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Dedicated
to my beloved family

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Abstract

Freeze desalination (FD) is a method in which saline water is cooled below its freezing point and freshwater is separated from the brine in the form of ice crystals. FD is relatively insensitive to the salinity of the feed solution, making it suitable for desalination of high concentration brines such as the brine rejected from the seawater desalination plants. The design of the FD system and the thermochemical behavior of the brine upon freezing are critical factors in the energy performance of this method. To date, thermochemical properties of the concentrated seawater during cooling, such as the threshold of formation of ice and salt-hydrates and their corresponding cooling load of formation, are not well known. Likewise, the optimal configuration of the FD system to achieve the maximum energy efficiency has not been investigated. This work provides comprehensive data about the cooling load of freezing of concentrated brine rejected from seawater desalination plants along with the threshold of formation of ice and salt-hydrates backed-up by validation. Furthermore, the optimal configuration of the FD system is identified and the effects of the compressor isentropic efficiency and effectiveness of the system's heat exchangers on the work consumption of the FD system were investigated. In addition, the lack of knowledge of FD's economic performances represents a critical research gap that impedes the technology's progression toward commercialization. To address the issue, this work presents a cost optimization framework for tuning the equipment size and identifying the optimal control parameters at the design stage. Utilizing the developed framework, the outcomes provide benchmark economic metrics for the FD technology considering practical ranges of electricity prices, brine disposal cost, and feed total dissolved solids (TDS). For a feed brine TDS of 75,000 ppm and at a freshwater selling price of 1.5 \$/ton, electricity price of 8 ¢/kWh, and brine disposal cost of 0.02 \$/bbl, the FD costs \$0.33 to treat 1 barrel (bbl) of feed. For feed brine TDS of 100,000 ppm and 200,000 ppm at the same electricity, disposal, and freshwater selling prices, FD costs 0.38 \$/bbl and 0.62 \$/bbl respectively. The generated benchmark cost metrics can inform the future market analysis and commercialization of the FD technologies.

In addition, this work investigates the potential for enhancing the power flexibility of the FD technology being a thermal desalination method known for its high energy consumption. The study introduces a design modification to the FD configuration, aiming to improve its adaptability to fluctuating power availability. By employing a causal modeling approach, the modified design is analyzed with a focus on minimizing brine treatment costs over a 24-hour period. The effectiveness of this design is evaluated through scenario-based testing, with a particular emphasis on its potential for brine treatment cost savings by participating in day-ahead electricity markets.

Nomenclature

C	cost [\$]
C_p	specific heat [J/kg°C]
Con	concentration [ppm]
h	enthalpy [J]
h_{sl}	latent heat of fusion [J]
m	mass [kg]
$\dot{m}$	mass flow rate [kg/s]
$\dot{P}$	electrical power [W]
Pr	price [\$]
Q	heat transfer rate [W]
RR/rr	water/ ice recovery ratio
S	salinity [ppm]
T	temperature [°C]
T_m	melting temperature [°C]
t	Time/ duration [s]
UA	combined heat transfer coefficient [W/°C]
u	fluid velocity in the x direction [m/s]
W	mechanical power [W]

Greek symbols

ϕ_{ice}	ice mass fraction
$\eta_{isentropic}$	isentropic efficiency
ρ	density [kg/m ³]
$\theta_1 - \theta_{10}$	calibration coefficients
$\alpha_1 - \alpha_{10}$	calibration coefficients
$\phi_1 - \phi_{10}$	calibration coefficients
Δ	change

Subscripts

amb	ambient
b	brine
bbl	barrel
c	convection
ch	brine freezing chamber
$CAPEX$	capital expenditure
cas	cascade heat exchanger
cl	construction labor
co	condenser
$cond$	condensing

<i>cv</i>	civil works
<i>cw</i>	cooling water
<i>cycA</i>	refrigeration cycle A
<i>cycB</i>	refrigeration cycle B
<i>d</i>	disposal
<i>des</i>	desalinated water selling price
<i>e</i>	electrical/ electricity
<i>ew</i>	electrical works
<i>ev</i>	evaporator
<i>evap</i>	evaporating
<i>f</i>	feed
<i>fz</i>	freezing
<i>H</i>	at the high-pressure side
<i>HX</i>	heat exchanger
<i>ICL</i>	intermediate cooling liquid
<i>i</i>	isentropic
<i>ice</i>	crystallized H ₂ O inside the freezing chamber
<i>in</i>	inlet
<i>interm</i>	cascade/ intermediate heat exchanger
<i>ion</i>	ionic components
<i>iwc</i>	additional initial working capital
<i>L</i>	at the low-pressure side
<i>l</i>	liquid phase
<i>la</i>	land acquisition
<i>lb</i>	labor
<i>m</i>	maintenance
<i>map</i>	corresponding to the compressor map superheat
<i>min</i>	minimum
<i>melt</i>	melting of formed ice
<i>out</i>	outlet
<i>pre</i>	precoolers
<i>rb</i>	rejected brine
<i>refr</i>	refrigerant
<i>r</i>	refrigeration system
<i>s</i>	solid phase/ section
<i>sf</i>	Refrigerant single-phase region
<i>sim</i>	corresponding to the compressor simulated superheat
<i>sl</i>	saturated liquid state
<i>st</i>	fluid stream
<i>sv</i>	saturated vapor state
<i>sw</i>	seawater
<i>T</i>	total cost of brine treatment
<i>tf</i>	Refrigerant two-phase region
<i>tw</i>	treated water
<i>w</i>	water/ wall

Abbreviations

CAPEX	capital expenditure
COP	coefficient of performance
FD	freeze desalination
ICL	intermediate cooling liquid
OPEX	operating expenditure
ppm	parts per million (unit)
SFDW	specific freeze desalination work consumption
TDS	total dissolved solids
TLM	logarithmic mean temperature
USD	United States dollar

1 Introduction

This chapter provides an in-depth examination of the challenges involved in treating high salinity brine and sets the stage for a detailed investigation into freeze desalination (FD) technology. FD is explored as a promising solution to these critical issues. The chapter also discusses the ethical and psychological motivations behind the research, focusing on the urgent crisis of water scarcity and the environmental and economic difficulties posed by current brine disposal practices. These practices are associated with essential industrial processes that produce significant quantities of brine as a byproduct, making it crucial to address these challenges due to their impact on economic development and societal well-being.

Additionally, the chapter introduces FD as a potential alternative to existing desalination technologies, which often face limitations when treating high salinity brine. It outlines the key features of FD, identifies current technical issues, and reviews recent advancements aimed at resolving these challenges. The chapter concludes by presenting the research methodology employed to evaluate FD's potential, detailing the process from identifying the problem to achieving meaningful and impactful research outcomes that could contribute significantly to solving the brine treatment issues.

1.1 Thrust of this research path

The global water scarcity crisis is an urgent and escalating issue that affects billions of people across the world [1]. Currently, over four billion individuals, experience water scarcity for at least one month each year [2]. This scarcity is particularly pronounced in agricultural regions, where approximately 3.2 billion people are subjected to high to very high water shortages [3]. Among these, roughly 1.2 billion individuals face severe water constraints, highlighting an immediate and critical need for effective water management strategies to support agricultural productivity and overall quality of life [4]. The situation underscores

the broader impact of water scarcity on food security and economic stability, emphasizing the need for innovative solutions to ensure sustainable water use and availability for future generations.

The projected exacerbation of water scarcity in the coming decades further underscores the urgency of addressing this crisis. By 2025, it is anticipated that half of the world's population could be living in regions experiencing water scarcity, a statistic that paints a dire picture of future water availability [5]. By 2030, intense water scarcity could potentially displace up to 700 million people, contributing to global migration and socio-economic instability [6]. By 2040, approximately one in four children worldwide is expected to live in areas of extremely high-water stress [7, 8]. These projections highlight the growing need for comprehensive and forward-thinking strategies to address both current and future water challenges. Addressing water scarcity not only involves increasing freshwater availability but also involves enhancing resilience to climate variability and ensuring equitable access to water resources.

Desalination technology emerges as a crucial response to the growing demand for water and the need to mitigate water scarcity. This process involves the removal of salts and other impurities from seawater or brackish water to produce freshwater, which is essential for meeting the needs of both populations and industries. Despite its critical role, desalination produces high salinity brine as a by-product, which poses significant environmental and economic challenges. As of 2019, there were approximately 16,000 desalination plants globally, collectively producing around 95 million cubic meters of freshwater daily while generating 141.5 million cubic meters of brine (water with higher TDS). This massive volume of brine disposal is a major environmental concern, requiring effective management strategies to mitigate its impact.

The disposal of high salinity brine presents considerable challenges. Traditional disposal methods such as surface water discharge and deep well injection have notable drawbacks. As an example, surface water discharge, where brine is released into natural water bodies

like lakes, rivers, or oceans, adversely impacts marine ecosystems by increasing salinity and temperature. This method is employed by over 90% of global seawater desalination plants, despite its environmental consequences. Another example is the deep well injection which involves injecting brine deep underground into geological formations, which can lead to potential groundwater contamination and seismic activity. The issues linked to the commonly utilized brine disposal methods [9] –[14] are presented in Table. 1:

Table 1: Commonly utilized brine disposal methods.

Brine disposal method	Primary issues
Deep well injection	Contamination of ground water and possibility of triggering earthquakes.
Land application	Salinization of the soil if the method is used on large scale production of crops and dependency on seasonal irrigation needs and climate.
Evaporation ponds	High capital costs due to expenses of land acquisition, contamination of underlying aquifers due to leakage issues and problems associated with migrating birds.
Seawater discharge	Negative impact on marine life due to improper dilution where it can possibly cause thermal pollution, reduction of dissolved oxygen in receiving waters, eutrophication, toxicity and pH increase.
Sewer discharge	Overload the existing capacity of the sewerage system while diminishing its usable hydraulic capacity.

These traditional methods underscore the need for more sustainable and effective brine management solutions. The challenge of managing high salinity brine is further complicated by its production from various industrial processes, including oil and gas operations. The oil and gas industry generates significant volumes of high salinity brine, with about 40% of this brine being discharged into the environment. This practice not only results in considerable disposal costs but also contributes to environmental pollution [15]. Therefore, addressing brine disposal through advanced desalination techniques is crucial for reducing environmental impacts and minimizing economic burdens.

Advanced desalination technologies such as FD offer promising solutions for brine treatment. FD involves cooling brine to form crystallized ice, which reduces the volume of disposed brine and recovers freshwater. This technology can help alleviate some of the environmental and economic burdens associated with brine disposal while providing additional freshwater resources. The potential benefits of freeze desalination make it a key area of research for addressing both water scarcity and brine disposal challenges.

In summary, this research focuses on tackling the dual challenges of water scarcity and high salinity brine disposal through research on FD technology. This aims to contribute to mitigating the global water crisis and aligns with global initiatives to enhance water availability, support sustainable development, and protect the environment for future generations.

1.2 Background

Desalination technology offers a promising solution for addressing the environmental and economic challenges associated with the disposal of high-salinity brine, particularly from seawater desalination plants and oil and gas operations. The adverse impacts linked to disposing the high salinity brine to the environment using the current methods (Table. 1) include the contamination of the ground water, the possibility of triggering earthquakes, salinization of the soil, problems associated with migrating birds and the negative impact on the marine life due to the thermal pollution as well as the reduction of dissolved oxygen [9] –[14].

By applying desalination processes to treat brine effluent, the volume of brine that must be disposed of is significantly reduced, which helps lower the associated disposal costs and mitigates the negative environmental impacts. Additionally, this process enables the recovery of a portion of usable water from the high-salinity brine, providing an additional freshwater resource that can help meet industrial, agricultural, or municipal water demands. As global water scarcity intensifies, these benefits position desalination as a critical tool in sustainable water management strategies.

1.2.1 Commercial desalination technologies

Globally around 92.5 million m³/day of water is generated from desalination plants [16]. Figure 1 presents the contribution of different desalination technologies in the overall water volume generated daily using desalination around the world [17].

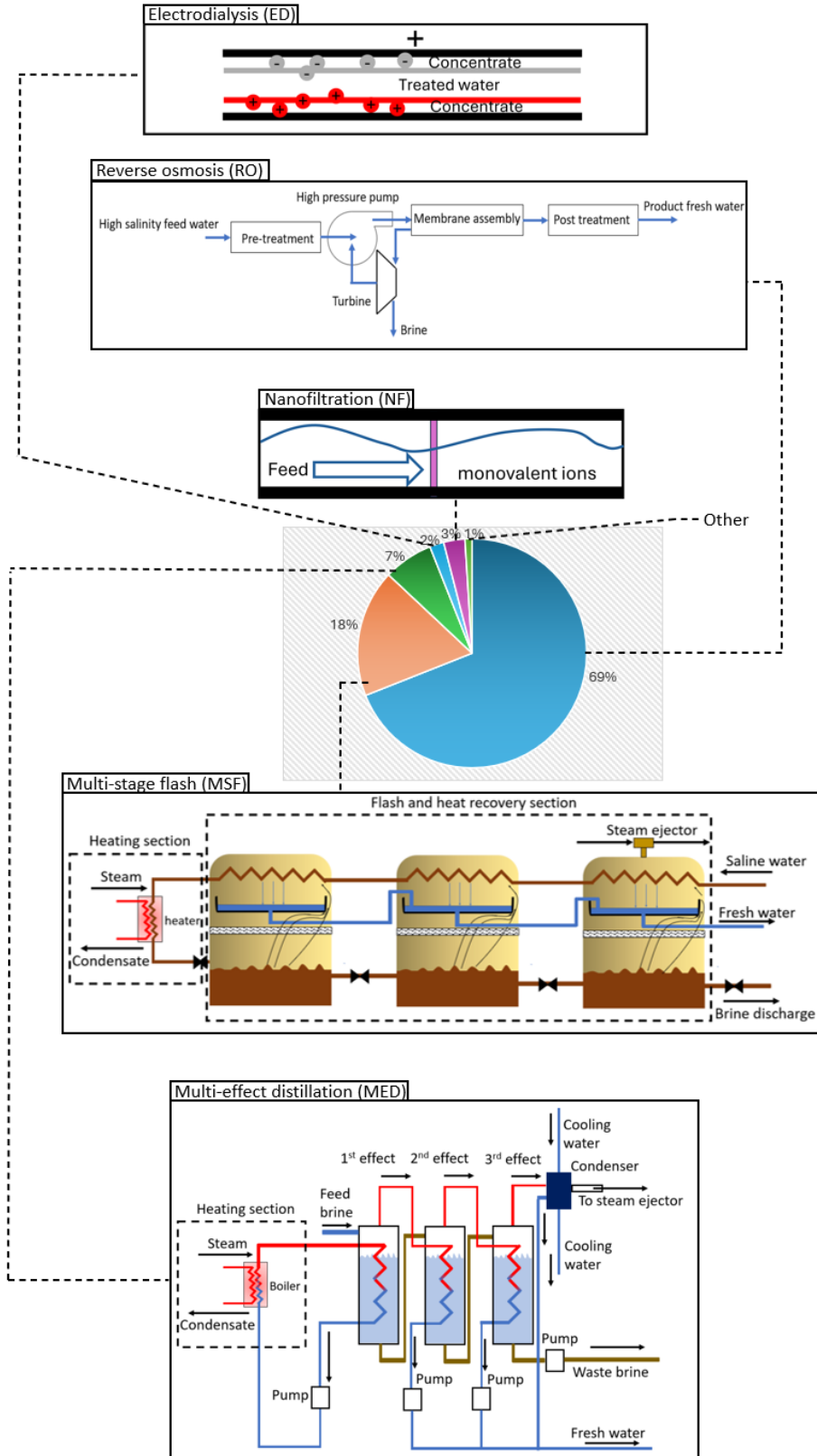


Figure 1: Commercial desalination technologies contribution [17].

Figure 1, shows that the most commonly used desalination techniques are reverse osmosis (RO) [18, 19, 20] (which falls under the category of membrane desalination (MD) technologies) followed by thermal desalination technologies (TD) [21]. In case of MD technologies, pressure has to be applied at a magnitude higher than the solution osmotic pressure transferring less concentration water across semi-permeable membrane while trapping significant amount of solute on the other side of the membrane [21]. The most commonly used thermal desalination technologies are Multi-effect distillation (MED) and multi-stage flash (MSF). MED and MSF techniques involve forms of water boiling and evaporation [22]. In the following subsections, the most widely used desalination techniques are going to be presented and reviewed in an additional layer of detail.

Reverse Osmosis (RO)

As previously described, in RO desalination method, an external pressure is applied to overcome the osmotic pressure. This would allow the water to cross the membrane in the direction from the higher concentration side to the lower concentration side. And thus no heating, cooling or phase separation is required. The major energy consumer in the RO process is work applied to generate the external pressure. In industry, the RO process can be broken down into four main stages. The membrane desalination process is presented in Fig. 2 and it's main stages are pre-treatment, high pressure pumping, membrane separation and post treatment [23, 24].

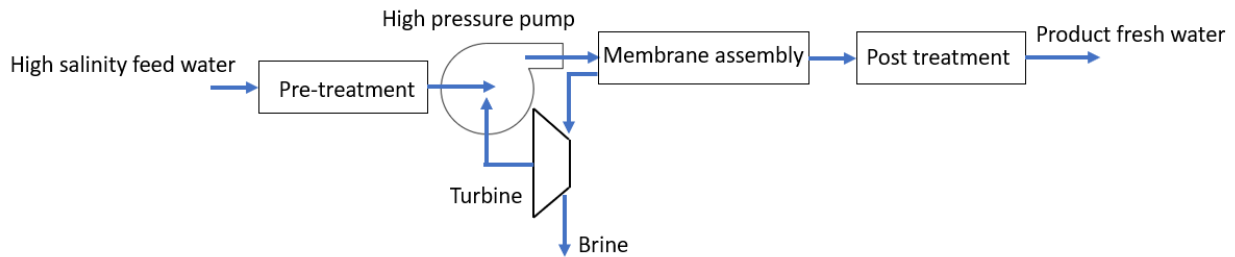


Figure 2: Schematic diagram of RO system [25].

The pre-treatment process includes logging the brine through multimedia filters. This would handle impurities larger in particle diameter size like granite and silica. Another step is chemical pre-treatment, for example, chlorination (which protects against pathogens) [26]. The pre-treatment stage is essential to limit salt precipitation and microbial growth on the membrane [27] which raises its life time as well as raising the pumps lifetime [28]. The following two stages include raising the pressure of stream and then allowing it to flow through the membrane. The most widely used RO process membrane types are hollow fiber and spiral wound [27, 29]. In the final stage, post-treatment of the stream takes place which might include disinfection and PH adjustment [27].

Multi-stage flash (MSF)

The multi-stage flash technology is a commonly used desalination technology. The operating principle is based on flash evaporation. To visualize the operating principle, Fig. 3 shows a simple illustration where the brine is logged to the low pressure chamber inside a tube and it's then directed to a heater (can be heated by any adequate heat source, for example as presented in Fig. 3 the heating is performed using steam) for raising the temperature of brine stream. The hot brine is then expanded into the low pressure chamber.

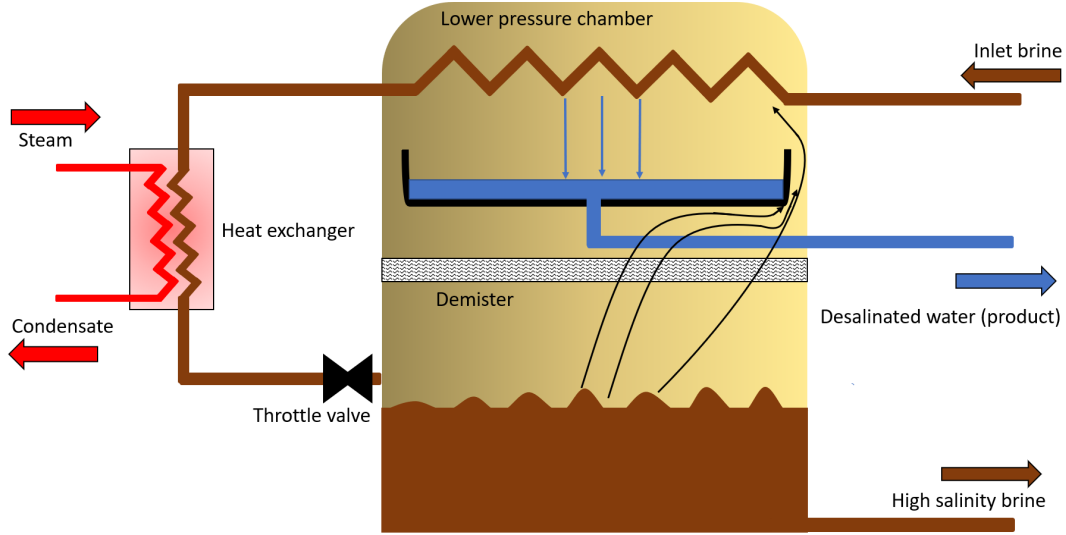


Figure 3: Illustration for describing the operating principle of flash desalination.

The pressure inside the chamber is low where the vacuum pressure can be achieved in various ways, for example using vacuum pump or by passing a stream through a nozzle connected to the chamber in order to create vacuum. The heated brine stream expanded into the chamber is now at a pressure lower than the saturation pressure corresponding to its temperature and thus vaporization occurs. The vapor separated from brine at the lower part of the chamber ascends upward carrying some droplets of brine where those droplets are characterized by high salinity concentration. A demister prevents the high salinity brine droplets from being carried over upwards in the chamber by the generated vapor. The vapor then transfers heat to the inlet brine stream inside tubes. This would pre-heat the inlet brine reducing the amount of energy required to raise its temperature to the desired level. In addition, this also cools down the vapor resulting in its condensation where it's collected in a sump. The extracted liquid from the sump is pure desalinated water product. An MSF system operates based on the explained principle. As previously explained, the inlet brine requires heating where an external source of steam can be used. As an example related to industrial multi-stage flash system, low pressure steam can be extracted from a steam power plant or co-generation plant [30, 31]. High temperature brine is then expanded into flash

evaporators (lower pressure chambers) where part of the brine evaporates while the rest is directed to following stages of flash evaporators that have lower pressure as shown in Fig. 4.

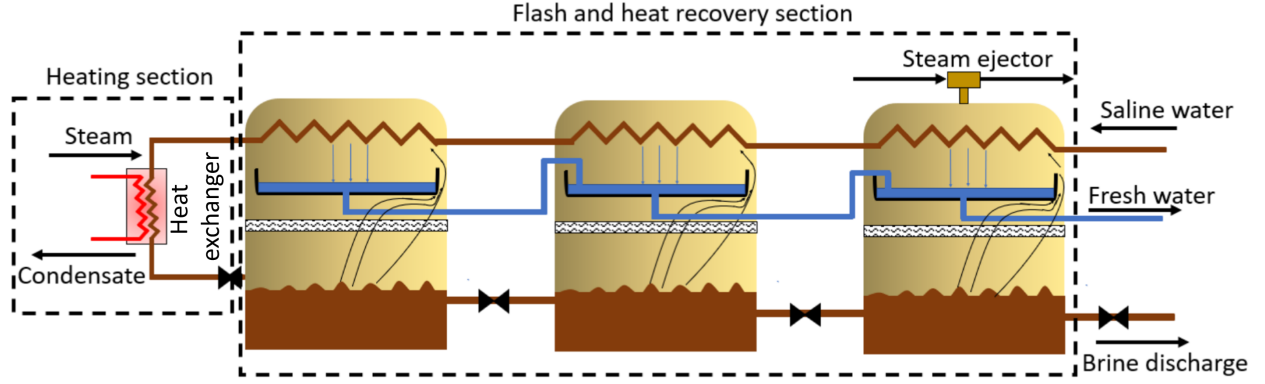


Figure 4: Multi-stage flash desalination system [32].

Similar to the illustration in Fig. 3, the H_2O vapor condenses when heat transfer occurs with the inlet brine (colder in temperature) inside the tubes. The vapor condenses (distillate is formed) where the water produced can have total dissolved solids as low as 2-10 ppm [28].

Multi-effect distillation (MED)

In Multi-Effect Distillation (MED) systems, the seawater or brine is heated and evaporated in multiple stages (referred to as "effects"), with each subsequent stage operating at a lower pressure. This pressure reduction allows for the reuse of vapor from each effect to provide heat for the next, thereby increasing energy efficiency. Figure 5 shows a simple multi-effect distillation system.

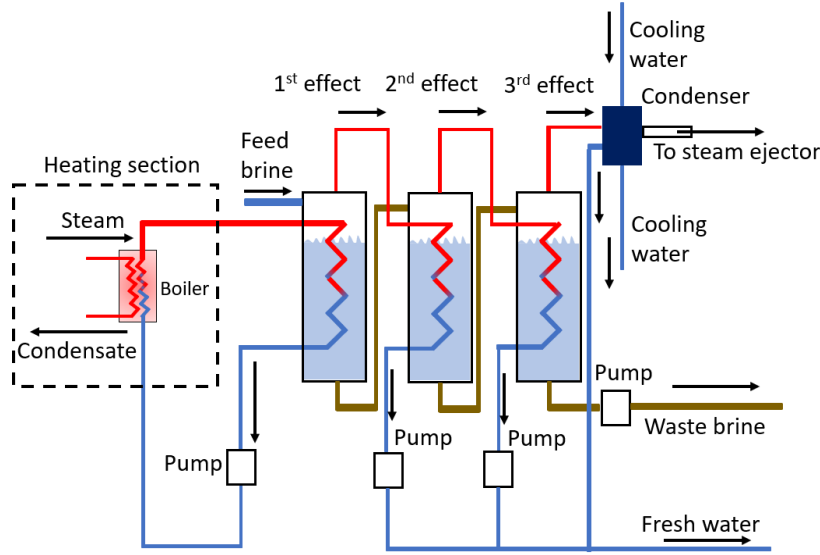


Figure 5: Multi effect distillation [33].

In a more detailed description of the process, an external heat source is utilized in the first effect to boil the brine [34]. Various pre-heating sources can be used including steam [35]. As a fraction of the water content evaporates in the first effect (evaporator), the brine in liquid state is directed to the following effects. The vapor generated within each effect is utilized as a heat source for the following effects. As a result of reduced pressure inside the effects, the brine continues to evaporate throughout the effects without the need to supply any further external heating other than the heat energy supplied in the first effect [36]. The difference between MED and MSF desalination techniques lie in the method of evaporation and heat transfer. For MED, the brine film in contact with the heat transfer surface evaporates. In case of MSF, convective heating of brine occurs within the tubes where in each stage, the vapor produced results from flashing liquid.

1.2.2 Limitations on treating high salinity brine with commercial desalination technologies

The concentration of the brine treated is a primary factor in identifying the most adequate desalination technology to utilize for a certain application. Electrodialysis (ED) is not

widely utilized in industrial desalination since it's only suitable for handling feed brine TDS up to approximately 12,000 ppm (which is significantly lower than typical seawater TDS) and requires periodic cleaning [37]. Nanofiltration (NF) is also not applied for seawater desalination on a large scale for problems related to fouling, the need of continuous membrane cleaning, short lifetimes of membranes, limited recovery ratios as well as the limitations on the feed TDS [38]. RO desalination technology is limited to a maximum brine concentration of approximately 70,000 ppm for the exit brine [39, 40] and their performance dramatically degrades at higher brine concentrations [41] –[44]. This concentration can be reached in various operational scenarios, for example, desalinating seawater typically at 35,000 ppm at a 50% recovery ratio. This is because the hydraulic pressure suitable to overcome the osmotic pressure related to higher salinity brine is more than the maximum allowable pressure for equipment and membranes related to the RO process [40, 45, 46]. Additional challenges related to RO include fouling which significantly affects the process efficiency resulting in raised operational cost [42, 43, 44]. In addition, fouling in RO might result in membrane damage at certain operational conditions [47]. Therefore, higher salinity brine requires adopting thermal desalination techniques (although higher in energy consumption than RO [40, 45, 46]). For the most widely used desalination techniques: MSF and MED, the raised energy consumption results from the relatively high latent heat of evaporation [48, 49]. Primarily, the applicability of thermal desalination plants at higher salinities is constrained by extensive fouling and corrosion and relatively high energy consumption [50].

1.3 Freeze desalination (FD) technology as a candidate to address critical limitations on high salinity brine treatment

Freezing desalination (FD) is considered one of the emerging desalination technologies [20] that can effectively address the described challenges as will be explained in detail through the following subsection. The FD process can be categorized based on contact of refrigerant with solution as: direct contact FD, indirect contact FD and vacuum freezing FD [51, 52, 53].

In some literature, FD process is also described as freezing melting process for desalination (FM) since the process is practically achieved first by the crystallization of ice followed by separation and melting [54] as shown in Fig. 6.

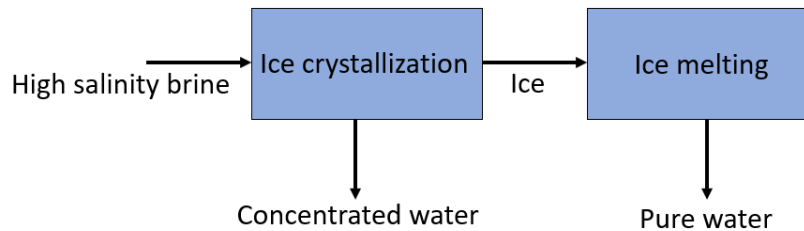


Figure 6: Stages of freezing melting process [54].

1.3.1 Key features of FD for high-salinity brine treatment

Theoretically, the thermal energy required to freeze H_2O is lower than that required for evaporation of seawater (approximately $1/7$) [18]. In addition, due to the low operating temperatures and the absence of membranes, FD requires no pre-treatment and experiences minimal fouling and corrosion [45]. This implies that adopting FD to treat high-salinity brine can potentially outperform commercially available technologies in terms of technical robustness and cost. Moreover, FD can selectively separate specific salts through controlling the operational parameters of the process [55, 56]. FD is also suitable for a wide range of feed TDS (and less sensitive for the change in feed salinity) [57].

Direct FD

In case of direct FD, a refrigerant is expanded through a nozzle into the brine and absorbs heat as it vaporizes after getting in direct contact with the brine [54]. A liquid hydrocarbon is commonly used in this process (for example butane) where it would have minimal mixing with water [57]. When injected into the brine, the refrigerant evaporates and withdraws heat from the brine resulting in ice crystals formation [57]. The formed mixture of brine and ice

is washed by water to obtain pure ice [57]. The pure ice is then melted to obtain liquid pure water [57]. Figure 7 shows direct freezing desalination process.

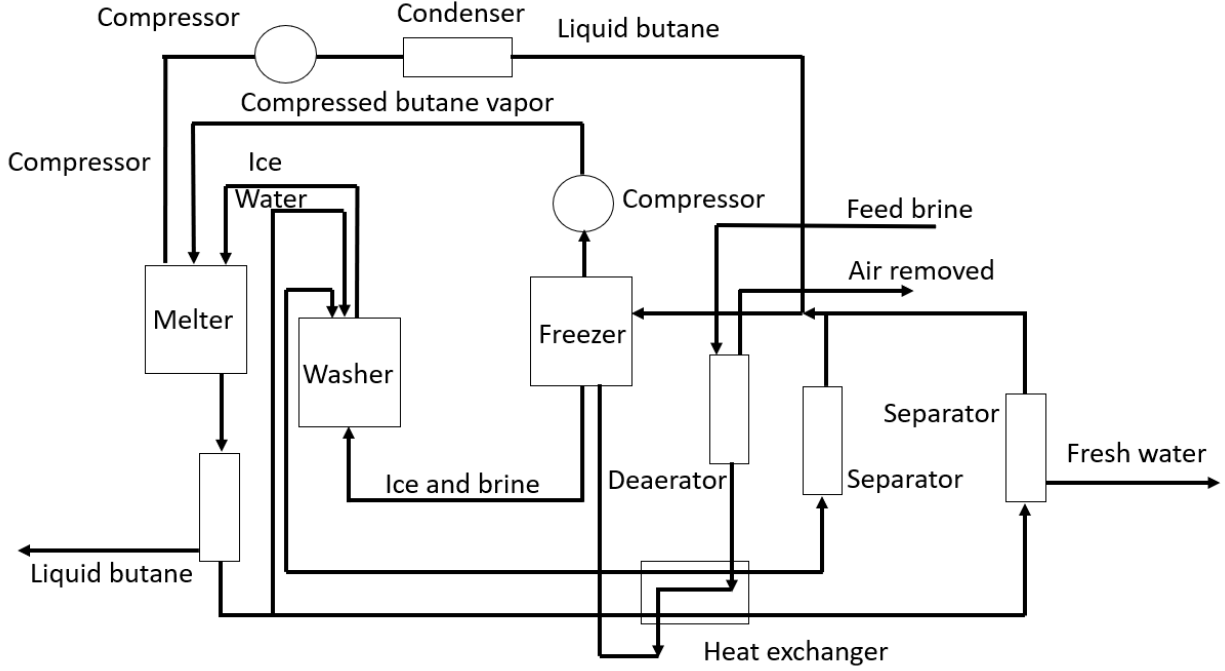


Figure 7: Schematic of direct freezing desalination process [57].

The refrigerant vaporized in the freezer is then compressed (temperature raised) and logged to the melter to transform ice into liquid water. The remaining refrigerant vapor is compressed and condensed at high pressure before being recycled to the freezer once more [57]. The disadvantage of this technique is that the ice usually contains trapped amounts of undesirable refrigerant which makes the generated water non-potable [57].

Vacuum FD

In this technique, a vacuum pressure is being pulled from the brine containing compartment or container where the water is used as the refrigerant [58]. First, when the pressure is reduced till reaching the saturation pressure value corresponding to the initial temperature of brine, part of the liquid evaporates and freezing takes place [59]. The amount of latent

heat required for the liquid to evaporate is being withdrawn from the liquid and therefore sensible cooling starts to occur for the liquid mass [60]. Cooling process of the brine continues further till hitting the freezing temperature and ice crystals start to form [61]. The temperature of the mixture becomes constant till all available freezable water changes to ice [62]. Afterwards, there might be a third stage to the process where further vacuum would result in sublimation of the solid (H_2O change of phase going from solid to gas phase directly) [62]. Pulling vacuum to adequate low levels is a high work consuming process when performed using vacuum pump and thus the technique might not be economically feasible. Figure 8 describes vacuum freezing desalination cycle.

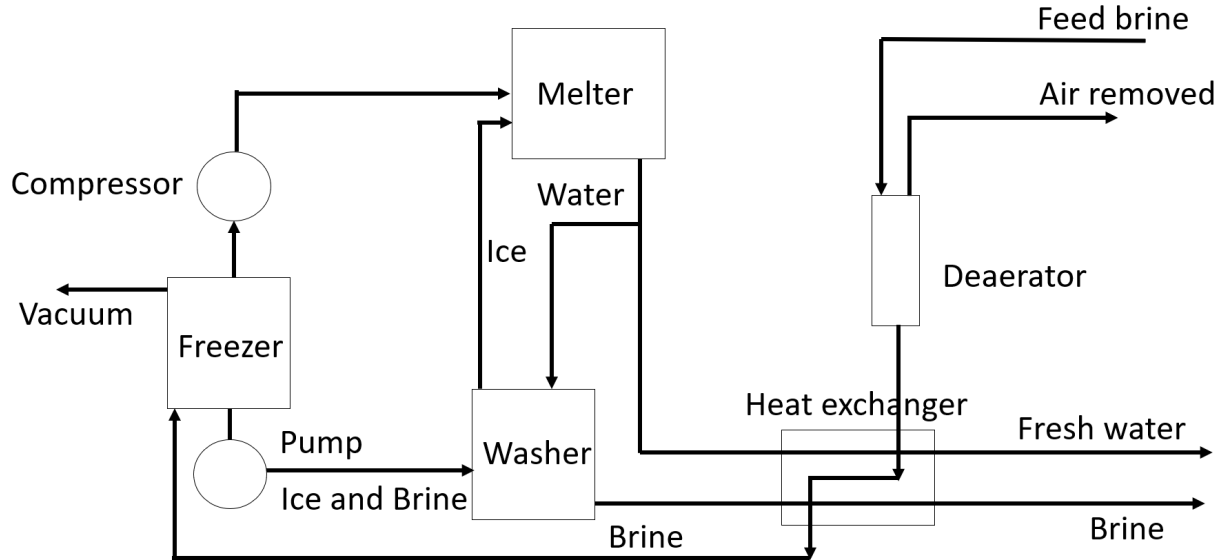


Figure 8: Schematic of vacuum freezing desalination process [57].

Indirect FD

In case of indirect FD, there is a separating boundary between the refrigerant and the brine during crystallization. The desalinated water generated from indirect FD cycles is refrigerant free [63] which saves the cost and complication of using special refrigerants to meet standards described previously. In this technique, a conventional vapor compression

refrigeration cycle is utilized to remove heat from the brine stream till the point of crystallization while the heat generated by the condenser of the refrigeration cycle is used to melt the generated ice after being washed and separated from the rest of the mixture as shown in figure 9. For applying indirect freezing desalination on a solid surface, there is difficulty on continuously removing the formed ice layer and maintaining low corrosion levels as well as acceptable life time for the solid surface.

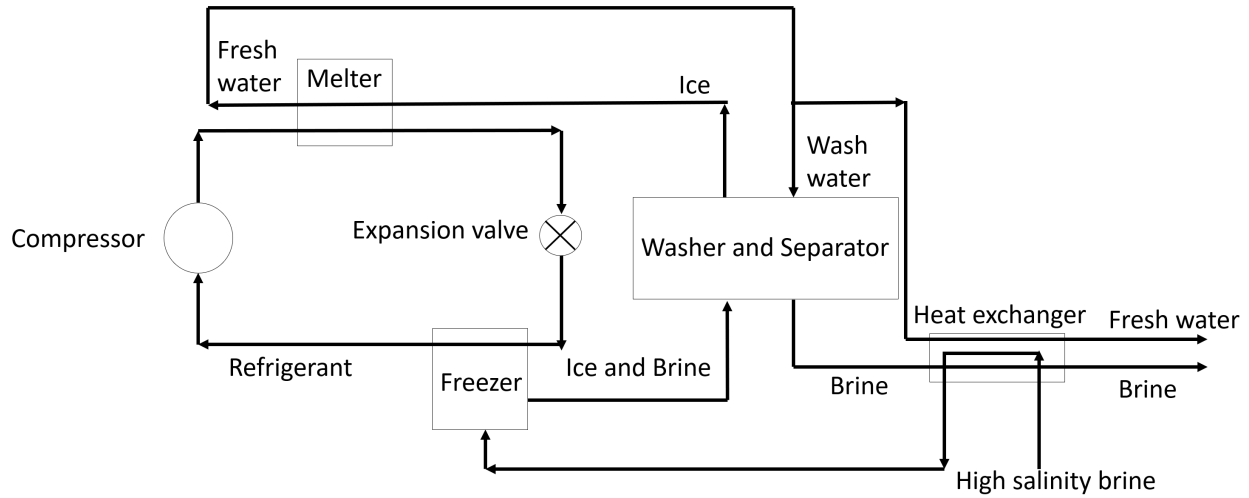


Figure 9: Schematic of indirect freezing desalination process [57].

1.3.2 Advances in overcoming technical challenges of FD

FD is a promising technology that has garnered significant interest in recent years. As highlighted briefly in the previous subsections, the standard FD systems showed a range of practical and technical difficulties. A common issue that emerged for both direct and indirect FD was the challenge of separation of the salt-hydrates and unfrozen brine from the ice (pure H_2O in solid state). Another technical challenge that degraded the quality of treated water generated by direct FD was the difficulty of separation of the refrigerant carried over with the desalinated water [54]. This technique is linked to poor quality of desalinated H_2O due to the chemical bonds formed between the refrigerant and water and imposes environmental concerns related to the refrigerant. In the case of indirect FD, the design involves a barrier

between the refrigerant and brine where the crystallization occurs over a solid surface (for example evaporator surface). The problem with this technique is the relatively poor heat transfer because of the ice layer formed on the surface in addition to high corrosion and lower life cycle. In other words, the ice layer formed on the cooling surfaces deteriorates the system's thermal efficiency unless a complex (and expensive) design to scrape the ice off the cold surface is applied. For vacuum FD technique, pulling the vacuum to adequate low levels significantly consumes work and thus deemed economically unfeasible.

Lately, research efforts have led to acceleration of FD development toward industrial implementation by addressing some of the major technical difficulties described above. Recent studies reported an FD system concept that bridges the direct and indirect FD techniques, alleviating the crucial issues associated with the standard configurations when used standalone [64, 65]. The proposed solution is based on the utilization of an intermediate cooling liquid (ICL) circulating between the refrigeration system (that provides cooling for the FD process) and a freezing chamber as shown in Fig. 10.

