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DESIGN AND ANALYSIS OF A NOVEL FREEZE DESALINATION SYSTEM FOR TREATMENT OF OIL AND GAS PRODUCED WATER

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PAOLO FRANCO MOGOLLON ACOSTA

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DESIGN AND ANALYSIS OF A NOVEL FREEZE DESALINATION SYSTEM FOR TREATMENT OF OIL AND GAS PRODUCED WATER

A THESIS APPROVED FOR THE

SCHOOL OF AEROSPACE AND MECHANICAL ENGINEERING

BY THE COMMITTEE CONSISTING OF

Dr. Hamidreza Shabgard, Chair

Dr. Ramkumar Parthasarathy

Dr. Jie Cai

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I would like to dedicate this work to my family, for their love and support through these years.

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Abstract

Freeze desalination is an alternative technology that has received a lot of attention due to several advantages. Among these, the lower energy consumption and low operation temperature are the most important ones. The operation and maintenance can also be considered simple in comparison to conventional technologies such as membrane-based ones, multistage flash, and Multi-effect distillation. However, the big scale implementation is the main concern for Freeze desalination due to the difficulty to operate it continuously. This study proposes a plant flow process that can operate continuously. Industrial components and actual efficiencies are considered in the development of this process. Moreover, this research is the first to study actual produced water compositions. To do that, a combination of engineering platforms is utilized, ASPEN Plus and OLI Chemical Wizard. Two different plants are proposed: a single-stage system and a two-stage system. Both systems are characterized for achieving temperatures lower than -20 ° by using a direct contact cooling liquid. The influence of different operation parameters is investigated. The results are presented in terms of pure water production, energy consumption, and a thermo-economic study that involves the operation and infrastructure costs. Water recovery ratios ranging from 0.67 to 0.87 were achieved depending on the brine composition. Similarly, the LCOW (Levelized cost of water) was found to be between 0.31 to 0.69 $/barrel of input brine.

Keywords: Freeze Desalination, ASPEN Plus, water recovery ratio, LCOW

1. Introduction

1.1. Topic Background

Water occupies 71% percent of the Earth's surface, however, only 2.6 % of that amount is fresh water and even a smaller percentage is accessible for consumption[1]. Water scarcity is a growing problem due to the increase in population and it affects all the countries around the world[2]. By 2025 is predicted that the global population will experience a rise of 40% with a water demand increase of 55%, which also includes the industry water requirement[3]. According to this situation, urgent action is required to tackle this problem. Besides, the existing freshwater access is worsening as the plants reject brine to the sea and soil, requiring action on wastewater management to save the planet. Industries such as mining and oil face problems of clean production because of water consumption and brine rejection[4]. As an example, the oil and gas industry has a production of 250 million barrels and more than 40% of this is discharged to the environment[5]. Consequently, desalination technologies have received a lot of attention and development to overcome the water scarcity problem and brine management.

There are different technologies among the desalination methods, some very well studied, and others in progress. They can be grouped into two main categories: membrane desalination, and thermal desalination. Reverse osmosis (RO) is the most commonly used desalination method as membrane desalination. Multistage flash (MSF) and Multiple effect distillation (MED) are types of thermal desalination. RO is applied 65% of the total desalination, while MSF and MED follow next with each being 21% and 7% of the total desalination process [6–8]. RO has been used because of its simple concept and feasibility to handle large-scale systems. However, there are some disadvantages such as the water acidity, high operation time, and waste of pure water in the process. On the contrary, thermal plants can be a solution if the energy input can be extracted from other industrial plants.

Among the thermal desalination plants, there are alternative technologies such as Freeze Desalination (FD). This method, instead of utilizing heat to evaporate, requires cold energy to freeze the brine and produce purified ice that later will be melted and supply as freshwater. This technology consumes one-seventh of the energy required by the conventional thermal methods. Other advantages are the low operation temperature, simple process, and easy maintenance. However, the main disadvantage is the complexity to operate continuously and the feasibility to build large-scale systems. Therefore, this research intends to provide a solution to overcome those limitations and apply it to the treatment of produced water.

1.2. Literature review

1.2.1. Current Desalination Technologies

A seawater desalination plant is capable of converting the seawater stream into freshwater and concentrated brine. To do that, energy and infrastructure are required. In the market, a variety of desalination technologies can be found such as thermal distillation, membrane separation, freezing, electrodialysis, etc.[7,9-10]. The status of desalination plants is promising. There around 20 000 desalination plants worldwide in 150 countries. In 2018, a production capacity of 100 000 000 cubic meters per day was achieved. Moreover, 300 million people drink water that is supplied by desalination plants[1](Figure 1). Among the existing desalination plants, Reverse Osmosis(RO) and Multistage flash(MSF) are the most utilized (Figure 2), with 60% and 26% of the total plants, respectively[11].

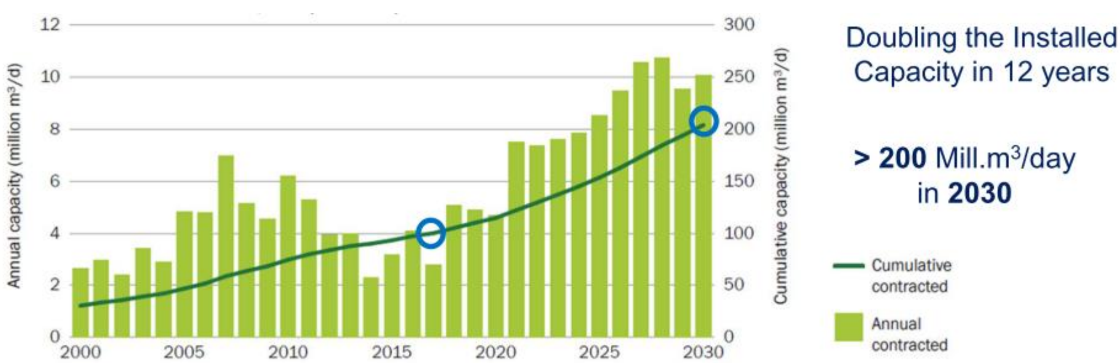

Figure 1. Desalination capacity history and forecast[1]

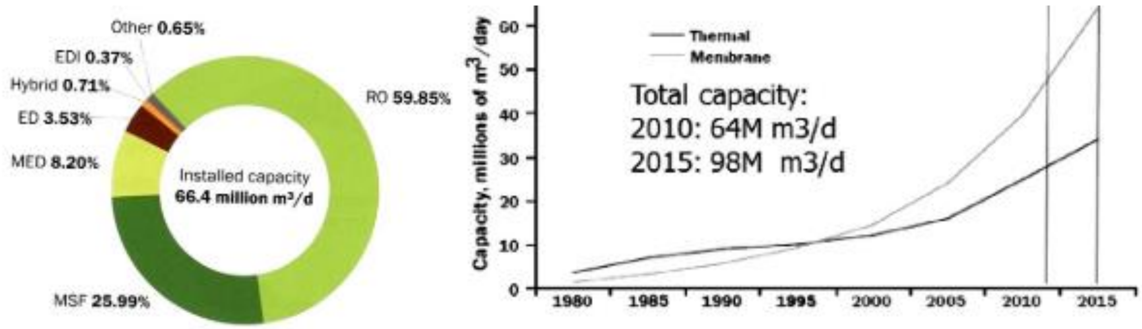

Figure 2. Distribution of current desalination technology[11]

Reverse Osmosis (RO)

The Reverse Osmosis process is categorized as part of the membrane methods and its operation is based on the application of osmotic pressure. To overcome the osmotic pressure, external pressure is applied, therefore, the water is forced to flow in the reverse direction across the membrane, leaving the dissolved salts in an increased concentration of brine. This process requires no heating or phase separation; however, energy is required to achieve the external pressure. RO plants consist of four major steps (Figure 3): feed, water pre-treatment, high pressure-pumping, membrane separation, and permeate post-treatment [7,12-13].

Raw seawater contains different impurities with different particle diameters and features. This way, the first process cleans and refines the raw brine utilizing multimedia filters. Common media are anthracite, silica, and granite. This process protects the pumps and the RO membranes. One of the major problems of untreated seawater is fouling, which greatly affects the membrane lifetime. The first filtering is complemented by a chemical pre-treatment. Typical pre-treatment includes chlorination, coagulation, dichlorination, etc.[7].

After the pre-treatment, the solution is pumped at high pressures that allow it to flow through the membranes. The membranes must withstand the pressure drop across them. The most utilized membrane configurations are spiral wound and hollow fiber [7,14].

The final step is the post-treatment, and it involves the addition of lime, removal of dissolved gases, pH adjustment, and disinfection.

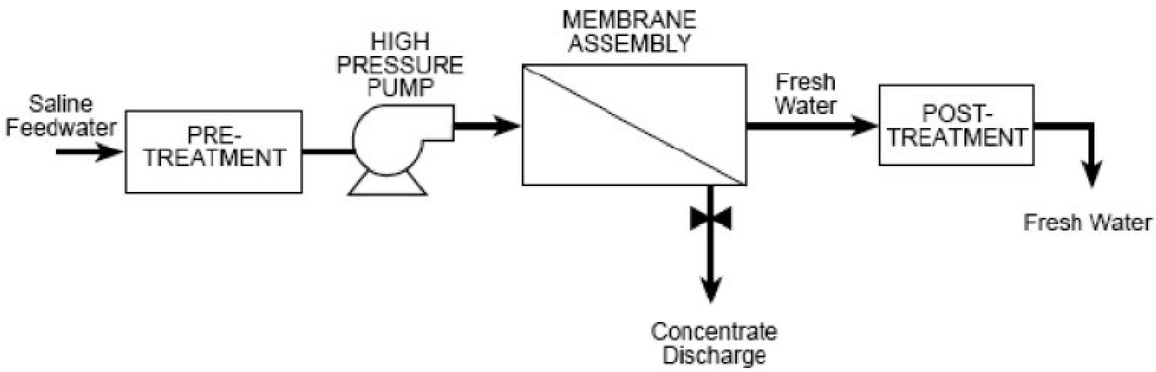

Figure 3. Schematic of a general Reverse Osmosis plant[15]

In the last decade, RO has advanced significantly due to the efficient energy recovery systems and more efficient and robust membranes. In the 1980s, the specific energy consumption was about 10kWh/m3 and it was reduced to below 4kWh/m3[2,16-17].

Multistage Flash

As mentioned, the Multistage Flash (MSF) is the second most utilized desalination technology and is considered part of the conventional thermal plants. MSF is based on the application of flash evaporation. In this technology, evaporation occurs due to the reduction of pressure rather than an increase of temperature. The condensation of the flashed seawater gradually raises the temperature of the incoming seawater to the next stage or chamber. The MSF comprises 3 major parts (Figure 4): heat input, heat recovery, and heat rejection[7].

To heat the seawater, external low-pressure steam is utilized, it can be supplied by a cogeneration plant or extracted from a steam power plant[7, 18-19]. The heated seawater directs to the flash evaporator that is composed of several stages from 19 to 28 in modern plants. In the evaporator, part of the brine is boiled until the flash temperature and the remaining brine passes to the next stage where pressure is lower to further flash. Each evaporator step has demisters, decarbonator, and deaerator to improve the quality of the distillate. Then, the flashed water is condensed by colder seawater to produce distillate. MSF produces freshwater from 2-10 ppm dissolved solids and is taken to a potabilization process[7].

MSF plants have improved in the last decades achieving a cost of $1.00/m3.

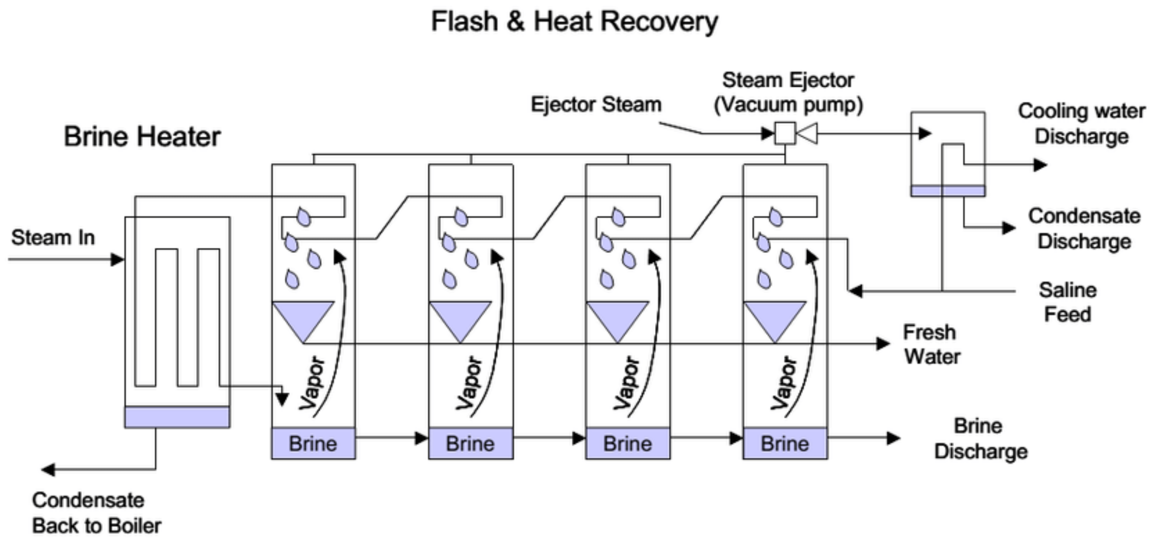

Figure 4. Schematic of a MSF plant[20]

Multi-effect distillation

Multi-effect distillation (MED) is one of the oldest desalination methods; however, it is very efficient thermodynamically [21,22]. A typical MED plant consists of a series of effects(evaporators), a steam supply, several preheaters, a condenser, a venting system, and a train of flashing boxes (Figure 5).

The array of effects will produce freshwater by a repetitive process of evaporation and condensation with reduction of pressure to avoid excessive heating. Theoretically, the number of effects is only limited by the temperature difference between the inlet seawater and inlet steam. However, economics can take part depending on the hot steam grand and the infrastructure investment[22].

To define the process, the maximum temperature must be below 120° C to avoid scaling, and the bottom end condenser temperature is limited by the seawater temperature used as cooling water[21].

In a MED plant, the seawater is preheated in the tubes and the temperature is raised in the effects until the boiling point. To do that, seawater is sprayed onto the evaporator tubes to enhance rapid evaporation. The tubes are heated by the external steam that commonly comes from an external power plant. That steam is condensed on the other side of the tubes and recycled back to the power plant as boiler-feed water. Only a fraction of the seawater evaporates in the first evaporator, the remaining part goes through the rest of the effects. The vapor condensates as distilled by heating the upcoming seawater entering the next effect. After all the effects, the condensate is accumulated. The cost of the plant is proportional to the number of effects[7].

Even though MED plants have a smaller capacity than MSF, their capacity has increased gradually achieving 22, 700 m3/day and 45,400 m3/day.

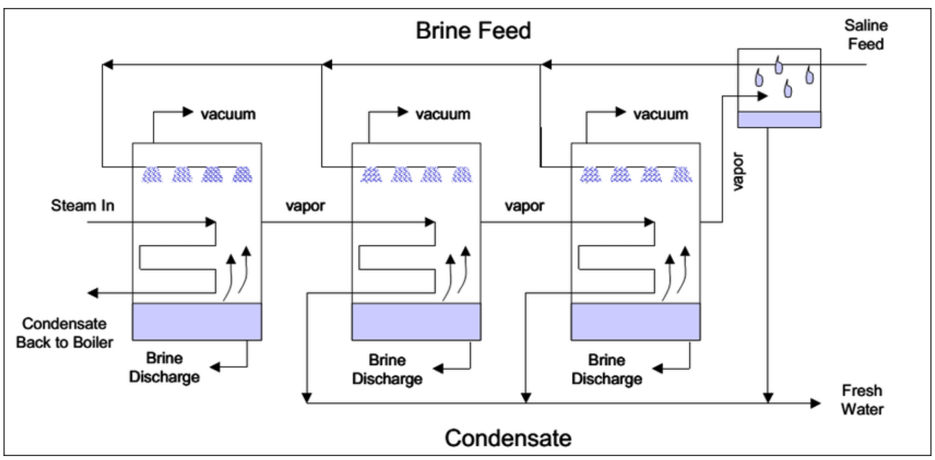

Figure 5. Schematic of a MED system[20].

1.2.2. Freeze Desalination

In general, the Freeze Desalination (FD) process is capable of supplying freshwater by freezing a saline solution such as seawater. In this technology, the partial freezing of the saline solution generates ice, that ideally is free of salts and residuals, then, the ice is melted and finally, supplied as freshwater. However, achieving pure ice requires different stages, being the separation stage, the most important[23].

A general FD plant comprises 3 major stages (Figure 6): crystallization, separation, and melting. The crystallization subprocess is characterized by the occurrence of nucleation, where ice crystals start to grow. The separation process, in a simple saline solution, is in charge of separating the crystals from the brine. Finally, in the melting step, ice is purified and melted to transform into freshwater[23]. Apart from the 3 major stages, an FD process has vital components like the refrigeration system, that supplies cold energy to the crystallization process, and pre-cooling systems that take place before the crystallization step.

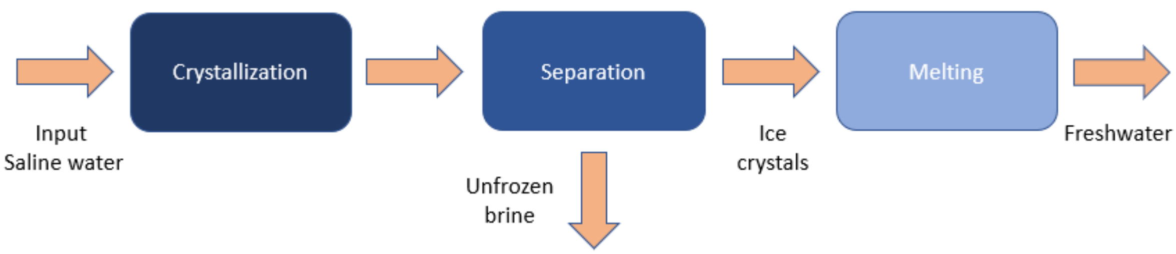

Figure 6. Simplified schematic of a FD system

The most utilized classification of FD is based on the type of contact between the refrigerant and the saline solution. Therefore, it can be direct contact, indirect contact, and vacuum. These types have different variations that are shown in table 1.

Table 1. Categories and types of FD systems[23]

A. Direct contact freezing
B. Indirect contact freezing
a. Internally cooled
1. Static layer growth system
2. Layer crystallization unit on rotating drum
3. Progressive crystallization unit
4. Dynamic layer growth system
5. Suspension crystallization
b. Externally cooled
1. Supercooled feed
2. Ripening vessels
C. Vacuum freezing

conventional direct contact freezing is defined by the use of a refrigerant in contact with the saline stream. The refrigerant removes heat from the solution, and that generates the production of ice crystals (Figure 7). Most commonly, the refrigerant is sprayed into the solution to enhance heat transfer and make the freezing process faster. Finding a suitable refrigerant can be tedious and expensive due to the nature of the brine and operating temperatures. There are four techno-economic requirements for the refrigerant: a) Boiling point lower than -4°C, b) non-toxicity and chemical stability, c) water-immiscible and no hydrate formation, and d) market availability and affordable price. A variety of refrigerants have been used but the most utilized are Freon-114, nitrous oxide, carbon oxide, and butane[23].

