# Salt recycling from fly ash; Process design and integration with a waste-to-energy plant

Master’s thesis within the Sustainable Energy Systems programme

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MASTER’S THESIS SEEX30

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# ABSTRACT

Fly ash is a by-product from waste-to-energy plants and is classified as hazardous waste due to its content of chlorides and heavy metals. Most of the generated fly ash is disposed of in special landfills for hazardous waste, which is expensive, requires transportation over long distances and is not sustainable in terms of a circular economy. Therefore, more sustainable ways of handling fly ash are being requested on the market. HaloSep AB, part of the Stena Metall Group, has developed an on-site fly ash recycling process that converts fly ash into a non-hazardous product. After treatment in several wet-chemical steps, chlorides from the fly ash end up in a brine as dissolved chloride salts, mainly $CaCl_2$, NaCl and KCl. Plants located close to a saltwater recipient can release the brine into the environment, but it is not possible for inland plants. An alternative way of handling the brine is therefore needed for inland plants.

The purpose of this thesis is to evaluate different salt recycling processes for recycling salt in the HaloSep brine. A literature study is performed where existing salt recycling methods and applications of salt are reviewed. Based on the results from the literature study, a salt recycling process is designed and simulated in Aspen Plus. Further on, heat-integration with an existing waste-to-energy plant is performed and the net energy loss in the plant is evaluated. A sensitivity analysis is performed to see how the concentration and composition of the brine affect the outcome of the process. A brief economic analysis is also done to determine when the process is motivated.

The findings in the literature study indicate that an evaporation-based process is the most suitable process to recycle the salts in the brine. The proposed design has two evaporation stages operating below atmospheric pressure, 0.65 bar and 0.14 bar, and results in three product streams that could be used as road salt for de-icing, dust suppression, or be further processed into purer salts. The net energy loss in the waste-to-energy plant is between 0.9-1.4% in electricity and 0-2.4% in heat, depending on the design conditions. The process is financially profitable considering the combination of revenue from energy costs and income generated from salt products.

Keywords: Salt recycling, fly ash, waste-to-energy, heat integration, Aspen Plus, multi-effect evaporation, NaCl, KCl, $CaCl_2$

Saltåtervinning från flygaska; Process design och integrering med en avfallsförbränningsanläggning
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## SAMMANFATTNING

Flygaska är en biprodukt från avfallsförbränningsanläggningar och klassas som farligt avfall på grund av dess innehåll av klorider och tungmetaller. Majoriteten av all flygaska som produceras deponeras i särskilda deponier för farligt avfall vilket är dyrt, kräver långa transporter, och är inte hållbart ur ett cirkulärt perspektiv. Därför finns en efterfrågan på mer hållbara sätt att hantera flygaska på. HaloSep AB, del av Stena Metallkoncernen, har utvecklat en lokal återvinningsprocess för flygaska där den omvandlas till ofarliga produkter. Efter behandling i flera våtkemiska steg hamnar kloriderna från flygaskan i en saltlösning som lösta salter, främst $CaCl_2$, NaCl och KCl. Anläggningar som är belägna nära saltvattenrecipienter kan släppa ut saltlösningen i naturen, men det är inte möjligt för anläggningar belägna inåt land. Därför finns det ett behov för alternativa sätt att hantera saltlösningen på för anläggningar inåt land.

Syftet med detta examensarbete är att undersöka olika saltåtervinningsprocesser för att återvinna salterna i saltlösningen från HaloSeps process. En litteraturstudie utförs för att evaluera existerande saltåtervinningsmetoder och dess användningsområden. Baserat på resultaten från litteraturstudien designas och simuleras en saltåtervinningsprocess i Aspen Plus. Vidare genomförs en värmeintegration med en existerande avfallsförbränningsanläggning och energiförlusten i anläggningen beräknas. En enkel ekonomisk analys genomförs även för att bedöma när processen är motiverad.

Resultaten från litteraturstudien tyder på att en förångingsbaserad process är mest lämplig för att återvinna salterna i saltlösningen. Den föreslagna processen har två förångningssteg vid undertryck, 0.65 bar och 0.14 bar, vilket resulterar i tre produktströmmar som kan användas som vägsalt för halkbekämpning, dammbindning, eller bearbetas vidare till högre renhet. Energiförlusten i avfallsförbränningsanläggningen är mellan 0.9–1.4% i el och 0–2.4% i värme, beroende på designparametrarna. Processen är ekonomiskt lönsam med hänsyn till intäkter från energikostnader och inkomster genererade från saltprodukterna.

Nyckelord: Saltåtervinning, flygaska, avfallsförbränning, värmeintegration, Aspen Plus, flerstegsförångning, NaCl, KCl, $CaCl_2$

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# Contents

# 1 Introduction

Incineration of solid waste is a common waste management method in Sweden and some other European countries. Incinerating such fuels in waste-to-energy (WtE) plants makes it possible to recover energy by producing heat and electricity. The incineration also produces two by-products, bottom ash and fly ash [1]. Bottom ash is the non-combustible waste fraction that remains at the bottom of the boiler after combustion, and fly ash is the fine particles that are removed from the flue gases through electrostatic precipitators or textile filters [2]. The fly ash contains high concentrations of volatile heavy metals and chloride salts [3]. The chlorides are water-soluble and some of the heavy metals are soluble at neutral pH conditions, which means that there is a leaching risk for these compounds. Therefore, fly ash is classified as a hazardous waste [2]. In 2021, around 7 000 000 tons of solid waste was incinerated in Sweden, which resulted in the generation of 300 000 tons of fly ash [4]. Today, most of the fly ash is deposited in special landfills for hazardous waste. This is expensive for the plant owners, requires long transportation, and is not sustainable in terms of a circular economy. Transforming the fly ash into non-hazardous waste and recycling valuable components is therefore of great interest not only for WtE plant owners but also from a sustainability perspective.

## 1.1 The HaloSep Process

The company HaloSep AB, part of the Stena Metall Group, has developed an on-site process that treats fly ash and converts it into non-hazardous waste. A full-scale plant has been installed and successfully operated at Denmark's largest waste management and energy company, Vestforbrænding. An overview of the HaloSep process is shown in Figure 1.

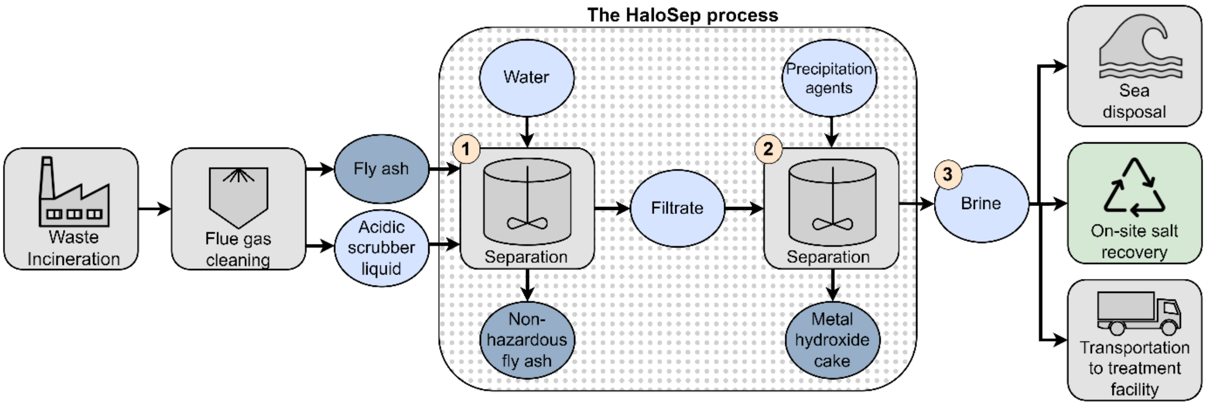


*Figure 1. Overview of the HaloSep process. The green box represents the focus of this thesis.*

The ash is treated with an acid, which is usually available at WtE plants that have wet flue gas treatment [2]. The acid is a weak hydrochloric acid with a pH near 0 and comes from the acid scrubber. The acid scrubber captures and dissolves acid gases from the flue gas, mostly HCl, which mainly comes from the combustion of PVC plastics in the waste [5]. Some plants add lime, which is alkaline, to the scrubber to increase the pH, which decreases the material costs of the equipment [2]. The pH will then be around 1.5, which makes it more difficult to use the acid for fly-ash treatment. In that case, and when another type of flue gas cleaning is used, the acid has to be supplied from an external source or lime dosing has to be reduced. In the first separation step, see 1 in Figure 1, the alkaline fly ash is mixed with the acid with pH near 0, and water. A neutralisation reaction will take place due to increased alkaline components from fly ash, and the resulting pH after the reaction will be ~ 4. At this pH, water-soluble salts and the mobile forms of heavy metals are leached from the fly ash. After a sieving step, the pH is further adjusted and the liquid is separated from the solid. The remaining solid fly ash is a non-hazardous product and the liquid filtrate contains salts and heavy metals. In the second separation step, see 2 in Figure 1, precipitation agents are added to the filtrate and the pH is increased up to 9-10, which results in a metal hydroxide filter cake that mainly consists of zinc hydroxide. A saltwater solution, see 3 in Figure 1, with 6-12% salts remain after the removal of the metal hydroxide cake. This solution can be released into the environment if the plant is located close to a saltwater recipient. However, if the plant is located inland, handling the brine becomes more problematic because it is difficult to get permits from authorities to release the brine to freshwater recipients and the regulation may be even more stringent in the future. Addressing possible ways of utilising the brine is therefore of interest for HaloSep, as it would make it possible for them to reach full market potential for inland plants.

The brine mainly contains $CaCl_2$, NaCl, KCl and some sulphates [2]. The ratio between the three salts varies depending on the composition of the fly ash, which is affected by the flue gas cleaning process. Usually, $CaCl_2$ is the most dominant salt because calcium-rich compounds are often added during flue gas cleaning. Sometimes, sodium-rich compounds are added instead, which leads to a brine high in NaCl. The brine from the HaloSep process at Vestforbrænding is shown as the calcium-rich brine in Figure 2. The sodium-rich brine in Figure 2 is from a HaloSep study at another plant. The compositions shown in Figure 2 are simplified, in reality 0.12 wt% and 1.6 wt% of the calcium-rich and sodium-rich brines, respectively, contain other components. Most of the other components are sulphates that can be removed in a pre-treatment step before a salt recycling process.

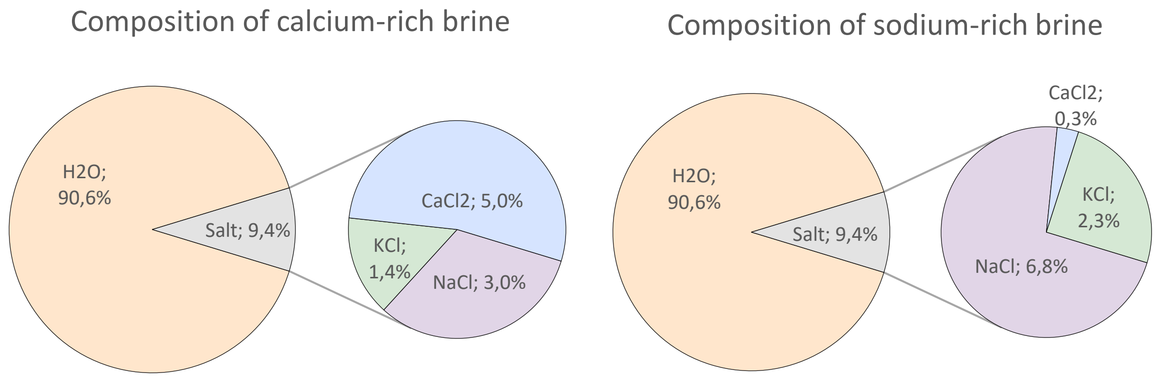


*Figure 2. Simplified composition of a calcium-rich (left) and sodium-rich (right) brine.*

The different salts have several different applications such as de-icing and dust control on roadways, aluminium recycling, PVC-manufacturing, oil drilling, and the paper and pulp industry [6]. Pure salts can also be used in the production of fertilisers and the food industry, but the question of acceptance of the origin of the salt probably becomes an obstacle for such applications [7], [6]. To use the brine, the different salts need to be separated. The fact that salts have different solubilities can be used for this purpose. By adjusting the temperature and pressure during an evaporation process, the salts can be separated [7]. Since the HaloSep process is on-site, waste heat from the WtE plant could be used for the evaporation process.

## 1.2 Gärstadverket – Tekniska Verken in Linköping

Integrating a salt-recycling process with a WtE plant is of interest because heat streams at the WtE plant could be efficiently used in a process located nearby. Additionally, it would allow the plant owners to independently handle their fly ash and convert it to useful products. Furthermore, this kind of integration has not been studied before.

To get a reality-based perspective on the possibility of integrating a WtE plant with the proposed salt-recycling process, the WtE plant Gärstadverket in Linköping is used as a case-study in this thesis. Gärstadverket belongs to Tekniska verken in Linköping, which is a municipally owned company that operates in many different areas, e.g., district heating and electricity production, waste management, and water purification [8]. Gärstadverket has five boilers that annually produce 1380 GWh of district heat and 293 GWh of electricity in total. Details of the streams are provided in Figure 3.

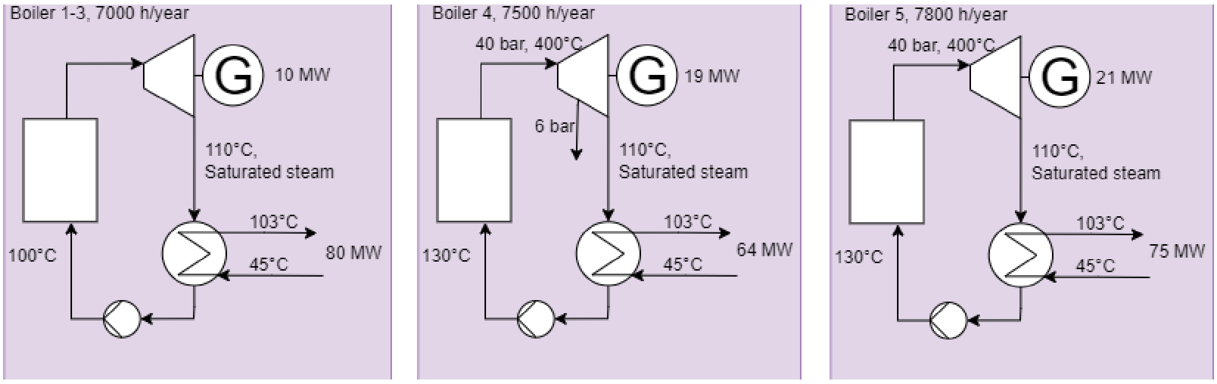


*Figure 3. Steam cycle with operating conditions at the five boilers of Gärstadverket - Tekniska Verken in Linköping,* [8].

All boilers are grate-fired, and the operation can be adjusted for heat-only production or simultaneous production of heat and electricity. The total electricity production is 50 MW, and the heat production is 219 MW [8].

## 1.3 Purpose

The main purpose of this thesis is to evaluate different processes for recycling the salts in the brine resulting from the HaloSep process. The aim is to obtain salt products with a market value to avoid landfilling and increase the circularity of fly ashes. The results are further utilised to get an insight into how the energy consumption for the salt recycling process can be integrated with a waste-to-energy plant.

## 1.4 Scope

The salt recycling process is modelled based on available data on one specific calcium-rich salt brine from the HaloSep process at Vestforbrænding. Simulations are run for salt concentrations between 6-12 wt% as these are the concentrations that can be expected from the process. Salt concentrations outside of this range are not considered. Furthermore, a sensitivity analysis is performed for a sodium-rich brine to evaluate the influence on the designed process. Other salt compositions are not considered. The energy requirement for start-up of the process is not considered and it is assumed that the process is under continuous operation. Pre-treatment of the brine for sulphur removal is assumed but is not researched in detail.

## 1.5 Objectives

The aim of this thesis is to address the following questions:

- What recycling methods are there for mixed salts, and what are the potential applications for the salt products?
- How can the salt recycling process be integrated with the existing waste-to-energy plant?
- What will be the net energy loss in the waste-to-energy plant output when it is integrated with the salt recycling process?
- How will the total salt concentration of the brine affect the net energy loss after integration with the salt recycling process?
- How will the salt recycling process be affected by a high concentration of NaCl or $CaCl_2$?
- When is the process motivated considering brief economic calculations based on cost of energy and income from selling salt, and brief environmental aspects?

# 2 Literature study

A literature review for salt recycling, for both processes and possible products for the salt is presented in this chapter. Brine treatment technologies that are available on the market and previous studies on mixed chloride salt separation are discussed, and existing plants that are available on the market today are mentioned. Finally, possible markets for utilisation of what the salts NaCl, KCl and $CaCl_2$ can be used for is presented. Chalmers library was used for literature searches as well as Google Scholar, Scopus and web of science. Literature was also provided by HaloSep containing their earlier projects.

## 2.1 Brine treatment technologies

There are many different brine-treatment technologies available on the market. The best brine-treatment technology depends on several factors, such as the concentration and composition of the brine, the volume of the brine, the geographic location of the plant, legal and public allowance, capital and operational costs, and availability for the disposal or second life for the salts [9]. The different brine treatment technologies can be divided into membrane-based, thermal-based, and solvent-based. In Figure 4, a summary of brine treatment technologies is presented. The limitation in terms of total dissolved solids (TDS) is shown for each treatment. High TDS means that the technology can handle high salinity and has no defined limit. The technologies are briefly discussed further down, and a more detailed description of the technologies is given in Appendix A.

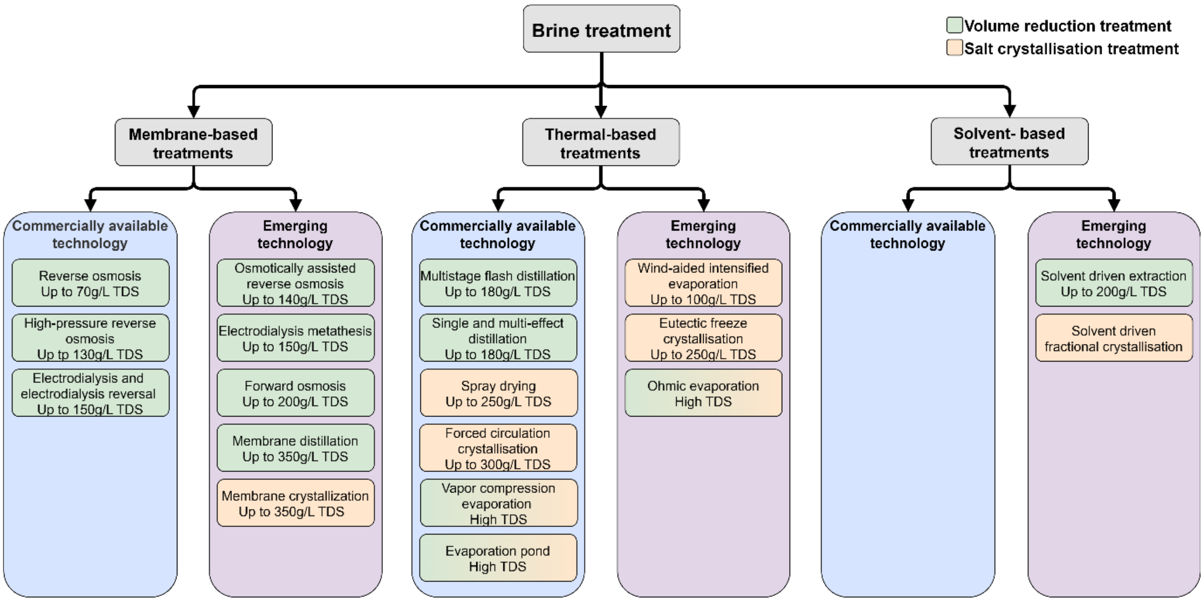


*Figure 4. A summary of brine treatment technologies and their limitation in terms of g/L total dissolved solids (TDS)* [9], [10], [11].

The technologies can be divided into volume reduction treatments (shown as green in Figure 4) and salt crystallisation treatments (shown as yellow in Figure 4). However, volume reduction treatments can sometimes also lead to salt crystallisation, although it is often not the main purpose. In salt crystallisation treatments, a solid salt product is formed. In order to crystallise the salt, the brine has to become supersaturated. This can be achieved in three ways, either by evaporation, cooling or a combination of both [12]. In Figure 5, the solubility graph for pure components of KCl, NaCl and $CaCl_2$ in water is shown. For $CaCl_2$, the solubility is shown for the most stable crystalline phase at the temperature in question.

