that supports them.

The "optimal" treatment train must balance a variety of cost, energy, and land use considerations. What water recovery to target, whether to include crystallization, how to balance crystallizer and concentrator operation, and which disposal method to use will depend on the severity of water insecurity, access to energy infrastructure, and access to geographic/geologic features for end disposal. ZLD/MLD processes may be especially crucial for inland, brackish water desalination with greater dependence on DWI and evaporation pond disposal methods (see

Methods for additional discussion), with this analysis demonstrating in particular the evaporation pond land use reductions associated with implementing ZLD/MLD treatment trains. Regardless of the specific ZLD/MLD treatment train design, shifting to renewable electricity and heat generation is vital for ensuring ZLD/MLD sustainability.

Efforts can be made to minimize these economic and energy impacts, but extracting additional water will always come at some cost. Yet as water insecurity and scarcity continue to threaten billions,⁴⁴ the need to secure water via any means will outweigh the added financial and energy requirements in many contexts. However, just as those least responsible for climate change are most likely to experience its earliest and severest consequences,⁴⁵ those most in need of clean water access may be those with the least capacity to construct large-scale desalination infrastructure. It is therefore imperative that funding and capacity-building efforts are enacted equitably to ensure that infrastructure barriers do not unjustly limit water access in an increasingly water stressed world.

Methods

We employed the WaterTAP model to characterize energy and material consumption, along with recoverable water and brine production in each treatment train in Figure 1. Utilizing the Institute for the Design of Advanced Energy Systems (IDAES) modeling framework, WaterTAP is a python-based model that enables steady-state modeling for a wide variety of water treatment operations. Users can specify water composition and target operating conditions, from which WaterTAP then estimates performance, LCOW, and SEC. For this analysis, unit operations are configured to optimize LCOW. There are different types of models available in WaterTAP: zero-order models calculate LCOW, SEC, and water recovery based on user-provided performance data. 0-dimensional and 1-dimensional models predict performance and calculate LCOW, SEC, and water recovery.

This analysis employs zero-order modeling for antiscalant+HCl addition and NF. In the absence of detailed fouling considerations, antiscalant+HCl addition does not change operation; its primary impacts revolve around the dosage and associated costs of the chemicals. 0dimensional NF models in WaterTAP did not account for ion-specific separations at the time of this analysis, though modeling efforts continue to improve in this area. A zero-order model is therefore employed to give the monovalent/divalent separation that is the primary purpose of NF in these treatment trains. At the time of this analysis, WaterTAP's zero-order NF model does not specify chloride selectivity; rather, chloride selectivity is calculated based on what is needed to preserve electroneutrality in NF permeate and brine streams. It is therefore difficult to measure the chloride levels in NF blending scenarios with certainty. However, given the order of magnitude difference between current chloride estimates and the chloride level acceptable for the most chloride-tolerant crops without even accounting for the chloride already present in the principal RO permeate, it is almost certain that chloride levels in full-blending cases will exceed regulatory requirements.⁴¹ The no blending and full blending scenarios are meant only to represent the most extreme lower and upper bounds of blending possibilities; exactly how much blending can occur will depend on permeate composition, final water use and corresponding regulatory requirements, and the ongoing development and deployment of improved ion-specific separation processes. Given this wide range of blending possibilities, only "no" and "full" blending cases are considered here, with downstream processes considered beyond the scope of this analysis.

RO is modeled with WaterTAP's 1-dimensional RO model, and the LSRRO model is based off of this 1-dimensioal RO model as well. The LSRRO model used in this analysis has been used in prior work as well.¹⁶ MVC and crystallization are modeled with WaterTAP's 0-dimensional MVC and crystallizer models, the most detailed models of these unit operations available in WaterTAP at the time of this analysis. Note that as modeling continues to improve, future efforts may find crystallization to come with a higher cost tradeoff than illustrated in this analysis. Evaporative crystallization operates based off principles similar to that of MVC, but the costs of the crystallizer in this analysis are notably lower than those of MVC (see Figure 3a). This is likely because the crystallizer is handling only the brine that emerges post-concentration, a much lower volume than the brine entering the concentrator step, and MVC utilizes compression, an expensive process step not part of the crystallizer in this analysis. Given the lack of widespread crystallizer use in full-scale operations, it is difficult to predict an exact heat recovery configuration. If compression is required, crystallizer costs will increase; for now, it is assumed that the steam condenses and the ensuing liquid is be pumped (see Table M.1 and SI Section 3.2). Future efforts should expand on heat integration aspects in more detail. Even if crystallizer costs prove higher than what is reported in this analysis, the end conclusion remains the same: crystallizer use for increased water recovery comes with significant tradeoffs.

Not all unit operations are compatible with all water property packages in WaterTAP; Table M.1 outlines the model type, property package, and key operating variables we provided to the WaterTAP models for each unit operation. Key parameters regarding water inlet conditions are based on the Dhekelia Desalination Plant's brine as described in SI Section 1.²⁴ The Dhekelia Desalination Plant is a seawater reverse osmosis desalination plant that employs SD.²⁴ Most of the world's desalinated water arises from seawater desalination, and over three-quarters of desalination operations are within 10 km of a coastline, making SD one of the most common disposal methods for desalination brine.⁸ Hence, SD is included in this analysis as one disposal option for the final brine. Additionally, brine disposal is a challenge particularly for inland brackish water desalination plants that do not have SD as a disposal option. Brackish water can have TDS concentrations ranging from approximately 1,000-20,000 mg/L, and brackish water desalination can reach water recoveries of approximately 70-90%.^{8,46} There is the potential, then, for overlap in the brine concentrations of relatively low recovery seawater desalination and high recovery brackish water desalination. Given the need to extract more freshwater in both seawater and

brackish contexts as climate change worsens water scarcity and the increasingly relevant need to explore concentrated brines as a source of critical minerals,⁴² this analysis uses seawater brine (the most prevalent brine by volume) with a range of final disposal options that span use in seawater and inland contexts to explore tradeoffs that come with different ZLD/MLD choices, including brine disposal options.

SD, DWI, and evaporation ponds are modeled in WaterTAP only as zero-order models, requiring user-provided performance data. We therefore characterized disposal options using literature sources. SD costs and energy are found to range from 0.049-0.298 \$/m³ brine and 0.035-0.105 kWh/m³ brine, respectively.^{9,47} DWI costs and energy use ranged from 0.47-2.63 \$/m³ brine and 3.39 kWh/m³ brine.^{9,48,49} Evaporation pond costs ranged from 0.784-9.97 \$/m³ brine and land use requirements are found to be 7.6*10³ acres/(m³/s brine).^{9,48} Salt disposal costs are taken as 0.051 \$/kg salt.⁴⁸

The supporting information provides detailed descriptions of all calculations and assumptions with the aim of allowing readers to reproduce the analysis in WaterTap, an open-source software package. Additionally, Table M.2-M.4. provide the life-cycle energy, water consumption, and GHG factors for energy (Table M.2), chemical addition (Table M.3), and salt disposal (Table M.4) based on the GREET model. Detailed descriptions of LCA calculations can be found in SI Section 9. All data can be found tabulated in Appendix 1, and modeling codes are provided at https://github.com/jenmbdunn/Data4Sustainability/tree/master/NexusApproachZLD_TrainModeling.

I able lilli	enne operation	litoating		
Unit	Model Type	Property	Key User-	Additional Comments
Operation		Package	Provided	
		_	Variables	
RO	1-dimensional	Seawater	Modeled across	RO membranes typically
		property	water	can withstand no more than
		package	recoveries until	85 bar. ^{15,31}
			pressure	
			exceeds 85 bar.	
Antiscalant	Zero-order	Water property	Use WaterTAP	LCOW and SEC
+HC1		package	default dosages	calculated, via WaterTAP
Addition			of 10 mg/L for	and additional TDS
			hydrazine and	accounted for as described
			HCl.	in SI Section 4.1.
NF	Zero-order	Seawater ion	Operating	Monovalent/divalent
		property	pressure of 10	selectivity for NF based on

Table M.1 – Unit Operation Modeling

		package (with the addition of K^+ , CO_3^{2-} , and HCO_3^-) adjusted to match the feedwater to the Dhekelia desalination plant. ²⁴	bar. Volumetric water recovery of 60% and 80%.	WaterTAP defaults for Na ⁺ , Ca ²⁺ , Mg ²⁺ , and SO4 ²⁻ , with assumptions that selectivities for K ⁺ would match that of Na ⁺ , CO3 ²⁻ would match that of SO4 ²⁻ , and HCO3 ⁻ found from literature. ³⁶
MVC	0-dimensional	Seawater property package	Single stage with water recovery varying from 40-70% by mass (42-74% by volume).	Beyond 74 vol% recovery, salt concentrations greatly exceed NaCl solubility levels and operation is deemed infeasible. MVC configured to operate on heat integration between steam and distillate streams with no external heating.
LSRRO	1-dimensional	Seawater property package	3 stage system with a permeate quality limit of 0.0007 kg TDS/kg in accordance with irrigation recommendatio ns of <700 mg TDS/L. ⁵⁰ Volumetric water recoveries ranged from 42.6-64.3% for Train 2, 54.3- 71.0% for Trains 3 and 5, and 52.1-73.2% for Trains 4 and 6.	Above the maximum water recoveries considered, LSRRO operation is found to be infeasible. Below the minimum recoveries considered, the third LSRRO stage operated with <10% recovery, indicating that the system is beginning to enter an operating region where optimization should focus on 2 vs 3 stage LSRRO systems. Optimization across LSRRO stages has been featured in other works and is considered beyond the scope of this analysis. ^{15,16}
Crystallizer	0-dimensional	Crystallization property package	Run for cases with solid salt yields of 50%, 70%, and 90%. It is assumed that through	The energy and costs associated with heat recovery are calculated assuming the steam would be brought to saturation conditions, pumped to

	steam	atmospheric pressure, and
	condensation	heat exchanged with the
	condensation	neut exchanged with the
	plus heat	inlet to the crystallizer (see
	exchange, 90%	SI Section 3.2). Future
	of the heat	work should especially
	requirement	focus on developing and
	could be	costing a more thorough
	recovered ³⁹ and	heat integrated crystallizer
	the condensed	in WaterTAP.
	steam could be	
	recovered.	

Table M.2 – Energy LCA Factors

Enorgy Type	Total Energy	Water Consumption	GHG Emissions
Energy Type	(kWh/kWh)	(m^3/kWh)	(kg CO _{2,eq} /kWh)
Electricity – Wind	1.09E+00	3.86E-05	1.04E-02
Electricity – U.S. Grid	2.08E+00	2.26E-03	4.69E-01
Heat – Natural Gas	1.13E+00	6.90E-05	2.54E-01

Table M.3 – Chemical LCA Factors

Chemical	Total Energy Water Consumpti		GHG Emissions	
Chemiear	(kWh/g)	(m^{3}/g)	$(\text{kg CO}_{2,\text{eq}}/\text{g})$	
Hydrazine	1.64E-02	4.81E-06	4.21E-03	
HCl	9.04E-03	5.45E-06	2.08E-03	

Table M.4 – Transportation LCA Factors

Transport	GHG Emissions (kg CO _{2,eq} /kg)
CIDI Vehicle: Conventional and LS Diesel	7.10E-04

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Works Cited

- (1) United Nations. Transforming Our World: The 2030 Agenda for Sustainable Development, 2015.
- United Nations Children Fund; World Health Organization. Progress on Household Drinking Water, Sanitation and Hygiene -- 2000-2017; 2019. https://www.unicef.org/media/55276/file/Progress%20on%20drinking%20water,%20sanita tion%20and%20hygiene%202019%20.pdf (accessed 2024-01-29).
- (3) *The State of Food Security and Nutrition in the World 2023*; FAO; IFAD; UNICEF; WFP; WHO;, 2023. https://doi.org/10.4060/cc3017en.
- (4) American Society of Civil Engineers. 2021 Report Card for America's Infrastructure --Drinking Water; 2021.
- (5) United Nations Department of Economic and Social Affairs. *World Population Prospects* 2022: Summary of Results; 2022.
- (6) World Meteorological Organization. State of Global Water Resources 2022; 2023.
- (7) U.S Department of Energy. *Bandwidth Study on Energy Use and Potential Energy Savings Opportunities in U.S. Seawater Desalination Systems*; 2017; p 136.
- (8) Jones, E.; Qadir, M.; van Vliet, M. T. H.; Smakhtin, V.; Kang, S. The State of Desalination and Brine Production: A Global Outlook. *Science of The Total Environment* 2019, 657, 1343–1356. https://doi.org/10.1016/j.scitotenv.2018.12.076.
- (9) Panagopoulos, A.; Haralambous, K.-J.; Loizidou, M. Desalination Brine Disposal Methods and Treatment Technologies - A Review. *Science of The Total Environment* 2019, 693, 133545. https://doi.org/10.1016/j.scitotenv.2019.07.351.
- (10) Missimer, T. M.; Maliva, R. G. Environmental Issues in Seawater Reverse Osmosis Desalination: Intakes and Outfalls. *Desalination* 2018, 434, 198–215. https://doi.org/10.1016/j.desal.2017.07.012.
- (11) Ihsanullah, I.; Atieh, M. A.; Sajid, M.; Nazal, M. K. Desalination and Environment: A Critical Analysis of Impacts, Mitigation Strategies, and Greener Desalination Technologies. *Science of The Total Environment* 2021, 780, 146585. https://doi.org/10.1016/j.scitotenv.2021.146585.
- (12) Tong, T.; Elimelech, M. The Global Rise of Zero Liquid Discharge for Wastewater Management: Drivers, Technologies, and Future Directions. *Environ. Sci. Technol.* 2016, 50 (13), 6846–6855. https://doi.org/10.1021/acs.est.6b01000.
- (13) Charisiadis, C. Brine Zero Liquid Discharge (ZLD) Fundamentals and Design, 2018. https://www.lenntech.com/processes/brine-treatment.htm (accessed 2023-02-02).
- (14) Poirier, K.; Al Mhanna, N.; Patchigolla, K. Techno-Economic Analysis of Brine Treatment by Multi-Crystallization Separation Process for Zero Liquid Discharge. *Separations* 2022, 9 (10), 295. https://doi.org/10.3390/separations9100295.
- (15) Du, Y.; Wang, Z.; Cooper, N. J.; Gilron, J.; Elimelech, M. Module-Scale Analysis of Low-Salt-Rejection Reverse Osmosis: Design Guidelines and System Performance. *Water Research* 2022, 209, 117936. https://doi.org/10.1016/j.watres.2021.117936.
- (16) Atia, A. A.; Allen, J.; Young, E.; Knueven, B.; Bartholomew, T. V. Cost Optimization of Low-Salt-Rejection Reverse Osmosis. *Desalination* 2023, 551, 116407. https://doi.org/10.1016/j.desal.2023.116407.
- (17) Panagopoulos, A. Techno-Economic Assessment of Zero Liquid Discharge (ZLD) Systems for Sustainable Treatment, Minimization and Valorization of Seawater Brine. *Journal of*

Environmental Management **2022**, *306*, 114488. https://doi.org/10.1016/j.jenvman.2022.114488.