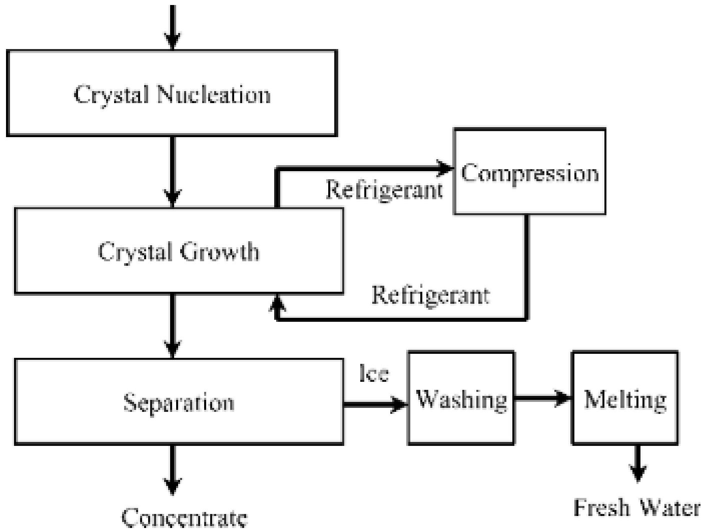

Figure 7. Process flow diagram of a direct contact FD system[23]

Like any other FD process, the direct contact type also has the freezing, separation and melting stages. One of the most common refrigerants is butane. In the crystallization unit (Figure 8), butane is sprayed in liquid form into the saline water stream. It vaporizes due to the lower pressure, by doing that, heat is removed from the saline water and tiny ice crystals are formed. Ice nucleation generation crystals of small sizes but then they start to grow by ripening. This process must be controlled to achieve a homogenous size distribution and a proper crystal diameter. These two particle properties are core for the separation process[23].

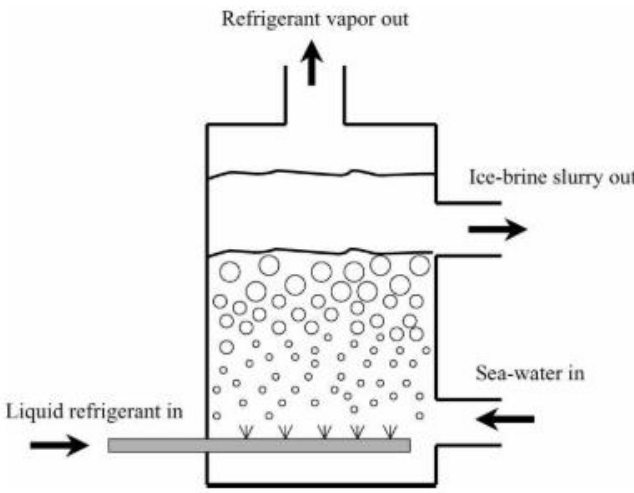

Figure 8. Schematic of a direct contact FD setup[23]

The separation process is one of the most concerning parts of FD because it defines the quality, and most importantly, the operation which can be batch or continuous. There are several types of separation methods such as gravitational, filters, centrifugal, wash columns, etc. All of them have pros and cons, like the operation time, efficiency, a type of operation. In a general FD plant, the goal is to separate the ice crystals from the unfrozen brine. The undesired brine is rejected from the system or part of it can be recycled back to the freezing stage. However, the separation process becomes more complicated with the nature of the brine. Simple saline solutions will work under the principle of a simple FD process. On the other hand, multi-component brines will form different products when frozen such as ice crystals, halites, and unfrozen brine, without considering the direct contact refrigerant. Then, a simple binary separation turned to a four-phase separation. One of the most difficult tasks is to separate the halites which are solid hydrated salts from the ice crystals and the other liquid phase. Therefore, extensive study of the components and separation methods is required.

Wash columns are probably the most accepted separation method for freezing technologies. This technology is capable of effectively separate pure ice crystals by washing them in a concentration unit. There are two types of wash columns (Figure 9), pressurized (mechanical or hydraulic) and gravity. In the first one, the crystals rises to the top and pressure pushes the wash liquid to flow down purifying the crystals. Moreover, the setup is implemented with filter tubes which allow the concentrated brine to flow through and be separated. This process is fast once a steady wash front (interface between washed and unwashed crystals) is achieved (Figure 10). The gravity column is very similar in concept, but to overcome applying the external pressure, the column must be very high so the hydraulic pressure can compact it[23].

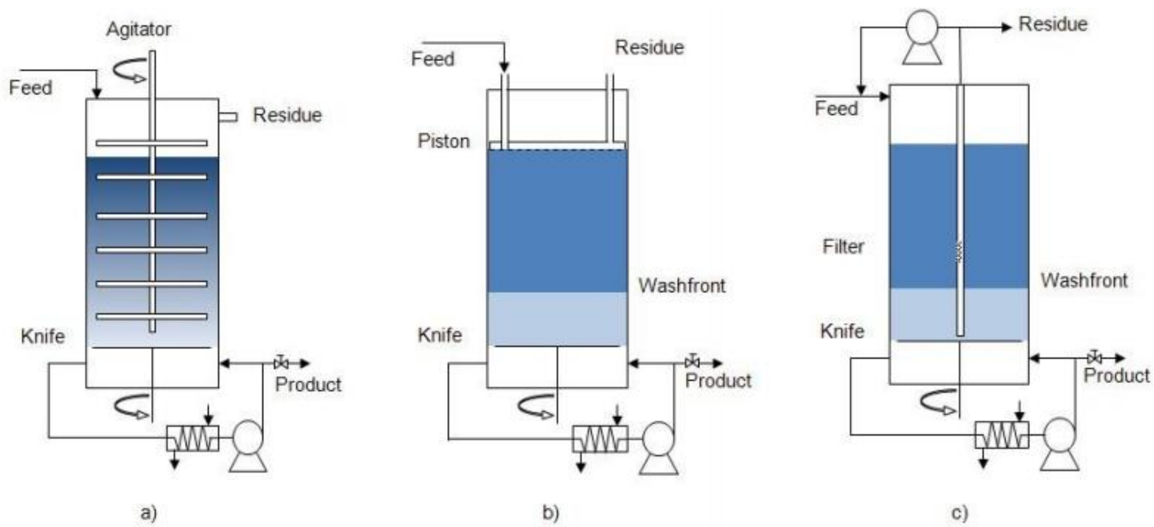

Figure 9. Wash column types: a) gravity, b) mechanical, c) hydraulic

The melting unit is a heat exchanger that will heat the ice crystals and pump them as freshwater. In some cases, the melting also occurs within the wash column by pumping hot washing liquid and melting a fraction of the crystals.

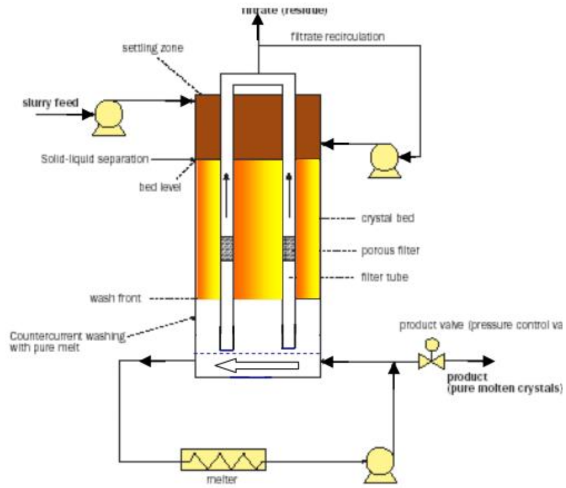

Figure 10. Schematic of zones and operation of wash columns[24]

The indirect contact freezing utilizes a refrigerant that does not mix with the saline water. Therefore, the cooling takes place through a typical heat exchanger. Indirect freezing can be categorized into two classes (Figure 11): suspension freezing and freezing on a cold plate. In the suspension freezing the ice crystals form a suspension in the mother liquor (Figure 12). This process occurs in two steps, ice nucleation (small crystals formed) and recrystallization (smaller crystals start to grow). The suspension method is commonly found in the food industry. Alternatively, the freezing on a cold plate forms a layer of ice in one dimension which is advantageous for easy operation. It can be of two types, progressive or falling film. The production of ice layers prevent trapping impurities in the ice[25].

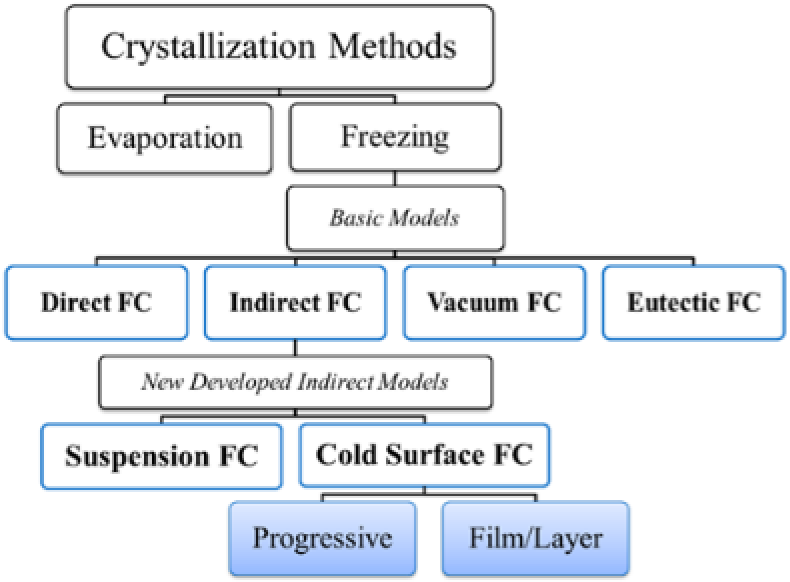

Figure 11. Classification of FD methods[25]

The progressive freezing utilizes a tube filled with solution, submerged in cold refrigerant (Figure 13). A stirrer is utilized inside the tube to lower the impurities in the ice layer. On the other hand, falling film freezing is a dynamic method. As the solution flows through the refrigerant, the heat transfer and mass transfer are enhanced which also make impurities away from the ice layer.

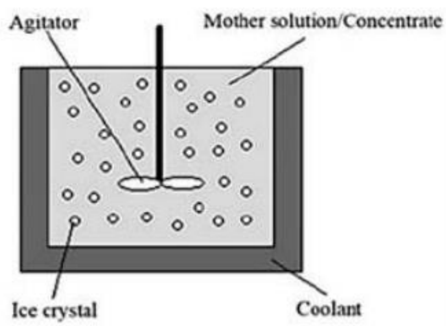

Figure 12. Schematic of suspension FD[25]

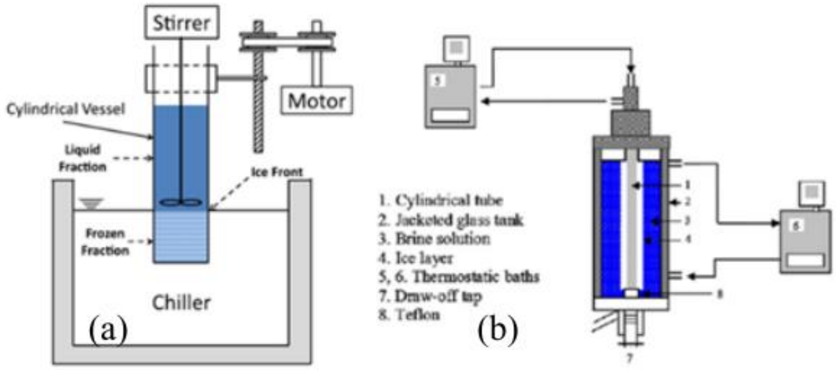

Figure 13. Schematic of progressive FD[25]

Vacuum freezing is the third most utilized method, and it employs high vacuum to vaporize a portion of the water, which provides the refrigeration effect by reducing the temperature and forming ice crystals[25].

Along with the three other described methods, eutectic freezing is a method that operates at very low temperatures (below the eutectic point)[25]. In this scenario, ice and salts are formed. Because of the lower temperatures, ice production is higher.

In the last decades, extensive research has been made in FD technologies. Experimental and numerical studies about the system, components, and operation have been developed. Madhavi et al. [26] experimentally test the FD process by reducing a sample brine of 33,351 to 15,885, 4,850, and 1,345 mg/L, after three successive FD cycles. Luo et al. [27] desalinated brackish water (1320 ppm to 8350 ppm). The results showed that FD could achieve a removal percentage between 57.88% to 48.38% of the TDS. Similarly, Mtombeni et al. [28] used the HybridICE^{TM} FD system and reached an average removal percentage of 98.5% with a specific consumption of 7.45 kWh per ton of ice produced. Melak et al. [29] utilized FD as a defluoridation technique. The method was able to purify tap water spiked with 10 mg/L F-1 and to obtain a fluoride removal of 62%, a water recovery ratio of 90%, consuming 91.8 KJ/L. Jayakody et al. [30] in an experimental and numerical investigation could reduce impurities from 1.5% to 0.1%. The use of N2 as a refrigerant in the freezer is also studied. It was found the higher N2 flow rates enhanced the ice production. Shin et al. [31] optimized the FD system by implementing a scraped surface crystallizer. It was found that utilizing a two-step process of 100 min each step can achieve a

40% water productivity and satisfying irrigation standards (1757 mg/L TDS). Chen et al. [32] include a supercooled dynamic ice machine as part of the freezing process in an FD system. The new system consumed 58% of the energy consumed by the indirect contact progressive freezing. Moreover, the new system achieved a water productivity of 60% with 0.05% of impurities. The investigation has also been developed at a component level to determine the factors that affect productivity and quality. Quin et al. [33] studied the wash column and its affection factors. The study showed that the ice size and shape, the thermal insulation, and the ice-packed bed compression are the predominant factors in the operation. Similarly, Yuan et al. [34] investigated the influencing factors of the ice shape. It was concluded that salt concentration is a key factor in the crystal morphology and growth. Eghtesad et al. [35] studied the influence of the freezer heat flux on ice generation and quality. The results showed that the increase in heat flux made the ice generation four times quicker, but the quality was reduced by 22%. On the contrary, the reduction in heat flux decreased the ice generation by 44%, but quality improved by 23.5%. Erlbeck et al. [36] compared the two scraped crystallizers with a different pitch. It was found that the 19°-pitch crystallizer achieved a removal efficiency of up to 29%, while the 4°-pitch unit reached a removal efficiency of 33%.

FD has been often integrated with other technologies to improve the quality and production of conventional methods. Wang and Chung [37] coupled a direct contact Membrane Desalination system with Freeze Desalination. The conceptual design could achieve drinkable water standards and a water recovery ratio of 71.5%. Baayyad et al. [38] numerically studied the integration of FD and RO. The results showed that energy savings were about 25% and the quality of freshwater improved 75%. The major electricity requirement comes from the refrigeration system in an FD plant; therefore, the utilization of other sources has been widely investigated. The regasification process of LNG involves a huge amount of cold energy which makes it a perfect fit for FD requirements. Lin et al.[39] experimentally integrated LNG cold energy and FD. The experimental study utilized liquid nitrogen and R410a as a cold energy source, and intermediate refrigerant, respectively. The system reached a freshwater capacity of 150 L/H by using 2 kg (freshwater)/kg (LNG) and the salt removal rate of the system is about 50%. Xie et al.[40] designed a novel freezer that was able to effectively use the LNG cold energy. It was found that the speed of refrigeration droplets, initial refrigeration temperature, and ice fraction are some of the most predominant factors. The novel designed included features that were suitable for LNG-FD plants. Ong and Cheng [41] studied the techno-economic feasibility of the integration of LNG cold energy with FD. The results showed that 1.64 kg/s of freshwater using 7.83 kg/s seawater when consuming 1.66kW of electric power. Similarly, Chong et al. [42] developed an economic study of the integration of LNG and FD. It was found that using a regasification rate of 200 t/h, the proposed system produced 260 m3/h of freshwater. The economic analysis showed that the FD operation cost can be reduced from $9.31/m3 to $1.11/m3 by cold energy integration. Lu et al. [43] developed a zero liquid discharge desalination system. The system was integrated by membrane distillation, crystallization, and freeze desalination plants. Moreover, sustainable sources as solar panels and LNG cold energy are utilized to supply energy to the system. The lab-scale pilot had a daily output of 2.52 kg of salt and 69.48 kg of water. Moreover, 50% of its heating energy can be supplied by solar panels with an effective area of 50.5 m2 and 100% of its cooling energy can be provided by the regasification of 207-kg LNG.

1.2.3. Brine management

In the last decades, the increasing amount of produced water from industrial plants has become a major issue for the environment. As an example, 250 million barrels of produced water are daily generated from Oil&Gas plants, and about 40% is discharged in the environment[5]. Furthermore, the number of seawater desalination plants has greatly increased due to the lack of potable water, in consequence, huge amounts of brine with high salinity are rejected from these plants. Therefore, different methods and technologies have been developed such as deep-well injection, surface water discharge, and sewer discharge[44]. The application of those depends on a variety of factors related to the brine and the environment. Similarly, Oil&Gas companies have been utilized the following methods: avoid productions, inject into formations, discharge to environments, reuse in operation, and beneficial uses[5].

Produced water is a mixture which components that come from different sources. In a reservoir, natural water with a little acidity is found below the hydrocarbons (Fig 14). In the extraction of oil and natural gas, the reservoir pressure is reduced then water is injected to overcome the pressure loss. Moreover, in some scenarios, water from outside the reservoir might leak into the reservoir. This way produced water becomes a mixture of different water, minerals, and hydrocarbon[5]. Produced water is characterized by the presence of minerals, contaminants, and salinity.

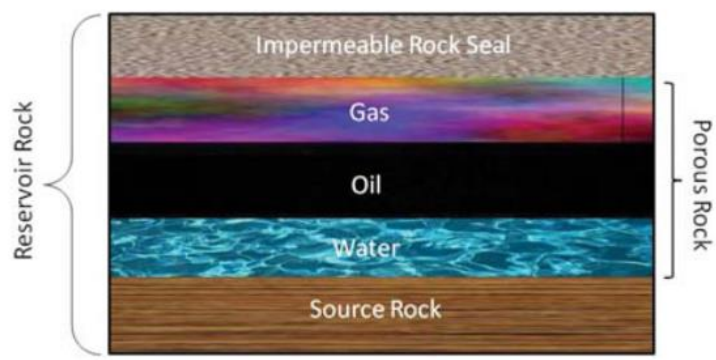

Figure 14. Layer stratification of a reservoir[5]

<u>Surface water discharge</u>

Surface water discharge is a method mostly used for seawater rejected brine. In this technology, the brine is discharged into the ocean, lakes, rivers, etc. This method is limited to the nature of the disposable brine, if the brine features do not match the water body requirements, it will not be implemented. The main constraints are the higher salinity of the brine and the presence of contaminants. One solution to the salinity issue is to mix the concentrated brine with brines of much lower salinity so the salinity requirement can be satisfied[44]. The cost of this technology ranges from U$$ 0.05/m^3 to USS 0.30 /m^3[45].