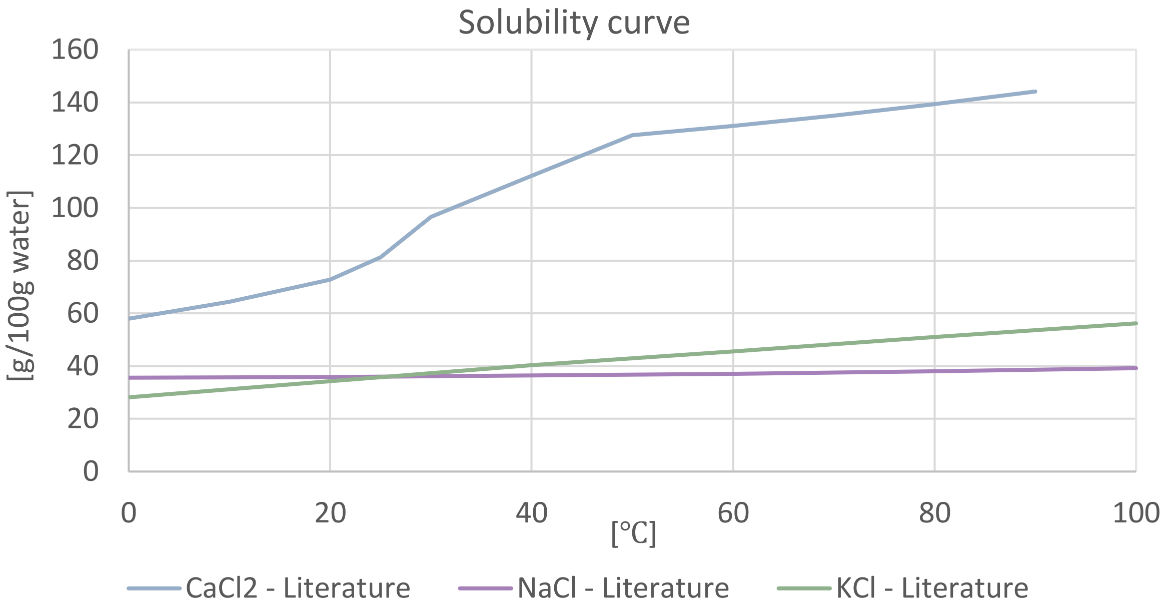


*Figure 5. Solubility curves for KCl, NaCl and $CaCl_2$, in water* [13], [14]

### 2.1.1 Membrane-based treatments

The most common membrane-based treatments for brine are reverse osmosis, high-pressure reverse osmosis, forward osmosis, osmotically assisted reverse osmosis, electrodialysis, electrodialysis reversal, electrodialysis metathesis, membrane distillation and membrane crystallisation [9]. The treatment is mostly used to reduce volume, but membrane crystallisation can be used for salt recovery. Furthermore, for membrane-based treatments, scaling and fouling are common problems and therefore an additional pre-treatment step is often needed, which increases the associated costs. Since the brine in this project has relatively high salinity, membrane-based methods will not be suitable. Therefore, membrane-based methods will not be further discussed but a more detailed description of the most common membrane-based treatments is presented in Appendix A.

### 2.1.2 Thermal-based treatments

The principle for thermal-based treatment is that thermal energy is used to evaporate water. This is often applied for brines with high salinity and when the required pressure when using membrane separation is higher than the bearing pressure for the membrane [15]. Thermal-based treatment often has high energy consumption and is often used when other applications do not work, e.g., in case of high fouling, too high salt concentration, or too complex compositions. However, the investment cost for thermal-based treatments is often high due to corrosion from the high concentration of salt, which will affect the material costs. Sometimes, a combination of membrane-based treatment and thermal-based treatment is used to reduce the operating cost. In that case, the membrane-based treatment can be used to concentrate the brine before thermal-based treatment. Like membrane-based treatments, thermal-based treatments can be aimed at either concentrating or crystallising the brine.

The most common thermal-based treatments are multistage flash distillation, multi-effect distillation, vapour compression evaporation, ohmic evaporation, wind-aided intensified evaporation, evaporation pond, spray drying, eutectic freeze crystallisation and forced circulation crystallisation [11]. Commercial technologies, except spray drying and evaporation pond, are considered to be suitable for this project, therefore more detailed descriptions for these technologies are presented below. For the other technologies, more detailed descriptions are in Appendix A. Spray drying and evaporation pond are not considered suitable as they cannot separate the individual salts.

#### *2.1.2.1 Multistage flash distillation*

Multistage flash distillation is a widespread thermal technology for treating high salinity brines [9]. In this technology, the brine is heated and led into a vessel with a lower pressure. Instantly, evaporation occurs, and the remaining solution is led into the next vessel with even lower pressure. This way, the brine gets more concentrated in steps. The flashed vapour is used to preheat the brine to save energy, and to condense the vapour to get freshwater. A multistage flash distillation plant normally has 4 to 40 stages where every following stage has a lower pressure and lower temperature [16]. For high TDS brines this technology has problems with corrosion which affects the cost of the construction material [11].

#### *2.1.2.2 Single and multi-effect distillation/evaporation*

The principle in single- and multi-effect evaporation is to evaporate water by supplying heat. An effect is an evaporator/condenser heat exchanger [17]. Hence, in a single effect evaporation, there is only one evaporator. Multi-effect evaporators on the other hand have sequential evaporators and the feed is pumped between them. The main difference between multi effect distillation and multistage flash distillation is that heat is only supplied before the multistage flash distillation, but in multi effect distillation heat is supplied in every stage by using the generated vapor. Compared to multistage flash distillation, multi-effect distillation is more thermodynamically efficient and can be connected to a wide range of heat sources as waste heat, but it has larger problems with scaling [15].

External heat is only supplied to the first effect, which vaporises water in the brine. The generated vapour is subsequently used as the heat source in the next effect. The generated vapour in the last effect is used to preheat the feed. To get high heat transfer, the brine is sprayed to create a thin fall film on the tubes, which constitutes of evaporation surfaces in the vessels where the heat exchange occurs. There are three different configurations of multi-effect evaporators. In a forward feed configuration, the brine flows co-currently with the vapor, i.e. from higher to lower temperature effects. Part of the brine is evaporated in the first effect, and the rest enters the next effect where more water is evaporated, and so on. In a backward feed configuration, the brine flows counter-currently with the vapor. The most common configuration is parallel feed, where the feed is distributed equally between the effects. The un-evaporated brine can either be directly discharged or enter the next effect. The technology has the same problems as multistage flash distillation with corrosion when the TDS is high in the brine [11].

#### *2.1.2.3* Vapour compression evaporation

Vapour compression evaporation utilises the produced vapour from the brine to evaporate the inlet brine [9]. The evaporation heat source comes from the produced vapour that is compressed either mechanically (MVC) or thermally (TVC). During the heat exchange between the vapour and the brine, vapour is condensed on the tube-side and forms a high-quality distillate. Since the energy from the vapour is utilised, the system gets high energy efficiency, but the technology has high investment costs, and water production costs partly due to possible corrosion of the compressor. The technology is mainly designed for small and medium-scale applications.

#### 2.1.2.4 Forced circulation crystallisation

A simplified description of forced circulation crystalliser is that the brine is fed into the bottom of the crystalliser and is mixed with the circulated brine [11]. The brine is circulated by force from the bottom through a heat exchanger and into the crystalliser again. Before the heat exchanger a stream consisting of crystals is taken out and led to a centrifuge or a filter for separation. There is an active volume in the crystalliser to achieve the required residence time for crystal growth [18]. Vapour exits from the crystalliser's top [11].

### 2.1.3 Solvent-based treatments

Emerging types of desalination techniques are solvent-based treatments. Compared to membrane- and thermal-based treatments, solvent-based treatments are not subjected to the practical limitations set by membranes and avoid high energy demands for evaporation [10]. Two solvent-based treatments that are being developed are solvent driven extraction and solvent-driven fractional crystallisation. An interesting aspect of these technologies is that an appropriate solvent could make it possible to separate salts that have similar solubilities in water, and therefore are difficult to separate with membrane- or thermal-based treatments. For example, it has been shown that the addition of alcohol or ammonia to solutions of mixed salts can cause KCl to crystallise. However, solvent regeneration also requires energy and solvent losses are unavoidable, which can lead to high costs. As these technologies mostly have been used on a laboratory scale, they are not considered suitable methods to treat the brine in this project. More details on solvent-driven extraction and solvent-driven fractional crystallisation are given in Appendix A.

## 2.2 Previous studies on mixed chloride salt separation

The aforementioned brine treatment technologies can be applied to a wide variety of brines. However, only a few of these technologies can separate and recover solid salts from mixed salt brines. To get an overview of the potential processes for the separation of mixed chloride salts, a summary of the previous research in this field is presented in this section. First, processes simulated in a software are presented, then lab-scale and commercial processes are summarised. For both lab-scale and commercial processes the brines come from fly ashes.

### 2.2.1 Simulated processes

There has been some previous work utilising Aspen Plus to simulate salt recycling processes. For example, an evaporation and cooling salt-recovery process for a brine containing $MgCl_2$, $MgSO_4$, KCl, and NaCl was modelled in Aspen Plus by Yang et al. where the purpose was to separate the salts [19]. The basic model had two single-effect evaporators operating at 0.1 MPa and 113°C. After the salt crystallised in the evaporator, it was removed, and the remaining solution was cooled (to 45°C after the first evaporator and 0°C after the second evaporator). The model was also improved from an energy-saving point of view by adding multi-effect evaporators, and mechanical vapour compression (MVC) and thermal vapour compression (TVC) heat pumps.

Kang et al. [20] modelled a process for the separation of NaCl and KCl in Aspen Plus. Two different brines were simulated, one high in sodium (8.7% NaCl, 4.3% KCl) and one high in potassium (8.7% KCl, 4.3% NaCl). The brine was fed to an evaporator-crystalliser, operating at 80°C and 0.325 bar, where the salt with the highest concentration crystallised. Part of the remaining stream was cooled to around 50°C, where the other salt crystallised. A mechanical vapour recompression was integrated with the process to improve the energy-efficiency. This means that the steam generated in the evaporator was mechanically compressed and condensed in a heat exchanger that pre-heats the feed.

A process for the separation of NaCl, $MgCl_2$ and KCl was modelled in Aspen Plus by Rempel et al [21]. The brine that enters the process contained 6.8% NaCl, 1% $MgCl_2$, and 0.5% KCl. The process consisted of three main parts, which were concentration and impurity removal, KCl recovery, and $MgCl_2$ recovery. Multi-stage flash evaporation (3 stages) was used in the first part, where most of the water was removed and a majority of the NaCl was crystallised. Filtering and crystallising units were used for the KCl and $MgCl_2$ recovery. $MgCl_2$ crystals were recovered at a purity of 98% and KCl at a purity of 60%.

### 2.2.2 Lab-Scale processes

A process for the separation and recovery of chlorides from fly ash was studied by Xie et al [22]. The fly ash was washed with water and the resulting wastewater contained KCl (8.91%), NaCl (8.16%), and $CaCl_2$ (7.93%). The wastewater was treated with an evaporation-crystallisation process, where a mixed crystallised salt of KCl-NaCl and a concentrated solution of $CaCl_2$ was obtained. The mixed KCl-NaCl salt was then separated through flotation. Citric acid was used as the depressant, dodecyl-amin as collector, and terpineol as frothier. Two concentrates were obtained, one with high KCl content and one with high NaCl content. The concentrates were washed with saturated solutions of the respective salts in order to increase the purity. Under optimal conditions, total recoveries of 91.4% and 90.0% for KCl and NaCl, respectively, were achieved. The grade was 98.1% for KCl and 96.6% for NaCl.

Another process for the separation of a brine containing $CaCl_2$, NaCl, and KCl, was studied by Tang et al. [23]. The brine originated from washing of fly ash from municipal waste incineration. The process was a three-step evaporation-crystallisation process where pure NaCl, KCl, and $CaCl_2$ was produced, a flowsheet of the process is shown in Figure 6. In the first step, water was evaporated from the brine and a fraction of the NaCl crystallised. The remaining solution was evaporated again, and the crystallised product contained NaCl and KCl. This precipitate was dissolved in water and ethanol was added, which caused precipitation of pure KCl. The remaining solution after the second evaporation was evaporated a third time. Then, the precipitate contained NaCl, KCl, and $CaCl_2$ and was therefore returned to the feed brine. Ethanol was added to the remaining solution, which precipitated pure KCl. The remaining solution only contained $CaCl_2$, which would crystallise if the water was evaporated [23]. At last, the ethanol was recycled through evaporation.

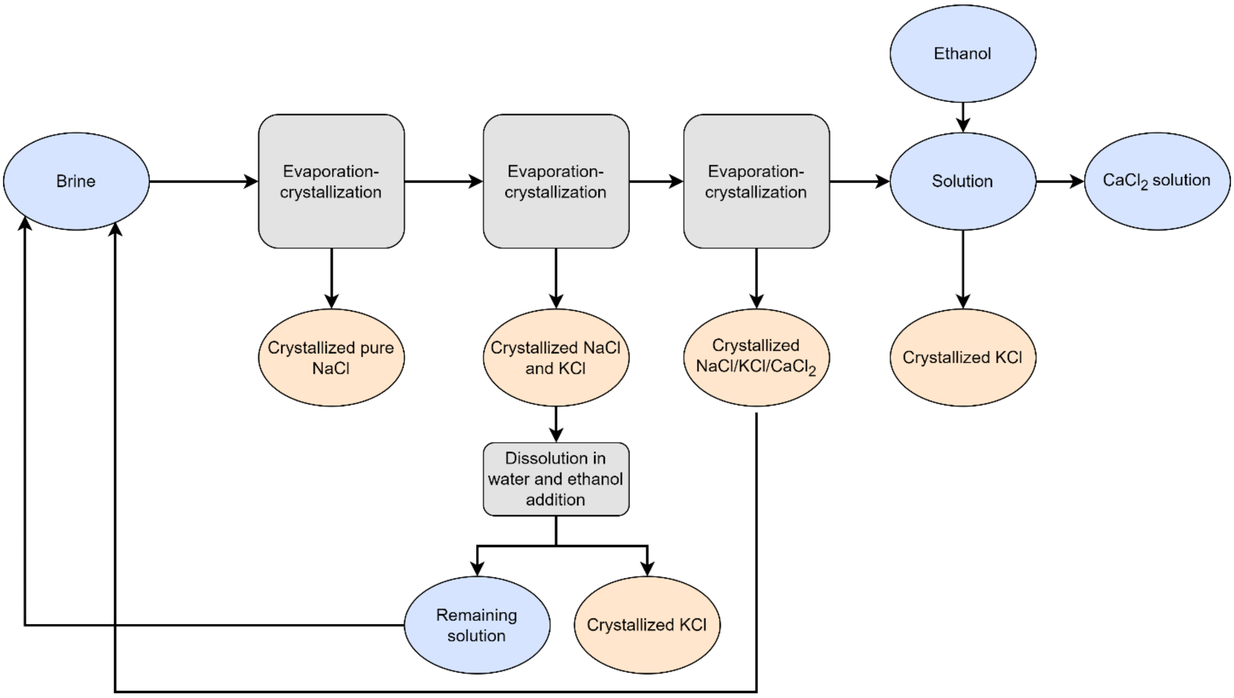


*Figure 6. A flowsheet of the process studied by Tang et al* [23].

### 2.2.3 Commercial processes

An industrial process for the separation of an aqueous solution with NaCl, KCl, and $CaCl_2$, which is a by-product from the washing of fly-ash, has been developed by Easy Mining. The process is called Ash2Salt. The process starts with enriching the brine with $CaCl_2$ so that the concentration of $CaCl_2$ is at least 15 wt% [24]. Water is removed from the solution through a single evaporation step, which causes NaCl and KCl to crystallise. The remaining solution contains dissolved $CaCl_2$, which can be dried so that $CaCl_2$ crystallises.

Another company that develops an industrial process is NOAH. NOAH AS is a Norwegian company that is planning to open a large-scale salt recycling process for salts from fly ash, the process is called Resalt [25]. A successful pilot scale process of Resalt was made in February 2022, where NaCl, KCl and $CaCl_2$ were recovered. The purity of the salt product is aimed to match the industrial requirements. HaloSep has together with NOAH performed pilot scale testing with brine from Vestforbrænding during the development of Resalt. The Resalt process evaporates the brine in three stages, where each stage has different pressures and temperatures, see Figure 7.

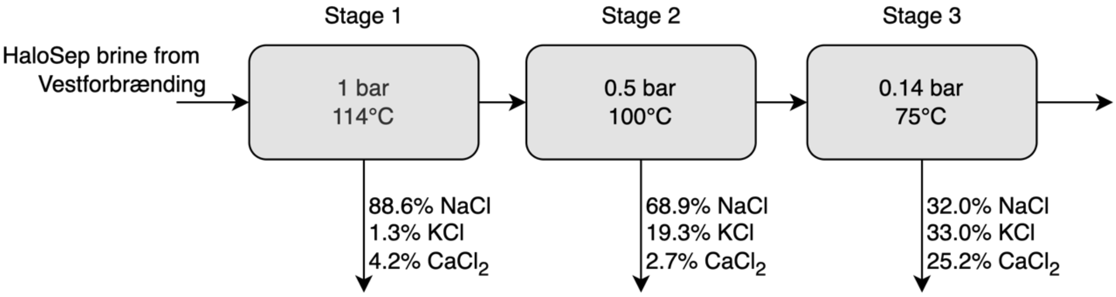


*Figure 7. A flowchart of the operating conditions for the Resalt process and results from the pilot scale test,* [26].

During the stages, salt will be crystallised and separated from the remaining liquid. For the pilot scale test, the HaloSep brine from Vestforbrænding was used for the first stage but for stage two and three a synthetic brine was used due to limited amount of brine.

## 2.3 Applications of salt

Although salt is often used as a synonym to table salt (NaCl), the chemical definition of salt is a compound that has been produced in the reaction between an acid and a base [27]. Different salts have different properties that make them suitable for various applications. The application depends not only on the type of salt, but also on the purity and physical properties. The origin of the salt is also a significant aspect regarding the acceptance of using salts in several applications, such as the food industry [6]. The three salts that are reviewed in this chapter are sodium chloride (NaCl), calcium chloride ($CaCl_2$), and potassium chloride (KCl). The main applications of the three different salts are presented in Figure 8.

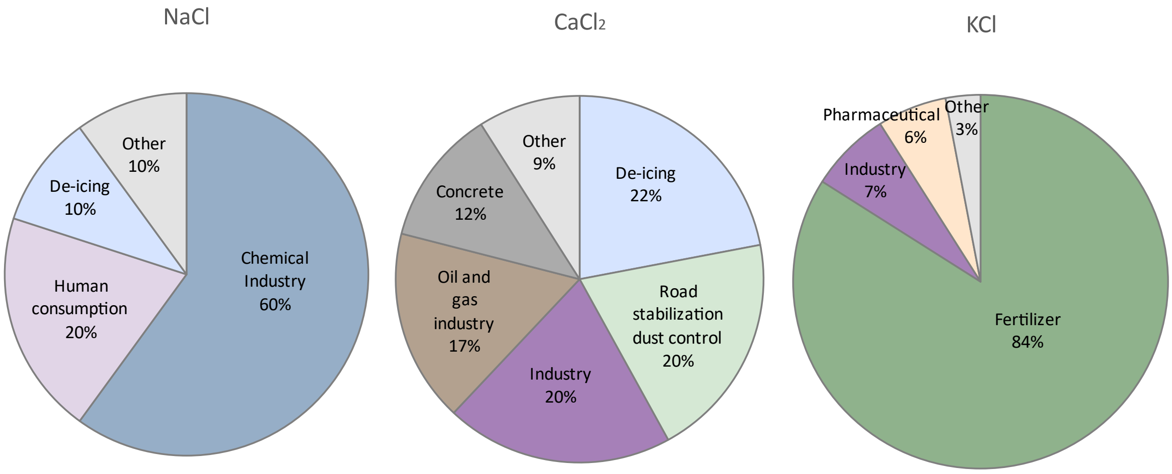


*Figure 8. Market share for NaCl, $CaCl_2$, and KCl by industry. Data source: (NaCl),* [28] *($CaCl_2$),* [29] *(KCl),* [30].

The global production of NaCl reaches more than 200 million tons each year and it has been estimated that there are 14 000 different uses of this salt [28], [31]. There are three major NaCl production methods. Solar salt, i.e. salt produced by solar evaporation of seawater in ponds, stands for the largest share of the salt production, followed by mined rock salt and solution mining [28]. Approximately 60% of the NaCl produced globally is used in the chemical industry, 20% is used for human consumption, 10% is used for de-icing of roads, and the rest is used for other applications such as water treatment and production of cooling brines [28].

$CaCl_2$ is produced as a by-product in the chemical process that produces soda ash (Solvay process) or from limestone. The salt is versatile and therefore useful in several different applications [32]. Around 22% of the calcium chloride produced globally is used for pavement de-icing, 20% for road stabilisation dust control, 20% for industrial processing, 17% in oil and gas well fluids, 12% concrete, and 9% for other uses [29].

KCl is produced from several natural resources, e.g., sylvite, carnallite and kainite [33]. The global KCl production is around 80 million tons and approximately 84% is used as fertiliser, 7% for industrial use, 6% for pharmaceutical use, and 3% for other use [30].

### 2.3.1 Chemical industry

Sodium chloride in the chemical industry is mainly used as raw material to produce other compounds such as chlorine, caustic soda, and soda ash [28]. The two largest processes that produce chlorine and caustic soda, and soda ash are the chlor-alkali process and the Solvay process, respectively.

#### *2.3.1.1 The chlor-alkali process*

The chlor-alkali industry is the largest user of NaCl in the chemical industry. In the process, a solution of NaCl is electrolysed so that chlorine and sodium hydroxide are produced [31]. The two products can further be used to manufacture other chemicals, e.g., detergents, pesticides, pharmaceuticals, plastics, and soaps. Production of polyvinyl chloride (PVC) is the largest consumer of chlorine. There are mainly three different kinds of electrolysis cells used for the chlor-alkali process. These are diaphragm cells, mercury cells, and membrane cells [34]. Membrane cells are the best available technology today because of comparably low power consumption, no use of harmful substances, and high-quality sodium hydroxide. However, this technology requires a high-quality brine with a calcium and magnesium concentration of less than 20 ppb because these compounds deposit on the membrane and reduce the lifetime of the equipment. Sulphates also need to be removed from the brine.

#### *2.3.1.2 The Solvay process*

In the Solvay process, a salt brine with NaCl absorbs ammonia and is carbonated with $CO_2$ [29]. This precipitates $NaHCO_3$ which is then filtered, dried, and calcinated to soda ash ($Na_2CO_3$). The brine used for the Solvay process needs to be purified from calcium and magnesium to prevent precipitation during the carbonation. The precipitation of calcium or magnesium compounds would lead to a decreased quality of the product and contamination of the equipment.