- (18) Panagopoulos, A. Techno-Economic Assessment of Minimal Liquid Discharge (MLD) Treatment Systems for Saline Wastewater (Brine) Management and Treatment. *Process Safety and Environmental Protection* 2021, *146*, 656–669. https://doi.org/10.1016/j.psep.2020.12.007.
- (19) Panagopoulos, A.; Giannika, V. Comparative Techno-Economic and Environmental Analysis of Minimal Liquid Discharge (MLD) and Zero Liquid Discharge (ZLD) Desalination Systems for Seawater Brine Treatment and Valorization. *Sustainable Energy Technologies and Assessments* 2022, 53, 102477. https://doi.org/10.1016/j.seta.2022.102477.
- (20) Zhang, C.; Shi, Y.; Shi, L.; Li, H.; Li, R.; Hong, S.; Zhuo, S.; Zhang, T.; Wang, P. Designing a next Generation Solar Crystallizer for Real Seawater Brine Treatment with Zero Liquid Discharge. *Nat Commun* 2021, *12* (1), 998. https://doi.org/10.1038/s41467-021-21124-4.
- (21) Chen, Q.; Burhan, M.; Shahzad, M. W.; Ybyraiymkul, D.; Akhtar, F. H.; Li, Y.; Ng, K. C. A Zero Liquid Discharge System Integrating Multi-Effect Distillation and Evaporative Crystallization for Desalination Brine Treatment. *Desalination* 2021, *502*, 114928. https://doi.org/10.1016/j.desal.2020.114928.
- (22) Cipolletta, G.; Lancioni, N.; Akyol, Ç.; Eusebi, A. L.; Fatone, F. Brine Treatment Technologies towards Minimum/Zero Liquid Discharge and Resource Recovery: State of the Art and Techno-Economic Assessment. *Journal of Environmental Management* 2021, 300, 113681. https://doi.org/10.1016/j.jenvman.2021.113681.
- (23) Panagopoulos, A. Brine Management (Saline Water & Wastewater Effluents): Sustainable Utilization and Resource Recovery Strategy through Minimal and Zero Liquid Discharge (MLD & ZLD) Desalination Systems. *Chemical Engineering and Processing - Process Intensification* 2022, *176*, 108944. https://doi.org/10.1016/j.cep.2022.108944.
- (24) Fritzmann, C.; Löwenberg, J.; Wintgens, T.; Melin, T. State-of-the-Art of Reverse Osmosis Desalination. *Desalination* 2007, 216 (1), 1–76. https://doi.org/10.1016/j.desal.2006.12.009.
- (25) Kolliopoulos, G.; Martin, J. T.; Papangelakis, V. G. Energy Requirements in the Separation-Regeneration Step in Forward Osmosis Using TMA–CO2–H2O as the Draw Solution. *Chemical Engineering Research and Design* 2018, *140*, 166–174. https://doi.org/10.1016/j.cherd.2018.10.015.
- (26) Bartholomew, T. V.; Mey, L.; Arena, J. T.; Siefert, N. S.; Mauter, M. S. Osmotically Assisted Reverse Osmosis for High Salinity Brine Treatment. *Desalination* **2017**, *421*, 3– 11. https://doi.org/10.1016/j.desal.2017.04.012.
- (27) Das, S.; O'Connell, M. G.; Xu, H.; Bernstein, R.; Kim, J.-H.; Sankhala, K.; Segal-Peretz, T.; Shevate, R.; Zhang, W.; Zhou, X.; Darling, S. B.; Dunn, J. B. Assessing Advances in Anti-Fouling Membranes to Improve Process Economics and Sustainability of Water Treatment. ACS EST Eng. 2022. https://doi.org/10.1021/acsestengg.2c00184.
- (28) Jafari, M.; Vanoppen, M.; van Agtmaal, J. M. C.; Cornelissen, E. R.; Vrouwenvelder, J. S.; Verliefde, A.; van Loosdrecht, M. C. M.; Picioreanu, C. Cost of Fouling in Full-Scale Reverse Osmosis and Nanofiltration Installations in the Netherlands. *Desalination* 2021, 500, 114865. https://doi.org/10.1016/j.desal.2020.114865.

- (29) WaterTAP contributors. WaterTAP: An Open-Source Water Treatment Model Library. Version 0.8. Sponsored by California Energy Commission, National Alliance for Water Innovation, and USDOE, 2023. https://github.com/watertap-org/watertap.
- (30) Quon, H.; Sperling, J.; Coughline, K.; Greene, D.; Miara, A.; Akar, S.; Talmadge, M.; Stokes-Draut, J. R.; Macknick, J.; Jiang, S. Pipe Parity Analysis of Seawater Desalination in the United States: Exploring Costs, Energy, and Reliability via Case Studies and Scenarios of Emerging Technology. ACS EST Eng. 2022, 2 (3), 434–445. https://doi.org/10.1021/acsestengg.1c00270.
- (31) DuPont. FilmTecTM Elements Operating Limits Temperature and Pressure Limits for 8-Inch FilmTecTM Seawater RO Elements: Tech Manual Excerpt, 2022. https://www.dupont.com/content/dam/dupont/amer/us/en/watersolutions/public/documents/en/RO-NF-FilmTec-Temperature-Pressure-Limits-Manual-Exc-45-D00691-en.pdf (accessed 2024-01-31).
- (32) Argonne National Laboratory. The Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies (GREET) Model, 2020.
- (33) Figueira, M.; López, J.; Reig, M.; Cortina, J. L.; Valderrama, C. Techno-Economic Analysis of Seawater Reverse Osmosis Brines Treatment Using Nanofiltration Modelling Tools. *Desalination* 2023, 568, 117013. https://doi.org/10.1016/j.desal.2023.117013.
- (34) Wang, R.; Lin, S. Thermodynamics and Energy Efficiency of Zero Liquid Discharge. ACS EST Eng. 2022, 2 (8), 1491–1503. https://doi.org/10.1021/acsestengg.2c00013.
- (35) Shamet, O.; Antar, M. Mechanical Vapor Compression Desalination Technology A Review. *Renewable and Sustainable Energy Reviews* **2023**, *187*, 113757. https://doi.org/10.1016/j.rser.2023.113757.
- (36) Vaseghi, G.; Ghassemi, A.; Loya, J. Characterization of Reverse Osmosis and Nanofiltration Membranes: Effects of Operating Conditions and Specific Ion Rejection. *Desalination and Water Treatment* 2016, 57 (50), 23461–23472. https://doi.org/10.1080/19443994.2015.1135825.
- (37) Telzhensky, M.; Birnhack, L.; Lehmann, O.; Windler, E.; Lahav, O. Selective Separation of Seawater Mg2+ Ions for Use in Downstream Water Treatment Processes. *Chemical Engineering Journal* 2011, 175, 136–143. https://doi.org/10.1016/j.cej.2011.09.082.
- (38) Nativ, P.; Leifman, O.; Lahav, O.; Epsztein, R. Desalinated Brackish Water with Improved Mineral Composition Using Monovalent-Selective Nanofiltration Followed by Reverse Osmosis. *Desalination* 2021, 520, 115364. https://doi.org/10.1016/j.desal.2021.115364.
- (39) Al-Anber, Z. A. Heat Saving in Evaporative Crystallization by Introducing a Heat Pump. *YJES* **2021**, *6* (1), 91–104. https://doi.org/10.53370/001c.24136.
- (40) El Azhar, F.; Tahaikt, M.; Zouhri, N.; Zdeg, A.; Hafsi, M.; Tahri, K.; Bari, H.; Taky, M.; Elamrani, M.; Elmidaoui, A. Remineralization of Reverse Osmosis (RO)-Desalted Water for a Moroccan Desalination Plant: Optimization and Cost Evaluation of the Lime Saturator Post. *Desalination* **2012**, *300*, 46–50. https://doi.org/10.1016/j.desal.2012.06.003.
- (41) Rhoades, J. D.; Kandiah, A.; Mashali, A. M. *The Use of Saline Waters for Crop Production*; Food and Agriculture Organization of the United Nations, 1992.
- (42) Sharkh, B. A.; Al-Amoudi, A. A.; Farooque, M.; Fellows, C. M.; Ihm, S.; Lee, S.; Li, S.; Voutchkov, N. Seawater Desalination Concentrate—a New Frontier for Sustainable Mining of Valuable Minerals. *npj Clean Water* 2022, *5* (1), 1–16. https://doi.org/10.1038/s41545-022-00153-6.

- (43) Wang, W.; Zhang, Y.; Tan, M.; Xue, C.; Zhou, W.; Bao, H.; Hon Lau, C.; Yang, X.; Ma, J.; Shao, L. Recent Advances in Monovalent Ion Selective Membranes towards Environmental Remediation and Energy Harvesting. *Separation and Purification Technology* 2022, 297, 121520. https://doi.org/10.1016/j.seppur.2022.121520.
- (44) United Nations Department of Economic and Social Affairs. *The Sustainable Development Goals Report 2023: Special Edition*; United Nations, 2023. https://doi.org/10.18356/9789210024914.
- (45) Althor, G.; Watson, J. E. M.; Fuller, R. A. Global Mismatch between Greenhouse Gas Emissions and the Burden of Climate Change. *Sci Rep* **2016**, *6* (1), 20281. https://doi.org/10.1038/srep20281.
- (46) Stanton, J. S.; Anning, D. W.; Brown, C. J.; Moore, R. B.; McGuire, V. L.; Qi, S. L.; Harris, A. C.; Dennehy, K. F.; McMahon, P. B.; Degnan, J. R.; Böhlke, J. K. *Brackish Groundwater in the United States*; 1833; U.S. Geological Survey, 2017. https://doi.org/10.3133/pp1833.
- (47) Rao, P.; Aghajanzadeh, A.; Sheaffer, P.; Morrow, W. R.; Brueske, S.; Dollinger, C.; Price, K.; Sarker, P.; Ward, N.; Cresko, J. Volume 1: Survey of Available Information in Support of the Energy-Water Bandwidth Study of Desalination Systems; LBNL--1006424, 1342538; 2016; p LBNL--1006424, 1342538. https://doi.org/10.2172/1342538.
- (48) Andrew H.P. Swift; Lu, H.; Becerra, H. Zero Discharge Waste Brine Management for Desalination Plants: Final Report; University of Texas at El Paso, 2002. https://www.usbr.gov/research/dwpr/reportpdfs/report089.pdf (accessed 2024-01-31).
- (49) Salih, H. H.; Li, J.; Kaplan, R.; Dastgheib, S. A. Life Cycle Assessment of Treatment and Handling Options for a Highly Saline Brine Extracted from a Potential CO2 Storage Site. *Water Research* 2017, *122*, 419–430. https://doi.org/10.1016/j.watres.2017.06.032.
- (50) Agriculture and Agri-Food Canada; Prairie Farm Rehabilitation Administration. Irrigation and Salinity, 2000.

Title: Water, Energy, and Cost: A Nexus Approach to Zero/Minimal Liquid Discharge Desalination Technologies

Margaret G. O'Connell,¹ Neha Rajendran,¹ Menachem Elimelech,² Jack Gilron,³ Jennifer B. Dunn^{1,*}

¹Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois 60208, United States

² Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06511, United States

³Zuckerberg Institute for Water Research, Ben-Gurion University of the Negev, Sde Boker 84990, Israel

*Corresponding author

Supporting Information

SECTION 1 – DHEKELIA DESALINATION PLANT BACKGROUND	4
SECTION 2 – TREATMENT TRAIN 0	5
Section 2.1 – RO Modeling	
Section 2.2 – Deep Well Injection (DWI) Calculations	6
Section 2.3 – Surface Discharge (SD) Calculations	
SECTION 2.4 – EVAPORATION POND (EP) CALCULATIONS	9
SECTION 3 – TREATMENT TRAIN 1	
Section 3.1 – MVC Modeling	
Section 3.2 – Crystallizer Modeling	
SECTION 3.3 – DWI, TRAIN 1	
SECTION 3.4 – SD, TRAIN 1	
SECTION 3.5 – EPS, TRAIN I	
SECTION 5.0 – $ADDITIONAL NOTES$	
SECTION 4 – TREATMENT TRAIN 2	
SECTION 4.1 – ANTISCALANT+HCL ADDITION	
SECTION 4.2 – LOW SALT REJECTION REVERSE OSMOSIS (LSRRO), TRAIN 2	
SECTION 4.5 – CRYSTALLIZER, TRAIN 2	
SECTION 4.4 – $DW1$, 1 RAIN 2 SECTION 4.5 – SD TRAIN 2	
SECTION 4.6 – EPS. TRAIN 2.	
Section 4.7 – Additional Notes	
SECTION 5 – TREATMENT TRAIN 3	
Section 5.1 – NF, Train 3	
Section 5.2 – LSRRO, Train 3	
Section 5.3 – Crystallizer, Train 3	
Section 5.4 – DWI, Train 3	
SECTION 5.5 – SD, TRAIN 3	
SECTION 5.6 – EPS, TRAIN 3	
SECTION 5.7 – ADDITIONAL NOTES	
SECTION 6 – TREATMENT TRAIN 4	
Section 6.1 – Additional Notes	
SECTION 7 – TREATMENT TRAIN 5	
Section 7.1 – NF, Train 5	
Section 7.2 – LSRRO, Train 5	
Section 7.3 – Crystallizer, Train 5	
Section 7.4 – DWI, Train 5	
SECTION 7.5 – SD, TRAIN 5	
SECTION 7.0 – EPS, TRAIN S	
SECTION $7.7 - ADDITIONAL INVIES$	
SECTION 8 – TREATMENT TRAIN 6	
SECTION 8.1 – ADDITIONAL NOTES	
SECTION 9 – LIFE CYCLE ANALYSIS	

List of Tables

4
5
12
15
25
27
32
39
39
39
40
40
41

Section 1 – Dhekelia Desalination Plant Background

All treatment trains begin with an inlet flow from the Dhekelia Desalination Plant's SWRO brine. Previous work identified the composition of the Dhekelia Desalination Plant's brine (Table S.1), with a brine composition of 80.0 kg TDS/m³ as well as a seawater feed composition of 40.5 kg TDS/m³ and a plant capacity of 40,000 m³/d (this value was taken to be the RO permeate flow rate in absence of more specific data).^{1,2} Using equations (1) and (2), the brine flow rate was found to be 0.474 m³/s. Note that, due to difference in how density is calculated in different water packages in WaterTAP, for the given mass flow rate, the volumetric flowrate of the brine entering the MVC unit in Train 1 was calculated as 0.448 m³/s; this flow rate was used for the volumetric recovery percentage calculations for Train1 only. Note that WaterTAP Version 0.8 was primarily used for modeling work, but the analysis work spanned many WaterTAP versions. Future analysis efforts are encouraged to use the most recent WaterTAP versions, looking to the provided codes as guides for process setup and variable specifications.

$$RR = 1 - \frac{TDS_{seawater}}{TDS_{brine}} \tag{1}$$

$$\dot{V}_{brine} = \frac{\dot{V}_{permeate}}{RR} * (1 - RR)$$
⁽²⁾

Where *RR* is the recovery ratio, $TDS_{seawater}$ is the seawater TDS concentration in kg/m³, TDS_{brine} is the brine TDS concentration in kg/m³, \dot{V}_{brine} is the SWRO brine volumetric flow rate in m³/s, and $\dot{V}_{permeate}$ is the SWRO permeate flow rate in m³/s (found to be 0.463 m³/s based on the plant's capacity). The brine is assumed to be at atmospheric pressure and at 298 K. The following sections will provide detailed modeling information on the different treatment trains.