Sewer discharge

Sewer discharge is another common technology that discharges the brine into a wastewater collector system. It is mostly applied by small brackish water desalination plants due to the risk of having big amounts of higher salinity brine entering the treatment plant. The brine may require further processes to treat metal traces[44]. The disposal cost of this method is found to be between US$0.32/m^3 to US$0.66/m^3[45].

Deep-well Injection

One of the most common disposal methods is deep-well injection. This method has been utilized mainly by the oil and gas industry, but desalination plants can also use it, especially in remote areas. In this technology, brine is injected in a defined deep below aquifers that are properly isolated. Usually, the injected brine and the aquifers are surrounded by casing, cementing, and ground to avoid filtrations[44]. However, this method has several disadvantages and concerns related to the filtration of the produced water and ground stability. This method is more expensive than sewer discharge and surface water discharge ranging from US$0.54/m^3 to US$2.65/m^3[45].

Evaporation ponds

Evaporation ponds are a technology utilized in shallow basins where the brine is stored and later evaporated by solar irradiation. After the brine is evaporated the precipitated minerals and salt crystals must be periodically removed. It is mostly used in dry and semi-dry areas. A lot of advances have been made in terms of ground conserving by using protection layers[44]. This method is not as economic as other methods and has a range of US$3.28/m^3 to US$210.24/m^3[45].

Desalination technologies

Desalination technologies can also be applied to treat produced water from oil and mining operations. Membrane technologies such as Reserve Osmosis, Microfiltration, and Ultrafiltration. These methods can be applied standalone or in a combination to achieve better results[5]. Similarly, thermal desalination methods such as MSF, vapor compression distillation, and MED have been widely applied. All the desalination methods will still produce residual brine to dispose of.

Biological methods

A different class of technology is biological treatment. Biological aerated filters (BAF) that comprises a permeable media that takes advantage of aerobic condition to facilitate oxidation and remove pollutants (Figure 15). It is proved that BAF can remove a wide range of contaminants, from oil, ammonia, solids, gases, sulfide to traces of heavy metals. Removal efficiencies are high and dependent on the contaminant like 80% for oil and 85% for suspended solids. Since this method, directly remove the contaminant in their natural and complete state, the water recovery ratio approach to 100%. The power consumption ranges from 1 to 4 kWh/day but the capital cost is expensive and more determinant[5].

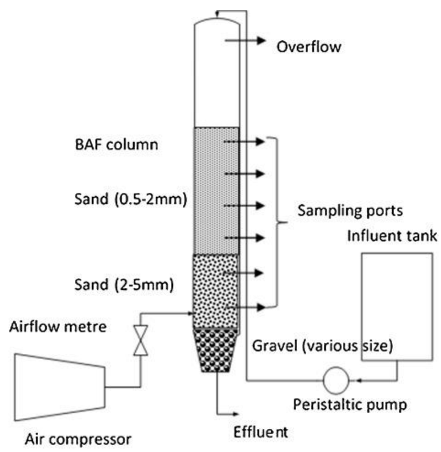

Figure 15. Schematic diagram of BAF system[46]

In the last decades, the design of zero liquid discharge (ZLD) systems has received a lot of attention. This type of system avoids the generation of a liquid brine, instead, treated water and solid crystals are produced.

1.3. Topic scope and proposed research

This research aims to develop a Freeze Desalination process flow that can handle industry-scale brine amounts and operate continuously throughout a year. Moreover, the system is designed to treat actual brine and include existing industrial equipment. Therefore, ASPEN Plus and OLI Chemical Wizard are utilized to build and analyze the model performance. The use of actual produced water compositions extracted from the Oklahoma Geological Survey and the implementation of a computation model are unique features of this research that will provide an accurate idea of the real feasibility of the proposed Freeze Desalination system.

In this study, current desalination and brine management technologies are described, then the Freeze desalination technology is investigated along with its benefits and disadvantages. The two main parts of this research are the proposals of the novel single stage and two-stage systems. Both systems are deeply evaluated in terms of freshwater productivity and energy consumption.

The systems analysis will be based on the effect of three major parameters:

- Brine composition: As previously mentioned, the compositions are not idealized, therefore, the brine is multicomponent and has more the five predominant ions that in their aqueous form represent more the twenty ionic components. In this investigation, compositions ranging from 75 000 ppm to 300 000 ppm are studied. Each brine will have a specific operating temperature that will promote higher production rates. Higher concentration brines require lower operating temperatures to supply considerable amounts of freshwater.
- Separation efficiency: Separation devices are fundamental parts of the FD process. They separate and classify the components based on density difference or size particle. Since the study considers actual devices, the separation efficiency is a parameter that must be taken into account. This efficiency influences the development of the process flow and will be critical to the water recovery ratio and energy consumption. A good design will be able to include low-efficiency devices without severely affecting freshwater production.

Throughout the chapter of this thesis, the influence of this parameter will be explained and quantified.

- Evaporator effectiveness: This is the first parameter that will not affect the process flow development on ASPEN plus, however, it is fundamental for the post-processing stage. This parameter represents the effectiveness of the coupling between the refrigeration system and the plant itself. It will greatly affect the total energy consumption since the refrigeration system is the one that provides the cold energy to the freezer. An engineered formula is presented in this study that relates the COP of the refrigeration system with the heat exchanger effectiveness and operating temperatures.

The study is completed by the development of a techno-economic analysis. This study uses the results from the systems evaluation as input data. The techno-economic study is represented in terms of the LCOW (Levelized Cost of Water) for a 30-year operation. Freshwater productivity, energy consumption, and the LCOW will determine the feasibility of the two proposed systems.

2. Study and proposal of single-stage system

2.1. Model description

In this study, the benefits of FD systems are going to be used to treat actual and complex brines such as produced water. Therefore, in the course of this chapter, the differences and requirements of this new process are described. A novel FD system is proposed, and it must be capable of treating produced water and supply freshwater.

In order to accomplish the objective, the novel plant must meet several requirements. These requirements are mostly techno-economic and environmental; however, qualitative requirements are also important and depend on the experience of the designer and other external factors. The main requirements are as follow:

- Treatment of actual brine compositions
- Computational design and simulation
- Continuous operation
- Large-scale operation
- Direct contact freezing
- Low number of mobile parts and devices
- Optimized production and energy consumption
- Process flow independent of the brine and temperature
- Eco-friendly

In this project, the brine composition data is realistic, and it was obtained from the “Oklahoma Geological Survey”. That document accounts for all the produced water information within the Oklahoma area. The presented data shows accurately the multi-component nature of produced water. The proposed plant can treat a wide range from brine compositions (70 000 ppm to 300 000 ppm). Table 2 shows the composition of studied brines.

Table 2. Brine compositions for Oklahoma basins

County	TDS (ppm)	Na+ (mg/L)	Cl– (mg/L)	Mg+2 (mg/L)	Ca+2 (mg/L)	HCO3 – (mg/L)	K+ (mg/L)	SO4 – 2 (mg/L)
Murray	70,000	21527	43298	1147	3824	35	56	113
Murray	92,798	28568	57400	1520	5070	46	74	150
Beaver	200,000	62140	112900	2350	6260	160	-	1175
Oklahoma	299,469	111477	182301	941	4459	44	-	246

The proposed system also includes the three main FD processes: freezing, separation, and melting. Since the plant will treat actual brines, those processes will become much more complex, and they will be a combination of several devices.

In the following section, the description of the processes and components of the novel plant are presented.

Freezing Unit

One of the unique features of this novel system is the design and components of the freezing unit. The freezing process is achieved by a direct-contact heat exchanger. In this unit, two fluids are in contact and very well mixed. Hot brine and an intermediate cooling liquid (ICL) enter the freezer. The ICL is an engineered fluid capable of standing freezing temperatures lower than -30°C without experiencing any crystallization and high increment of viscosity [47-48]. The ICL must be immiscible with water, chemically stable, and eco-friendly. The specific gravity of ICL is 0.85 (Table 3). The hot brine is cooled down to temperatures between -20° and -30° depending on the brine composition. The mass flow rate of ICL is about 30 times higher than the brine mass flow rate. The choice of a direct-contact freezer is to reach higher and more effective heat transfer rates. The good mixing of both fluids is core for this process to enhance ice nucleation and the unit effectiveness.

Table 3. Commercial ICL properties[47]

Viscosity @25°C	**Specific gravity**	**Flash point**	**Pour point**	Specific Heat (KJ/kg-K)
1.5cSt	0.85	63°C	-90°C	1.5

Very low temperatures are required, especially for higher saline brines (200 000 ppm and above). In general, produced water requires freezing temperatures to reach acceptable water recovery ratios.

In the steady state the heat required ($\dot{Q}_{Fr}$) in the freezing process is modeled by:

$$\dot{Q}_{Fr} = \dot{m}_{ICL} * c_{p.ICL} * \left(T_{Fr,out} - T_{ICL,in}\right) \quad \text{Eq. 1}$$

Where $\dot{m}_{ICL}$, $c_{p.ICL}$, $T_{ICL,in}$, and $T_{Fr,out}$ are the mass flow rate, the specific heat, the ICL inlet temperature, and the freezer outlet temperature.

$$\dot{m}_{rc} + \dot{m}_{br} = \dot{m}_{ubrine} + \dot{m}_{ice} + \dot{m}_{hal} \quad \text{Eq. 2}$$

Where $\dot{m}_{br}$, $\dot{m}_{rc}$, $\dot{m}_{ice}$, $\dot{m}_{hal}$, and $\dot{m}_{ubrine}$ are the mass flow rates of the input brine, recycled brine, ice crystals, halites, and unfrozen brine, respectively. The inclusion of the recycled brine in this equation is vital for the project and it is further explained in the following sections.

Similarly, the freezer load is also calculated by the following:

$$\dot{Q}_{Fr} = \dot{m}_{br} * c_{p,br,in} * \left(T_{br,in} - T_{Fr,out}\right) + \dot{m}_{rc} * c_{p,\mathrm{rc}} * \left(T_{rc,in} - T_{Fr,out}\right) + \dot{m}_{ice} * H_{w,aq,sol} + \dot{m}_{hal} * H_{w,aq,\mathrm{disc}} \qquad \text{Eq. 3}$$

Where $T_{br,in}$, $T_{Fr,out}$, and $T_{rc,in}$ are the temperatures of the inlet brine, freezer outlet, and recycled stream, respectively. $c_{p,br,in}$, $c_{p,\mathrm{rc}}$ are the specific heats of the inlet brine and recycled stream, respectively. These parameters change its value with the temperature. $H_{w,aq,sol}$ and $H_{w,aq,\mathrm{disc}}$ are the latent heat of solidification for water and the halite, respectively.

In eq.3 four different components can be distinguished. The first term represents the sensible heat required to cool the brine. The second term calculates the sensible heat involved in the recirculating brine. The third term accounts for the latent heat of solidification of water. The fourth term represents the latent heat of dissociation.

The freezing of produced water involves sensible and latent heat of different components. In this system, the supercooled temperatures at the freezer outlet generate the formation of a multiphase system. This system comprises ice, unfrozen brine, halites, and ICL. Ice and halites (hydrated salt crystals) represent the solid phases while the unfrozen brine and ICL are the liquid phase. The nature of the multiphase flow becomes a difficulty to the separation process. In a simple saline solution, the separation step only treats ice and saline brine; however, in an actual brine such as produced water, the separation becomes a four-phase step. The separation process is described in the next section.

Separation Process

The objective of an FD system is to melt pure ice crystals and supply them as freshwater. At the freezer outlet, the stream comprises ice, halites, ICL, and unfrozen brine. In this project, the separation process is accomplished by the use of three technologies: hydrocylones, gravity, and wash column. The design of the separation stage accounts for the following:

- Actual industrial devices and efficiencies (no perfect separation nor recycling)
- The ICL must be fully recycled
- Combination and array of separation devices instead of single devices
- Incorporation of recycling and collector lines
- Continuous operation

As mentioned before, the separation step is now a combination of technologies and devices. The selection of the proper device depends mainly on the properties and nature of the components to be separated. The most determinant property in the separation process is density. The solid halites are the densest particle, unfrozen brine is the second, ice crystals are the third, and the ICL is the lightest component. The order of densities is vital for the selection of the technology.

The process flow of the new system is characterized by having two big branches, one carries the heavy components (unfrozen brine and halites), while the other is composed of ice and ICL. To achieve this division, an array of gravity separation devices is utilized where the heavy components settle and go through the bottom outlet. The lighter components raise and flow through the top outlet of the gravity devices. After that, the components already separated undergo different separation steps. The heavy line comprises halites that are heavier than the unfrozen brine. That density difference is suitable for hydrocyclone operation; therefore, an array of hydrocylones where the solid phase goes through the underflow and the liquid phase leaves the hydrocyclone through the overflow. On the other hand, the lighter component line has ice as the lightest phase. Based on that, wash columns are a suitable technology. Wash columns allow to have almost perfect separation and include a washing process which is core to remove micro impurities on the ice crystals surface. After the wash column, one stream is pure ice, and the other stream contains the ICL.

Since the system accounts for realistic efficiencies, other component traces can be found in the separated streams. Therefore, the combination of several devices is utilized to minimize those contaminants. A consequence of that strategy is that in the system, some streams carry a big number of contaminants. Hence, the idea to include collector lines raises as a good solution, these collector lines carries all the residual flows and then they all end up in a single line which is mostly liquid (ICL and unfrozen brine). To recover the full ICL several settling devices are placed and the unfrozen brine is rejected from the system.

Melting and Dissociation Process

The melting process is the last step of the FD system. The unit is a simple tank in which the ice crystals are heated and melted to be supplied as freshwater. In the proposed system, pure inlet crystals from the wash column enter the melting unit. The heat required to melt the crystals is calculated as follows:

$$\dot{Q}_{MELT} = \dot{m}_{ice} * c_{p,ice} * \left(T_{ice,sol} - T_{Fr,out}\right) + \dot{m}_{ice} * H_{ice,sol} + \dot{m}_{ice} * c_{p,w} * \left(T_{w,out} - T_{ice,sol}\right) \quad \text{Eq. 4}$$

Where $T_{ice,sol}$, $T_{Fr,out}$, and $T_{w,out}$ are the water solidification, freezer outlet (melting inlet), and melting tank outlet temperatures. The properties $c_{p,ice}$, $c_{p,w}$,and $H_{ice,sol}$ are the specific heat of ice, water, and latent heat of solidification. $\dot{m}_{ice}$ is the mass flow rate of the ice crystals stream.

One unique feature of the proposed system is the inclusion of a second heating process that is called dissociation. As explained, from the freezing of produced water, two solid phases were achieved: ice crystal, and halite crystals. The previous equation only accounts for the heat required for the ice. The halite crystals are hydrated salts formed at freezing temperatures. By heating (dissociating) these halites, two main components are obtained, one is solid salts and the other is saturated brine. The dissociation process is modeled as follows:

$$\dot{m}_{hal} = \dot{m}_{salt} + \dot{m}_{conc} \qquad \text{Eq. 5}$$

Where $\dot{m}_{hal}$, $\dot{m}_{salt}$, and $\dot{m}_{conc}$ represented the mass flow rate of the halites, the formed salts, and formed concentrated brine, respectively.

$$\dot{Q}_{DIS} = \dot{m}_{hal} * c_{p,hal} * \left(T_{hal,dis} - T_{Fr,out}\right) + \dot{m}_{hal} * H_{hal,dis} + \dot{m}_{salt} * c_{p,salt} * \left(T_{salt,out} - T_{hal,dis}\right) + \dot{m}_{conc} * c_{p,conc} * \left(T_{salt,out} - T_{hal,dis}\right) \qquad \text{Eq. 6}$$

Where $c_{p,hal}$, $c_{p,salt}$, $c_{p,conc}$ are the specific heats of the halites, solid salts, and saturated brine. $T_{hal,dis}$ and $T_{salt,out}$ are the halites dissociation temperature and the dissociation tank outlet temperature, respectively. $H_{hal,dis}$ is the latent heat of dissociation.

<u>Refrigeration System</u>

In the previous sections, the FD processes that take place within the proposed system have been described at a conceptual and numerical level. However, the mechanism of the energy supply has not been explained. The refrigeration system is the unit in charge of supplying cold energy to the freezer. The refrigeration plant is composed the evaporator, condenser, compressor, and throttling valve.

The refrigeration plant, through the evaporator, cools down the ICL to a temperature low enough to enter the freezer of the FD system. The refrigeration system transfers (release) heat through the condenser to complete the refrigeration cycle. Under this scenario, there are two possible choices. The first is to transfer heat to the environment, for that to be possible, the condenser temperature must be above the environment temperature. However, there would be a huge temperature difference between the condenser (higher than 20°C) and the evaporator (lower than -20°C) which generates a very low COP that finally reflects in higher energy consumption. The second approach is a much more thoughtful and useful solution. The condenser heat is transferred to the melting and dissociation units. We would expect to supply the right amount of energy to the two units, but the consumption is a little lower than the total heat released in the condenser. The remaining heat is accounted for by a secondary refrigeration system. This way, the main refrigeration system has a high COP (coefficient of performance), and the energy savings are considerable. The cost operation and installation of the secondary refrigeration system is lower than the savings obtained by the improvement of the main COP.

By conducting experimental and numerical studies, a COP expression was calculated and modeled for the proposed FD Plant:

$$\begin{aligned} COP = \big(&-5.3364x10^{-5}{T_c}^3 + 3.3852x10^{-5}{T_c}^2T_e + 0.0038x10^{-5}{T_c}^2 \\ &- 6.450x10^{-5}T_c{T_e}^2 - 0.0085x10^{-5}T_cT_e - 0.3294T_c \\ &- 1.3285x10^{-5}{T_e}^3 + 0.0013{T_e}^2 + 0.2868T_e + 12.054\big)x0.75 \\ &/0.65 \end{aligned} \qquad \text{Eq. 7}$$

Where T_e and T_c are the evaporator and condenser temperature, respectively.

That expression results in higher COP values when the difference between the evaporator and condenser temperatures is not huge.

The refrigeration system and the FD parameters are related by:

$$T_e = T_{Fr,out} - \Delta T_{ICL}/\varepsilon \qquad \text{Eq. 8}$$

Where ΔT_{ICL} is the ICL temperature difference and ε is the heat exchanger effectiveness.

2.2. Proposed single stage system

The system was developed to treat produced water. It includes the units previously described and is capable of supplying freshwater in a continuous operation. Figure 16 shows the conceptual process flow of the novel system.