### 2.3.2 Road salts for de-icing

Salts are commonly used as de-icing agents to prevent slippery roads in countries with cold climate. Both NaCl and $CaCl_2$ can be used for this purpose [35]. NaCl is the least expensive option, and it is effective at temperatures above -12°C. $CaCl_2$ is effective at lower temperatures, but it is five times more expensive than NaCl. KCl can in principle also be used as a de-icing agent, but it is only effective at temperatures above -4°C and is slower at melting ice than the other mentioned chloride salts [36]. The reason why $CaCl_2$ is most effective at de-icing and KCl the least effective is because $CaCl_2$ has the highest solubility in water and KCl the lowest solubility, see Figure 5.

In Sweden, spreading of road salt on roads owned by the state is handled by the authority for the Swedish Transport Administration, Trafikverket [37]. On municipal or private roads, it is handled by the municipalities or the road owners. Trafikverket has a requirement that the salt used for their roads must have a purity of at least 97% NaCl. The remaining 3% contains moisture, gypsum, and anti-caking agents (sodium ferrocyanide). The reason why NaCl is used instead of any other salt is because it gives the best trade-off between cost, environmental impact, and de-icing effect, according to Trafikverket. The purity requirement of at least 97% NaCl is because a lower content usually contributes to unwanted contamination that can have a negative effect on the environment [6]. The total amount of de-icing salt spread on roads owned by Trafikverket is around 200 000 tons each year [37]. The salt is applied to the roads either directly as dry salt, or as salt brine. D. Eriksson at Trafikverket (2023-02-22) states that it is up to the contractors hired by Trafikverket to apply the salts and decide how they should be applied. The advantage of applying it as a brine is that it will be effective instantly. If it is applied as dry salt, the salt will not be effective until it has been processed mechanically by traffic. However, the municipalities or private road owners are not required to follow the requirement set by Trafikverket.

### 2.3.3 Road salt for unsealed roads

Salts are applied to unsealed roads to prevent dust and wear of the roads. Dust prevention is important because it causes decreased visibility, poses a health hazard for pedestrians, and increases the vehicle operating costs [38]. $CaCl_2$ is effective at dust control because it has deliquescent and hygroscopic properties. Deliquescent means that the salt becomes liquid by absorbing moisture from the surroundings and hygroscopic means that it can absorb and retain moisture.

In Sweden, road salts used for this purpose are usually applied as salt flakes of either $CaCl_2$ or $MgCl_2$ [39]. The salts can also be applied as a brine. It was found in a study by Gustafsson and Gabrielsson [39] that the most effective dust prevention agent was a solution of magnesium- or calcium chloride. No significant difference in performance between the two salts was concluded.

### 2.3.4 Food- and fertiliser industry

Salt in the form of NaCl is added to food for flavour enhancement, preservation, as a binder, and fermentation control, among others [31]. $CaCl_2$ is also used in the food industry for processing of milk products, fruits, and vegetables [40]. KCl can be used as a low-sodium salt substitute for NaCl [41]. It decreases the health risks associated with high intakes of NaCl but has a bitter and metallic taste.

KCl is also an important fertiliser since potassium is one of the macronutrients that plants need [42]. The KCl fertiliser is commonly referred to as potash and it is applied to farmland to enhance nutrient value and to improve water retention and soil structure. There are several different kinds of potassium fertilisers, but potash is the most economical and the most widely used potassium fertiliser worldwide [33].

### 2.3.5 Oil and gas drilling

Drilling fluids or muds are used in the oil and gas industry to facilitate drilling [43]. The drilling fluids have several different functions, e.g., to remove drill cuttings from the wellbore and to cool and lubricate the drill bit. There are different types of drilling fluids, and the choice of fluid depends on the geographic conditions in the drilling location among others. Most of the drilling fluids used today are water-based and contain additives to reach certain properties. One type of additive is salt, for example NaCl or $CaCl_2$, which can be added to increase the density of the drilling fluid and flocculate [31]. Salts are also added in order to saturate the water when salt deposits are encountered during the drilling operation. This prevents the dissolution of salt from the surroundings.

### 2.3.6 Paper and pulp-industry

The pulp- and paper industry uses $CaCl_2$ to improve the printability of high-quality paper by decreasing the static electricity of the surface [6], [44]. The salt is added as a solution with 35-40% salt and it cannot contain solid particles or heavy metals [6]. The dosage of $CaCl_2$ is usually 6-8 kg /ton paper but it can be up to 12 kg/ton paper [45].

### 2.3.7 Concrete

$CaCl_2$ is often used as an additive to cement to increase the hydration speed and reduce the set time [46]. It is especially used in areas with cold weather, because in too hot areas it could cause the cement to set too quickly. It can be added in a concentration up to 2% in the cement.

### 2.3.8 Aluminium recycling

There are not many applications where mixtures of chloride salts are used, but one common application for mixtures of NaCl and KCl is aluminium recycling. The salts are added to the aluminium scraps that are heated up in a furnace [47]. This increases the aluminium yield because the salts strip the aluminium oxide layer, which facilitates the release of aluminium. The salt mixture should have a melting point near the melting point of aluminium (660°C) in order to fuse with it [48]. In America, the salt mixture is usually an equimolar mixture of NaCl and KCl because it gives the lowest melting point (645 °C) [49]. In Europe it is however more common to use a NaCl:KCl ratio of 70:30 by weight because it has been historically shown to give an acceptable yield. There is reason to decrease the KCl content because KCl is more expensive than NaCl. It has been shown that a decreased share of KCl does not affect the metal yield because it is the chloride, and not the cation, that is active in the reaction on the metal surface. However, a decreased KCl content increases the melting point, which means that an increased process temperature is required, and it decreases the coagulation efficiency slightly. Adding fluorides to the salt mixture, usually in the form of $CaF_2$ and $Na_3AlF_6$ at around 2-5 wt%, has also been shown to increase the aluminium yield.

### 2.3.9 Emerging Applications

The applications stated in the previous section are the most common applications being used at an industrial scale today. However, there are also some emerging applications that are presented in the following section.

#### *2.3.9.1 Production of titanium*

Titanium is commercially produced through the Kroll or the Hunter process, both of which are thermochemical processes based on the reduction of $TiCl_4$ [50]. These processes are however expensive and not very energy efficient. Therefore, new methods for titanium production have been studied during the last several decades. One kind of process that is being developed are electrochemical processes that convert $TiO_2$ into Ti through molten salts. For example, the Cambridge FFC method uses molten $CaCl_2$, and other methods have used melts of NaCl, KCl, and NaF. However, these processes are not commercially implemented yet and it is expected that it will take several years before they are.

#### *2.3.9.2 Molten salts for thermal energy storage*

Molten nitrate salts are currently being used as a medium for thermal energy storage in concentrated solar power plants [51]. These salts are thermally stable up to 600°C but there is an interest to use molten salts at higher temperatures to reach higher efficiencies. Different mixtures of chloride salts are being studied for this purpose. The molten salts should have several desired properties, such as a low melting point, high heat capacity, and high thermal conductivity. Some chloride salts that have been identified to have suitable properties are listed in Table 1. The downside of using chloride salts is that they are corrosive if any oxygen or water is present in the salt. Therefore, they must be treated to remove these compounds before being used.

Table 1. Salt mixtures in molten salts for thermal energy storage.

| Salt mixture (wt%) | | Reference |
|---|---|---|
| $ZnCl_2$ | 68.6 | [51] |
| KCl | 23.9 | |
| NaCl | 7.5 | |
| KCl | 62.5 | [51] |
| $MgCl_2$ | 37.5 | |
| NaCl | 39.6 | [52] |
| $MgCl_2$ | 39 | |
| $CaCl_2$ | 21.4 | |
| $MgCl_2$ | 48.6 | [52] |
| KCl | 30.9 | |
| NaCl | 20.5 | |

#### 2.3.9.3 Carbon capture through mineral carbonation

Aqueous solutions of metal cations, such as concentrated brines, can be used to absorb carbon dioxide through a mineral carbonation reaction [53]. Gaseous carbon dioxide is absorbed by the solution where it dissolves into a reactive, ionic form. The metal cations will react with the dissolved $CO_2$ and form an inorganic material. For example, calcium ions form calcium carbonates, which have a high value in several industries. Finding solutions with metal cations has been limiting the implementation of large-scale processes for this application.

# 3 Method

The methodology flowchart for this thesis is shown in Figure 9. First, salt recycling methods and salt applications were researched. Based on the literature study, a salt recycling method was chosen. The recycling method predictive capability in Aspen Plus V12.1 was validated, and the process was then constructed. Energy integration with a waste-to-energy plant was performed and the process was further evaluated based on energy consumption. Finally, a sensitivity analysis was performed.

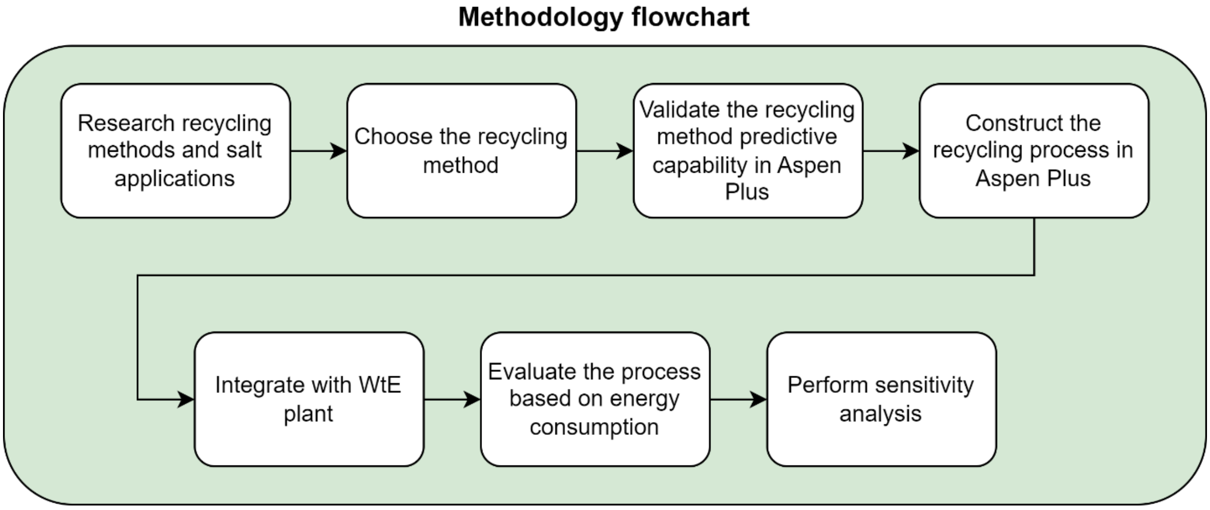


*Figure 9. A flowchart over the methodology in this thesis. The methodology is divided into seven steps: literature study, choosing the recycling method, validation, construction of the process, heat integration, evaluation of the process, and sensitivity analysis.*

The literature review showed that thermal based brine treatment is the most suitable method to handle the brine because it can handle high salt concentrations and has the possibility to separate the individual salts through crystallisation. It is desirable to separate the individual salts because there are more areas of applications for pure salts than for mixed salts, as shown in the literature study regarding salt applications. Furthermore, there is validation data available from NOAH which can be used to validate the settings in Aspen if a similar process is simulated. The thermal based treatments also require large amounts of energy which provides an opportunity for heat integration with a WtE plant.

Aspen Plus V12.1 was chosen as the simulation software for the salt recycling process because previous studies have used it for similar purposes. Aspen Plus uses basic engineering relationships such as balance equations for thermodynamic properties and thermodynamic relationships for reactions [54]. This allows a prediction of the behaviour for the process and gives an indication of the energy demand for the process. To see if the software provides reliable results, experimental data from literature and NOAH was used for validation. Data used in Aspen for salt solubility was validated by plotting two solubility curves for each salt in Aspen, one with water as solvent and one with inlet brine as solvent, and comparing it with data found in literature. To further validate Aspen's predictive capability of product compositions from the chosen salt recycling method, a model of NOAH's existing pilot-scale process (Resalt), which uses a similar brine treatment method as the chosen one, was constructed in Aspen and simulated. The simplified calcium-rich brine presented in Figure 2 was used for the simulations to reduce the computational time. The result from this simulation was compared with the experimental data obtained from the real process. Further, the complex brine composition containing 0.12 wt% of other components such as sulphur, was simulated to assess the effect and validate the decision of neglecting the complex composition.

The aim of the design of the salt recycling process was to obtain the purest possible salts. The design was based on the solubilities of the salts. Temperature levels in the process were based on available heat streams from Gärstadverket and the pressures were adjusted to meet the aim. It was assumed that the lowest feasible pressure level was 0.14 bar. With lower pressures, the size of the equipment and associated costs increase. Since the Resalt process that was used for validation had 0.14 bar in the last evaporator, see Figure 7, it is used as the lowest pressure limit in this study. The minimum temperature difference in evaporators was assumed to be 7℃ and in heat exchangers it was assumed to be 12℃. The minimum temperature differences were based on Gärstaverkets temperature difference in the heat exchanger for the district heating and previous experiences. It was assumed that there are no energy losses in the process except for the compressors. Different configurations were evaluated to minimise energy consumption and maximise product streams.

Heat integration with an existing waste-to-energy plant was done by simulating heat streams from Gärstadverket as heat sources in the process. Data was provided by Tekniska verken, see Figure 3. Based on the results from the simulation, the process was evaluated by analysing the net energy loss in the waste-to-energy plant when integrating the salt recycling process. This was used as a metric to evaluate when the salt recycling process is motivated together with a brief economic calculation. The environmental benefits and drawbacks of the salt recycling process were also briefly discussed.

The brief economic calculation included the loss in revenue from decreased heat and electricity production and the income from selling salt products. It was assumed that the process is operating 7800 h/year and the hours are evenly distributed over the year. Prices for district heating were taken for 2023 from Tekniska verken's website [55]. Electricity prices were taken from Nord Pool for the area SE3 for both 2022 and the average value for the prices from 2013 to 2022 [56]. The prices for NaCl and $CaCl_2$ are based on an interview with an actor trading with salts and it is assumed that the mixed salt with NaCl and KCl has the same market prices as NaCl. Further details can be found in Appendix B.

Different brine concentrations and compositions were used for the sensitivity analysis. The total salt concentration for the calcium-rich brine was varied between 6 wt% and 12 wt%. It was analysed how the mass flow and the net energy loss in Gärstadverket was affected. The sensitivity analysis for brine composition was performed by comparing the simulation results from the calcium-rich brine with the sodium-rich brine. Changes in the composition of the product streams were studied. Further, the process was optimised for the sodium-rich brine by adjusting the pressure and another configuration was proposed. The net energy loss was compared between the proposed processes.

## 3.1 Set up of the Aspen model

To start the simulation with Aspen Plus, the template "Chemicals - Electrolytes with Metric Units" was chosen. NaCl, $CaCl_2$ and KCl are strong electrolytes and electrolytes cannot be assumed to be ideal due to interaction between the ions [54], [57]. In Aspen, electrolytes can be simulated with the model "ELECNRTL", and this is the default property model by Aspen when choosing the template "Chemicals - Electrolytes with Metric Units" [54]. ELECNRT can handle aqueous and mixed-solvent systems at any concentration [58]. The model is based on the like-ion repulsion assumption and the local electroneutrality assumption.

For the component list, water was provided from the template and NaCl, $CaCl_2$ and KCl were added. With the help of the tool "Electrolyte wizard" in Aspen, the ionic species and salt that can be generated from the base components were automatically defined [57]. The simulation approach was chosen to be true component. This means that Aspen solves both equations describing solution chemistry and unit operation equations at the same time. If apparent component should be chosen instead, Aspen Plus would be modifying the physical properties and the state of the molecules, as ions or salt, would not been seen by the operation units.

The process in Aspen was built using models of the required equipment from the model palette, and material streams were used to represent the flows. The evaporators were modelled using *Flash2*. This is a two-outlet separator that can be used to model e.g., evaporators by using rigorous vapor-liquid equilibrium calculations. For heat exchangers, the model *HeatX* was used. *HeatX* models a two-stream heat exchanger, and it was set to operate counter-currently. The solid-liquid separation was modelled using *CFuge,* which is a model of a centrifuge. It was set to be a decanter centrifuge and the residual moisture content was set to 10 wt% on dry basis. The value for moisture content is based on a real decanter centrifuge where the moisture in the salt does not exceed 10 wt% [59]. Compressors were modelled using *Compr* where the isentropic efficiency was set to 0.85, because this is a typical efficiency for compressors [60]. Pumps were modelled using *Pump* and throttles using *Valve*. *Compr, Pump* and *Valve* were specified by the discharge pressure. Since the process is operating below atmospheric pressure, the solid streams also need to be adjusted to atmospheric pressure before being discharged from the process. This is not simulated in Aspen, but instead calculated by hand as sluices. It is assumed that it will be emptied one time a day, and the volume of the sluice is 10% larger than the volume of the salt products produced during one day.

# 4 Results

The simulation results are presented and briefly discussed in the following section. First, it is shown how the results are validated by comparison with experimental data from literature and from Resalt. Then, the salt recycling process is designed and it is shown how pressure and temperature levels were chosen. It is explained in chapter 3 how the salt recycling process was selected. The product streams and the energy demand in the process is presented in the following section. Internal energy integration is further performed, and the new energy demand is presented together with the impact it has on Gärstadverket. A brief economic analysis of the energy costs and income from selling salts is presented. Finally, a sensitivity analysis is presented where the brine concentration and composition are varied.

## 4.1 Validation of the predictive capability in Aspen

Validation of the simulation results from Aspen was first performed by comparing the solubilities of pure salts with literature values. Then the process was evaluated by comparing the results with experimental data from Resalt.

### 4.1.1 Validation of data used in Aspen for salt solubility

Solubility curves that were produced in Aspen for the different salts when the solvent was water are shown in Figure 10 and are compared with the literature.

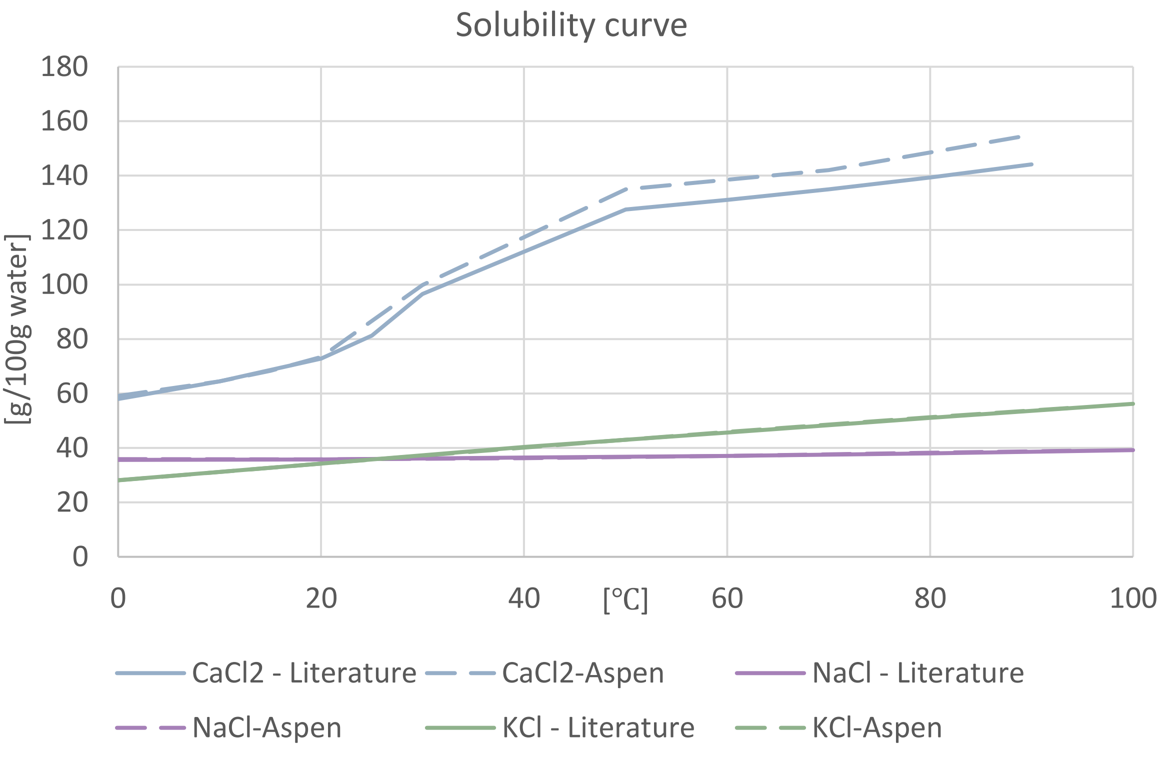


*Figure 10. Solubility curves for the salts KCl, NaCl and $CaCl_2$ in water. Comparison between values obtained from Aspen and literature,* [13], [14].

As shown in Figure 10, both NaCl and KCl are in good agreement with the literature, but for $CaCl_2$ the agreement with the literature is slightly worse. Why $CaCl_2$ does not match as well may be because Aspen is missing equilibrium constants for $CaCl_2$. Instead of using equilibrium constants, Aspen calculates the solubility using minimisation of Gibbs free energy of the participating components [57].

Further, the solubility curves of the salts when the solvent is the inlet brine were produced by Aspen and is shown in Figure 11 together with the earlier results.