WaterTAP modeling codes used for this analysis available at: https://github.com/jenmbdunn/Data4Sustainability/tree/master/NexusApproachZLD_TrainModeling

Table 5.1 – Drifte Composition					
Brine Composition	Concentration (mg/L)	Flow rate (kg/s)			
Total Flow Rate		474			
H2O		436			
Ca	891	0.423			
Mg	2.88e3	1.36			
Na	2.46e4	11.7			
K	888	0.421			
HCO3	315	0.150			

Table S.1 – Brine Composition

CO3	0.40	1.90e-4
SO4	6.74e3	3.20
Cl	4.37e4	20.7
TDS	8.00e4	38.0

Section 2 – Treatment Train 0

This treatment train represents conventional brine disposal using RO to produce water in accordance with the assumption that additional water *must* be extracted from the brine.

Section 2.1 – RO Modeling

The RO unit operation was modeled in WaterTAP, using the platform's 1-dimensional RO model paired with WaterTAP's seawater property package. Note that the seawater property package performs calculations based on TDS concentration, not on an ion-specific basis. A pump was added from WaterTAP's unit models as well. After initializing the RO unit, the pump outlet pressure and RO membrane area was unfixed to allow for optimization of the LCOW. The RO model was configured to assume no concentration polarization, no pressure change along the membrane, and no solubility limits – essentially making the RO operation conditions as favorable as possible. Beginning at 2% volumetric recovery, the model was run for increasing recoveries until the pump outlet pressure reached 85 bar, beyond which RO membranes generally cannot operate.^{3,4} LCOW and SEC calculations performed in WaterTAP were calculated per m³ of RO permeate. RO operational variables are tabulated in Table S.2. Table S.2 gives the operational values required to run the RO model, indicating which variables were left at their WaterTAP default value vs customized based on our specifications. These are the initial variables input to the model; Table S.2 indicates which variables were subsequently unfixed for optimization purposes. Note that as WaterTAP continues to be updated, default values may change.

Variable	Value	Unit	Default/Custom	Fix/Unfix
Feed Pressure	101325	Pa	Default	Fix
Feed Temperature	273.15 + 20	K	Default	Fix
Feed TDS Mass Fraction	0.08	-	Custom	Fix
Feed H ₂ O Mass Flow Rate	436.35	kg/s	Custom	Fix
Pump Efficiency	0.80	-	Default	Fix

Pump Pressure Outlet	70e5	Pa	Custom	Unfix
Membrane area	11100	m^2	Default	Unfix
Solvent permeability coefficient (A)	4.2e-12	m/Pa/s	Default	Fix
Solute permeability coefficient (B)	3.5e-8	m/s	Default	Fix
Atmospheric Pressure	101325	Pa	Default	Fix
Permeate Pressure	101325	Pa	Default	Fix
Length	16	m	Custom	Unfix
Volumetric Recovery Rate	0.02-0.22	-	Custom	Fix

The brine from the RO unit is subsequently sent to one of three disposal options: DWI, SD, or EPs, each one evaluated separately. Note that the LCOW and SEC of these disposal options were estimated based on data found in literature (cited in the following sections) as disposal models in WaterTAP are currently zero order models. Zero order models do not predict performance and rely on user-supplied data to generate LCOW and SEC based on an assumed performance. In the absence of more detailed, predictive models, literature data was used for the disposal methods.

Section 2.2 – Deep Well Injection (DWI) Calculations

The costs of DWI were calculated based on a U.S. Department of the Interior (DOI) Desalination Research and Development Program Report.⁵ For a plant with a feed of 22.83 MGD (the feed rate in the study most comparable to that of the Dhekelia plant), the disposal cost for DWI was given as 0.5 \$/kgal produced water.⁵ The report gives a disposal rate of 6.85 MGD, so water is produced at a rate of 15.98 MGD, yielding a disposal cost of 0.31 \$/m³ brine via equation (3). The report was written in 2000, so it was assumed that these figures were in 2000\$. Converting to 2018\$ (the year basis used throughout this analysis as it is the default in WaterTAP), the DWI disposal cost was found to be 0.47 \$/m³ brine.

$$Disposal Cost \left[\frac{\$}{m^{3} brine}\right] = Disposal Cost \left[\frac{\$}{kgal prod.water}\right] *$$

$$Produced Water \left[\frac{kgal prod.water}{d}\right] * \frac{1}{Disposal Rate} \left[\frac{d}{m^{3} brine}\right]$$
(3)

A DWI cost of 0.47 \$/m³ brine is lower than values found in literature, which have been reported as 0.54-2.65 \$/m³ brine (in 2019\$ based on the publication year).⁶ Disposal costs will inevitably vary by location according to the plant's distance from a geologic formation suitable for DWI, so the value of 2.63 \$/m³ brine in 2018\$ was taken as a maximum DWI cost case while 0.47 \$/m³ brine was taken as a minimum DWI cost case. SEC for DWI was taken from a study that

found an energy use of 3.39 kWh/m³ brine.⁷ It was assumed that DWI injection drives much of the energy use and is consistent enough across desalination DWI operations to warrant using only this energy value. To convert from a basis of per m³ brine to per m³ usable water (RO permeate, in this case), equations (4) and (5) were used for LCOW and SEC, respectively. The RO brine and permeate flow rate data were given as part of the WaterTAP model output for each RO volumetric recovery case.

$$DWI \ LCOW \left[\frac{\$}{m^3 \ Usable \ Water}\right] = DWI \ Cost \left[\frac{\$}{m^3 \ brine}\right] *$$
$$RO \ Brine \ Flow \left[\frac{m^3 \ brine}{s}\right] * \frac{1}{RO \ Permeate \ Flow} \left[\frac{s}{m^3 \ RO \ permeate}\right]$$
(4)

$$DWI SEC \left[\frac{kWh}{m^{3} Usable Water}\right] = DWI SEC \left[\frac{kWh}{m^{3} brine}\right] *$$

$$RO Brine Flow \left[\frac{m^{3} brine}{s}\right] * \frac{1}{RO Permeate Flow} \left[\frac{s}{m^{3} RO permeate}\right]$$
(5)

Once on a per m³ RO permeate basis, the DWI LCOW and SEC can be added to the RO LCOW and SEC, respectively, to calculate an overall treatment train LCOW and SEC on a per m³ usable water basis. A minimum and maximum case were generated for each RO volumetric recovery case, where the minimum case utilizes the lower bound for DWI LCOW of 0.47 \$/m³ brine and the maximum case utilizes the upper bound of 2.63 \$/m³ brine. The LCOW is given in 2018\$/m³ usable water (RO permeate) and the SEC is given in kWh/m³ usable water (RO permeate). Equations (6) and (7) give the overall treatment train LCOW and SEC, respectively.

$$Total Train LCOW \left[\frac{\$}{m^{3} Usable Water}\right] = RO LCOW \left[\frac{\$}{m^{3} RO permeate}\right] + DWI LCOW \left[\frac{\$}{m^{3} RO permeate}\right]$$
(6)

$$Total \ Train \ SEC\left[\frac{kWh}{m^3 \ Usable \ Water}\right] = RO \ SEC\left[\frac{kWh}{m^3 \ RO \ permeate}\right] + DWI \ SEC\left[\frac{kWh}{m^3 \ RO \ permeate}\right](7)$$

Section 2.3 – Surface Discharge (SD) Calculations

Costs ranging from 0.05-0.3 \$/m³ brine were reported for SD (assumed to be in 2019\$ based on publication year).⁶ Converting to 2018\$ to match the default costing year in WaterTAP, a minimum case assuming an SD cost of 0.049 \$/m³ brine and a maximum case assuming 0.298 \$/m³ brine were performed for each RO volumetric recovery case. Minimum and maximum cases

were also performed for SD SEC, given that SD energy is dependent on distance from the end water discharge point which may widely vary across desalination SD operations. A report by Lawrence Berkeley National Laboratory that supplied information for the U.S. Department of Energy's 2017 Seawater Desalination Bandwidth Study gave a low intensity SEC value of 0.035 kWh/m³ brine and a high intensity SEC value of 0.105 kWh/m³ brine.⁸ It was assumed that all costs and energy requirements reported for SD included the costs and energy needed for the intake of additional water used to dilute the brine before discharge as this is an integral step of SD operations. Equations (8) and (9) were used to convert these LCOW and SEC values to a per m³ RO permeate (i.e. usable water) basis.

$$SD \ LCOW \left[\frac{\$}{m^3 \ Usable \ Water}\right] = SD \ Cost \left[\frac{\$}{m^3 \ brine}\right] *$$

$$RO \ Brine \ Flow \left[\frac{m^3 \ brine}{s}\right] * \frac{1}{RO \ Permeate \ Flow} \left[\frac{s}{m^3 \ RO \ permeate}\right]$$
(8)

$$SD \ SEC \left[\frac{kWh}{m^{3} \ Usable \ Water}\right] = SD \ SEC \left[\frac{kWh}{m^{3} \ brine}\right] *$$

$$RO \ Brine \ Flow \left[\frac{m^{3} \ brine}{s}\right] * \frac{1}{RO \ Permeate \ Flow} \left[\frac{s}{m^{3} \ RO \ permeate}\right]$$
(9)

For minimum cases, the overall brine treatment train minimum LCOW and SEC was the sum of the RO LCOW and SEC and SD LCOW and SEC, respectively (calculated with the minimum SD LCOW and SEC values from literature) found for each RO volumetric recovery case. Maximum cases utilize the maximum SD LCOW and SEC values from literature. The LCOW is given in 2018\$/m³ usable water (RO permeate) and the SEC is given in kWh/m³ usable water (RO permeate). Equations (10) and (11) give the overall treatment train LCOW and SEC, respectively.

$$Total Train LCOW \left[\frac{\$}{m^3 Usable Water}\right] = RO LCOW \left[\frac{\$}{m^3 RO permeate}\right] + SD LCOW \left[\frac{\$}{m^3 RO permeate}\right]$$
(10)

$$Total Train SEC\left[\frac{kWh}{m^3 \, Usable \, Water}\right] = RO \, SEC\left[\frac{kWh}{m^3 \, RO \, permeate}\right] + SD \, SEC\left[\frac{kWh}{m^3 \, RO \, permeate}\right] (11)$$
Section 2.4 – Evaporation Pond (EP) Calculations

The costs of EPs were calculated based on a U.S. DOI report regarding desalination brine discharge.⁵ For a plant with a feed of 22.83 MGD (the feed rate in the study most comparable to that of the Dhekelia plant), the disposal rate is given as 6.85 MGD, meaning water is produced at a rate of 15.98 MGD.⁵ The disposal cost for EPs was given as 1.36 \$/kgal produced water.⁵ This disposal cost includes the cost of salt disposal; this salt disposal cost needed to be separated from the total disposal cost to distinguish between the cost of the evaporation ponds themselves versus the cost of salt disposal. Given that there are multiple ways to approach the leftover salt – disposal or turning into a product such as road salt – it is important to distinguish between the cost of 3.08e6 \$/yr was reported (or 0.53 \$/kgal produced water);⁵ removing the salt disposal cost yields an evaporation pond disposal cost of 0.51 \$/m³ brine following equation (12). Based on the publication year of the report, this value was assumed to be in 2000\$. A final evaporation pond cost of 0.78 \$/m³ brine in 2018\$ (the year that is the basis for all WaterTAP calculations) was utilized for the analysis.

$$Disposal Cost \left[\frac{\$}{m^{3} brine}\right] = \left(Disposal Cost (incl. salt disposal) \left[\frac{\$}{kgal prod.water}\right] - \left(Salt Disposal Cost \left[\frac{\$}{yr}\right] * \frac{1}{Produced Water} \left[\frac{yr}{kgal prod.water}\right]\right)\right) *$$

$$Produced Water \left[\frac{kgal prod.water}{d}\right] * \frac{1}{Disposal Rate} \left[\frac{d}{m^{3} brine}\right]$$
(12)

This evaporation pond cost is noticeably lower than reported literature values, which give estimates of 3.28-10.04 m^3 brine (in 2019 based on publication year).⁶ Accordingly, the value of 0.78 m^3 brine served as a lower bound while 9.97 m^3 brine (in 2018) was taken as the upper bound. For each RO volumetric recovery case, both a minimum and a maximum LCOW case was calculated using 0.78 and 9.97 m^3 brine respectively. Equation (13) converted the LCOW to be on a per m³ of RO permeate basis, where RO brine and permeate flows are included in WaterTAP outputs for each volumetric recovery case. It was assumed that the EP disposal process is entirely driven by sunlight with no additional energy input (EP SEC = 0 kWh/m³ brine).

$$EP \ LCOW \left[\frac{\$}{m^3 \ Usable \ Water}\right] = EP \ Cost \left[\frac{\$}{m^3 \ brine}\right] *$$

$$RO \ Brine \ Flow \left[\frac{m^3 \ brine}{s}\right] * \frac{1}{RO \ Permeate \ Flow} \left[\frac{s}{m^3 \ RO \ permeate}\right]$$
(13)

Additionally, the same DOI report on desalination brine discharge gives a salt disposal cost of 30 \$/ton (or 0.051 \$/kg salt in 2018\$).⁵ For this treatment train, it was assumed that all TDS in the RO brine entering the evaporation pond would require disposal. Using RO brine TDS flow rates given as part of WaterTAP's output, equation (14) illustrates how salt disposal costs were calculated on a per m³ RO permeate basis for each RO volumetric recovery case.

Salt Disposal Cost
$$\left[\frac{\$}{m^3 \, Usable \, Water}\right] = Salt \, Disposal \, Cost \left[\frac{\$}{kg \, salt}\right] *$$

RO Brine TDS Flow $\left[\frac{kg \, TDS}{s}\right] * \frac{1}{RO \, Permeate \, Flow} \left[\frac{s}{m^3 \, RO \, permeate}\right]$ (14)

Once on a per m³ RO permeate basis, the EP LCOW and salt disposal cost can be added to the RO LCOW to get an overall treatment train LCOW on a per m³ usable water basis. A minimum and maximum case were generated for each RO volumetric recovery case, where the minimum case utilizes the lower bound for EP LCOW of 0.78 \$/m³ brine and the maximum case utilizes the upper bound of 9.97 \$/m³ brine. The LCOW is given in 2018\$/m³ usable water (RO permeate). As no SEC was associated with the evaporation pond disposal route, the SEC for this train is comprised only of the RO SEC on a per m³ RO permeate basis. Equations (15) and (16) give the overall treatment train LCOW and SEC, respectively. In equation (15), the salt disposal is the cost of disposing the salt generated from the evaporation pond step. Unlike in the other treatment trains, there is no salt produced from a crystallization step as the brine from the RO is not concentrated enough for feasible crystallizer operation.

$$Total Train LCOW \left[\frac{\$}{m^{3} Usable Water}\right] = RO LCOW \left[\frac{\$}{m^{3} RO permeate}\right] +$$

$$Salt Disposal Cost \left[\frac{\$}{m^{3} Usable Water}\right] + EP LCOW \left[\frac{\$}{m^{3} RO permeate}\right]$$
(15)

$$Total Train SEC\left[\frac{kWh}{m^{3} Usable Water}\right] = RO SEC\left[\frac{kWh}{m^{3} RO permeate}\right]$$
(16)

Evaporation ponds also require large land areas. The DOI report on desalination brine discharge used in several prior calculations reported an acreage of 2,286 acres for the 22.83 MGD feed plant with a disposal rate of 6.85 MGD.⁵ Based on this, an acreage requirement of 334 acres/MGD brine (or 7,612 acres/(m³ brine/s)) was used for the analysis. For each RO volumetric

recovery case, equation (17) gives the evaporation pond land area requirements. Note that a 0.9 utilization factor is the default utilization assumed in WaterTAP. This utilization factor cancels out when LCOW and SEC are reported per m³ of produced water, but not when evaporation pond area is calculated.

$$EP Area[acres] = Acreage Rate\left[\frac{acres}{m^{3} brine/s}\right] * RO Brine Flow\left[\frac{m^{3} brine}{s}\right] *$$

$$Utilization Factor$$
(17)

Section 3 – Treatment Train 1

This treatment train gives an example of thermally-driven ZLD/MLD brine treatment trains. The Dhekelia plant's SWRO brine is sent first to a mechanical vapor compression (MVC) unit which produces a distillate stream (the usable water basis for LCOW and SEC calculations) and a brine stream. The MVC brine proceeds to a crystallizer step which produces solid salt, water vapor, and a more condensed brine stream. The brine from the crystallizer then goes to one of three disposal processes: DWI, SD, or EPs. In some scenarios, the MVC brine goes straight to disposal. As noted in the main text, the separation in the MVC is thermally driven through heat exchange; in the cases evaluated here, the MVC was configured such that no external heating is required, only electricity use.