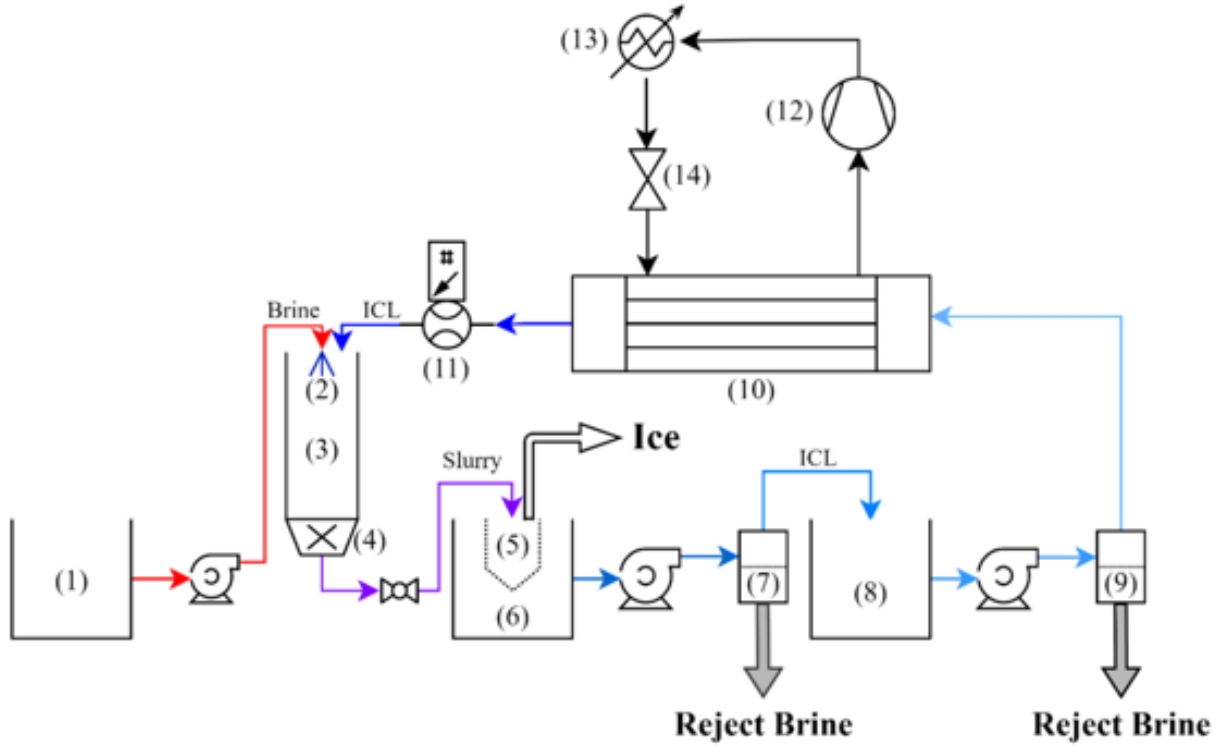


Figure 10: Schematic of FD system utilizing intermediate cooling liquid (ICL) [65].

The feed brine is injected into the cold ICL fluid inside the freezing chamber where crystallization takes place. The freezing column assembly setup is shown in Fig. 11.

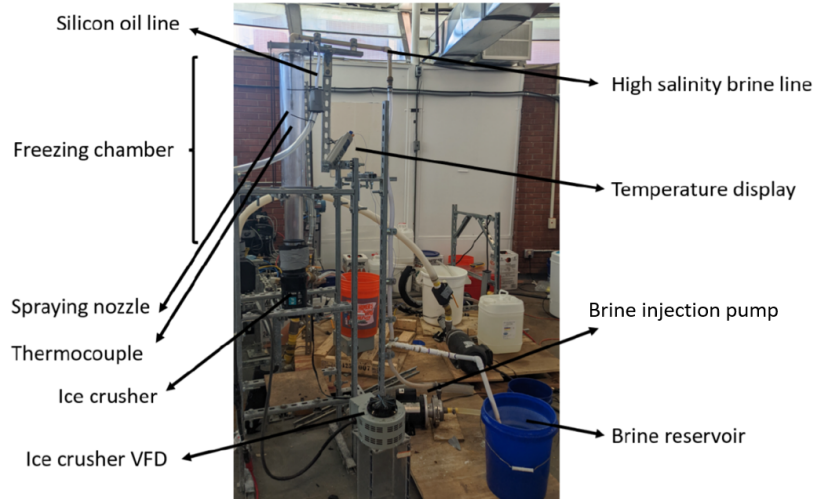
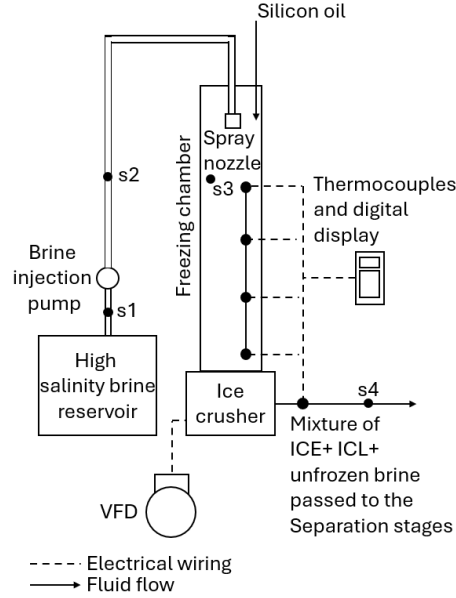
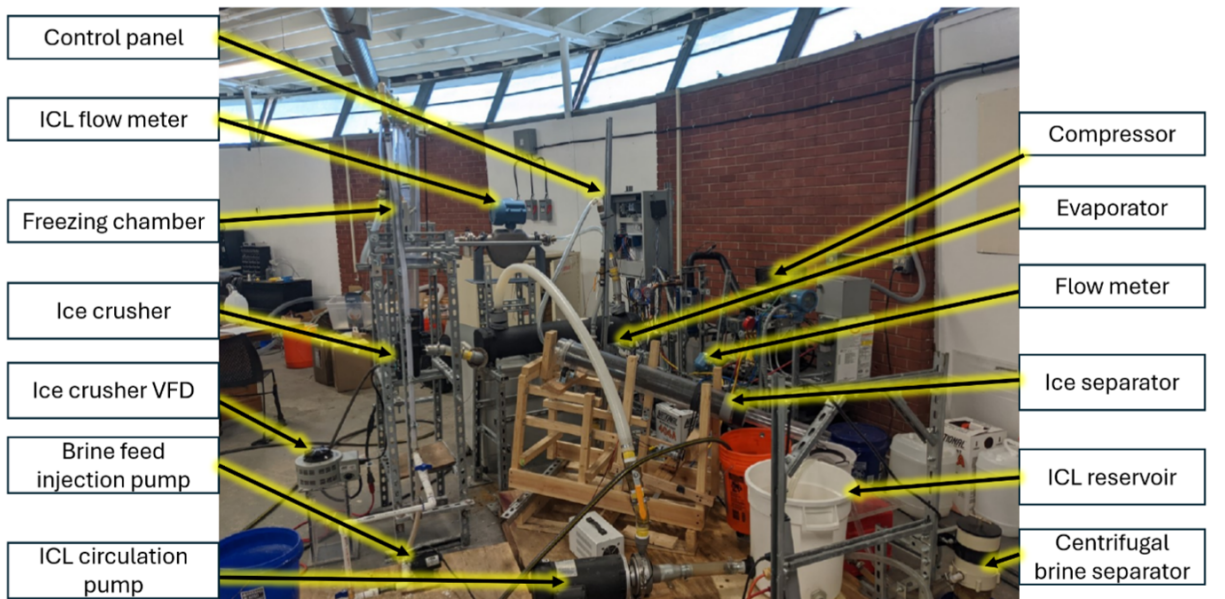


Figure 11: Freezing column assembly prototype.

The feed brine is collected inside the container (high salinity brine reservoir shown in Fig. 11) before being pulled by the pump (s1 to s2) and injected into the freezing chamber through a fine nozzle. The ICL and brine mix inside the freezing chamber (s3) and ice crystallizes. The mixture is then crushed by a crusher before the slurry (s4) is passed to the separator. Ice is then separated from the concentrate (unfrozen brine+ any formed salts) and the ICL. The separated ICL is circulated back into the system to be cooled inside the evaporator of the refrigeration system before being fed again into the freezing chamber.

The experimental characterization of the FD system utilizing the ICL has proved its ability to generate ice at acceptable TDS values. Yet, the concept still suffers from significant energy and cost penalties. The full lab setup used for the experimental characterization of the concept is shown in Fig 12.

First, the intermediate fluid is cooled by the refrigeration cycle. The refrigeration cycle composes of a compressor, a condenser, an expansion valve, and an evaporator and utilizes the R404-A refrigerant where the compressor is a low temperature compressor manufactured by Copeland compressors model 2DL3F20KE-TFC. The compressor operates within an evaporating temperature range of -18°C to -40°C and a condensing temperature range of 4°C to 60°C . The heat transfer between the intermediate fluid and the refrigerant takes place in the shell and tube evaporator. The heat exchanger is a Westermeyer DX5-1 horizontal shell-and-tube heat exchanger where the shell is manufactured of steel and the tubes are manufactured of copper. The evaporator is equipped with baffles to enhance the cooling effect. It is also notable to mention that the entire outer surface is wrapped in 20 mm of thermal insulation to reduce thermal losses. Once cooled, the intermediate fluid is transferred to the top of the freezing chamber. The intermediate fluid is circulated using a pump controlled by a variable frequency drive (VFD). The pump is a three-phase, low-temperature, stainless-steel, corrosion-resistant model from Weg. To accurately quantify the intermediate fluid's flow rate, an Emerson Micro Motion Coriolis mass flow meter is installed downstream of the evaporator heat exchanger. Brine is extracted from a container, pressurized by a diaphragm pump (at a rate of 0.13 kg/min), and introduced into the intermediate fluid through a nozzle, initiating nucleation in the crystallization column. The nozzle tip is positioned at a level higher than the intermediate fluid's level in the freezing chamber. The nozzle sprays brine droplets ranging in size from 50 to 100 micrometers where the smaller size of the brine droplets enhance heat transfer by increasing the contact surface area between the brine and the cold intermediate fluid. The ice, unfrozen brine and ICL mixture leaving the freezing chamber is then directed to a gravity separation column (where unfrozen brine



2 Thermochemical modeling and configuration optimization of FD

Freeze desalination (FD) is considered one of the emerging desalination technologies that can effectively address the challenges facing the current commercial desalination techniques when treating high salinity brine [20, 67, 68]. To date, the energy performance of FD is not well understood due to limited knowledge of the behavior of brine upon freezing and the optimal configuration of the system [69]. This includes lack of knowledge about the brine's cooling load of freezing and thermochemical properties at different freezing temperatures of the system. This section contributes to a better understanding of the FD process by addressing the following primary knowledge gaps:

1. Knowledge about the concentrated seawater cooling load of freezing and threshold of freezing, where cooling the seawater results in variation of the cooling load of freezing and each of the salt-hydrates forms at a specific temperature, introducing a new source of thermal load that needs to be determined carefully for accurate energy analysis of FD systems. In addition, the study introduces knowledge about the concentrated seawater's other thermochemical properties.
2. Knowledge about the FD system's optimal configuration (most energy efficient configuration) and its optimal operational parameters along with the corresponding energy consumption performance.

The following subsections focus on addressing the described research gaps which are critically essential for maximizing the FD system's energy efficiency.

2.1 Contextualizing the issues and research objectives for maximizing the FD system energy efficiency

This subsection sets the stage for critical findings of this research work through establishing the context and scope of the issues, highlighting the solutions novelty, and providing insight into the selected research methodology. As described previously, the FD technology can effectively address the challenges facing the currently adopted commercial desalination techniques when treating high salinity brine [20, 67, 68]. However, utilizing the FD technology at an industrial scale is still unattainable due to major issues and knowledge gaps. The most prominent issue with the FD technology is the raised energy requirement (it consumes less energy than the evaporative techniques, yet the energy consumption is still high and the FD system’s energy efficiency has not been previously optimized). The question is, what is the FD system’s configuration that maximizes its energy efficiency?. In FD technology, a dominant fraction of the consumed energy is used to achieve the low temperatures inside the freezing chamber. Therefore, to significantly enhance the energy efficiency of FD, the recovery of the cooling energy is indispensable.

Vapor compression is a widely utilized energy efficient cooling technology that is suitable to provide cooling for FD. For an FD system cooled by vapor compression technology, cooling energy recovery can be realized in the condenser or through precooling the inlet brine feed. This builds an impression that an FD system configuration utilizing vapor compression technology with cooling energy recovery feature will raise the FD process’ energy efficiency. Yet the FD system’s configuration issue raised earlier cannot be fully addressed without answering the following questions:

- To maximize the FD system’s energy efficiency, what is the best vapor compression system configuration to utilize (single stage/ cascade)?
- What is the best approach for cooling energy recovery within the FD system to maximize its energy efficiency (cooling energy recovered in the condenser of

the vapor compression cycle/ cooling energy recovered through precooling of the input brine)?

This also raises a pivotal concern about selecting the optimal configuration of the FD system (the configuration with maximized energy efficiency). Given the infinite number of possible configurations for an FD system and the wide variety of components that can be utilized, how would we prove that a selected FD system configuration is the optimal one (such that -theoretically- no other FD configuration can prove more energy efficient)?. For that, a heuristic-driven brute-force with early termination approach is adopted as described in Fig. 13.

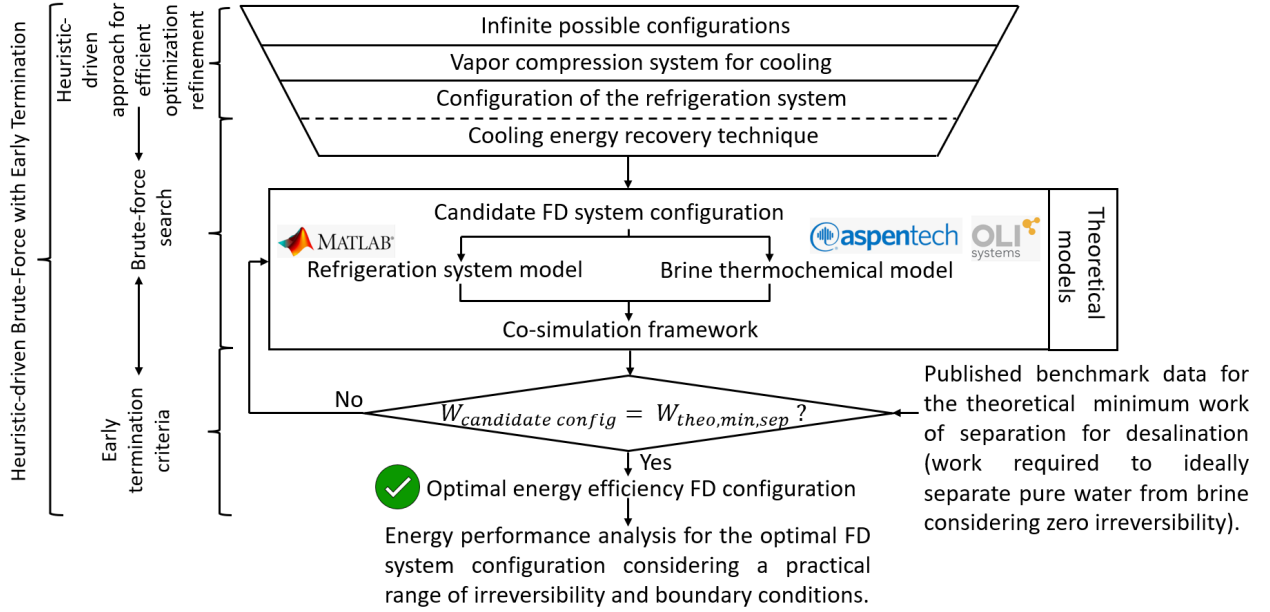


Figure 13: Schematic of the heuristic-driven brute-force with early termination approach adopted to identify the optimal FD system configuration.

In Fig. 13, the approach adopted to identify the optimal FD system configuration is explained. The number of possible configurations for an FD system are infinite, and critical literature review and calculations have been performed offline to narrow down the possibilities of the optimal FD configuration. Such preliminary analysis let us know that a vapor compression system would be suitable to provide cooling for the FD system. The following step

is related to the technique of cooling energy recovery adopted which then narrows down the configurations even more. In other words, starting with infinite possible configurations for the FD system, optimization refinement narrows down the search pool based on deep literature review along side with offline calculations and analysis. Theoretical analysis considering no irreversibility are adopted and the optimal FD system configuration can be identified when the theoretical outcomes converge with the early termination criteria based on the published benchmark theoretical minimum work of separation for desalination (work required to ideally separate pure water from brine considering zero irreversibility) [70]. The refrigeration model is developed in MATLAB and the brine thermochemical properties are estimated using ASPEN PLUS + OLI model (each of those models will be explained in details in the following sections), where the simulation is orchestrated using a MATLAB master code to estimate the work of the treatment process and the quality of the purified water under different operational parameters. Different FD system configurations were simulated to find the most energy efficiency one. During the brute-force search, the different FD system configurations are tested till the optimal configuration has been identified (when the work consumption matches the corresponding minimum work of separation for desalination as the stop criteria for the search). Details about the selection process and the FD configuration selected is meticulously described later in this section. The validation of the models developed is presented in the next section to support the optimal FD system configuration claimed.

The optimal FD system configuration selected is generalized for FD systems (direct, indirect, ...). Another general issue linked to FD technology is the significant difficulty of separating the brine and salt-hydrates from the ice. Typically, a fraction of unfrozen brine gets carried over with the generated ice (will be described in detail through a following subsection). The questions central to understanding the relevant knowledge gap encompass:

- What is the amount of the unfrozen brine carried over with the formed ice?
- What are the FD system parameters affecting the amount of unfrozen brine car-

ried over with the formed ice?

- How would the unfrozen brine carried over with the generated ice affect the treated water salinity collected at the output of the FD system?

2.2 Thermochemical behavior of concentrated seawater upon freezing

To accurately model the thermochemical transformation of the brine and formation of ice and salt-hydrate compounds as the brine goes through the freezing process, the OLI Alliance engine for Aspen PLUS is utilized [71, 72]. The OLI utilizes the mixed solvent electrolyte model (MSE) that can predict electrolyte behavior from infinite dilution to molten salts. The MSE model is based on readily predicted equilibrium constants and other standard state partial molal thermodynamic properties. The activity coefficient model is based on a Uniquac term, an extended Debye-Huckel term, and a middle-range electrolyte term. The developed integrated ASPEN PLUS + OLI model includes a heat exchanger unit with fixed outlet temperature. The seawater at various levels of concentration is introduced to the heat exchanger. The model determines the chemical composition of the output stream at the prescribed outlet temperature, including the volume fractions of generated ice, salt-hydrates (if any), and the unfrozen concentrated brine. In this study, the typical composition of seawater is used for the feed stream at different concentrations of 35,000 ppm, 50,000 ppm, 75,000 ppm, 100,000 ppm, 150,000 ppm, and 200,000 ppm. The ionic composition of all the investigated brines is that of typical seawater [73] shown in Table 2. Various concentrations are formed by changing the pure H_2O content of this standard composition where the adopted pure water mass fraction values per unit mass of feed are 0.96, 0.95, 0.925, 0.9, 0.85 and 0.8. This is consistent with seawater desalination where the reject brine is created by extracting freshwater from the seawater.

Table 2: Typical ionic composition of seawater [73].

	Cl^- (ppm)	Na^+ (ppm)	SO_4^{2-} (ppm)	Mg^{+2} (ppm)	Ca^{+2} (ppm)	K^{+1} (ppm)	HCO_3^- (ppm)
Typical Seawater	18980	10556	2649	1262	400	380	140

2.3 Heuristic refinement for optimizing the FD system configuration

This part discusses the primary set of analysis performed to narrow down the huge amount of configuration alternatives of the FD system. To achieve that, it is useful to answer the following question: is it possible to recover all the cooling energy through precooling by transferring heat to the incoming brine ?.

To answer this question, the configuration presented in Fig. 14 is investigated where both of the separated cold streams (ice and concentrate) are passed directly to parallel the precooling heat exchangers to exchange heat with the feed brine.

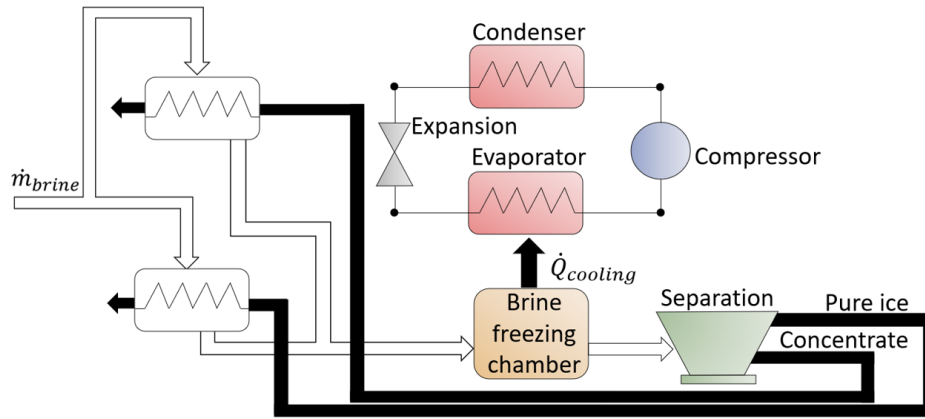


Figure 14: Proposed FD configuration considering energy recovery through precooling the feed brine.

Enthalpy method correlations are utilized to estimate the temperature and the ice fraction for each of the return and feed streams as shown through the following equations:

$$u \frac{\delta h}{\delta x} = U A (T_{st} - T_w) \quad (1)$$

$$T_{st} = \begin{cases} T_m + \frac{h}{C_s} & h \leq 0 \\ T_m & 0 < h < h_{sl} \\ T_m + \frac{h-h_{sl}}{C_l} & h \geq h_{sl} \end{cases} \quad (2)$$

$$\phi_{ice} = \begin{cases} 1 & h \leq 0 \\ 1 - \frac{h}{h_{sl}} & 0 < h < h_{sl} \\ 0 & h \geq h_{sl} \end{cases} \quad (3)$$

$$h_{sl} = \begin{cases} C_s (T_{st} - T_m) & T_{st} < T_m \\ C_l (T_{st} - T_m) + h_{sl} & T_{st} > T_m \end{cases} \quad (4)$$

Where u is the relative velocity between each of the two fluid streams and the interface in m/s, h is the enthalpy of the fluid in J and δx resembles the spatial coordinate step in the domain of interest in m. UA is the local overall heat transfer coefficient in W/°C, T_{st} is the temperature of the stream in °C and T_w is the temperature of the interface or wall in °C. T_m is the melting temperature in °C, C_s is the solid phase specific heat capacity in J/kg K, C_l is the liquid phase specific heat capacity in J/kg K, h_{sl} is the latent heat of fusion (or solidification) in J and ϕ_{ice} represents the phase of fluid.

The enthalpy is first estimated using Eq. 1, then the stream temperature is updated with Eq. 2. The crystallized ice fraction is estimated using Eq. 3 and the enthalpy of the stream at the current timestep is updated utilizing Eq. 4.

Figure 15 shows plots of the thermal behavior of the return ice stream in the case of 35,000 ppm feed salinity, a freezing temperature of -35°C, ambient temperature of 25°C, and unfrozen brine stream (high salinity return liquid stream) resembling 2.5 % of the mass of the return ice stream (unfrozen brine entrapped in pockets within the generated ice).

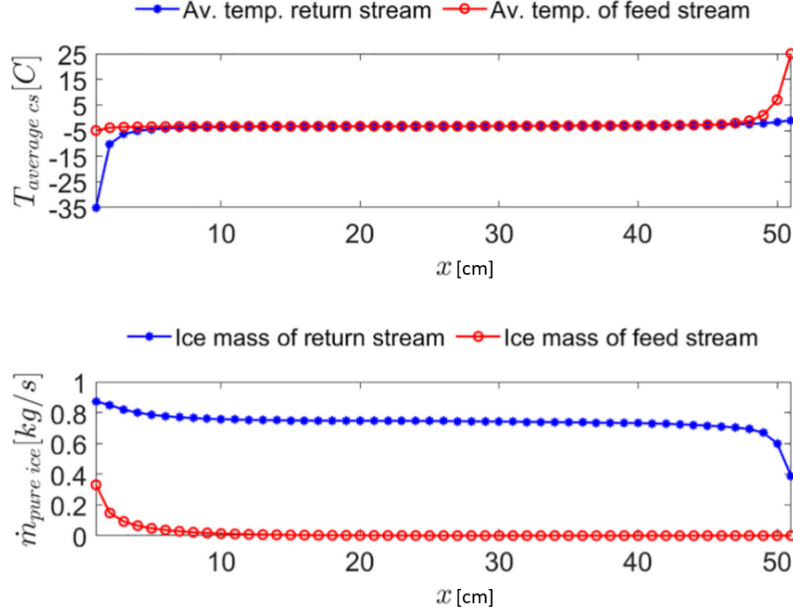


Figure 15: Ice mass and temperature illustration along the FD system's precooler.

Figure 15 shows the temperature profile and the mass of pure ice related to the return ice and feed brine streams. The two streams exchange heat in a counter flow configuration precooling heat exchanger. The results show that the entire mass of formed ice cannot be completely melted through the precooling of the feed brine stream only, and accordingly further energy recovery should be adopted in the FD configuration utilized.

Based on the outcomes of this analysis, the pool of the possible optimum FD configurations has been narrowed down to the ones with a cascade coupling heat exchanger which is essential for complete energy recovery.

2.4 The optimal FD system configuration

The generalized optimal FD system (direct and indirect) configuration corresponds to the maximum efficiency of the system in terms of the energy used per unit mass of treated water. The maximum efficiency can be achieved by maximizing the coefficient of performance (COP) of the vapor compression cycle providing cooling, and by maximizing the energy recovery from the discharging streams. After the problem refinement presented in the previous section,

brute-force search is conducted to select the most energy efficient among different possible FD configuration candidates.

To establish a clear early termination criteria, the searched configurations will be investigated based on theoretical analysis disregarding the irreversibility of the systems. Therefore, the published benchmark theoretical minimum work of separation for work-driven desalination process [70] can be used for the early termination criteria (once the theoretical work consumption of a certain tested configuration matches the corresponding theoretical minimum work of separation, the search terminates). The refrigeration cycle adopted is a reversed Carnot cycle (Carnot refrigerator) presented in Fig. 16.

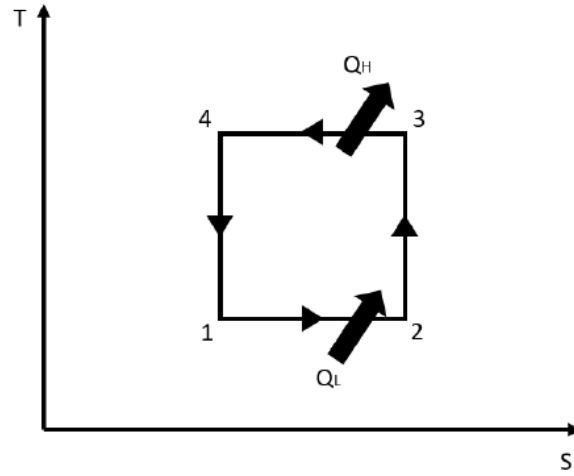


Figure 16: Refrigeration cycle utilized for theoretical analysis of different freeze desalination system configurations.

In figure 16, process 1 to 2 is isothermal heat addition, process 2 to 3 resembles isentropic compression, 3 to 4 is isothermal heat rejection and 4 to 1 counts for isentropic expansion. A summary of the assumptions applied for the theoretical analysis:

- No heat losses to the ambient.
- Perfect heat transfer inside the system's heat exchangers (the heat transfer effectiveness inside the condenser, the evaporator and the brine freezing chamber equals 1).

- The evaporating temperature equals the brine freezing chamber temperature.
- The condensing temperature matches the ambient temperature.
- The ambient temperature is fixed to a value of 25°C.
- The crystallized ice can be perfectly separated from the concentrate after leaving the freezing chamber (without any carried over contamination or heat losses during the process).
- No friction losses.

Based on the above assumptions, the coefficient of performance of the investigated configurations is calculated using Eq. 5:

$$COP_{cycle} = \frac{T_{evap}}{T_{cond} - T_{evap}} \quad (5)$$

where T_{evap} is the evaporating temperature and T_{cond} is the condensing temperature. The work applied by compressor is calculated using Eq. 6:

$$W_{compressor} = \frac{Q_{evap}}{COP_{cycle}} \quad (6)$$

where Q_{evap} presents the heat absorbed by the refrigerant at the evaporator which is equal to the load of the freezing chamber. The heat released from the condenser is presented by Eq. 7:

$$Q_{cond} = W_{compressor} + Q_{evap} \quad (7)$$

In case of utilizing cascade refrigeration cycles, the heat generated by the condenser of one cycle is passed to the evaporator of the following cycle and the mass of ice generated by the system might be fully or partially melted to recover cold energy. This reduces the load

on the evaporator of the following cycle as presented in Eq. 8:

$$Q_{evap,i+1} = Q_{cond,i} - Q_m \quad \text{where } i > 1 \quad (8)$$

where i is the refrigeration cycle number, $Q_{evap,i+1}$ is the load carried by the evaporator of the following cycle, $Q_{cond,i}$ is the amount of heat rejected at the condenser of the cycle i and Q_m corresponds to the heat absorbed by the ice melted inside the condenser shell of cycle i . The overall work of the freeze desalination cycle is the summation of the work consumed by all the utilized cycles' compressors as shown in Eq. 9:

$$W_{desal} = \sum_{i=1}^n W_{compressor,i} \quad (9)$$

where W_{desal} is the overall work of the freeze desalination system and n is the total number of refrigeration cycles utilized. The details of the investigated configurations are described through Appendix A. An example of the investigated configurations during brute-force search is presented in Fig. 17:

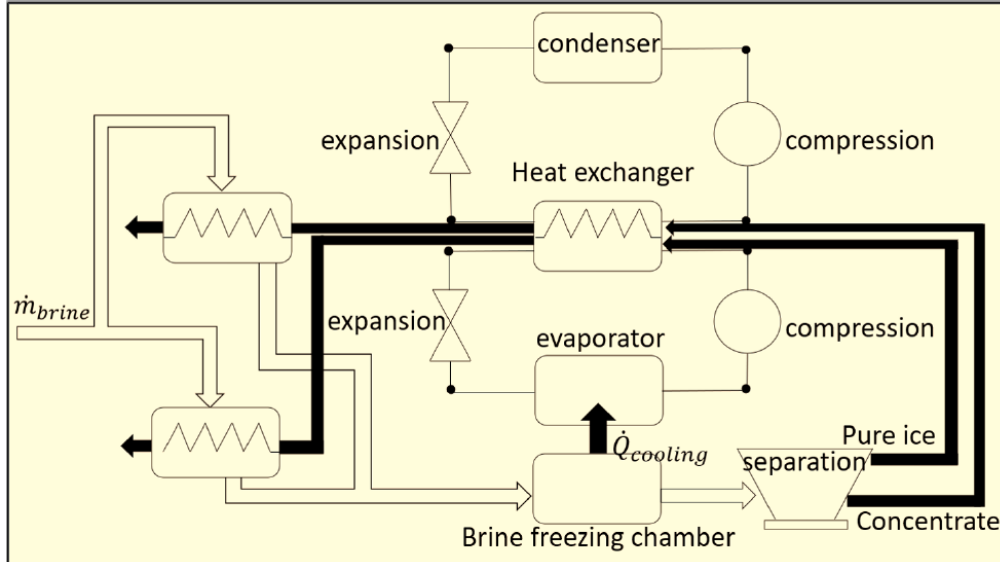


Figure 17: Candidate configuration with both cold streams passed to the intermediate heat exchanger then to the precoolers.

In this configuration, both of the separated streams are directed to the condenser shell for energy recovery. The two streams exit the condenser's shell at 0°C and are then passed to perform precooling of the entering brine. The cooling load and the work of separation was calculated as shown in Figs. 18 and 19 :

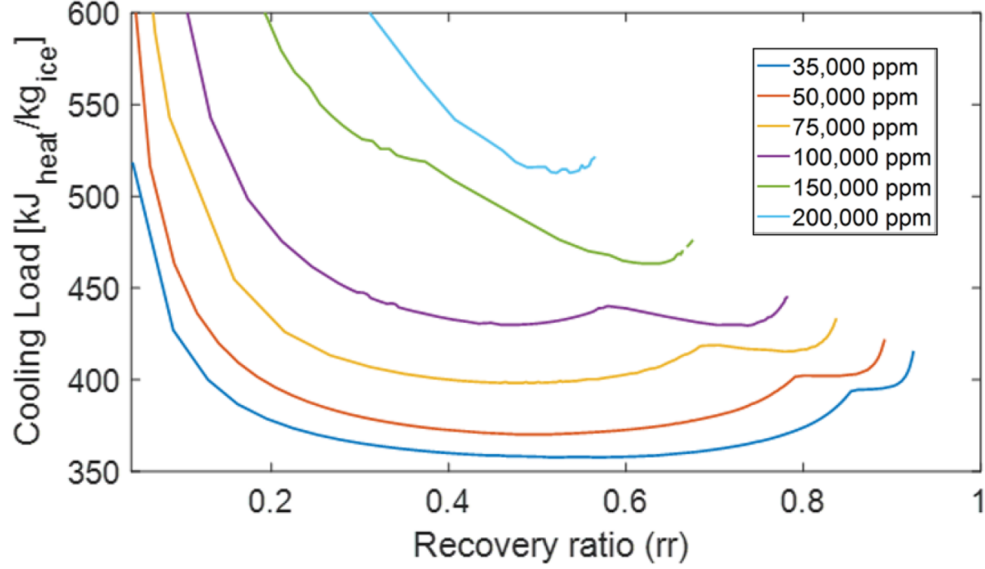


Figure 18: Cooling load at different recovery ratio values for the candidate configuration with both cold streams passed to the intermediate heat exchanger then to the precoolers.

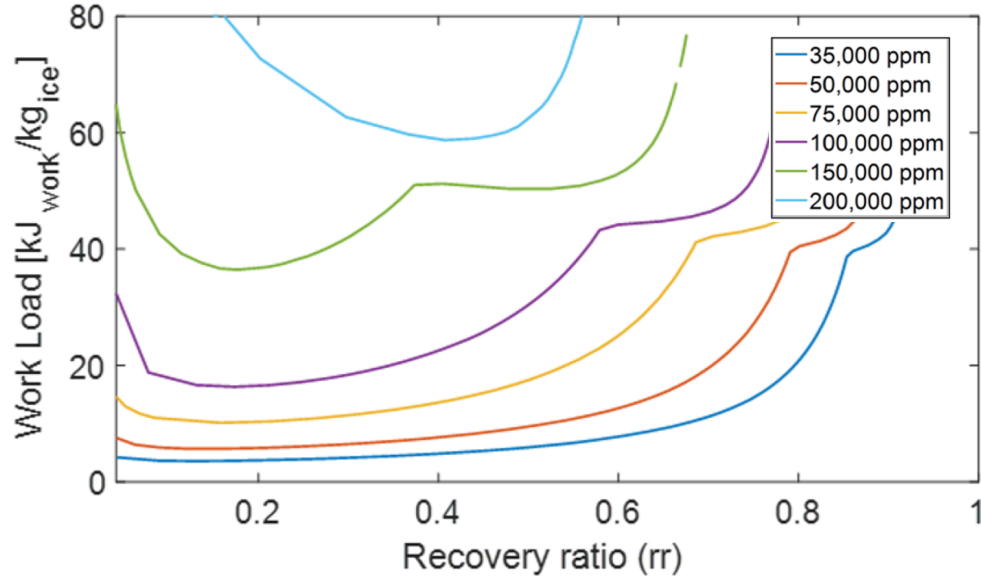


Figure 19: Work of separation at different recovery ratio values for the candidate configuration with both cold streams passed to the intermediate heat exchanger then to the precoolers.

In Fig. 18, the cooling load of the brine per unit mass of ice crystallized (related to the configuration shown in Fig. 17) is illustrated at each recovery ratio value for different feed TDS values. At lower recovery ratio values, the specific cooling load is relatively high because of the low efficiency of the cooling energy recovery. As the recovery ratio value increases, more ice is being formed and the specific cooling load value starts to decrease. In the case of higher recovery ratio values, the energy requirement further increases which results in a rise in the specific cooling load values. Also, the higher the feed TDS, the lower the temperature needs to go (inside the freezing chamber) to crystallize the same amount of ice compared to lower TDS feed. Accordingly, the specific cooling load of the brine increases by the increase in the feed TDS. This reflects directly on the specific work load of the system (Fig. 19) where the specific work is calculated from dividing the specific cooling load (18) by the coefficient of performance (COP).

Another configuration investigated is shown in Fig. 20 where the generated ice is first passed to the intermediate heat exchanger for melting, then logged to the precooler for further cooling energy recovery. The ice stream exits the condenser shell as liquid H_2O at $0^\circ C$. The cold concentrate stream is passed to the precoolers directly for raising the system's energy efficiency.

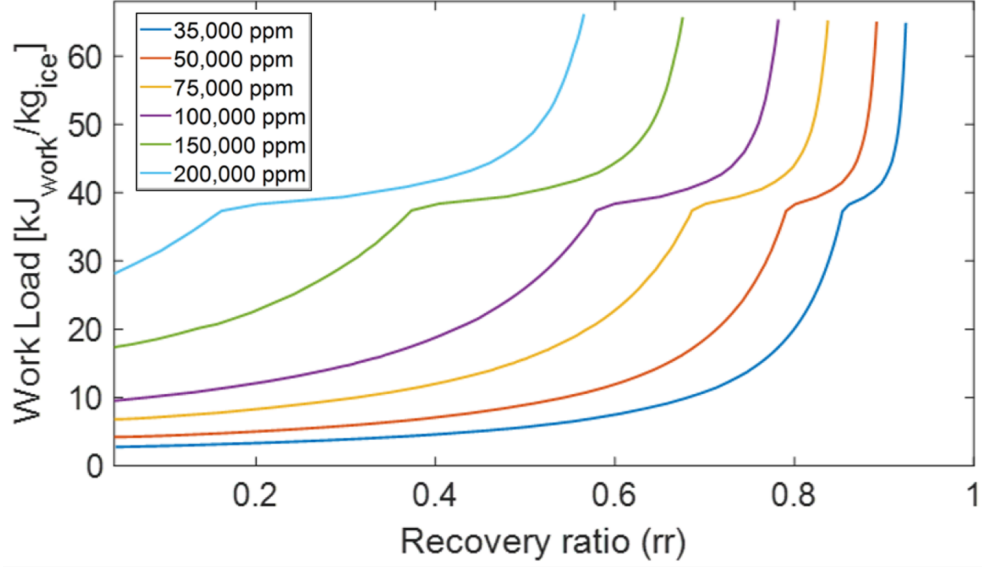


Figure 22: Work of separation at different recovery ratio values for the candidate configuration with ice passed to the intermediate heat exchanger then to the precooler and concentrate stream passed directly to the precooler.

In Fig. 21, the specific cooling load related to the FD system configuration in Fig. 20 is presented. Compared to the previously discussed FD configurations, the results clearly show an increase in the efficiency of the cooling energy recovery process which reflects on the specific cooling load. At lower recovery ratio values, the cooling load is relatively low. As the recovery ratio increases the cooling load increases. As explained previously, higher feed TDS is associated with higher cooling load requirement to reach the same recovery ratio values which is shown in the results. This also reflects on the specific load values presented in Fig. 22 which is calculated based on dividing the specific cooling load by the COP.

The results presented above are not only useful to identifying the optimal FD system configuration but also supports the understanding of the thermal performance of FD systems. The results figures above show that the work load of separation increases at higher brine concentrations since the higher the concentration of the brine, the more cooling energy it needs to freeze. Curves (corresponding to all the simulated concentrations) experience a significant bump at temperature of -23°C (plots indicating the temperatures along with detailed explanation is presented in the following sections). This indicates the start of formation

of hydrohalites ($\text{NaCl} \cdot 2\text{H}_2\text{O}$). When hydrohalites start to form, the rate of ice generation experiences a significant rise while the rate of brine fraction reduction reduces significantly at this temperature. This is a result of the amount of salts precipitated from the brine. The reduction in mass of ions in the brine solution makes freezing less energy intensive which explains the change of trend for all curves at the temperature of -23°C .

Based on the results above, the FD system configuration presented in Fig. 23 can achieve the maximum efficiency by full energy recovery from the ice and discharging streams and maximizing the COP by using a cascade configuration.

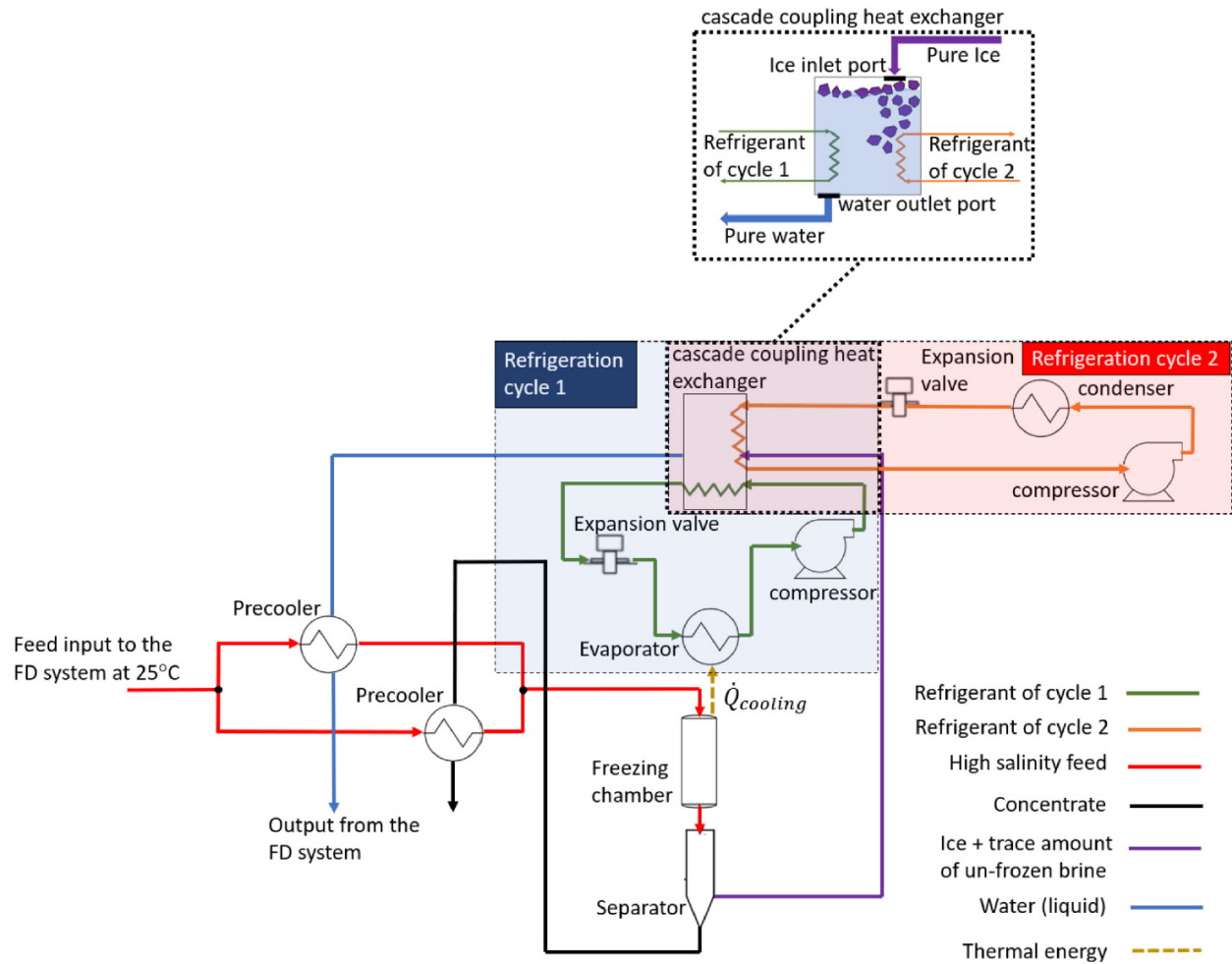


Figure 23: Optimal freeze desalination system configuration.