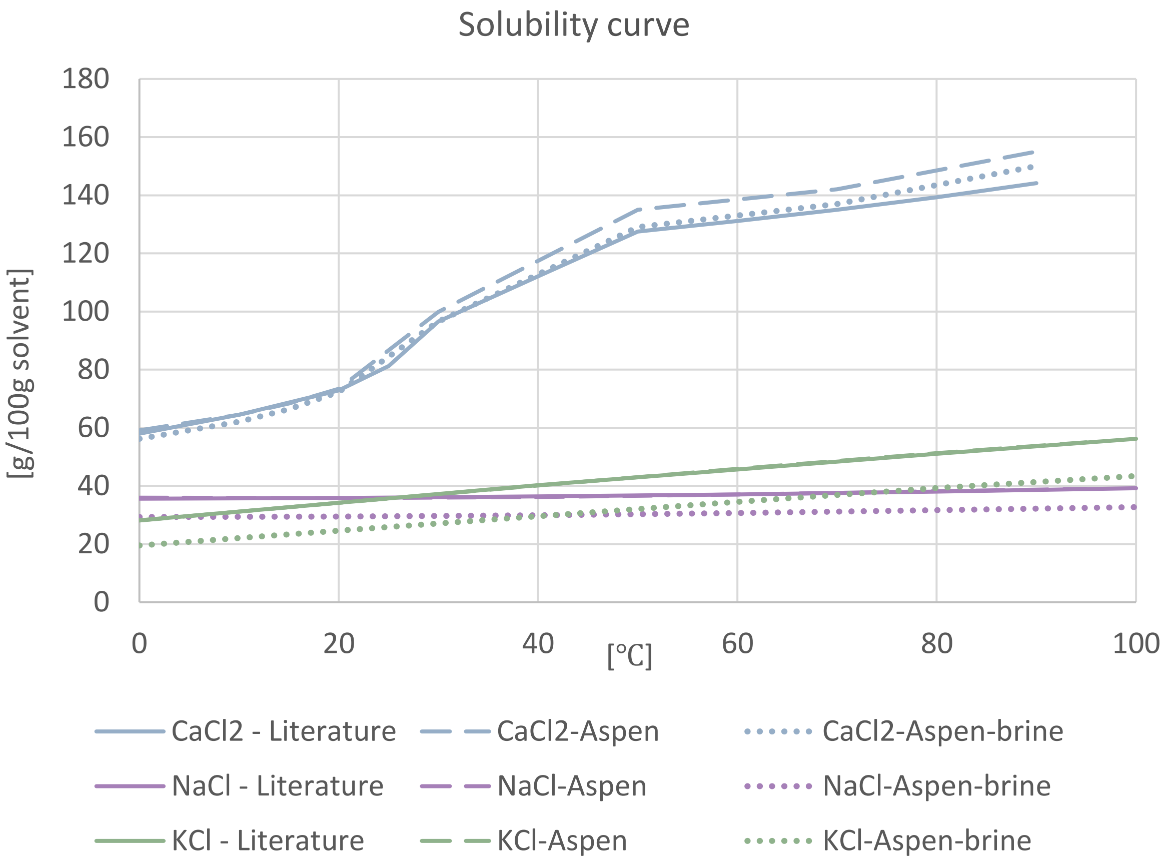


*Figure 11. Solubility curves for the salts KCl, NaCl and $CaCl_2$ in water (literature* [13], [14] *and Aspen) and inlet concentration of the brine (Aspen).*

As can be seen in Figure 11, using the inlet brine as the solvent has an impact on the solubility of the salts, but it does not affect the trend of the curves. It lowers the solubility curves and makes NaCl and KCl solubility curves slightly more similar to each other.

### 4.1.2 Validation of product composition for the chosen salt recycling method

The Resalt process was built in Aspen according to the process flow chart shown in Figure 12. It is unknown how the solid-liquid separation-step was performed in the Resalt tests, but it is simulated as a decanter centrifuge in Aspen in this work.

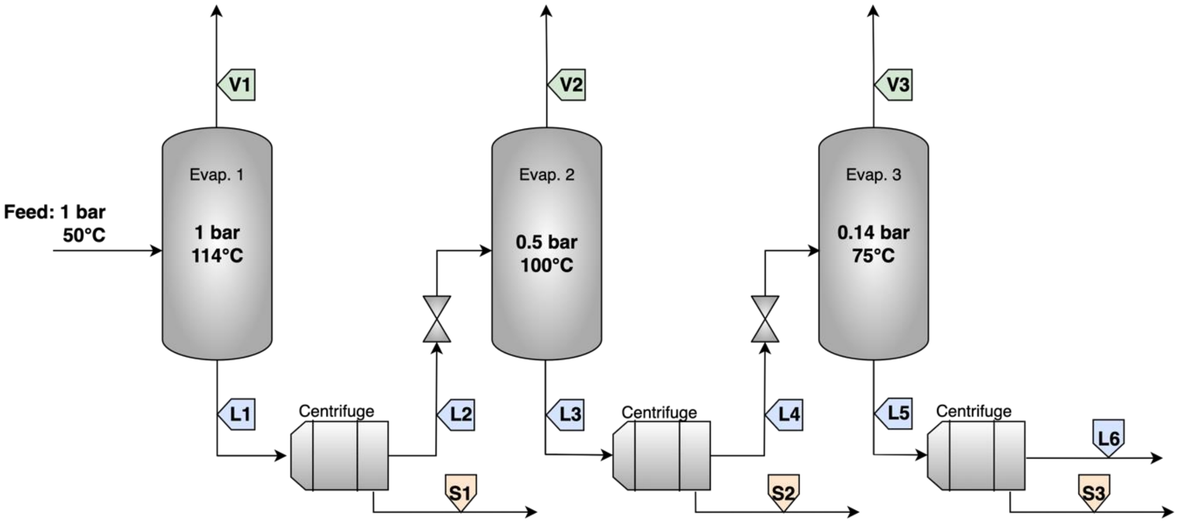


*Figure 12. Flowchart of the Resalt process simulated in Aspen, the streams marked with V are vapour, L are liquid, and S are solid.*

S1, S2, and S3 in Figure 12 are the solid fractions received after the solid-liquid separation after each evaporator and L2, L4, and L6 are the liquid fractions. In Figure 13, the dark-coloured bars represent the composition of salt in the solid products from the simulation with the simplified brine, see section 1.1 for explanation. The light-coloured bars are the experimental values.

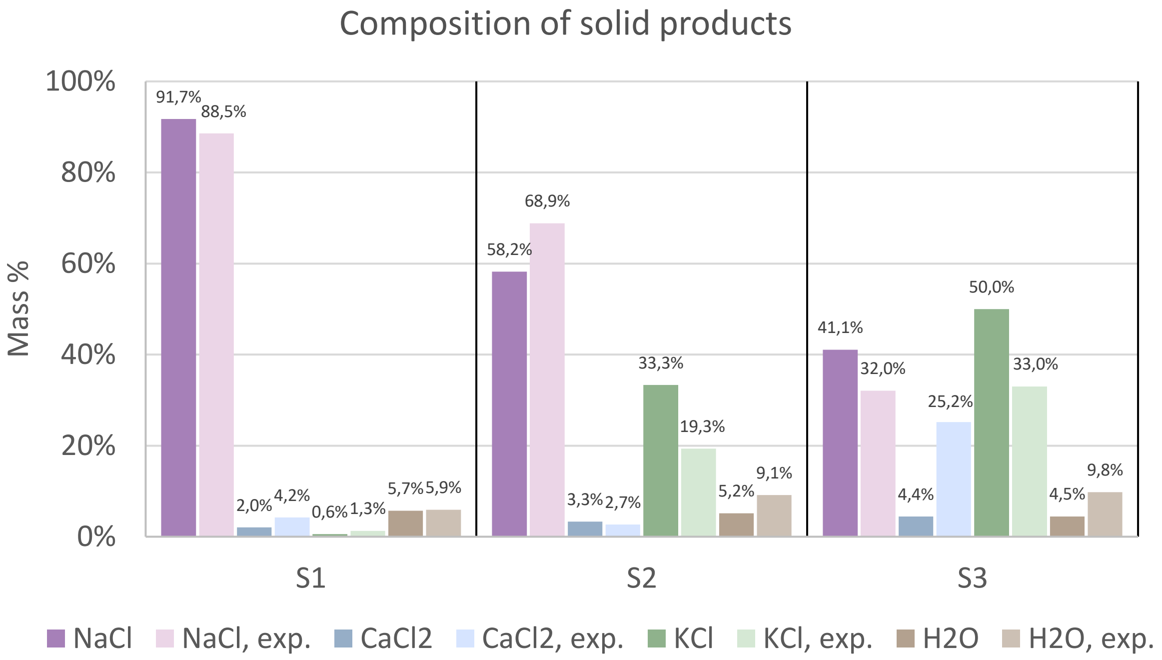


*Figure 13. Comparison of composition in the solid products from a simulation with simplified brine and the experimental data. The dark-coloured bars are for the result from the simulation and the light-coloured bars are from the experimental data shown in Figure 7.*

The simulation results fit well with the experimental results for S1, but there are larger deviations in S2 and S3. This is reasonable because simulation errors will accumulate throughout the process so more steps will give more uncertainties. It should be noted that the moisture fraction in the solid product was defined by the decanter centrifuge to 10 wt% in the simulation, while it is unknown how the solid-liquid separation was performed in Resalt. This brings uncertainty to the results. Another uncertainty is that a synthetic brine was used for the second and third evaporation steps in the experimental tests, which also could contribute to the deviations. However, the overall trend of the simulations fits the experimental data.

In Figure 14, the comparison of simulated results and experimental results is shown for the liquid products. Just as for the solid products, there are some deviations, but the general trend is similar for the simulated and the experimental results. Overall, the results are shown to be well-aligned with the experimental results. Thus, the created Aspen model is deemed to predict the solid and liquid properties well with the chosen settings and databases.

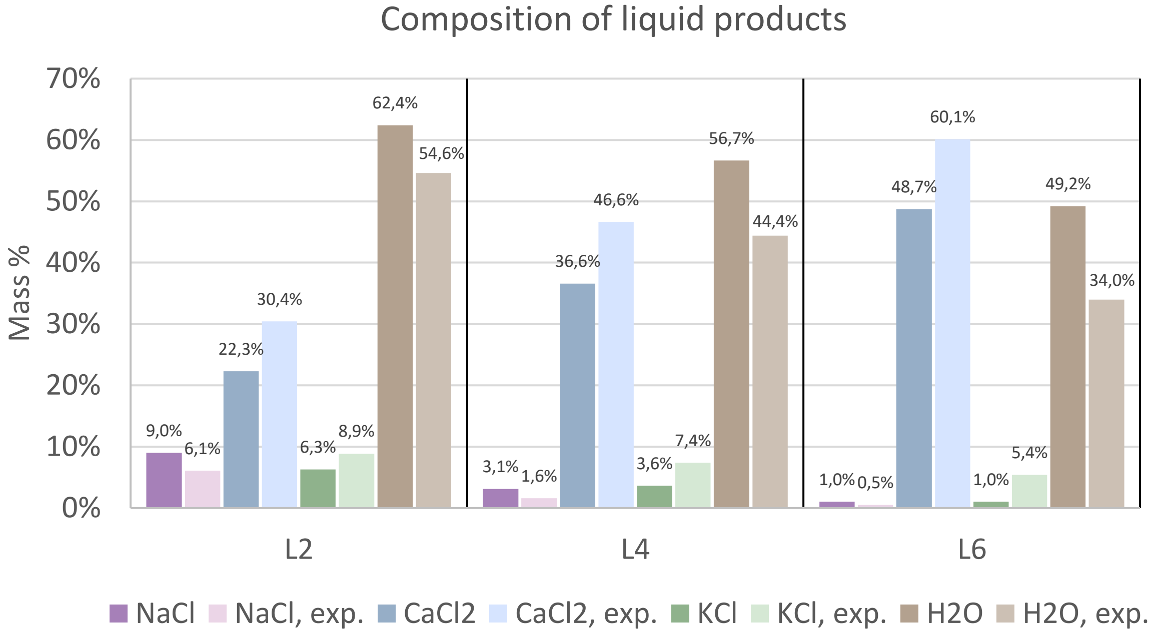


*Figure 14. Comparison of composition in the liquid products from a simulation with simplified brine and the experimental data. The dark-coloured bars are for the result from the simulation and the light-coloured bars are from the experimental data shown in Figure 7.*

The results shown in Figure 13 and Figure 14 were simulated with a simplified brine. The simulation results for the first solid and liquid products (S1 and L2) with the complex brine composition are shown in Figure 15. No experimental data was available for the other streams but the simulated results for the other streams are shown in Appendix C.

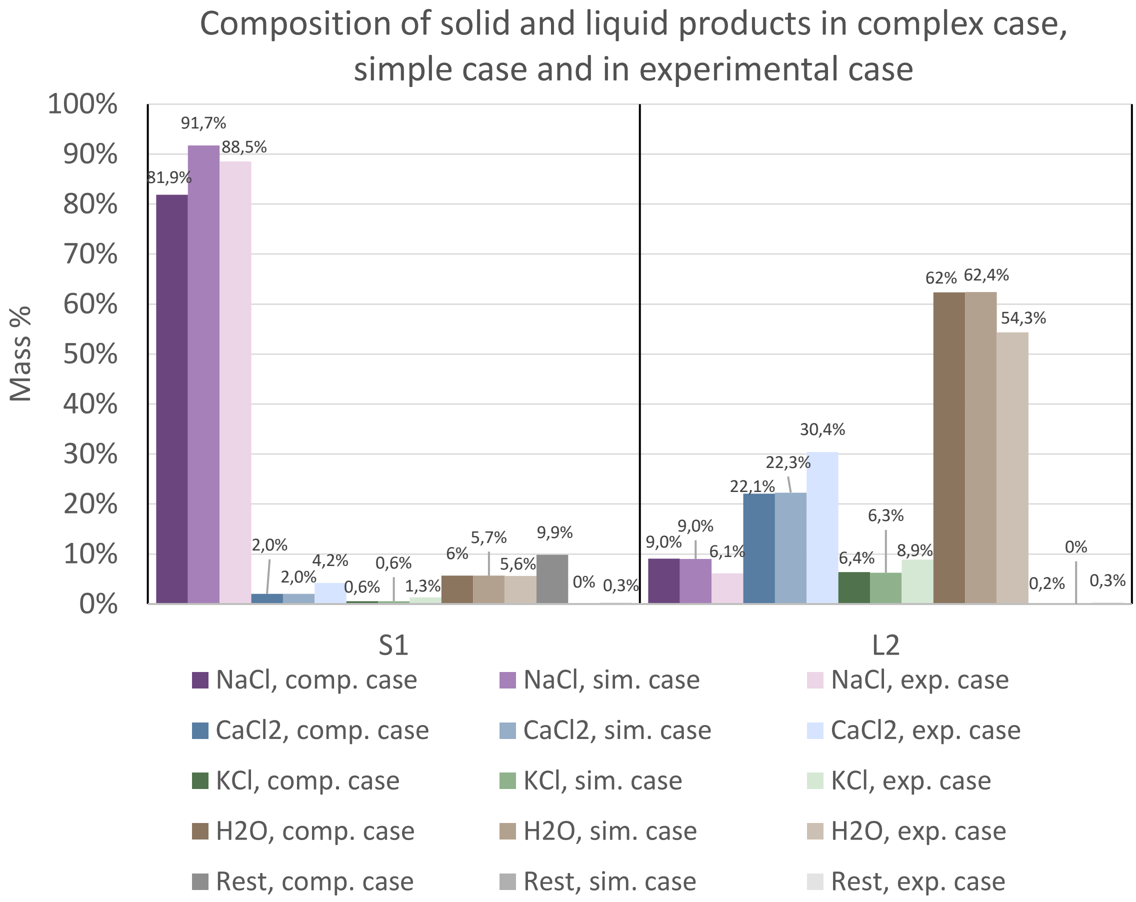


*Figure 15. Comparison of composition for the first solid and first liquid product. The darkest-coloured bars are for the result from the simulation with complex brine composition, the middle bars are for the result from the simulation with the simplified brine composition and the lightest-coloured bars are from the experimental data.*

The darkest bars are the results from the simulation with the complex (comp.) case, the middle bars are for the simplified (sim.) case, and the light bars are for the experimental (exp.) case. The fraction named *Rest* includes all components that are not NaCl, KCl, $CaCl_2$, or $H_2O$. For the complex brine composition case, most of the rest fraction is $CaSO_4 \cdot \frac{1}{2} H_2O$. There is not a large difference between the complex and simple brine, except for the large rest fraction in S1. The reason for this is the presence of sulphates in the complex brine composition case, which easily precipitate as $CaSO_4 \cdot \frac{1}{2} H_2O$. However, sulphates can be removed with a pre-treatment step. Therefore, the simplified brine is used for further simulations, and it is assumed that sulphates are removed before the salt recycling process.

## 4.2 Design of the model

Based on the validation process shown in Figure 12, a similar process was designed but instead of three evaporators, only two were used because it was deemed to be sufficient with regards to the aim of extracting salt products with market value. The first evaporator focused on getting the purest possible product stream of solid NaCl, while the second evaporator focused on getting as much crystallised NaCl and KCl in one product stream and as pure $CaCl_2$ as possible in the liquid product stream, see Figure 16. NaCl and KCl have similar solubilities, as shown in Figure 11, which means that they are difficult to crystallise separately when they have similar concentrations. In the first evaporator, the concentration of NaCl is significantly higher than KCl, which is why it is possible to retrieve a pure crystallised stream of NaCl. However, the concentration of NaCl and KCl is similar in the second evaporator, which is why a mixed NaCl/KCl salt is formed. To separate the mixed salt, a different technique needs to be used [23].

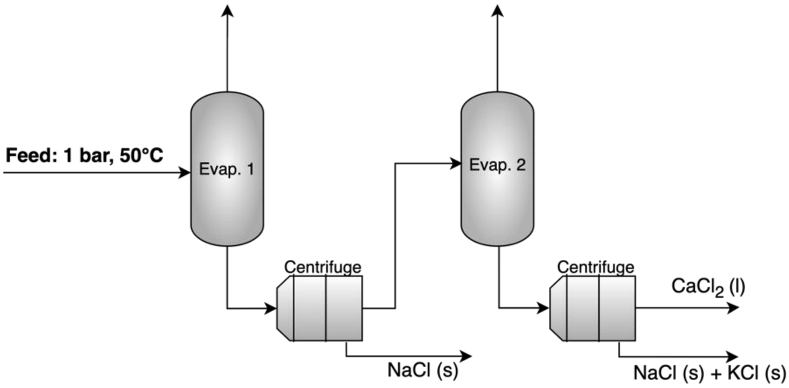


*Figure 16. Flowchart for the designed model of the process, where two evaporators are used to get three products streams.*

### 4.2.1 Temperature and pressure levels

The temperature in the first evaporator was set based on the desired heat integration with Gärstadverket. Based on the available information, it was chosen to integrate the salt recycling process with boiler 5 because it has the highest operating hours. The heat integration is done by sending a part of the flow from the turbine outlet to the salt recycling process, where it will be condensed and then returned to the steam cycle after the condenser, see Figure 17.

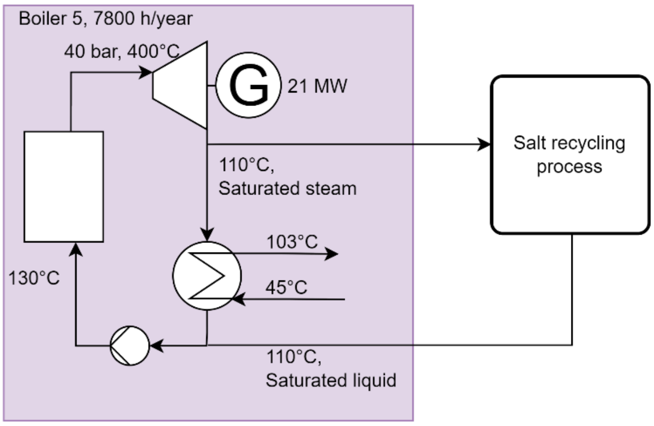


*Figure 17. How the salt recycling process is connected to boiler 5 at Gärstadverket.*

To not affect the actual production of electricity, it is planned to take the heat from the flow out of the turbine with a temperature of 110°C. However, this will have an effect on the district heating production because some of the stream will go to the salt recycling process instead of producing district heating. Since the minimum driving force for heat exchange in the evaporator was set to 7°C, the temperature in evaporator 1 was set to be 103°C.

The starting point for the first evaporator was to crystallise as much NaCl as possible, without crystallising KCl. Therefore, the pressure was changed until the pressure was found where the maximum amount of NaCl solid products was received without crystallising KCl, while the temperature was kept constant at 103°C. In Table 2, the result for the optimal pressure for 103°C is presented and compared with the simulation results from the first evaporator in the Resalt process, see the flowchart of the simulated Resalt process in Figure 12.

*Table 2. Pressure, temperature, heat demand and mass flow of solid salt from the first evaporator in the simulated Resalt process and in the designed model with the optimal pressure value for 103°C in the first evaporator.*

| Evaporator 1 | | | | | |
|---|---|---|---|---|---|
| Case | Pressure [bar] | Temperature [°C] | Heat demand [MW] | Mass flow of NaCl [kg/h] | Mass flow of KCl [kg/h] |
| Resalt evap. 1 | 1 | 114 | 5.8 | 106 | 0 |
| Optimal pressure when the temperature is 103°C | 0.65 | 103 | 5.9 | 186 | 0 |

As shown in Table 2, 0.65 bar was the optimal pressure for the first evaporator when the temperature was set to 103°C. Therefore, these conditions were set for the first evaporator while the second evaporator was tested with different conditions, see Table 3. The optimal temperature/pressure refers to the condition where as much NaCl and KCl as possible are crystallised, with no $CaCl_2$.

*Table 3. Pressure, temperature, heat demand and mass flow of solid salt from the second and third evaporator in the simulated Resalt process and in the second evaporator in the designed model with different optimal values. Evaporator 1 is kept constant at 0.65 bar and 103℃.*

| Evaporator 2, with evaporator 1 at 0.65 bar and 103℃ | | | | | |
|---|---|---|---|---|---|
| Case | Pressure [bar] | Temperature [℃] | Heat demand [MW] | Mass flow of NaCl [kg/h] | Mass flow of KCl [kg/h] |
| Resalt evap. 2 | 0.5 | 100 | 0.25 | 89 | 95 |
| Optimal temperature when the pressure is 0.5 bar | 0.5 | 132 | 0.63 | 130 | 143 |
| Optimal pressure when the temperature is 100℃ | 0.22 | 100 | 0.56 | 130 | 143 |
| Resalt evap. 3 | 0.14 | 75 | 0.41 | 122 | 136 |
| Optimal temperature when the pressure is 0.14 bar | 0.14 | 86 | 0.54 | 129 | 143 |

As shown in Table 3, the three cases with optimal conditions have similar results for the mass flows of NaCl and KCl. Since the availability of lower temperature heat is higher, the process design for the second evaporator was set to 0.14 bar and 86℃.