Section 3.1 – MVC Modeling

The MVC unit in WaterTAP is a 0-dimensional model that was run using WaterTAP's seawater property package. Stream compositions therefore comprise of H₂O and TDS, not individual ions. The Dhekelia plant's SWRO brine was used as the inlet to the MVC unit, with the individual ions summed to an overall TDS value. The MVC was modeled as a single stage, and optimization of the MVC's evaporator area, outlet brine temperature, compressor pressure ratio, and heat exchanger areas was performed to minimize LCOW. Results were produced for water recoveries of 40-70% by mass (42.3-74.1% by volume). While the input of salt concentration as TDS does not allow for ion-specific saturation calculations, recoveries greater than 70% by mass began to yield brine streams with concentrations roughly 50-114 TDS wt%, far exceeding solubility of NaCl.⁹ These situations were considered infeasible for the operation of the MVC unit modeled here. MVC operational variables are tabulated in Table S.3. Both the MVC LCOW and SEC are calculated per m³ of MVC distillate. The brine from the MVC unit then proceeds either straight to disposal steps or to a crystallization unit followed by disposal.

When Train 1 was modeled with no crystallizer, the usable water produced is equal to the MVC distillate. When a crystallizer is included in the treatment train, the usable water is equal to the MVC distillate plus the water recovered from crystallizer steam.

Variable	Value	Unit	Default/	Fix/Unfix
			Custom	
Mass Flow Rate				
Liq TDS		kg/s	Custom	Fix
Liq H ₂ O		kg/s	Custom	Fix
Feed Temperature	273.15 + 25	K	Default	Fix
Feed Pressure	101325	Pa	Default	Fix
Feed Recovery	0.4-0.75	-	Custom	Fix
External Heat	0	Watt	Default	Fix
Feed Pump				
Efficiency	0.8	-	Default	Fix
Control Volume deltaP	7e3		Default	Fix
Distillate Heat Exchanger				
Overall Heat Transfer Coefficient	2e3	$W/K-m^2$	Default	Fix
Heat transfer area	700	m^2	Custom	Unfix
Cold deltaP	7e3		Default	Fix
Hot deltaP	7e3		Default	Fix
Brine Heat Exchanger			•	·
Overall Heat Transfer Coefficient	2e3	W/K-m ²	Default	Fix
Heat transfer area	644	m ²	Custom	Unfix
Cold deltaP	7e3		Default	Fix
Hot deltaP	7e3		Default	Fix
Evaporator				
Inlet Feed Temperature	50 + 273.15	K	Default	Fix
Outlet Brine Temperature	70 + 273.15	K	Default	Unfix
Overall Heat Transfer Coefficient	3e3	W/K-m ²	Default	Fix
Evaporator Heat Transfer Area	5e4	m^2	Default	Unfix
Compressor				
Pressure ratio	1.6	$W/m^2.K$	Default	Unfix
Efficiency	0.8	-	Default	Fix
Brine Pump				·
Efficiency	0.8	-	Default	Fix
Control Volume deltaP	4e4		Default	Unfix

Table S.3 – MVC Variables

Distillate Pump						
Efficiency	0.8	-	Default	Fix		
Control Volume deltaP	4e4		Default	Unfix		
Brine Outlet Pressure	101325	Pa	Default	Fix		
Distillate Outlet Pressure	101325	Pa	Default	Unfix		

Section 3.2 – Crystallizer Modeling

The WaterTAP crystallizer model is a 0-dimensional model based on continuous evaporative crystallization. The crystallizer unit was modeled using WaterTAP's crystallizer property package which is based on the crystallization of NaCl-H2O systems. Accordingly, the TDS concentrations from the MVC brine were input into the crystallizer unit as NaCl, assuming a direct 1:1 conversion from TDS to NaCl in the absence of more ion-specific modeling capabilities. The crystallizer produces a vapor stream of steam, a liquid brine, and solid NaCl. It was assumed that the steam is entirely recovered during heat recovery processes, while the liquid brine proceeds to DWI, SD, or EP. The solid NaCl is disposed of using the same assumptions as described in SI Section 2.4 (i.e. salt disposal is 0.051 \$/kg salt with no additional energy use) and equation (18) gives the associated costs.

$$Salt Disposal Cost \left[\frac{\$}{m^{3} Usable Water}\right] = Salt Disposal Cost \left[\frac{\$}{kg salt}\right] *$$

$$Solid NaCl from Crystallizer \left[\frac{kg NaCl}{s}\right] * \left(\frac{1}{MVC Distill te Flow} \left[\frac{s}{m^{3} MVC distillate}\right] + \frac{1}{Crys Steam Flow} \left[\frac{s}{m^{3} crys steam}\right]\right)$$
(18)

For each MVC recovery, cases with no crystallizer and crystallization at 50, 70, and 90% yield were analyzed. These yields refer to how much of the NaCl entering the crystallizer is converted to solid NaCl salt. For the 40% MVC mass recovery case, 50%, 70%, and 90% crystallizer yields could not be accomplished; the inlet to the crystallizer was not concentrated enough for feasible operation. For the 45% MVC mass recovery case, 70% and 90% crystallizer yields also proved infeasible due to the relatively low concentration entering the crystallizer.

WaterTAP provides results regarding the LCOW, SEC, and heat requirements for the crystallizer. The SEC from WaterTAP accounts only for electricity requirements; heat requirements were subsequently added after setting up a heat recovery process. Specifically, it was assumed that 90% of the heat required to operate the crystallizer could be provided from condensing the produced steam and heat exchanging the resulting liquid water with the crystallizer

inlet stream. Previous work indicates that 90% heat recovery falls within heat recovery ranges for evaporative crystallization,¹⁰ and condensing the steam alone generates more heat than required for 90% recovery, though additional losses would occur in reality. In the absence of a condensing heat exchange model in WaterTAP, the process was modeled using WaterTAP's condenser and pump models plus the heat exchanger model from IDAES to a) calculate the heat released from condensing the steam from its crystallizer outlet conditions (328.15 K, 11992 Pa) to saturation conditions (320.9 K, 11992 Pa) b) pump the liquid water up to atmospheric pressure, and c) heat exchange the condensed stream with the liquid inlet to the crystallizer to a hot side temperature difference of 10 K. Future studies should especially focus on developing more detailed heat exchange schematics.

From this system, heat recovery values were pulled to ensure that more than enough heat was supplied to achieve 90% heat recovery, electricity consumption estimates for pumping were generated, and the LCOW of the pump plus heat exchanger was calculated. Note that WaterTAP does not provide LCOW calculations for condensers. To ensure that the costs of the heat recovery process encapsulated the additional costs of more complex condensing heat exchange processes, the LCOW of the pump plus heat exchanger was doubled to give the final LCOW of the heat recovery process. Heat recovery implies that less steam is required to heat the crystallizer, so the crystallizer LCOW was adjusted for this based on equation (19), with the initial cost of steam provided for in WaterTAP's output. The overall crystallizer LCOW including heat recovery, crystallizer electricity SEC, and crystallizer heat SEC were initially calculated per second, then converted to a per m³ usable water basis via equations (20), (21), and (22), respectively. Variables to model the crystallizer operation are tabulated in Table S.4.

$$Crystallizer \ LCOW\left[\frac{\$}{s}\right] = \left(Crystallizer \ LCOW, initial\left[\frac{\$}{m^3 \ crys \ inlet}\right] \ast Crystallizer \ Inlet \ Flow\left[\frac{m^3 \ crys \ inlet}{s}\right]\right) - \left(\frac{Initial \ Steam \ Cost\left[\frac{\$}{yr}\right]}{Initial \ Heat \ Required\left[\frac{J}{s}\right]} \ast Adjusted \ Heat \ Required\left[\frac{J}{s}\right] \ast \frac{1}{365 \ast 24 \ast 3600} \left[\frac{yr}{s}\right]\right) + \left(2 \ast \left(Pump \ \& \ HX \ LCOW\right)\left[\frac{\$}{m^3 \ crys \ steam}\right] \ast Crys \ Steam \ Flow\left[\frac{m^3 \ crys \ steam}{s}\right]\right)$$
(19)

$$Crystallizer \ LCOW\left[\frac{\$}{m^3 \ Usable \ Water}\right] = Crystallizer \ LCOW\left[\frac{\$}{s}\right] * \\ \left(\frac{1}{MVC \ Distillate \ Flow}\left[\frac{s}{m^3 \ MVC \ distillate}\right] + \frac{1}{Crys \ Steam \ Flow}\left[\frac{s}{m^3 \ crys \ steam}\right]\right)$$
(20)

$$Crystallizer SEC, electric \left[\frac{kWh}{m^{3} Usable Water}\right] = \left(Crystallizer SEC, electric \left[\frac{kWh}{m^{3} crys inlet}\right] * Crystallizer Inlet Flow \left[\frac{m^{3} crys inlet}{s}\right] + \left(Pump \& HX SEC\right) \left[\frac{kWh}{m^{3} crys steam}\right] * Crys Steam Flow \left[\frac{m^{3} crys steam}{s}\right] \right) * \left(\frac{1}{MVC Distillate Flow} \left[\frac{s}{m^{3} MVC distillate}\right] + \frac{1}{Crys Steam Flow} \left[\frac{s}{m^{3} crys steam}\right] \right)$$
(21)

$$Crystallizer SEC, heat \left[\frac{kWh}{m^{3} Usable Water}\right] = 0.1 * Crystallizer Heat, initial \left[\frac{kWh}{m^{3} crys inlet}\right] * Crystallizer Inlet Flow \left[\frac{m^{3} crys inlet}{s}\right] * \left(\frac{1}{MVC Distillate Flow}\left[\frac{s}{m^{3} MVC distillate}\right] + \frac{1}{Crys Steam Flow}\left[\frac{s}{m^{3} crys steam}\right]\right)$$
(22)

Variable	Value	Unit	Default/	Fix/Unfix
			Custom	
Inlet H ₂ O (Liquid)	Concentrator	kg/s	Custom	Fix
	brine			
Inlet NaCl (Aqueous)	Concentrator	kg/s	Custom	Fix
	brine			
Inlet NaCl (Solid	1e-6	kg/s	Default	Fix
Inlet H ₂ O (Vapor)	1e-6	kg/s	Default	Fix
Inlet Pressure	101325	Pa	Default	Fix
Inlet Temperature	273.15 + 20	K	Default	Fix
Operating Temperature	273.15 + 55	K	Default	Fix
Crystal Growth Rate	3.7e-8	m/s	Default	Fix
Souders Brown Constant	0.04	m/s	Default	Fix
Crystal Median Length	0.5e-3	m	Default	Fix
Crystallization Yield	0.5, 0.7, or 0.9	-	Custom	Fix

Table S.4 – Crystallizer Variables

Section 3.3 – DWI, Train 1

The costs of DWI were calculated according to SI Section 2.2, with a minimum DWI cost of 0.47/m^3 brine and a maximum of 2.63/m^3 brine in 2018\$ and with an SEC of 3.39 kWh/m^3 brine. To convert from a basis of per m³ brine to per m³ usable water (MVC distillate plus crystallizer steam, where applicable), equations (23) and (24) were used for LCOW and SEC,

respectively. Note that in cases without a crystallizer, the brine flow rate is that of the brine exiting the MVC and the usable water consists of MVC distillate only. In cases with crystallization, the brine flow rate is that of the liquid brine exiting the crystallizer and the usable water is the sum of MVC distillate and steam (recovered as liquid water) exiting the crystallizer. The brine flow rate, MVC distillate flow rate, and steam flow rate data were given as part of the WaterTAP model output for each MVC recovery case in combination with each crystallizer yield case (when applicable).

$$DWI \ LCOW\left[\frac{\$}{m^{3} \ Usable \ Water}\right] = DWI \ Cost\left[\frac{\$}{m^{3} \ brine}\right] *$$

$$MVC \ or \ Crystallizer \ Brine \ Flow\left[\frac{m^{3} \ brine}{s}\right] * \left(\frac{1}{MVC \ Distillate \ Flow}\left[\frac{s}{m^{3} \ MVC \ distillate}\right] +$$

$$\frac{1}{Crys \ Steam \ Flow}\left[\frac{s}{m^{3} \ crys \ steam}\right]\right)$$

$$(23)$$

$$DWI SEC \left[\frac{kWh}{m^{3} MVC \ distillate} \right] = DWI SEC \left[\frac{kWh}{m^{3} \ brine} \right] *$$

$$MVC \ or \ Crystallizer \ Brine \ Flow \left[\frac{m^{3} \ brine}{s} \right] * \left(\frac{1}{MVC \ Distillate \ Flow} \left[\frac{s}{m^{3} \ MVC \ distillate} \right] +$$

$$\frac{1}{Crys \ Steam \ Flow} \left[\frac{s}{m^{3} \ crys \ steam} \right] \right)$$

$$(24)$$

Once on a per m³ usable water basis, the DWI LCOW and SEC can be added to the MVC LCOW and SEC and the crystallizer LCOW and SEC, respectively, and the salt disposal cost to get an overall treatment train LCOW and SEC on a per m³ usable water basis. MVC LCOW is initially on a per m³ MVC distillate basis and, when crystallization is used, is converted via equation (25). Note, salt disposal costs are only included in trains using DWI when crystallization is used. No salt disposal costs are present when MVC brine goes straight to DWI in cases without crystallization. A minimum and maximum case were generated for each MVC recovery case in combination with each crystallizer yield case, where the minimum case utilizes the lower bound for DWI LCOW of 0.47 \$/m³ brine and the maximum case utilizes the upper bound of 2.63 \$/m³ brine. The LCOW is given in 2018\$/m³ usable water and the SEC is given in kWh/m³ usable water. Equations (26) and (27) give the overall treatment train LCOW and SEC, respectively. In equation (26), the salt disposal cost is the cost of disposing the solid salt produced from the crystallizer step.

$$MVC \ LCOW \left[\frac{\$}{m^3 \ Usable \ Water}\right] = MVC \ LCOW \left[\frac{\$}{m^3 \ MVC \ distillate}\right] *$$
$$MVC \ Distillate \left[\frac{m^3 \ MVC \ distillate}{s}\right] * \left(\frac{1}{MVC \ Distillate \ Flow}\left[\frac{s}{m^3 \ MVC \ distillate}\right] +$$
$$\frac{1}{Crys \ Steam \ Flow}\left[\frac{s}{m^3 \ crys \ steam}\right]\right)$$
(25)

$$Total Train LCOW \left[\frac{\$}{m^{3} Usable Water}\right] = MVC LCOW \left[\frac{\$}{m^{3} Usable Water}\right] + Crystallizer LCOW \left[\frac{\$}{m^{3} Usable Water}\right] + Salt Disposal Cost \left[\frac{\$}{m^{3} Usable Water}\right] + DWI LCOW \left[\frac{\$}{m^{3} Usable Water}\right]$$
(26)

$$Total Train SEC\left[\frac{kWh}{m^{3} Usable Water}\right] = MVC SEC\left[\frac{kWh}{m^{3} Usable Water}\right] + Crystallizer SEC\left[\frac{kWh}{m^{3} MVC distillate}\right] + DWI SEC\left[\frac{kWh}{m^{3} MVC distillate}\right]$$
(27)