For the optimal FD configuration presented in Fig. 23, the inlet feed brine is first pre-cooled (using cooling energy recovered from the return streams), then further cooled down in

the freezing chamber to partially freeze. The freezing chamber is cooled by a cascade refrigeration cycle. The stream leaving the freezing chamber is introduced to a separation stage to separate the ice in the slurry from the concentrate (including unfrozen brine and other formed solids). The separated ice may have a percentage of high salinity unfrozen brine encapsulated in pockets within the ice [74, 75, 76] (the exact amount of entrapped brine is quantified based on laboratory experiments described later in this section). The concentrate stream leaving the separator is utilized for precooling the inlet feed brine. The return ice stream is also utilized for cooling energy recovery through melting inside the shell-side of the cascade coupling heat exchanger (explained in the following) and then precooling the inlet feed brine.

Effectiveness of the separation process

After generating ice in the freezing chamber, it must be separated from the rest of the slurry before being melted. Researchers have used several separation methods for this purpose, including presses, gravity drainage, centrifugal drainage, filter, wash column and sweating ice [77]–[82]. None of these methods can perfectly separate the unfrozen brine from the ice and in all cases the separated ice will contain some amount of unfrozen brine. This brine is later mixed with the melted ice during melting and degrades the quality of the final treated water. It has been shown that generally the higher the recovery ratio (rr), corresponding to lower freezing chamber temperature, the higher the TDS of the treated water [83]. In other words, as the recovery ratio - and the salinity of the rejected unfrozen brine - increases, the quantity of the unfrozen brine contaminating the treated water also increases. In this work, effectiveness of the separation process is approximated using the data obtained from an experimental freeze-desalination prototype developed by the authors [84, 66]. The experimental setup utilized composes of two primary system loops: The refrigeration loop and the intermediate cooling liquid (ICL) loop coupled together through a shell and tube evaporator heat exchanger as shown in Fig. 24:

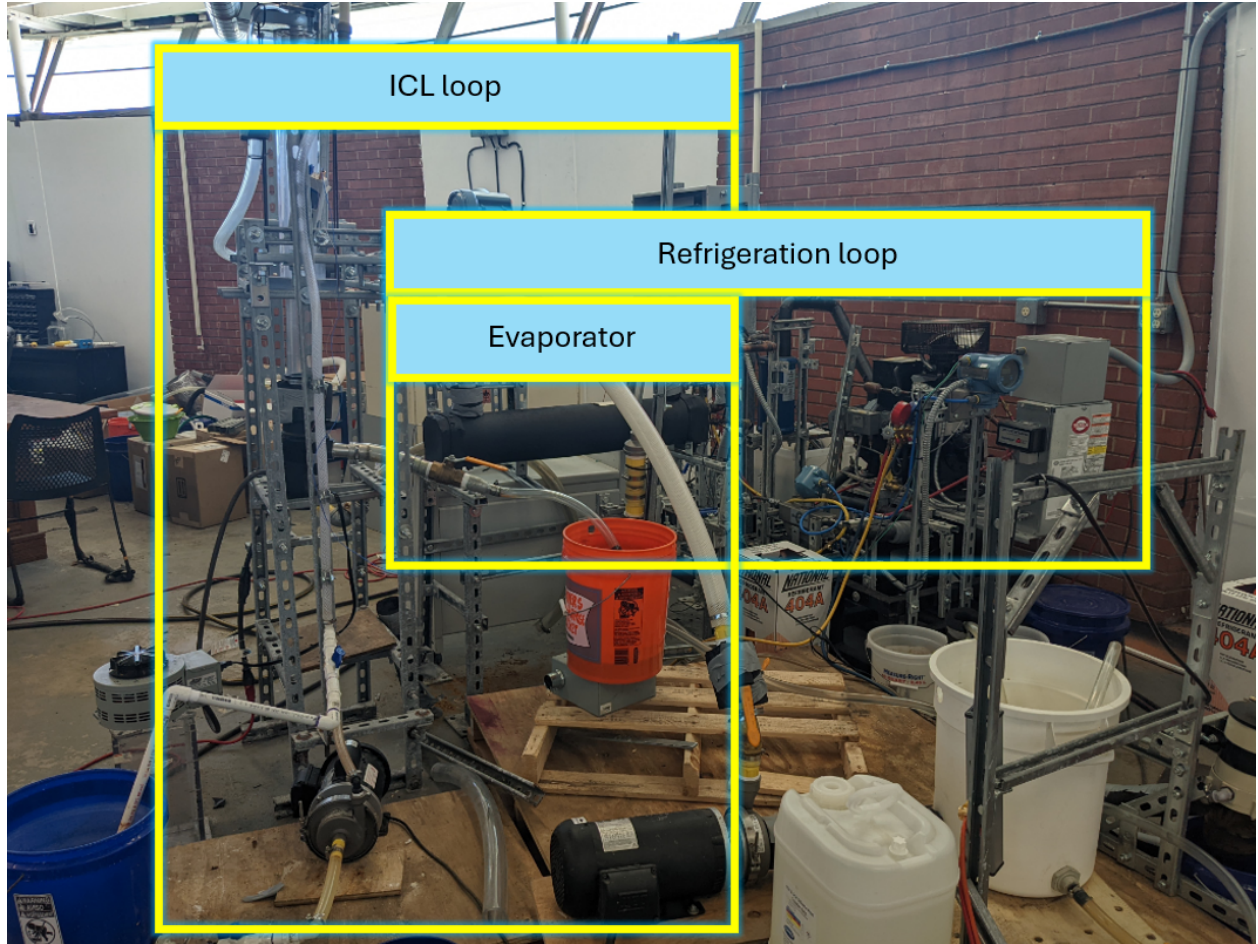


Figure 24: Primary loops of the experimental setup utilized to estimate the effectiveness of the separation process for the proposed FD system.

As explained earlier, one of the purposes from developing the experimental setup presented in Fig. 24 is to investigate the quality of the extracted water form the FD system that adopts the ICL solution (adopted to improve the thermal performance and the water quality generated by the FD process). Studying the quality of water generated provides knowledge about the separation effectiveness of the proposed FD system configuration. The refrigeration system cools down the ICL inside the evaporator then the cold ICL is passed to the freezing chamber. The feed brine is injected inside the freezing chamber into the cold ICL stream through a nozzle and ice crystallizes as shown in Fig. 25.

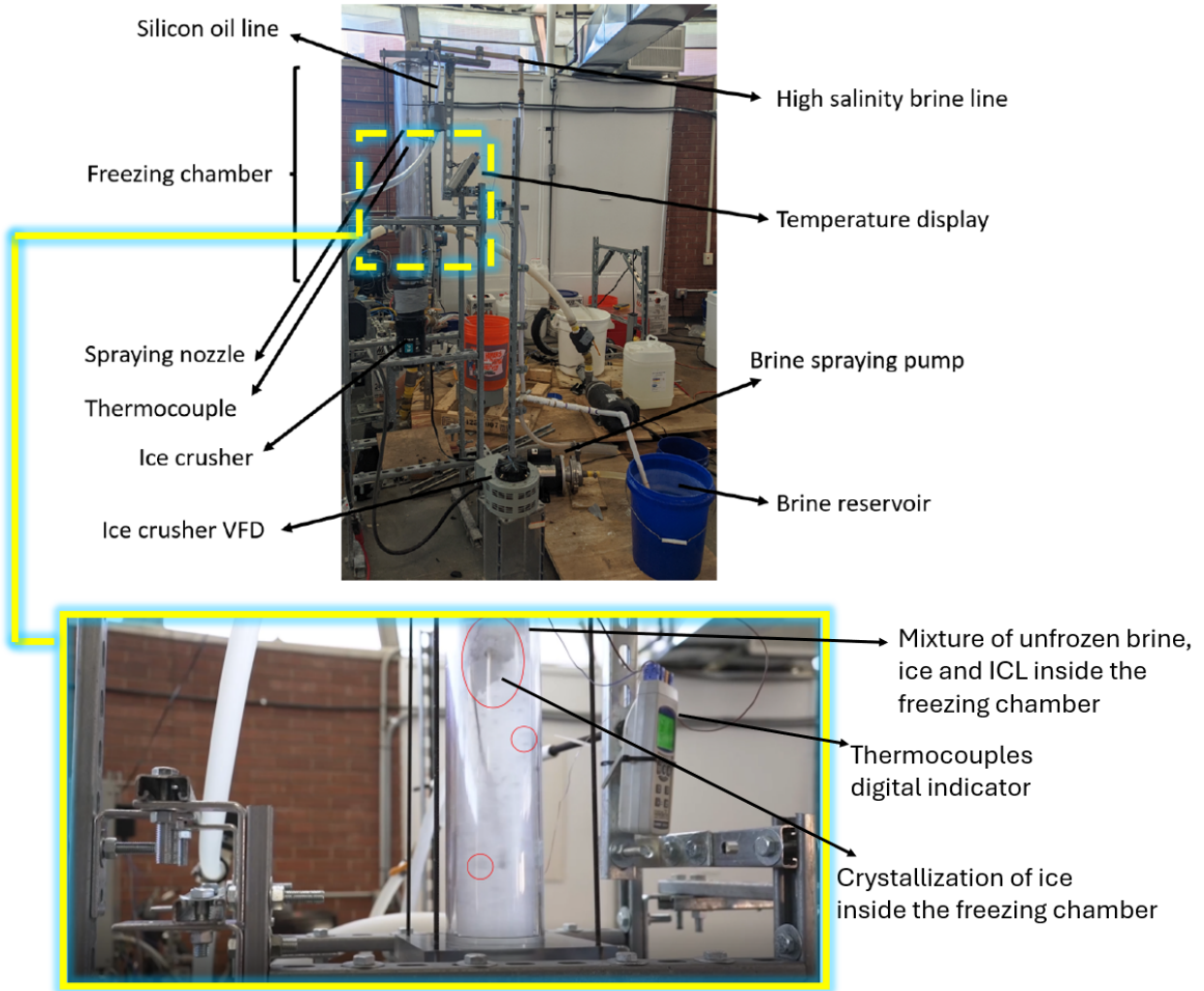


Figure 25: Freezing chamber of the FD system.

The freezing chamber contains a mixture of the ice crystallized inside the freezing chamber, the unfrozen brine and the ICL. To separate the ice, the mixture (ice+ ICL+ concentrate) undergoes multiple separation stages as shown in Fig. 26.

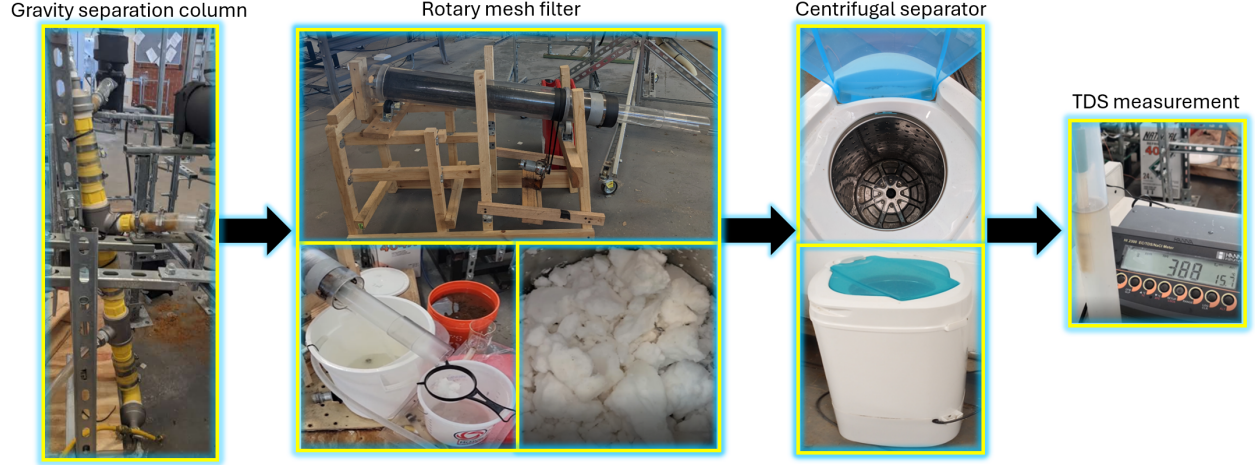


Figure 26: The primary separation stages of the proposed FD system.

The mixture leaving the freezing chamber is crushed and directed to a gravity separation column where most of the unfrozen brine is separated. Following that, a mesh rotary filter developed by the authors [66] is utilized to extract solid ice from the liquid ICL which is circulated back to the system. The extracted solid ice still carries quantities of unfrozen brine in pockets and the centrifugal separation stage is utilized to remove the majority of the carried over unfrozen liquid brine from the extracted ice. Finally, the ice is melted and the TDS of the water extracted from the system is accurately quantified. The experimental data showed that the salinity ratio of the treated water to the rejected unfrozen brine, S_{tw}/S_{rb} , remained almost constant at about 0.02. For any given feed brine salinity and recovery ratio, S_{tw}/S_{rb} can be used to find the salinity of the treated water from the following equation:

$$S_{tw} = \left(\frac{S_{tw}}{S_{rb}} \right) \frac{S_f}{1 - rr \left(1 - \frac{S_{tw}}{S_{rb}} \right)} \quad (10)$$

Where S_{tw} is the treated water salinity in ppm, S_{rb} is the return brine salinity in ppm, S_f is the feed salinity and rr is the ice recovery ratio. Equation. 10 is obtained from a mass balance of the salt and water through the desalination system (derivation is presented in Appendix B). Considering the experimentally determined salinity ratio of $S_{tw}/S_{rb} \approx 0.02$, Eq. 10 is rewritten as:

$$S_{tw} = \frac{0.02 S_f}{1 - 0.98 rr} \quad (11)$$

The cascade coupling heat exchanger

The cascade coupling heat exchanger is a heat exchanger serving as the condenser for the refrigeration cycle 1 and as the evaporator for the refrigeration cycle 2 (Fig. 23). The ice stream leaving the separator is introduced to the shell-side of the cascade coupling heat exchanger to completely melt before leaving as liquid water (schematically illustrated in the excerpt of Fig. 23). The cascade coupling heat exchanger is utilized in the optimal FD system design to provide essential support in raising the system's thermal efficiency. It can be shown that without melting the ice to cool the condenser of refrigeration cycle 1, the cooling capacity of the ice associated with its latent heat of fusion cannot be fully recovered. Therefore, utilizing the cascade coupling heat exchanger is essential in the optimal configuration of the FD system to ensure the complete energy recovery from the ice on the return stream side which plays a dominant role in maximizing the FD system's thermal efficiency. The shell-side temperature of the cascade coupling heat exchanger strongly affects the work consumption of the system [84]. The optimal shell-side temperature of the cascade coupling heat exchanger is the minimum temperature that guarantees full melting of the ice since it enables full recovery of the latent cooling capacity of the ice and provides greater capacity for precooling of the feed brine due to lower temperature of the melted ice. The melting temperature of the separated ice depends on its entrapped brine content. As such, the amount of salt entrapped in the ice affects the optimal shell-side temperature of the cascade coupling heat exchanger.

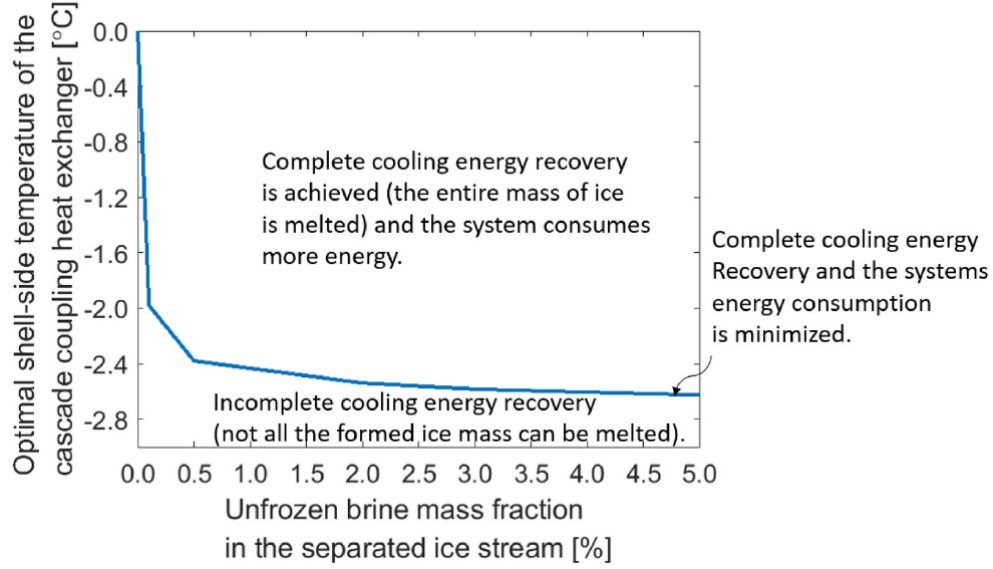


Figure 27: Optimal shell-side temperature of the cascade coupling heat exchanger for various unfrozen brine mass fractions in the return ice stream (obtained for feed salinity of 35,000 ppm and ambient temperature of 25°C).

Fig. 27 (corresponding to feed salinity of 35,000 ppm and ambient temperature of 25°C) indicates the minimum condenser shell-side temperatures that allow for the complete melting of ice at different unfrozen brine mass fractions (the mass ratio of the liquid brine in the ice stream to the total mass of the ice stream). For a theoretical case of perfect ice separation (no liquid brine entrapped within the ice stream), the optimal cascade coupling heat exchanger shell-side temperature is 0°C. Higher percentages of salts carried over in the return ice stream are associated with higher recovery ratios and vice versa. This explains the temperature trend in Fig. 27 having a relatively higher slope at lower brine mass fractions. In the case of higher freezing temperatures, the lower mass of formed ice along with the corresponding higher quantities of unfrozen brine (carried over within the return ice stream) allows the melting of the ice at relatively lower intermediate condenser temperatures due to the relatively higher overall concentration of the return stream (more high salinity brine and less ice). On the other hand, in the case of lower freezing temperatures (higher recovery ratios), the higher mass of formed ice and lower quantities of unfrozen brine make it necessary to reach higher temperatures for the complete melting of ice due to the lower overall concentration.

2.5 Thermochemical modeling of the FD system

A freeze desalination system model should cover the brine thermochemical transformation as it goes through freezing and melting processes in the system. The model should also predict thermal performance and work consumption of the process for various feed qualities and recovery ratios.

The following assumptions are adopted in developing the freeze desalination model:

- The analysis is conducted under the assumption of a steady-state condition.
- The effectiveness of heat transfer within the system's evaporator, condenser and cascade coupling heat exchanger is represented by a temperature difference ΔT between the hot and cold media reported in the literature [85].
- An inert water-immiscible intermediate cooling liquid (ICL) circulates between the evaporator of the refrigeration cycle 1 and the freezing chamber to cool the feed brine.
- Well-mixed slurry at the outlet of the freezing chamber; the ice, unfrozen brine, possible salt-hydrates, and the ICL are at thermal equilibrium.
- All phases are presumed to be in a state of equilibrium throughout the analysis.
- Negligible heat gain/loss from/to the ambient.

2.5.1 Refrigeration cycles model

The optimal freeze desalination cycle configuration is composed of a two-level cascaded refrigeration cycle [84]. The T-s diagram for each of the two cycles is presented in Fig. 28, where the transition of the refrigerant state from 1 to 2 results from irreversible compression. Constant pressure heat rejection occurs from state 2 to 3. Isenthalpic expansion occurs from

state 3 to 4 and constant pressure heat addition takes place from state 4 to 1. The model accounts for the two dominant sources of irreversibility in vapor compression refrigeration cycles, namely the compression isentropic efficiency, and heat transfer effectiveness of the heat exchangers.

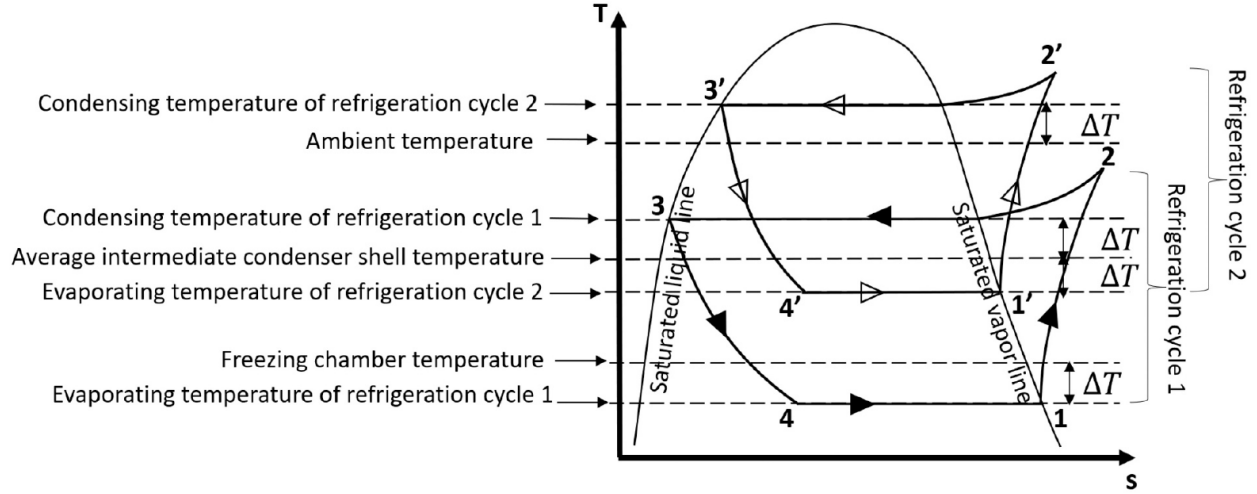


Figure 28: The T-s diagram corresponding to each of the two refrigeration cycles utilized in the optimal FD system configuration.

The variation in heat transfer effectiveness is modeled by applying a temperature difference between the two fluids in each of the systems' primary heat exchangers [85]. As shown in Fig. 23, the studied freeze desalination system is composed of three primary heat exchangers: the evaporator, the condenser, and the cascade coupling heat exchanger. The temperature difference corresponding to variation in heat transfer effectiveness is applied as described in Fig. 28. Fig. 28 also shows the evaporating temperature of refrigeration cycle 1 below the desired ICL temperature (the temperature desired for the ICL to reach at the outlet of the evaporator) by a designated temperature difference, ΔT . Similarly, the condensing temperature of refrigeration cycle 2 is above the ambient temperature by a designated temperature difference, ΔT .

The shell-side temperature of the cascade coupling heat exchanger is maintained at the optimal temperature. In addition, Fig. 23 shows the evaporating and condensing tempera-

tures corresponding to the refrigeration cycles 2 and 1, respectively, relative to the cascade coupling heat exchanger shell-side temperature. To account for the irreversibility of the compression process, the compressor's isentropic efficiency is calculated using the following two equations for refrigeration cycles 1 and 2, respectively.

$$\eta_{isentropic,1} = \frac{h_{2s} - h_1}{h_2 - h_1} \times 100\% \quad (12)$$

where, h_1 and h_2 are the refrigerant's enthalpy at points 1 and 2, respectively, and h_{2s} is the refrigerant outlet enthalpy under ideal isentropic compression.

$$\eta_{isentropic,2} = \frac{h_{2's} - h_{1'}}{h_{2'} - h_{1'}} \times 100\% \quad (13)$$

Similar to Eq. 12, $h_{1'}$ and $h_{2'}$ represent the enthalpy at points 1' and 2', respectively, and $h_{2's}$ represents the refrigerant outlet enthalpy under ideal isentropic compression.

Considering the operating temperatures in this system, R404A is the selected refrigerant for both refrigeration cycles and its thermodynamic properties are obtained using the CoolProp package [86]. Note that the system performance using other refrigerants shows a deviation of <5% compared to the refrigerant R404A.

2.5.2 Co-simulation framework

The freeze desalination system behavior and performance are analyzed through co-simulation of the component models as illustrated in Fig. 29.

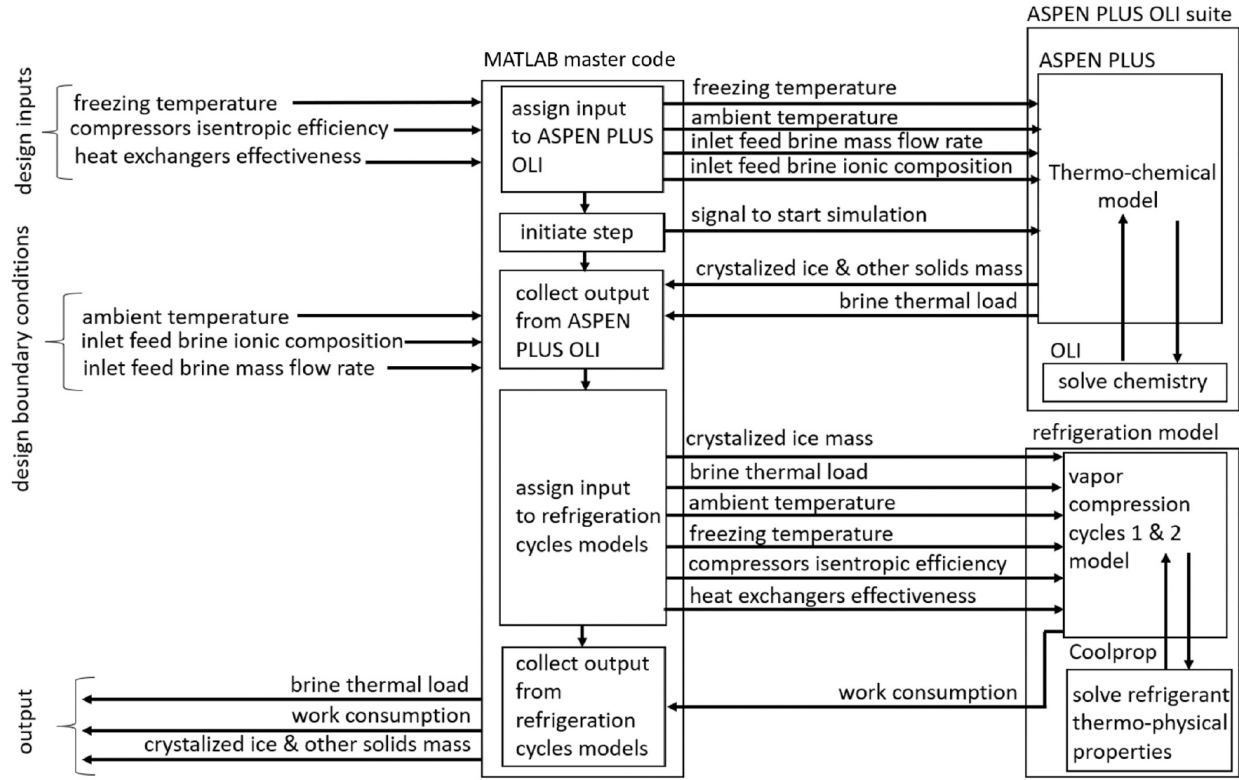


Figure 29: Layout of the co-simulation framework developed to identify the optimal FD system configuration and its thermochemical performance.

The significance of adopting this approach is that it allows for the extrapolation of results beyond the available experimental points used to validate the framework (validation presented in the next Section). A master code orchestrates the simulation of the feed thermo-chemical properties in ASPEN PLUS + OLI engine along with the cascade refrigeration cycles model. In the following subsections, the three main blocks of the co-simulation framework (MATLAB master code, refrigeration model and ASPEN PLUS OLI suite) are described in detail.

Master code of the co-simulation framework

The master code running the co-simulation framework is written in MATLAB. The code establishes a connection with ASPEN PLUS, assigns input, runs the ASPEN simulation

file for a specified period then collects the output. The master code also utilizes MATLAB functions for estimating the cascade refrigeration cycle performance. Fig. 30 shows the detailed structure of the framework's master code.

MATLAB master code

```

% Link MATLAB with ASPEN PLUS

Aspen = actxserver('Apwn.Document.39.0');

% Get attributes of folder (necessary to establish the location of the simulation
folder) and assign simulation file name

[stat,mess] = fileattrib;
Sim_Name = 'file1';
Aspen.invoke('InitFromArchive2',[mess.Name '\' Sim_Name '.bkp']);

% Identify the ASPEN PLUS window and dialogues visibility
Aspen.SuppressDialogs = 1;
Aspen.Visible = 0;

% Run simulation
Aspen.Engine.Run2(1);

% Assign inputs
% Example of input assignment:
Aspen.Tree.FindNode("\Data\Blocks\CLR1A\Input\TEMP").value = temperature_value_assigned;
% Call to variable in ASPEN

% Initiate, run & stop ASPEN simulation
Aspen.Reinit;
Aspen.Engine.Run2(1);

time = 1;
while Aspen.Engine.IsRunning == 1
    pause(0.5);
    time = time+1;
    if time == desired_simulation_stop_time
        Aspen.Engine.Stop;
    end
end

% Collect outputs
% Example of output collection:
load_value_collected = Aspen.Tree.FindNode("\Data\Blocks\COOLER\Output\QCALC").value;

% Utilize refrigeration cycle model using MATLAB functions
[outputs_from_function] = refrigeration_cycles_model(inputs_to_function);

% Save output
save('data_file_name.mat','variable1','variable2','variable3',.....)

```

Figure 30: MATLAB master code of the co-simulation framework.

Refrigeration model application in the co-simulation framework

The refrigeration cycles model is utilized to estimate its energy performance as part of the integrated FD system model. The evaporating temperature of refrigeration cycle 1 is less than the temperature inside the freezing chamber by the heat exchanger's approach temperature, ΔT (as explained earlier, the variation in heat transfer effectiveness is modeled by applying a temperature difference between the two fluids in each of the systems' heat exchangers). Eq. 14 represents the evaporating temperature for refrigeration cycle 1. Similarly, the condensing temperature for refrigeration cycle 2 is higher than the ambient temperature by the heat exchanger's approach temperature, ΔT as shown in Eq. 15. The evaporating temperature of refrigeration cycle 2 is lower than the cascade coupling heat exchanger shell side temperature by the exchanger's approach temperature, ΔT while the condensing temperature of refrigeration cycle 1 is higher than the shell side temperature by ΔT . The compression irreversibility is counted for using the isentropic efficiency values calculated by Eqs. 12 and 13:

$$T_e = T_{ch} - \Delta T \quad (14)$$

$$T_c = T_a + \Delta T \quad (15)$$

Where T_e is the evaporating temperature in $^{\circ}\text{C}$, T_{ch} is the freezing chamber average temperature in $^{\circ}\text{C}$, T_c is the condensing temperature in $^{\circ}\text{C}$ and T_a is the ambient temperature in $^{\circ}\text{C}$.

The evaporating load of refrigeration cycle 1 required to cool the brine down to the desired temperature inside the freezing chamber is the product of the refrigerant mass flow rate and the difference between the enthalpies at the exit and inlet of the evaporator as presented in Eq. 16:

$$Q_e = m_r(h_{e,o} - h_{e,i}) \quad (16)$$

Where Q_e is the evaporating load in W, m_r is the refrigerant mass flow rate in kg/s, $h_{e,o}$ is the enthalpy of the refrigerant leaving the evaporator in J and $h_{e,i}$ is the enthalpy of the refrigerant entering the evaporator in J.

The condensing heat and the work of each of the two compressors are estimated using Eqs. 17 and 18 respectively.

$$Q_c = m_r(h_{c,i} - h_{c,o}) \quad (17)$$

$$W_{comp} = m_r(h_{comp,o} - h_{comp,i}) \quad (18)$$

Where Q_c is the condensing load in W, m_r is the refrigerant mass flow rate in kg/s, $h_{c,i}$ is the enthalpy of the refrigerant entering the condenser in J, $h_{c,o}$ is the enthalpy of the refrigerant leaving the condenser in J, W_{comp} is the work of the compressor in W, $h_{comp,o}$ is the enthalpy of the refrigerant leaving the compressor in J and $h_{comp,i}$ is the enthalpy of the refrigerant entering the compressor in J.

The evaporating load of refrigeration cycle 2 handles the condensing heat of refrigeration cycle 1 minus the cooling energy recovered from melting the ice inside the intermediate condenser shell as shown in Eq. 19. The overall work requirement of the FD system is the sum of the work of each of the system's compressors.

$$Q_e = Q_c - Q_m \quad (19)$$

In Eq. 19, Q_m resembles the cooling energy recovery rate from the melted ice in W.

ASPEN PLUS OLI suite description

As described previously, the utilized ASPEN PLUS + OLI model includes a heat exchanger unit with fixed outlet temperature where the mixed solvent electrolyte model (MSE) of OLI is adopted to predict the brine's thermochemical behavior. In the following subsections, the ASPEN PLUS and the OLI models are described in more detail.

ASPEN PLUS model

The ASPEN PLUS model consists of a heat exchanger and a separator as shown in Fig. 31. The adopted seawater composition (ionic composition defined in Table 2) is configured in the ASPEN PLUS model and utilized for the input seawater brine stream (S1). The input stream is then logged to a separator that removes a certain amount of liquid H_2O from the stream. The removal of H_2O (S2) raises the mixture's salinity and enables modeling different concentrations of the high salinity brine feed to the FD system (S3), namely, 35,000 ppm, 50,000 ppm, 75,000 ppm, 100,000 ppm, 150,000 ppm, and 200,000 ppm. The brine feed is cooled down to the freezing chamber temperature assigned by the master code. The thermal load and the chemical behavior of the brine is calculated using OLI (explained in more detail through the following subsection). The thermal load associated with the process and the chemical composition of the product stream are collected by the master code. Similarly, the cooling energy recovered inside the cascade coupling heat exchanger and through the precooling process is counted for in the calculations of the master code using data generated by an ASPEN PLUS model coupled with OLI.

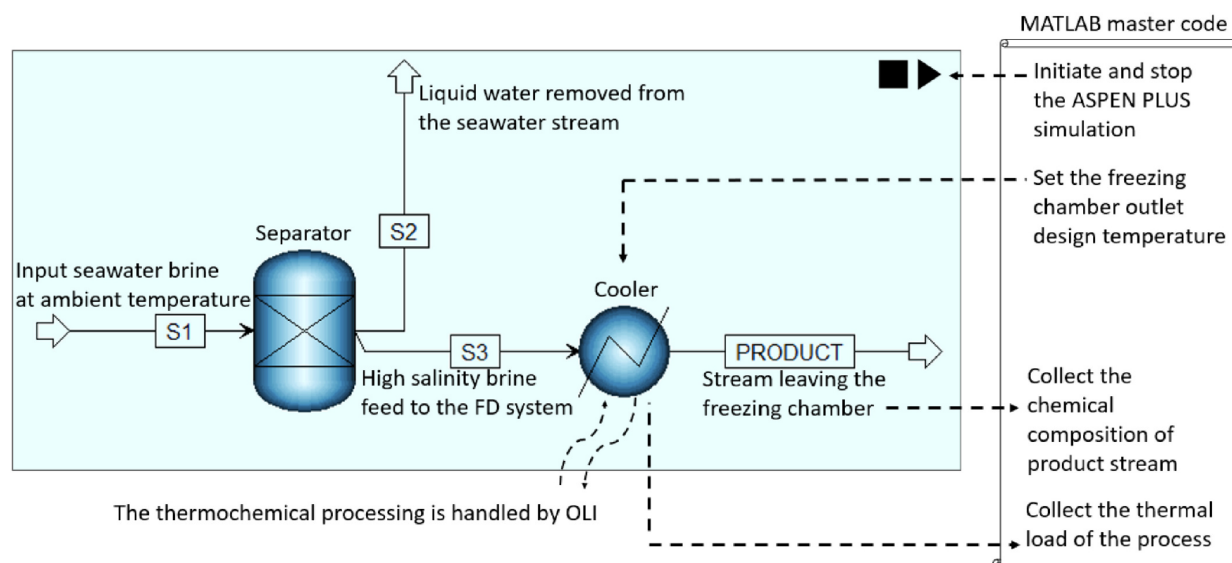


Figure 31: ASPEN PLUS model.

OLI model

As described briefly, OLI utilizes the mixed solvent electrolyte model (MSE) which represents the chemical and phase equilibria in addition to the volumetric and thermal properties for mixed solvent electrolyte systems from infinite dilution to molten salts [87]. The MSE model has been extensively validated against experimental data [87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97]. The experimental data utilized to determine the MSE model parameters included the heat capacities, the densities, the Gibbs energy of transfer of electrolytes, the heats of mixing and dilution, the osmotic coefficients in aqueous solutions, the acid dissociation constants as a function of the solvent composition, the solubility of salts, and the activity coefficients in completely dissociated aqueous systems [87].

The electrolyte solution nonideal behavior is affected primarily by the electrostatic (long-range) effects due to the electric charges of the ionic species [87, 98, 99], the physical dispersion forces and structural differences between the species [87, 100, 101], and the chemical forces leading to complex formation or association [87]. To consider the described effects, the MSE model combines the excess Gibbs energy expression with chemical equilibrium re-

lations. The chemical equilibrium calculations involve the simultaneous use of the standard state thermodynamic properties (linked to the species engaging in the chemical reactions) and activity coefficients [87]. The excess Gibbs energy and the activity coefficient expressions adopted by the MSE model are presented in Eqs. 20 and 21, respectively. For the MSE model, comprehensive data has been published about the selection of the reference state and the standard state chemical potentials conventions [87]. The published work included detailed information about the long, the short and the middle range interaction contribution as well as density, enthalpy and heat capacity calculations [87].

$$\frac{G}{R_g T_K} = \frac{G_L}{R_g T_K} + \frac{G_M}{R_g T_K} + \frac{G_S}{R_g T_K} \quad (20)$$

$$\ln \gamma = \ln \gamma_L + \ln \gamma_M + \ln \gamma_S \quad (21)$$

where G_L is the contribution of the long-range electrostatic interactions, G_M is the contribution of the middle range ionic interactions, and G_S represents the short-range contribution resulting from ion/ion, molecule/molecule and molecule/ion interactions. Similarly, γ_L , γ_M and γ_S are the activity coefficients linked to the long, medium and short-range interactions.

Concluding remarks

The present section devised a thermochemical model for a FD system configuration capable of achieving maximum efficiency in terms of power consumption per unit mass of treated water. The model comprised a co-simulation framework combining state-of-the-art tools to simulate the thermochemical behavior of the brine upon freezing and the FD system's thermal performance. This section findings and contributions can be summarized in the following points:

- Proposing a FD system configuration that maximizes energy efficiency. The claim is verified through the proximate between the system's theoretical work of separation with the published benchmark minimum work of separation for desalination.
- A co-simulation framework to simulate the thermochemical behavior of the brine upon freezing and the FD system's thermal performance.

The contributions of this study present a reference for selection, sizing, operation and techno-economic analysis of FD systems which will be presented in the coming sections.

3 Thermochemical performance of the optimal FD system configuration

In the previous section, the optimal freeze desalination system configuration has been identified based on theoretical analysis that disregarded the system's irreversibility. Although such analysis are suitable for the configuration optimization process, studying the FD system's performance considering irreversibility is an essential step towards the technology's commercialization.

This section addresses the knowledge gap about the specific mechanical work required to treat brine using the FD system considering the system's irreversibility, answering the following research questions:

- What is the cooling load of freezing of the high salinity brine ?
- How does the brine's cooling load change with the change of the freezing temperature ?
- What is the effect of the feed brine TDS on the cooling load ?
- How would the feed TDS and the different primary sources of irreversibility affect the work of the FD system ?

The section composes of two main parts: part 1 presents, the cooling load required for freezing of standard and concentrated seawater at different temperatures and the correspondingly formed compounds along a temperature range of -35°C to 0°C . Part 2 is dedicated to the FD system's work consumption considering the effects of the compressors' isentropic efficiency and effectiveness of the primary heat exchangers.

3.1 Thermal performance of the optimal FD configuration

The brine thermochemical model is validated by comparing the ice recovery ratio values with the previously reported experimental data for standard and concentrated seawater presented in Figs. 32–37 [102]. The maximum error between the model predictions and the actual measurements is $<5\%$ for concentrations of 35,000, 50,000 and 75,000 ppm (Figs. 32–34). For the concentrations of 100,000 ppm and 150,000 ppm, the maximum error is within the 10% margin (Figs. 35 and 36).