Inlet brine composed of several ions and salts enters the freezer when is cooled down to freezing temperatures (lower than -20°C). At the same time, the supercooled ICL enters the freezer in direct contact with the inlet brine. The ICL experiences a temperature rise when cooling down the brine. At the freezer outlet, a multiphase system is formed, the new mixture is composed of ice crystals, halites, unfrozen brine, and ICL. Therefore, the resulting flow undergoes several separation processes. These incorporated devices such as hydrocylones, settling tanks, and wash columns. Once all the products are separated, they lead to the next steps. The ice crystals stream goes through the melting tank and is supplied as freshwater. The ICL stream is recycled through the evaporator so It can be cold enough to reenter the freezer. The ICL forms a loop through the plant and the refrigeration system. On the other hand, the halites stream leads to the dissociation tank, where it is converted to solid salts and concentrated brine. The concentrated brine is recycled into the freezer. That recycling is vital to optimize the production and avoid rejection of higher amounts of brine to the environment. It will be very useful when the system incorporates actual devices and efficiencies are not perfect. The fourth product is the rejected brine, it represents a small percentage of the inlet brine and is rejected from the system.

At an energy level, the refrigeration systems perform a vital role in the operation. The main system provides enough cold energy to the freezer through the ICL cooling. Besides, the heat rejected from this system is utilized to heat the melting and dissociation tanks. However, the rejected heat is bigger than the heat load and there is a remaining amount. The remaining amount is treated by a secondary refrigeration system. This system is the one that rejects heat to the environment. Therefore, the energy input of the proposed plant mainly comes from the electricity consumption of the compressors. There is small equipment such as pumps or actuators that require electric power but those are small quantities that will be taken care in the following sections.

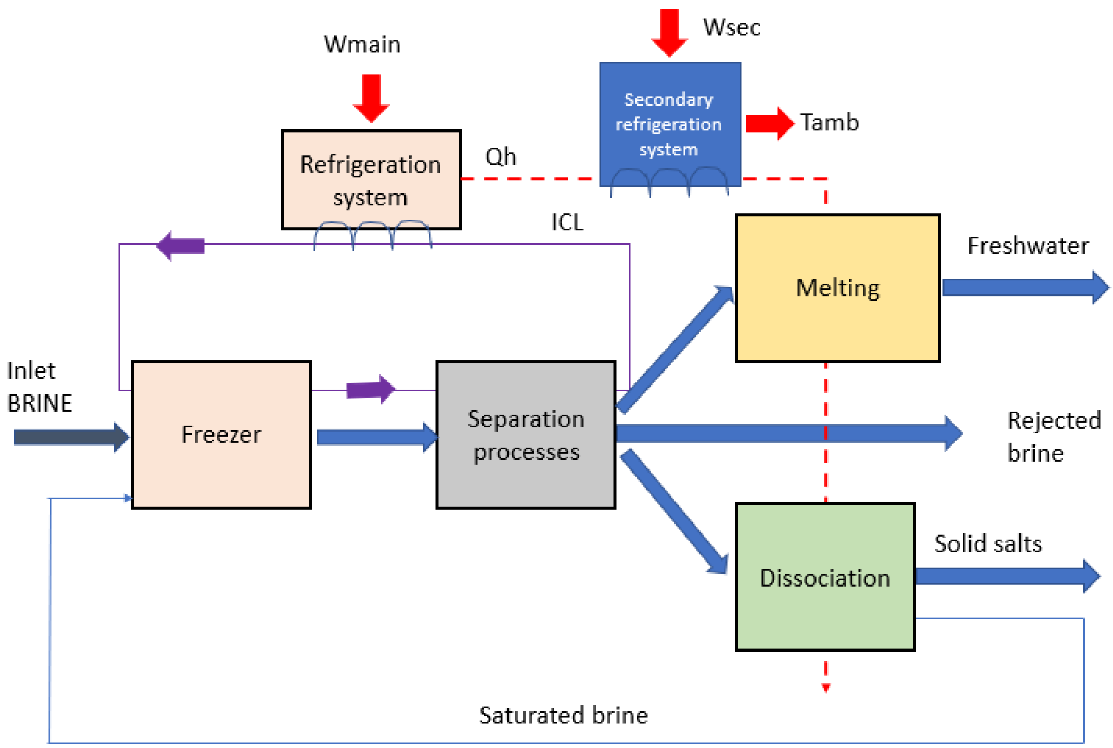

Figure 16. Schematic diagram of the conceptual process integrated with the refrigeration system

The conceptual process provides a good idea of the steps of this system; however, it doesn't approach industrial operation. The most predominant parameter for the development of the actual process flow is the separation efficiency. Having actual efficiencies involves that there are contaminants in the lines that are desired to be pure. Hence, the flow process must somehow account for it and solve the issue. To do that, a much more detailed and ideal process flow is designed on ASPEN Plus. This model has a 100% separation and recycling efficiency. The importance of this ideal model falls in two aspects: provides a better understanding and works as a threshold for water productivity and energy consumption.

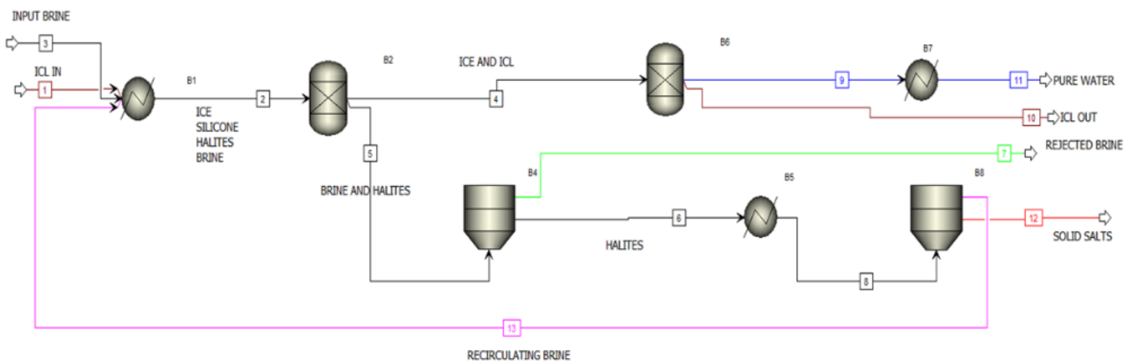

Figure 17. Process flow diagram of the ideal single stage system on ASPEN Plus

The proposed ideal model is shown in Figure 17. Once the components are cooled in the freezer, they lead to a gravity separation device. This device separates the lighter components (ICL and ice) and they leave through the top outlet. The ICL and ice undergo the wash column where they are perfectly separated, and the ice is later melted and supplied as freshwater. Similarly, the halites and unfrozen brine escape the gravity separator and are separated in the hydrocyclone. The unfrozen brine is rejected from the system and the halites are dissociated. The dissociation produces two components, concentrated brine, and solid salts. The salts are rejected from the system while the concentrated brine is recycled back to the freezer. Due to the perfect separation, the rejected brine is the minimum generating that the freshwater productivity is the maximum. The energy consumption is the lowest because the recycled stream has the minimum amount, as well.

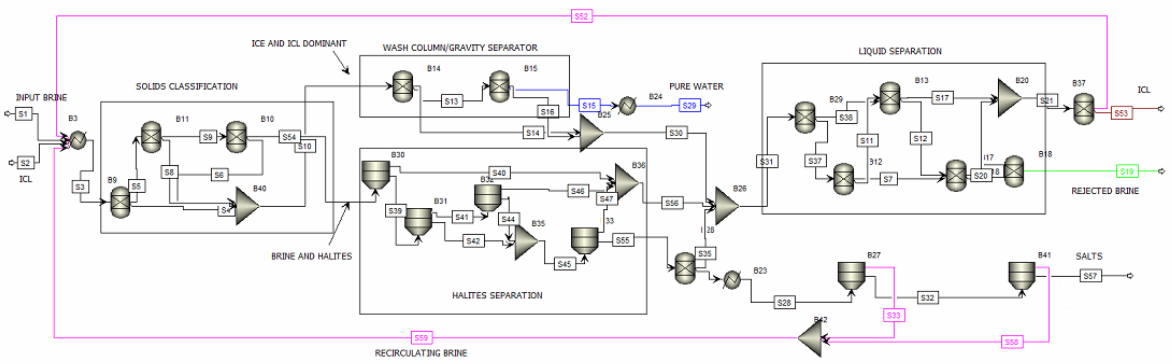

Figure 18. Process flow diagram of actual single stage plant on ASPEN Plus

With a better understanding of the system, the actual single-stage system is shown in Figure 18. This model accounts for actual efficiencies for all separation processes. The main difference with the ideal model is the incorporation of multiple separation devices in each separation step. Another feature of this new model is the use of collector lines. The process flow show collectors that carry contaminants that later are separated in the liquid-liquid separation step. This allows to overcome the drop in efficiency and achieve the requirements previously specified. In the next section, the new process flow is tested and analyzed in terms of productivity and energy consumption. It is expected that the productivity is not affected by the change of separation efficiency to be a successful design.

2.3. Simulation

In this section, the parameters and settings required to simulate different scenarios are explained. Sensitivity analyses are conducted for the three major parameters:

- Brine composition: In this study, brines are denominated by the amount of total dissolved solids (TDS). In table 2 the compositions were showed. There is a direct relation between energy and freshwater productivity of the saline brines. Higher TDS brine consumes less energy per kg of input brine than lower TDS ones when reaching the same temperature. Moreover, lower TDS brine can produce more freshwater than the higher TDS brines. At first, it is very likely to assume that higher TDS (much more complex chemistry) should require a higher amount of energy to treat. However, it is not the case because higher TDS brines have a much lower presence of water that results in less consumption of latent heat of solidification (much higher value than the sensible heat of the other components). On the other hand, in terms of specific energy consumption per kg of freshwater, higher TDS brine may have higher values because the water production is lower.

- Separation Efficiency: This is the most relevant operating parameter since it depends on the devices. The system incorporates industrial devices with actual efficiencies. The system response to the variation of efficiency is one of the biggest concerns, in terms of successful process flow. The sensitivity analysis accounts for a change of nominal efficiency in the range of 70% to 100%. If the development of the system is successful, freshwater productivity will only have marginal variations for the drop of efficiency.
- Evaporator effectiveness (HX effectiveness): This parameter is fundamental for the coupling of the refrigeration system and the freezer of the FD plant. Values ranging from 0.5 to 1 are considered. Moreover, this parameter depends on the operating temperatures of the freezer and the refrigeration plant. It is a vital parameter in the techno-economic study.

Brine composition and separation efficiency are analyzed on the ASPEN Plus interface while the evaporator effectiveness effect is studied in the techno-economic section.

The incorporation of actual brine compositions (multi-ionic) and process flow simulation involves challenges that cannot be solved analytically. Therefore, the use of engineering tools is the most valid approach. OLI Chemical wizard and ASPEN Plus were the engineering platforms integrated to develop this study.

OLI Chemical Wizard is a tool part of the OLI software that allows us to work with multi-ionic compositions. This tool creates files that incorporate the concentration, models, and libraries that are later uploaded into ASPEN Plus. Within the OLI Chemical Wizard, three different models can be selected: Aqueous, MSE, and MSE-SRK. The Aqueous model is the original and incipient model created by OLI it is only capable of working with simple solutions, in a limited range of temperature and pressure. The MSE model is a much more robust and advanced model that is able to work with complex concentrations, concentrations ranging from 0 to 1, a vast range of temperatures, and commercial operating pressures. The MSES-RK is a model developed to work with gases and liquids that work under very high pressures. For this project, the MSE model offer the necessary features to approach our modeling.

Setting up the brine composition is a user-friendly process because the steps are clear, and the library of brine components is extensive. One of the most useful features of the OLI wizard is the ability to create engineered fluids (not commercial fluids but the specific heat and density are known). Through the definition of pseudo-materials, OLI allows specifying the properties so the fluid can be modeled. The ICL is modeled by using that feature. After the chemistry is defined, the files can be exported to be opened on ASPEN Plus.

ASPEN Plus is one of the most utilized platforms among process engineers, designers, and researchers. Its extensive blocks and libraries are suitable to develop almost any process flow in the industry. Besides, the platform is user-friendly and provides automated tools such as calculators and sensitivity analysis. Once the OLI files are read on ASPEN Plus, the next step is to build the process flow and set the parameters and efficiencies of the components.

The flowsheet development starts with the brine creation. Due to the OLI wizard, the brine has more than 30 ionic components. First, we set a brine with the compositions extracted from the Oklahoma Geological Survey and the brine is computed to have the actual ionic components. The actual brine is now a brine with more than 20 ionic components with the same TDS as the first brine. In this analysis, the brine temperature is set at 1° C and a pressure of 1 atm. At the same time, the ICL is specified by a brine with a mass fraction of 1 for the ICL component. In this simulation the mass flow rate of brine, and ICL are 1kg/s and 41 kg/s, respectively.

Once the brine is defined, the plant blocks must be set. The first Unit is the freezer, the block heater is utilized. In this block, the outlet freezer temperature (depending on the brine composition) and the pressure (1 atm) are assigned. Table 3 shows the operating temperatures of different brines.

The separation process composes three types of devices, hydrocylones, wash columns, and gravitational separators. As one of the project requirements is to consider actual efficiencies, the definition of efficiency is a bit complicated to approach reality.

ASPEN Plus provides a hydrocyclone block in which several ways to define can be found. For this design, the solid outlet (desired) is defined by the nominal efficiency of the device. As an example, if the device efficiency is 80%, the solid outlet carries 80% of the total amount of solids. However, the effect of impurities is accounted for; therefore, in the liquid outlet, the efficiency of the liquid phase has a fixed value of 98% which means that 2% of the total inlet liquid phase is going through the solid outlet. Similarly, the gravity separators (or settling tanks) are defined in a uniquely. To model those, the separator block is utilized. In this kind of block, the mass fraction of each component can be specified. It also has two outlets. In this block, the ICL and ICE are expected to go through the top outlet; hence, if the device has a nominal efficiency of 90%, the mass fraction of the two components is 90%. To account for the inefficiencies, the remaining components have a fixed efficiency of 5% at the top outlet, as well. The wash column definition is a very special process because it is placed on the process flow at the end after several gravitational processes. Therefore, the amount of ICL is not as big as it was at the inlet of the FD process. Moreover, the ICL purity is proven to achieve almost a 100%. Under these assumptions, the ice outlet is considered to have 99% of efficiency and the ICL leaves the wash column completely through the other outlet.

The melting and dissociation tanks are defined by using the heater blocks. The outlet temperature and pressure are 1°C and 1 atm.

Table 4. Freezer operation temperatures

Brine composition (TDS)	Freezer Temperature (°C)
70,000	-24
92,798	-24
200,000	-25
299,469	-26

2.4. Results

To evaluate the feasibility of this proposal two aspects must be investigated, freshwater productivity and energy consumption. Thereby, a deep analysis of the affecting parameters is fundamental. It has been mentioned that the brine composition, separation efficiencies, and heat exchanger effectiveness are the predominant factors. The first two are evaluated on the ASPEN Plus interface while the effectiveness is studied after the simulations.

Sensitivity analyses were performed for the three parameters and the water productivity and energy consumption of the plant were evaluated. The analysis keeps the input data mentioned in previous sections and tables.

<u>Brine composition</u>

The study of the brine composition is fundamental because it provides an accurate prediction on the capability of the proposed plant to perform in different scenarios (different basins have different compositions). Produced water composition is highly dependent on the geographical location and the extracted fuel, as an example, natural gas and oil reservoirs do not share similar ionic distributions. Therefore, it is meaningful to evaluate a wide range of produced water compositions using table 2. Figure 19 shows that relation between water productivity ratio (eq. 9) and brine composition.

$$water\ recovey\ ratio = \frac{\dot{m}_{freshwater}}{\dot{m}_{input,brine}} \qquad \text{Eq. 9}$$

It can be noticed in Fig 19, that a maximum water recovery ratio of 0.85 is achieved for the treatment of a 70000-ppm produced water. On the other hand, the minimum water recovery ratio achieved was 0.66 and belonged to the 300000-ppm. The behavior is supported by the fact that the amount of pure water in higher compositions is much less than in more dilute brines. However, the water recovery ratio only decreases 23% for a brine with a composition more than three times higher.

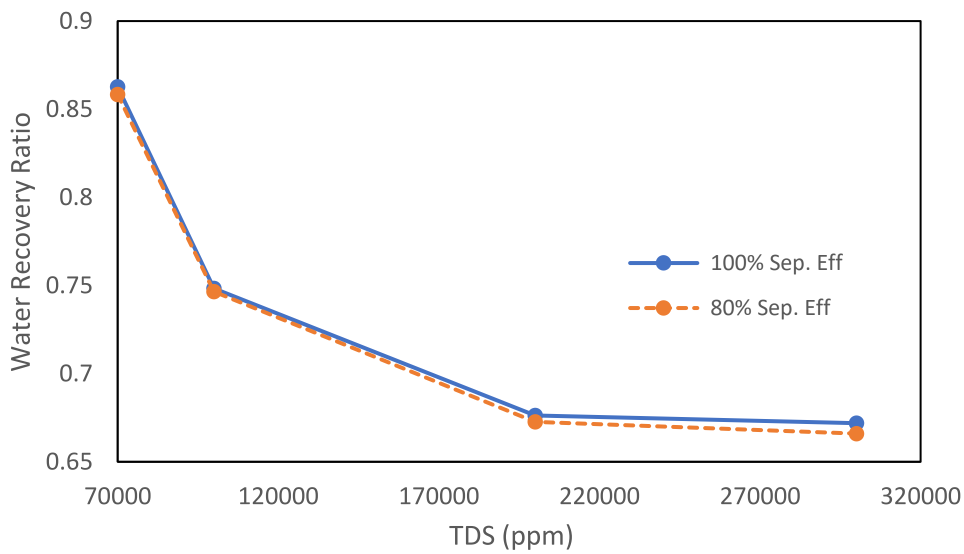

Figure 19. Water recovery ratio as function of brine composition for 100% and 80% separation efficiency system

Understanding the energy consumption of the existing process is vital because it is the most important input to develop the techno-economical study. In figure 20, the cooling and melting specific consumption are presented. It can be extracted that the consumption per brine does not show a unique trend due to the complexity of the brine. The 300000-ppm brine consumes about 8% more energy than the 70000-ppm brine, mainly due to the lower freezer temperature.