Section 3.4 – SD, Train 1

From the sources described in SI Section 2.3, a minimum case assuming an SD cost of 0.049 \$/m³ brine and SEC of 0.035 kWh/m³ brine and a maximum case assuming 0.298 \$/m³ brine and SEC of 0.105 kWh/m³ brine were performed for each MVC recovery case in combination with each crystallizer yield, when applicable. Equations (28) and (29) were used to convert these LCOW and SEC values from a per m³ brine to a per m³ usable water basis. As before, in cases with no crystallizer the brine flow rate is from the MVC brine and the usable water is MVC distillate. In cases with crystallization, the brine flow rate is from the liquid brine exiting the crystallizer and the usable water is the sum of MVC distillate and steam (condensed to liquid water) from the crystallizer.

$$SD \ LCOW \left[\frac{\$}{m^{3} \ Usable \ Water}\right] = SD \ Cost \left[\frac{\$}{m^{3} \ brine}\right] *$$

$$Crystallizer \ Brine \ Flow \left[\frac{m^{3} \ brine}{s}\right] * \left(\frac{1}{MVC \ Distillate \ Flow}\left[\frac{s}{m^{3} \ MVC \ distillate}\right] + \frac{1}{Crys \ Steam \ Flow}\left[\frac{s}{m^{3} \ crys \ steam}\right]\right)$$

$$(28)$$

$$SD \ SEC \left[\frac{kWh}{m^{3} \ Usable \ Water}\right] = SD \ SEC \left[\frac{kWh}{m^{3} \ brine}\right] *$$

$$Crystallizer \ Brine \ Flow \left[\frac{m^{3} \ brine}{s}\right] * \left(\frac{1}{MVC \ Distillate \ Flow}\left[\frac{s}{m^{3} \ MVC \ distillate}\right] + \frac{1}{Crys \ Steam \ Flow}\left[\frac{s}{m^{3} \ crys \ steam}\right]\right)$$

$$(29)$$

For minimum cases, the overall brine treatment train minimum LCOW and SEC was the sum of the MVC LCOW and SEC, crystallizer LCOW and SEC (in cases with crystallization), SD LCOW and SEC (calculated with the minimum SD LCOW and SEC values from literature), respectively, plus salt disposal cost (in cases with crystallization) found for each MVC recovery case in combination with each crystallizer yield case in scenarios involving crystallization. Maximum cases utilize the maximum SD LCOW and SEC values from literature. Equations (30) and (31) give the overall treatment train LCOW and SEC, respectively. In equation (30), the salt disposal cost is the cost of disposing the solid salt produced from the crystallizer step.

$$Total Train LCOW \left[\frac{\$}{m^{3} Usable Water}\right] = MVC LCOW \left[\frac{\$}{m^{3} Usable Water}\right] + Crystallizer LCOW \left[\frac{\$}{m^{3} Usable Water}\right] + Salt Disposal Cost \left[\frac{\$}{m^{3} Usable Water}\right] + SD LCOW \left[\frac{\$}{m^{3} Usable Water}\right]$$
(30)

$$Total Train SEC\left[\frac{kWh}{m^{3} Usable Water}\right] = MVC SEC\left[\frac{kWh}{m^{3} Usable Water}\right] + Crystallizer SEC\left[\frac{kWh}{m^{3} Usable Water}\right] + SD SEC\left[\frac{kWh}{m^{3} Usable Water}\right]$$
(31)

Section 3.5 – EPs, Train 1

The costs of EPs were calculated according to SI Section 2.4, giving a minimum cost of $0.78 \text{ }/\text{m}^3$ brine and a maximum cost of $9.97 \text{ }/\text{m}^3$ brine. Equation (32) converts the LCOW to be on a per m³ of usable water basis, where MVC brine, MVC distillate, crystallizer brine, and crystallizer steam flows are included in WaterTAP outputs for each MVC recovery case in combination with each crystallizer yield, when applicable. In cases with no crystallizer, usable water is MVC distillate and brine is MVC brine. In cases with crystallization, usable water is MVC distillate plus steam from the crystallizer recovered as liquid water and brine is liquid brine exiting the crystallizer. It was assumed that the EP disposal process is entirely driven by sunlight with no additional energy input (EP SEC = 0 kWh/m³ brine).

$$EP \ LCOW \left[\frac{\$}{m^3 \ Usable \ Water}\right] = EP \ Cost \left[\frac{\$}{m^3 \ brine}\right] *$$

$$Crystallizer \ Brine \ Flow \left[\frac{m^3 \ brine}{s}\right] * \left(\frac{1}{MVC \ Distillate \ Flow}\left[\frac{s}{m^3 \ MVC \ distillate}\right] + \frac{1}{Crys \ Steam \ Flow}\left[\frac{s}{m^3 \ crys \ steam}\right]\right)$$

$$(32)$$

When there is no crystallization, it is assumed that all TDS present in the MVC brine will require disposal. When there is crystallization, it was assumed that all NaCl in the crystallizer brine entering the evaporation pond would require disposal along with the solid NaCl produced via crystallization (ultimately equaling the amount of salt disposal required in no crystallization cases). Equation (33) illustrates how salt disposal costs were calculated for cases without crystallization. Equation (34) illustrates how salt disposal costs were calculated on a per m³ usable water in cases with crystallization, using crystallizer brine NaCl flow rates and solid NaCl data given as part of WaterTAP's output.

$$Salt Disposal Cost \left[\frac{\$}{m^{3} Usable Water}\right] = MVC Brine TDS Flow \left[\frac{kg TDS}{s}\right] * Salt Disposal Cost \left[\frac{\$}{kg salt}\right] * \frac{1}{MVC Distillate Flow} \left[\frac{s}{m^{3} MVC distillate}\right]$$
(33)

$$Salt Disposal Cost \left[\frac{\$}{m^{3} Usable Water}\right] = \left(Crystallizer Brine NaCl Flow \left[\frac{kg NaCl}{s}\right] + Crystallizer Solid NaCl \left[\frac{kg NaCl}{s}\right]\right) * Salt Disposal Cost \left[\frac{\$}{kg salt}\right] * \left(\frac{1}{MVC Distillate Flow}\left[\frac{s}{m^{3} MVC distillate}\right] + \frac{1}{Crys Steam Flow}\left[\frac{s}{m^{3} crys steam}\right]\right)$$
(34)

Once on a per m³ usable basis, the EP LCOW and salt disposal cost can be added to the MVC and crystallizer LCOWs to get an overall treatment train LCOW on a per m³ usable water basis. A minimum and maximum case were generated for each MVC recovery case in combination with each crystallizer yield (where applicable), with the minimum cases utilizing the lower bound for EP LCOW of 0.78 \$/m³ brine and maximum cases utilizing the upper bound of 9.97 \$/m³ brine. The LCOW is given in 2018\$/m³ usable water. As no SEC was associated with the evaporation pond disposal route, the SEC for this train is comprised only of the MVC and, where applicable, crystallizer SECs on a per m³ usable water basis. Equations (35) and (36) give the overall treatment train LCOW and SEC, respectively.

$$Total Train LCOW \left[\frac{\$}{m^{3} Usable Water}\right] = MVC LCOW \left[\frac{\$}{m^{3} Usable Water}\right] + Crystallizer LCOW \left[\frac{\$}{m^{3} Usable Water}\right] + Salt Disposal Cost \left[\frac{\$}{m^{3} Usable Water}\right] + EP LCOW \left[\frac{\$}{m^{3} Usable Water}\right]$$
(35)

$$Total Train SEC\left[\frac{kWh}{m^{3} Usable Water}\right] = MVC SEC\left[\frac{kWh}{m^{3} Usable Water}\right] + Crystallizer SEC\left[\frac{kWh}{m^{3} Usable Water}\right]$$
(36)

As described in SI Section 2.4, an evaporation pond acreage requirement of 334 acres/MGD brine (or 7,612 acres/(m³ brine/s)) was used for the analysis. For each MVC recovery case in combination with each crystallizer scenario, equation (37) gives the evaporation pond land area requirements. The brine flow is given by the MVC brine flow in cases with no crystallization and by the liquid brine exiting the crystallizer in cases with crystallization.

$$EP Area[acres] = Acreage Rate\left[\frac{acres}{m^{3} brine/s}\right] * Brine Flow\left[\frac{m^{3} brine}{s}\right] * Utilization Factor$$
(37)

Section 3.6 – Additional Notes

- In cases with no crystallizer operation, Train 1 achieves higher water recoveries than Trains 2-4, with the MVC achieving a maximum 74.1 vol% water recovery while the LSRRO reaches 64.3, 56.8, and 42.6 vol% in Trains 2, 3, and 4 respectively.
 - A change occurs with the addition of the crystallizer: antiscalant+HCl and LSRRObased Train 2 achieves higher water recoveries than MVC-based Train 1. WaterTAP modeling assumes that the distillate of the MVC is salt-free, while some concentration of salt remains in the LSRRO permeate. As a result, there is a lower concentration of salt in the brine entering the crystallizer in Train 2 (as some salt is in the LSRRO permeate) compared to Train 1 (all salt exits the MVC in liquid brine and enters the crystallizer), so more water must be removed as steam during crystallization in Train 2 cases to achieve the same solid salt yields than for Train 1, resulting in somewhat higher water recoveries.

- When operating at similar recoveries in no crystallizer scenarios and under the same disposal conditions, the LCOW of Train 1 is generally higher than that of the LSRRObased trains until LSRRO costs increase steeply as they approach recovery limits.
- When there is no crystallizer, the LCOW of the MVC initially decreases with increasing water recovery as the increase in recovery outpaces the increase in cost, but increases after 58.2 vol% recovery beyond which the increase in costs outpaces the increase in recovery. In situations involving crystallization where additional water recovered from crystallization steam results in more constant water recovery– MVC costs per m³ increase with increasing MVC recovery.
 - In cases with SD and no crystallization, Train 1 experiences relatively little variation in costs and energy compared to LSRRO-based trains, largely because SD does not drive LCOW or SEC and MVC LCOW and SEC initially become more efficient with increasing recovery, likely because of the heat exchange dynamics that improve with greater steam formation.
- For these cases not utilizing a crystallizer, Train 1 (MVC-based) achieves an optimum LCOW for cases involving SD (at both minimum and maximum values) and DWI (at its minimum value); however, as disposal costs increase for cases involving DWI at its maximum value and evaporation ponds at both minimum and maximum values, the increasing recovery leads to decreasing LCOW for all points of MVC operation.
- The LCOW impacts of crystallizer yield varied based on disposal method; for SD and DWI, increasing crystallizer yield lead to an increase in salt disposal and crystallizer costs that outweighed the decrease in SD and DWI costs, leading to an increase in LCOW despite the increase in recovery at higher crystallizer yields. The same amount of salt is disposed of in evaporation pond cases independent of crystallizer yield (i.e. all salt exiting the concentrator step), so for cases involving evaporation ponds, the decrease in evaporation pond cost outweighed the increased crystallizer costs, leading to lower LCOWs plus higher recoveries as crystallizer yield increased. In terms of costs, preferred crystallizer operation will therefore depend greatly on the disposal method and the target water recovery. (Applies to all ZLD/MLD Trains)
- Disposal costs do not vary much with recovery when crystallization is employed since the ratio of water recovered to liquid brine disposed of remains relatively constant compared

to cases when no crystallizer is present. Disposal costs vary with recovery, but overall recovery does not vary much when crystallization is used.

- The increase in water recovery from crystallizer use drives costs down compared to those without crystallization as the crystallizer itself is not a large cost contributor. However, see **Methods** for discussion on the potential for increased crystallizer costs. (Applies to all ZLD/MLD Trains).
- When evaporation ponds are used, salt disposal costs are independent of crystallizer salt yield as all salt exiting the concentrator will be disposed of either as solid salt from the crystallizer or salt recovered from the brine that undergoes evaporation. On a per m³ basis there may be some variation in salt costs when evaporation ponds are used just due to the slightly higher water recovery that goes with increasing crystallizer solid salt yield from 50, 70, to 90%. (Applies to all ZLD/MLD Trains)
- For Train 1, it is assumed that MVC distillate contains no TDS, increasing salt concentration but not salt mass flowrate with increasing water recovery. At a given crystallizer yield of 50, 70, or 90% solid salt, the same amount of liquid brine and solid salt will exit the crystallizer, with lower quantities of steam formed as MVC recoveries increase. Hence, the same evaporation pond area is required for scenarios with a given crystallization yield across all MVC recovery cases.
- Train 1 typically has higher energy requirements than membrane-based Trains 2-6 when comparing similar water recovery and disposal cases under no crystallizer scenarios, with an exception occurring as Train 2 reaches its upper recovery limit and LSRRO SEC exceeds that of the MVC.
- In cases with no crystallization, the SEC of MVC initially decreases with increasing water recovery, indicating that at lower recoveries, improved recovery improves energy efficiency. At high enough recoveries, though, MVC energy requirements outpace increases in water recovery and associated decreases in disposal energy requirements, and overall SEC increases. Hence, in cases with no crystallizer, Train 1 reaches an optimum SEC under each disposal scenario.
- For cases involving a crystallizer step, SEC increases with increasing crystallizer yield. It
 may appear that the highest SEC values decrease for Train 1 as crystallizer yield increases
 from 50% to 70%/90%, but this is because the lowest MVC recovery cases that generate

the highest overall SECs at 50% crystallizer recoveries are not feasible for 70% and 90% crystallizer recoveries due to the larger, less concentrated brine volumes at low MVC recoveries.

Section 4 – Treatment Train 2

This treatment train represents one possible membrane-based option for ZLD/MLD brine treatment. As demonstrated by treatment train 0, standard RO is neither cost nor energy effective in terms of improving water recovery from brine. RO that has been adjusted – in this case, low salt rejection reverse osmosis (LSRRO) – to better handle brines is one treatment option. LSRRO was selected as the membrane-based option as there is currently a lack full-train analyses utilizing this innovative technique, and initial studies indicated promising results for increasing water recovery with reasonable cost and energy impacts.^{3,11}

Prior to a membrane-based brine treatment, it is necessary to have a pre-treatment step to limit the impacts of membrane fouling and scaling. Including reductions in fouling and/or scaling impacts would generate more economical and energy efficient results, but the quantification of these impacts will be highly case dependent based on foulant/scalant and membrane chemistry data not available.^{12,13} Moreover, the LSRRO models themselves are limited in their ability to include highly complex fouling impacts. The models are steady-state and rely on broad TDS values rather than the component-specific calculations necessary to attempt fouling representation. Given that the models are largely unable to capture fouling impacts, it was necessary to neglect fouling/scaling reductions introduced by pre-treatments to maintain a balanced analysis. This treatment train examines the use of antiscalant and HCl addition that are used to reducing the scaling potential of brine and adjust the brine's pH.