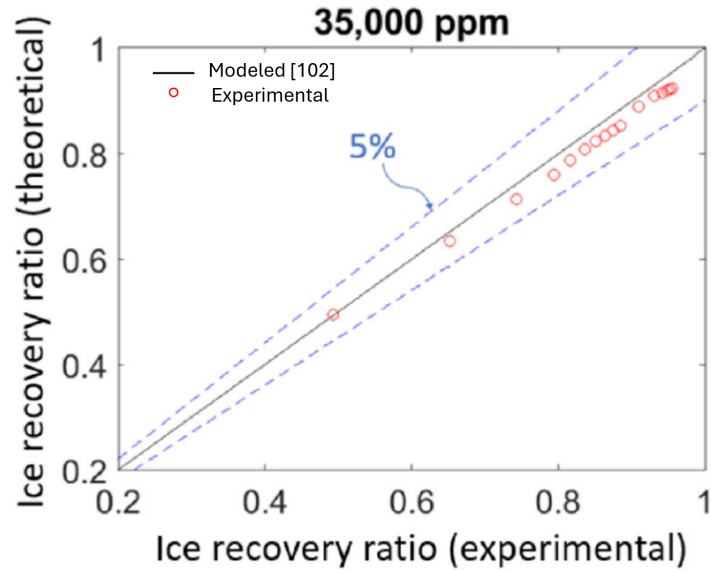


Figure 32: Calculated ice recovery ratio vs. experimental values for the standard seawater feed of 35,000 ppm.

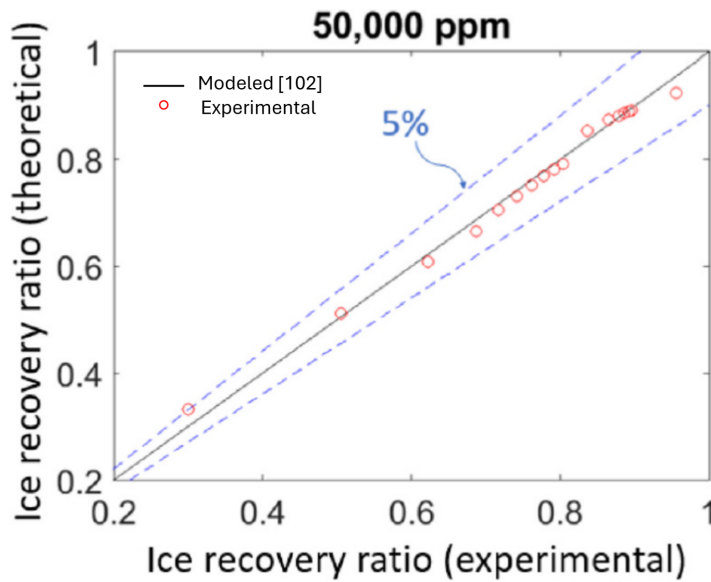


Figure 33: Calculated ice recovery ratio vs. experimental values for the concentrated seawater feed of 50,000 ppm.

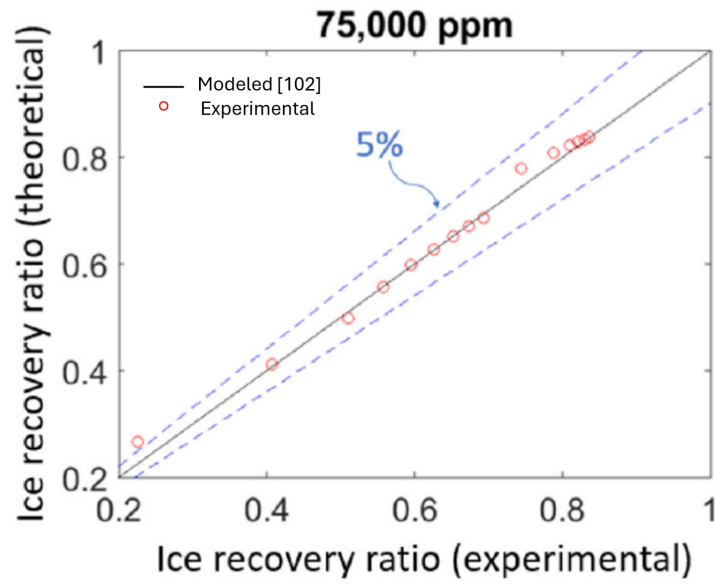


Figure 34: Calculated ice recovery ratio vs. experimental values for the concentrated seawater feed of 75,000 ppm.

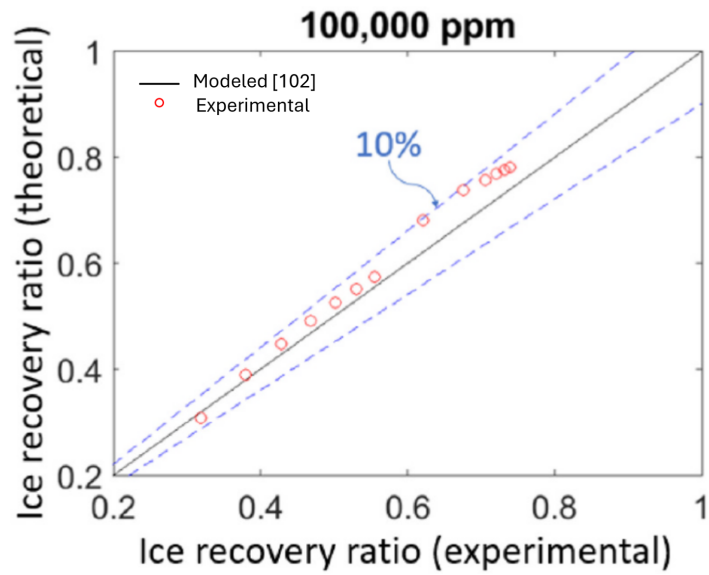


Figure 35: Calculated ice recovery ratio vs. experimental values for the concentrated seawater feed of 100,000 ppm.

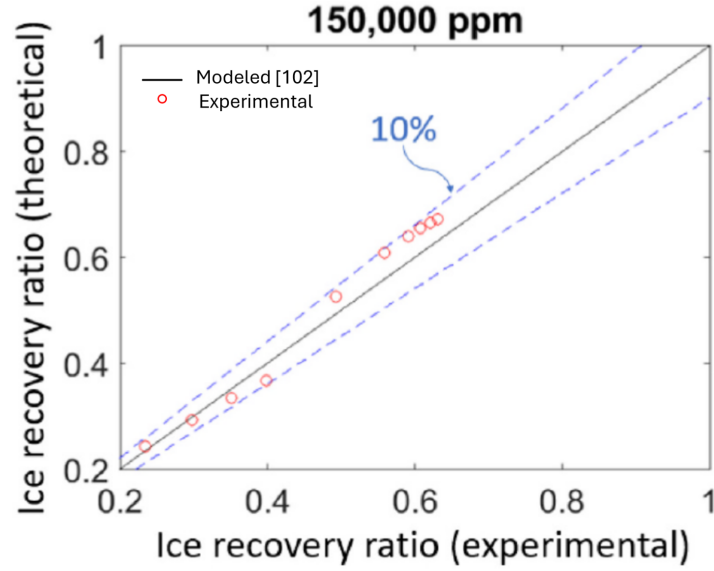


Figure 36: Calculated ice recovery ratio vs. experimental values for the concentrated seawater feed of 150,000 ppm.

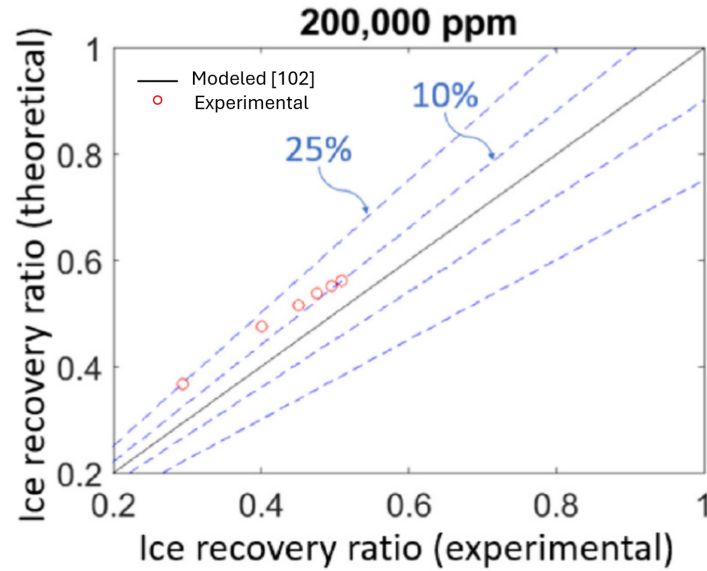


Figure 37: Calculated ice recovery ratio vs. experimental values for the concentrated seawater feed of 200,000 ppm.

In the case of the 200,000 ppm feed salinity, the estimated values lie within a 25% error margin, with the theoretical results overpredicting the mass of formed ice compared to the experimental data (Fig. 37). The relatively large error for TDS of 200,000 ppm is possibly

due to the difficulty of the complete separation of the ice from the formed hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) in the experimental studies which is exacerbated at higher brine salinities.

Utilizing the validated model to predict the ice mass fractions for the different feed concentrations at different freezing temperatures, a phase diagram presented in Fig. 38 is generated to highlight the input stream, output stream and the onset of freezing within the FD system.

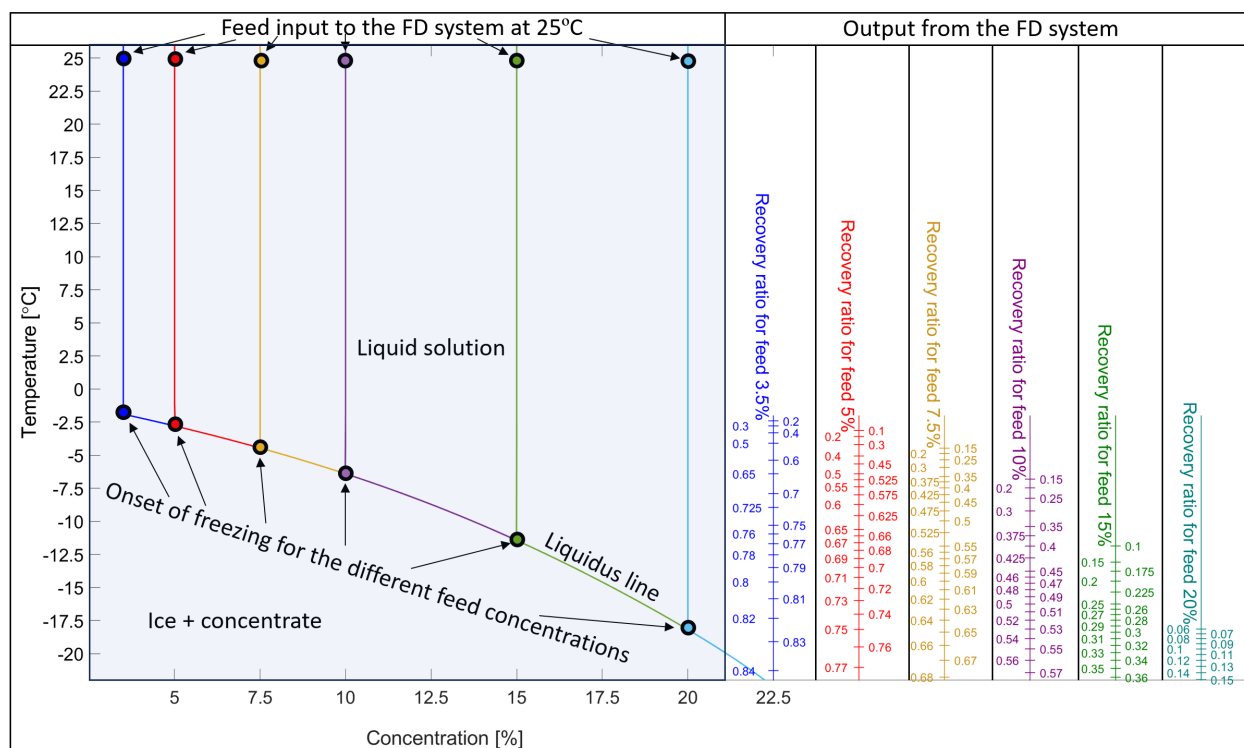


Figure 38: Phase diagram for seawater feed at different concentrations.

Upon freezing, the brine is decomposed into four main components, namely, unfrozen brine (will be referred to as brine), pure ice, hydrohalite and solids (salt-hydrates and other suspended solids). Figs. 39–44 show the mass fractions of each of these components at various temperatures (from 0°C to -35°C) for standard and concentrated seawater (35,000 ppm, 50,000 ppm, 100,000ppm, 150,000ppm, 200,000 ppm).

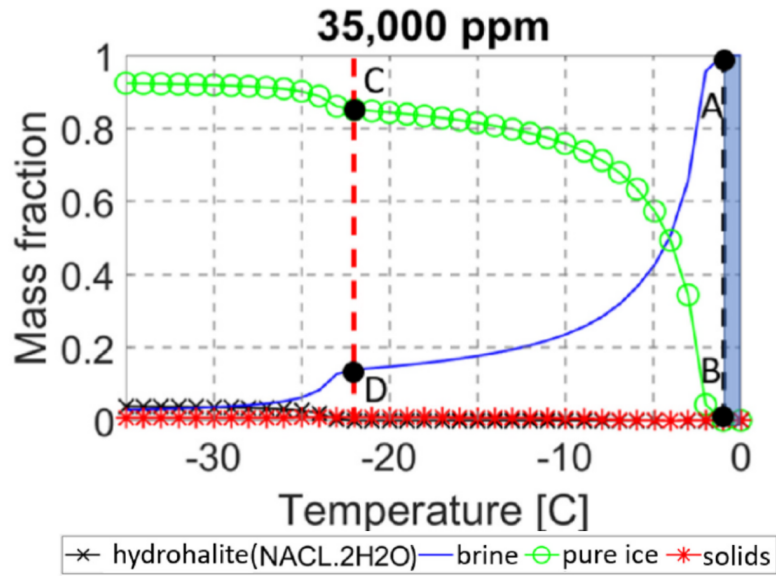


Figure 39: Mass fractions of various components formed upon cooling of standard seawater at 35,000 ppm between 0°C and -35°C.

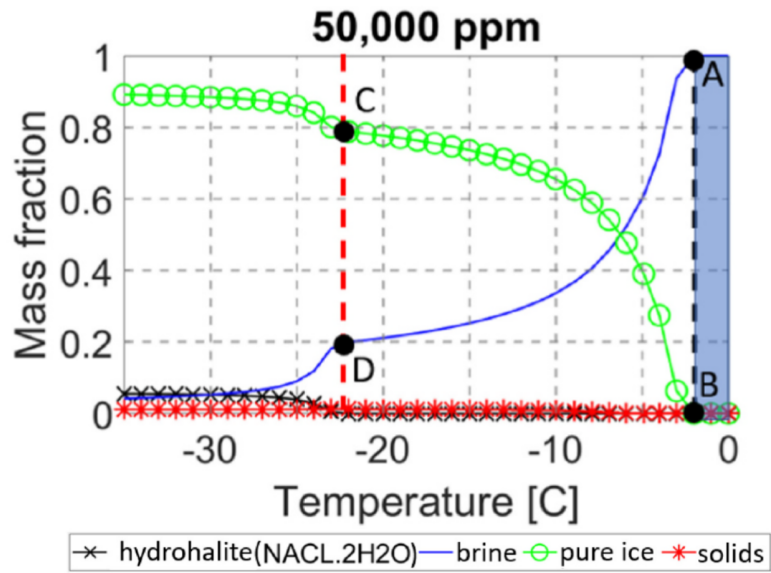


Figure 40: Mass fractions of various components formed upon cooling of concentrated seawater at 50,000 ppm between 0°C and -35°C.

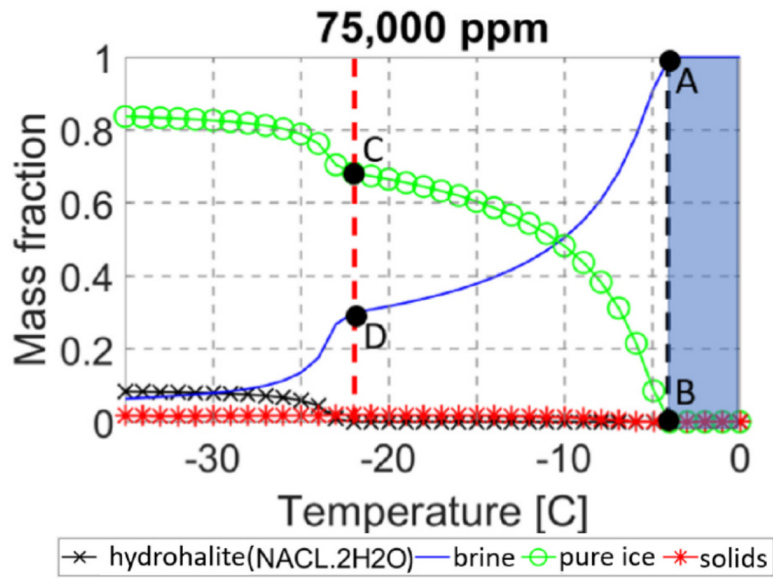


Figure 41: Mass fractions of various components formed upon cooling of concentrated sea-water at 75,000 ppm between 0°C and -35°C.

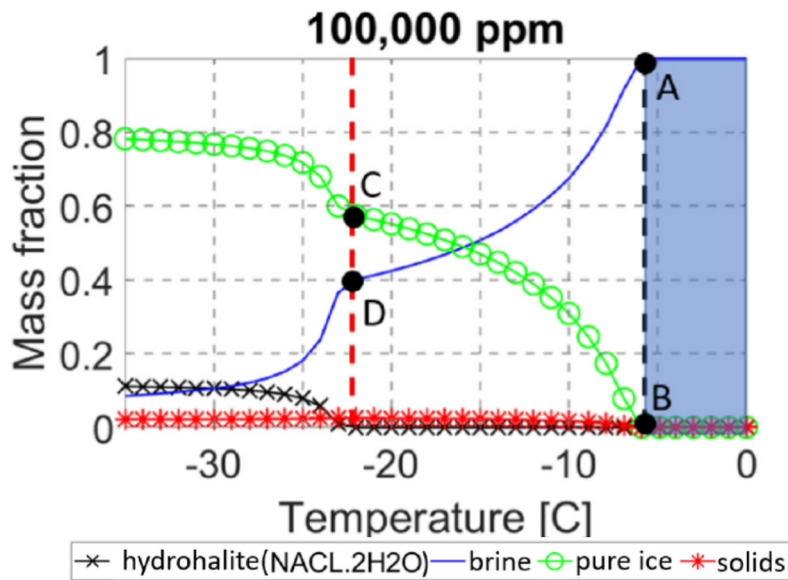


Figure 42: Mass fractions of various components formed upon cooling of concentrated sea-water at 100,000 ppm between 0°C and -35°C.

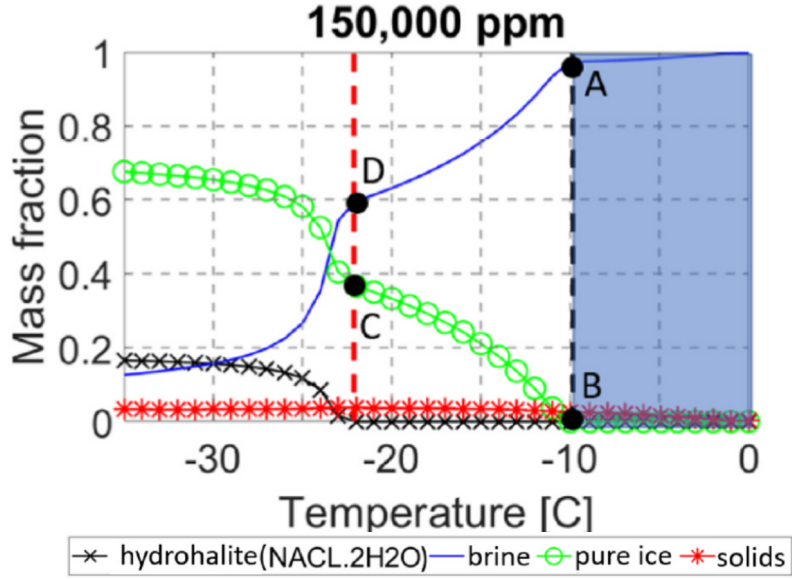


Figure 43: Mass fractions of various components formed upon cooling of concentrated sea-water at 150,000 ppm between 0°C and -35°C.

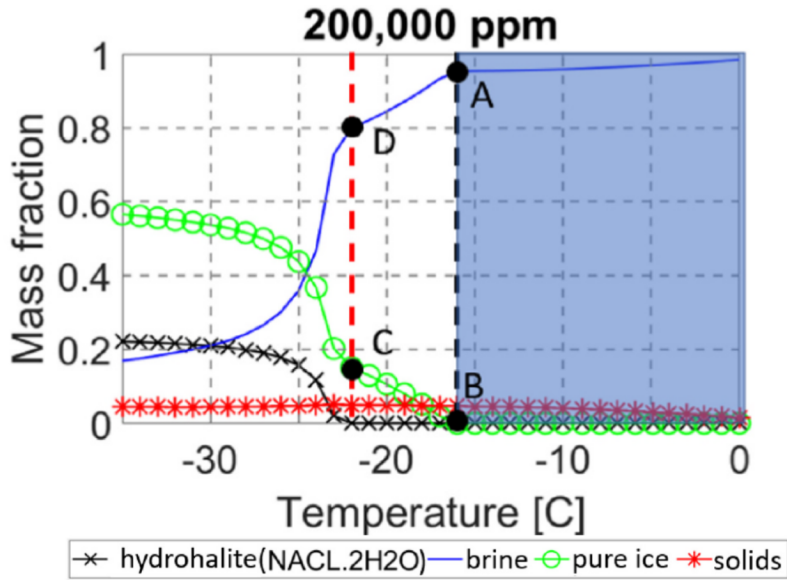


Figure 44: Mass fractions of various components formed upon cooling of concentrated sea-water at 200,000 ppm between 0°C and -35°C.

In Figs. 39– 44, the brine refers to liquid phase containing water and dissolved ions. Three regions can be identified in Figs. 39– 44, separated by two vertical dashed lines, namely line AB connecting points A and B, and line CD connected points C and D. Line AB shows the onset of freezing, where the first ice crystals are formed, and line CD shows

the onset of hydrohalite formation. In an analogy with a binary NaCl-water solution, line CD is equivalent to the eutectic temperature. It is noted, however, that due to its diverse composition, seawater does not have a single eutectic temperature. As evident in Figs. 38–44, the onset of freezing temperature is suppressed significantly as the brine TDS increases; decreasing by almost 15°C as the brine TDS increases from 35,000 ppm to 200,000 ppm. On the other hand, the formation temperature of hydrohalite remains almost constant at about -23°C for various brine salinities, that is consistent with previous studies [103].

In the region to the right of line AB, there is no ice, and the mixture is primarily composed of liquid and small amounts of solids that start to precipitate below 0°C . In the middle region, between lines AB and CD, ice, brine, and some solids are present. Further cooling in this region leads to an increasing amount of ice and decreasing amount of brine with no noticeable change in the amount of precipitated solids. In the region to the left of line CD, hydrohalite is added to the mixture.

Figs. 39–44 also shows that the higher the concentration of the feed brine, the higher the temperature at which solids precipitation commences. In addition, for temperatures lower than -23°C , the mass fraction of hydrohalite is higher for higher feed salinities. The higher mass fraction of solids and hydrohalite is explained by the mixture saturation occurring at higher temperatures for higher concentration feed brine.

Reducing the temperature below the formation threshold of hydrohalite induces a sharp rise (drop) in both the ice and hydrohalite (liquid brine) mass fraction. These significant changes near -23°C can be explained by the fact that the Na^{+} and Cl^{-} ions largely dominate the ionic composition of the brine. Therefore, the behavior of the brine near -23°C is very similar to the behavior of binary NaCl- H_2O system near -21.1°C where it undergoes eutectic freeze with no leftover liquids.

The specific cooling load is the amount of cooling energy required to generate 1 kg of purified water, in the form of ice, by removing sensible and latent heat from the brine. Fig. 45 shows the specific cooling load of the feed brine starting at 0°C cooled down to different

temperatures below the threshold of freezing. The effect of the supercooling phenomenon has been considered in the cooling load analysis. The outcomes presented in Fig. 45 are based on supercooling of 0.383°C (below the threshold of freezing) for the different feed concentrations. At the same freezing temperature, the higher the feed concentration, the lower the mass of the ice crystallized (compared to lower feed concentration) as described earlier (Figs. 39– 44). This explains the higher cooling load per kg of crystallized ice in the case of higher feed concentrations. Also at higher concentrations, the cooling load (per kg of crystallized ice) decreases at lower freezing temperatures. This is linked to the higher recovery ratio values where a larger portion of the cooling energy (provided to reach the desired freezing temperature) is consumed to crystallize ice rather than sensibly cool high salinity unfrozen brine.

3.2 Work load of the optimal FD configuration

The freeze desalination system's specific work is the amount of work consumed by the system to generate 1 kg of purified water. The minimum possible specific work of separation (separation of water from the feed brine) corresponds to a water recovery ratio (mass ratio of the purified water to the saline feed water) approaching zero as proved in published studies [104, 105]. From Fig. 45, as the water recovery ratio approaches zero ($R \rightarrow 0$), the freezing chamber temperature approaches the onset of freezing for each feed concentration. Therefore, the desalination minimum work of separation corresponds to temperatures approaching the start of freezing for each feed concentration as presented in Eq. 22.

$$SWFD_{min} \equiv \lim_{T_{ch} \rightarrow T_{fz}} SWFD \quad (22)$$

where $SWFD$ is the specific work of freeze desalination corresponding to various feed concentrations and brine freezing chamber temperatures, T_{ch} and T_{fz} are the temperatures inside the freezing chamber and the freezing temperature for each of the feed concentrations, re-

spectively.

To validate the proposed FD system's configuration in terms of minimizing the work of separation for desalination, the proposed system's model has been simulated adopting Carnot cycle (for the purpose of comparison with the published benchmark theoretical work of separation values [70]). The theoretically estimated FD work consumption showed agreement with the established values of theoretical work of separation [70] within $\pm 5\%$ error range.

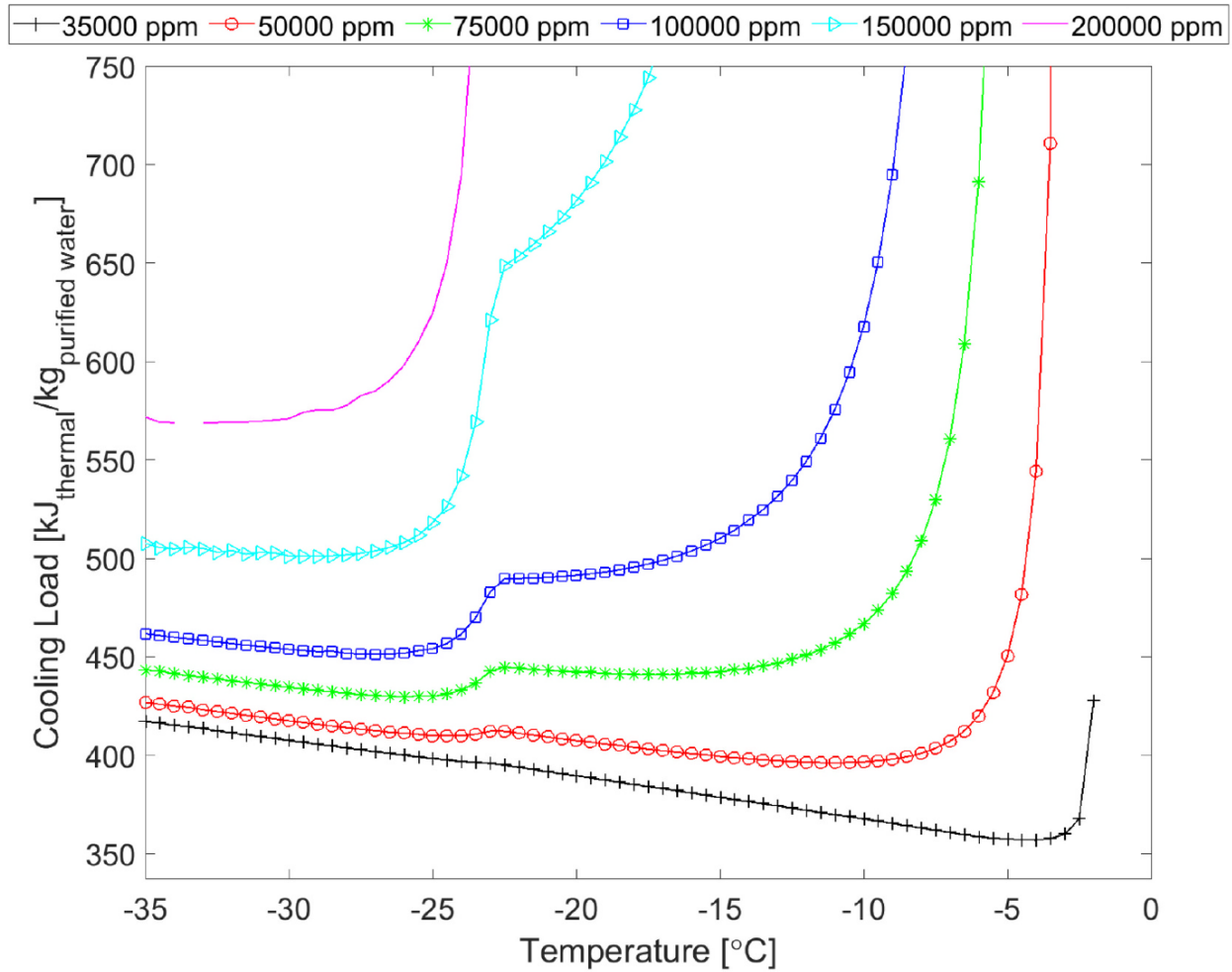


Figure 45: Brine specific cooling load at different freezing temperatures for various feed concentrations.

Since the minimum work of separation is achieved as $R \Rightarrow 0$, the maximum energy efficiency of the FD system will be achieved at the onset of freezing for any brine concentration.

Figs. 46– 49 show the effect of compressor isentropic efficiency on the FD system minimum work of separation for different feed concentrations and heat exchangers' approach temperature, ΔT . As noted, $\Delta T = 0$ °C corresponds to an isentropic heat exchanger with an effectiveness of 1 and larger ΔT values represent larger irreversibilities and smaller effectiveness values.

Figures. 46– 49 show that the minimum work of separation of the FD system decreases for all feed concentrations as the isentropic efficiency of the system's compressor increases. Also, the lower the heat transfer effectiveness of the system's heat exchangers (higher ΔT values), the greater the minimum work of separation is. These results also show that the higher the feed concentration, the higher the specific work. The lower intermolecular forces among the molecules of the solvent at higher feed concentrations makes it more energy demanding to freeze the water content within the mixture compared to less concentration feeds. In the case of imperfect salt separation, the work load of the FD system was found to be lower (compared to the perfect salt separation case) which complies with the published entropy-based analysis outcomes [104]. The reduced work consumption comes at the penalty of lower water quality which defies the purpose of desalination.

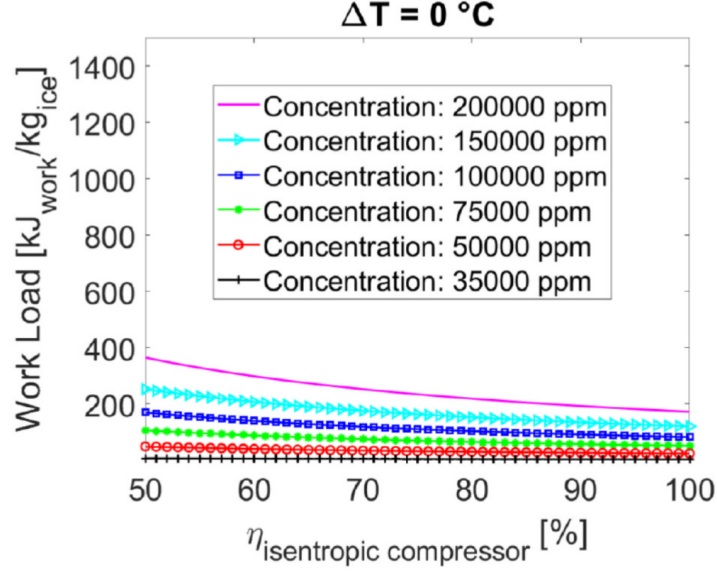


Figure 46: The minimum work of separation of the freeze desalination system at different concentrations versus compressors' isentropic efficiency for heat exchanger approach temperatures $\Delta T = 0$ °C.

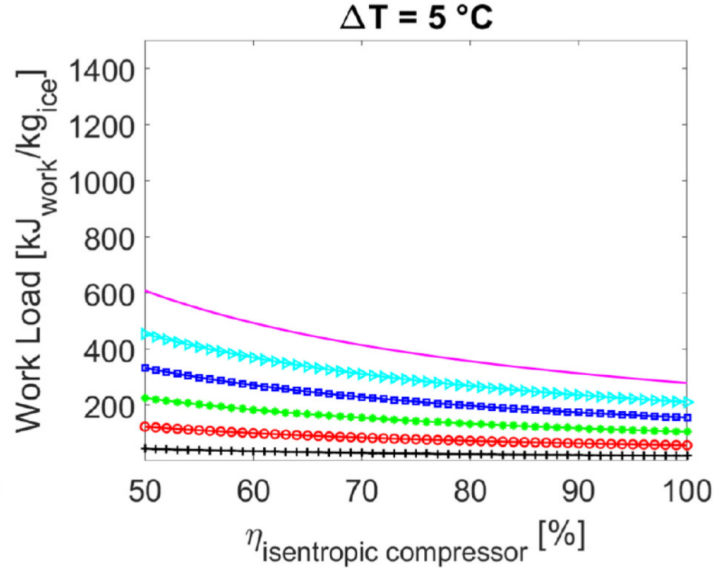


Figure 47: The minimum work of separation of the freeze desalination system at different concentrations versus compressors' isentropic efficiency for heat exchanger approach temperatures $\Delta T = 5$ °C.

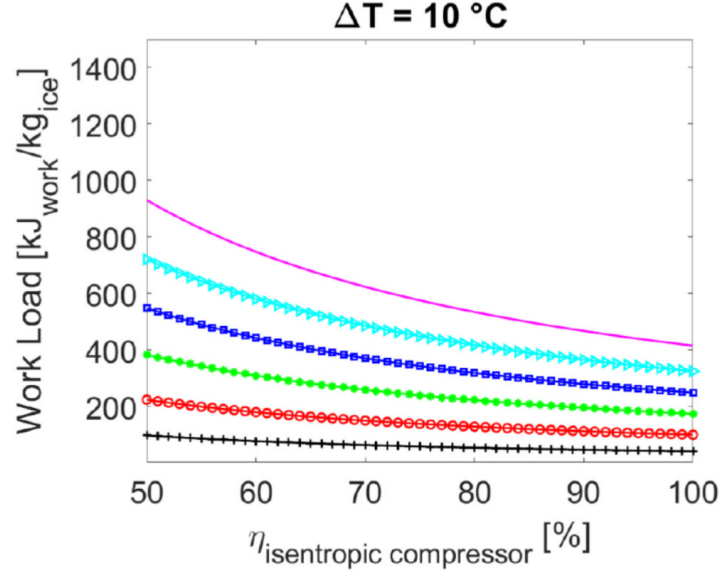


Figure 48: The minimum work of separation of the freeze desalination system at different concentrations versus compressors' isentropic efficiency for heat exchanger approach temperatures $\Delta T = 10\text{ }^{\circ}\text{C}$.

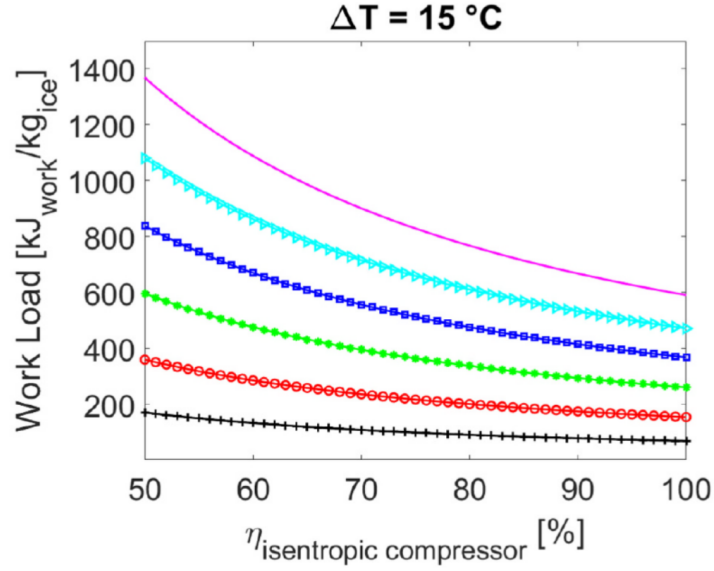


Figure 49: The minimum work of separation of the freeze desalination system at different concentrations versus compressors' isentropic efficiency for heat exchanger approach temperatures $\Delta T = 15\text{ }^{\circ}\text{C}$.

Concluding remarks

The effect of the isentropic efficiency of the compressors and effectiveness of the primary heat exchangers on the work of desalination were investigated. The study findings and contributions can be summarized in the following points:

- Thermochemical maps documenting the behavior of the standard and concentrated seawater (feed TDS 35,000 ppm, 50,000 ppm, 75,000 ppm, 100,000 ppm, 150,000 ppm, 200,000 ppm) at a freezing temperature range between -35°C and 0°C . The thermochemical maps were generated using the co-simulation framework described in the previous section and supported by validation using experimental data.
- Comprehensive maps documenting the effect of isentropic efficiency of the compressors and the heat exchangers' effectiveness on the energy performance of the FD system.
- Maps documenting the thermal load of the standard and concentrated seawater upon cooling for feed TDS: 35,000 ppm, 50,000 ppm, 75,000 ppm, 100,000 ppm, 150,000 ppm, 200,000 ppm) at a freezing temperature range between -35°C and 0°C .

In the next section, a technoeconomic optimization framework will be presented as a reliable tool to estimate the cost of brine treatment using FD technology.

4 Technoeconomic optimization framework for FD technology

High salinity brine is rejected in massive amounts from desalination plants, oil and gas operations, and other industrial activities [106, 107]. The process of disposal of the high salinity brine causes a notable added cost and a rising threat to the environment [108, 109]. Desalination of the high salinity brine reduces the disposed volume and thus minimizes the adverse impact on the environment as well as the disposal cost. It also creates a new source of freshwater to supply some of the water demand of the industrial, agricultural, or municipal sectors.

Currently, reverse osmosis (RO), multi-stage flash (MSF), and multi-effect distillation (MED) are the most technically mature and widely implemented desalination technologies [110]. In the case of treating the high salinity brine using the commercially available RO technology, major technical and economic barriers exist primarily related to the accelerated aging of the membranes [111, 112]. In the case of utilizing MSF or MED, the limitation on treating high salinity brine is the relatively high energy consumption besides the extensive corrosion [113]. Freeze desalination (FD) can effectively treat the high salinity brine and address the above challenges [114, 115, 116] because it experiences minimal fouling and corrosion.

Theoretically, the thermal energy required to freeze H_2O is lower than that required for evaporation (approximately 1/7) [18]. This implies that adopting FD to treat high-salinity brine can potentially outperform commercially available technologies in terms of technical robustness and cost. FD is a promising technology that has garnered significant interest in recent years. As highlighted in the previous sections, there are two main categories of FD systems: direct FD, and indirect FD. Direct FD involves a refrigerant in direct contact with the feed brine. In case of indirect FD, a solid surface always separates the refrigerant from the brine. In the early stages, the developed FD systems showed a range of practical

and technical difficulties. A common issue that emerged for both direct and indirect FD was the challenge of separation of the salt-hydrates and unfrozen brine from the ice (pure H_2O in solid state). Another technical challenge that degraded the quality of treated water generated by direct FD was the difficulty of separation of the refrigerant carried over with the desalinated water [54]. In the case of indirect FD, the ice layer formed on the cooling surfaces deteriorates the system’s thermal efficiency unless a complex (and expensive) design to scrape the ice off the cold surface is applied.

Lately, research efforts have led to acceleration of FD development toward industrial implementation by addressing the primary technical difficulties and filling key knowledge gaps. As presented in the previous chapter, our research group’s recent work reported an FD system configuration that bridges the direct and indirect FD systems, alleviating the crucial issues associated with each of the two standard configurations when used standalone [117, 118]. In general, FD is comprised of three main stages, namely, (i) freezing, (ii) separation, (iii) cold recovery (including cold recovery from melting ice). Several configurations can be devised to recover cold energy from ice during melting and other discharging streams. Assuming a reversible refrigeration system and perfect separation, the optimal cold recovery configuration must yield the least work of separation of 2.71 kJ/kg [117]. The energy consumption of the optimal FD configuration under various operating conditions has been extensively studied [117, 118]. However, the cost of brine treatment using the identified configuration has not been studied.