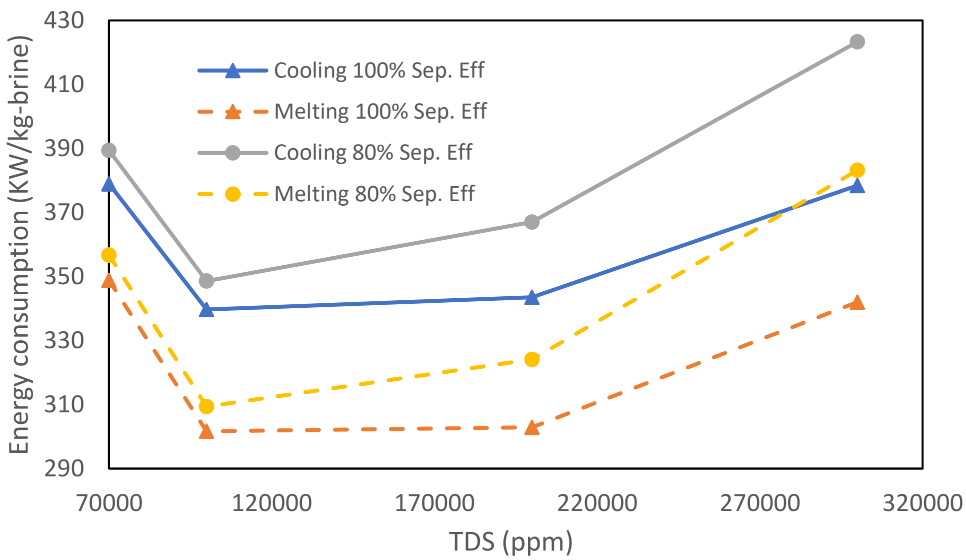

Figure 20. Cooling and melting loads as function of brine composition for a 100% and 80% separation efficiency plant

Separation efficiency

Separation efficiency is one of the two most important parameters along with brine composition. It is the parameter that helps us approach industrial applications. In other words, considering this parameter allows us to study actual field scenarios by using industrial efficiencies. It was previously mentioned the procedure to assign efficiencies to the different separation technologies that comprise the FD plant. Figure 21 shows the evaluation of the separation efficiency between 70% to 100%, where the 100% corresponds to the ideal scenario. The results show that the change of separation efficiency has an almost negligible effect on the water recovery ratio (about

0.5%) and it is not dependent on the brine composition. Achieving this system response is a sign of a very robust plant that is capable of working with actual devices. The key behind the good process flow is the inclusion of recycling and collector lines that accounts for recovering the inefficiencies of the separation devices.

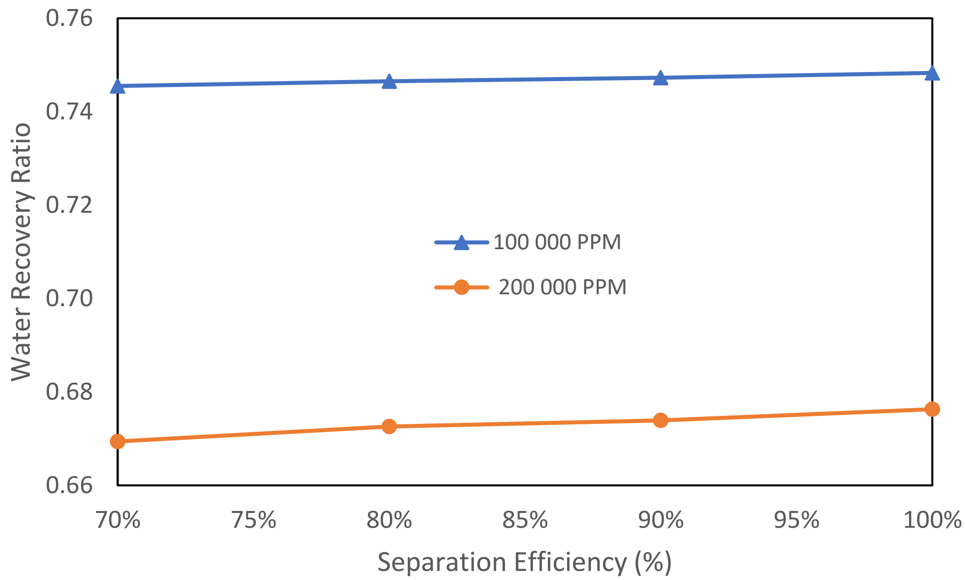

Figure 21. Relation between water recovery ration for 100 000 ppm and 200 000 ppm brine compositions

In figure 22, the cooling and melting specific consumption is presented. The trend shows that lower separation efficiencies require more energy (about 12%). Since the objective is to supply as much freshwater as possible, the collector and recycling lines have higher flows at lower separation efficiencies. That increase in flow is reflected as an increase in energy consumption; however, the increase of energy is lower than the reduction of efficiency. It is also extracted from figure 22, that higher composition brines consume more specific energy than lighter ones.

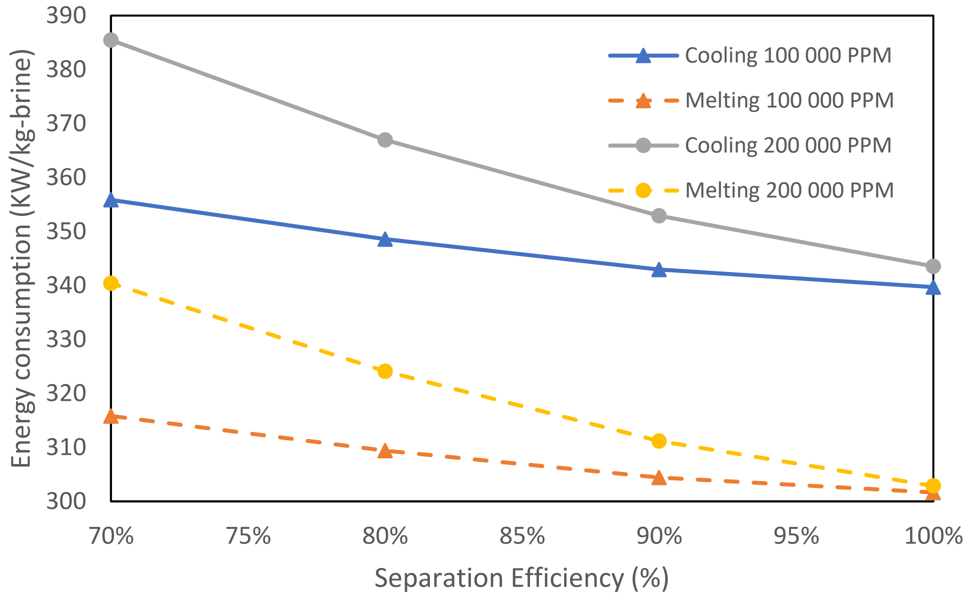

Figure 22. Relation between cooling and melting loads as function of separation efficiency for 100 000 ppm and 200 000 ppm brines

Table 5 summarizes the results extracted from ASPEN Plus. It provides all possible combinations for brine composition and separation efficiency. One interesting behavior to point out is the cooling relation with the change of composition. In previous results, the specific consumption per freshwater has been explained. However, the consumption per input brine shows (or FRZ and MLTG as in Table) that there is a reduction in the cooling for higher saline brines. The key to understanding that relation is that the amount of pure water contained in higher saline solutions is much less than in lower saline brines. Therefore, there is less amount of water that requires latent heat of solidification, instead, there are more solid salts that only require its specific heat which is much lower than the latent heat value.

Table 5. Mass and Energy analysis for different compositions and separation efficiencies

Summary table Mass and Energy analysis													
TDS (ppm)	Separation Efficiency	Mass Analysis					Energy Analysis						
		Pure water (kg/s)	Brine (kg/s)	Salts (kg/s)	Max. MFR (kg/s)	Max. VFR (m3/s)	FRZ (KW)	MLTG (KW)	DSCTR (KW)	Pump Power (KW)	Cooling Load (KW)	Total Melting (KW)
70000	100%	0.8627	0.0863	0.05082	42.049	0.0332	360.936	332.61	16.199	3.36	378.98	348.81
	90%	0.86035	0.092	0.0475	42.171	0.03336	364.214	331.676	19.571	3.38	382.42	351.25
	80%	0.8583	0.0961	0.0455	42.3204	0.0334	370.916	330.902	25.821	3.38	389.46	356.72
	70%	0.8582	0.0979	0.043	42.7	0.0337	378.584	330.85	34.301	3.41	397.51	365.15
100000	100%	0.7483	0.214	0.0375	42.042	0.03324	323.524	288.488	13.17	3.37	339.70	301.66
	90%	0.7473	0.2153	0.0373	42.1788	0.03334	326.615	288.096	16.296	3.38	342.95	304.39
	80%	0.7465	0.2166	0.0367	42.3621	0.0334	331.983	287.795	21.587	3.38	348.58	309.38
	70%	0.7455	0.2188	0.0355	42.7703	0.0337	338.909	287.408	28.417	3.41	355.85	315.83
200000	100%	0.6763	0.207	0.1166	42.1233	0.03325	327.184	262.033	40.82	3.37	343.54	302.85
	90%	0.6739	0.2104	0.1156	42.4138	0.0334	336.096	261.12	50.08	3.38	352.90	311.20
	80%	0.6726	0.2138	0.1135	42.7755	0.0336	349.518	260.603	63.516	3.40	366.99	324.12
	70%	0.6694	0.2206	0.1099	43.6623	0.0342	367.108	259.356	81.069	3.46	385.46	340.43
300000	100%	0.6719	0.1033	0.2246	42.2409	0.0333	360.429	261.629	80.399	3.37	378.45	342.03
	90%	0.6688	0.1055	0.2255	42.7235	0.0336	378.118	260.395	98.756	3.40	397.02	359.15
	80%	0.666	0.1117	0.2222	43.297	0.0339	403.158	259.305	123.918	3.43	423.32	383.22
	70%	0.6604	0.1242	0.2152	44.7984	0.0348	436.274	257.122	157.191	3.53	458.09	414.31

3. Study and proposal of a two-stage system

3.1. Model description

The freezing process of produced water is complicated in terms of the chemistry involved and requires a lot of energy to produce ice crystals mainly due to the water latent heat of solidification. To achieve commercial amounts of freshwater, the system operates at very low temperatures.

A deeper understanding of the chemistry of ice formation in produced water shows a key behavior. Several brine compositions were studied for this project, besides the ones presented and most of them, especially the higher concentrated ones have a very particular property. The ice formation occurs in an abruptly and suddenly. In other words, it can be possible to not have ice until -12°C; however, at -13° a 20% of ice can be formed. Therefore, it is fundamental to find the ice formation temperature and the amount of ice formed.

Following the previous finding, if the FD plant has a freshwater production of 70% and, it is found that 30-35% of the production happens at a greater temperature, cooling down that mass of ice that is already pure results in a waste of energy and money. Hence, it is a good criterion to extract that high amount of ice at that temperature and only freeze the remaining brine to grow more ice.

The extraction of ice at an intermediate temperature leads to the development of the 2-stage system.

The new system must meet the requirements specified for the single-stage system such as continuous operation, maximum freshwater production, full ICL recycling, etc. Similarly, three main processes are involved: freezing, separation, and melting.

The main difference is that the freezing process happens in two stages. The first stage operates at intermediate temperatures between -10 ° C to -20 °C, depending on the brine composition. The second stage operates at much lower temperatures reaching the same temperature as the single-stage system.

3.2. Proposed two-stage system

The new system is also capable of desalinating input produced water, supply freshwater, and reject brine and solid salts. Two freezers, different separation units, and the melting (and dissociation) tanks comprise the process. The two-stage system conceptual diagram is presented in figure 23.

The main difference between this system and the single-stage is the utilization of two freezing stages. The incorporation of an intermediate freezer has consequences in the whole process flow. The two-stage plant now has two stages of separation, that are different in terms of separation objectives.

The input produced water enters the system through the freezer where it is cooled down at an intermediate temperature. The freezer temperature allows to grow ice crystals and unfrozen brine; the amount of halites is zero or negligible. The stream composed of ice crystals, unfrozen brine, and ICL undergoes the first separation process. The separator removes pure ice crystals from the slurry, generating the first pure ice stream. The ICL is also recycled in this step and looped it back to the evaporator of the refrigeration system. The unfrozen brine leads to the second freezer, where it becomes a slurry of ice, halites, and unfrozen brine. The slurry composed of ice crystals, halites, unfrozen brine, and ICL undergoes the separation process where ice crystals are extracted, unfrozen brine is rejected, the ICL is recycled, and the halites are also separated. The pure ice stream along with the other ice stream is heated in the melting tank and supplied as freshwater. The unfrozen brine is rejected from the system. The halites are heated in the dissociation tank, forming solid salts and concentrated brine. The concentrated brine is recycled to the second freezer to maximize the system productivity.

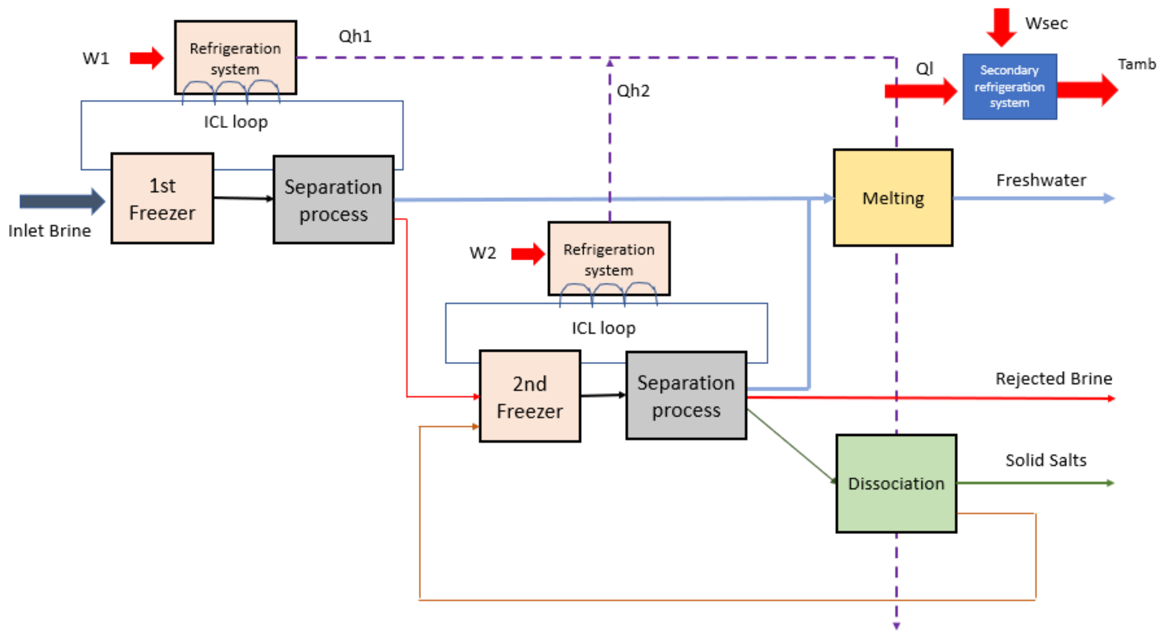

Figure 23. Conceptual diagram of a two-stage system

The refrigeration system is also modified by the inclusion of an intermediate freezer. The refrigeration plant now has three components. The first supplies cold energy to the first freezing stage through the cooling of the ICL. The second refrigeration component supplies cold energy to the second freezer. Alike any other refrigeration system, heat must be released in the condenser. For this design, both systems released heats are utilized to provide heat to the melting and dissociation tanks. However, the total heat released is bigger than the tanks' consumption; therefore, the remaining heat is absorbed by the third refrigeration component (secondary system). The secondary refrigeration system absorbs the heat and finally rejects it to the environment.

The conceptual process is important to provide a clear idea of the different processes that take place in the plant. However, it differs from actual application mainly by the separation inefficiencies. Incorporating the inefficiencies results in a robust and complex system that must be developed on ASPEN Plus.

To start with the development of the real process flow, first, a 100% model is developed in ASPEN Plus. Figure 24 shows the 100% separation efficiency process flow in ASPEN Plus.

The system is characterized by the use of one separator device in each separation step. After the first freezing, one separator extracts pure ice crystals and ICL, rejecting brine to the second freezer. The ice crystals and ICL are separated in a wash column where pure ice is extracted and the ICL is recycled. On the other hand, the unfrozen brine is cooled in the second freezer, forming ice crystals, halites, a little amount of unfrozen brine, and ICL. One separator extracts the ICL and ice crystals from the slurry. The ICL and ice crystals also undergo a wash column. The halites and brine are separated in a hydrocyclone where the halites are extracted and the brine is rejected. The halites are finally melted in the dissociation tank, forming solid salts and concentrated brine which is recycled to the second freezer.

The benefit of modeling an ideal process flow is that it establishes a threshold value for maximum freshwater productivity and minimum energy consumption. Achieving the maximum freshwater production also involves that the rejected brine is the minimum possible.

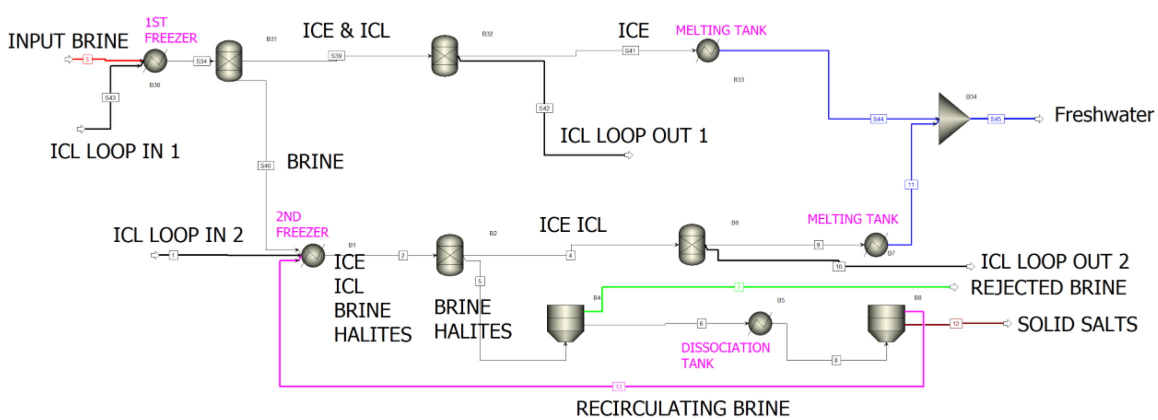

Figure 24. Process flow diagram of the ideal two-stage system in ASPEN Plus

The real two-stage system process flow is depicted in figure 25. The system is depicted in two vertical big blocks. In the first part of the system, the input brine enters in contact with the ICL, and the first freezing and separation step happens. The unfrozen brine resulting from the first freezing process is directed to the second freezer, where it transforms into ice crystals, halites, unfrozen brine, and ICL slurry. Through several devices and separation steps, the ice crystals are finally separated and later melted. This second part of the process is very similar to the single-stage system previously presented with the difference that the brine inlet temperature is lower. The main difference at the device level is that the separation process comprises a combination of several devices rather than unique devices like the ideal system.