While accounting for detailed impacts on membrane scaling is beyond the scope of this analysis, the antiscalant+HCl addition step factors into the treatment train costs as well as the composition of the water entering the LSRRO unit. Namely, the additional chloride ions from the HCl addition are factored into the Dhekelia desalination plant's brine TDS concentration entering the LSRRO unit. The LSRRO unit then produces two streams: a permeate stream (the usable water used in combination with crystallizer steam (when applicable) as a basis for treatment train LCOW and SEC calculations) and a brine stream. The LSRRO brine then proceeds either straight to

disposal in cases with no crystallization or to a crystallizer, which produces steam, liquid brine, and solid NaCl salt. The crystallizer brine then undergoes either DWI, SD, or enters EPs.

Section 4.1 – Antiscalant+HCl Addition

The antiscalant and HCl addition were modeled using WaterTAP's chemical addition zero order model. As a zero order model, this model does not predict performance; rather, performance is specified by the user (see Table S.5 for details). Noted above, the detailed impacts of scaling reduction that may occur due to the use of these chemicals (impacts such as reduced energy use, reduced membrane cleaning requirements, elongated membrane life, etc.) are considered beyond the scope of this analysis for treatment Trains 2-6. The addition of these chemicals is included in this analysis primarily to account for the costs associated with these chemical treatments compared to alternative pre-treatments (i.e. nanofiltration, used in treatment Trains 3-6). Hydrazine is the antiscalant included in WaterTAP, and WaterTAP's default dosage levels were used (see Table S.5). The additional chloride ions dissolved as a result of the HCl addition were added to the Dhekelia desalination plant's brine TDS concentration, slightly increasing the TDS concentration from 80.03 kg/m³ to 80.04 kg/m³. The LCOW and SEC (given by electricity intensity for zero order models in WaterTAP) were calculated per m³ brine flow and converted to per m³ usable water (LSRRO permeate plus crystallizer steam in scenarios with crystallization) via equations (38) and (39), respectively.

$$Antiscalant + HCl LCOW \left[\frac{\$}{m^{3} Usable Water}\right] = Antiscalant + HCl Cost \left[\frac{\$}{m^{3} inlet brine}\right] *$$

$$Inlet Brine Flow \left[\frac{m^{3} inlet brine}{s}\right] * \left(\frac{1}{LSRRO Permeate Flow} \left[\frac{s}{m^{3} LSRRO permeate}\right] + \frac{1}{Crys Steam Flow} \left[\frac{s}{m^{3} crys steam}\right]\right)$$

$$(38)$$

$$Antiscalant + HCl SEC \left[\frac{kWh}{m^{3} Usable Water}\right] = Antiscalant + HCl SEC \left[\frac{kWh}{m^{3} inlet brine}\right] *$$

$$Inlet Brine Flow \left[\frac{m^{3} inlet brine}{s}\right] * \left(\frac{1}{LSRRO Permeate Flow} \left[\frac{s}{m^{3} LSRRO permeate}\right] + \frac{1}{Crys Steam Flow} \left[\frac{s}{m^{3} crys steam}\right]\right)$$

$$(39)$$

Variable	Value	Unit	Default/ Custom	Fix/Unfix
Feed Mass Flow Rate	·		·	·
H ₂ O	436.3464	kg/s	Custom	Fix
Cl	20.7086	kg/s	Custom	Fix
Na	11.6911	kg/s	Custom	Fix
Mg	1.3649	kg/s	Custom	Fix
SO_4	3.1992	kg/s	Custom	Fix
Ca	0.4227	kg/s	Custom	Fix
К	0.4212	kg/s	Custom	Fix
CO ₃	0.00018972	kg/s	Custom	Fix
HCO ₃	0.1495	kg/s	Custom	Fix
Dosages				
Antiscalant (hydrazine) Dosage	10	mg/L	Default	Fix
HCl Dosage	10	mg/L	Default	Fix

 Table S.5 – Antiscalant+HCl Addition Variables

Section 4.2 – Low Salt Rejection Reverse Osmosis (LSRRO), Train 2

The LSRRO model in WaterTAP uses builds off of the 1-dimensional RO model. This analysis utilized a 3-stage LSRRO process. In such a process, the first stage operates as a typical RO process, generating a permeate comparable to that of the primary SWRO step (i.e. the usable water produced in this treatment train). The brine from this stage proceeds to a subsequent RO step, but this RO operates as "impaired RO"; meaning, some salt passage through the membrane is intentionally allowed to reduce the osmotic pressure difference between the permeate and the concentrate, thereby reducing pressure requirements while still further concentrating the brine.³ The permeate from this second stage is recycled to the inlet of the first stage while the brine proceeds to stage three. Stage three again uses impaired RO, with the permeate recycled to the inlet of the second stage and the final, most concentrate brine exiting the LSRRO process and entering either disposal or crystallizer steps. After the first and last stages, energy recovery devices take advantage of the pressurized concentrate to supply energy to the pumps. Other studies have explore LSRRO optimization in more detail, analyzing the balance between water composition, water recovery, energy use, LCOW, and the number of stages.^{3,11} This analysis, though exploring LSRRO as a membrane-based ZLD/MLD option, is not focused specifically on LSRRO only. Rather, this analysis looks to situate LSRRO within a broader ZLD/MLD landscape, comparing pre-treatments, comparing against thermal-based MVC, and comparing against conventional disposal options. Therefore, only a 3-stage LSRRO configuration is considered here, allowing existing LSRRO-focused studies to supply an understanding of additional LSRRO arrangements.

The LSRRO model for this analysis was configured to calculate concentration polarization impacts and calculate pressure drop along the membranes. WaterTAP's seawater property package was used; meaning the concentration of the Dhekelia plant brine was input as TDS in the absence of more ion-specific modeling capabilities. As a result, WaterTAP's NaCl solubility limit feature was not included as in reality, the NaCl concentration used in modeling represents a much more diverse mixture of ions. WaterTAP continues to be developed to better model more detailed water compositions, and future analyses should explore these impacts on solubility and the potential for membrane fouling/scaling. The model, however, did include a permeate quality limit; namely, the permeate must have no more than 0.0007 mg TDS/L to align with agriculture irrigation water recommendations.¹⁴

WaterTAP's parameter sweep tool allows for rapid modeling of numerous cases. The parameter sweep tool was used to run the LSRRO model for the same inlet composition and flow rate, but targeting different water recoveries. An initial parameter sweep from 10-90% volumetric water recovery with 20 evenly spaced runs indicated that recovery could potentially range from 39.5-68.9%. Below 39.5% volumetric water recovery, the third LSRRO stage has less than 1% water recovery, indicating two stages may be more optimal for such a situation. Beyond 68.9% recovery, simulations were infeasible, likely requiring more pressure in the first stage than RO membranes can tolerate. A subsequent, more focused sweep between these values (again with 20 evenly spaced runs) showed that feasible, optimized solutions were possible for recoveries from 42.6-64.3% volumetric water recovery; lower than this, the first two stages are operating at recoveries an order of magnitude higher than those of stage 3, indicating that 2 stages may be more optimal. Optimization of treatment trains utilizing different LSRRO configurations are considered beyond the scope of this analysis. Beyond 64.3%, simulations were infeasible.

The LSRRO model is set up to optimize performance in regards to the LCOW. For the range of recoveries tested, optimized results showed the first stage operating at 85 bar (near the upper limit of current RO membrane capabilities) to recover as much water as possible, while stages 2 and 3 generally operate at 65 bar. While almost all cases operated at the same pressure

independent of water recovery, the lower the water recovery (at the same pressure), the lower the required membrane area. Membrane costs are a driving factor of LCOW, so optimizing around LCOW generally means minimizing membrane area even if this increases energy requirements.^{13,15} Future analyses can explore the relationship between optimizing LCOW versus SEC; for now, optimization focused LCOW, with the goal of this analysis examining how to cost effectively produce additional water while assessing the impacts such increased energy use could have via life cycle analysis.

In all LSRRO volumetric recovery cases, the LCOW and SEC are calculated on a per m³ LSRRO permeate basis, with the LCOW reported in \$/m³ LSRRO permeate (2018\$) and the SEC reported in kWh/m³ LSRRO permeate. This basis is equivalent to the per m³ usable water basis for scenarios with no crystallization, and is converted to per m³ LSRRO permeate plus crystallizer steam for scenarios with crystallization (as in equation (25), but with LSRRO permeate instead of MVC distillate). The brine from the LSRRO unit, exiting the third stage, proceeds either to disposal or to the crystallizer unit. Table S.6 outlines the variables used in LSSRO modeling.

Variable	Value	Unit	Default/ Custom	Fix/Unfix
Number of Stages	3	-	Custom	Fix
Water Recovery	Sweep	-	Custom	Fix
Inlet TDS Concentration	Depends on pre- treatment	kg/m³	Custom	Fix
Inlet Volumetric Flow Rate	Depends on pre- treatment	m³/s	Custom	Fix
Membrane Water Permeability Coefficient	4.2e-12	m/s-Pa	Default	Fix
Membrane Salt Permeability Coefficient	3.5e-8	m/s	Default	Fix
Permeate Quality Limit	0.0007	kg/kg	Custom	Fix
AB Gamma Factor	1	-	Default	Fix
Pump Efficiency	0.75	-	Default	Fix
Energy Recovery Device Efficiency	0.8	-	Default	Fix
Channel Height in Membrane Stage	1e-3	m	Default	Fix
Spacer Porosity in Membrane Stage	0.85	-	Default	Fix
Effective Membrane Width	5 * Qin / 1e-3	m	Default	Unfix

Table S.6 – LSRRO Variables

Membrane Area	100 * Qin /	m ²	Default	Unfix
	1e-3			
Atmospheric Pressure	101325	Pa	Default	Fix
Feed Temperature	273.15 +	K	Default	Fix
	20			

Section 4.3 – Crystallizer, Train 2

The crystallizer was modeled in WaterTAP as described in SI Section 3.2, taking the final brine from the third stage of the LSRRO as the crystallizer feed. For each LSRRO recovery, three crystallizer cases were analyzed: 50% yield, 70% yield, and 90% yield. These yields refer to how much of the NaCl entering the crystallizer is converted to solid NaCl salt. For the 42.5-47.2% LSRRO volumetric recovery cases, 50%, 70%, and 90% crystallizer yields could not be accomplished; the inlet to the crystallizer was not concentrated enough for feasible operation. For the 48.8-51.9% LSRRO volumetric recovery cases, 70% and 90% crystallizer yields also proved infeasible due to the relatively low concentration entering the crystallizer. Finally, 90% crystallizer yields could only be accomplished for LSRRO volumetric recovery cases >56.5%. Crystallization calculations were performed as described in SI Section 3.2, with the usable water given as the LSRRO permeate plus crystallizer steam.

Section 4.4 – DWI, Train 2

DWI calculations were performed as described in SI Sections 2.2 and 3.3. In cases with no crystallization, DWI costs and energy usage were calculated for disposal of the LSRRO brine on a per m³ LSRRO permeate (usable water) basis. In cases with crystallization, DWI costs and energy usage were calculated for disposal of the liquid brine exiting the crystallizer on a per m³ LSRRO permeate plus crystallizer steam (usable water) basis. Total train LCOW is the sum of antiscalant+HCl, LSRRO, and DWI LCOWs in cases without crystallization. Total train LCOW is the sum of antiscalant+HCl, LSRRO, crystallizer, DWI, and salt disposal LCOWs in cases with crystallization. Total train SEC is the sum of antiscalant+HCl, LSRRO, crystallizer, and DWI SECs in cases with crystallization. Total train SEC is the sum of antiscalant+HCl, LSRRO, crystallizer, and DWI SECs in cases with crystallization.

Section 4.5 - SD, Train 2

SD calculations were performed as described in SI Sections 2.3 and 3.4. In cases with no crystallization, SD costs and energy usage were calculated for disposal of the LSRRO brine on a per m³ LSRRO permeate (usable water) basis. In cases with crystallization, SD costs and energy usage were calculated for disposal of the liquid brine exiting the crystallizer on a per m³ LSRRO permeate plus crystallizer steam (usable water) basis. Total train LCOW is the sum of antiscalant+HCl, LSRRO, and SD LCOWs in cases without crystallization. Total train LCOW is the sum of antiscalant+HCl, LSRRO, crystallizer, SD, and salt disposal LCOWs in cases with crystallization. Total train SEC is the sum of antiscalant+HCl, LSRRO, crystallizer, and SD SECs in cases with crystallization.

Section 4.6 – EPs, Train 2

EP calculations were performed as described in Sections 2.4 and 3.5. In cases with no crystallization, SD costs and energy usage were calculated for disposal of the LSRRO brine on a per m³ LSRRO permeate (usable water) basis. In cases with crystallization, SD costs and energy usage were calculated for disposal of the liquid brine exiting the crystallizer on a per m³ LSRRO permeate plus crystallizer steam (usable water) basis. Total train LCOW is the sum of antiscalant+HCl, LSRRO, EP, and salt disposal LCOWs in cases without crystallization, and includes the LCOW of the crystallizer in cases with crystallization. Total train SEC is the sum of antiscalant+HCl and LSRRO SECs in cases with no crystallization. Evaporation pond area is calculated via equation (37), with the brine flow is given by the LSRRO brine flow in cases with no crystallization and by the liquid brine exiting the crystallizer in cases with crystallizer in cases with crystallization.

Section 4.7 – Additional Notes

• Train 2 can achieve higher recoveries than Trains 3 and 4 since using antiscalant+HCl as a pre-treatment instead of nanofiltration (NF) further increases the amount recovered as no initial water is diverted to disposal after the pre-treatment step. However, the increased costs of LSRRO operation make this method more expensive than NF80,Disp at certain recoveries. However, as Train 3 reaches its upper limit for water recovery, the higher

LSRRO and disposal costs (due to NF brine disposal) make Train 3 more expensive in its higher recovery scenarios than Train 2 at comparable recoveries.

- Essentially, Train 2 initially has higher LCOW at similar recoveries than Train 3 but becomes the more economic choice as recovery increases, indicating that the economical choice between operating a larger LSRRO unit at lower recovery versus a smaller LSRRO unit at a higher recovery will depend specifically on the targeted water recovery amount.
- Unlike Trains 3-6, Train 2 reaches an LCOW optimum for DWI,Min cases when no crystallizer is used; the greater volume entering the LSRRO post-antiscalant+HCl addition compared to post-NF means that initially Train 2 includes lower water recoveries than Trains 3-6, at which point the volume of brine requiring disposal leads to an optimum for DWI,Min as well. Less volume enters the LSRRO in Trains 3-6 due to the diversion of NF brine, so a three-stage LSRRO system cannot attain as high of a maximum recovery as Train 2, but also does not operate at as low of a recovery as Train 2 since the lesser volume requires higher recovery in Trains 3-6 to warrant a three-stage LSRRO system.
- Because Train 2 involves the largest quantities of brine exiting the LSRRO at low recoveries and going to the crystallizer step compared to Trains 3-6, at too low of concentrator recoveries, crystallizer operation for Train 2 is infeasible.
- For Trains 2-6, increasing LSRRO water recovery increases the TDS concentration in the LSRRO brine, but the mass flowrate of TDS in the brine decreases as some TDS is present in the LSRRO permeate. A given crystallizer yield necessitates a specific crystallizer outlet brine concentration, so a decrease in the amount of TDS entering the crystallizer leads to a decrease in the amount of liquid brine exiting the crystallizer for a given crystallizer yield and a decrease in land requirement. The change in TDS mass flow rate in the brine with LSRRO recovery is slight, so the change in liquid brine discharge from the crystallizer (and subsequent change in land use) is largely unnoticeable compared to the order of magnitude of land required. (Applies to Trains 2-6)

Section 5 – Treatment Train 3

This treatment train employs nanofiltration (NF) as the pre-treatment step ahead of LSRRO. Divalent ions have a lower solubility and are more prone to precipitate onto the LSRRO

membranes, resulting in membrane scaling which leads to increased energy use, increased membrane cleaning, and membrane replacement. NF produces a divalent-rich brine and a monovalent-rich permeate.^{16,17} The permeate, now with reduced divalent concentrations and therefore reduced scaling tendencies, is sent to the LSRRO unit. The NF brine is sent to the disposal steps (i.e. DWI, SD, or EPs); an alternative handling of the NF brine is presented in treatment Trains 5-6. The LSRRO unit produces a permeate in the first stage that serves as the usable water basis for LCOW and SEC calculations in cases with no crystallization, while the brine from the LSRRO unit's third stage proceeds to disposal. In cases with crystallization, LSRRO brine proceeds to the crystallizer and the usable water basis of LSRRO permeate plus the steam produced via crystallization. The liquid brine exiting the crystallizer then proceeds to either DWI, SD, or EPs.