### 4.2.2 Products and energy demand

A process flow diagram of the resulting process, with the first evaporator, Evap.1, at a temperature of 103℃ and pressure of 0.65 bar and the second evaporator, Evap. 2, at a temperature of 86℃ and a pressure of 0.14 bar, is shown in Figure 18.

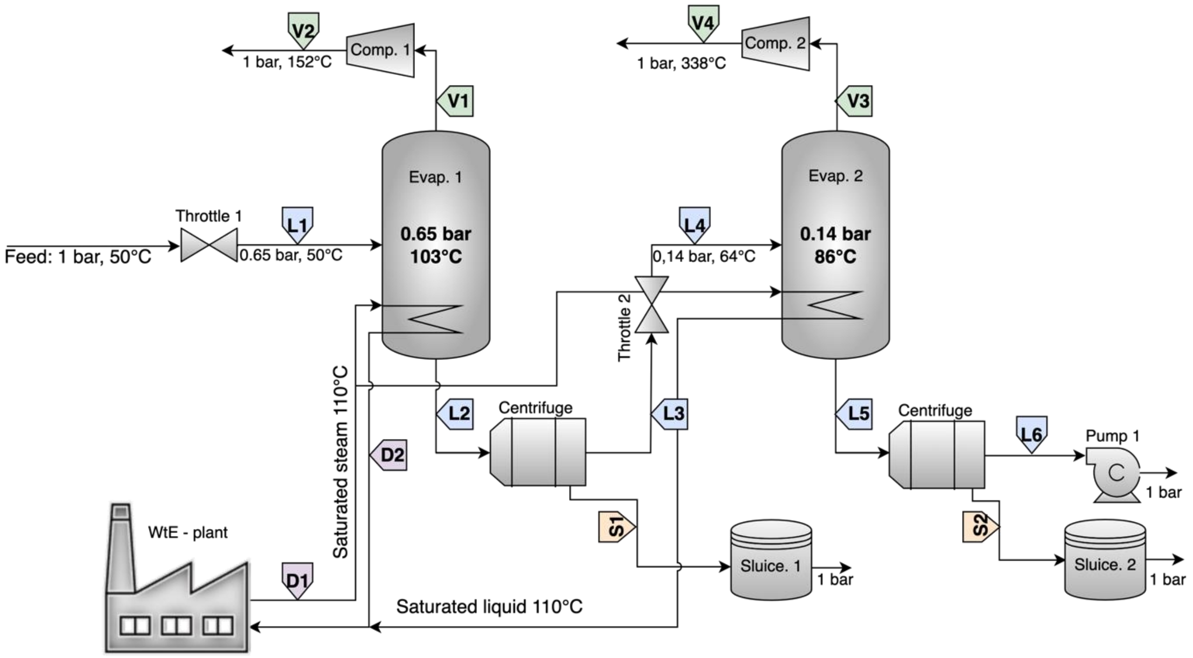


*Figure 18. Flowchart of the designed salt recycling process and integration with Gärstadverket. The streams marked with V are vapour, L are liquid, S are solid and D stands for district heating streams.*

The vapour streams (V1 and V3) are compressed to 1 bar (V2 and V4) before leaving the process because otherwise, their pressure would be lower than atmospheric pressure. Similarly, the liquid stream (L6) that leaves the process is pumped up to 1 bar and the crystallised salt products (S1 and S2) go through sluices where the pressure is increased to 1 bar. The temperature, flow rate and composition of the streams are shown in Table 4.

*Table 4. Temperature, flow and composition of the streams from the salt recycling process.*

| Composition of streams | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Stream | Temp. [°C] | Flow [kg/h] | $H_2O$ [wt%] | $Na^+$ [wt%] | $Ca^+$ [wt%] | $K^+$ [wt%] | $Cl^-$ [wt%] | NaCl(s) [wt%] | KCl(s) [wt%] |
| L1 | 50 | 10 622 | 91 | 1.2 | 1.8 | 0.73 | 5.7 | - | - |
| L2 | 103 | 2232 | 55 | 2.4 | 8.5 | 3.5 | 22 | 8.3 | - |
| L3 | 103 | 2028 | 60 | 2.6 | 9.3 | 3.8 | 24 | - | - |
| L4 | 64 | 2028 | 60 | 2.6 | 9.3 | 3.8 | 24 | - | - |
| L5 | 86 | 1144 | 30 | 0.13 | 17 | 0.21 | 30 | 11 | 12 |
| L6 | 86 | 845 | 39 | 0.17 | 22 | 0.27 | 39 | - | - |
| V1 | 103 | 8390 | 100 | - | - | - | - | - | - |
| V2 | 152 | 8390 | 100 | - | - | - | - | - | - |
| V3 | 86 | 884 | 100 | - | - | - | - | - | - |
| V4 | 338 | 884 | 100 | - | - | - | - | - | - |
| S1 | 103 | 204 | 5.5 | 0.23 | 0.85 | 0.35 | 2.2 | 91 | - |
| S2 | 86 | 299 | 3.6 | 0.015 | 2.0 | 0.024 | 3.5 | 43 | 48 |

The composition of the product streams in terms of salt can be seen in Figure 19. This is the composition when the solid product has been dried from excess water.

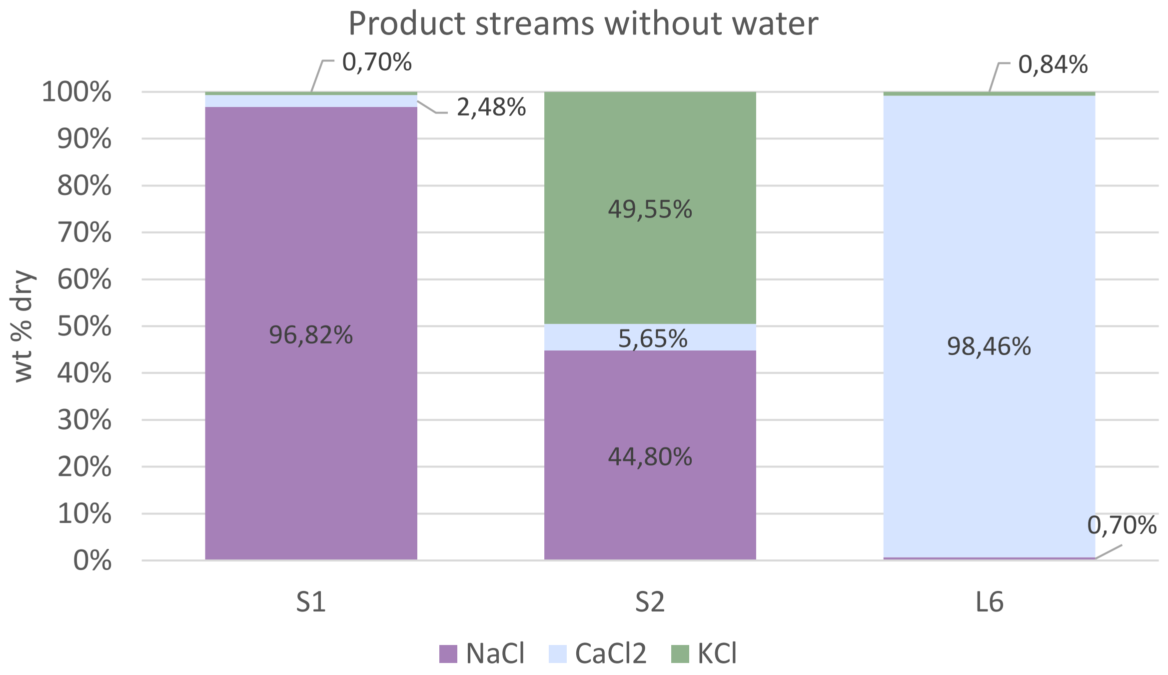


*Figure 19. Dewatered product streams for when evaporator 1 operates at 103°C and 0.65 bar and evaporator 2 at 86°C and 0.14 bar. S1 is the solid product stream from Evap. 1 and S2 and L6 are the solid and liquid product streams from Evap. 2.*

The heat demand for the evaporators and the electricity consumption for the other equipment is presented in Table 5. The values for evaporators, compressors and pump are given by Aspen and the values for sluices are calculated, see Appendix D for the calculations. The energy consumption for centrifuge is taken from literature [61].

*Table 5. Heat and electricity consumption for different equipment in the salt recycling process.*

| Equipment | Energy consumption [kW] |
|---|---|
| Evaporator 1 | 5862 |
| Evaporator 2 | 537 |
| Total heat demand | 6399 |
| Compressor 1 | 215 |
| Compressor 2 | 120 |
| Centrifuge 1 & 2 [61] | 65 + 65 |
| Pump 1 | 0.04 |
| Sluice 1 | 0.6 |
| Sluice 2 | 3.3 |
| Total electricity demand | 469 |

In addition to the continuous energy demand, energy will also be required for vacuum pumps during the start-up of the process since the process operates below atmospheric pressure. This energy demand was not accounted for, as this energy demand is assessed to be outside the scope of this study. The fact that the process operates at low pressures also brings additional challenges when it comes to equipment sizing and related investment cost. When the pressure is decreased, the volume flow increases to keep the same mass flow in the process, which will further affect the sizing of equipment. Over throttle 1 the volume flow does not change significantly since the fluid is in liquid state. However, over throttle 2 there is a volume flow increase with a factor of 614. Before throttle 2, the volume flow is 0.00042 $m^3$/s and after it is 0.26 $m^3$/s. This is because 4% of the fluid transforms into gas when the pressure is decreased.

### 4.2.3 Internal heat integration

The heat demand for the process is reduced if some of the required heat is provided through the compressed vapour streams (V2 and V4) from the evaporators. Since the vapour streams need to be compressed to at least 1 bar before leaving the process, the increased temperature of the streams can be used as a heat source. A process flow diagram with internal heat integration is shown in Figure 20. The compressed vapour from Evap. 2 (V4) can release heat inside Evap. 2 because it has enough energy to supply all of the required heat when it is compressed to 1 bar. However, it will not be possible to use internal heat to cover the energy demand during the start up of the process. Therefore, an external heat source, such as heat from a WtE plant, will be needed during start-up, see schematics in Figure 18. The compressed vapour from Evap. 1 (V2) does not have enough energy to supply all of the heat demand when it is compressed to 1 bar. Therefore, external heat from the WtE plant will be necessary for the first evaporator, even if the vapour is compressed to 1 bar. Hence, the configuration for heat exchange in Evap. 1 is different from Evap. 2. See how the process was modelled in Aspen in Appendix E.

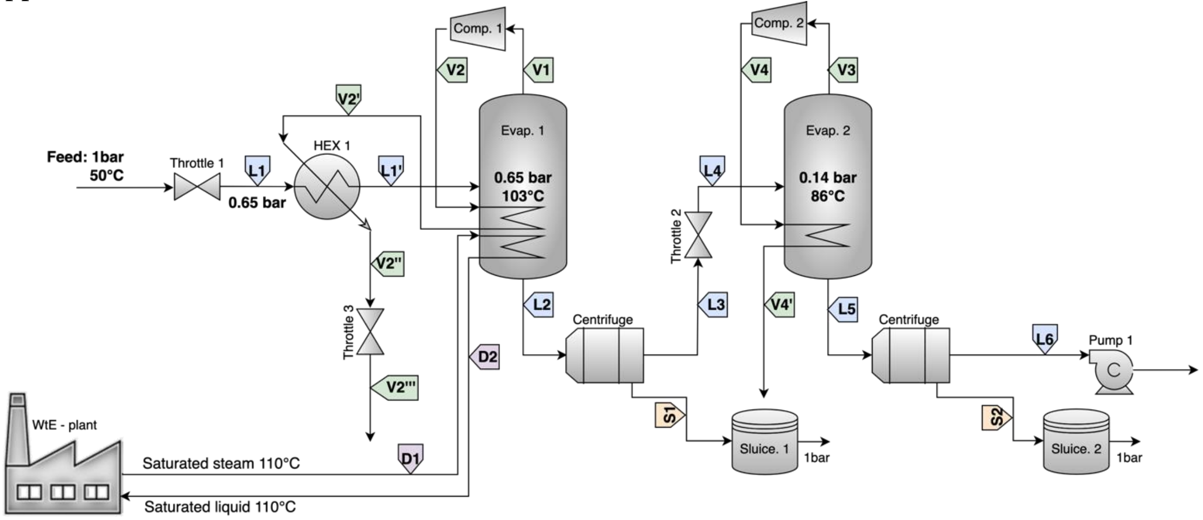
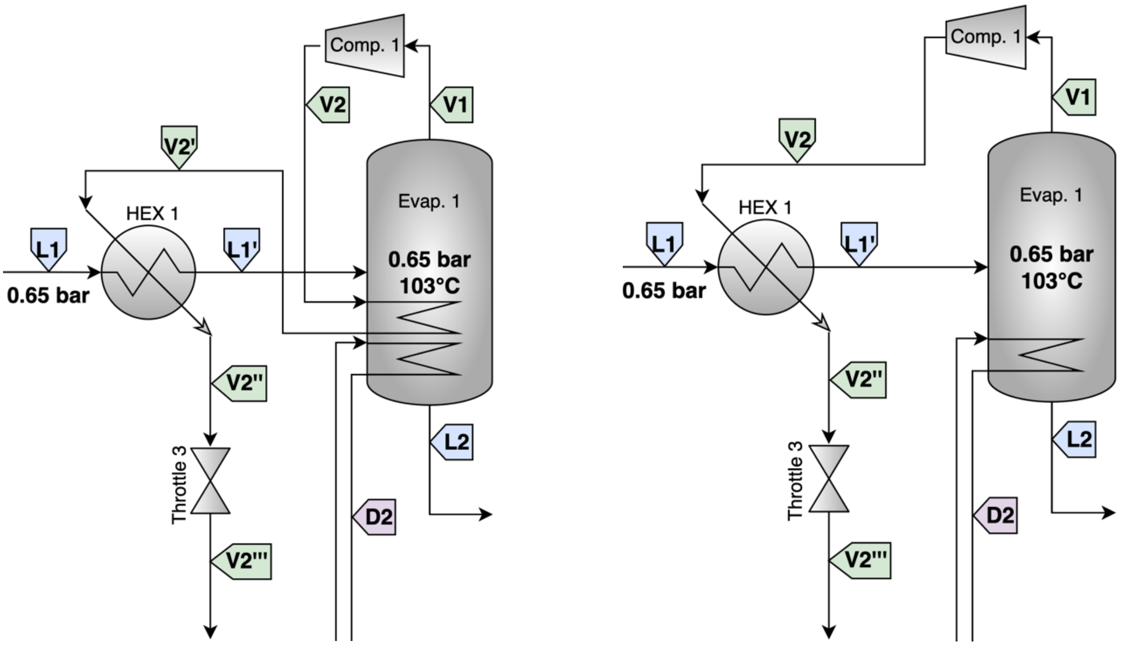


*Figure 20. Flowchart of the salt recycling process with internal heat integration. The streams marked with V are vapour, L are liquid, S are solid and D stands for district heating streams.*

In Figure 20, vapour V2 first enters Evap. 1, where it can release heat until it reaches 110°C, i.e. the same temperature that the external heat source has. Then, vapour (V2') exits Evap. 1 and enters heat exchanger 1 (HEX 1) where it pre-heats the feed. This is one possible configuration. Another possibility is that the compressed vapour V2 enters the heat exchanger, HEX 1, directly, and never takes part in the heat exchange inside of Evap. 1. The two possible configurations are shown in Figure 21, where the configuration on the left side (Configuration (A)) is the same as in Figure 20, and the configuration on the right side (Configuration (B)) is the other one. Configuration (B) is however only possible if no crystallised salt is formed in the heat exchanger. If there is crystallised salt in the stream that exits the heat exchanger (L1'), configuration (A) will have to be applied because crystallised salt would clog the heat exchanger. Technically, a third configuration where vapour (V2) enters Evap. 1 and then is discharged, is also possible. In other words, this would be the same configuration as in Evap. 2. However, this configuration requires that the flow that leaves Evap. 1, (V2') has a temperature of at least 110°C, which means that there would be a significant heat loss in the discharged stream. As the purpose of this part of the thesis is to improve the energy efficiency of the process, this configuration will not be considered.



(A) (B)

*Figure 21. Flowcharts of two possible configurations for the first evaporator.*

If the discharge pressure of the first compressor (Comp. 1) is increased to more than 1 bar, more electricity will be needed for the compression, but it will be possible to recover more heat, so less external heat will be needed. The electricity demand in the compressor versus the heat that has to be supplied externally in Evap. 1 depending on the discharge pressure of Comp. 1 is shown in Figure 22.

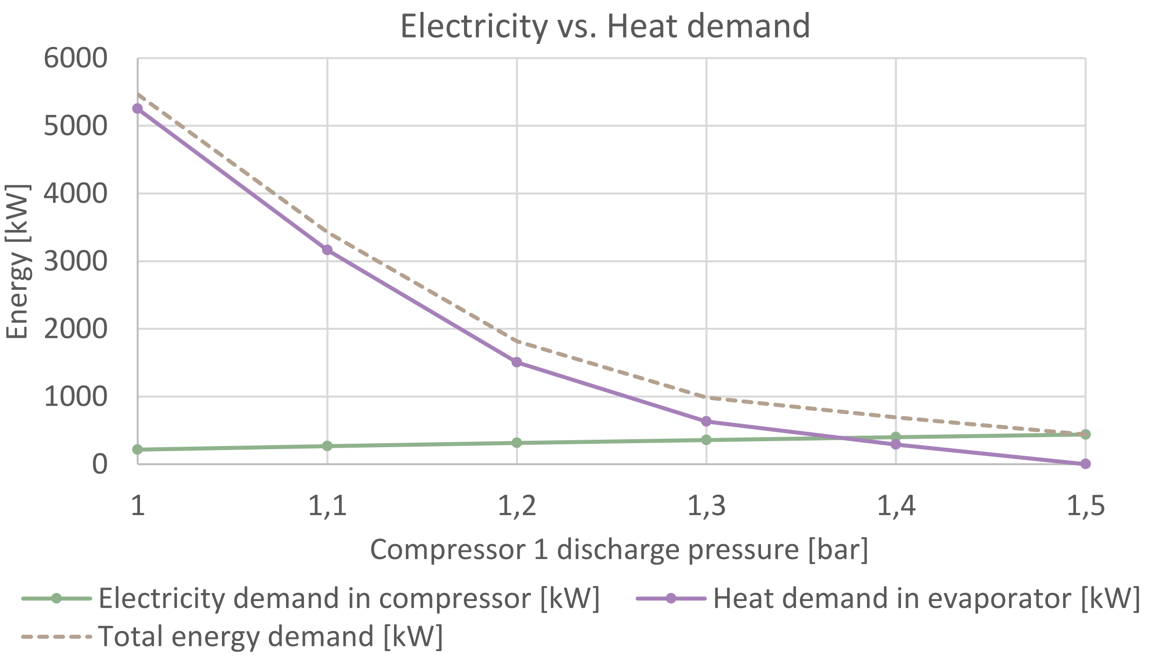


*Figure 22. Electricity demand in compressor 1 and heat demand in evaporator 1, based on discharge pressure of compressor 1. Configuration B is used up to 1.3 bar, configuration A is used for pressures over 1.3 bar.*

It can be seen in Figure 22 that there is enough heat in the vapour to cover the entire heat demand of Evap. 1 when the steam is compressed to 1.5 bar in Comp. 1. This is also the pressure that gives the lowest total energy demand. When the discharge pressure of Comp. 1 is above 1.3 bar, there will be enough energy to evaporate so much water from the feed that some salt will start to crystallise. When this is the case, it will not be possible to use configuration (B).

The cases where the discharge pressure of Comp. 1 is 1 bar, 1.3 bar, and 1.5 bar were studied in more detail. 1 bar and 1.5 bar were chosen because these are the minimum and maximum pressures and 1.3 bar was chosen because it is the highest pressure before configuration (A) in Figure 21 will be required. The results for the total electricity demand, the total heat demand, and the effect on Gärstadverket for these pressures are shown in Table 6. For 1 bar an energy balance over the whole process was checked and can be seen in Appendix FAppendix .

*Table 6. Total electricity and heat demand for the salt recycling process depending on discharge pressure of compressor 1 and the effect on Gärstadverket.*

| Case | 1 bar | 1.3 bar | 1.5 bar |
|---|---|---|---|
| Electricity demand [kW] | 469 | 611 | 693 |
| Heat demand [kW] | 5250 | 629 | 0 |
| Decrease in electricity production at Gärstadverket [%] | 0.9 | 1.2 | 1.4 |
| Decrease in heat production at Gärstadverket [%] | 2.4 | 0.3 | 0 |

As seen in Table 6, the electricity demand for the process corresponds to 0.9-1.4% of the total electricity production in Gärstadverket and the heat demand is between 0-2.4% of the heat production. It is expected that if the brine composition is the same, the energy demand of the process will be around this range regardless of plant size. If the WtE plant is smaller, it will produce less fly ash and less brine, so it will also require less energy.

In addition to affecting the electricity and heat consumption, the discharge pressure of Comp. 1 also affects the process design in several ways. The heat exchanging area in HEX 1 and inside Evap. 1 will be affected due to heat exchange taking place in different parts of the process for the three cases. Sizing of the equipment will also be affected due to the volumetric flow rate being different in the different cases. The results for these parameters are shown in Table 7. Configuration (A) is used for 1.5 bar and configuration (B) is used for 1 bar and 1.3 bar. The total heat exchange area is not the same in the three cases, this is because the driving force for the heat exchange in the three cases will vary.