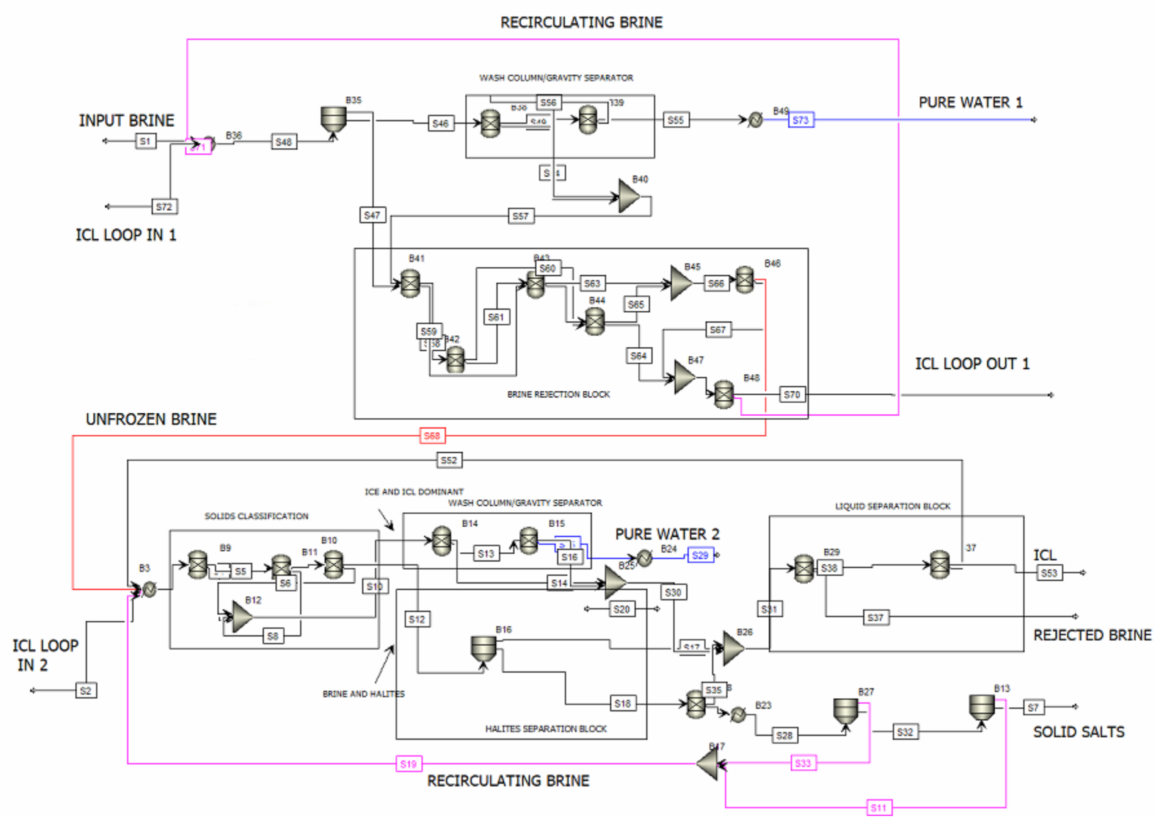

Figure 25. Process Flow diagram of the real two-stage system in ASPEN Plus

3.3. Simulation

The development and inclusion of devices from the ASPEN Plus libraries are similar to the ones described in the previous chapter. The files exported from OLI are utilized and the plant is built on the flowsheet of ASPEN Plus with the models and properties of the OLI Chemical Wizard. For a detailed description of the devices and parameters assignation such as efficiency and temperature, refer to the simulation section in Chapter 2.

The brine inlet temperature and pressure are 1°C and 1 atm, respectively. The mass flow ration between the ICL and brine is still 41 such as the previous model. In this new system, two operating temperatures are required, intermediate (first freezing) and second freezing. The assigned temperatures are dependent on the brine composition. Table 6 shows the temperatures for each brine. The freezers are assigned with their proper temperature at 1 atm. Finally, the melting and dissociation tanks have an outlet temperature of 1°C.

Mass flow rates and energy are extracted for each stream and heat exchanger, respectively.

The system is simulated for four brine compositions (Table 2) and four separation efficiencies 70%, 80%, 90%, and 100% (ideal case).

Table 6. Operating temperature for different brine compositions

Brine composition (TDS)	1st Freezer Temperature (°C)	2nd Freezer Temperature (°C)
70,000	-11	-24
92,798	-11	-24
200,000	-18	-25
299,469	-22	-26

3.4. Results

Following a similar approach to the single-stage system. Mass and energy analysis is developed for the two-stage proposed system.

Firstly, the sensitivity analysis for brine composition is presented. Water productivity and cooling and melting energy are evaluated. Secondly, the effect of separation efficiency on water productivity and energy is studied. Graphs and tables are included throughout this chapter to show the obtained data.

Brine composition

It is one of the most relevant parameters because it provides an idea of the flexibility of this plant to treat produced water from different wells or even different industries. Proving that is feasible for low and high concentration brines is core for this study.

Water productivity analysis is depicted in figure 26 as a relation between water recovery ratio and brine composition. It is noticed that the new plant can achieve high water recovery rations in the range of 0.67 (300 000-ppm brine) to 0.87 (70 000- ppm). Higher concentration brines have lower recovery rations because of the lower amount of water available in the solution. It can also be extracted that there is a considerable difference between the 100 000-ppm brine and the 300 000-ppm brine. It is a signal that brines more concentrated than 100 000-pm have more complicated chemistry, mainly due to the likely formation of hydrates.

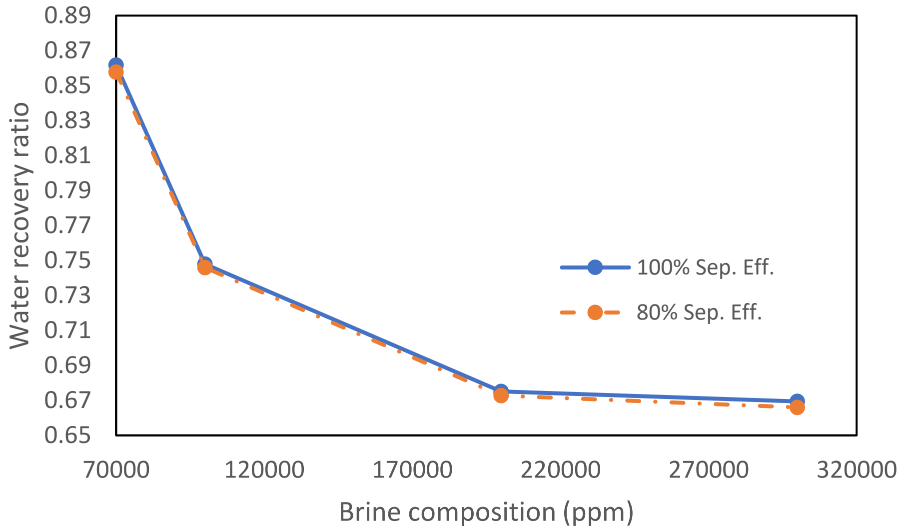

Figure 26. Water recovery ratio as function of brine composition for 80% and 100% separation efficiency

The incorporation of an intermediate freezer allows us to take a deeper look at the chemistry of the solution in terms of required energy. In figure 27, the specific consumption per brine is depicted. It shows that the first freezing does not have a defined trend. It is explained by the different compositions of the brines. In other words, the 200 000-ppm brine is not proportional to the 100 000-ppm brine. Each brine has a unique ionic composition like a greater number of sulfates or bicarbonates. On the other hand, the second freezing and melting have a defined trend that suggests that higher concentration brines have higher specific consumption. Understanding of the shown behavior was not possible in the single-stage system since it only works with one freezing, and it is not possible to read the chemistry at intermediate points.

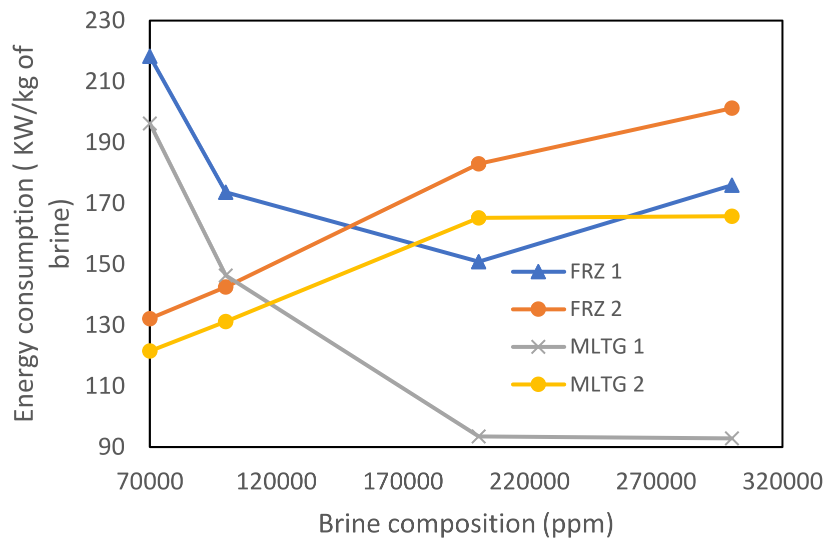

Figure 27. Cooling and Melting loads as function of brine composition for a 90% separation efficiency.

After the subcomponent's consumption is explained, understanding the total process consumption is key for the project. Figure 28 shows the relation between the specific consumption of the cooling and melting processes. The depicted cooling represents the cooling required by the freezer including 5% of heat gains. The total melting is composed of the two melting and the dissociation processes. The trend is not unique because of the actual compositions of the brine. The higher concentration brines show a higher consumption because they operate at lower freezer temperatures. This finding agrees with the single-stage system.

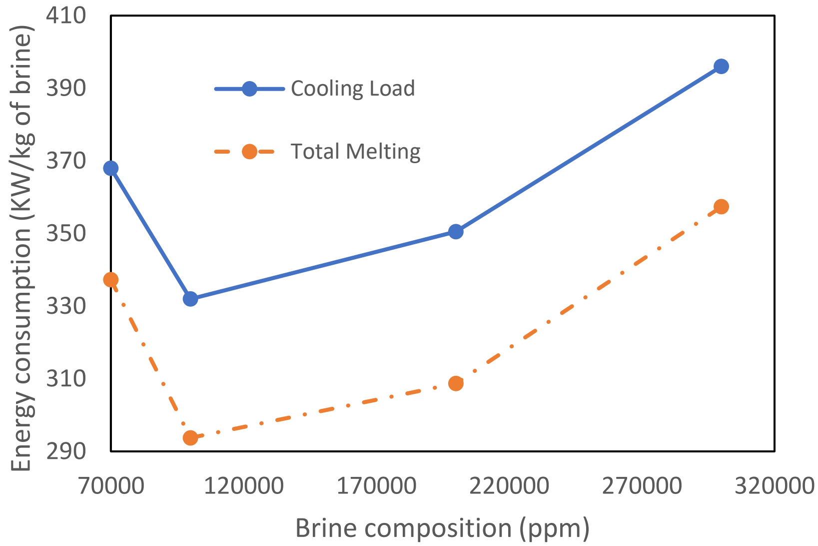

Figure 28. Cooling and melting load as relation of brine composition for a 90% separation efficiency

<u>Separation Efficiency</u>

Separation efficiency is a parameter that allows approaching the functioning of actual industrial separation devices. In figure 29, the relation between water recovery ratio and separation efficiency is shown. The variation is almost negligible and independent of the brine composition. The difference between the 100% efficiency and 70% efficiency plants results in a variation of 0.3%. The small variation suggests that the proposed system can easily overcome the drop in efficiency and incorporate actual devices without problems.

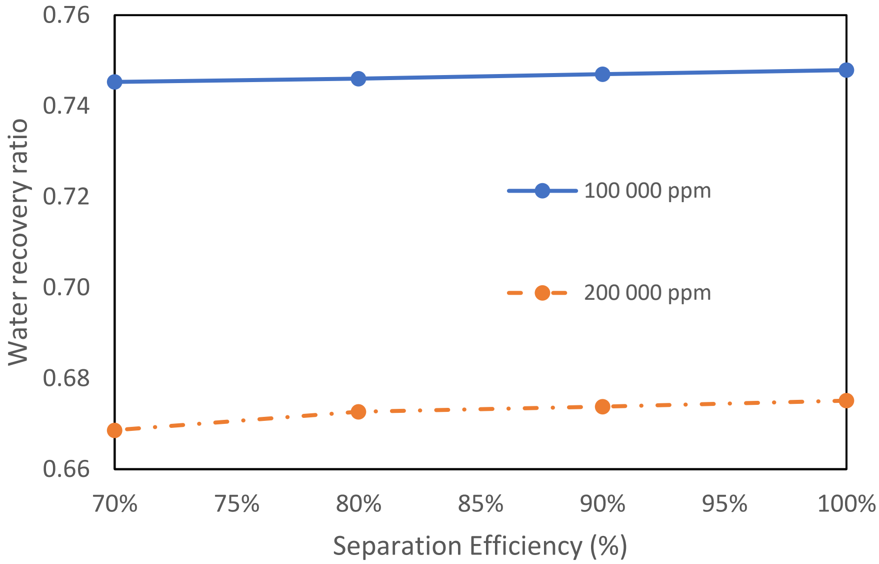

Figure 29. Water recovery ratio as function of separation efficiency for 100 000 ppm and 200 000 ppm

To have a better understanding of the insider behavior. The use of an intermediate freezer allows one to look at the specific energy consumption for the two stages. Figure 30 shows the behavior of melting and cooling processes for a 200 000-ppm brine. It can be noticed that the second Freezing is much more affected by the change efficiency than the first Freezing. The Melting processes are not deeply affected by this change.

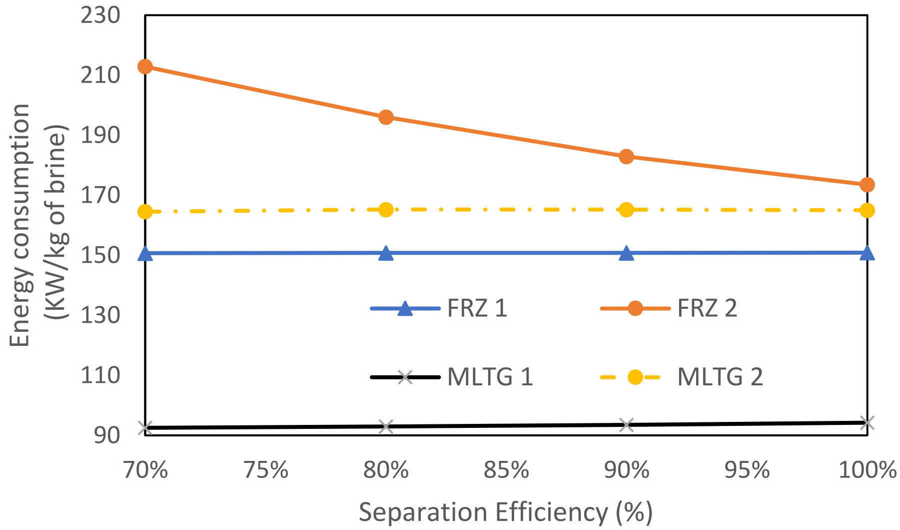

Figure 30. Relation between cooling and melting load and separation efficiency for a 200 000 ppm brine

Towards the economic analysis, the processes of consumption must be studied. Figure 31 represents the cooling and melting consumption as a function of separation efficiency for the 200 000-ppm brine. The cooling includes both freezer and an extra 5% of heat gains. The total melting Lower separation efficiencies result in higher energy consumption. Both cooling and melting loads experience an increase of 12% for a 30% drop in separation efficiency.

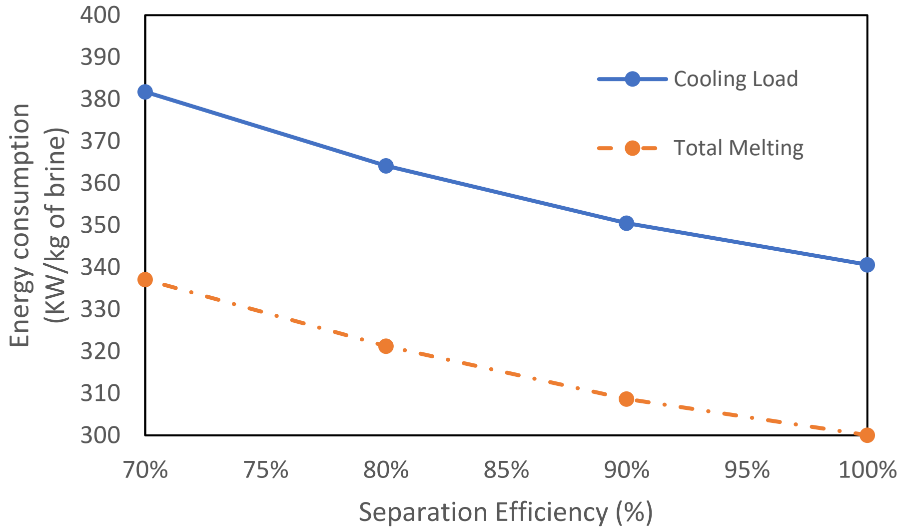

Figure 31. Relation between cooling and melting load and separation efficiency for a 200 000 ppm brine

The main reason to develop the two-stage system is to save energy and money. In figure 32, the consumptions for both single and two-stage systems are compared. It can be noticed that for all brine compositions the 2-stage system has lower compositions. It can also be extracted that the difference between both systems increases at lower brine compositions.

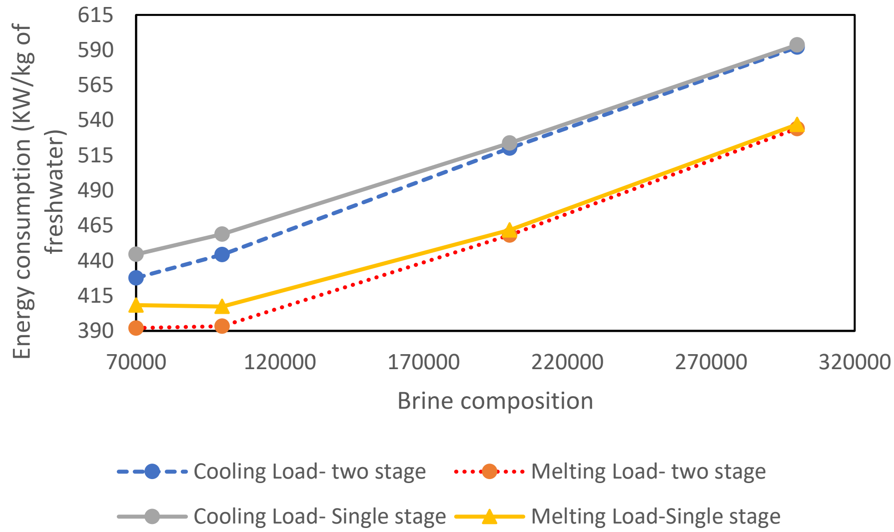

Figure 32. Energy consumption comparison between single stage and two-stage systems

Complete data for all the simulation scenarios are presented in Table 7. Four brine compositions and four separation efficiencies were run. The presented data is a key input for the techno-economic analysis.