4.1 Current technoeconomic assessments for FD: Key Issues and Gaps

A few studies have reported the costs associated with various FD processes, none of which resemble the optimal single-stage FD system configuration [117, 118]. One study estimated the cost of water to be 37.69 USD per cubic meter ($\$/m^3$) based on experimental and numerical analysis of a small tray unit with 35,000 ppm feed brine, prepared using

deionized water (Water Purification System, Human Corp., Korea) and table salt (Nouryon Functional Chemicals, Netherlands) [19]. Several other studies have considered the cost of water to be 0.34 $\$/m^3$ [119]–[123], all referencing a report published around 25 years ago based on groundwater from the Dakota Aquifer at 5040 ppm [124]. An older study introduced the cost of water generated through energy recovery from the liquefied natural gas (LNG) handling process as 0.96 $\$/m^3$ for treating seawater [125]. More recently, a study reported a lower cost of water at 0.148 $\$/m^3$ utilizing cooling recovery from LNG for seawater desalination [126]. On a pilot scale, the HybridICETM achieved a water cost ranging from 0.42 $\$/m^3$ to 0.58 $\$/m^3$ for synthetic brine samples using sodium chloride aqueous solution feed ranging from 1–25 mg/L [127, 128]. Other studies have reported the cost of water generated by the freezing melting process as 0.93 $\$/m^3$ based on seawater, RO reject brine, food liquids, and a diluted solution of hexavalent chromium (Cr(VI)) prepared from potassium dichromate (Riedel-de Haen, Seelze, Germany) in double-distilled water [54, 57, 49, 129, 130]. As evident, there are notable inconsistencies among the published cost estimates. Most of the available studies estimate the unit cost of water based solely on capital and energy costs [19], 125–128, [54, 57, 49, 129, 130]. Few studies additionally considered the disposal costs of rejected brine and adopted a refined definition of the capital costs (reporting the costs for the installation, equipment, instrumentation, personnel, maintenance, utilities, insurance as well as research and engineering support for the first year of the project) [119]–[123]. Table. 3 shows a summary of the available cost of water treatment figures using FD:

Table 3: Summary of the published cost of water treatment using FD technology

Cost of water	Context of the estimation
37.69 \$/m ³	Based on experimental and numerical analysis of a small tray unit with 35,000 ppm feed brine, prepared using deionized water (Water Purification System, Human Corp., Korea) and table salt (Nouryon Functional Chemicals, Netherlands) ¹¹ .
0.34 \$/m ³	Several studies have considered the cost of water referencing a report published around 25 years ago ¹²⁻¹⁶ based on groundwater from the Dakota Aquifer at 5040 ppm ¹⁷ .
0.96 \$/m ³	An older study introduced the cost of water generated through energy recovery from the liquefied natural gas (LNG) handling process for treating seawater ¹⁸ .
0.148 \$/m ³	A recent study reported a relatively lower cost of water utilizing cooling recovery from LNG for seawater desalination ¹⁹ .
0.42 \$/m ³ - 0.58 \$/m ³	On a pilot scale, the HybridICE™ achieved the presented water cost range for synthetic brine samples using sodium chloride aqueous solution feed ranging from 1-25 mg/L ^{20, 21} .
0.93 \$/m ³	Several studies have reported the cost of water generated by the freezing melting process based on seawater, RO reject brine, food liquids, and a diluted solution of hexavalent chromium (Cr(VI)) prepared from potassium dichromate (Riedel-de Haen, Seelze, Germany) in double-distilled water ²²⁻²⁶ .

Despite numerous studies on the techno-economic analysis of FD systems, the reported data are afflicted by several issues summarized as follows:

- Published costs are determined based on specific electricity prices. However, in reality, electricity prices vary significantly across different locations and times [131, 132]. Notably, prices can even change within a day to support grid balancing in specific regions [133, 134]. Accordingly, generalizing the available energy and economic figures for FD technology becomes challenging.
- Crystalizing ice (pure water/ desalinated water) out of the feed brine creates an effluent with a higher concentration than the feed brine. The disposal cost of the reject brine (effluent) has not been considered in the previous studies, despite being considerably high in some regions [135, 136].
- The specific load associated with FD varies with the feed TDS. At a given desalinated water generation rate, higher feed salinities require more energy. The relation between the energy consumption of the freezing process and the brine

TDS and composition requires a thermodynamic model that takes into account the chemistry of the brine and its changes upon freezing. This factor, despite its notable effect on the system’s energy requirements and economics, was not properly considered in the literature.

- Specific freezing temperatures were adopted in previous studies. In addition, the amount of ice formation at a certain freezing temperature varies with the TDS of the feed brine. Therefore, the energy consumption of the FD system, and thus the desalination cost, depends on the TDS of the feed brine in addition to the freezing temperature. This was not considered in the previous work.
- Preliminary sensitivity analysis has shown the significance of the equipment size on the unit cost of the brine treatment at various boundary conditions. However, this tradeoff has not been comprehensively investigated by any of the prior studies

In this work, to account for variations in electricity prices, we’ve adopted an electricity price range for the economic analysis to make the analysis applicable to FD systems running within the standard market range of electricity prices. In addition, the reject brine disposal cost has been considered in the economic analysis of the system, covering the critical information gap described earlier.

For closing the knowledge gap about the effect of the feed TDS on the cooling load and thus on the system’s economics, the present study considers the coupling between the feed brine TDS, the recovery ratio, and the cooling load using thermochemical modeling of the brine. Various freezing temperatures (corresponding to different amounts of ice formed) were investigated to present comprehensive outcomes that can be generalized for the FD technology. In addition, the detailed capital expenditures (CAPEX) are part of the economic analysis.

To optimize the equipment size and the control (to minimize the brine treatment cost), a framework has been developed that balances the tradeoff between the various cost terms.

Addressing the presented issues by adopting the described methodologies contributes to the progression of FD technology towards commercialization.

4.2 FD system design model

In this subsection, the developed design models of the FD system are discussed in detail. The optimal FD system configuration identified in the previous section is adopted for the technoeconomic analysis presented in this section (Fig. 50).

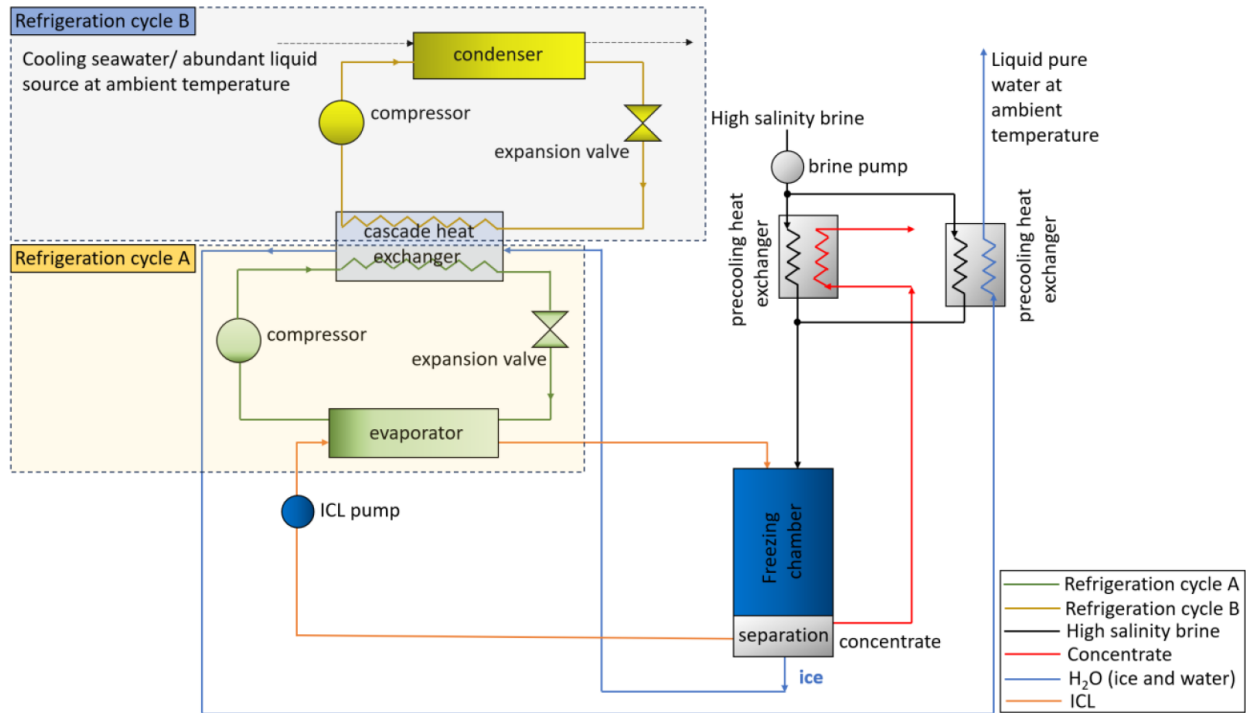


Figure 50: Freeze desalination (FD) system configuration utilized in this study.

The primary models involved in estimating the FD system's energy performance and the corresponding economics include the brine thermochemical property model, the refrigeration cycle model, the co-simulation framework, and the techno-economic model. The following assumptions were employed in model development:

1. Steady-state condition.
2. Well-mixed slurry at the outlet of the freezing chamber.

3. The ice, unfrozen brine, possible salt-hydrates, and the ICL are at thermal equilibrium.
4. All phases are assumed to be in a state of equilibrium throughout the analysis.
5. Negligible heat gain/loss from/to the ambient.

Thermochemical modeling of high salinity brine upon cooling

The estimation of the thermochemical state of the brine upon freezing is performed using the OLI Alliance engine for ASPEN PLUS [137, 138] based on its mixed solvent electrolyte (MSE) model. The model relies on readily predicted values of the equilibrium constants and other standard state partial molal thermodynamic properties. The ASPEN PLUS + OLI model utilizes a heat exchanger unit model with a fixed outlet temperature. A detailed description of the ASPEN PLUS and OLI models has been presented in the previous section.

Refrigeration cycle design model

In the utilized FD system configuration (Fig. 50), cooling is provided using a cascade refrigeration cycle. The refrigeration cycle is composed primarily of compressors, evaporator, cascade heat exchanger (an integrated evaporator-condenser set), and condenser. The refrigeration cycle accounts for a dominant fraction of the FD system's total energy consumption. Modeling the refrigeration system accurately is essential for estimating the overall system energy performance. The amount of energy rejected at the condensing side of each refrigeration cycle balances with the summation of the evaporator's thermal load and the compressor's work of the same cycle as shown in Eq. 23:

$$Q_{co} = Q_{ev} + W \quad (23)$$

As described previously, the cascade heat exchanger connects the two refrigeration cycles thermally. The load carried by the evaporator of refrigeration cycle B (Fig. 50) is the summation of the evaporating load and compressor work of refrigeration cycle A after considering the cooling energy recovered from melting the formed ice as shown in Eq. 24:

$$Q_{ev,cycB} = W_{cycA} + Q_{ev,cycA} - Q_{ice,melt} \quad (24)$$

Compressor

The cascade refrigeration cycle is composed of two compressors exerting work on the refrigerant to circulate it through the cycle. Based on the design capacity and the high-efficiency requirement, the commercial screw compressors models HSK9583-320 and HSK8591-180 manufactured by Bitzer are selected for refrigeration cycles A and B, respectively [139].

To model the compressors' performance, the statistical ten-coefficient ARI540 correlation is utilized [140]. The refrigerant mass flow rate and the compressor electrical power consumption are calculated using Eq. 25 and 26 as a function of the evaporating and condensing temperatures (adopted within the manufacturer's map limits [139]):

$$\begin{aligned} \dot{m}_{refr} = & \theta_1 + \theta_2.T_{evap} + \theta_3.T_{cond} + \theta_4.T_{evap}^2 + \theta_5.T_{evap}.T_{cond} + \theta_6.T_{cond}^2 + \theta_7.T_{evap}^3 \\ & + \theta_8.T_{evap}^2.T_{cond} + \theta_9.T_{evap}.T_{cond}^2 + \theta_{10}.T_{cond}^3 \end{aligned} \quad (25)$$

$$\begin{aligned} \dot{P}_e = & \alpha_1 + \alpha_2.T_{evap} + \alpha_3.T_{cond} + \alpha_4.T_{evap}^2 + \alpha_5.T_{evap}.T_{cond} + \alpha_6.T_{cond}^2 + \alpha_7.T_{evap}^3 \\ & + \alpha_8.T_{evap}^2.T_{cond} + \alpha_9.T_{evap}.T_{cond}^2 + \alpha_{10}.T_{cond}^3 \end{aligned} \quad (26)$$

where $\dot{m}_{refr}$ is the refrigerant mass flow rate in kg/s, P_e is the electrical power in W, and T_{evap} and T_{cond} are the evaporating and condensing temperatures in °C, respectively. The correlation coefficients are represented by θ_1 to θ_{10} and α_1 to α_{10} .

The ARI540 correlation parameters have been calibrated using manufacturer performance data for the selected compressors [139]. Since the design superheat is different from the one at which the manufacturer data was generated, correction is applied to the refrigerant mass flow rate and the compressor power (estimated from Eq. 25 and 26) using Eq. 27 and 28, respectively [141]:

$$\frac{\dot{m}_{sim}}{\dot{m}_{map}} = 1 + 0.75 \left(\frac{\rho_{s,sim}}{\rho_{s,map}} - 1 \right) \quad (27)$$

$$\frac{\dot{P}_{sim}}{\dot{P}_{map}} = \frac{\dot{m}_{sim}}{\dot{m}_{map}} \frac{\Delta h_{i,sim}}{\Delta h_{i,map}} \quad (28)$$

where $\dot{m}_{sim}$ and $\dot{m}_{map}$ are the simulated and the map mass flow rates in kg/s, and $\rho_{s,sim}$ and $\rho_{s,map}$ are the simulated and the map suction densities in kg/m^3 , respectively. The isentropic enthalpy change is represented by $\Delta h_{i,sim}$ and $\Delta h_{i,map}$ in J.

Evaporator, condenser and cascade heat exchanger

The optimal FD system configuration utilizes three primary heat exchangers; the evaporator where the ICL is cooled down before entering the freezing chamber, the cascade heat exchanger where the generated ice is melted for cooling energy recovery and the condenser where heat is rejected to a cooling stream entering the condenser at ambient temperature. The size of those heat exchangers considerably affects the FD system's brine treatment cost. Using larger heat exchangers (larger heat transfer areas) is associated with higher energy efficiency, which lowers energy costs. On the other hand, utilizing larger heat exchangers raises the system's CAPEX along with the associated maintenance and labor costs. Accordingly, optimizing the heat exchangers' size becomes critical for minimizing the brine treatment cost.

The temperature difference between the fluids inside each heat exchanger ΔT is the con-

trollable variable linked to the design size of each of the heat exchangers, as presented in Fig. 51. The evaporator's temperature difference (ΔT_A) resembles the average temperature of the ICL inside the evaporator minus the refrigerant's evaporating temperature of refrigeration cycle A. For the condenser, ΔT_D is the difference between the refrigerant's condensing temperature of refrigeration cycle B and the average cooling water temperature across the condenser. The cascade heat exchanger's design size is associated with the controllable variable ΔT_C defined as the difference between the refrigerant's condensing temperature (of cycle A) and the shell side temperature of the cascade heat exchanger. For the cascade heat exchanger, previous work proved that the optimal shell side temperature is 0°C assuming perfect ice separation [117].

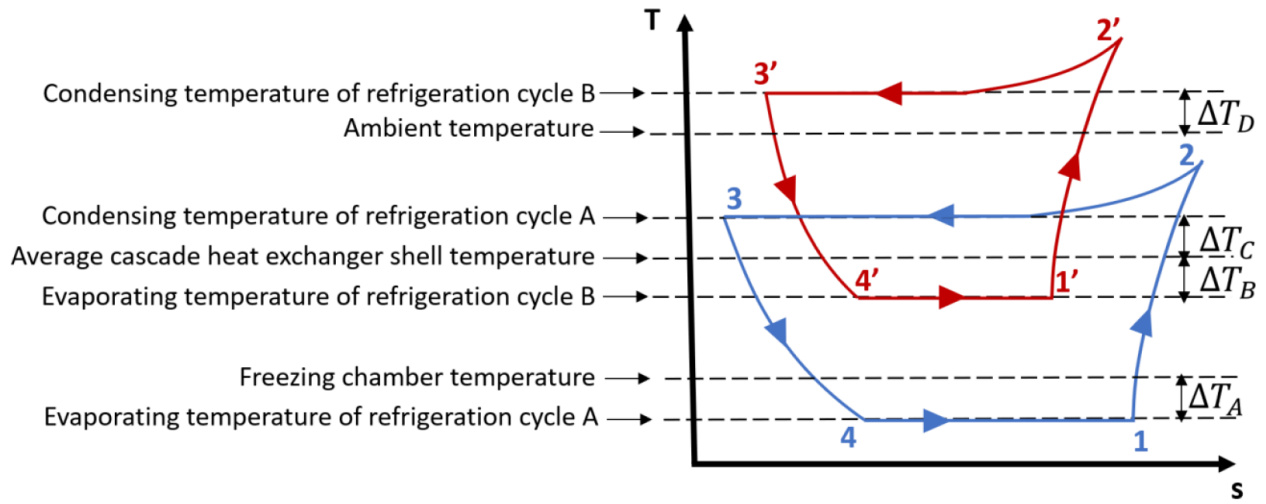


Figure 51: The temperature differences (ΔT) utilized as the controllable variable linked to the design size of the evaporator, the condenser and the cascade heat exchanger of the freeze desalination (FD) system.

The temperature difference values (ΔT) presented in Fig. 51 allow calculating the logarithmic temperature difference (ΔT_{LM}) for each of the heat exchangers as shown in Eq. 29–33:

$$\Delta TLM_{ev,cycA} = \frac{(T_{ev,cycA,ICL,in} - T_{ev,cycA,refr,out}) - (T_{ev,cycA,ICL,out} - T_{ev,cycA,refr,in})}{\ln\left(\frac{T_{ev,cycA,ICL,in} - T_{ev,cycA,refr,out}}{T_{ev,cycA,ICL,out} - T_{ev,cycA,refr,in}}\right)} \quad (29)$$

$$\Delta TLM_{interm,sf} = \frac{(T_{co,cycA,refr,in} - T_{melt}) - (T_{co,cycA,refr,sv} - T_{melt})}{\ln\left(\frac{T_{co,cycA,refr,in} - T_{melt}}{T_{co,cycA,refr,sv} - T_{melt}}\right)} \quad (30)$$

$$\Delta TLM_{interm,tf} = \frac{(T_{co,cycA,refr,sv} - T_{melt}) - (T_{co,cycA,refr,out} - T_{melt})}{\ln\left(\frac{T_{co,cycA,refr,sv} - T_{melt}}{T_{co,cycA,refr,out} - T_{melt}}\right)} \quad (31)$$

$$\Delta TLM_{co,cycB,sf} = \frac{(T_{co,cycB,refr,in} - T_{cw,out,sf}) - (T_{co,cycB,refr,sv} - T_{cw,in,sf})}{\ln\left(\frac{T_{co,cycB,refr,in} - T_{cw,out,sf}}{T_{co,cycB,refr,sv} - T_{cw,in,sf}}\right)} \quad (32)$$

$$\Delta TLM_{co,cycB,tf} = \frac{(T_{co,cycB,refr,sv} - T_{cw,out,tf}) - (T_{co,cycB,refr,out} - T_{cw,in,tf})}{\ln\left(\frac{T_{co,cycB,refr,sv} - T_{cw,out,tf}}{T_{co,cycB,refr,out} - T_{cw,in,tf}}\right)} \quad (33)$$

Where ΔTLM represents the logarithmic mean temperature different in $^{\circ}C$ and T is the temperature in $^{\circ}C$. The subscript *ev* refers to the evaporator, the subscript *ICL* is for the intermediate cooling liquid and the subscript *in* is for the inlet. The subscript *refr* is for the refrigerant and subscript *out* refers to the fluid leaving the heat exchanger. The subscript *co* refers to the condenser and the subscript *sv* refers to the saturated vapor phase. The variable T_{melt} is the melting temperature in $^{\circ}C$. The subscript *sf* refers to the single phase and the subscript *tf* is for the two phase. Subscript *interm* refers to the intermediate heat exchanger and subscript *cw* is for the cooling water. The subscript *cycA* and *cycB* refer to refrigeration cycles A and B, respectively.

The combined heat transfer coefficient UA (in $W/^{\circ}C$) of each of the heat exchangers is calculated using Eq. 34–38.

$$UA_{ev,cycA} = \frac{Q_{ev,cycA}}{\Delta TLM_{ev,cycA}} \quad (34)$$

$$UA_{interm,sf} = \frac{Q_{co,cycA,sf}}{\Delta TLM_{interm,sf}} \quad (35)$$

$$UA_{interm,tf} = \frac{Q_{co,cycA,tf}}{\Delta TLM_{interm,tf}} \quad (36)$$

$$UA_{co,cycB,sf} = \frac{Q_{co,cycB,sf}}{\Delta TLM_{co,cycB,sf}} \quad (37)$$

$$UA_{co,cycB,tf} = \frac{Q_{co,cycB,tf}}{\Delta TLM_{co,cycB,tf}} \quad (38)$$

Where UA is the combined heat transfer coefficient in $W/^\circ C$, Q is the cooling load in W and ΔTLM is the logarithmic mean temperature different in $^\circ C$. The subscript *interm* refers to the intermediate heat exchanger, the subscript *sf* is the single phase and the subscript *tf* represents the two phase. The subscript *cycA* and *cycB* refer to refrigeration cycles A and B, respectively.

The capital cost of the evaporator, the condenser, and the cascade heat exchanger are estimated based on the published data correlating the capital cost with the combined heat transfer coefficient UA (heat exchanger capital cost: 850 \$/kW/K) [142, 143]. Accordingly, the heat exchangers' capital cost is estimated using Eq. 39–41.

$$C_{ev,cycA} = 850 (UA_{ev,cycA}) \quad (39)$$

$$C_{interm} = 850 (UA_{interm,sf} + UA_{interm,tf}) \quad (40)$$

$$C_{co,cycB} = 850 (UA_{co,cycB,sf} + UA_{co,cycB,tf}) \quad (41)$$

4.3 FD cost optimization framework

This section presents the co-simulation framework developed to optimize the FD system's design and control. The optimization problem aims to minimize the brine treatment cost by tuning the controllable variables; feed brine injection rate and temperature differences ($\Delta T_A, \Delta T_C$ and ΔT_D) linked to the design size of each of the heat exchangers. To explain the co-simulation framework's operation, Table 4 shows the input-output correspondence for the FD system's primary component models utilized to estimate the electrical power consumption. The single-underscored variables are external inputs, and the double-underscored ones represent internal variables solved iteratively by satisfying Eq. 42–44.

Table 4: Freeze desalination (FD) design model input-output form.

Model	Input – output form
Freeze chamber	$[Q_{ch}, T_{fz}, \dot{m}_{ice}] = \text{chamber}(\dot{m}_b, \dot{m}_{\underline{\underline{ICL}}}, T_{\underline{\underline{ch,ICL,in}}}, T_{\underline{\underline{ch,b,in}}}, \underline{\underline{TDS_b}})$
Evaporator _{cycA}	$[T_{\text{cycA,refr,evap}}, T_{\text{ev,ICL,out}}] = \text{evap}(Q_{ch}, \dot{m}_{\underline{\underline{ICL}}}, T_{fz}, \underline{\underline{\Delta T_A}})$
Compressor _{cycA}	$[\dot{P}_{e,\text{cycA}}, Q_{\text{ev,cycA}}] = \text{comp}(T_{\text{cycA,refr,evap}}, T_{\underline{\underline{melt}}}, \underline{\underline{\Delta T_C}})$
Intermediate heat exchanger	$[Q_{\text{ev,cycB}}] = \text{interm}(Q_{\text{ev,cycA}}, \dot{P}_{e,\text{cycA}}, \dot{m}_{ice}, T_{fz})$
Compressor _{cycB}	$[\dot{P}_{e,\text{cycB}}, T_{\text{cycB,refr,evap}}] = \text{comp}(Q_{\text{ev,cycB}}, T_{\underline{\underline{amb}}}, \underline{\underline{\Delta T_D}})$
Condenser _{cycB}	$[T_{\text{co,cw,out}}] = \text{cond}(\dot{m}_{\underline{\underline{cw}}}, T_{\underline{\underline{co,cw,in}}}, \dot{P}_{e,\text{cycB}}, Q_{\text{ev,cycB}})$
Precoolers	$[T_{\text{pre,b,out}}] = \text{precoolers}(\dot{m}_b, \dot{m}_{ice}, T_{\underline{\underline{melt}}}, T_{\underline{\underline{amb}}})$

In Table. 4, Q_{ch} is the freezing chamber's thermal load in W, T_{fz} is the temperature inside the freezing chamber in °C and $\dot{m}_{ice}$ is the ice crystallization rate in kg/s. $\dot{m}_b$ is the brine injection rate into the freezing chamber in kg/s, $\dot{m}_{\underline{\underline{ICL}}}$ is the ICL mass flow rate in kg/s, $T_{\underline{\underline{ch,ICL,in}}}$ is the temperature of the ICL entering the freezing chamber in °C, $T_{\underline{\underline{ch,b,in}}}$ is the temperature of the brine entering the freezing chamber in °C and $\underline{\underline{TDS_b}}$ is the TDS of the feed brine in ppm. $T_{\text{cycA,refr,evap}}$ resembles the evaporating temperature of the refrigerant of cycle A in °C, $T_{\text{ev,ICL,out}}$ is the temperature of the ICL leaving the evaporator in °C and $\underline{\underline{\Delta T_A}}$

is a controllable variable (explained earlier) related to the size of the evaporator of refrigeration cycle A in °C. $\dot{P}_{e,cycA}$ resembles the electrical power consumption of the compressor of refrigeration cycle A in W. $Q_{ev,cycA}$ is the thermal load carried by the evaporator of refrigeration cycle A in W, T_{melt} is the ice melting temperature in °C and ΔT_C is a controllable variable related to the size of the intermediate heat exchanger coupling refrigeration cycle A and B °C. $Q_{ev,cycB}$ is the thermal load on the evaporator of refrigeration cycle B in W, $\dot{P}_{e,cycB}$ is the electrical power consumption of the compressor of refrigeration cycle B in W, $T_{cycB,refr,evap}$ is the evaporating temperature of the refrigerant of cycle B in °C, T_{amb} is the ambient temperature and ΔT_D is a controllable variable related to the size of the condenser of refrigeration cycle B °C. $T_{co,cw,out}$ is the temperature of the cooling water leaving the condenser in °C, $\dot{m}_{cw}$ is the cooling water mass flow rate in kg/s, $T_{co,cw,in}$ is the temperature of the cooling water entering the condenser in °C and $T_{pre,b,out}$ is the temperature of the brine leaving the precooler in °C.

$$T_{ch,ICL,in} = T_{ev,ICL,out} \quad (42)$$

$$T_{ch,b,in} = T_{pre,b,out} \quad (43)$$

$$Q_{ch} = Q_{ev,cycA} \quad (44)$$

For the freeze chamber model, well mixing and sufficient column length are assumed such that the temperatures of the brine, ice, and ICL streams leaving the chamber are equivalent (T_{fz}). The co-simulation framework is developed in MATLAB to orchestrate the numerical solution among the component models also developed in MATLAB in addition to leveraging the brine thermochemical model (part of the freeze chamber model) in ASPEN PLUS + OLI engine.

Techno-economic analysis of the FD system is critical for minimizing the treatment cost.

Sensitivity analysis showed that the factors with significant effects on the economics of the FD system are the feed brine TDS, the electricity price, the brine (concentrate) disposal cost, the desalinated water selling price, the CAPEX cost as well as the maintenance and the labor costs. The CAPEX of the FD system is calculated using Eq. 45:

$$C_{CAPEX} = C_r + C_{cv} + C_{ew} + C_{la} + C_{cl} + C_{iwc} \quad (45)$$

where C_{CAPEX} represents the CAPEX cost, C_r is the refrigeration system cost, C_{cv} is the civil works cost, C_{ew} is the electrical works cost, C_{la} is the land acquisition cost, C_{cl} is the construction labor cost and C_{iwc} represents the additional initial working capital all in \$ (USD). The C_r is calculated based on the market prices of the refrigeration system's equipment [142, 143]. The percentages adopted for the contribution of the various categories to the total CAPEX are presented in Table 5 [142] –[148].

Table 5: Freeze desalination (FD) system's CAPEX primary cost categories.

CAPEX cost category	[%] of total CAPEX cost
Refrigeration system cost (C_r) (Compressors+ Heat exchangers+ Other hardware & instrumentation)	30%
Civil works cost (C_{cv})	30%
Electrical works cost (C_{ew})	10%
Land acquisition cost (C_{la})	10%
Construction labor cost (C_{cl})	15%
Additional initial working capital (C_{iwc})	5%

The cost of electricity is found using Eq. 46:

$$C_e = 2.7778(10^{-9}) \times \dot{P}_e \times Pr_e \times t \quad (46)$$

where C_e is the total cost of electricity in \$, $\dot{P}_e$ represents the electrical power consumption of the system in W, Pr_e is the electricity price in ¢/kWh and t is the operational time in seconds. The disposal cost is estimated using Eq. 47:

$$C_d = 0.0062898 \times Pr_d \times m_b \times (1 - RR) \quad (47)$$

where C_d is the total cost of disposing high salinity brine in \$, Pr_d is the brine disposal cost in \$/bbl, m_b is the feed brine mass in kg and the recovery ratio (RR) represents the mass ratio between the desalinated water generated and the feed brine. The maintenance cost (C_m) emerges from the capital equipment utilized as well as the intensity and duration of operation [144, 149, 150]. Based on published industrial data, Eq. 48 is developed to estimate the maintenance cost (C_m) of the FD system [144, 149, 150]:

$$C_m = 0.228 \times C_e + 0.248 \times C_{CAPEX} \quad (48)$$

where C_e is the total cost of electricity in \$ and C_{CAPEX} represents the CAPEX cost. The labor cost (C_{lb}) is considered as 1.5 the maintenance cost (C_m) [144, 149, 150]. The desalinated water selling price (C_{des}) is also considered in estimating the cost of treatment. The total cost of the brine treatment (C_T) in \$ is calculated using Eq. 49:

$$C_T = C_e + C_d + C_{CAPEX} + C_m + C_{lb} - C_{des} \quad (49)$$

Concluding remarks

This section introduces a cost optimization framework for the FD technology. The framework is built based on a detailed FD system model, which has been developed and validated against both experimental and manufacturer data. The developed framework is a novel contribution that serves as a critical tool for the selection and the design optimization (sizing and operational parameters) of the FD technology. This section resulted in a number of critical conclusions summarized in the following points:

- The electricity prices change significantly across different locations and times, and the calculation method to estimate the accurate cost of brine treatment using FD should consider the effect of the varying electricity price.
- The cost of disposal is a dominant component in the overall brine treatment cost utilizing FD systems. An accurate and beneficial cost estimation framework has to consider the practical range of the brine disposal prices.
- One of the primary advantages of the FD technology is the lower sensitivity to the feed TDS. Therefore, a cost optimization framework for FD can only be practically beneficial when it considers a range of feed TDS including higher TDS brines.
- Different boundary conditions require the change in the FD system's operational parameters to enhance the energy efficiency. This includes controlling the freezing chamber temperature by changing the rate at which the feed brine is injected into the system.
- The FD system's equipment size and particularly its primary heat exchangers (evaporator, intermedaite heat exchanger, and condenser) has a significant effect

on the system's energy performance and brine treatment cost. This resembles a critical tradeoff balancing problem at each set of boundary conditons.

5 Benchmark cost maps for FD technology

The primary contributions of this section is to provide accurate quantitative results related to the system's economics. The following subsections, discuss the validation of the brine thermochemical model and the compressor models using published experimental data and manufacturer data, shows the sensitivity analysis for the optimization variables highlighting the tradeoffs, and present the techno-economic metrics necessary for the design of the FD system under different realistic scenarios. To achieve that, the following critical research questions are addressed throughout this section:

- What is the cost of brine treatment using the identified optimal FD system configuration ?
- What is the effect of varying electricity price on the cost of brine treatment ?
- What is the effect of change in disposal price on the cost of brine treatment ?
- What is the effect of adopting different freezing temperatures on the cost of brine treatment ?
- What is the effect of feed TDS on the cost of brine treatment ?
- What are the optimal equipment sizes and operational parameters for minimizing brine treatment cost using FD ?

5.1 Models validation

As described in the previous section, the estimation of the thermochemical properties of the brine flowing through the FD system is handled by models developed based on the OLI Alliance engine for ASPEN PLUS [137, 71]. The outputs predicted by the thermochemical model include the mass of crystallized ice and the cooling load of the brine. The cooling load estimation model has been verified using published experimental data for a binary aqueous

Na^+ and Cl^- solution at the same concentrations showing a maximum error of less than 5% [151]. The prediction accuracy of the ice mass production has been verified against published experimental data for freezing brine [102]. The outcomes showed that for TDS of 35,000, 50,000, and 75,000 ppm, the error between the model predictions and the actual measurements is less than 5%. For the TDS of 100,000 ppm and 150,000 ppm, the error is below 10%. In the case of higher TDS (200,000 ppm), the calculated values showed significant overpredictions compared to the experimental data with a 25% margin error. This large error in the case of the high salinity feed is suggested to emerge from the practical difficulties in the experiment performed to generate the data, primarily, associated with the separation of ice from the hydrohalite without losing part of the formed ice.

The commercial screw compressors HSK95103-320 and HSK8591-180 (manufactured by Bitzer) are utilized for each of the refrigeration cycles 1 and 2 respectively. The compressors' developed models (discussed in the previous section) have been validated against manufacturer data showing an error of less than 5% for the estimated refrigerant mass flow rate and the electrical power consumption as presented in Figs. 52–55.

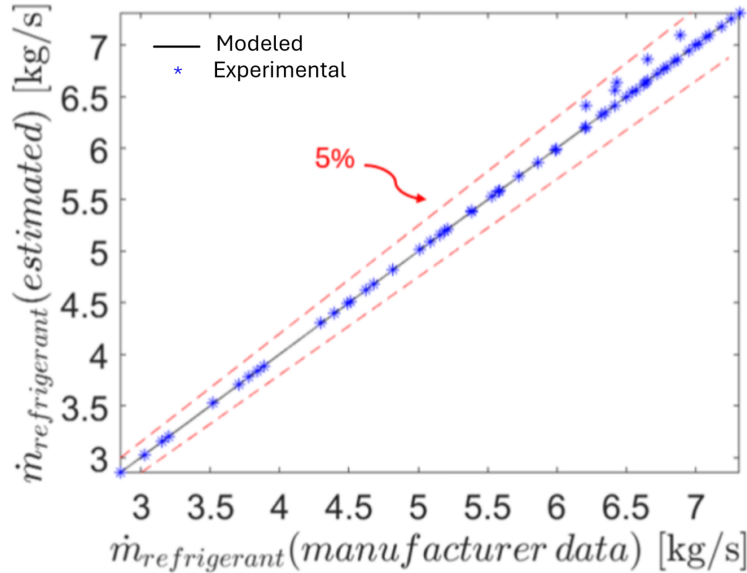


Figure 52: Model estimated vs. manufacturer's values of the refrigerant mass flow rate related to the HSK95103-320 compressor.

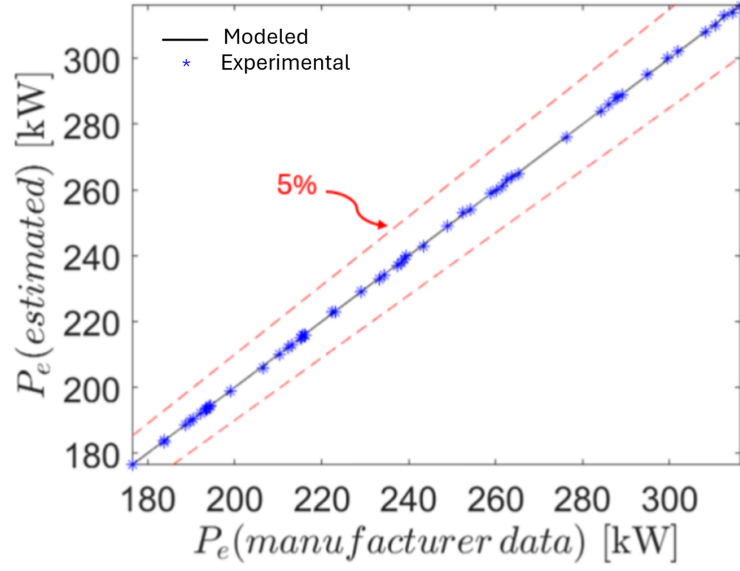


Figure 53: Model estimated vs. manufacturer's values of the electric power related to the HSK95103-320 compressor.

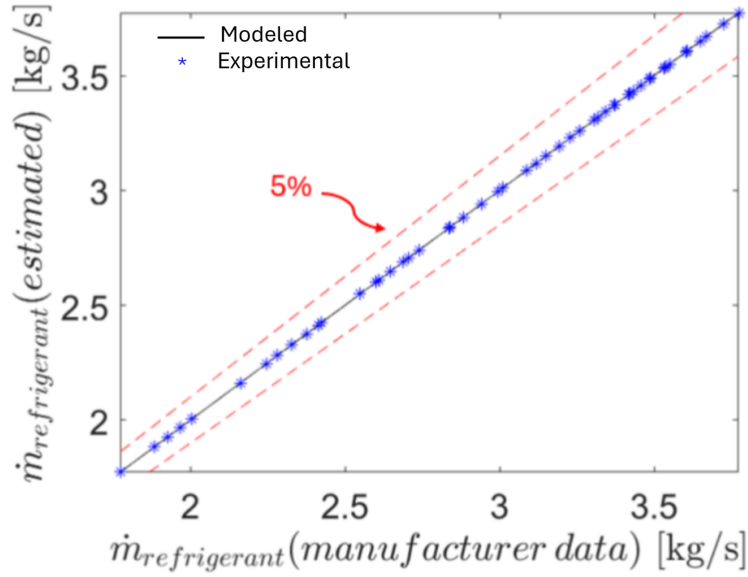


Figure 54: Model estimated vs. manufacturer's values of the refrigerant mass flow rate related to the HSK8591-180 compressor.

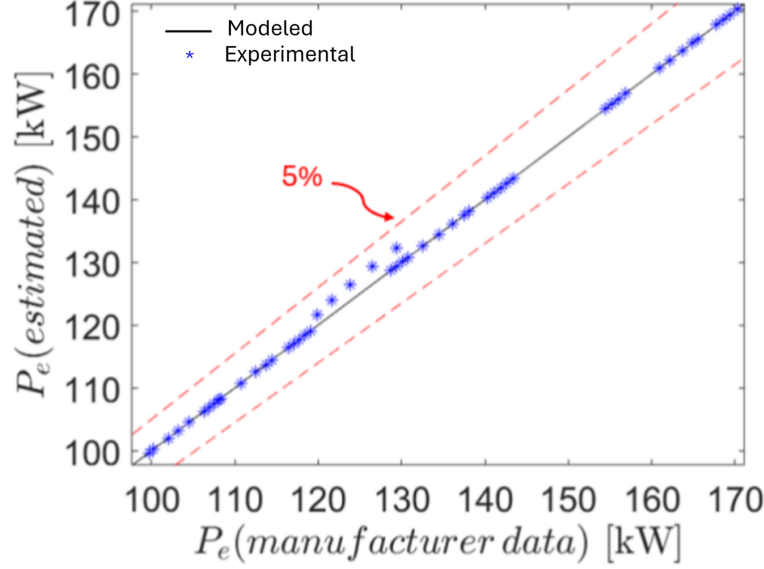


Figure 55: Model estimated vs. manufacturer's values of the electric power related to the HSK8591-180 compressor.

5.2 Sensitivity analysis

As described earlier, the heat exchangers' size is optimized to minimize the cost of brine treatment. The temperature difference (ΔT) is the controllable variable linked to the design size of each of the heat exchangers. Figure 56 is an example illustration of the cost of brine treatment at different values of ΔT_{HX} , assuming a feed TDS of 75,000 ppm, a brine disposal cost of 0.02 \$/bbl, an electricity price of 8 ¢/kWhr, a freezing chamber temperature of -15°C and considering $\Delta T_A = \Delta T_C = \Delta T_D = \Delta T_{HX}$ for this example case. After accounting for the profit collected from selling the purified water, the cost of brine treatment is the summation of the electricity cost, the disposal cost, the maintenance cost, the labor cost, and the CAPEX. At the same freezing chamber temperature, changing the ΔT values result in a change in each of those cost categories except for the disposal cost. The ratio between the summation of the electricity cost, the maintenance cost, and the labor cost to the CAPEX showed compliance with the published values with a ratio ranging between 4.15 to 20.75 [144].

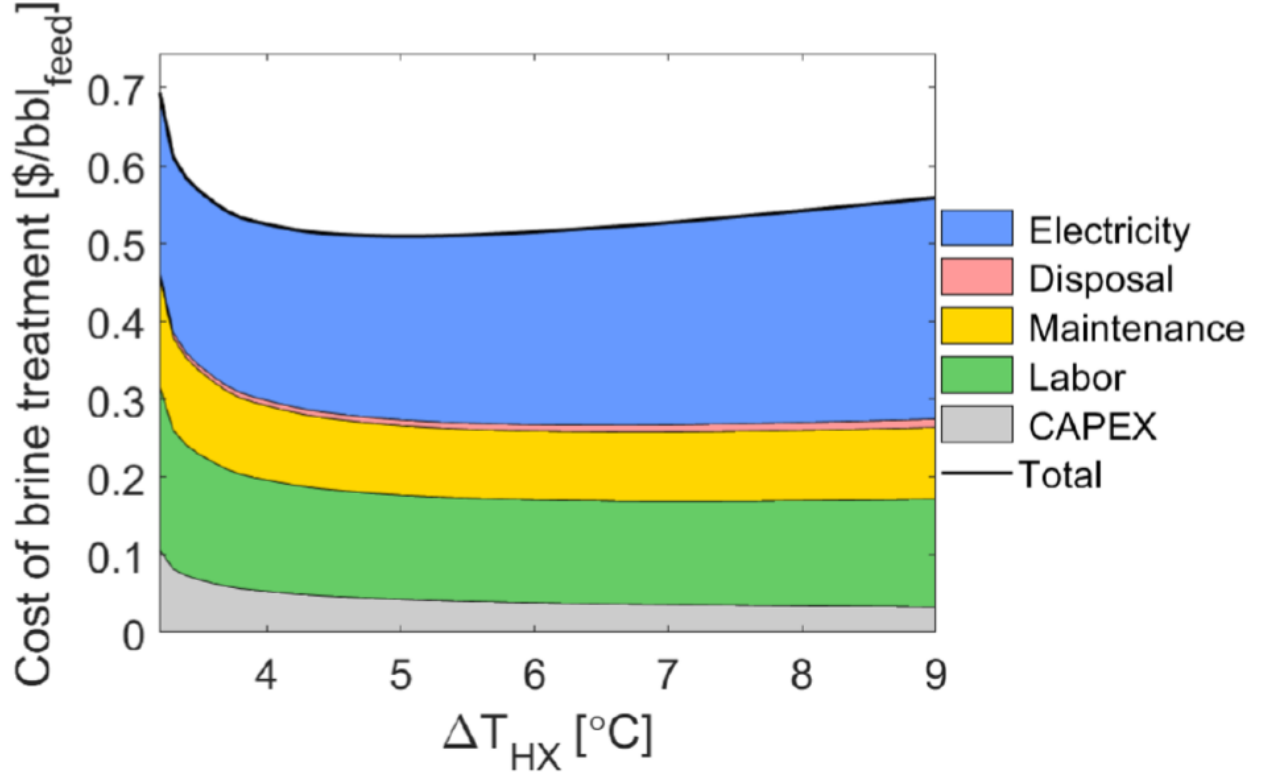


Figure 56: Illustration of the change in the cost of brine treatment throughout a ΔT range.