*Table 7. The heat exchanging area in HEX 1 and Evap. 1, and the volume flow expansion factor over HEX 1 for the discharge pressure in Comp. 1 at 1 bar, 1.3 bar and 1.5 bar.*

| Case | 1 bar | 1.3 bar | 1.5 bar |
|---|---|---|---|
| Heat exchanging area in HEX 1 [$m^2$] | 24 | 348 | 7 |
| Heat exchanging area in Evap. 1 [$m^2$] | 370.4 | 76.9 | 321.8* |
| Volume flow expansion factor over HEX 1 | 75 | 1951 | 1.01 |

*Covered only with internal heat

## 4.3 Brief economic analysis

Based on Tekniska Verken's price on district heating and electricity price from Nord Pool, the loss in revenue has been calculated, see Table 8, and see Appendix B for the price data.

*Table 8. Revenue from heat and electricity costs for the discharge pressure in Comp. 1 at 1 bar, 1.3 bar and 1.5 bar.*

| Loss in revenue for the heat and electricity production [MSEK/year] | | | |
|---|---|---|---|
| Case | 1 bar | 1.3 bar | 1.5 bar |
| Electricity* | -5.0 | -6.6 | -7.4 |
| Heat | -14.1 | -1.7 | 0 |
| Sum | -19.1 | -8.3 | -7.4 |

*Electricity price based on 2022

Three product streams with market values will be obtained from the process. This means that the products can be sold to the market and some revenue can be obtained. The NaCl stream and the mixed stream with NaCl and KCl are sold as solids and $CaCl_2$ is sold as a liquid of 36 wt% $CaCl_2$. The revenue for selling the products is shown in Table 9, the products is not affected by different configurations or pressure and therefore it is the same revenue for different pressures, see Appendix B for the price data.

*Table 9. Income generated from selling the salt products.*

| Revenue [MSEK/year] | |
|---|---|
| NaCl(s) | +1.2 |
| NaCl(s) + KCl(s) | +1.7 |
| $CaCl_2$(l) | +21.9 |

The difference in loss in revenue from decreased heat and electricity production and the gain in revenue for the product streams can be seen as a result in Table 10.

*Table 10. Result based on revenue from energy costs and income generated from selling salt for the discharge pressure in Comp. 1 at 1 bar, 1.3 bar and 1.5 bar.*

| Result [MSEK/year] | | |
|---|---|---|
| 1 bar | 1.3 bar | 1.5 bar |
| +5.7 | +16.6 | +17.4 |

For all three cases, there is a gain in revenue, but it is the smallest when Comp. 1 has a discharge pressure of 1 bar. This is because this configuration needs a lot of external heat since the condensing temperature is too low in the vapour stream from Evap. 1 to fulfil the temperature difference of 12°C between the vapour stream and the feed. During winter months it will be expensive to run with this configuration. The economic result can however be affected by many different factors and can change a lot from plant to plant. For example, in the summer less heat will be used and then electricity may be more valuable and for a plant in southern Europe heat has probably lower value than electricity. The variation in revenue based on the price difference for each month can be seen in Figure 23.

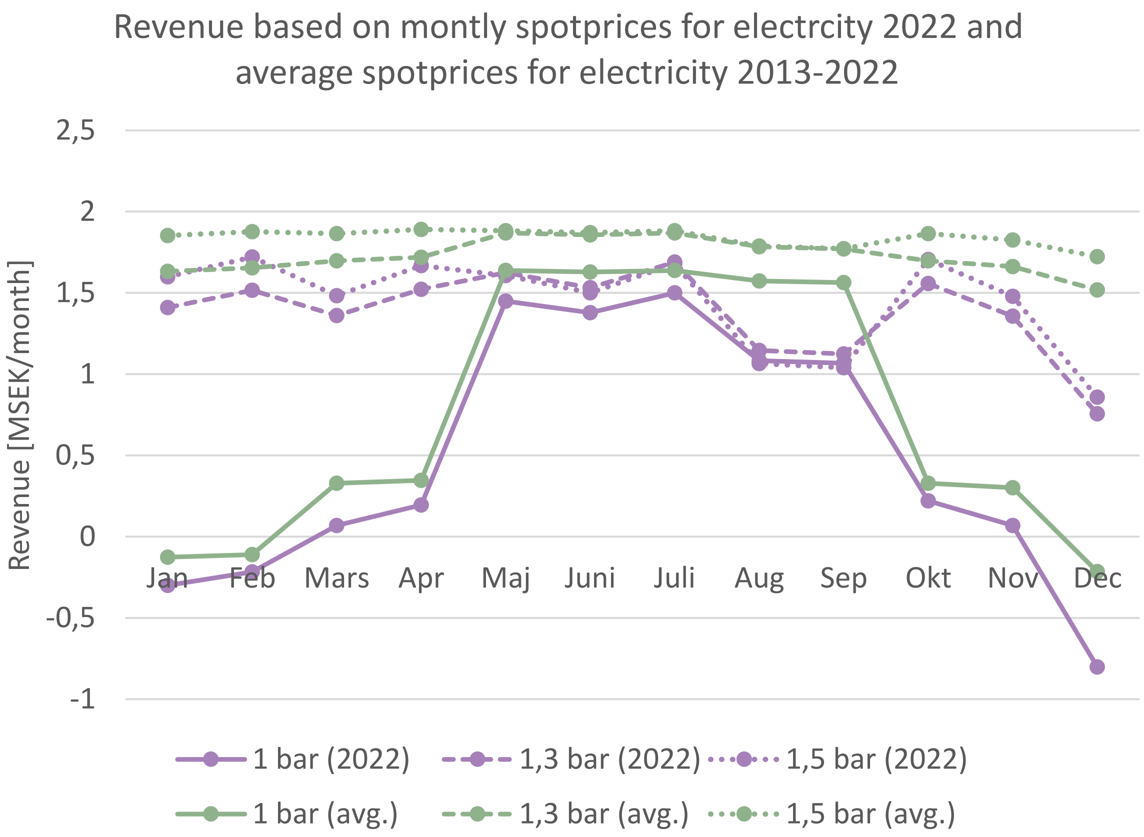


*Figure 23. Revenue for each month based on both spot price for 2022 and average spot prices 2013-2022 depending on discharge pressure of compressor 1. The solid lines are for 1 bar, the dashed lines are for 1.3 bar and the dotted lines are for 1.5 bar.*

As can be seen in Figure 23, the revenue will be negative during the winter months due to the higher price for district heating when Comp.1 has a discharge pressure of 1 bar. During these months it will be beneficial to have Comp. 1 at a higher discharge pressure. The figure does not show the availability of waste heat during the summer months, therefore the revenue is probably higher for the summer months than shown in the figure. Based on the figure and the assumption that there is waste heat during the summer, a mix of different pressures for Comp. 1 is probably most beneficial from the point of revenue.

## 4.4 Sensitivity analysis

Results from the sensitivity analysis are shown below. In the first section, the salt composition is kept constant while the total salt concentration is varied. In the second section, the total salt concentration is constant while the composition is changed.

### 4.4.1 Brine concentration

In Table 11, mass flows of the product streams based on brine concentration are shown. The medium salt case, which has a total salt concentration of 9.4 wt%, is the same brine that was used in the previous simulations. For the low salt and high salt case, the ratio between $CaCl_2$, NaCl, and KCl is the same as in the medium salt case but the amount of water is different. The total mass flow of the feed is the same in all cases.

*Table 11. Mass flow of product streams based on three different salt concentrations.*

| | Low salt (6 wt%) | Medium salt (9.4 wt%) | High salt (12 wt%) |
|---|---|---|---|
| S1 mass flow (kg/h) | 131 | 204 | 261 |
| S2 mass flow (kg/h) | 192 | 299 | 383 |
| L6 mass flow (kg/h) | 541 | 845 | 1104 |

As can be seen in Table 11, the mass flow of the products increases when the salt concentration increases. This is reasonable because a higher salt concentration means that there is more salt in the feed, and therefore more salt also leaves the process.

Increasing the salt concentration not only affects the mass flow of the product streams but also the heat and electricity demand for the process. See the results in Figure 24, where darker line colour represents higher salt concentration. The dashed lines show the decrease in electricity production at Gärstadverket and the solid lines show the decrease in heat production.

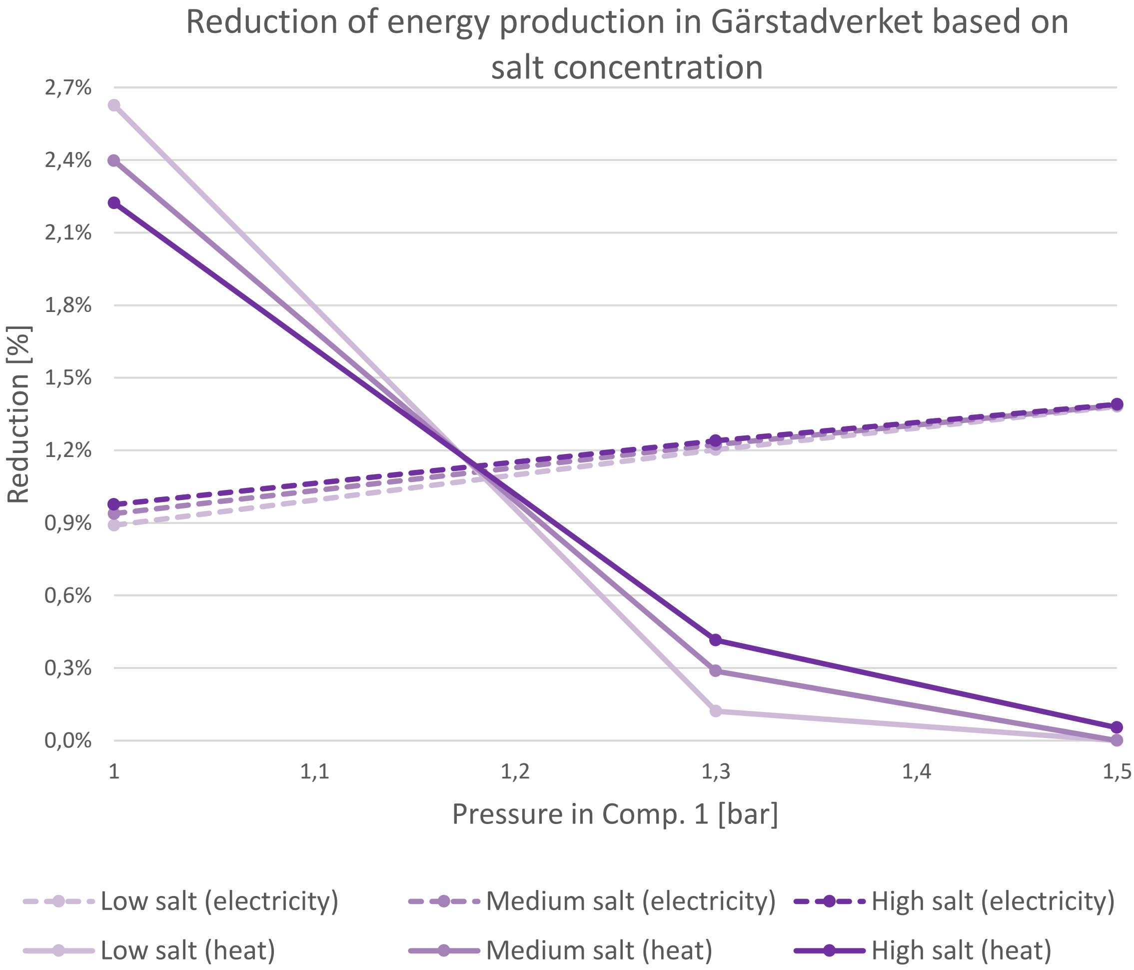


*Figure 24. Sensitivity analysis results regarding the effect of brine concentration on energy consumption. The dashed lines show the decrease in electricity production at Gärstadverket and the solid lines show the decrease in heat production. Darker colours represent higher salt concentration.*

The heat consumption depends on how much water is evaporated in the first evaporator. Lower salt concentration means that more water will evaporate, which requires more heat. As can be seen in Figure 24, this agrees with the results at 1 bar but not at the higher pressures. This is because a larger amount of evaporated water also means that there will be more heat available for heat exchange between the compressed steam and the feed. Therefore, there is a turning point where more external heat is required for the more concentrated brine. For electricity consumption, most electricity is required for the most concentrated brine. The electricity consumption depends on the amount of steam that is compressed in Comp. 1 and Comp. 2. Out of the three brine concentrations, the low salt case has the most steam in Comp. 1 and the high salt case has the most steam in Comp. 2. Since Comp. 2 has a higher compression ratio than Comp. 1, the high salt case will require the most electricity in total. However, as the pressure in Comp. 1 increases, the difference in electricity consumption between the three brine concentrations becomes smaller. At the highest pressure, it is almost equal in all three brines. This is because the electricity consumption of Comp. 1 increases when the compression ratio increases, but in Comp. 2 it remains the same.

### 4.4.2 Brine composition

Instead of using the calcium-rich brine, the sodium-rich brine was used to see how the process was affected see composition of the brine in Figure 2. The results can be seen in Table 12.

*Table 12. Temperature, flow and composition of the streams with the sodium-rich brine with the original design of the process.*

| Brine with high Na+ content | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Stream | Temp. [°C] | Flow [kg/h] | $H_2O$ [wt%] | $Na^+$ [wt%] | $Ca^+$ [wt%] | $K^+$ [wt%] | $Cl^-$ [wt%] | NaCl(s) [wt%] | KCl(s) [wt%] |
| Feed | 50 | 10 622 | 91 | 2.7 | 0.11 | 1.2 | 5.4 | - | - |
| L6 | 86 | 13.7 | 39 | 0.17 | 22 | 0.27 | 39 | - | - |
| S1 | 103 | 1040 | 5.5 | 0.24 | 0.83 | 0.37 | 2.2 | 68 | 23 |
| S2 | 86 | 5.1 | 3.6 | 0.015 | 2.0 | 0.024 | 3.5 | 42 | 49 |

The process was operated with the same conditions in Evap. 1 and Evap. 2 and the same mass flow as when the calcium-rich brine was used. It resulted in, as can be seen in Table 12, that also KCl crystallised in the first evaporator. This is because the equilibrium conditions are different in the different brines. To solve this, the pressure in Evap. 1 was changed from 0.65 bar to 0.77 bar, the result can be seen in Table 13.

*Table 13. Temperature, flow and composition of the streams with the sodium-rich brine with the changed conditions in Evap. 1, optimised base model.*

| Brine with high Na+ content, optimal conditions | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Stream | Temp. [°C] | Flow [kg/h] | $H_2O$ [wt%] | $Na^+$ [wt%] | $Ca^+$ [wt%] | $K^+$ [wt%] | $Cl^-$ [wt%] | NaCl(s) [wt%] | KCl(s) [wt%] |
| Feed | 50 | 10 622 | 91 | 2.7 | 0.11 | 1.2 | 5.4 | - | - |
| L3 | 103 | 1501 | 63 | 7.3 | 0.76 | 8.4 | 20 | - | - |
| L6 | 86 | 1.1 | 39 | 0.17 | 22 | 0.27 | 39 | - | - |
| S1 | 103 | 476 | 5.8 | 0.66 | 0.069 | 0.76 | 1.8 | 91 | - |
| S2 | 86 | 568 | 3.6 | 0.015 | 2.0 | 0.024 | 3.5 | 49 | 42 |

Changing the pressure in Evap. 1 resulted in a quite pure NaCl in S1. It should be noted that with the changed condition in Evap. 1 the flow in L6 is very small, hence a two-stage evaporation process may not be preferable for brine with a low content of $CaCl_2$. Therefore, a new model is created with only one evaporator. In Table 14, the energy demand for the base model, the optimised base model when Evap. 1 has a pressure of 0.77 bar and the new model with only one evaporator is shown.

*Table 14. Total energy demand for the salt recycling process with the calcium rich brine in the original configuration and the sodium-rich brine for three different configurations and the effect on the WtE plant. The discharge pressure of Comp. 1 is 1 bar.*

| | Calcium-rich brine, base model | Sodium-rich brine, base model | Optimised base model | New model |
|---|---|---|---|---|
| Electricity demand [kW] | 469 | 380 | 395 | 198 |
| Heat demand [kW] | 5250 | 5945 | 5495 | 5495 |
| Effect on electricity production at Gärstadverket [%] | 0.9 | 0.8 | 0.8 | 0.4 |
| Effect on heat production at Gärstadverket [%] | 2.4 | 2.7 | 2.5 | 2.5 |

In comparison with the calcium-rich brine the base model with the sodium-rich brine requires more heat and less electricity. This is because most of the water is evaporated in Evap. 1 and there is a very small flow in Evap. 2, so Comp. 2 has a very low energy demand. For the Optimised base model, where the pressure is changed in Evap. 1, the heat demand is still higher than when the calcium-rich brine is used, but lower than for the base model. This is because, in comparison to the calcium-rich brine, the water will need to be evaporated to a higher extent if there is a low concentration of Ca. The heat consumption is lower than for the base model because the evaporation step is now divided between the two evaporators and for Evap. 2 no external heat is required. Electricity consumption is lower compared to calcium-rich brine because the first evaporator operates at a higher pressure than before. However, the electricity consumption is higher compared to the base model because there is now a larger flow in Comp. 2. The new model is the same as the optimised model but ends after the first centrifuge. Therefore, it has the same heat demand as the optimised base model but lower electricity demand since Comp. 2 does not exist.

# 5 Discussion

As shown in the literature study, there are many areas of applications for pure salts while the demand for mixed salt products is evidently lower. This makes it more desirable to separate salts from the brine into individual products, but this also brings more challenges to the brine treatment method. Among the different technologies that were reviewed in this work, a two-staged evaporation method was chosen as the most suitable technology to treat the brine in question. The evaporation method is a mix between multistage flash distillation, multi-effect distillation and vapor compression evaporation. The evaporation steps will be used as crystallisers.  Though, depending on the brine composition a combination of different brine treatment technologies could be suitable, and there are some interesting emerging technologies that could be considered in the future e.g., solvent driven fractional crystallisation to separate NaCl from KCl.

The validation process for the chosen technology showed that Aspen Plus can simulate the process with good predictive ability. Further, the results from the process design and heat integration, the changed brine concentration and composition, the application of product streams, and the economic and environmental aspects will be discussed.

## 5.1 Process design and heat integration

Integrating a WtE plant with a salt recycling process appears to be beneficial since available heat streams could be effectively utilized for the energy-demanding process and produce products with a market value that would increase the revenue of the plant. The process design was based on receiving as pure product streams as possible, while considering available heat streams that could be used for heat integration from the WtE plant. In the design, the condition for the evaporation was set based on this integration and resulted in two quite pure salt streams. However, in reality, the limit values for the pressure and temperature are often not as precise as in the simulation program. Therefore, it could impact the purity of the product streams and the actual pressure and temperature will need to be set according to the most valuable product stream. It should also be emphasized that the equilibrium of the brine and its components are the main drivers for the calculations, and in this way no kinetic effects are taken into account, which could have implications with respect to yield and sizing of equipment.

For the design, only one type of integration with the WtE plant has been investigated. Both primary steam and the available steam extraction at 6 bar from boiler 4, illustrated in Figure 3, could be other potential streams for heat integration. If streams with higher temperatures are chosen, it will be possible to have higher temperature and pressure levels in the salt recycling process. If the pressure is higher, the problems associated with low pressure such as large equipment size, difficulties with process start-up and maintaining low pressure in the process will be minimised. On the other hand, the energy consumption for the vapour compressors will increase since the discharge pressure of the compressors needs to be higher in order to utilise the energy in the vapor. A process below atmospheric pressure will be energy-demanding concerning the start-up, but a process in a more ambient environment could have higher running costs. Depending on if the process is run continuously during the year or if the process will follow the cycle of fly ash production, another process design than the chosen one could be more favourable.

The design choice of a minimum temperature difference of 7°C at the pinch point in the evaporator and 12°C in the heat exchanger will affect the investment costs. Lower temperature differences require larger heat exchange areas, while higher differences give higher energy losses. In this work, the minimum temperature differences were based on Gärstaverkets temperature difference in the heat exchanger for the district heating and previous experiences. However, these values could be optimised by for example, a techno-economic analysis. This was however outside the scope of this work. Another design choice that could be investigated more is the condition in Evap. 2. It was only based on the pressure of the validation process's, Resalt's, minimum pressure. When analysing the pinch, see in Appendix F, it is higher than 7°C. Thus, both the pressure and temperature in the evaporator could be higher and still supply all its required heat by itself. If the pressure would be higher, less energy in Comp. 2 would be required.

## 5.2 Applications of product streams

The three product streams that are received from the process can be used for different purposes. The first solid stream contained almost 97 wt% NaCl when dried from excess water, and the rest was $CaCl_2$ and KCl. In reality, there would be other minor components present as well. For instance, the simulations with the complex brine composition showed that calcium sulphate hemihydrate ($CaSO_4 \cdot \frac{1}{2} H_2O$) could be one such compound. The presence of this compound was neglected in the results as it was assumed that sulphates would be removed in a pre-treatment step. It should be noted that the investment and running costs for the pre-treatment also have to be considered before the implementation of the salt recycling process. Without a pre-treatment step, the purity of the first solid product would be compromised and the economic outcome of the process would be affected. There will also be other compounds in the brine that cannot be expected to be removed in a pre-treatment step. Although other compounds will be present in very small amounts, they will impact the purity of the salt and make it unfeasible to use the salt in the chemical- or food industry. The application that appears to be most feasible for the NaCl product is as road salt for de-icing. Trafikverket has quite strict requirements for their salt, but municipalities or private road owners do not have the same requirements and could therefore be interested in recycled salt from fly ash.