Table 7. Mass and Energy analysis summary

Conc. PPM	Separation Efficiency	Mass Analysis: Pure water 1 (kg/s)	Pure water 2 (kg/s)	Total freshwater	Brine (kg/s)	Salts (kg/s)	Max. MFR (kg/s)	Max. VFR (m3/s)	Energy Analysis: FRZ 1 (KW)	FRZ 2 (KW)	MLTG 1 (KW)	MLTG 2 (KW)	DSCTR (KW)	Pump Power (KW)	Cooling Load (KW)	Total Melting (KW)
70000	100%	0.55	0.31	0.86	0.09	0.05	28.00	0.022	218.37	128.14	197.52	120.72	16.19	2.25	363.83	334.42
	90%	0.55	0.32	0.86	0.09	0.05	28.13	0.022	218.29	132.18	196.26	121.49	19.53	2.26	368.00	337.28
	80%	0.54	0.32	0.86	0.10	0.05	28.28	0.022	218.18	137.26	195.27	121.75	24.64	2.28	373.20	341.66
	70%	0.54	0.32	0.86	0.10	0.04	28.51	0.023	218.00	144.59	194.19	122.36	31.66	2.30	380.71	348.21
100000	100%	0.41	0.34	0.75	0.21	0.04	28.00	0.022	173.63	139.43	147.29	130.59	13.32	2.25	328.71	291.19
	90%	0.41	0.34	0.75	0.22	0.04	28.12	0.022	173.64	142.51	146.36	131.23	16.14	2.24	331.95	293.73
	80%	0.40	0.34	0.75	0.22	0.04	28.29	0.022	173.62	147.18	145.60	131.88	20.75	2.27	336.85	298.23
	70%	0.40	0.34	0.75	0.22	0.04	28.53	0.023	173.62	152.74	144.83	132.53	26.36	2.30	342.68	303.71
200000	100%	0.25	0.43	0.68	0.21	0.12	28.00	0.022	150.88	173.53	94.23	164.96	40.87	2.24	340.62	300.05
	90%	0.25	0.43	0.67	0.21	0.12	28.12	0.022	150.85	182.99	93.45	165.26	49.99	2.25	350.53	308.69
	80%	0.25	0.43	0.67	0.21	0.11	28.30	0.022	150.81	196.04	93.00	165.26	63.02	2.26	364.19	321.29
	70%	0.24	0.42	0.67	0.22	0.11	28.56	0.023	150.72	212.87	92.52	164.53	80.04	2.29	381.77	337.09
300000	100%	0.25	0.42	0.67	0.10	0.22	28.00	0.022	175.74	182.02	93.82	165.27	80.25	2.23	375.64	339.34
	90%	0.24	0.43	0.67	0.11	0.23	28.12	0.022	175.93	201.23	92.84	165.78	98.70	2.24	396.02	357.33
	80%	0.24	0.43	0.67	0.11	0.22	28.29	0.022	176.39	226.79	91.97	165.54	123.43	2.26	423.34	380.94
	70%	0.24	0.42	0.66	0.12	0.22	33.18	0.025	182.01	260.28	91.04	164.18	156.01	2.56	464.40	411.23

4. Techno-economic analysis

To complete the project development, it is mandatory to evaluate the economic feasibility. In the previous chapters, the technical feasibility has been extensively studied showing satisfactory results such as a high-water recovery ratio and system robustness to the drop in separation efficiency.

The importance behind the economic study relies first on providing an accurate estimate of the investment and second, making the proposal competitive with existing technologies.

The costs involved in this project can be categorized into two big groups, fixed and variable costs. The fixed costs are mostly related to the infrastructure cost, while the variable represents the energy cost.

4.1. Fixed Cost

The fixed cost is mostly represented by the infrastructure. It can include investments such as licenses, preparing the site, and purchasing devices. In this study, it is intended to cover as many of the predominant costs required to build and operate the plant.

The cost of the devices and equipment is part of this category. It is composed of the cost of the refrigeration system, the ICL, and the cost of the rest of devices such as separators, tanks, etc.

The cost of site preparation and the installation of the devices are also included in the budget.

The cost of those items is based on commercial quotations and accurate estimates (Table 8).

Table 8. Itemized fixed costs

Item	Cost
1510 Refrigeration System	$1,510,000
Intermediate Cooling Liquid	$452,000
Maintenance	$9,350,121
Other equipment	$200,000
Installation	$200,000
Site preparation	$100,000

The previous items account for the infrastructure and site but it does not include other costs like the labor. Therefore, the maintenance cost is added to the budget, and it has several components.

Maintenance Cost

The O&M costs have been included in the economic analysis based on the following criteria:

- The maintenance cost now includes the replacement, the labor, and the cleaning and maintenance cost
- The cost analysis was developed for an operation of 30 years
- The replacement time of the mechanical devices have been assigned based on reported industry cases:

Table 9. Lifetime for plant devices

Component	Lifetime (years)
HX	20[49]
Pumps	15[50]
Separation devices	20[51]
Valves	10[52], [53]
Piping	+50[54]

- The components of the maintenance cost have been identified and estimated based on industrial desalination plant reports[53], [55]–[60]
- The labor cost represents the salary of three workers during the 30-year operation time. Two of them report a salary of 100 000 dollars per year and the third one has an annual income of 60 0000 dollars.
- Similarly, the cleaning and preventive maintenance cost is considered as 4% of the total cost.
- The cost percentage distribution is shown in Table 10 and Figure 33.

Table 10. Percentage of maintenance costs

Component	COST	% Total Plant cost
Replacement	$202,000	1%
Labor	$7,800,000	25%
Preventive maintenance and cleaning	$1,348,121	4%

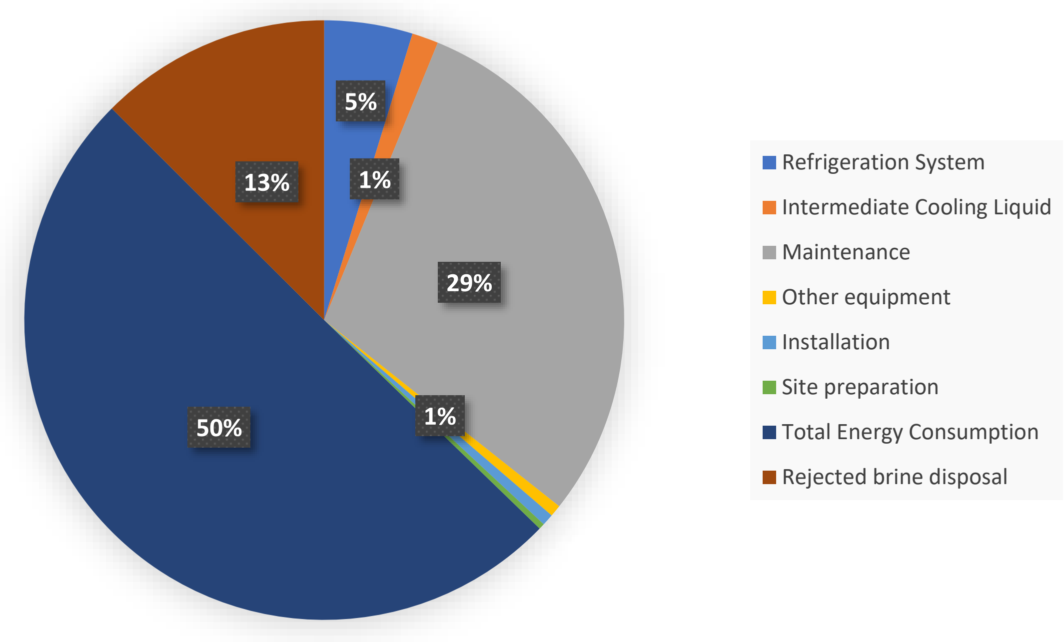

Figure 33. Pie diagram of total costs (fixed and variables)

4.2. Variable costs

Under this category, two components are considered, total energy cost and the brine disposal cost.

To build this analysis, the mass and energy analysis developed in previous chapters are the principal inputs with a special focus on energy consumption.

The main energy contribution happens through the refrigeration systems since they supply the cooling and heating to the freezing and melting processes, respectively. Within, the refrigeration system, the compressors are the ones receiving the electric power input. Therefore, the compressor power shows the highest consumption. The heat exchanger effectiveness takes place in this part.

However, the total energy consumption has another component, the auxiliary systems. The auxiliary system is mainly represented by the pumping system.

Brine disposal cost is sometimes taken for granted; however, it must be considered to develop an accurate economic analysis. The proposed system rejects an amount of unfrozen brine and salts that cannot be dumped into the environment without previous treatment. Therefore, managing the rejected brine results in a cost that depends on the amount of brine. The brine disposal cost is $0.3 per barrel.

4.3. Results

In this section, the economic analysis results are presented for the single-stage and two-stage systems. First, a detailed description of the energy cost is presented. The conversion from the cooling and heating load to compressor power is explained. Later, the electricity consumption for compressors and auxiliary systems is translated to dollars.

The fixed costs (infrastructure, maintenance, etc.) are also included in the economic analysis. To uniformize the variable and fixed cost, the Levelized Cost of Water (LCOW). The LCOW is calculated for an operation of 30 years. The LCOW is calculated as follows:

$$LCOW = \frac{\sum_{i=1}^{30} C_i Q_{brine,i}}{\sum_{i=1}^{30} Q_{brine,i}} \quad \text{Eq. 10}$$

Where C_i is the total annual cost and $Q_{brine,i}$ is the annual brine intake.

<u>Single Stage system</u>

In this system, most of the energy consumption comes from the compressors (main and secondary). The freezing and melting process load are supplied by the refrigeration system. The input power for compressors is calculated using the COP of each system. The COP value is highly dependent on operation temperatures and heat exchanger effectiveness (ε).

The main compressor power is calculated by the following:

$$\dot{W}_{main} = \frac{\dot{Q}_{FRZ}}{COP_{main}} \qquad \text{Eq. 11}$$

Where $\dot{Q}_{FRZ}$ is the freezer load including a 5% of heat gains and the COP_{main} is the coefficient of performance of the main system calculated by eq. 7.

The total melting heat is calculated by:

$$\dot{Q}_{heat} = \dot{Q}_{MLTG} + \dot{Q}_{DSCT} \qquad \text{Eq. 12}$$

Where $\dot{Q}_{MLTG}$ and $\dot{Q}_{DSCT}$ are the melting tank and dissociation tank loads, respectively.

The second main component of the energy cost is the secondary compressor power that is obtained by:

$$\dot{W}_{sec} = \frac{\dot{Q}_{FRZ} + \dot{W}_{main} - \dot{Q}_{heat}}{COP_{sec}} \qquad \text{Eq. 13}$$

Where COP_{sec} is the coefficient of performance of the secondary refrigeration system.

The auxiliary systems are also part of the energy cost and it is calculated by the following:

$$\dot{W}_{pumps} = \dot{v}_{max} \Delta P_{max} \qquad \text{Eq. 14}$$

Where $\dot{v}_{max}$ and ΔP_{max} are the maximum flow rate and pressure drop in the system.

Once the three components of the energy consumption are obtained, the total consumption is obtained by:

$$W_{total} = \frac{\dot{W}_{main} + \dot{W}_{sec} + \dot{W}_{pumps}}{3.6} \quad \frac{KWh}{TON} \qquad \text{Eq. 15}$$

Finally, the energy cost is calculated by:

$$C_{energy} = W_{total} * c_{elec} \qquad \text{Eq. 16}$$

Where c_{elec} is the cost of electricity and has a value of 0.0439 $/KWh.

One of the main concerns is the compressors' consumption and the relation with the effectiveness. Figure 34 shows the relation between both parameters for a plant operating with a 90% separation efficiency. It can be noticed that higher effectiveness results in lower compressor power. Reducing the effectiveness from 1 to 0.5 results in a power increase of about 27%. The highest variation is produced in the main refrigeration system compressor. It is also shown that both brines (100 000 ppm and 200 000 ppm) behave in a similarly. Higher composition brines have greater consumption.

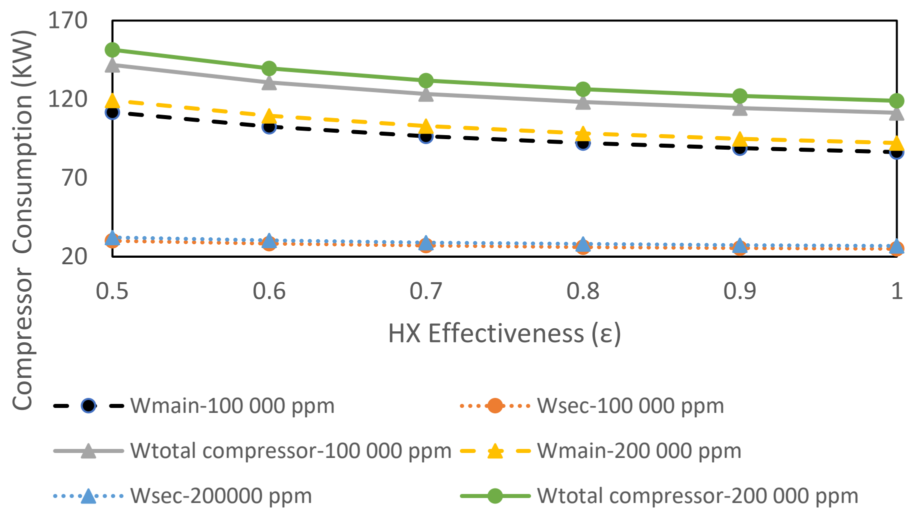

Figure 34. Relation between compressors power and HX effectiveness for 100 000-ppm and 200000-ppm

The main component of the total cost is the energy cost. This component, that involves the compressors and auxiliary systems consumption, is depicted in Figure 35 as a relation of heat exchanger effectiveness. The energy cost is presented as a function of tons of brine and tons of freshwater production. The trend is very similar to the compressors' consumption since it is the predominant component of this cost. The energy cost achieved for a 100 000 ppm treatment ranges between 1.44 to 1.77 $/ ton of brine. Similarly, for the 200 000 ppm brine the cost falls between 1.49 to 1.89 $/ton of brine.

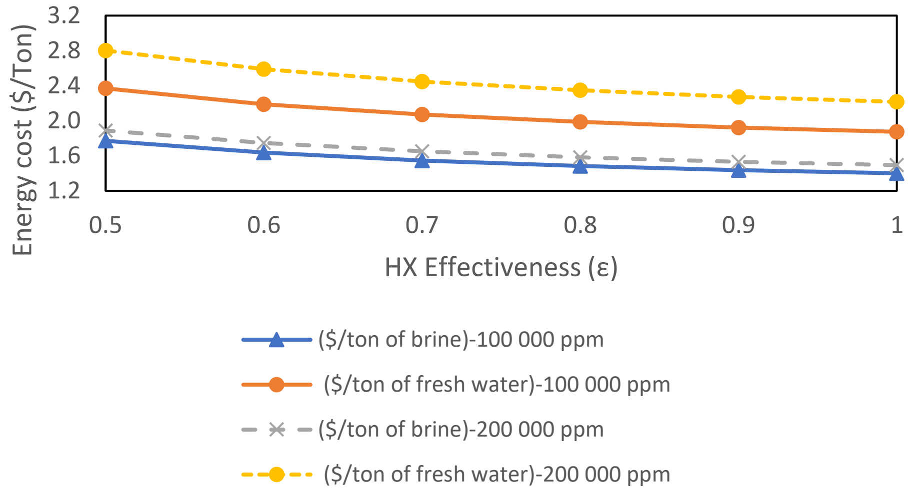

Figure 35. Energy cost and HX effectiveness for 100 000 ppm and 200 000 ppm

To calculate the LCOW, the energy cost must be added with the fixed and the brine disposal costs. Since this project is oriented to the Oil&Gas industry, the results are calculated in per unit of barrel. Figure 34 shows the LCOW for the 200 000-ppm brine in relation to heat exchanger effectiveness and separation efficiency. It is noted that lower effectiveness and lower separation efficiency results in higher LCOW. The LCOW of this brine has a range between $0.59 to $0.71. The study of the 200 000 ppm is relevant because it represents a typical highly concentrated produced water.

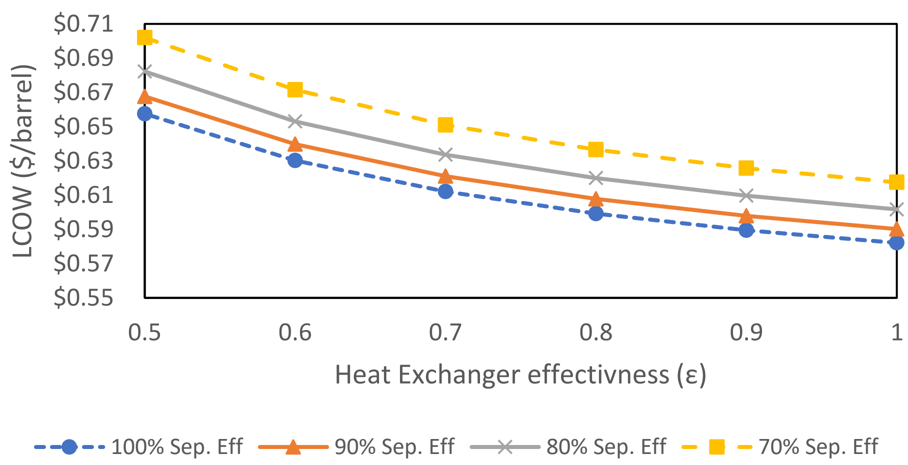

Figure 36. LCOW as function of HX effectiveness for different separation efficiencies

To have a better understanding on the system cost, it is necessary to calculate the results for the different brines. The LCOW for different brines are presented in Figure 37 as a relation of effectiveness. Higher concentration brines are more expensive. The 70 000-ppm brine has a maximum LCOW of 0.55 $/barrel of brine, while the 300 000 ppm has a maximum LCOW of almost 0.80 $/barrel of brine.

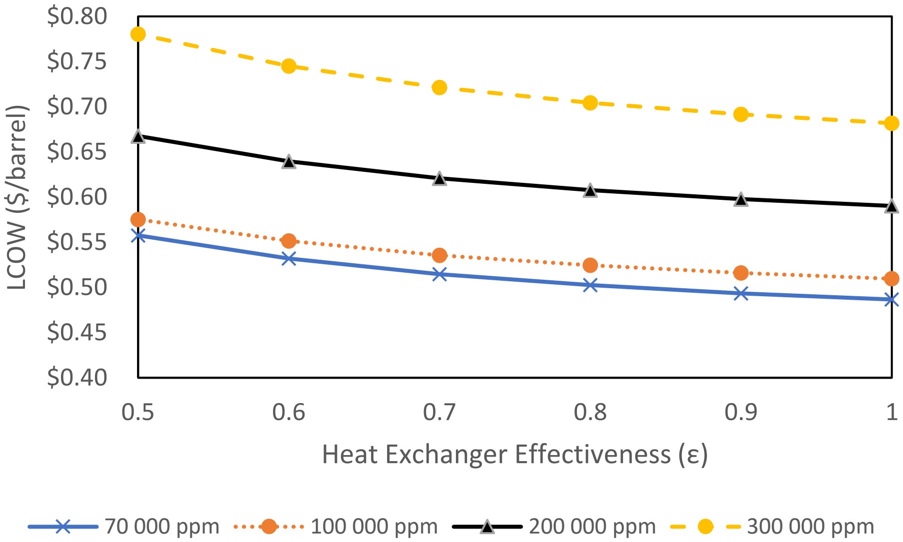

Figure 37. LCOW and HX effectiveness relation for different brine compositions

<u>Two-stage system</u>

The compressors' power is the main component of the energy cost. In this system, there are three refrigeration systems. The first two provides cold energy to the two freezers y the third system accounts for the released heat of the previous two.