Figure 56 shows that higher ΔT values correspond to lower CAPEX (smaller-size heat exchangers). The higher ΔT values are also associated with increased electricity costs due to the deterioration of the heat transfer efficiency. On the other hand, lower ΔT values are associated with lower electricity costs and higher CAPEX, maintenance, and labor costs. The cost optimization framework balances the tradeoff and identifies the optimal sizes for each of the FD system's heat exchangers.

The feed brine injection rate is the other optimization variable tuned to minimize the brine treatment cost. Changing the amount of brine injected into the freezing chamber results in changing the freezing chamber temperature as shown in Fig. 57 (for a feed TDS of 75,000 ppm). The change in the freezing chamber temperature is linked to a change in the ice recovery ratio (the amount of formed ice) [117] as well as the treatment cost. Figure 58 illustrates the effect of the change of the freezing temperature on the treatment cost and the recovery ratio values corresponding to the feed salinity of 75,000 ppm, brine disposal cost of

0.5 \$/bbl, and electricity price of 8 ¢/kWhr.

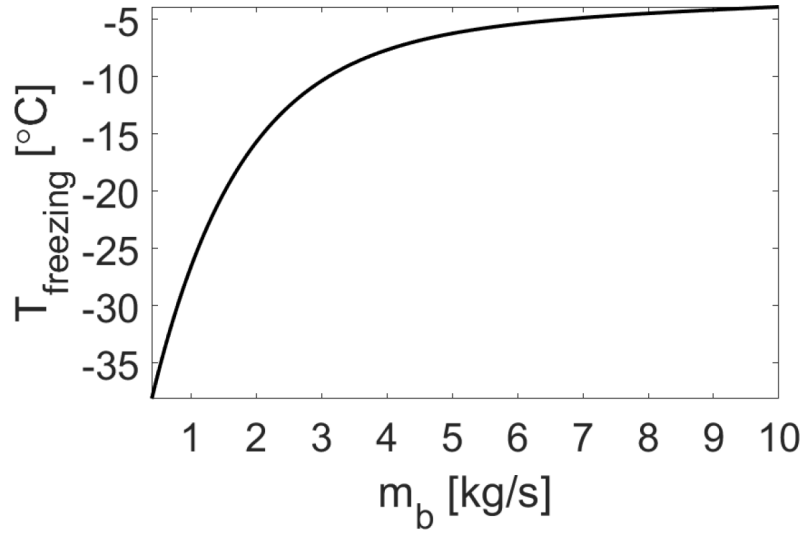


Figure 57: The change in the freezing chamber temperature at different brine injection rates corresponding to a feed TDS of 75,000 ppm.

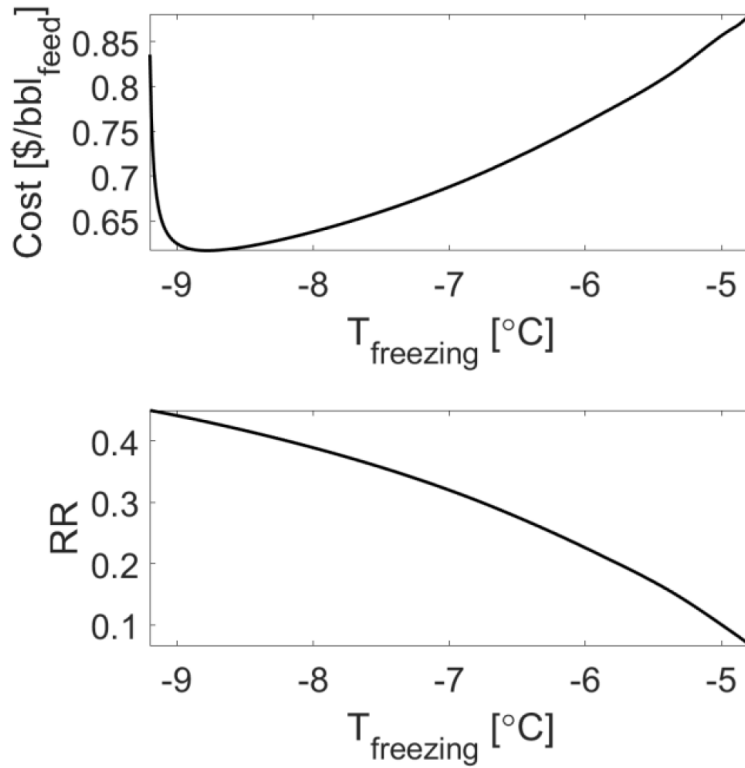


Figure 58: The change of the water recovery ratio and the cost of brine treatment at different freezing temperatures corresponding to a feed salinity of 75,000 ppm, brine disposal cost of 0.5 \$/bbl, and electricity price of 8 ¢/kWhr.

At lower freezing chamber temperatures, more ice is generated (higher recovery ratio). However, this is accompanied by an increase in electricity consumption and thus an increase in the overall treatment cost. On the other hand, the rise in the freezing temperature approaching the start of freezing temperature causes the treatment cost to significantly increase due to the higher mass of disposal. Therefore, optimizing the feed brine injection rate is critical for minimizing the cost of treatment linked to the FD technology.

5.3 Technoeconomic metrics of the FD system

Comprehensive knowledge about the economics of processing high-salinity brine utilizing the FD system is essential for the commercialization of the technology (critical for the selection, design, and further analysis of the FD system). The accurate and reliable technoeconomic analysis for the FD system became possible with the models and treatment cost optimization framework developed in this study.

Besides the CAPEX, the cost of treatment of the high salinity brine is affected primarily by the feed TDS, the electricity price, the brine disposal cost, the costs associated with the labor and maintenance, and the desalinated water selling price. Currently, the price of freshwater produced from conventional desalination plants is typically between \$0.5 to \$1.5 per ton [144, 145, 152]. Sensitivity analysis showed a minimal effect of changing the water selling price within the typical range on the overall treatment cost, and accordingly, a constant desalinated water selling price of \$1.5 per ton is adopted.

The electricity price and the brine disposal cost vary tremendously at different geographical locations. Thus, a range of electricity prices is considered from ¢4 to ¢27.83 per kWhr [153]. The assumed brine (concentrate) disposal costs are \$0.02, \$0.5, \$1.5, \$2.5, and \$3.5 per barrel [154, 155, 156, 157, 158, 159].

Table 6 presents the CAPEX for an FD plant with a treatment capacity of 1000 tons of brine per day corresponding to a feed TDS of 100,000 ppm, an electricity price of 4 ¢/kWhr, and a brine disposal cost of 0.5 \$/bbl. The CAPEX is calculated based on the optimized

equipment size and brine injection rate, assuming a plant life cycle of 30 years.

Table 6: CAPEX of the freeze desalination (FD) plant (1000 tons of brine per day).

Refrigeration plant [57][71-74]	\$ 106,716
Civil works [61,62]	\$ 106,716
Electrical works [61,62]	\$ 35,572
Land acquisition [61,62]	\$ 35,572
Construction labor [61,62]	\$ 53,358
Initial working capital [61,62]	\$ 17,786
Total CAPEX	\$ 355,720

The FD system runs at its full capacity and the temperature inside the freezing chamber is directly affected by the feed brine injection rate. Higher brine injection rates lead to higher freezing temperatures as well as lower recovery ratio values (RR). Utilizing the FD cost optimization framework (to tune the heat exchangers' size as well as the brine injection rate), the optimal cost of treatment is identified for a wide range of electricity prices, brine disposal costs, and different feed TDS values, as presented in Figs. 59– 73. The controllable variables are tuned using gradient based optimization technique utilizing the models discussed previously.

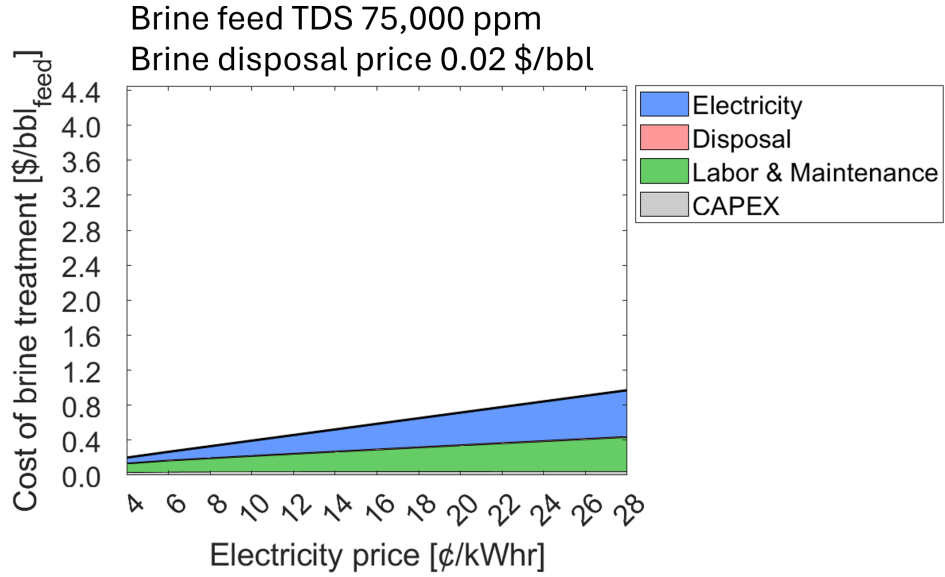


Figure 59: The treatment cost of brine using FD technology for a feed TDS of 75,000 ppm and a brine disposal price of 0.02 \$/bbl.

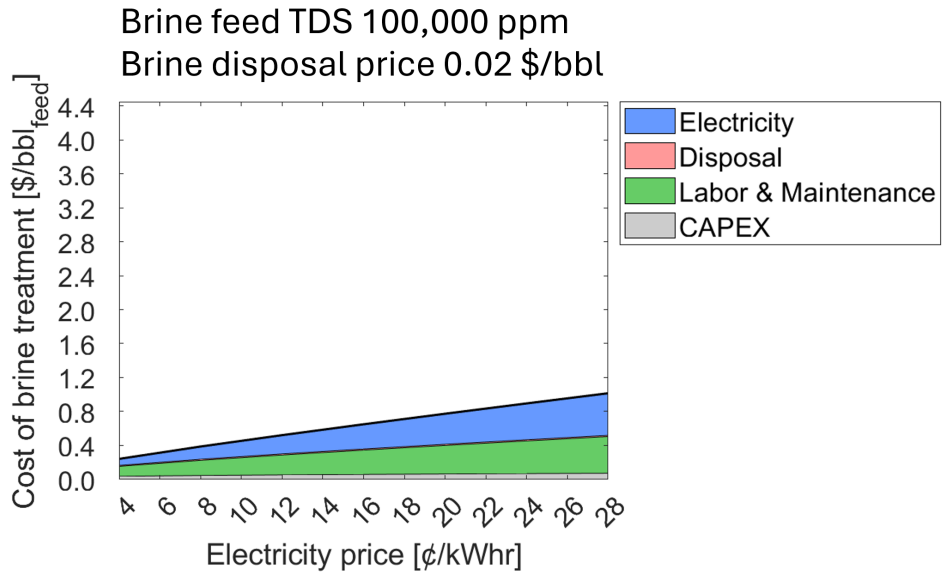


Figure 60: The treatment cost of brine using FD technology for a feed TDS of 100,000 ppm and a brine disposal price of 0.02 \$/bbl.

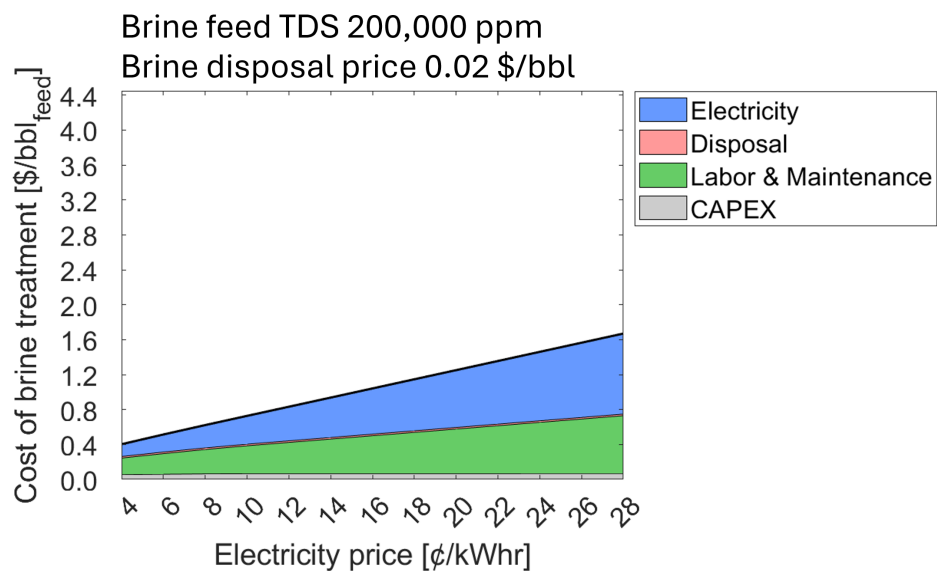


Figure 61: The treatment cost of brine using FD technology for a feed TDS of 200,000 ppm and a brine disposal price of 0.02 \$/bbl.

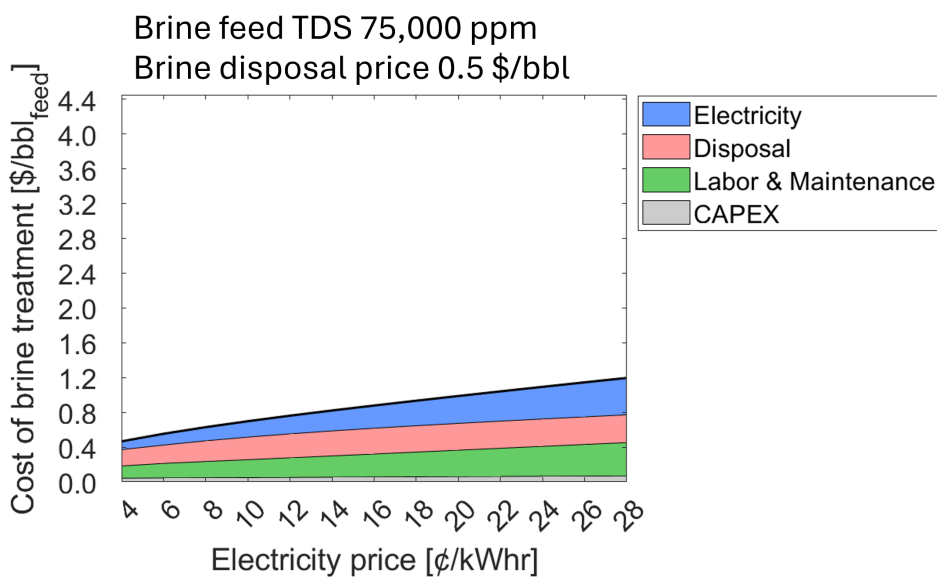


Figure 62: The treatment cost of brine using FD technology for a feed TDS of 75,000 ppm and a brine disposal price of 0.5 \$/bbl.

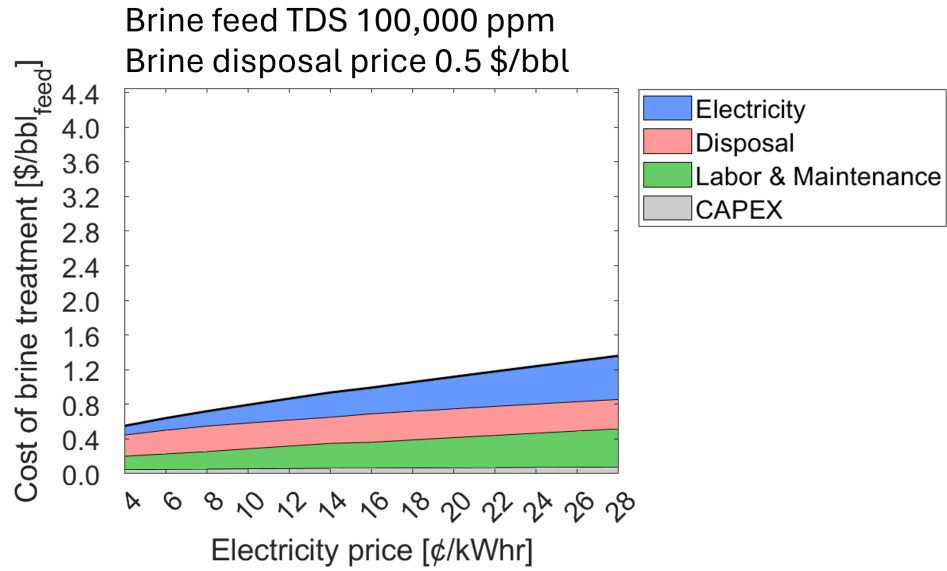


Figure 63: The treatment cost of brine using FD technology for a feed TDS of 100,000 ppm and a brine disposal price of 0.5 \$/bbl.

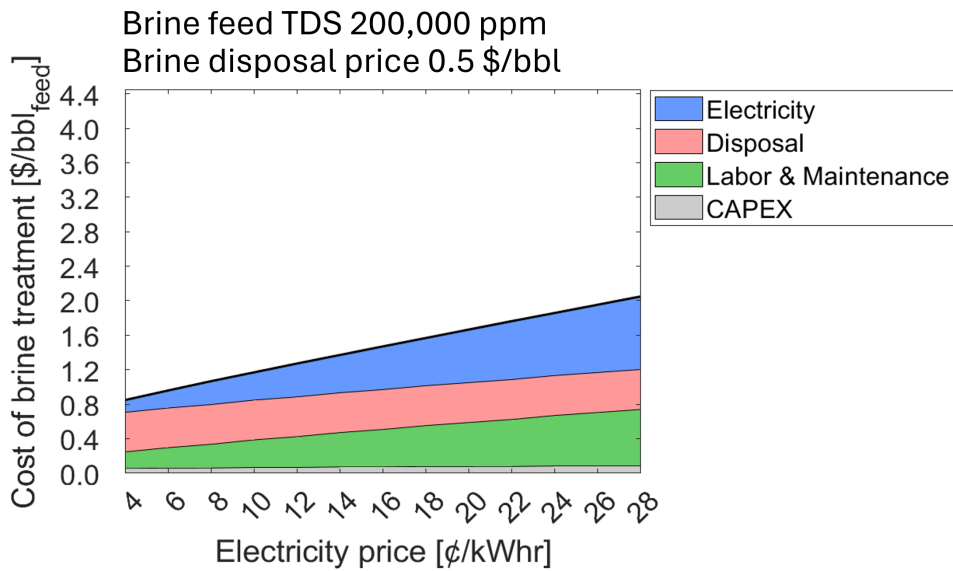


Figure 64: The treatment cost of brine using FD technology for a feed TDS of 200,000 ppm and a brine disposal price of 0.5 \$/bbl.

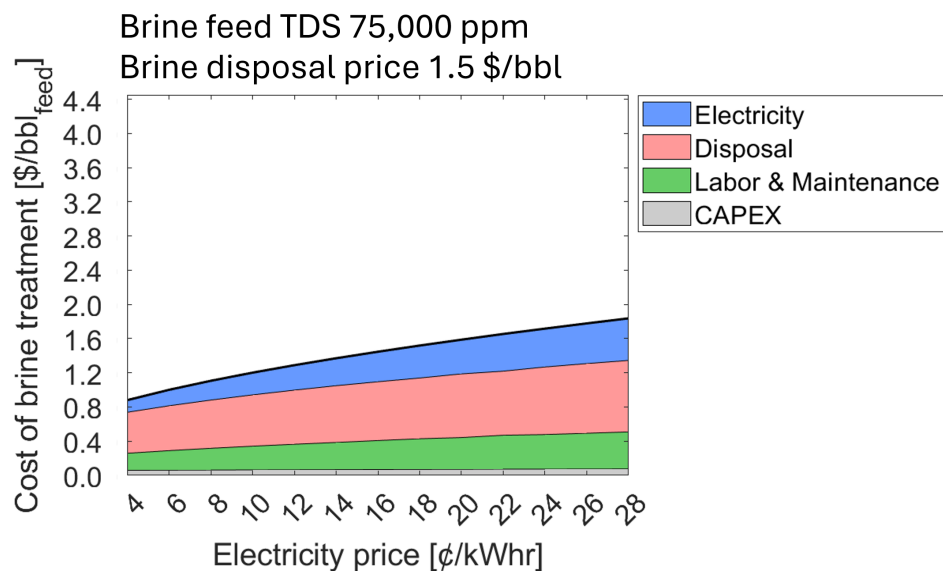


Figure 65: The treatment cost of brine using FD technology for a feed TDS of 75,000 ppm and a brine disposal price of 1.5 \$/bbl.

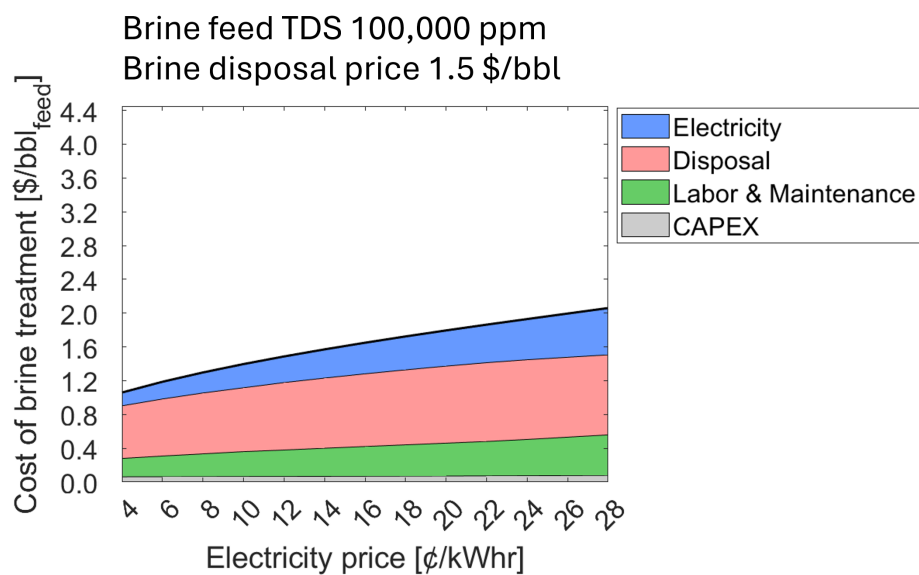


Figure 66: The treatment cost of brine using FD technology for a feed TDS of 100,000 ppm and a brine disposal price of 1.5 \$/bbl.

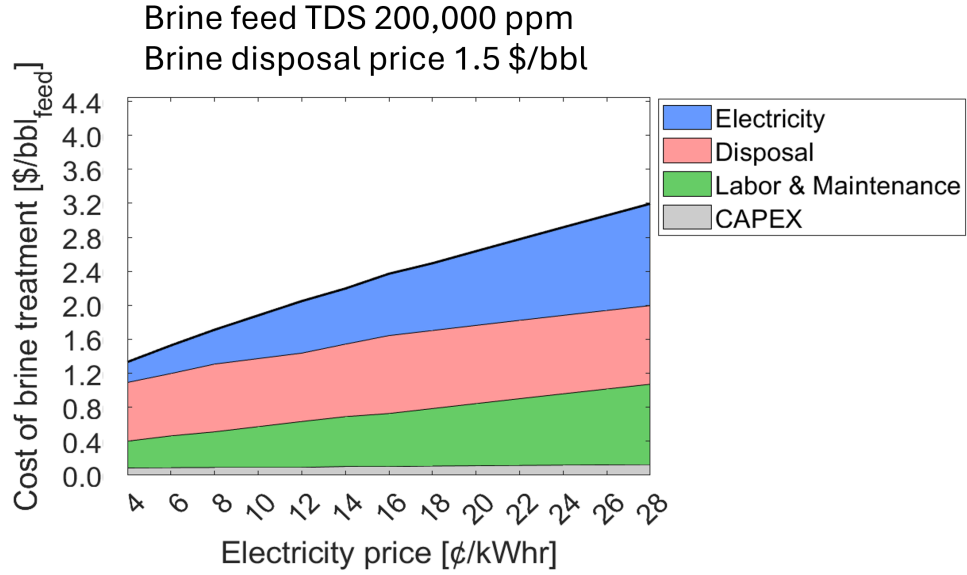


Figure 67: The treatment cost of brine using FD technology for a feed TDS of 200,000 ppm and a brine disposal price of 1.5 \$/bbl.

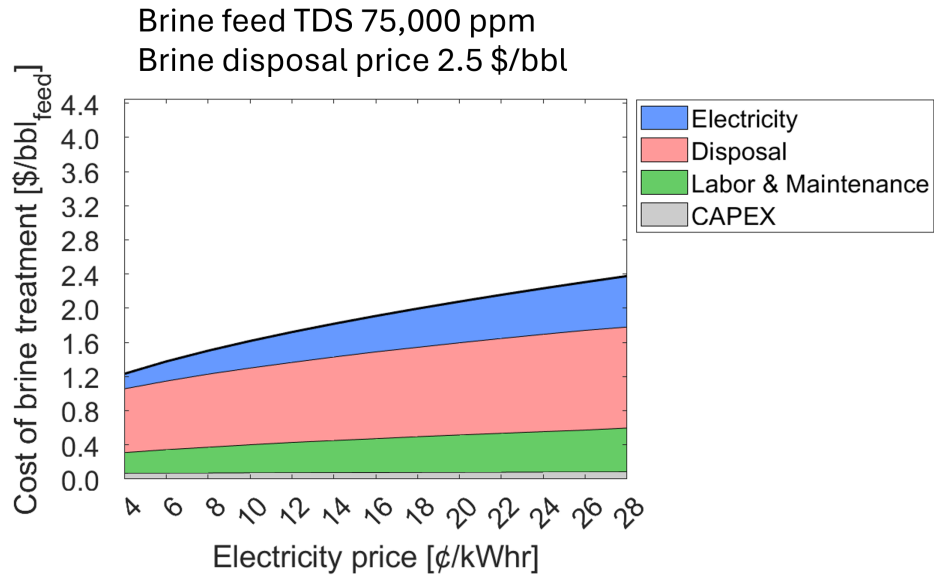


Figure 68: The treatment cost of brine using FD technology for a feed TDS of 75,000 ppm and a brine disposal price of 2.5 \$/bbl.

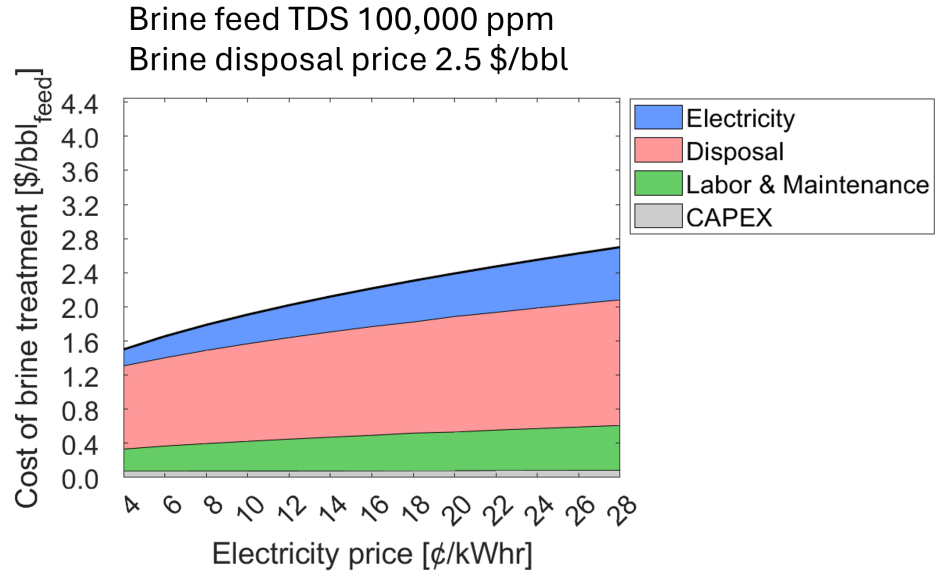


Figure 69: The treatment cost of brine using FD technology for a feed TDS of 100,000 ppm and a brine disposal price of 2.5 \$/bbl.

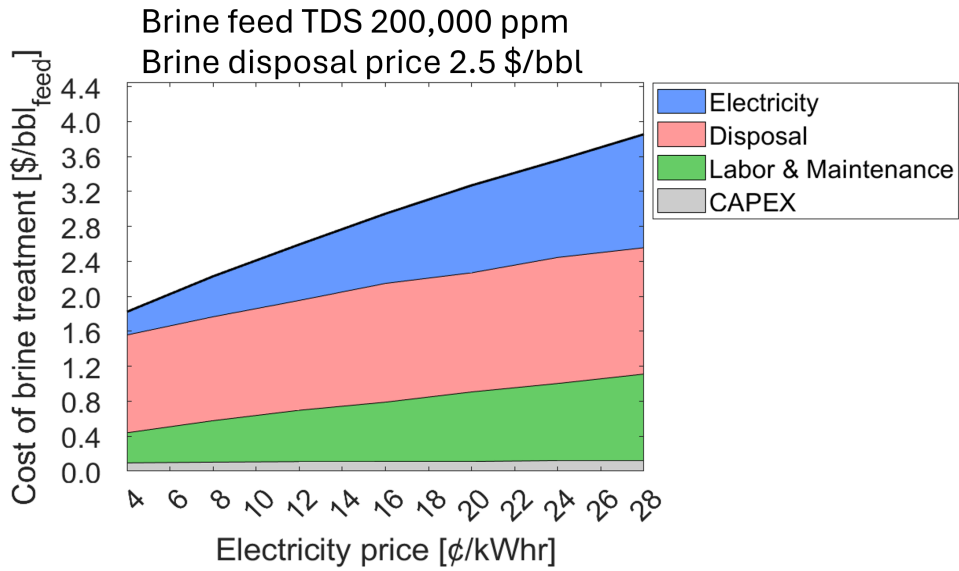


Figure 70: The treatment cost of brine using FD technology for a feed TDS of 200,000 ppm and a brine disposal price of 2.5 \$/bbl.

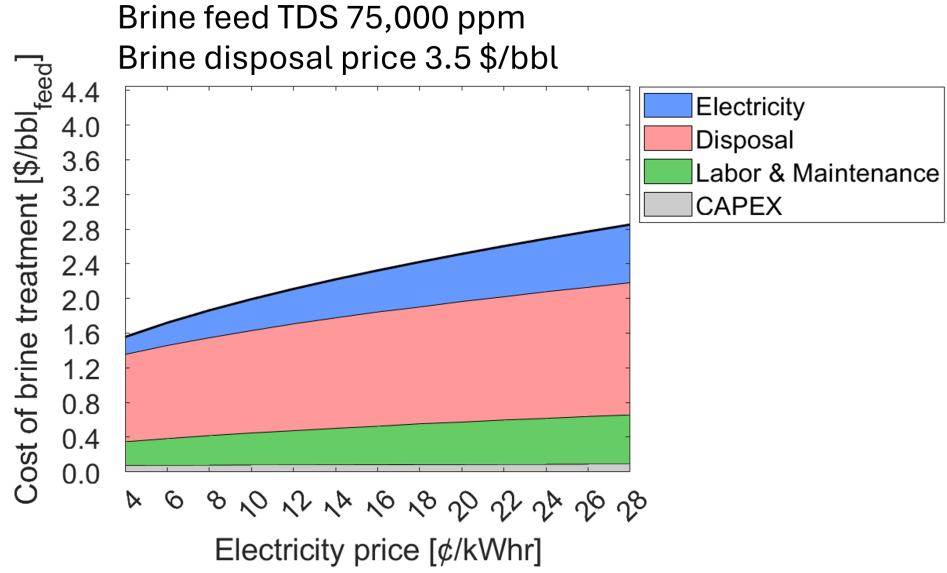


Figure 71: The treatment cost of brine using FD technology for a feed TDS of 75,000 ppm and a brine disposal price of 3.5 \$/bbl.

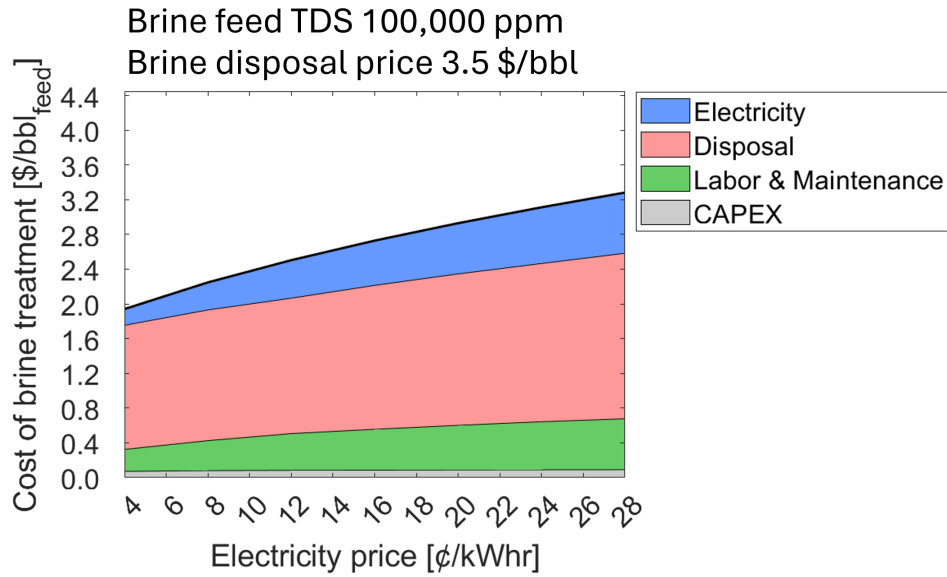


Figure 72: The treatment cost of brine using FD technology for a feed TDS of 100,000 ppm and a brine disposal price of 3.5 \$/bbl.

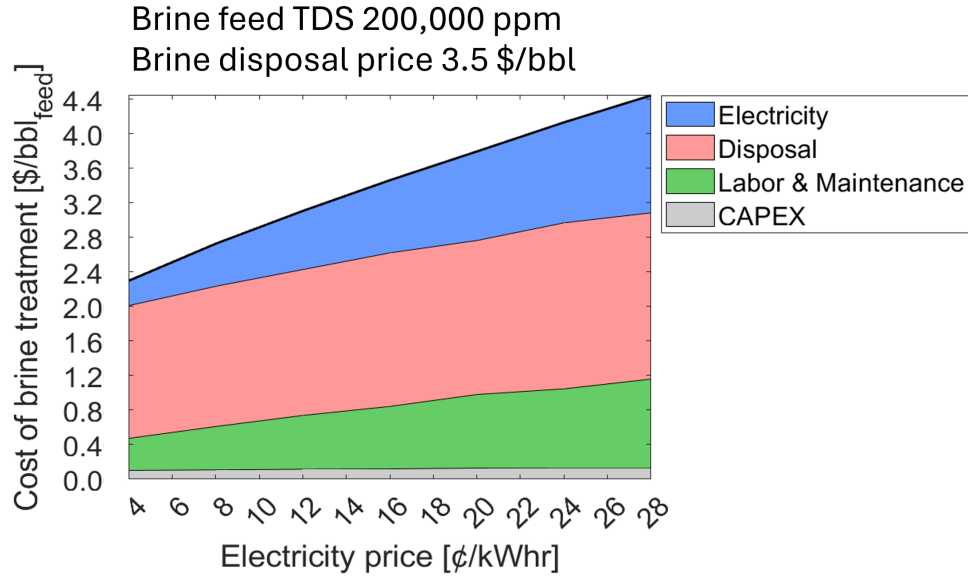


Figure 73: The treatment cost of brine using FD technology for a feed TDS of 200,000 ppm and a brine disposal price of 3.5 \$/bbl.

Figures 59– 73 shows that lower electricity prices are associated with lower brine treatment costs due to the reduced electricity costs. The figure also illustrates the rise in the treatment cost corresponding to the increase in disposal costs. Figures 59– 73 also shows that increased feed TDS is associated with higher treatment costs, primarily due to elevated disposal and electricity expenses, which also impact maintenance and labor costs. This can be explained by the fact that, at the same freezing chamber temperature, injecting higher TDS feed brine into the freezing chamber generates less ice (less purified water) and more disposable mass compared to lower TDS feed. The percentage of the contribution of each of the primary cost categories to the total cost is presented in Figs. 74– 88 for an electricity cost of 8 ¢/kWhr. Similar to the results presented in Figs. 59– 73, the outcomes presented in Figs. 74– 88 are generated using the optimal values of the brine injection rate and the heat exchangers' sizes.

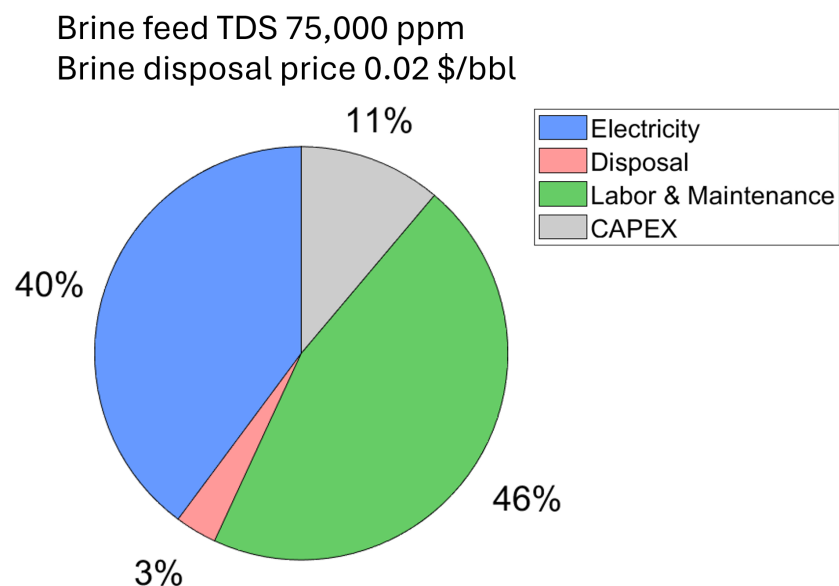


Figure 74: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 75,000 ppm and a brine disposal price of 0.02 \$/bbl.

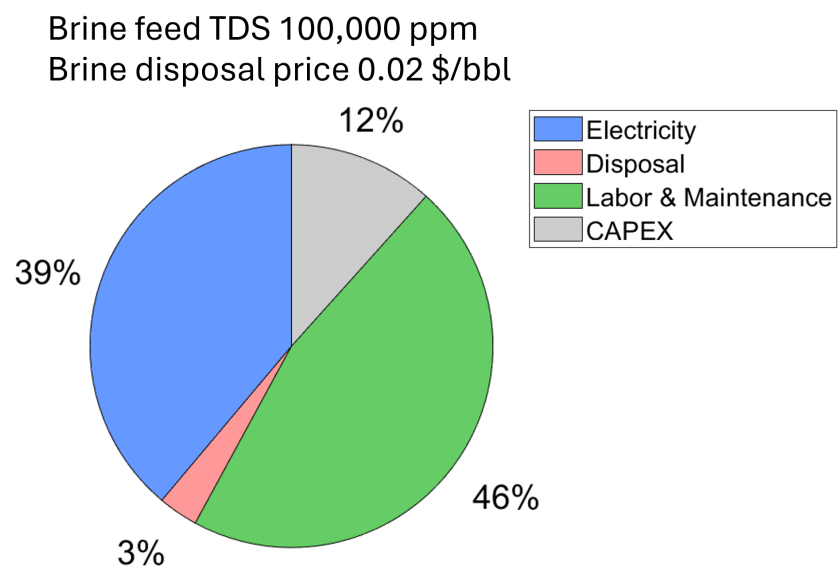


Figure 75: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 100,000 ppm and a brine disposal price of 0.02 \$/bbl.