According to the findings in the literature study, there is no direct application for the second solid product stream, which has around 50 wt% KCl, 45 wt% NaCl and 5 wt% $CaCl_2$ when dewatered. It could possibly also be used as road salt, but it will probably be less effective as a de-icing agent than commercial road salt due to the high content of KCl. Another option is to continue treating the salt in a process that separates NaCl from KCl. This could be achieved with a solvent-based treatment.

The liquid product stream from the process has a high purity (> 98 wt%) of $CaCl_2$. It could for example be used as road salt for unsealed roads. Another alternative is to use the calcium-rich solution to absorb $CO_2$ and produce calcium carbonate. This could be especially interesting for the WtE plant owner as it could provide an opportunity to reduce the $CO_2$ emissions of the plant. As calcium carbonate has several industrial applications, it would be further interesting to evaluate the economic feasibility in future studies.

New areas of application for mixed salts are also emerging, meaning that different kinds of products could be desirable in the future. The mixed salt stream of (> 44 wt%) NaCl and (> 49 wt%) KCl can in the future have a larger application area. However, if the aim of the salt recycling was to produce a mixed salt, the design would probably look significantly different from the current design.

## 5.3 Impact of brine concentration and composition

The sensitivity analysis showed that changing the brine concentration but keeping the same mass flow in the feed constant has a large impact on the amount of salt products but smaller impact on the energy consumption. It is interesting that changing the brine concentration impacted the heat demand in two ways, lower concentration means that more water must be evaporated, but it also creates more steam that can supply heat internally. Logically, more salt products are formed when the salt concentration is increased since more salt enters the process.

The mass flow of brine that enters the salt recycling process was kept constant in the simulations. It can be argued that this is a less realistic scenario than keeping the mass flow of the salts constants and changing the salt concentration by adjusting the amount of water instead. This is because the amount of salts that end up in the fly ash in a WtE plant correlates to the amount of generated fly ash. Therefore, the amount of salt that enters the salt recycling process will be constant in relation to the generated fly ash. The amount of water can however vary, depending on how the HaloSep process is adjusted. Therefore, it might be more interesting to keep the amount of salt constant but change the inlet mass flow of brine in a future study.

Changing from a calcium-rich to a sodium-rich brine had a major impact on the outcome since the process was optimised for the calcium-rich brine. It indicates that the process needs to be adjusted in pressure and temperature depending on the brine. For the sodium-rich brine, changing the pressure in Evap. 1 was a simple adjustment that improved the outcome. A notable difference from the calcium-rich brine was that the liquid product stream from the process was very small. The advantage of this is that it is easier to handle solid products as the volume is much smaller. On the other hand, the calcium-rich liquid product has a relatively high economic value. Since it will not be possible to receive this product with the sodium-rich brine, the question is whether it even is worth it to have a second evaporator. Having only one evaporator would decrease the investment cost, but only one solid product with NaCl and one liquid stream with NaCl, KCl and $CaCl_2$, would be received.

## 5.4 Economic impact of the process

Depending on how the process is designed both running costs and investment costs will impact the economic outcome of the process. As shown in the sensitivity analysis the best economic condition will be given when the process is designed for the specific brine that it is going to handle. Regarding the running cost, the demand for different energy sources and availability of waste heat in the summer will also have an impact on the economic outcome. The process can be varied depending on this demand, and during summer months when more waste heat is available, the process will create value by producing salt from heat that otherwise would have been wasted.

Further, the economic calculation is only based on the energy consumption of the process and the revenue for the product streams. For the energy consumption, Aspen does not account for energy losses, and it has been assumed that no energy losses will occur in the process. This means that in reality there is a slightly higher energy consumption than calculated. Compressors are the only simulation step that considers the efficiency. Beyond energy losses in the different steps, there will be energy losses in pipes and energy will need to be used to retain the low pressure in the process.

The electricity and heat prices that were used for the economic analysis are from Sweden. It is important to consider that the prices differ depending on country and therefore, the economic analysis might have a different outcome if it was applied to a different country. Sweden is also a relatively cold country where large amounts of district heat are required during the cold months. In warmer countries and especially in countries without a district heating grid, there could be more waste heat that could be used for the salt recycling process without any significant cost.

The prices of the product streams are not constant and for the $CaCl_2$-rich product, it has varied a lot in the recent past. Depending on the market value of the product, the process will be more or less profitable. Furthermore, it has also been assumed that the product stream with a mixture of NaCl and KCl has the same market value as the NaCl-rich product stream, since potassium has a significantly larger market price. In the future, an additional separation step that can separate NaCl and KCl would be a good idea to meet full market potential for the process.

Moreover, the investment cost and all running costs other than energy and salt products have not been investigated in this thesis, but for a future study, it would be interesting to investigate to get a more accurate measurement of the economic viability of the process. For example, the brine requires a material that can handle corrosion conditions due to the presence of chlorides which might lead to a higher investment cost. Also, the pressure will affect the investment cost. With a lower pressure, the volume is increasing for the equipment which means more material. If the process should be flexible and adapt depending on the prices and demand of heat and electricity, it will require additional configurations. For example, during the summer months waste heat can be used and then it is favourable to have Comp. 1 at a discharge pressure of 1 bar. When the price for heat increases the discharge pressure of Comp. 1 could be changed to 1.3 bar. This will however require other process specifications. If heat is expensive, it will be more desirable to use more electricity, so the design process with 1.5 bar as discharge pressure in Comp. 1 would be preferable. However, if the pressure is adjusted to over 1.3 bar the salt will crystallise in the heat exchanger and a whole new configuration is required. An alternative could be to only separate the salts during summer when waste heat is available, and produce a mixed salt stream during winter when the separation is more expensive. There would be a trade-off in the revenue of selling salt and the cost of performing the separation, which would be interesting to evaluate in a future study.

Another example of a significant cost that has not been considered is the cost of landfilling hazardous waste (fly ash). Today, this is a large cost for WtE plant owners and implementing a fly ash and salt recycling process could be profitable considering that this cost is avoided. It is more difficult for plants located inland to implement fly ash recycling processes without also implementing a salt recycling process, as the brine must be handled in some way. Therefore, further development of salt recycling processes is important to reduce the amount of fly ash that is landfilled today. Even though plants located close to the sea often can release the brine into the environment, it could be of interest for these plants as well to implement salt recycling processes, because there might come stricter environmental regulations in the future that make it harder to dispose of the brine in saltwater recipients.

## 5.5 Environmental impact of the process

The underlying reason for this study was the need for a recycling process with a low heat demand that converts the salts from fly ash into useful products. Implementing such a process increases the circularity of materials, which is important in terms of a circular economy-perspective. However, the environmental sustainability of the salt recycling process also depends on the energy consumption and the required material resources for the equipment.

The energy requirement in the integrated salt recycling process will be met by the WtE plant. This is advantageous considering that there will be less energy losses when the energy does not have to be transported for long distances. Also, in the summer months waste heat can be utilised to produce valuable products. The process was also designed to minimise the energy consumption, but the process does still require energy. Since the WtE plant sells less heat and electricity by being integrated with the salt-recycling process, more heat and electricity has to be produced somewhere else in society. The environmental impact of this additional energy production should be accounted for when assessing the environmental impact of the salt recycling process.

The salt recycling process designed in this thesis is attractive for WtE-plants located inland because it provides a way to handle the brine from the HaloSep process for the fly ash treatment. If more plants are motivated to implement the process, there will be less hazardous waste generated and landfilled, which reduces the risks associated with hazardous waste.

# 6 Conclusions

In this thesis, a salt recycling process that treats brine from the HaloSep process has been designed. There is a wide range of salt recycling methods, but only a few can handle highly concentrated brines and are suitable for separating salts from fly ashes. Evaporation-based methods with several stages are suitable for this purpose but require large amounts of energy. The applications of salts retrieved from the salt recycling process are limited since the purity will not be as high as commercially produced salt. The NaCl-rich (> 96 wt%) product could be useful as road-salt for de-icing and the $CaCl_2$-rich (> 98 wt%) product could be useful as road-salt for unsealed roads. The mixed product of NaCl and KCl could also work as a de-icing salt or be further processed into two separate salts.

The designed salt recycling process presented in this thesis can be integrated with a waste-to-energy plant by using steam from the plant as a heat source. The temperature and pressure levels in the salt recycling process can be adjusted to fit the temperature level of the steam.

Net energy loss in the WtE plant output will depend on the design conditions in the salt recycling process. In the design that was proposed in this thesis, the compression ratio in the first compressor determines the net energy loss. A higher compression ratio leads to a larger electricity consumption but lower energy consumption in total since the heat demand is reduced more than the electricity demand increases. The electricity loss is between 0.9-1.4% and the heat loss is between 0-2.4%.

The total salt concentration in the brine impacts the electricity consumption slightly. Higher salt concentration requires more electricity. The heat demand is highest for the low concentration salt when the compression ratio in the first compressor is low. At higher compression ratios, it is the opposite. However, it should be noted that brines with higher salt concentrations also produce more salt products.

The process design that was created in this thesis was optimised for a calcium-rich brine. When it was run with a sodium-rich brine, the outcome of the process was affected significantly. Two solid product streams with a mix of NaCl and KCl and a liquid product with a small flow were received. Changing the pressure level in the first evaporator improved the outcome, but changing the process design could be more profitable for the sodium-rich brine.

According to the brief economic analysis based on the cost for energy and income from selling salt, the salt recycling process has a positive revenue of 5.7-17.4 MSEK/year, depending on the compression ratio in the first compressor and assuming the electricity price from 2022. Since the net energy loss in the plant was lowest at the highest compression ratio, it also gives the highest revenue. However, this should only be used as a very brief hint of the economic outcome, and it is recommended that the other running costs and the investment cost is investigated in a future study. From an environmental aspect, the process is motivated in terms of circularity and because it could give more incentive for the plant owners to implement a fly-ash recycling process which would produce less hazardous waste. However, a more thorough analysis must be performed to see the entire environmental impact of the process.

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# Appendix A

## Brine treatment technologies

### A.1 Membrane-based treatments

#### A.1.1 Reverse osmosis (RO) and high-pressure reverse osmosis (HPRO)

Reverse osmosis and high-pressure reverse osmosis are pressure-driven separations where water molecules are forced through a semipermeable membrane by pressure [11]. The pressure needs to be higher than the osmotic pressure between the brine and the permeate liquid and pressure will gradually increase when operating. Reverse osmosis uses pressure up to 82 bar and has a limitation between 55 000-70 000 mg/L of total dissolved solids (TDS). High-pressure reverse osmosis is when the pressure is over 100 bar. It requires higher demands on the membrane and only a few membranes are commercially available today [9], [11]. Saltworks Technologies Inc. has a membrane that can reach a salt concentration of 130 000 mg/L TDS with high-pressure reverse osmosis [62].

#### A.1.2 Forward osmosis (FO)

Forward osmosis uses osmotic pressure gradient to drive the separation [11]. With the help of a draw solution that has high concentration, the water molecule moves from the brine with lower concentration through the membrane. The draw solution is connected in a recovery cycle where water can be separated and removed from the system. Compared to reverse osmosis and high-pressure reverse osmosis, this method is more energy efficient since no external pressure is needed. The method is also more suitable to deal with high salinity brines. For example, Lenntech has equipment that can handle a concentration of about 200 000 mg/L TDS [63]. Forward osmosis has high potential but still today it is not fully commercialised due to challenges such as reverse salt flux, high energy cost for regeneration of draw solution, and low membrane flux [64]. There is also no ideal draw solution. An ideal draw solution is a solution that is inexpensive, provides high water flux, is commercially available, has low fouling potential, low toxicity to microorganisms, is easy to regenerate, and has low reverse solute diffusion [11].

#### A.1.3 Osmotically assisted reverse osmosis (OARO)

Osmotically assisted reverse osmosis combines the technologies of reverse osmosis and forward osmosis. Like reverse osmosis, it is a pressure driven process where static pressure forces water molecules through a semipermeable membrane [11]. However, for osmotically assisted reverse osmosis, also the osmatic pressure is decreased with a lower osmotic pressure sweep solution that is added on the permeate side. The pressure can therefore be much lower than for reverse osmosis and can therefore treat a higher concentrated brine. This type of technology is often in series where the final step in the series is using the technology for ordinary reverse osmosis. The same core technology is used in Cascading Osmotically Mediated Reverse Osmosis and Counter Flow Reverse Osmosis, but the configuration of stages or modules are different. This technology has successfully been used to concentrate a brine to 250 000mg/L TDS. The disadvantage is that it is more complex compared to other pressure membrane-based technologies [65].

#### A.1.4 Electrodialysis and electrodialysis reversal

Electrodialysis and electrodialysis reversal are membrane-based technologies that are voltage driven [11]. Between a cathode and an anode, alternate cation-exchange membrane and anion-exchange membrane is set up, see Figure 25 (a) [9]. Anions, as chloride molecules, move towards the anode and will pass the anion-exchange membrane but not the cation-exchange membrane. While cations, as sodium or potassium, will move towards the cathode and pass the cation-exchange membrane and not the anion-exchange membrane. This will create a higher concentration of ions between every other membrane, that alternates with a flow with a low ion concentration. Electrodialysis is seen as an efficient method to concentrate the brine before a crystallisation process due to low energy consumption compared to thermal concentration methods. Fouling and scaling, as in other membrane-based technologies, are the major problems for electrodialysis. Electrodialysis reversal uses the same technique as in electrodialysis but 3 to 4 times per hour reversal DC voltage is used to minimise fouling and scaling by removing charge particles on the membranes.

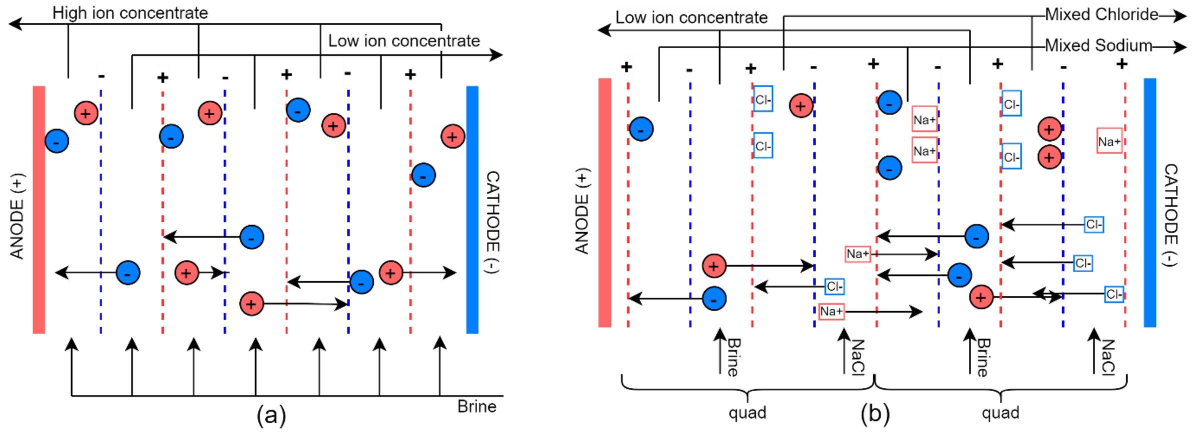

*Figure 25. A sketch of the working principle in (a) electrodialysis and electrodialysis reversal, (b) electrodialysis metathesis*

### A.1.5 Electrodialysis metathesis

Electrodialysis metathesis is a variant of electrodialysis [66]. The same set up with a cathode and an anode is used with alternating anion-exchange and cation-exchange membrane between. For electrodialysis metathesis, five membranes that form four compartments are called a quad, the quad is then repeated between the cathode and the anode, see Figure 25 (b). The quad consists of four different flows, the first compartment is used for a substitution solution that is chosen depending on which mixed concentrate is desired, in Figure 25 (b) NaCl is chosen. The third compartment is the feed (brine) which will constitute the low ion concentrated stream when it goes out of the electrodialysis metathesis. The second and fourth compartment are the concentrate where ions are collected. If the cathode is to the right and the first compartment is next to it, the second compartment will be dominated by cations from the feed and the fourth compartment will be dominated by anions from the feed. The chosen substitution solution will decide the composition of the concentrate. The anion from the substitution solution will end up in the second compartment and the cations will end up in the fourth compartment, the cations will come from the second quad. In this way, a desired composition for the concentration can be obtained and the exchange of ions is called metathesis. This method can minimise scaling problem with multivalent ions that are intended to scale with for example $Ca^{2+}$ [11].

### A.1.6 Membrane distillation and membrane crystallisation

Membrane distillation is a thermal-driven membrane-based separation method where the brine is heated. It will create a vapour pressure gradient across the hydrophobic microporous membrane due to a temperature difference compared to the other side of the membrane [11]. Liquid molecules are prevented from moving through the membrane while vapour molecules can pass through by the hydrophobic nature of the membrane. There are four main different configurations for membrane distillation, the most common for brine treatment applications is direct contact membrane distillation. This configuration is also the simplest where both the feed and permeate are in direct contact with the membrane [67]. The vapour from the feed stream condensates directly into the liquid on the permeate side. Other configurations are air gap membrane distillation, sweep gas membrane distillation and vacuum membrane distillation. The advantage of membrane distillation is that it can treat brine up to 350 000 mg/L TDS but theoretically there are no restrictions on the salinity of the feed brine [11]. The operation is at low temperature, between 40-80°C and the application can therefore use waste heat streams. Significant problems with this technology are low permeate flux, high energy consumption and membrane fouling.

Membrane crystallisation is a hybrid approach of membrane distillation and crystallisation [68]. This method can both provide volume reduction and recovery for solid crystal salts [11]. During the membrane distillation process, the feed brine will reach supersaturation conditions and start crystallising. The crystallisation process is well-controlled compared to conventional crystallisation process. This is due to uniform evaporation rate through the membrane, and it results in crystals with high purity and uniform size [69].

## A.2 Thermal-based treatments

### A.2.1 Ohmic evaporation

Ohmic evaporator, also called Joule-heating, is a technology that uses electric currents of 60 Hz frequency at an applied voltage between 110-330V to evaporate the brine [70]. This method is a brine volume minimiser and is efficient for treatment of highly concentrated brines [9]. The brine is directly heated when the current travels through the non-ideal conductor (the brine) between the electrodes [71]. It results in vapour production and a more concentrated TDS liquid. In larger scale applications this technology needs to be further investigated and the experimental data for multicomponent hypersaline brines is scarce [9], [71].

### A.2.2 Wind-aided intensified evaporation

Wind-aided intensified evaporation is used foremost for brine volume minimisation [11]. It is based on vertical plates that are placed parallel to each other with gaps between where the wind can pass through. The plates are adjusted so the vertical surface is parallel to the wind direction [72]. With the help of a pump, the brine is pumped up to the top of the plates and evenly distributed so that the whole side of the plate is wetted. An accelerated evaporation process takes place when the wind blows between the plates and picks up the moisture driven by mass and thermal transfer gradients. The excess water is collected under. This method is both energy efficient and land efficient, the only energy supply is for the pump since it exploits wind energy for evaporation and the vertical plates create a large surface on a small land area [11].

### A.2.3 Evaporation pond

Evaporation ponds use the solar energy directly to evaporate the brine in large ponds. It is a nature-based technology that is most suitable for large areas with a high sun exposure [9]. The purpose is to remove the water from the brine and the advantage of this technology is that the ponds are relatively easy to construct and have low operating cost [73]. However, the technology has some problems with leaching that can contaminate the ground water together with that it requires high need of land [9].

### A.2.4 Spray drying

A spray dryer converts the brine into solid powder of the mixed solid salts [11]. This technology has been used for a long time in the food, chemical and pharmaceutical industries. The technology works as the brine is distributed in droplets using for example a centripetal atomizer. This is to maximise the surface area between the brine and the hot air. The droplets are mixed with heated air that will evaporate all the moisture in a vertical spray drying chamber. The dried solid particles from the brine will then be collected with a bag filter and the vapour stream is released to the environment.

### A.2.5 Eutectic freeze crystallisation

Eutectic freeze crystallisation uses the density difference of ice, solution, and salt [11]. The ice will flow at the top and the salt will sink to the bottom. Operation is under equilibrium condition between ice, salts, and a specific concentration of the solution. This point is called eutectic point and the temperature and the specific concentration for this point calls eutectic temperature and eutectic concentration. The eutectic point is different for different solutions. The technology has mostly been used to separate solutions with only one salt component, and multicomponent brine has not been fully investigated. Further, each salt has its own unique eutectic temperature so it could be feasible to separate multicomponent mixtures. This technology has significantly less energy requirement for the separation since the heat of fusion of ice is six times less than for evaporation of water [74]. However, the cost for the energy required for freezing is more expensive than for heating.

## A.3 Solvent based treatments

### A.3.1 Solvent driven extraction

In solvent driven extraction, a low-polarity solvent is added to the brine at an extraction temperature ($T_{ex}$), where it is immiscible with water. The solvent will however have hydrophilic functional groups that attract water to the solvent phase while the salts remain in the aqueous phase [75]. As the volume of water in the aqueous phase decreases, the concentration of the salt will increase and eventually, the salt will crystallise [10]. To recover the solvent and water, the temperature of the mix can be decreased to a discharge temperature ($T_{dis}$) where the solubility of water is lower and the solvent-phase can be decanted. Subsequently, the water separates from the solvent and a clean water stream and a solvent that can be reused is attained. However, it is costly to recover the solvent completely as some solvent will be dissolved and lost in the water [75]. A flow-chart of the solvent driven extraction process is shown in Figure 26. It has been shown in previous studies that solvent driven extraction can recover water from brines with up to 200 000 mg/L TDS and recover valuable minerals [10]. However, the technology has mostly been tested on laboratory brine solutions with only NaCl and not on complex brines with different salts and contaminants. Therefore, more research on real brines is needed before the technology is commercialised [75].