The two main refrigeration system power is calculated by the following equations:

$$\dot{W}_1 = \frac{\dot{Q}_{FRZ1}}{COP_1} \qquad \text{Eq. 17}$$

$$\dot{W}_2 = \frac{\dot{Q}_{FRZ2}}{COP_2} \quad \text{Eq. 18}$$

Where $\dot{Q}_{FRZ1}$, $\dot{Q}_{FRZ2}$, COP_1, and COP_2 are the first freezer cooling, second freezer cooling, the first coefficient of performance, and the second coefficient of performance, respectively. The freezer loads utilized in the equations includes an extra 5% that accounts for heat gains. The COPs are calculated with eq. 7.

The total melting load is calculated by:

$$\dot{Q}_{heat} = \dot{Q}_{MLTG1} + \dot{Q}_{MLTG2} + \dot{Q}_{DSCT} \quad \text{Eq. 19}$$

Where $\dot{Q}_{MLTG1}$, $\dot{Q}_{MLTG2}$, and $\dot{Q}_{DSCT}$ are first melting, second melting and dissociation loads, respectively.

The third compressor (secondary) load is calculated by the following expression:

$$\dot{W}_{sec} = \frac{\dot{Q}_{FRZ1} + \dot{Q}_{FRZ2} + \dot{W}_1 + \dot{W}_2 - \dot{Q}_{heat}}{COP_{sec}} \quad \text{Eq. 20}$$

The pumping system power consumption is calculated by using:

$$\dot{W}_{pumps} = \dot{v}_{max}\Delta P_{max} \qquad \text{Eq. 21}$$

Where $\dot{v}_{max}$ and ΔP_{max} are the maximum flow rate in the system and the maximum pressure drop, respectively.

The specific energy consumption of the plant is calculated by:

$$W_{total} = \frac{\dot{W}_1 + \dot{W}_2 + \dot{W}_{sec} + \dot{W}_{pumps}}{3.6} \quad \frac{KWh}{TON} \qquad \text{Eq. 22}$$

Finally, the energy cost of the plant operation is calculated by:

$$C_{energy} = W_{total} * c_{elec} \qquad \text{Eq. 23}$$

In this section, the key parameter is the heat exchanger effectiveness. As previously mentioned, the compressor consumption is the main component of the energy cost. Figure 38 depicts the relation between power compressor and HX effectiveness for 100 000 ppm and 200 ppm brine compositions. It can be extracted that the reduction of effectiveness from 1 to 0.5 results in a total power consumption increase of 26%. The 200 000-ppm brine is slightly more affected than the 100 000 ppm. It is also noticed that the secondary compressor power shows very small variations with the change of effectiveness.

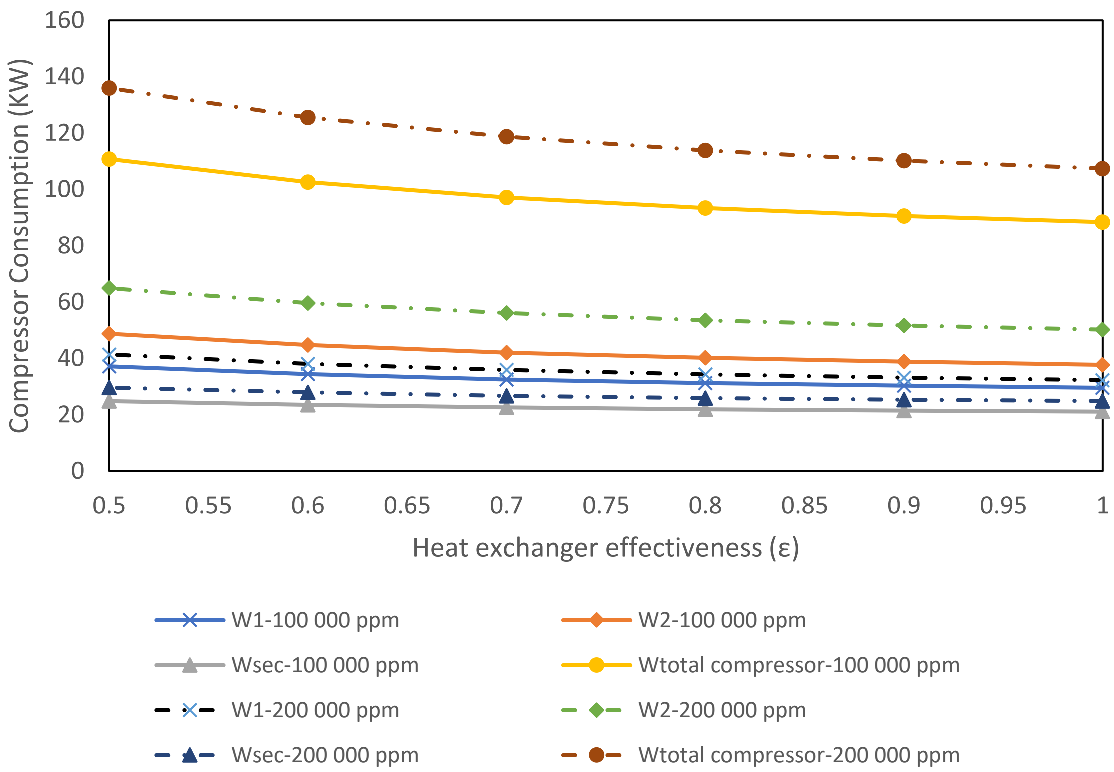

Figure 38. Relation between compressor and HX effectiveness for 100 000 ppm and 200 000 ppm brines

Using the expressions presented in this section, the energy cost is calculated. The relation between energy cost and HX effectiveness is presented in Figure 39. The reduction of heat exchanger effectiveness from 1 to 0.5 results in an increase of energy cost of about 26%. Higher concentration brines are slightly more affected than lower concentration brines.

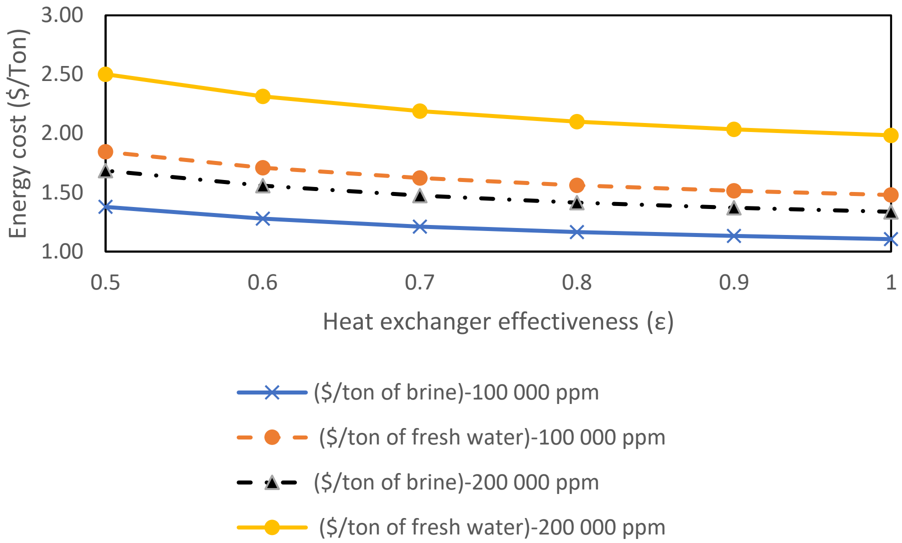

Figure 39. Relation between energy cost and HX effectiveness for 100 000 ppm and 200 000 ppm

The interaction between separation efficiency and HX effectiveness must be evaluated to cover all possible scenarios. Figure 40 depicts the relation between those parameters for a 200 000-ppm brine. It is observed that the LCOW has a range maximum cost of 0.54 $/barrel of brine and a minimum cost of 0.42 $/barrel of brine. It shows that the decrease of 30% in separation efficiency combined with a reduction of 50% in HX effectiveness only results in a 23% increase in the LCOW.

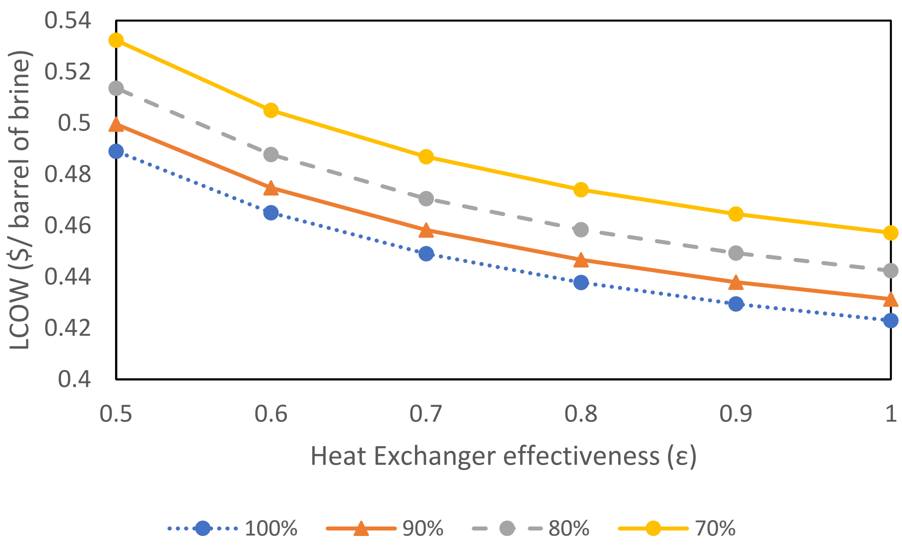

Figure 40. LCOW as function of HX effectiveness for different separation efficiencies

The LCOW dependence between the LCOW and HX effectiveness is one of the most important. This relation is depicted in Figure 41. It shows that treating lower brine compositions has a maximum LCOW under 0.4 $/barrel of brine. Higher brine compositions result in an LCOW ranging from 0.5 to 0.65 $/barrel of brine.

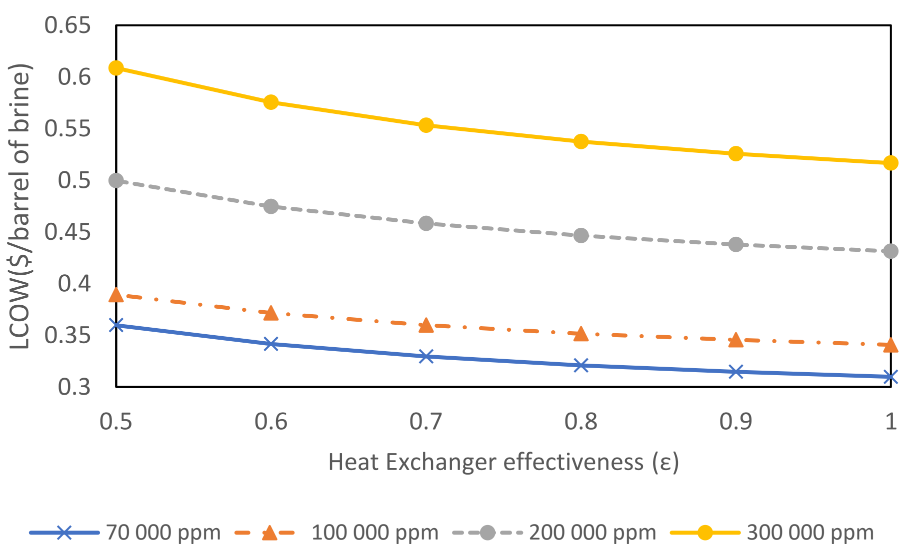

Figure 41. LCOW as function of HX effectiveness for different brine compositions

The main motivation to develop the two-stage system is the expected savings. Hence, evaluating the LCOW for each system is vital. The LCOW for both systems is depicted in figure 42 for all studied brines. Firstly, it is noticed that higher concentration brines show bigger savings by the second-stage system. Secondly, the LCOW savings between 28% and 55%

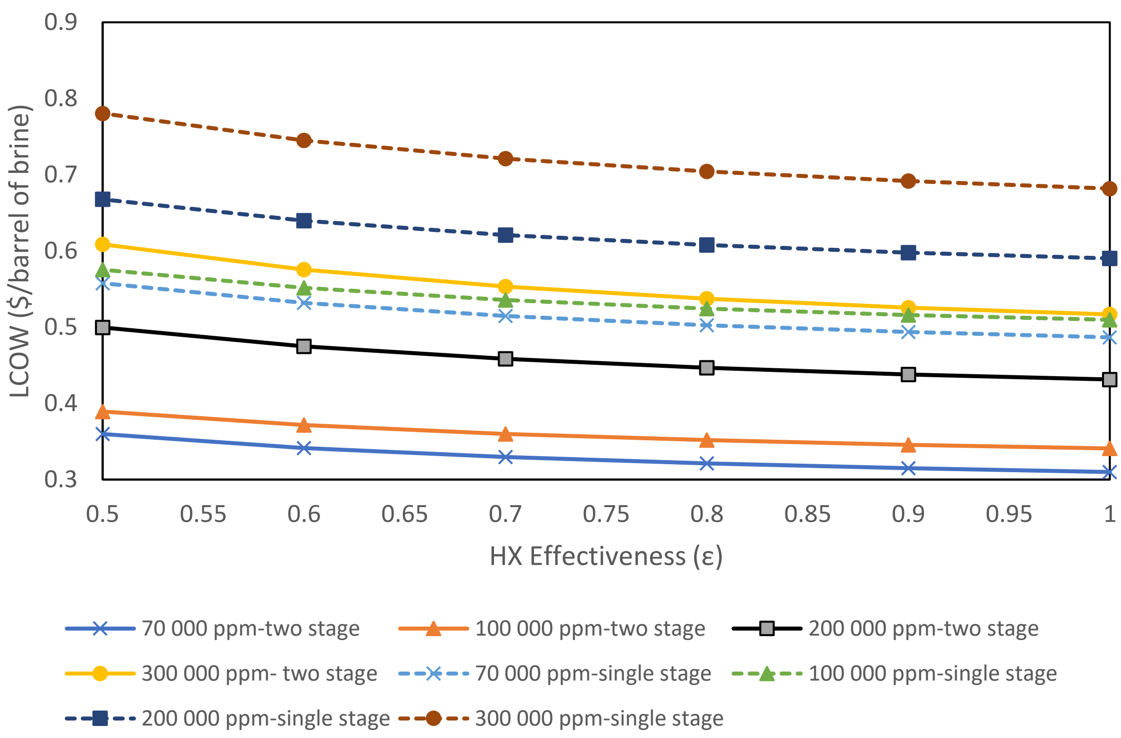

Figure 42. LCOW comparison between single and two-stage system as function of HX effectiveness

5. Conclusions

This research is focused on the development of a novel freeze desalination system. First, the conventional Freeze Desalination technology is thoroughly described, along with its advantages and disadvantages. Current desalination technologies like RO and MSF are also described to identify the main drawbacks. Similarly, industrial brine management technologies are presented to provide a solid background of produced water treatment.

The proposed system is designed to treat actual brine compositions such as produced water. Realistic data obtained from the "Oklahoma Geological Survey" is studied in the present thesis. Moreover, the novel FD system must overcome the main drawbacks of existing FD systems and includes features that make it unique. The new FD process operates continuously and includes commercial separation devices. Besides, to enhance the freezing process, the freezing occurs by direct contact of the brine with ICL (commercial intermediate cooling liquid). The freezing process and the refrigeration system, that provides cold energy to the freezer, are studied in detail. In this study, two systems are proposed, single-stage, and two-stage systems. The two-stage system is developed to generate energy savings compared to the single stage.

As one of the requirements is to include actual brine compositions and devices, this thesis utilizes a computational approach. OLI Chemical Wizard and ASPEN Plus are the platforms used to build the complex chemistry, develop the process flow, and obtain results. Firstly, mass and energy analyses are conducted in ASPEN Plus for both proposed systems. This provides the results in terms of freshwater productivity and energy consumption. Secondly, a techno-economic study is presented. It includes fixed costs (infrastructure, maintenance, etc.) and variable costs like energy cost. Freshwater productivity and energy consumption are inputs of the techno-economic study.

In this study, the response of the proposed systems to brine composition, separation efficiency, and evaporator effectiveness is investigated in terms of freshwater productivity, energy consumption, and LCOW (Levelized cost of water). After conducting several sensitivity analyses of the mentioned parameters, the following conclusions were found:

- Direct-contact freezing can be achieved due to the existence of commercial heat transfer fluids with suitable properties. Several industrial direct-contact heat exchangers can be used for this purpose.
- It is possible to operate the system continuously. Using different separation technologies such as hydrocyclone, wash columns, and gravity separators allows to achieve that type of operation. The development of the process flow plays a key role in the operation. The inclusion of recycling and recirculating lines is fundamental.
- One of the main concerns was the presence of low-efficiency separators. However, it was proved due to the robust process flow that the water recovery ratio has negligible changes to the drop of separation efficiency. Reducing the separation efficiency from 100 to 70% results in only a 0.3% reduction in the water recovery ratio. Similarly, the cooling and melting loads only experience a rise of 13% as a consequence of the reduction.
- The flexibility of the process to handle different produced water compositions coming from different basins was put to test. It was possible to achieve high water recovery ratios by modifying the operating temperature. Higher concentration brines require lower freezer temperatures. The system achieved water recovery ratios of 0.86, 0.75, 0.68, and 0.67 for the 70 000, 100 000, 200 000, and 300 000-ppm produced water, respectively. The cooling and melting loads (KW/kg of brine) for the 300 000-ppm brine are about 8% higher than the required for 70 000 ppm.
- As expected, the two-stage system provides more benefits than the single-stage process. Firstly, it allows us to better understand the energy and chemistry involved in the freezing process. Secondly, up to 28% of energy savings are achieved for cooling and melting loads. Both systems have the same water recovery ratio.
- The evaporator effectiveness is the parameter that links the energy analysis to the economic analysis since it is used to calculate the compressor power. The total

compressors consumption increases by 26% as a result of dropping the HX effectiveness from 100% to 50%.

- The combined effect of variating separation efficiency and evaporator effectiveness is studied to evaluate the robustness of the design. Reducing the separation efficiency by 30% and the evaporator effectiveness by 50% resulted in only a 23% increase of the LCOW.
- The two-stage system has savings from 28% to 55% in the LCOW compared to the single-stage system.
- For the single stage plant, the treatment of the 70 000, 100 000, 200 000, and 300 000 ppm has a maximum LCOW of 0.57, 0.59, 0.70 and 0.85 $/ barrel of brine.
- For the two-stage plant, the treatment of the 70 000, 100 000, 200 000, and 300 000 ppm has a maximum LCOW of 0.37, 0.40, 0.53 and 0.69 $/ barrel of brine.

The results show that the plant accomplish the requirements and it is viable to build this plant. Features such as high-water recovery ratios and low LCOW make the novel system compete with current desalination and brine management technologies. Further work is recommended to refine the fixed costs. The next design step would be to develop P&ID diagrams to include instrumentation and control of the devices and parameters.

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