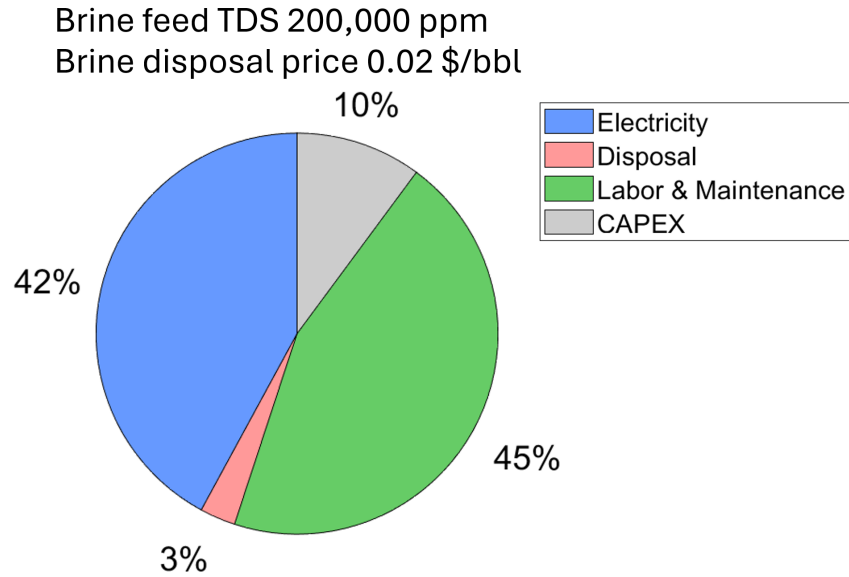


Figure 76: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 200,000 ppm and a brine disposal price of 0.02 \$/bbl.

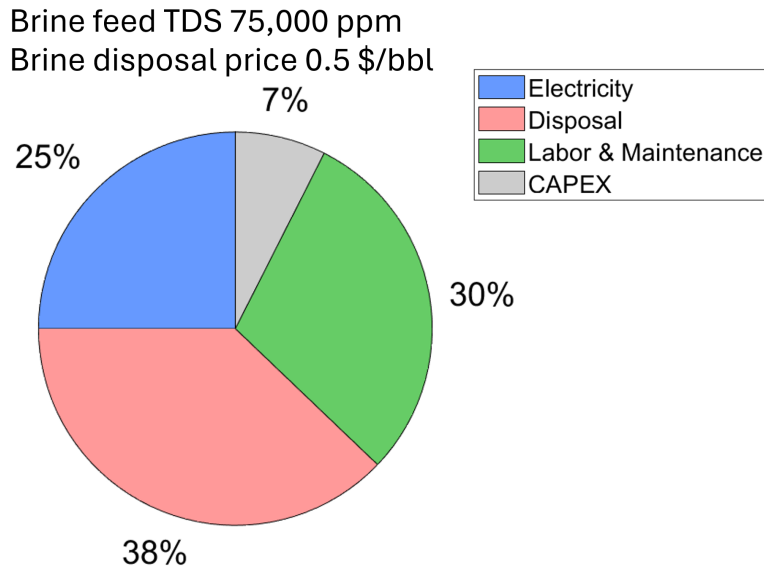


Figure 77: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using freeze desalination (FD) for a feed TDS of 75,000 ppm and a brine disposal price of 0.5 \$/bbl.

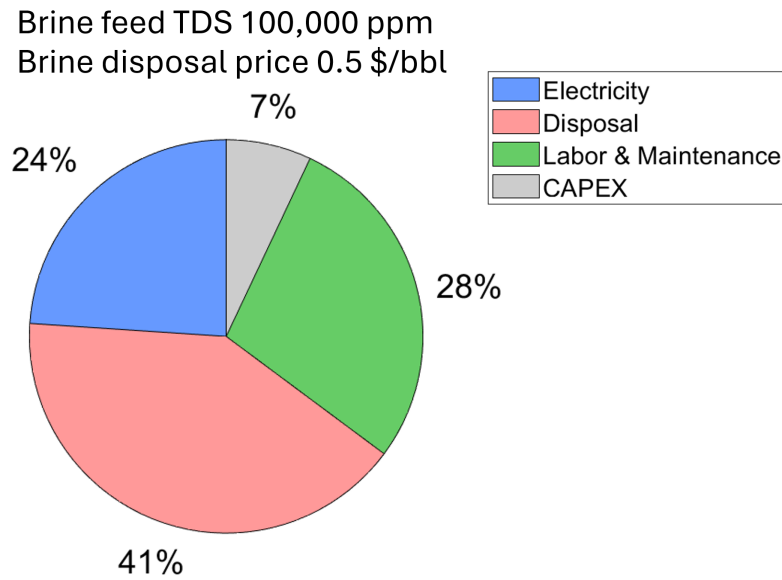


Figure 78: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 100,000 ppm and a brine disposal price of 0.5 \$/bbl.

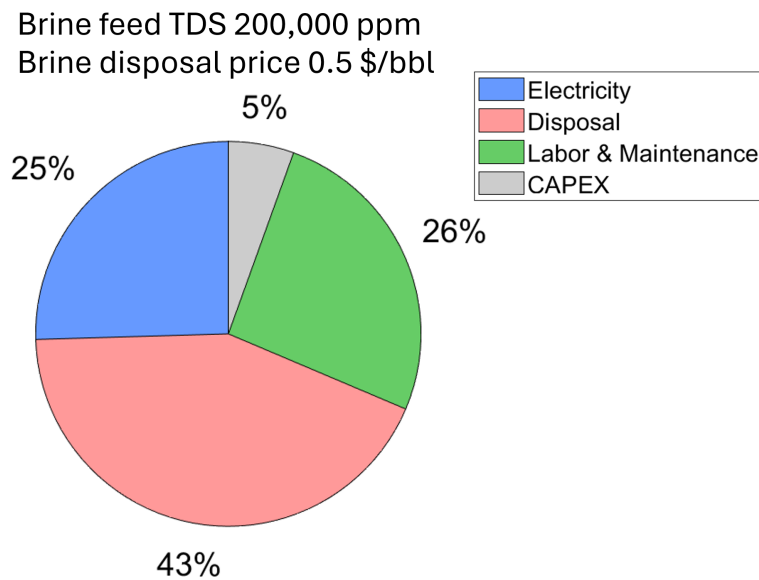


Figure 79: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 200,000 ppm and a brine disposal price of 0.5 \$/bbl.

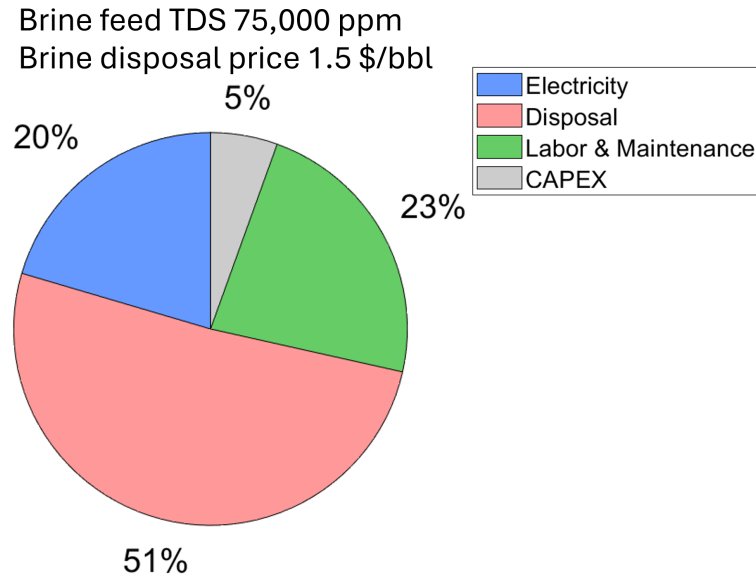


Figure 80: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 75,000 ppm and a brine disposal price of 1.5 \$/bbl.

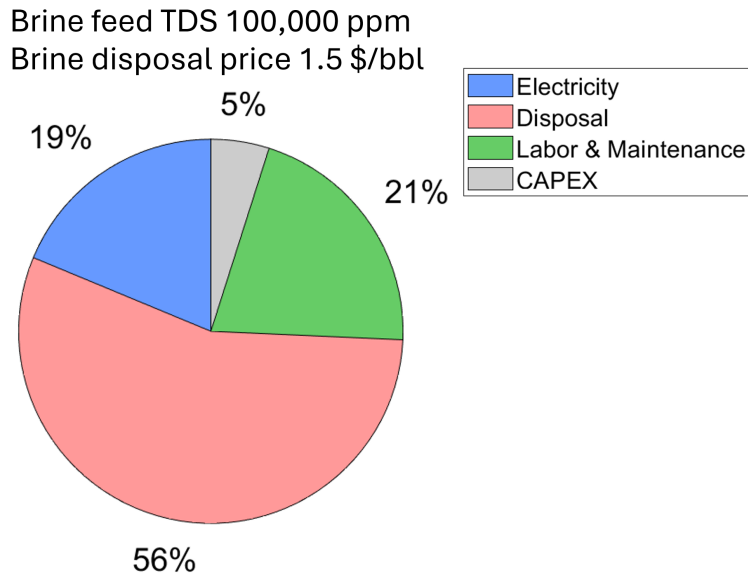


Figure 81: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 100,000 ppm and a brine disposal price of 1.5 \$/bbl.

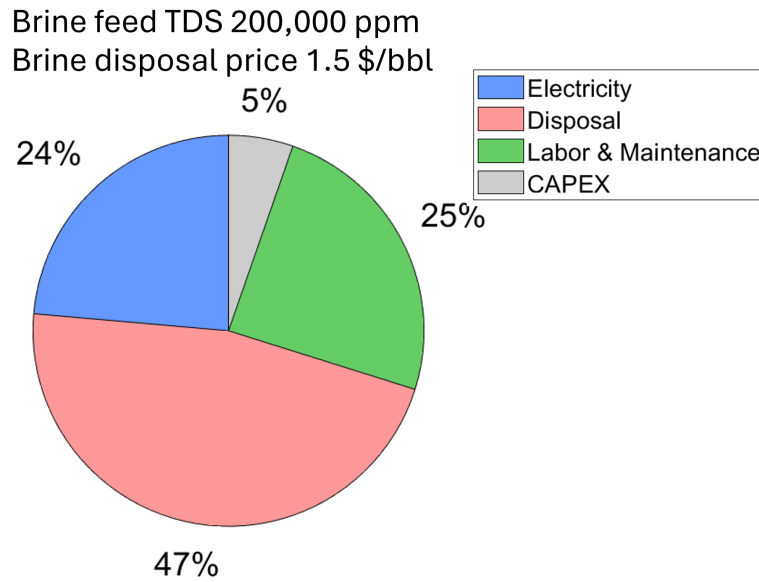


Figure 82: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 200,000 ppm and a brine disposal price of 1.5 \$/bbl.

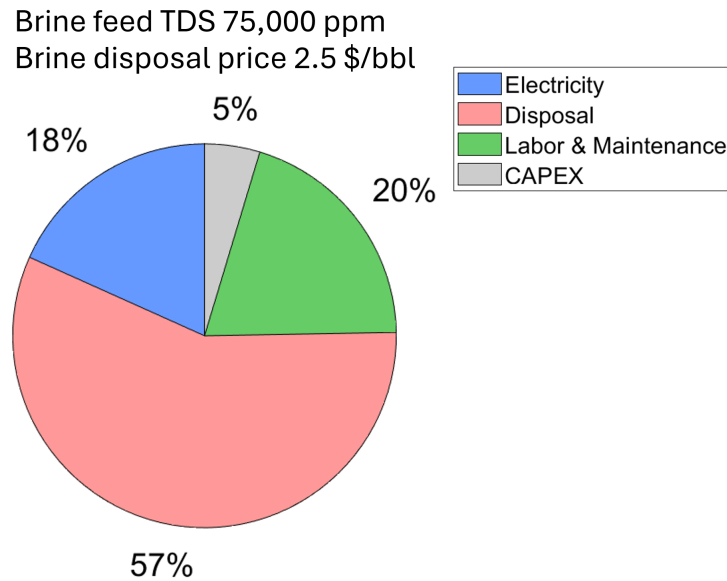


Figure 83: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment FD for a feed TDS of 75,000 ppm and a brine disposal price of 2.5 \$/bbl.

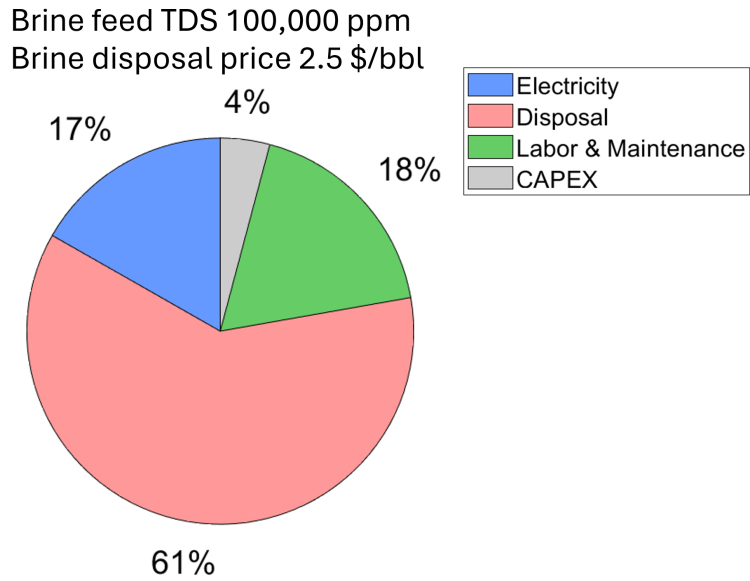


Figure 84: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 100,000 ppm and a brine disposal price of 2.5 \$/bbl.

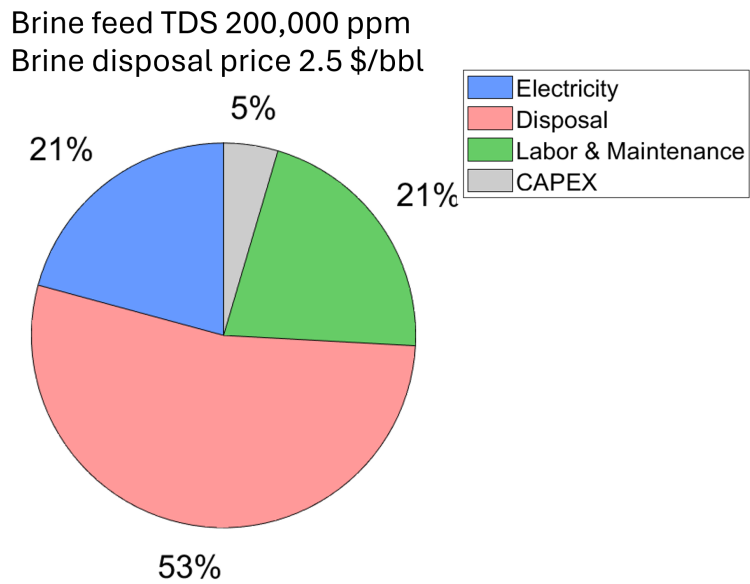


Figure 85: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 200,000 ppm and a brine disposal price of 2.5 \$/bbl.

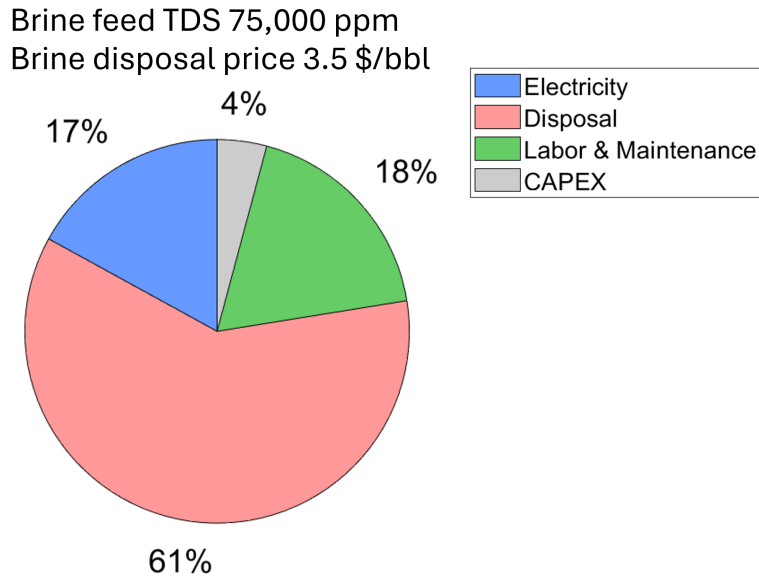


Figure 86: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 75,000 ppm and a brine disposal price of 3.5 \$/bbl.

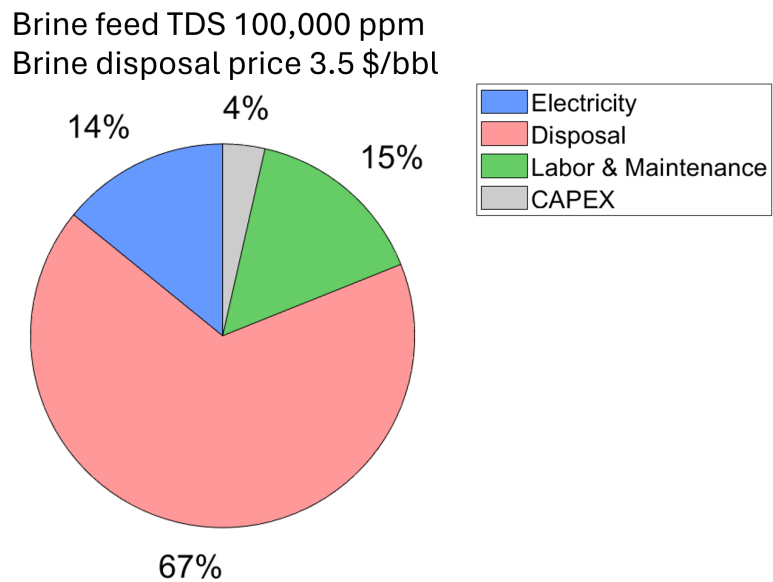


Figure 87: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 100,000 ppm and a brine disposal price of 3.5 \$/bbl.

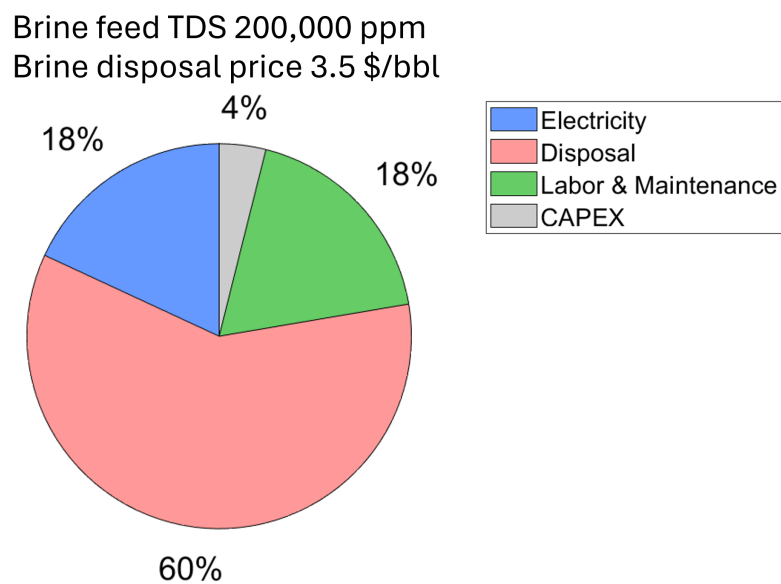


Figure 88: The percentage of the contribution of each of the primary cost categories to the total cost of brine treatment using FD for a feed TDS of 200,000 ppm and a brine disposal price of 3.5 \$/bbl.

Concluding remarks

This section provides benchmark economic metrics (maps) considering practical ranges for key boundary conditions affecting the brine treatment costs. For feed brine TDS levels of 75,000 ppm, 100,000 ppm, and 200,000 ppm, with a desalinated water selling price of 1.5 \$/ton, electricity price of 8 ¢/kWh, and brine disposal cost of 0.02 \$/bbl, the FD technology demonstrates optimal costs of 0.33 \$/bbl, 0.38 \$/bbl, and 0.62 \$/bbl, respectively. The increase in electricity price, feed TDS, or brine disposal cost results in higher brine treatment costs. However, the calculations show that the contribution of each cost category (electricity, disposal, maintenance, labor, and CAPEX) varies disproportionately due to changes in the optimized design parameters aimed at cost minimization. These benchmark cost metrics can guide future market analysis and commercialization efforts for FD technology.

6 Leveraging FD power flexibility in day-ahead electricity market

Freeze desalination (FD), as one of the thermal desalination techniques, consumes relatively high amounts of energy [69, 117], yet the technology remains one of the most promising options for treating higher salinity brine [57, 69, 117, 118].

The day-ahead electricity market (DAM) is a crucial component of modern electricity markets, designed to ensure grid reliability and economic efficiency. Flexible loads can participate in day-ahead electricity markets, leading to benefits for the grid through effective load shifting and cost savings for users by allowing them to pay less for electricity. This section explores the power flexibility of FD technology by examining a proposed design modification on the FD configuration presented in the previous sections aimed at improving this flexibility. The modified design is modeled using a causal framework, with control strategies targeting to minimize brine treatment costs throughout the day. The performance of this design is then tested with scenarios to evaluate its effectiveness and potential cost savings through participation in a day-ahead electricity market.

6.1 Configuration upgrade to enhance FD power flexibility

Previous sections analyzed how to maximize the energy efficiency of FD technology and minimize costs. This section focuses on enhancing the power flexibility of the FD system. The original optimal configuration includes cascade refrigeration system with an intermediate heat exchanger to couple the refrigeration cycles and facilitate ice melting on the shell side. In this setup, the cascade refrigeration cycles provide cooling to the intermediate cooling liquid (ICL), which is circulated to the freezing chamber. In the freezing chamber, brine is injected to form ice, which is then melted to recover cooling energy before being extracted as the output.

The proposed modification to the FD system configuration incorporates a well-insulated

ice storage device. Ice formed inside the freezing chamber of the FD system, after being separated from the concentrate and the ICL, is transferred to the ice storage device. Portions of the stored ice are released from the storage device at various times throughout the day based on a control signal. The exiting ice is then directed to a heat exchanger, where it exchanges heat with refrigerant to facilitate melting. The melted water is subsequently sent to the precooler for further cooling energy recovery before leaving the system as shown in Fig. 89. The following sections will discuss the modeling and control of the proposed configuration.

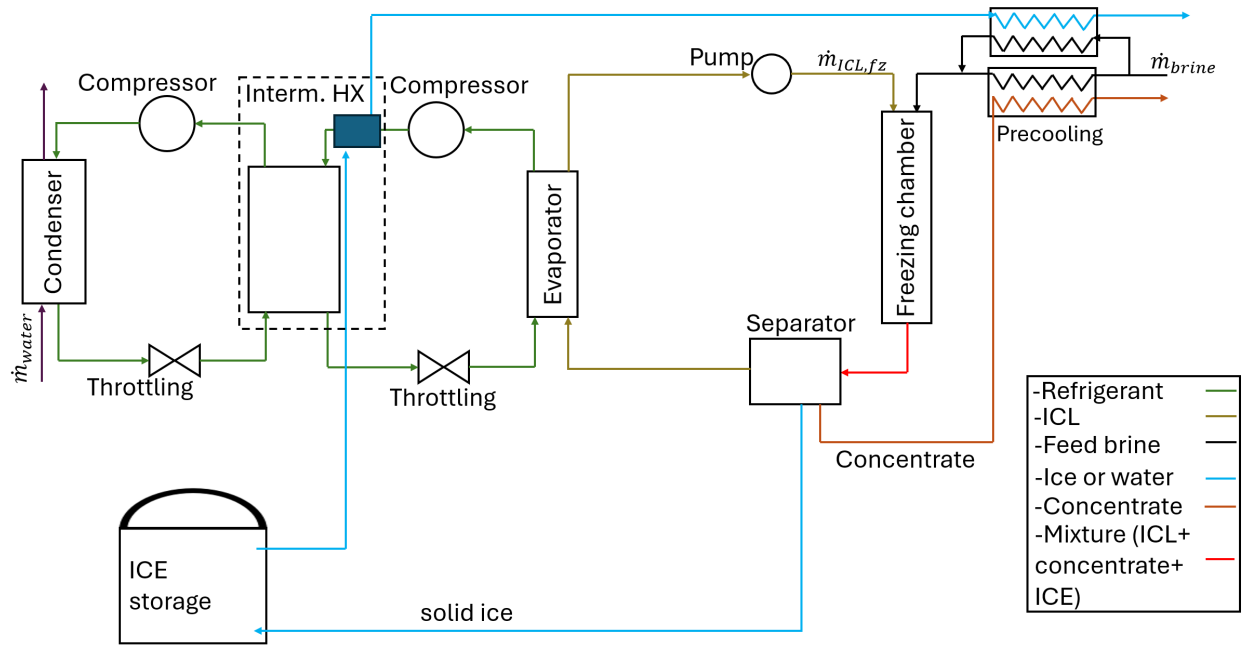


Figure 89: Modified FD configuration with load shifting feature.

6.2 Co-simulation framework for the control of FD

In this section, the co-simulation framework developed for the control of FD is discussed. The compressors models remain consistent with the ones presented in previous sections. The operational limits of the compressors are considered based on the manufacturer's data where the minimum power consumption of the compressor of the primary refrigeration cycle is 122.1 kW [139]. During the hours when the amount of ice melted out of the ice storage device

enable the condensing temperature of the primary refrigeration cycle to reach its minimum map value [139], the secondary refrigeration cycle is turned off. For the evaporator and condenser, the heat transfer effectiveness values were established through lab experimentation as described in [160]. The primary and significant change from the system component models presented in earlier sections is the method of modeling the intermediate heat exchanger. Additionally, in contrast to the design models previously employed, the component models are now integrated and solved collectively as a causal model, as will be elaborated upon later in this section.

The cascade heat exchanger is a shell and tube type and establishes thermal coupling between the two parts of the cascade refrigeration cycle, namely cycle A and cycle B as shown in Fig. 90. A counter-flow finite volume model is used for the cascade heat exchanger where the refrigerant of cycle A condenses on the tube side while the refrigerant of cycle B boils on the shell side.

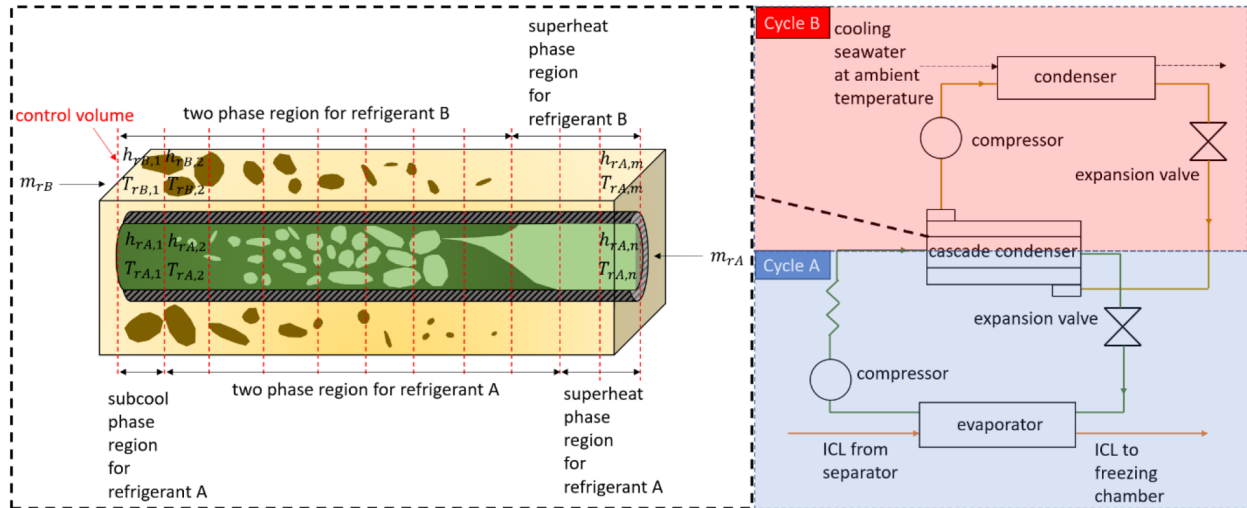


Figure 90: Schematic diagram for the counter-flow finite volume model of the cascade heat exchanger.

The enthalpy method is adopted to estimate the state of the refrigerant inside the cascade heat exchanger assuming a well-mixed flow. From the temperature difference, the enthalpy is first calculated using Eqs. 50,51 and 52, then the stream temperature and phase are updated

using the refrigerant thermophysical properties package CoolProp [86].

$$u \frac{\delta h}{\delta x} = UA(T_{st} - T_{wa}) \quad (50)$$

$$h_2(i+1) = h_2(i) + \Delta h_{23}(i) \quad (51)$$

$$h_1(i+1) = h_1(i) - \Delta h_{12}(i) \quad (52)$$

To calculate the local heat transfer (UA) on both sides of the cascade heat exchanger, the heat transfer coefficients values are estimated locally. For estimating the heat transfer coefficient for the condensing refrigerant on the tube side, Eq. 53 is developed and calibrated based on various sets of experimental data [161, 162]:

$$HTC_{c,R404A} = HTC_l[\phi_1(1-x)^{\phi_2} + \phi_3x^{\phi_4}T_{cond}^{\phi_5}] \quad (53)$$

where $HTC_{c,R404A}$ is the condensing heat transfer coefficient in $W/m^2 \text{ } ^\circ C$, HTC_l is the liquid phase heat transfer coefficient in $W/m^2 \text{ } ^\circ C$ and x is the refrigerant quality. ϕ_1 to ϕ_5 are calibration parameters. The heat transfer coefficient of the boiling refrigerant on the shell side is calculated using Shah's general correlation for heat transfer during evaporation of falling films on horizontal plain tube [163].

The component models presented in Table. 7 are numerically solved to estimate the power consumption of the FD system and the pure water recovery ratio which are then translated into cost of treatment for the feed brine, where Eqs. 54–61 are satisfied. In Table. 7, the underscored variables refer to the external boundary conditions and the double underscored are the internal unknown variables. It is assumed that the ice can be perfectly separated from the concentrate and ICL ($T_{melt} = 0^\circ C$). Well mixing and having adequate length for thermal equilibrium is also assumed for the mixture inside the freezing chamber where the

temperatures of the ICL, concentrate and ice leaving the chamber are the same.

Table 7: Freeze desalination (FD) causal model Input-output form.

Model	Input – output form
Freeze chamber	$[T_{ev,ICL,in}, \dot{m}_{ice\ generated}] = chamber(\underline{\dot{m}_{brine}}, \underline{T_{ICL,in,fz}}, \underline{\dot{m}_{ICL,fz}}, \underline{T_{br,in,fz\ chamber}}, \underline{TDS_{br}})$
Precoolers	$[T_{br,out,precooler}] = precoolers(\underline{\dot{m}_{ice\ melted}}, \underline{T_{melt}}, \underline{T_{ambient}}, \underline{\dot{m}_{brine}}, \underline{\dot{m}_{ice\ generated}}, \underline{T_{br,fz,out}})$
Compressor _{cycA}	$[P_{e,cycA}, \dot{m}_{refr,cycA}, h_{refr,cycA,in,interm}] = comp(\underline{T_{condensing,cycA}}, \underline{T_{evaporating,cycA}})$
Compressor _{cycB}	$[P_{e,cycB}, \dot{m}_{refr,cycB}, h_{refr,cycB,in,co}] = comp(\underline{T_{evaporating,cycB}}, \underline{T_{condensing,cycB}})$
Intermediate heat exchanger	$[h_{refr,cycA,out,EXV}, h_{refr,cycB,out,interm}] = interm(\underline{\dot{m}_{refr,cycA}}, \underline{h_{refr,cycA,in,interm}}, \underline{\dot{m}_{refr,cycB}}, \underline{h_{refr,cycB,in,interm}}, \underline{\dot{m}_{ice\ melted}}, \underline{T_{ice}})$
Evaporator _{cycA}	$[T_{ev,ICL\ out}, h_{refr,cycA,in,evap}] = evap(\underline{\dot{m}_{ICL,fz}}, \underline{T_{ev,ICL,in}}, \underline{\dot{m}_{refr,cycA}}, \underline{h_{refr,cycA,in,evap}})$
Condenser _{cycB}	$[h_{refr,cycB,out,EXV}] = cond(\underline{\dot{m}_{cw}}, \underline{T_{cw,in}}, \underline{\dot{m}_{refr,cycB}}, \underline{T_{condensing,cycB}}, \underline{h_{refr,cycB,in,co}})$

In Table. 7, $T_{ev,ICL,in}$ refers to the temperature of the ICL entering the evaporator in °C, $\dot{m}_{ice\ generated}$ is the amount of ice crystallized inside the freezing chamber in kg/s, $\dot{m}_{brine}$ is the brine injection rate into the freezing chamber in kg/s, $T_{ICL,in,fz}$ is the temperature of the ICL entering the freezing chamber in °C, $\dot{m}_{ICL,fz}$ is the ICL mass flow rate entering the freezing chamber in kg/s, $T_{br,in,fz\ chamber}$ is the temperature of the brine injected into the freezing chamber in °C and TDS_{br} is the total dissolved solids (TDS) of the brine feed in ppm. The variable $T_{br,out,precooler}$ resembles the temperature of the brine leaving the precooler in °C, the $\dot{m}_{ice\ melted}$ is the rate of ice leaving the storage device and melted from heat transfer with the refrigerant before being passed to the precooler in kg/s, T_{melt} is the temperature at which the ice leaving the storage device melts in °C. Assuming perfect separation of ice from the concentrate where no quantities of unfrozen brine are carried over with the generated ice, the melting temperature is 0°C. $T_{ambient}$ is the ambient temperature in °C, $T_{br,fz,out}$ is the temperature of the brine leaving the freeze chamber. $P_{e,cycA}$ is the electrical power consumption of the compressor of refrigeration cycle A in W, $\dot{m}_{refr,cycA}$ is the refrigerant mass flow rate of refrigeration cycle A in kg/s, $h_{refr,cycA,in,interm}$ is the enthalpy of the refrigerant

of cycle A entering the intermediate heat exchanger in J, $T_{evaporating,cycA}$ is the evaporating temperature of cycle A in °C and $T_{condensing,cycA}$ is the condensing temperature of cycle A in °C. $P_{e,cycB}$ is the power consumption of refrigeration cycle B in W and $\dot{m}_{refr,cycB}$ is the refrigerant mass flow rate of cycle B in kg/s. $h_{refr,cycB,in,co}$ is the enthalpy of the refrigerant of cycle B entering the condenser in J, $T_{evaporating,cycB}$ is the evaporating temperature of cycle B in °C and the $T_{condensing,cycB}$ is the condensing temperature of cycle B in °C. T_{ice} is the temperature of the ice leaving the storage device in °C, $h_{refr,cycB,in,interm}$ is the enthalpy of the refrigerant of cycle B entering the intermediate heat exchanger in J, $h_{refr,cycB,out,interm}$ is the enthalpy of the refrigerant of cycle B leaving the intermediate heat exchanger in J. $h_{refr,cycA,out,EXV}$ is the enthalpy of the refrigerant of cycle A leaving the expansion valve in J. $h_{refr,cycA,in,evap}$ is the enthalpy of the refrigerant of cycle A entering the evaporator in J. $T_{ev,ICL,out}$ is the temperature of the ICL leaving the evaporator in °C, $h_{refr,cycA,in,evap}$ is the enthalpy of the refrigerant of cycle A entering the evaporator in J, $h_{refr,cycB,out,EXV}$ is the enthalpy of the refrigerant of cycle B leaving the expansion valve in J. $\dot{m}_{cw}$ resembles the cooling water mass flow rate provided to the condenser in kg/s and $T_{cw,in}$ is the temperature of the cooling water entering the condenser in °C.

$$h_{refr,cycA,out,EXV} = h_{refr,cycA,in,evap} \quad (54)$$

$$M_{refr,cycA,charge} = M_{refr,cycA,resided\ in\ evapr} + M_{refr,cycA,resided\ in\ cond} \quad (55)$$

$$h_{refr,cycB,out,EXV} = h_{refr,cycB,in,evap} \quad (56)$$

$$M_{refr,cycB,charge} = M_{refr,cycB,resided\ in\ evapr} + M_{refr,cycB,resided\ in\ cond} \quad (57)$$

$$T_{ev,ICL,out} = T_{ICL,in,fz} \quad (58)$$

$$T_{br,out,precooler} = T_{br,in,fz\ chamber} \quad (59)$$

$$SH_{cycA} = 0 \quad (60)$$

$$SH_{cycB} = 0 \quad (61)$$

where $M_{refr,cycA,charge}$ is the amount of refrigerant charged into the refrigeration cycle A in kg, $M_{refr,cycA,resided\ in\ evapr}$ is the amount of refrigerant resided inside the evaporator of refrigeration cycle A in kg, $M_{refr,cycA,resided\ in\ cond}$ is the amount of refrigerant mass resided in the condenser of cycle A in kg and SH_{cycA} is the superheat of refrigeration cycle A. $M_{refr,cycB,charge}$ is the amount of refrigerant charged into the refrigeration cycle B in kg, $M_{refr,cycB,resided\ in\ evapr}$ is the amount of refrigerant resided inside the evaporator of refrigeration cycle B in kg, $M_{refr,cycB,resided\ in\ cond}$ is the amount of refrigerant mass resided in the condenser of cycle B in kg and SH_{cycB} is the superheat of refrigeration cycle B.

6.3 Optimization Problem Overview

The scope of this section of the work is to utilize the proposed FD system configuration integrated with the ice storage device (described in Fig. 89) to investigate further potential brine treatment savings. The controllable variable is the amount of ice leaving the ice storage device to melt ($\dot{m}_{ice\ melted}$). The amount of ice melted out of the ice storage device is always less than or equal to the amount of ice resided inside the storage device. Also for any set of operating conditions, the amount of ice melted out of the ice storage device does not exceed the amount that would reduce the condensing temperature of the primary refrigeration cycle below its compressor's map limits [139]. Additionally, the constraint on each of the simulated cases implies that the entire ice mass must be completely melted by the end of each day. The cost function is formulated to minimize the operational treatment cost of the brine, which considers the electricity cost, the disposal cost, the maintenance cost and the labor cost (described in details in the previous chapters).

6.4 Optimized FD operation in day-ahead electricity market

In this section, the outcomes for controlling the FD system configuration with ice storage device (Fig. 89) are presented. The cost of the brine treatment using the FD system is calculated from Eqs. 55–59, adopting a brine disposal price of 0.5 \$/bbl, purified water selling price of 1.5 \$/ton and feed brine TDS of 75,000 ppm. The first case corresponds to a summer day in California with the hourly day-ahead electricity price values presented in Fig. 91 where the peak to average ratio is 3.63 [164].

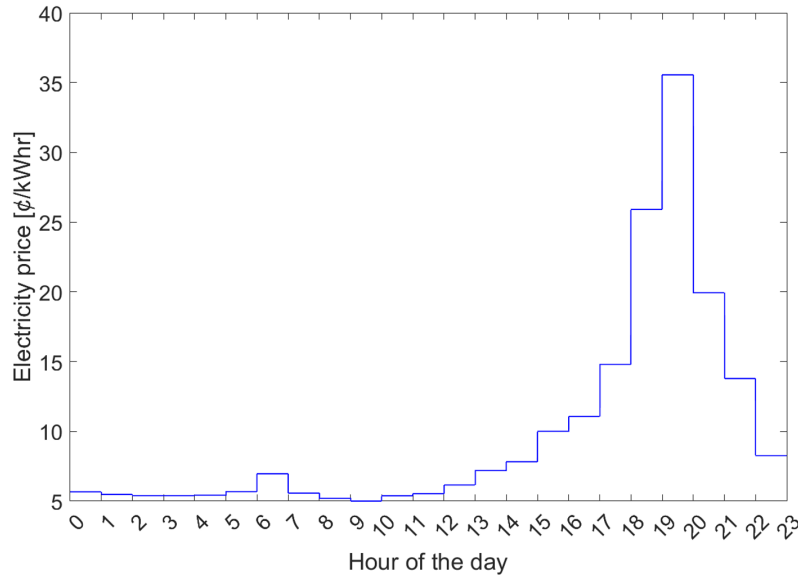


Figure 91: Electricity hourly price for a summer day in California.

The brine injection rate is fixed at the optimal value (discussed in the previous sections) for both the baseline and the controlled case. Both of the baseline and the controlled cases are compared based on treating the same amount of brine throughout a day. In the baseline case, the operator manually shuts down the system during the hour(s) of the highest electricity price based on the treatment capacity requirement of each day. All the ice generated by the system is directed to the shell side of the cascade heat exchanger for melting then passed to the precooler for further energy recovery before leaving the system as shown in Fig. 23. In the optimized scenarios, a gradient based optimization technique determines the precise amount of ice to be extracted from the ice storage device each hour of the day. Fig. 92

compares the optimized power consumption and the baseline power consumption of the FD system operating in the summer day with the electricity price presented in Fig. 91.

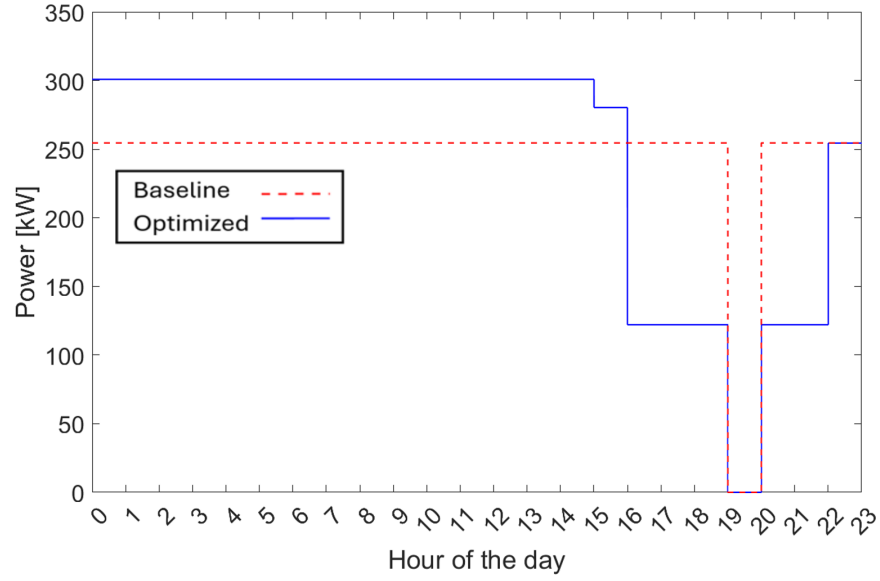


Figure 92: Power consumption of the optimized case vs. baseline case for a summer day in California.