Section 5.1 – NF, Train 3

While WaterTAP developers continue to improve models to include ion-specific behavior, at the time of this analysis the 0-dimensional NF model runs only based on single solute (NaCl) dynamics. Given that the primary purpose of using NF in treatment Trains 3-6 is to separate divalent species form monovalent species, NF was modeled using WaterTAP's zero order nanofiltration model which enables the user to specify ion separation data (see Table S.7).

The NF model was run using WaterTAP's seawater ion property package adjusted to represent typical Mediterranean seawater composition, emulating the seawater desalinated at the Dhekelia plant in Cyprus.¹ Within this property package, the upper bound on mass flow rate was also removed to enable the full-scale modeling of the treatment train (see https://github.com/jenmbdunn/Data4Sustainability). The NF model then consists of a pump connecting to the NF unit, with water composition specified by ion based on the SWRO brine from the Dhekelia desalination plant. The rejection levels of Na⁺, Ca²⁺, Mg²⁺, and SO₄²⁻ ions were based on WaterTAP defaults. The rejection data for HCO₃⁻ was pulled from Vaseghi et. al,¹⁷ while in the absence of more detailed data, the rejection of K⁺ was assumed to be the same as for Na⁺, and the rejection is calculated based on what is necessary to preserve electroneutrality. NF membrane area and operating pressure were left unspecified and solved for based on the targeted volumetric

recovery of 80%. WaterTAP outputs gave an NF operating pressure of 10 bar and a membrane area of 6.50e3 m².

The LCOW and SEC of the NF unit were calculated in WaterTAP on a per m^3 NF permeate basis, with the LCOW given in m^3 NF permeate (2018\$) and the SEC given in kWh/m³ NF permeate. The LCOW and SEC were converted to per m^3 usable water (LSRRO permeate plus crystallization steam, when applicable) via equations (40) and (41), respectively.

$$NF \ LCOW\left[\frac{\$}{m^{3} \ Usable \ Water}\right] = NF \ LCOW\left[\frac{\$}{m^{3} \ NF \ permeate}\right] *$$

$$NF \ Permeate \ Flow\left[\frac{m^{3} \ NF \ permeate}{s}\right] * \left(\frac{1}{LSRRO \ Permeate \ Flow}\left[\frac{s}{m^{3} \ LSRRO \ permeate}\right] +$$

$$\frac{1}{Crys \ Steam \ Flow}\left[\frac{s}{m^{3} \ crys \ steam}\right]\right)$$

$$(40)$$

$$NF SEC \left[\frac{kWh}{m^{3} Usable Water}\right] = NF SEC \left[\frac{kWh}{m^{3} NF permeate}\right] *$$

$$NF Permeate Flow \left[\frac{m^{3} NF permeate}{s}\right] * \left(\frac{1}{LSRRO Permeate Flow} \left[\frac{s}{m^{3} LSRRO permeate}\right] +$$

$$\frac{1}{Crys Steam Flow} \left[\frac{s}{m^{3} crys steam}\right]$$

$$(41)$$

Variable	Value	Unit	Default/ Custom	Fix/ Unfix
Feed Pressure	101325	Pa	Default	Fix
Feed Temperature	273.15 + 25	K	Default	Fix
Feed Mass Fractions				
Ca	0.000891	-	Custom	Fix
Mg	0.002878	-	Custom	Fix
SO_4	0.006745	-	Custom	Fix
Cl	0.04366	-	Custom	Fix
Na	0.02465	-	Custom	Fix
К	0.00088799	-	Custom	Fix
CO_3	3.99997E-07	-	Custom	Fix
HCO ₃	0.0003153	-	Custom	Fix
Feed Mass Flow Rate		•		
H ₂ O	436.346	kg/s	Custom	Fix
Operation		•		
Pump Efficiency	0.80	-	Default	Fix
Pump Pressure Outlet	10e5	Pa	Default	Fix

|--|

Solvent Volumetric Flux	2e-5	$m^3/m^2/s$	Default	Fix
Across Membrane				
Membrane area	Not specified	m^2	-	Unfix
Volumetric Recovery Rate	0.6, 0.8	-	Custom	Fix
Permeate Pressure	101325	Ра	Default	Fix
Observed Solute Rejection			-	
Na ⁺	0.01	-	Default	Fix
Ca^{2+}	0.79	-	Default	Fix
Mg^{2+}	0.94	-	Default	Fix
SO ₄ ²⁻	0.87	-	Default	Fix
\mathbf{K}^+	0.01	-	Custom	Fix
CO_{3}^{2-}	0.87	-	Custom	Fix
HCO ₃ -	0.75	-	Custom	Fix
Cl-	0.15	-	Default	Unfix

Section 5.2 – LSRRO, Train 3

The LSRRO unit is configured in the manner described in SI Section 4.2, with the NF permeate serving as the LSRRO inlet. For this treatment train, parameter sweeps identified 54.3-71.0% LSRRO volumetric recoveries as the likely operating range. In all LSRRO volumetric recovery cases, the LCOW and SEC are calculated on a per m³ LSRRO permeate basis, with the LCOW reported in \$/m³ LSRRO permeate (2018\$) and the SEC reported in kWh/m³ LSRRO permeate. This basis is equivalent to the per m³ usable water basis for scenarios with no crystallization, and is converted to per m³ LSRRO permeate plus crystallizer steam for scenarios with crystallization (as in equation (25), but with LSRRO permeate instead of MVC distillate). The brine from the LSRRO unit, exiting the third stage, proceeds either to disposal or to the crystallizer unit.

Section 5.3 – Crystallizer, Train 3

The crystallizer unit was configured as described in SI Section 4.3, now with 50%, 70%, and 90% crystallizer yields possible for all tested LSRRO volumetric recoveries. The NF removed enough flow from entering the LSRRO unit that now all LSRRO recoveries produce a brine concentrated enough for crystallizer operation at each tested yield.

Section 5.4 – DWI, Train 3

The DWI unit was configured as described in SI Section 4.4, with the exception that now LCOW and SEC calculations were performed based on both the liquid brine from the LSRRO and the brine from the NF unit in scenarios without crystallization and based on the liquid brine from the crystallizer and NF units in scenarios with crystallization. Overall treatment train LCOW and SEC calculations were found as described in SI Section 4.4, with NF LCOW and SEC substituting the antiscalant + HCl addition LCOW and SEC.

Section 5.5 - SD, Train 3

The SD unit was configured as described in SI Section 4.5, with the exception that now LCOW and SEC calculations were performed based on both the liquid brine from the LSRRO and the brine from the NF unit in scenarios without crystallization and based on the liquid brine from the crystallizer and NF units in scenarios with crystallization. Overall treatment train LCOW and SEC calculations were found as described in SI Section 4.5, with NF LCOW and SEC substituting the antiscalant + HCl addition LCOW and SEC.

Section 5.6 – EPs, Train 3

The EP unit was configured as described in SI Section 4.6, with the exception that now LCOW and SEC calculations were performed based on both the liquid brine from the LSRRO and the brine from the NF unit in scenarios without crystallization and based on the liquid brine from the crystallizer and NF units in scenarios with crystallization. Overall treatment train LCOW and SEC calculations were found as described in SI Section 4.6, with NF LCOW and SEC substituting the antiscalant + HCl addition LCOW and SEC. Note that salt disposal costs also include costs of disposing the TDS in the NF brine entering the evaporation ponds. Evaporation pond area is calculated via equation (37), with the brine flow given by the LSRRO and NF brine flows in cases with no crystallization and by the liquid brine exiting the crystallizer and NF brine flow in cases with crystallization.

Section 5.7 – Additional Notes

• Trains 3 and 4, involving the disposal of the NF brine generated as an LSRRO pretreatment step, reach the lowest water recoveries out of the ZLD/MLD cases. Operating at 80% (Train 3) or 60% (Train 4) NF recovery, the NF steps reduce the volume of brine sent to the LSRRO and crystallizer steps, reducing water recovery potential.

Section 6 – Treatment Train 4

Each unit of this treatment train is configured in the same manner described in SI Section 5, with the exception that the NF pre-treatment step now targets 60% volumetric recovery. This NF recovery was tested to identify how a different volume entering the LSRRO and crystallizer units would impact LCOW and SEC, exploring the balance of decreased energy and capital requirements for the LSRRO and crystallizer steps with the increased disposal requirements and decreased usable water production.

The modeling in WaterTAP resulted in an NF unit operating at the same pressure (10 bar) but with lower membrane area requirements (5.80e3 m²). In this treatment train, 60% NF recovery means a lower flow enters the LSRRO unit. The LSRRO unit is then capable of achieving higher volumetric recoveries (52.1-73.2%), but less total water is captured and a greater amount of NF brine is sent to disposal. LCOW and SEC calculations are performed as described in SI Section 5.

Section 6.1 – Additional Notes

- Train 4 does not achieve as high of recoveries as Train 3 since Train 3 (at 80% NF recovery) sends more volume to the LSRRO for water recovery.
- Achieving water recoveries comparable to those of Trains 1, 2, and 3 with only 60% NF recovery (the rest going to disposal Train 4) is possible only by operating the LSRRO unit towards the upper range of its recovery potential, resulting in higher LCOWs for Train 4, operating at the upper end of its recovery range, than Trains 1, 2, and 3 achieving similar recoveries but at the lower end of their recovery range.
 - An exception occurs when evaporation ponds are the disposal method and the lowest recovery of Train 2 proves more expensive than the highest recovery case for Train 4 primarily due to Train 4's reduced salt disposal cost resulting from some salt present in the LSRRO permeate as opposed to all salt being disposed of in Train 2 cases.
- LSRRO energy demand increases with increasing recovery at the recoveries assessed here, so Trains 2-4 reach optimum overall SEC values (in cases with no crystallization) only in

DWI disposal scenarios, where the increase in LSRRO energy consumption with increasing water recovery is initially offset by a decrease in DWI disposal requirements.

Section 7 – Treatment Train 5

This treatment train employs NF as the pre-treatment step ahead of LSRRO. As discussed in earlier sections, NF produces a divalent-rich brine. Desalination plants employing RO for the principal treatment step often have to re-supply divalent species such as calcium and magnesium in post-treatment steps to meet water quality standards.^{16,18} Treatment trains 5-6 assume that the entire NF brine is blended with the LSRRO permeate in order to supply divalent species that would otherwise be added via post-treatment steps. Treatment train LCOW and SEC calculations were therefore generated on a per m³ LSRRO permeate+NF brine basis in cases with no crystallization and on a per m³ LSRRO+crystallizer steam+NF brine basis in cases with crystallization; i.e. the NF brine is defined as usable water in this treatment train. In reality, the amount of blending possible will be dependent on the exact composition of the LSRRO permeate and end-use regulatory requirements, varying on a case-by-case basis. Given this variation, treatment Trains 3-6 were modeled to represent the most pessimistic and most optimistic scenarios. Namely, Trains 3-4 assume none of the NF brine can be blended and all must go to disposal while Trains 5-6 assume all of the NF brine can be blended and none goes to disposal. Depending on the exact operating situation of a plant, the answer in actuality will lie somewhere between these bounds. Given the case-by-case nature of salt addition both in terms of the quantity added and the addition method, the cost savings of replacing Ca²⁺ and Mg²⁺ addition with NF brine blending is not accounted for in this analysis. Accounting for these avoided costs would make treatment Trains 5-6 even more economically favorable.

As in treatment Trains 3-4, the NF permeate is sent to the LSRRO unit. The LSRRO unit produces a permeate from the first stage that, blended with the NF brine and, in scenarios with crystallization, crystallizer steam, serves as the usable water basis for LCOW and SEC calculations. The brine from the LSRRO unit's third stage proceeds either to disposal in the absence of a crystallizer or to a crystallizer followed by DWI, SD, or EPs.

Section 7.1 – NF, Train 5

The NF unit for this treatment train was modeled in the same manner described in SI Section 5.1. The LCOW and SEC of the NF unit were calculated in WaterTAP on a per m³ NF permeate basis, with the LCOW given in \$/m³ NF permeate (2018\$) and the SEC given in kWh/m³ NF permeate. The LCOW and SEC of the NF unit were calculated as described in SI Section 5.1, but with NF brine included as part of the usable water basis.

Section 7.2 – LSRRO, Train 5

The LSRRO unit is configured in the manner described in SI Section 5.2, with the NF permeate serving as the LSRRO inlet and NF brine added to the usable water basis.

Section 7.3 – Crystallizer, Train 5

The crystallizer unit was configured as described in SI Sections 4.3 and 5.3, but with NF brine included in the usable water basis.

Section 7.4 – DWI, Train 5

The DWI unit was configured as described in SI Section 4.4 and 5.4, with the NF brine now also included in the usable water basis and no NF brine entering disposal.

Section 7.5 - SD, Train 5

The SD unit was configured as described in SI Section 4.5 and 5.5, with the NF brine now also included in the usable water basis and no NF brine entering disposal.

Section 7.6 – EPs, Train 5

The SD unit was configured as described in SI Section 4.6 and 5.6, with the NF brine now also included in the usable water basis and no NF brine entering disposal. Salt disposal also does not include any salt from the NF brine, and evaporation pond area is based on LSRRO brine in cases with no crystallization and liquid brine exiting the crystallizer in scenarios with a crystallizer unit.

Section 7.7 – Additional Notes

- Trains 5 and 6 result in lower LCOWs at higher recoveries than the other treatment trains because of both the increase in usable water volume and the decrease in liquid and salt disposal costs.
- Trains 5 and 6 have the least volume of brine entering the final disposal step, so the decrease in disposal energy does not offset the increase in LSRRO energy demand and no SEC optimums are reached in cases without crystallization.

Section 8 – Treatment Train 6

Each unit of this treatment train is configured in the same manner described in SI Section 7, with the exception that the NF pre-treatment step now targets 60% volumetric recovery.

Section 8.1 – Additional Notes

- In Trains 2-6, the cost of LSRRO operation increases with increasing recovery, but in cases involving more expensive disposal options (DWI,Max, Evap,Min, and Evap,Max) and no crystallization, LCOW optimums are reached based on the balance of increasing LSRRO costs and decreasing disposal costs with increasing water recovery.
- Evaporative crystallization is an energy-intensive process, so total SEC declines as concentrator recovery increases and crystallization energy requirements accordingly decrease. Exceptions occur in Trains 2-6 as the LSRRO approaches its upper recovery limit and the increase in LSRRO energy demand outweighs the decrease in crystallizer and disposal energy demands.