The amount of ice resided inside the storage each hour of the day is presented in Fig. 93. During the lower electricity price hours of the day, all the ice formed is stored. Later on when the electricity price starts to increase, the stored ice gets released out to melt and decrease the system's energy consumption to save money during those hours. During the final hours of the day, the controlled case acts similar to the baseline where any ice formed is melted directly.

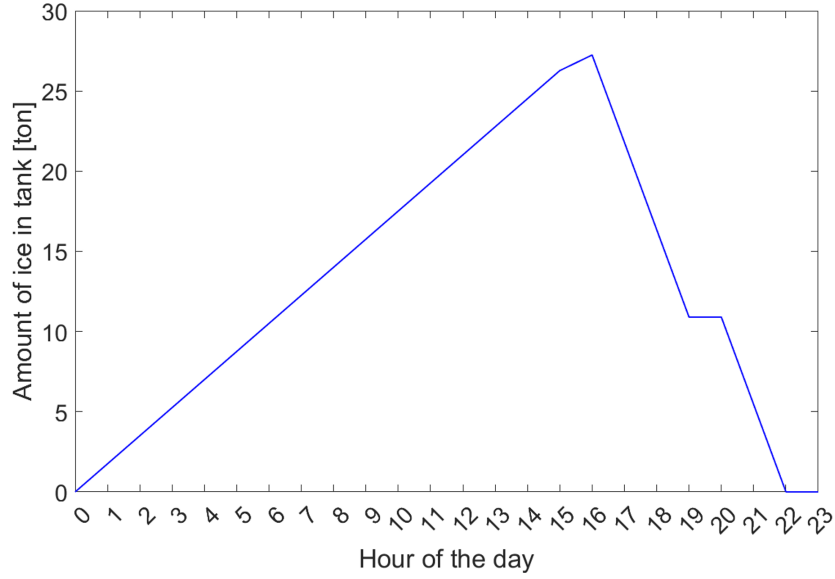


Figure 93: The amount of ice resided inside the storage device for a summer day in California.

For the summer day case (Fig. 91), the operational costs of brine treatment throughout the entire day for the baseline case and the optimized case are presented in Fig. 94 where the operational costs of brine treatment for the optimized case has shown to be 14.6% less than the baseline case.

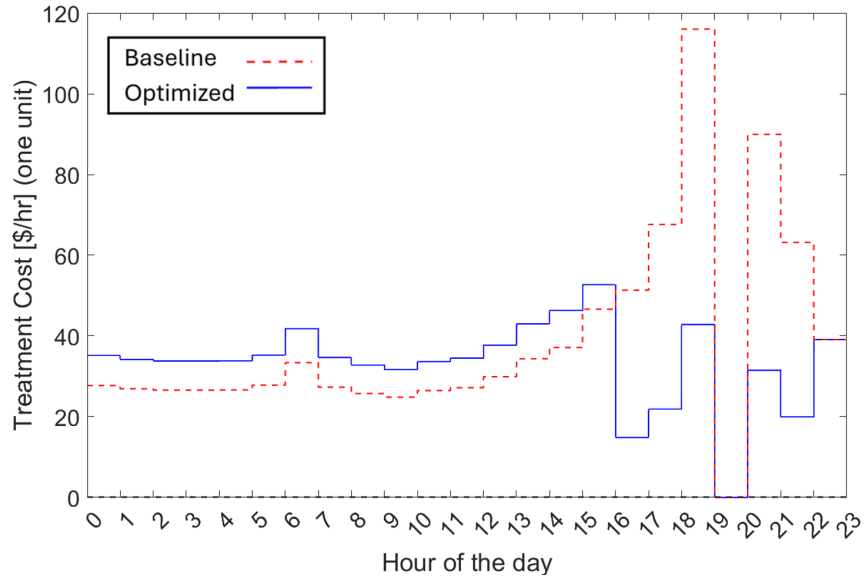


Figure 94: Operational costs of brine treatment for the baseline vs. optimized case for a summer day in California.

A winter day in California is analyzed, with the day-ahead electricity price depicted in Fig. 95 [164] (peak to average ratio: 1.7). The power consumption of the optimized and the baseline cases is presented in Fig. 96.

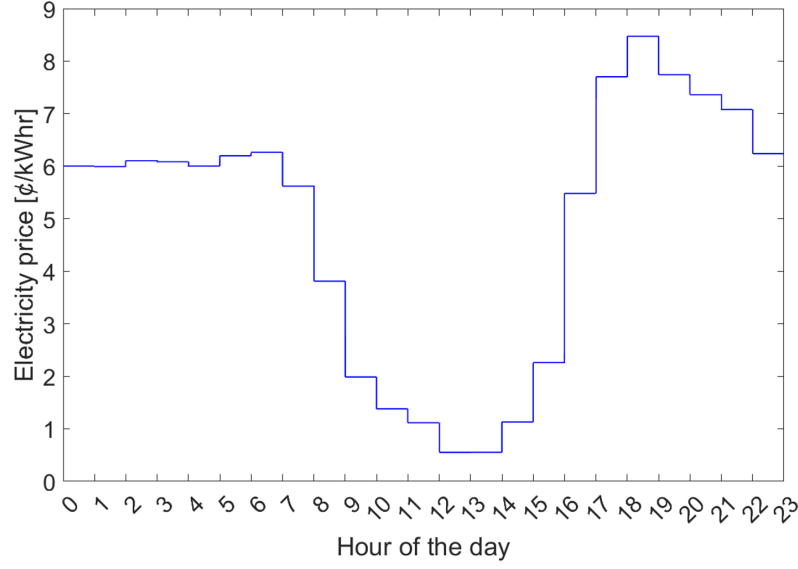


Figure 95: Electricity hourly price for a winter day in California.

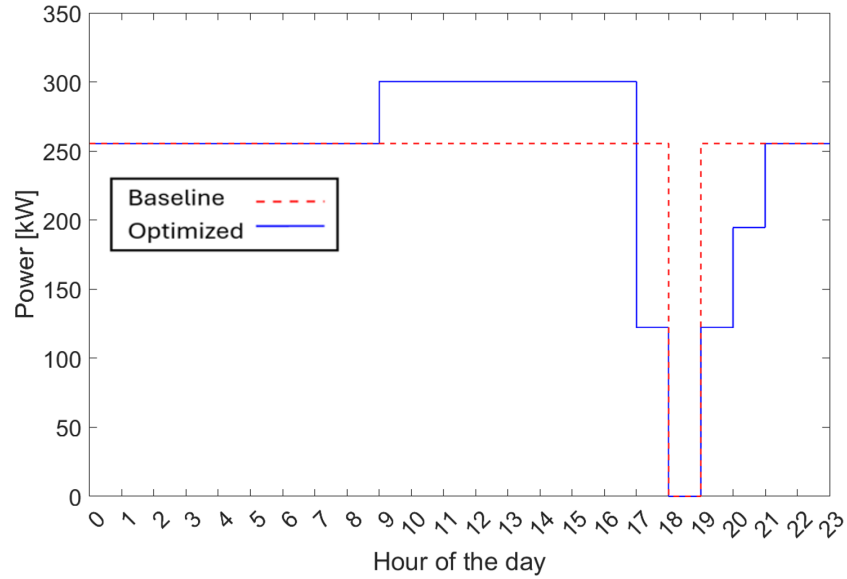


Figure 96: Power consumption of the optimized case vs. baseline for a winter day in California.

At the early hours of the day, both the baseline and the optimized cases melt the formed

ice directly without storage. When the electricity prices go lower during the middle hours of the day, the optimized case stores ice and consumes more power. The stored ice is then melted later in the day during the hours of higher electricity prices reducing the energy consumed notably during those hours which results in a decrease in the treatment cost during that period of the day. Finally during the last hours of the day, both the baseline and the controlled cases show similar behavior where all the ice formed is melted directly as shown in Fig. 97.

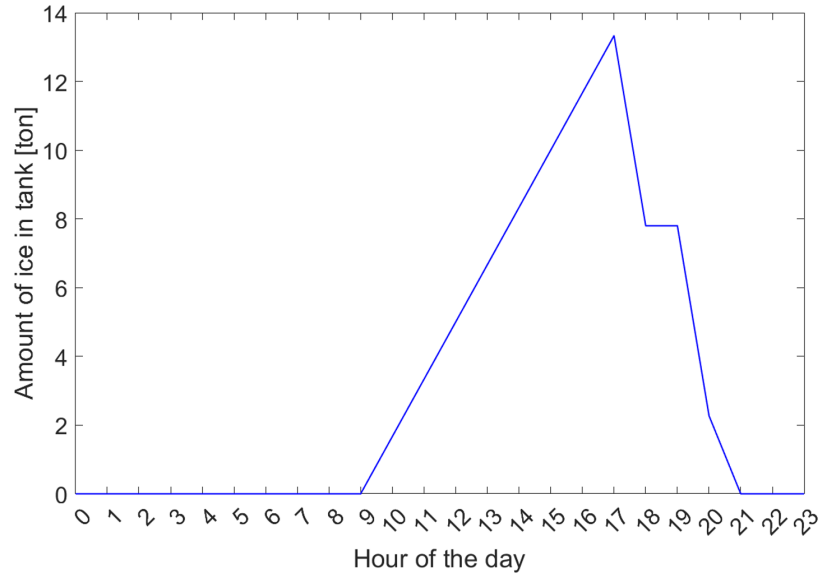


Figure 97: The amount of ice resided inside the storage device for a winter day in California.

For the winter day case (Fig. 95), the costs of the brine treatment throughout the day are presented in Fig. 98 where the operational costs of the brine treatment for the optimized case has shown to be 6.6% less than the baseline case.

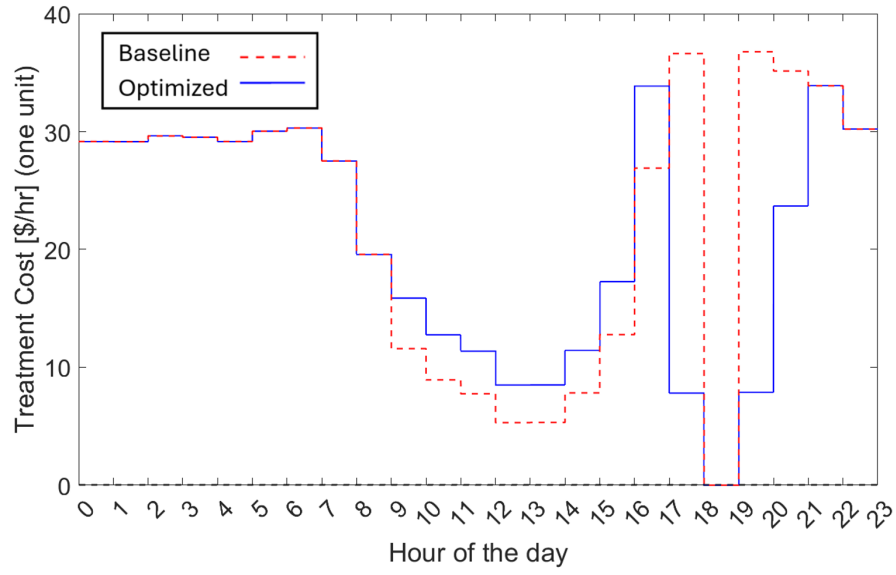


Figure 98: Cost of brine treatment for the baseline vs. optimized case for a winter day in California.

Concluding remarks

This section investigates leveraging the power flexibility of the FD technology. A novel design of the FD system is introduced including an ice storage device which accumulates the separated ice generated inside the freezing chamber to be melted at certain times of the day. This enables the FD system to contribute in the day-ahead electricity market and reduces the brine treatment cost accordingly. A causal co-simulation framework is developed to optimize the ice melting rate out of the ice storage device for minimizing the brine treatment cost. For a summer day of California, the results showed that the optimized operation of the new design reduces the operational cost of the brine treatment by 14.6% compared to the baseline case handling the same amount of feed brine at the same day. In a winter day, the brine treatment cost is reduced by 6.6% compared to baseline.

7 Conclusions and Future Work

In this dissertation, the optimal FD system configuration has been identified and validated. Reliable FD thermochemical models and co-simulation framework were developed and validated and the detailed thermochemical performance of the FD system has been analyzed. Technoeconomic models and a co-simulation framework were developed and validated to offer accurate and reliable cost estimations for the FD technology related to any set of practical boundary conditions. Detailed maps for the cost of brine treatment using FD were offered to support FD system's selection and design optimization. A novel FD system configuration is introduced as a solution to enhance the power flexibility of the FD system. A causal co-simulation framework is developed along with additional component models to support the analysis of the new concept. The optimization of the system's operation is then explored in the context of a day ahead electricity market, highlighting the potential savings in the brine treatment costs. Accordingly, this work has bridged a number critical research gaps covering the path of the FD technology from the concept to close stages from starting large scale commercial application. Analyzing the overall outcomes of this work framed the following summary of conclusions and remarks:

- The optimal FD configuration composes of a cascade vapor compression refrigeration system to provide cooling for the brine down to low temperatures where cooling energy recovery is indispensable for economically feasible utilization of the FD technology. The cooling energy recovery cannot be completely realized through precooling but found optimal when combining precooling with melting the generated ice inside the intermediate heat exchanger of the cascade vapor compression refrigeration system.
- A combination of theoretical analysis, heuristic estimations and offline calculations can significantly support in minimizing complex configuration characterization problems which make it possible to converge to the solution.

- The cost of brine treatment using FD technology is strongly affected by a set of boundary conditions, primarily: the electricity prices, the brine disposal cost, the feed brine TDS as well as the water selling price (with a lower effect on the treatment cost compared to the other boundary conditions). Cost or performance maps linked to the FD technology are practically useful to the system’s designer when the maps cover the practical ranges of the described boundary conditions.
- Integrating an ice storage device as a modification to the optimal FD system configuration showed effectiveness in raising the power flexibility of the FD system allowing additional cost savings in the context of day-ahead electricity markets.
- In FD, the adopted freezing temperature which is primarily controlled by changing the feed brine injection rate significantly affects the cost of treatment. Accordingly, to raise the energy efficiency of the FD system, the brine injection rate should be accurately controlled at each set of boundary conditions.
- The FD system’s equipment size, and specifically the size of the primary heat exchangers (evaporator, intermediate heat exchanger and condenser) significantly affects the cost of brine treatment over the life cycle of the FD system. The equipment size is a factor in the capital expenditures and affects the heat transfer efficiency which reflects on the cost of energy of the FD system.

Future work should address raising the efficiency of the separation process which will further reduce the cost of brine treatment. In addition, future work should focus on merging and applying the features of this newly developed technology with the critical real-world applications to fully leverage the potential of this innovative desalination approach. The following paths are highly rewarding topics to explore as the next steps for this work:

- As highlighted in this work, the current separation techniques that can be economically adopted as part of the FD system are far from being perfect where a percentage of

unfrozen brine would be carried over with the generated ice. Although the percentage of salt contamination can be contained down to levels that suit a lot of applications (including potable water), there are applications that require highly critical levels of purity for the generated water. For those, the FD technology won't be able to meet the process requirements and therefore the significant economical advantages from utilizing FD with lower energy requirement cannot be leveraged. Optimizing the design of the separation process along with the associated operational parameters like the (separation duration and speed) might result in significant increase in the FD technology's applications spectrum.

- From the thermal and thermochemical performance explored in this work, it is obvious that FD technology can be a very good candidate for zero liquid discharge (ZLD) applications primarily for its energy consumption and its low sensitivity to the feed salinity which is critical for ZLD applications that reach extremely high TDS values.

The second research gap described above has been explored in an additional level of detail to open doors for future work and analysis for this research path as will be explained through the following section.

7.1 FD for enhancing the energy efficiency of ZLD applications

7.1.1 Background

High salinity produced water is generated in abundance through oil and gas operations. Disposing of the brine presents a significant added cost and imposes an adverse impact on the environment. Zero liquid discharge (ZLD) techniques can be utilized to crystallize salts out of the brine, thus significantly minimizing the disposal cost and producing clean useable water. So far, the studied ZLD techniques linked to treating high salinity brines are energy intensive. This gives the classical high salinity brine disposal methods a tremendous cost advantage. This section introduces a concept for a novel zero liquid discharge high salinity

brine treatment system characterized by raised energy efficiency. The system adopts freeze desalination and thermal crystallization techniques both powered by waste energy recovered from a gas turbine's exhaust. The system treats high salinity brine feed and produces fresh water, electricity, and solid salts. A comprehensive model has been developed to support the hypothesized arguments. The study also highlights the proposed system's thermal performance and water generation capability. Technoeconomic analysis has been performed considering a practical range of boundary conditions within an industrial context. The outcomes document the profitability scenarios through maps supporting the implementation of the proposed concept.

7.1.2 The proposed system configuration

Throughout this study, the proposed system is referred to as the gas turbine zero liquid discharge system (GTZLD). The GTZLD system treats high salinity brine at ZLD and produces electricity. Although the GTZLD system is new, the proposed configuration is based on widely adopted engineering equipment which facilitates the industrialization of this technology. Besides the ability to build the system from scratch, the proposed GTZLD system configuration is designed to be retrofit friendly. To turn older industrial systems into GTZLD, almost any classical industrial GT engine can be upgraded by additional components installed around the GT. Only a minor modification to GT's inlet air manifold is required.

The GTZLD system is primarily powered by fuel (injected to the combustion chamber of the GT engine). One advantage of this configuration is that it doesn't require additional fuel beyond the original quantities injected into the GT to generate electrical energy at a certain rate. The part of the GTZLD system responsible for the treatment of the high salinity brine is primarily powered by the waste heat recovered from the exhaust of the GT engine. Besides the GT, the proposed system composes of a vapor compression cycle, a crystallizer, a turboexpander, and two-heat exchangers installed in the inlet air manifold of a GT engine as shown in Fig. 99.

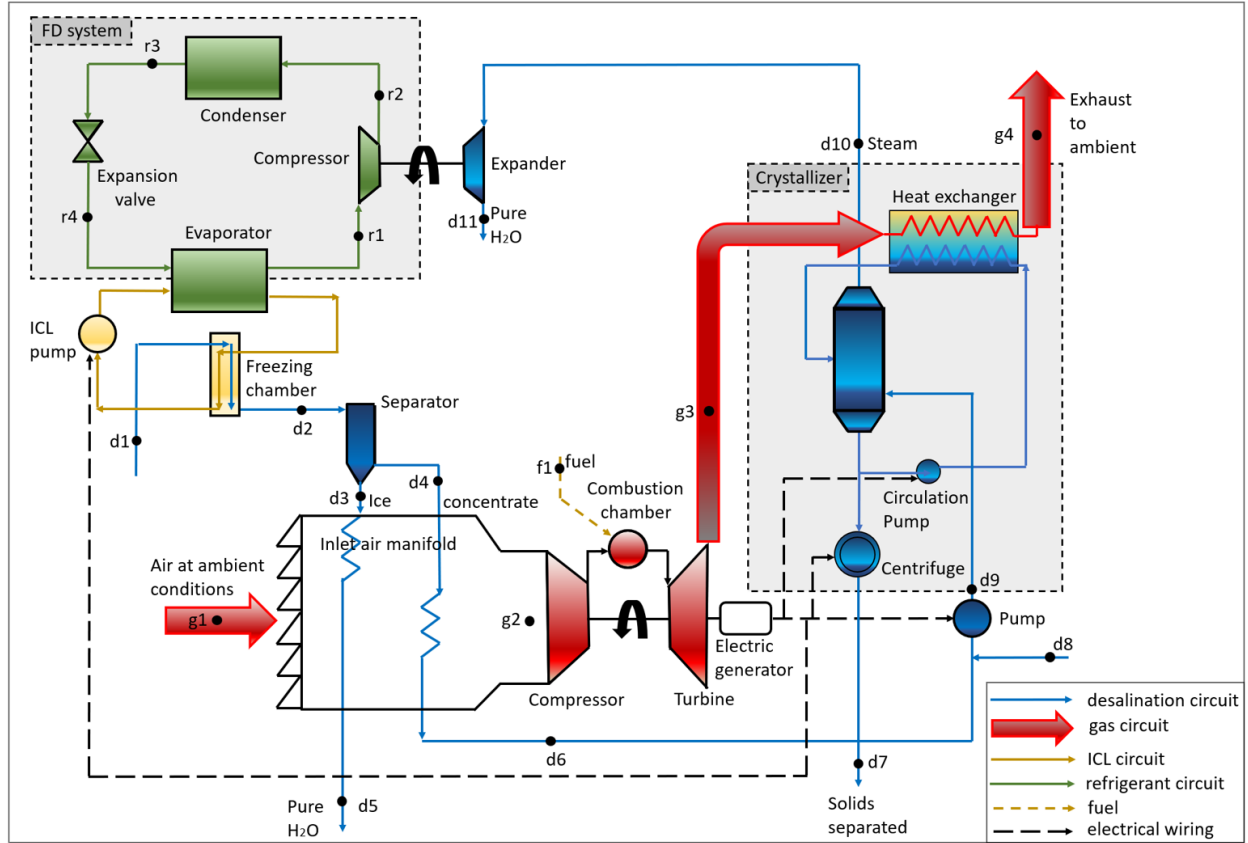


Figure 99: GTZLD system configuration.

As described in the previous paragraph, heat energy is recovered from the GT's exhaust. The recovered heat is utilized to heat up the high salinity brine to boiling temperatures in the crystallizer. The generated steam is then expanded in the turbine side of the turboexpander, and work is generated. The turboexpander's generated work drives the vapor compression cycle's compressor. In addition to the compressor, the vapor compression refrigeration cycle primarily composes of a condenser, an evaporator, and an expansion valve. The refrigeration cycle provides cooling to the high salinity brine feed entering the system. In the context of freeze desalination (FD) systems, extensive research has been published on the best way to deliver cooling to the brine [118, 117]. The published outcomes showed the effectiveness of utilizing an intermediate cooling liquid (ICL) for thermal coupling. The ICL is a silicon-based fluid with the ability to withstand low temperatures without a significant difference in its desirable viscosity and doesn't react with the brine. In the GTZLD system, the ICL

gets cooled down in the evaporator then enters the freezing chamber. The high salinity brine is sprayed into the freezing chamber to be in direct contact with the cold ICL. Inside the freezing chamber, the brine gets cooled down to freezing temperatures allowing a designed amount of ice to crystallize. The cold stream then passes through a separation stage where the crystallized ice is separated from the concentrate (high salinity unfrozen liquid). The separation process is not perfect where the ice carries small quantities of liquid brine encapsulated in pockets [165]. The cold streams (ice and concentrate) are passed through two heat ex-changers in the GT's inlet air manifold for cooling energy recovery. This reduces the temperature of the air inlet to the GT's compressor, raising its energy efficiency. The ice is melted, and water leaves the system at ambient temperature. The concentrate stream also exists the GT's inlet air manifold heat exchanger at the ambient temperature. The concentrate is then pumped at higher pressures and directed to the crystallizer. Besides the concentrate stream, another inlet brine stream is fed to the crystallizer where steam is generated.

A Appendix

In this appendix, the various freeze desalination (FD) system configurations tested during the brute-force search to identify the optimal FD system configuration are presented. The optimal FD system configuration refers to the configuration that maximizes the process' energy efficiency and matches the published benchmark theoretical minimum work of separation for desalination (work required to ideally separate pure water from brine considering zero irreversibility) [70]. Figure 100 shows a configuration tested performing cooling energy recovery from the return streams through series heat transfer of the incoming brine with the return pure ice then the concentrate streams. The cooling is provided to the freezing chamber using a single vapor compression refrigeration cycle that reduces the temperature of the brine down the desired freezing temperatures and ice crystallizes. The ice and concentrate are separated after leaving the freezing chamber before the cooling energy recovery is performed with the incoming brine feed.

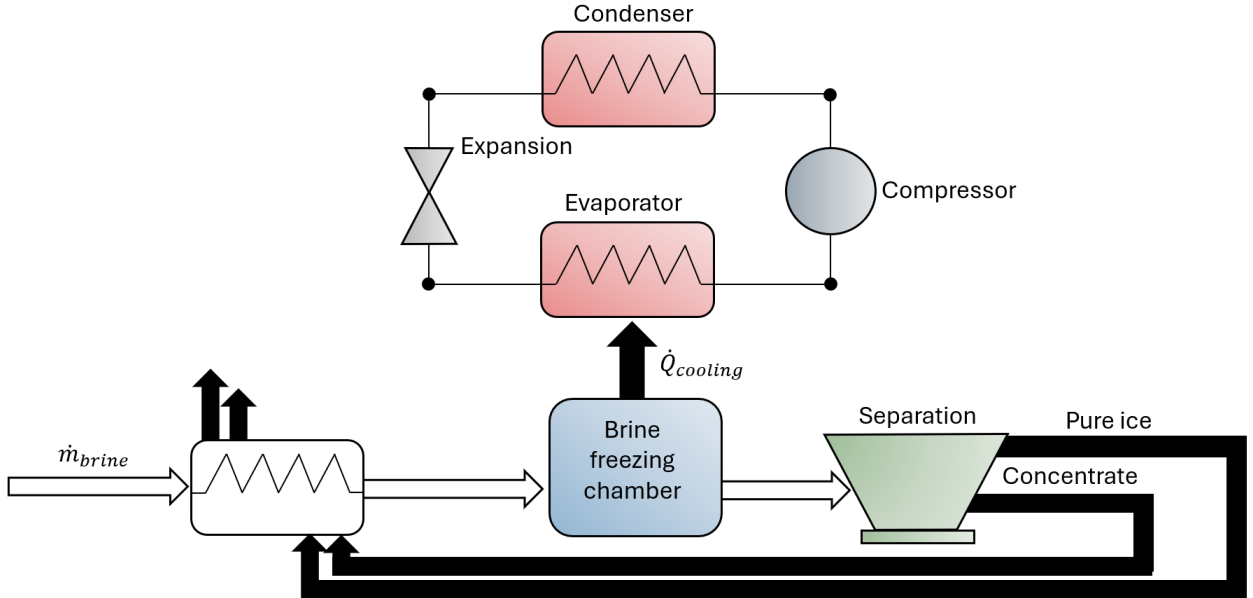


Figure 100: FD configuration utilizing a single vapor compression refrigeration cycle and cooling energy recovery from the return streams through series heat transfer of the incoming brine with the return pure ice then the concentrate streams.

The cooling energy recovery from the return ice and concentrate streams through parallel heat exchangers has also been investigated utilizing a single stage vapor compression refrigeration system, as illustrated in Fig. 101.

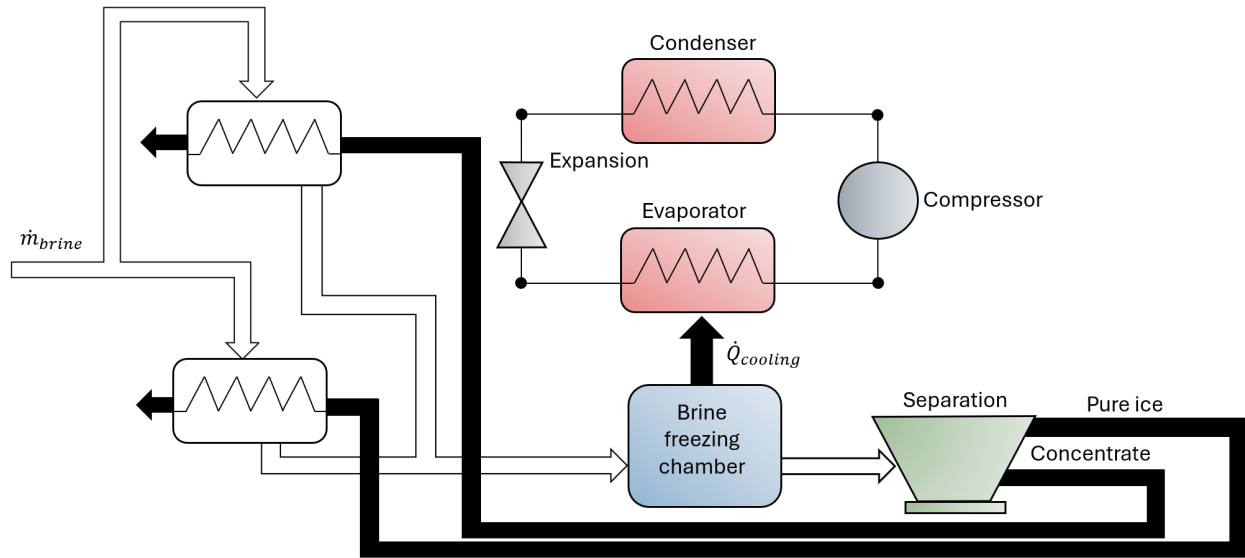


Figure 101: FD configuration utilizing a single vapor compression refrigeration cycle and the cooling energy recovery from the return ice and concentrate streams is performed through parallel heat exchangers.

Recovering the cooling energy from the return streams by passing through the condenser's shell side of the single vapor compression refrigeration cycle has been investigated as shown in Fig. 102.

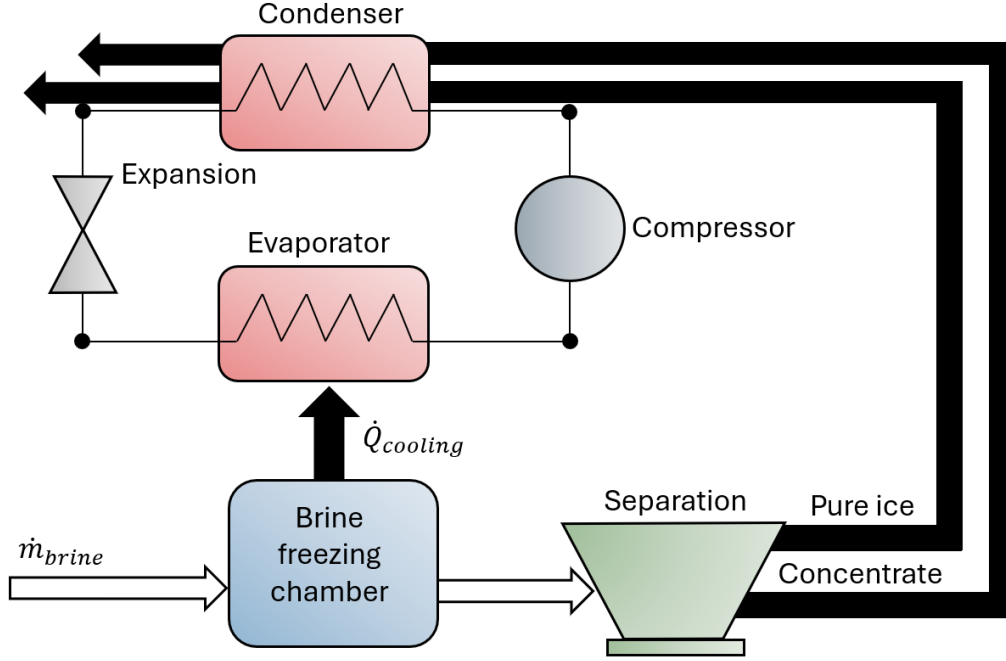


Figure 102: FD configuration utilizing a single vapor compression refrigeration cycle and the cooling energy recovery from the return ice and concentrate streams is performed in the condenser.

Since none of the FD system configurations described above showed a match with the published benchmark minimum work of separation for desalination (brute-force search termination criteria) [70], cascade vapor compression refrigeration cycles were investigated. Figure 103 illustrates the FD configuration utilizing cascade vapor compression refrigeration cycle to provide cooling to the freeze chamber. The cooling energy recovery takes place by passing the two return cold streams (ice and concentrate) through the shell side of the intermediate heat exchanger (intermediate condenser coupling the two refrigeration cycles). Further energy recovery is performed using the return streams after leaving the intermediate condenser through series precooling of the incoming brine.

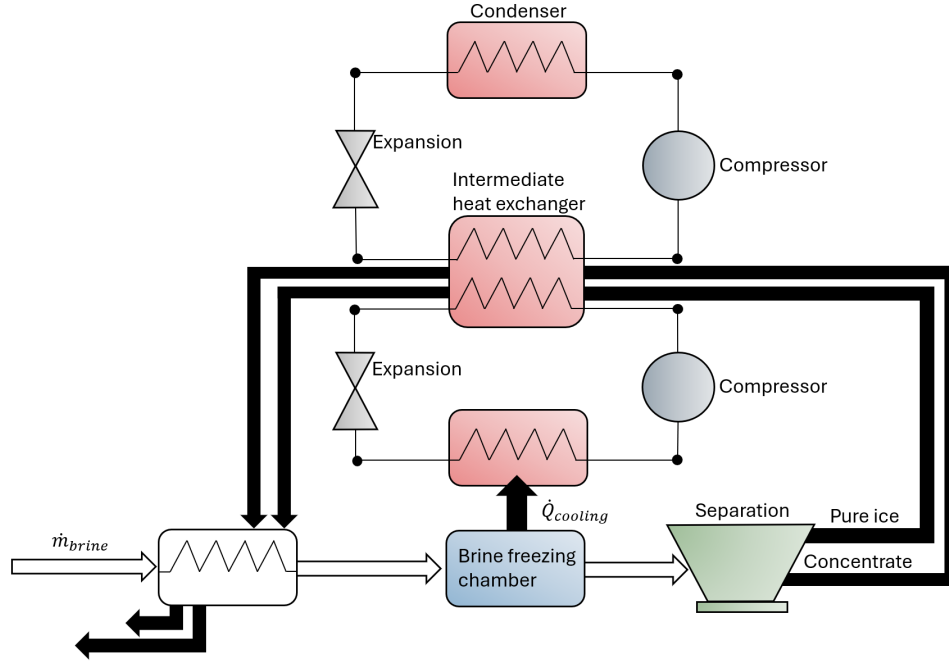


Figure 103: FD configuration utilizing cascade vapor compression refrigeration cycle and the cooling energy recovery is performed in the condenser then through feed precooling.

Another approach for the cooling energy recovery has been tested where the concentrate stream is passed directly to the pre-cooler. The pure ice stream is first melted inside the shell of the intermediate condenser before further precooling the incoming feed brine as illustrated in Fig. 104.

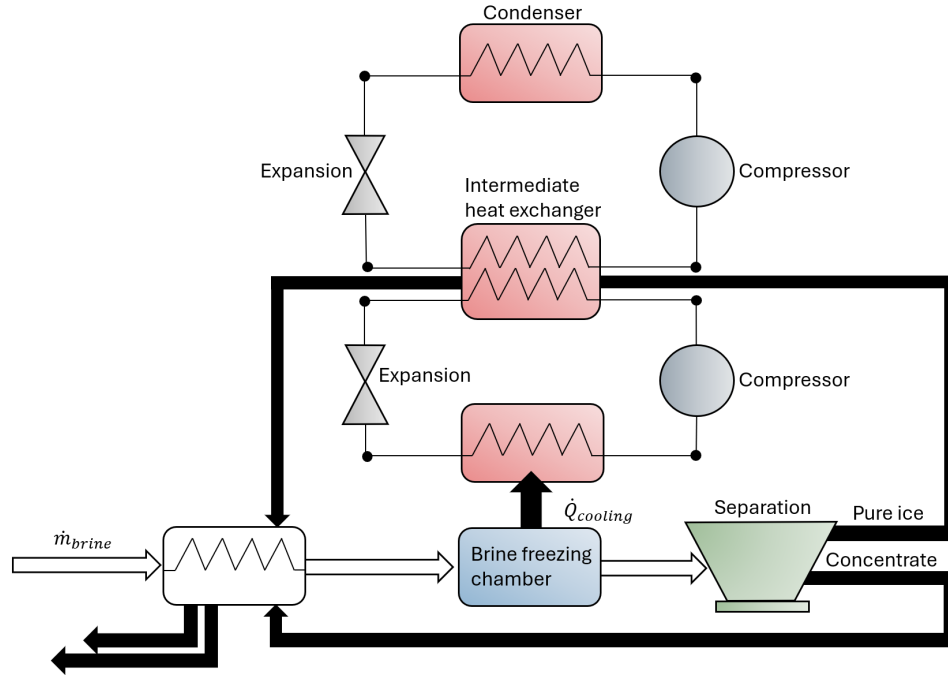


Figure 104: FD configuration utilizing cascade vapor compression refrigeration cycle where the concentrate stream precools the incoming brine and the ice stream melts in the intermediate condenser then further precools the brine feed.

Passing both return streams by the shell side of the intermediate heat exchanger of the cascade refrigeration system then utilizing them in parallel heat exchangers to further precool the brine feed has been investigated as shown in Fig. 105.

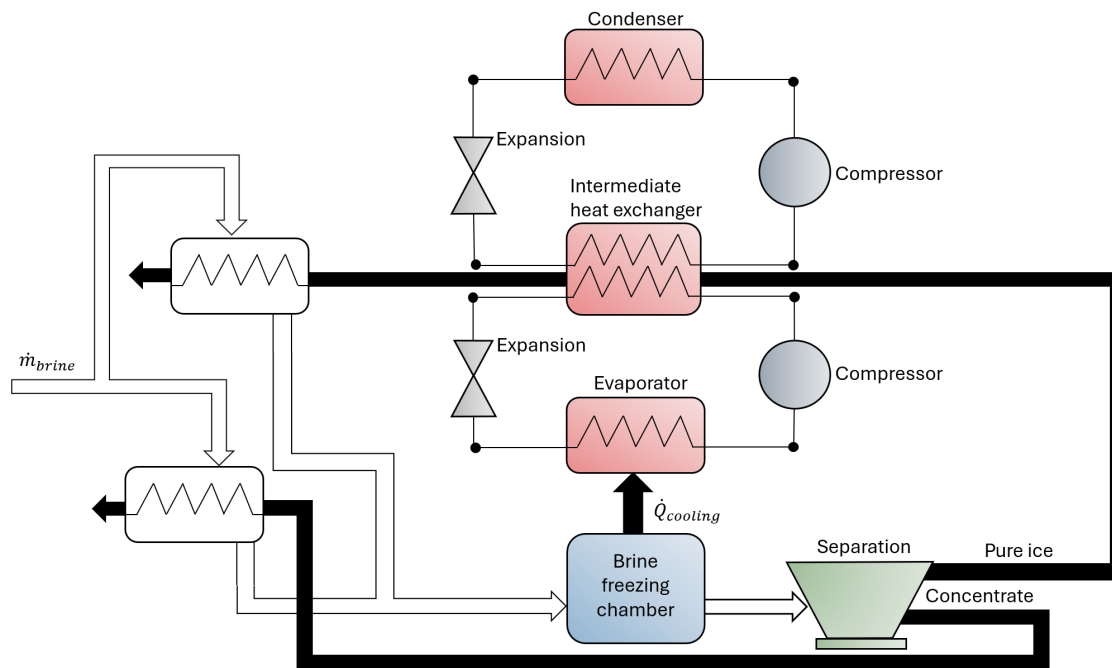


Figure 106: FD configuration utilizing cascade vapor compression refrigeration cycle where the concentrate stream precools the incoming brine and the ice stream melts in the intermediate condenser then further precools the brine feed utilizing parallel precooling heat exchangers.

B Appendix

In this appendix, the correlation for finding the salinity of the treated water is deduced, based on mass balance of the salt through the desalination system (62)

$$m_{s,tw} + m_{s,rb} = m_{s,f} \quad (62)$$

The mass rate of salts can be replaced by the corresponding total mass rate (mass rate of salts + mass rate of water) multiplied by the salinity for each of the feed, treated and rejected streams. Thus, Eq. 62 can be rewritten as Eq. 63 and re-arranged in the form of Eq. 64.

$$m_{tw}S_{tw} + m_{rb}S_{rb} = m_fS_f \quad (63)$$

$$\frac{m_{tw}}{m_f}S_{tw} + \frac{m_{rb}}{m_f}S_{rb} = S_f \quad (64)$$

The mass rate balance between the feed, treated and rejected streams (Eq. 65) is applied to Eq. 64 to obtain Eq. 66.

$$m_{tw} + m_{rb} = m_f \quad (65)$$

$$\frac{m_{tw}}{m_f}S_{tw} + \frac{m_f - m_{tw}}{m_f}S_{rb} = S_f \quad (66)$$

The pure water recovery ratio (R) is defined as the ratio between the treated mass rate to the feed mass rate. Accordingly, Eq. 66 can be rewritten as Eq. 67 then re-arranged through Eqs. 67– 70 to find the salinity of the rejected stream.

$$RS_{tw} + (1 - R)S_{rb} = S_f \quad (67)$$

$$R\left(\frac{S_{tw}}{S_{rb}}\right) + (1 - R) = \frac{S_f}{S_{rb}} \quad (68)$$

$$1 - R\left[1 - \left(\frac{S_{tw}}{S_{rb}}\right)\right] = \frac{S_f}{S_{rb}} \quad (69)$$

$$S_{rb} = \frac{S_f}{1 - R\left[1 - \left(\frac{S_{tw}}{S_{rb}}\right)\right]} \quad (70)$$

By multiplying the salinity of the rejected stream (presented by Eq. 70) by the salinity ratio of the treated water to the rejected stream, the salinity of the treated water can be calculated using Eq. 71.

$$S_{tw} = S_{rb}\left(\frac{S_{tw}}{S_{rb}}\right) = \left(\frac{S_{tw}}{S_{rb}}\right) \frac{S_f}{1 - R\left(1 - \frac{S_{tw}}{S_{rb}}\right)} \quad (71)$$

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