Section 9 – Life Cycle Analysis

This analysis calculates life cycle impacts from greenhouse gas emissions (GHG) factors, total energy factors, and water consumption factors provided by Argonne National Laboratory's 2022 Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies Model (GREET).¹⁹ These factors include the GHGs and energy associated with petroleum well infrastructure, natural gas (NG) well infrastructure, coal well infrastructure, wind turbine

materials, and power plant infrastructure. Table S.8-S.9 give the factors associated with electricity from a wind-based grid and a U.S. mix grid, respectively.

Electricity – Wind			
	Feedstock	Fuel	Total
Total Energy (kWh/kWh elec)	0	1.09	1.09
Water Consumption (m ³ /kWh elec)	0	3.86E-05	3.86E-05
GHGs (kg CO _{2,eq} /kWh elec)	0	0.01	0.01

Table S.8 – LCA Factors, Wind Electricity

Table S.9 – LCA Factors, U.S. Grid Electricity

Electricity – U.S. Mix			
	Feedstock	Fuel	Total
Total Energy (kWh/kWh elec)	0.10	1.98	2.08
Water Consumption (m ³ /kWh elec)	1.21E-04	2.14E-03	2.26E-03
GHGs (kg CO _{2,eq} /kWh elec)	0.05	0.42	0.47

The evaporative crystallization unit requires external heat supply, and here it is assumed that the heat is provided via natural gas (NG) combustion with a boiler efficiency of 90%. Table S.10 outlines the factors for total energy, water consumption, and GHGs for NG as a stationary fuel.

Heat – Natural Gas Boiler NG as Combustion Total Stationary Fuel Total Energy (kWh/kWh 1.28E-01 1.00 1.13 heat) Water Consumption (m³/kWh 6.90E-05 0 6.90E-05 heat) GHGs (kg CO_{2,eq} /kWh heat) 5.12E-02 2.03E-01 2.54E-01

Table S.10 – LCA Factors, Natural Gas Heating

Next, for the LCA calculations were performed for the chemicals involved in Train 2, namely hydrazine (antiscalant) and HCl. These chemicals were dosed at WaterTAP's default dosage level: 10 mg/L inlet brine. Total energy, water consumption, and GHG factors for HCl were pulled from GREET and are listed in Table S.11.

/		
Chemical Addition – HCl production in the U.S.		
	Total	
Total Energy (kWh/g)	9.04E-03	
Water Consumption (m ³ /g)	5.45E-06	
GHGs (kg CO _{2,eq} /g)	2.08E-03	

Table S.11 – LCA Factors, HCl Addition

Hydrazine information is not directly available in GREET. To best approximate it, factors for ammonia and hydrogen peroxide were pulled from GREET and converted to factors for hydrazine based on the reaction given in equation (42).

$$2 NH_3 + H_2O_2 \to N_2H_4 + 2 H_2O \tag{42}$$

Given that this reaction is exothermic, it was assumed that no additional heat supply would be required. Table S.12 gives the factors for hydrazine, where the contributions of ammonia and hydrogen peroxide to hydrazine were found via equations (43) and (44), respectively.

Table S.12 – LCA Factors, Antiscalant (Hydrazine) Addition

Chemical Addition – Hydrazine						
	Ammonia (GREET)	Hydrogen Peroxide (GREET)	NH ₃ contribution to N ₂ H ₄	H ₂ O ₂ contribution to N ₂ H ₄	Hydrazine Total	
Total Energy (kWh/g)	1.06E-02	4.80E-03	1.13E-02	5.09E-03	1.64E-02	
Water Consumption (m ³ /g)	2.02E-06	2.51E-06	2.14E-06	2.67E-06	4.81E-06	
GHGs (kg CO _{2,eq} /g)	2.88E-03	1.08E-03	3.06E-03	1.15E-03	4.21E-03	

$$NH_{3} \ contribution = \frac{NH_{3} \ GREET \ Factor[\frac{x}{ton \ NH_{3}}] * 2[\frac{mol \ NH_{3}}{mol \ N_{2}H_{2}}] * 1.88 * 10^{-5}[\frac{ton \ NH_{3}}{mol \ NH_{3}}]}{3.53 * 10^{-5}[\frac{ton \ N_{2}H_{2}}{mol \ N_{2}H_{2}}]}$$
(43)

$$H_2O_2 \ contribution = \frac{H_2O_2 \ GREET \ Factor\left[\frac{x}{ton \ NH_3}\right] * 1\left[\frac{mol \ H_2O_2}{mol \ N_2H_2}\right] * 3.75 * 10^{-5}\left[\frac{ton \ H_2O_2}{mol \ H_2O_2}\right]}{3.53 * 10^{-5}\left[\frac{ton \ N_2H_2}{mol \ N_2H_2}\right]}$$
(44)

Where x is mmBTU, gal, or g $CO_{2,eq}$ for total energy, water consumption, and GHG emission factors, respectively. Numbers given in ton/mol represent molar mass in U.S. tons.

The final aspect of the LCA involved emissions associated with salt disposal. It is assumed that the salt would be trucked a distance of 50 mi in a diesel truck (Compression-Ignition Direct-Injection vehicle) capable of holding 22 tons.²⁰ Table S.13 gives the associated emissions factor.

Table S.13 – LCA Factor, Salt Disposal

Vehicles CIDI Vehicle: Conventional and LS Diesel				
GHGs (g CO _{2,eq} /(mi*vehicle))	2.84E+02			
Distance (mi)	50			
Salt per vehicle (ton/vehicle)	22			
GHGs (kg CO _{2,eq} /kg salt)	7.10E-04			

Total full cycle energy, water consumption, and GHGs were calculated for each treatment train according to equations (45), (46), and (47). TEF indicates "Total Energy Factor", WCF indicates "Water Consumption Factor", and GHG_{EF} indicates "GHG Emissions Factor" as tabulated in Table S.8-S.13.

$$Full Cycle Energy Consumption \left[\frac{kWh}{m^{3} Usable Water}\right] = Treatement Electricity \left[\frac{kWh}{m^{3} Usable Water}\right] * TEF, elec \left[\frac{kWh}{kWh}\right] + Treatement Heat \left[\frac{kWh}{m^{3} Usable Water}\right] * \frac{TEF,heat}{NG Boiler Efficiency} \left[\frac{kWh}{kWh}\right] + N_{2}H_{2} Dose \left[\frac{g N_{2}H_{2}}{m^{3} Usable Water}\right] * TEF, N_{2}H_{2} \left[\frac{kWh}{g N_{2}H_{2}}\right] + H_{2}O_{2} Dose \left[\frac{g H_{2}O_{2}}{m^{3} Usable Water}\right] * TEF, H_{2}O_{2} \left[\frac{kWh}{g H_{2}O_{2}}\right]$$
(45)

$$Water \ Consumption\left[\frac{m^{3} \ Consumed}{m^{3} \ Usable \ Water}\right] = Treatement \ Electricity\left[\frac{kWh}{m^{3} \ Usable \ Water}\right] *$$

$$WCF, elec\left[\frac{m^{3} \ Consumed}{kWh}\right] + Treatement \ Heat\left[\frac{kWh}{m^{3} \ Usable \ Water}\right] *$$

$$\frac{WCF, heat}{NG \ Boiler \ Efficiency}\left[\frac{m^{3} \ Consumed}{kWh}\right] + N_{2}H_{2} \ Dose\left[\frac{g \ N_{2}H_{2}}{m^{3} \ Usable \ Water}\right] * WCF, N_{2}H_{2}\left[\frac{m^{3} \ Consumed}{g \ N_{2}H_{2}}\right] +$$

$$H_{2}O_{2} \ Dose\left[\frac{g \ H_{2}O_{2}}{m^{3} \ Usable \ Water}\right] * WCF, H_{2}O_{2}\left[\frac{m^{3} \ Consumed}{g \ H_{2}O_{2}}\right]$$

$$(46)$$

$$GHG\ Emissions\left[\frac{kg\ CO_{2,eq}}{m^{3}\ Usable\ Water}\right] = Treatement\ Electricity\left[\frac{kWh}{m^{3}\ Usable\ Water}\right] * \\GHG_{EF}, elec\left[\frac{kg\ CO_{2,eq}}{kWh}\right] + Treatement\ Heat\left[\frac{kWh}{m^{3}\ Usable\ Water}\right] * \frac{GHG_{EF},heat}{NG\ Boiler\ Efficiency}\left[\frac{kg\ CO_{2,eq}}{kWh}\right] + \\N_{2}H_{2}\ Dose\left[\frac{g\ N_{2}H_{2}}{m^{3}\ Usable\ Water}\right] * GHG_{EF}, N_{2}H_{2}\left[\frac{kg\ CO_{2,eq}}{g\ N_{2}H_{2}}\right] + H_{2}O_{2}\ Dose\left[\frac{g\ H_{2}O_{2}}{m^{3}\ Usable\ Water}\right] * \\GHG_{EF}, H_{2}O_{2}\left[\frac{kg\ CO_{2,eq}}{g\ H_{2}O_{2}}\right] + Solid\ Salt\left[\frac{kg\ salt}{m^{3}\ Usable\ Water}\right] * GHG_{EF}, Salt\left[\frac{kg\ CO_{2,eq}}{kg\ salt}\right]$$
(47)

Where contributions from N₂H₄ and HCl dosing are included only for Train 2 and treatment heat contributions are included only for scenarios involving crystallization. Treatment electricity is the sum of the SECs for antiscalant+HCl addition (Train 2), NF (Trains 3-6), MVC (Train 1), LSRRO (Trains 2-6), crystallization electricity (when applicable), SD, and DWI. GHG contributions from salt disposal are included for all scenarios involving crystallization and for scenarios employing evaporation ponds when there is no crystallization.

Works Cited

- (1) Fritzmann, C.; Löwenberg, J.; Wintgens, T.; Melin, T. State-of-the-Art of Reverse Osmosis Desalination. *Desalination* **2007**, *216* (1), 1–76. https://doi.org/10.1016/j.desal.2006.12.009.
- (2) The World Bank. Seawater and Brackish Water Desalination in the Middle East, North Africa and Central Asia, 2004. https://documents1.worldbank.org/curated/en/813191468191928325/pdf/335150v70Seawate r0annex060cyprus.pdf (accessed 2023-10-16).
- (3) Du, Y.; Wang, Z.; Cooper, N. J.; Gilron, J.; Elimelech, M. Module-Scale Analysis of Low-Salt-Rejection Reverse Osmosis: Design Guidelines and System Performance. *Water Research* 2022, 209, 117936. https://doi.org/10.1016/j.watres.2021.117936.
- (4) DuPont. FilmTecTM Elements Operating Limits Temperature and Pressure Limits for 8-Inch FilmTecTM Seawater RO Elements: Tech Manual Excerpt, 2022. https://www.dupont.com/content/dam/dupont/amer/us/en/watersolutions/public/documents/en/RO-NF-FilmTec-Temperature-Pressure-Limits-Manual-Exc-45-D00691-en.pdf (accessed 2024-01-31).
- (5) H.P. Swift, A.; Lu, H.; Becerra, H. Zero Discharge Waste Brine Management for Desalination Plants; Desalination Research and Development Program Report 89; University of Texas at El Paso, 2002. https://www.usbr.gov/research/dwpr/reportpdfs/report089.pdf (accessed 2023-10-16).
- (6) Panagopoulos, A.; Haralambous, K.-J.; Loizidou, M. Desalination Brine Disposal Methods and Treatment Technologies - A Review. *Science of The Total Environment* 2019, 693, 133545. https://doi.org/10.1016/j.scitotenv.2019.07.351.
- (7) Salih, H. H.; Li, J.; Kaplan, R.; Dastgheib, S. A. Life Cycle Assessment of Treatment and Handling Options for a Highly Saline Brine Extracted from a Potential CO2 Storage Site. *Water Research* 2017, *122*, 419–430. https://doi.org/10.1016/j.watres.2017.06.032.
- (8) Rao, P.; Aghajanzadeh, A.; Sheaffer, P.; Morrow, W. R.; Brueske, S.; Dollinger, C.; Price, K.; Sarker, P.; Ward, N.; Cresko, J. Volume 1: Survey of Available Information in Support of the Energy-Water Bandwidth Study of Desalination Systems; LBNL--1006424, 1342538; 2016; p LBNL--1006424, 1342538. https://doi.org/10.2172/1342538.
- (9) Pinho, S. P.; Macedo, E. A. Solubility of NaCl, NaBr, and KCl in Water, Methanol, Ethanol, and Their Mixed Solvents. J. Chem. Eng. Data 2005, 50 (1), 29–32. https://doi.org/10.1021/je049922y.
- (10) Al-Anber, Z. A. Heat Saving in Evaporative Crystallization by Introducing a Heat Pump. *YJES* **2021**, *6* (1), 91–104. https://doi.org/10.53370/001c.24136.
- (11)Atia, A. A.; Allen, J.; Young, E.; Knueven, B.; Bartholomew, T. V. Cost Optimization of Low-Salt-Rejection Reverse Osmosis. *Desalination* 2023, 551, 116407. https://doi.org/10.1016/j.desal.2023.116407.
- (12)AlSawaftah, N.; Abuwatfa, W.; Darwish, N.; Husseini, G. A Comprehensive Review on Membrane Fouling: Mathematical Modelling, Prediction, Diagnosis, and Mitigation. *Water* 2021, 13 (9), 1327. https://doi.org/10.3390/w13091327.
- (13)Das, S.; O'Connell, M. G.; Xu, H.; Bernstein, R.; Kim, J.-H.; Sankhala, K.; Segal-Peretz, T.; Shevate, R.; Zhang, W.; Zhou, X.; Darling, S. B.; Dunn, J. B. Assessing Advances in Anti-Fouling Membranes to Improve Process Economics and Sustainability of Water Treatment. *ACS EST Eng.* 2022. https://doi.org/10.1021/acsestengg.2c00184.

- (14)Agriculture and Agri-Food Canada; Prairie Farm Rehabilitation Administration. Irrigation and Salinity, 2000.
- (15)Jafari, M.; Vanoppen, M.; van Agtmaal, J. M. C.; Cornelissen, E. R.; Vrouwenvelder, J. S.; Verliefde, A.; van Loosdrecht, M. C. M.; Picioreanu, C. Cost of Fouling in Full-Scale Reverse Osmosis and Nanofiltration Installations in the Netherlands. *Desalination* 2021, 500, 114865. https://doi.org/10.1016/j.desal.2020.114865.
- (16)Nativ, P.; Leifman, O.; Lahav, O.; Epsztein, R. Desalinated Brackish Water with Improved Mineral Composition Using Monovalent-Selective Nanofiltration Followed by Reverse Osmosis. *Desalination* **2021**, *520*, 115364. https://doi.org/10.1016/j.desal.2021.115364.
- (17)Vaseghi, G.; Ghassemi, A.; Loya, J. Characterization of Reverse Osmosis and Nanofiltration Membranes: Effects of Operating Conditions and Specific Ion Rejection. *Desalination and Water Treatment* **2016**, *57* (50), 23461–23472. https://doi.org/10.1080/19443994.2015.1135825.
- (18)Telzhensky, M.; Birnhack, L.; Lehmann, O.; Windler, E.; Lahav, O. Selective Separation of Seawater Mg2+ Ions for Use in Downstream Water Treatment Processes. *Chemical Engineering Journal* **2011**, *175*, 136–143. https://doi.org/10.1016/j.cej.2011.09.082.
- (19)Argonne National Laboratory. The Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies (GREET) Model, 2020.
- (20) Bulk Delivery Methods & Equipment. Midwest Salt. https://midwestsalt.com/delivery-service/bulk-delivery-methods-equipment/ (accessed 2024-02-08).