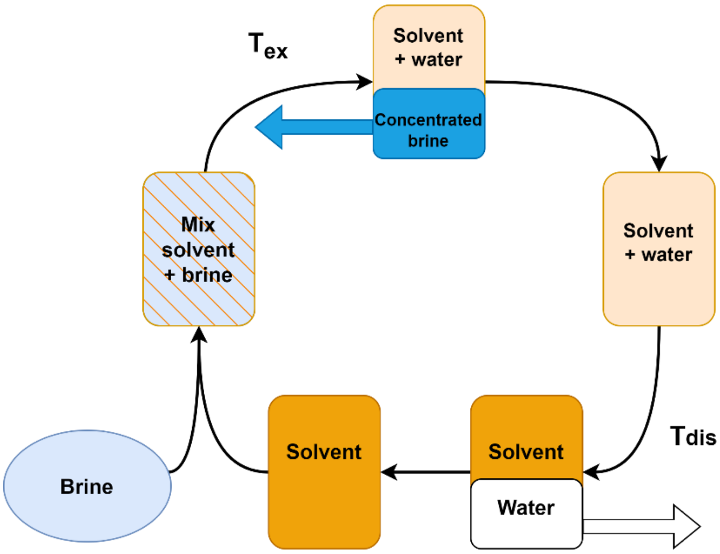

*Figure 26. A sketch of the working principle in solvent driven extraction.*

### A.3.2 Solvent driven fractional crystallisation

In solvent driven fractional crystallisation, a water-miscible solvent is added to the brine [10]. This will affect the solubility of the salt so that it will eventually crystallise. In contrast to solvent driven extraction, there is only one liquid phase. The choice of solvent is very important because it must have the right properties to cause the target salt to precipitate. For example, it has been shown that addition of alcohol or ammonia to solutions of mixed salts can cause KCl to precipitate.

# Appendix B

## Electricity and salt prices

Prices for electricity taken as spot price for both 2022 and average price 2013-2022, see Table 15. Prices for district heating is shown in Table 16 and salts in Table 17. The prices for different salts is from an interview (2023-05-03) with an actor trading with salts and an assumption that the mixed stream has the same market price as NaCl.

*Table 15. Spot price for electricity for each month in 2022 and average spot price for electricity for each month for 2013-2022* [56].

| Spot price for each month [SEK/MWh] | | | | | | |
|---|---|---|---|---|---|---|
| 2022 | Jan | 1043.32 | | Average 2013-2022 | Jan | 479.3572 |
| 2022 | Feb | 774.8 | | Average 2013-2022 | Feb | 427.5923 |
| 2022 | Mars | 1303.3 | | Average 2013-2022 | Mars | 454.3364 |
| 2022 | Apr | 892.16 | | Average 2013-2022 | Apr | 396.7303 |
| 2022 | Maj | 1028.63 | | Average 2013-2022 | Maj | 412.967 |
| 2022 | Juni | 1263.09 | | Average 2013-2022 | Juni | 440.8077 |
| 2022 | Juli | 866.13 | | Average 2013-2022 | Juli | 412.8103 |
| 2022 | Aug | 2230.47 | | Average 2013-2022 | Aug | 624.4132 |
| 2022 | Sep | 2286.33 | | Average 2013-2022 | Sep | 659.3036 |
| 2022 | Okt | 806.45 | | Average 2013-2022 | Okt | 453.8664 |
| 2022 | Nov | 1308.81 | | Average 2013-2022 | Nov | 542.1891 |
| 2022 | Dec | 2690.18 | | Average 2013-2022 | Dec | 769.5363 |

*Table 16. Price for district heating from Tekniska verken's webpage, without tax* [55].

| District heating [SEK/MWh] | |
|---|---|
| Jan | 600.8 |
| Feb | 600.8 |
| Mars | 469.6 |
| Apr | 469.6 |
| Maj | 89.6 |
| Juni | 89.6 |
| Juli | 89.6 |
| Aug | 89.6 |
| Sep | 89.6 |
| Okt | 469.6 |
| Nov | 469.6 |
| Dec | 600.8 |

*Table 17. Price for the salt products, the prices is for impure salt.*

| Salt Price [SEK/ton] | |
|---|---|
| NaCl | 750 |
| NaCl + KCl | 750 |
| $CaCl_2$ | 2000 |

# Appendix C

## Compositions of solid and liquid products in simulated complex case

Composition of solid and liquid products when the complex brine is used in the simulation is shown in Figure 27.

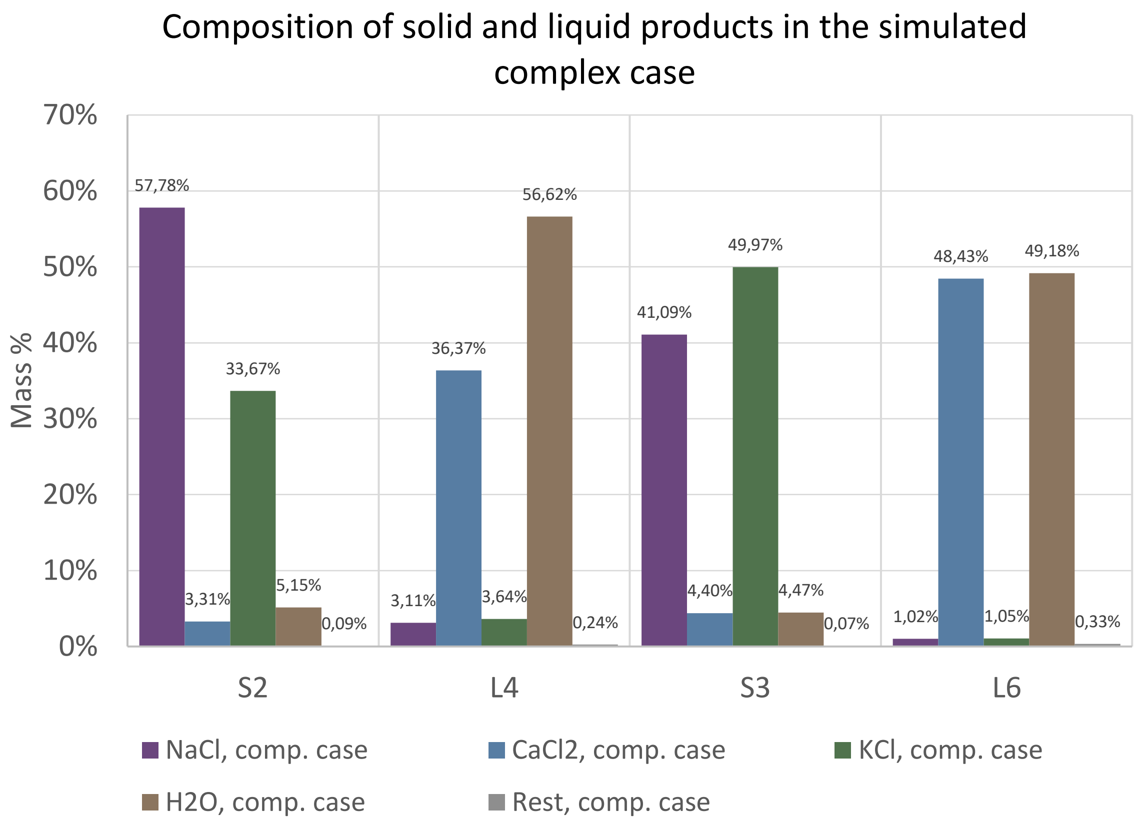

*Figure 27. Composition of solid and liquid products in the simulated complex case.*

# Appendix D

## Calculations for sluice

The solid product is under atmospheric pressure and therefore a sluice is needed to get the solid product. It is calculated that the container needs to be emptied every day and that the container is 10% larger than the salt volume produced in one day. To get the product out of the container it is closed off from the process and air is released into the container. The solids are then emptied and the air in the container is vacuum pumped out to the right pressure before it is connected to the process again. With Equation 1 the energy consumption for the vacuum pump is calculated [76]. Note that the value will be negative because the net energy in the container is decreased, it is the atmosphere outside the container that gains energy.

$$\text{Adiabatic hp} = \frac{\kappa}{\kappa - 1}\,\frac{\omega RT}{M(550)(3600)}\left[\left(\frac{P_2}{P_1}\right)^{(\kappa-1)/\kappa} - 1\right] \tag{1}$$

Where: hp = Horsepower
$\omega$ = Flow of air, Ib/h
$\kappa$ = Ratio of heat capacity at constant pressure to heat capacity at constant volume.
M = Molecular weight, Ib/mol
R = Gas constant, 1544ft·Ib$_f$/(Ib·mol)(°R)
T = Absolute temperature, °R
P = Absolute pressure, torr

Calculations for sluice 1 are shown in Table 18.

*Table 18. Calculations for sluice 1.*

| Calculations for sluice 1, pump from 1 bar to 0.65 bar | | | |
|---|---|---|---|
| Flow of salt | 2.4 | m3/day | From Aspen |
| Container for salt | 2.64 | m3 | 10% more than the salt volume |
| Density air at 20℃, 1 bar | 1.293 | kg/m3 | Literature |
| Total mass air | 3.41 | kg | Calculate the mass of the air in the container. |
| Time it will take | 1 | h/day | Iteration value to get the optimal energy consumption for the vacuum pump. [77] |
| Flow | 3.41 | kg/h | Calculate the mass flow |
| Volume flow | 2.64 | m3/h | Change to volume flow |
| Molar mass air | 28.97 | g/mol | Literature |
| w | 7.53 | Ib/hr | Change mass flow to Ib/hr |
| k | 1.39 | | Literature |
| R | 1544 | ftIbf/Ib mol R | Literature |

| | | | |
|---|---|---|---|
| T | 527.67 | R | Assuming 20C for the temperature |
| M | 0.0639 | Ib/mol | Change g/mol to Ib/mol |
| P2 | 487.54 | torr | Pressure 0.65 bar in torr |
| P1 | 750.06 | Torr | Pressure 1 bar in torr |
| Ad hp | -19.67 | hp | Calculate adiabatic hp from Equation 1 |
| Energy | -14.47 | kW | Change unit from hp to kW, ideal values are below 15 kW for vacuum pumps. |
| Calculate the energy consumption over the whole day, since its only active 1h per day. | | | |
| | -14.47 | kWh/day | |
| | 24 | h/day | |
| | -0.603 | kW | |

Calculations for sluice 2 are shown in Table 19.

*Table 19. Calculations for sluice 2.*

| Calculations for sluice 2, pump from 1 bar to 0.14 bar | | | |
|---|---|---|---|
| Flow of salt | 3.5 | m3/day | From Aspen |
| Container for salt | 3.85 | m3 | 10% more than the salt volume |
| Density air at 20°C, 1 bar | 1.293 | kg/m3 | Literature |
| Total mass air | 4.97805 | kg | Calculate the mass of the air in the container. |
| Time it will take | 5.5 | h/day | Iteration value to get the optimal energy consumption for the vacuum pump. [77] |
| Flow | 0.9051 | kg/h | Calculate the mass flow |
| Volume flow | 0.7 | m3/h | Change to volume flow |
| Molar mass air | 28.97 | g/mol | Literature |
| w | 1.995402 | Ib/hr | Change mass flow to Ib/hr |
| k | 1.392758 | | Literature |
| R | 1544 | ftIbf/Ib mol R | Literature |
| T | 527.67 | R | Assuming 20C for the temperature |
| M | 0.063868 | Ib/mol | Change g/mol to Ib/mol |
| P2 | 105.0086 | Torr | Pressure 0.65 bar in torr |
| P1 | 750.06 | Torr | Pressure 1 bar in torr |
| Ad hp | -19.4023 | hp | Calculate adiabatic hp from Equation 1 |

| | | | |
|---|---|---|---|
| Energy | -14.2704 | kW | Change unit from hp to kW, ideal values are below 15 kW for vacuum pumps. |
| Calculate the energy consumption over the whole day, since it is only active 1h per day. | | | |
| | -78.4872 | kWh/day | |
| | 24 | h/day | |
| | -3.2703 | kW | |

# Appendix E

## Flowchart in Aspen

The flowchart of the salt recycling process when designed in Aspen is shown in Figure 28.

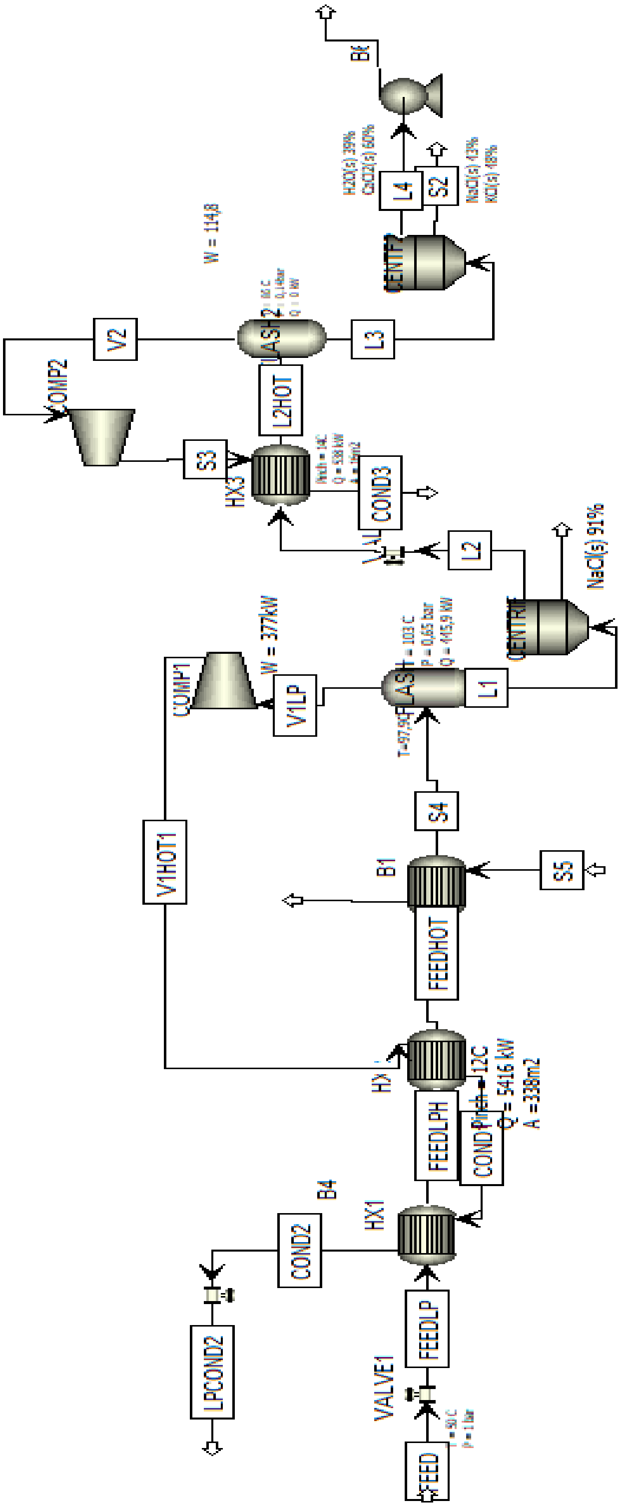

Figure 28. Flowchart of the salt recycling process in Aspen.

# Appendix F

## Energy balance investigations

### Energy balance over the process:

An energy balance is performed with values from Aspen. Since Aspen does not calculate the energy for the centrifuges, that energy is assumed to be zero. See Table 20 for the calculations and result, and Figure 29 for the system boundary.

*Table 20. Energy balance calculations for the process when Comp. 1 has an outlet pressure of 1 bar.*

| Energy in [kW] | | Energy out [kW] | |
|---|---|---|---|
| Feed | -44 184.4 | S1 | -422.654 |
| D1 | -31 117.7 | S2 | -563.756 |
| Comp. 1 | 215.1 | L6 | -2 559.9 |
| Comp. 2 | 120.2 | V2 | -31 364.9 |
| | | V4 | -3 687.81 |
| | | D2 | -3 6367.7 |
| Sum | -74 966.8 | Sum | -74 966.7 |

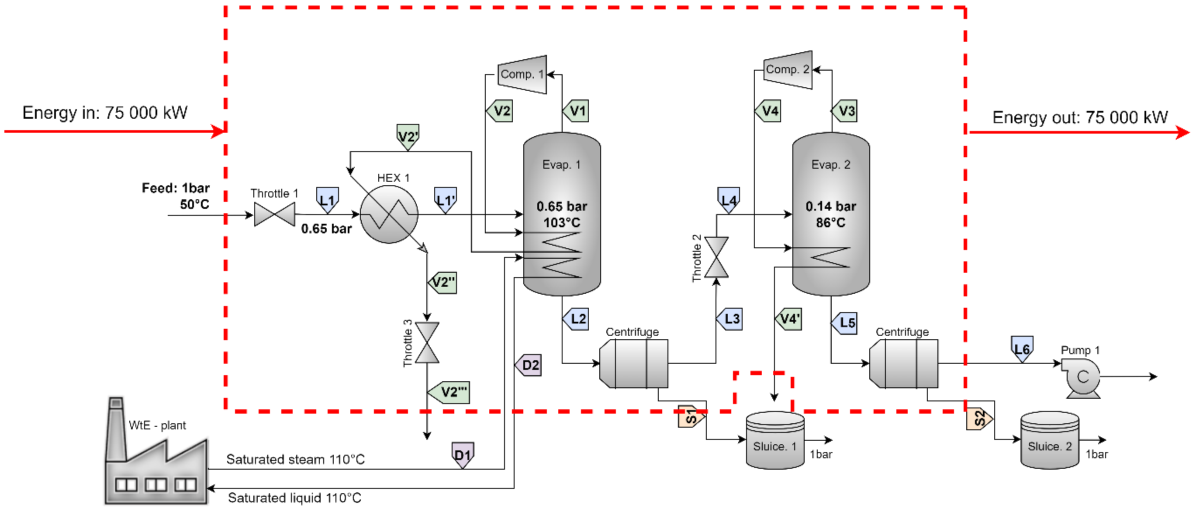

*Figure 29. The system boundary for the energy balance.*

### Cold and Hot composite curves for the process

To check that no pinch violation occurs through the process, cold and hot composite curves are checked. See Figure 30, Figure 31 and Figure 32 for the curves when the process operates with an outlet pressure of 1 bar for Comp. 1.

.

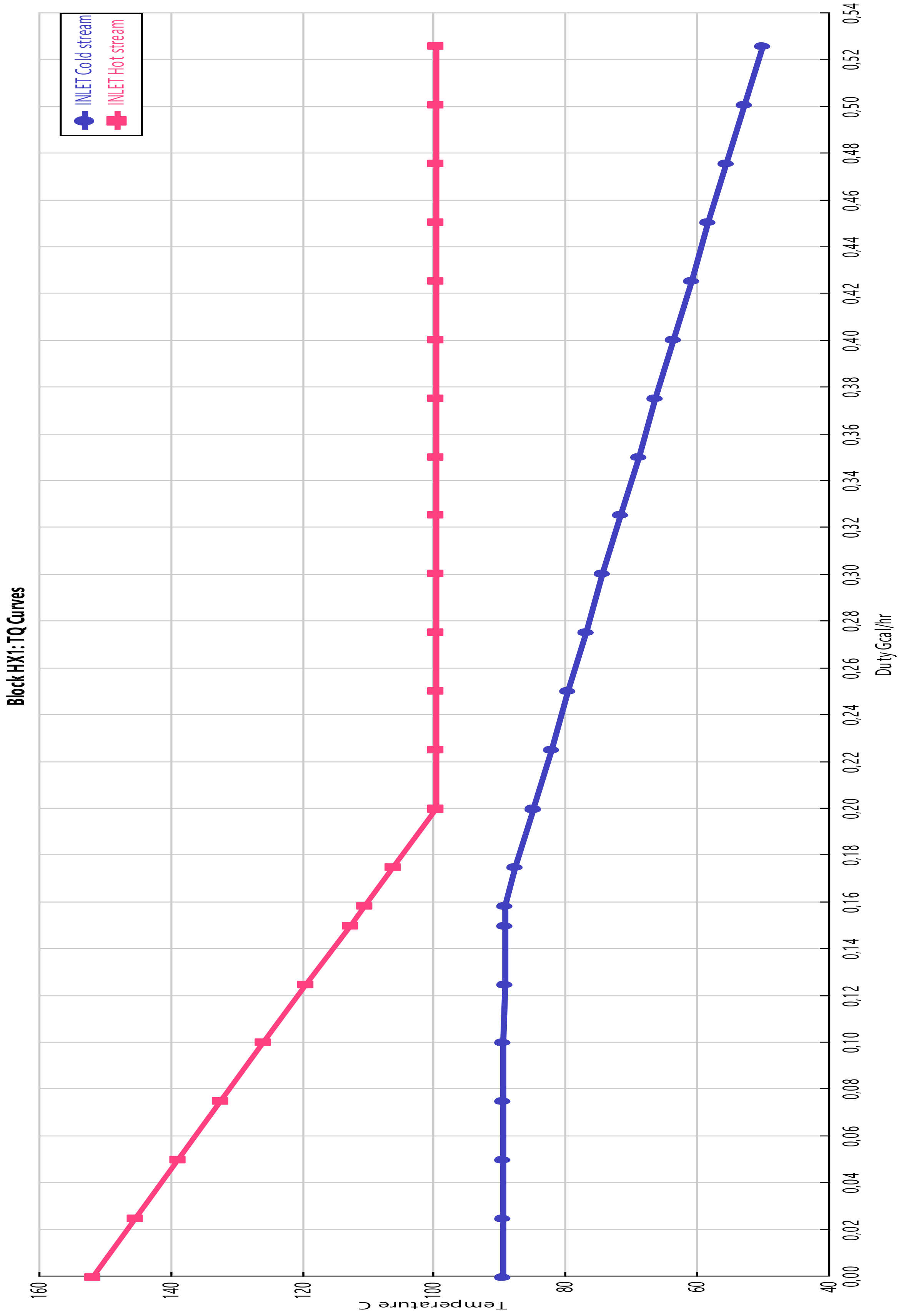

*Figure 30. Cold and hot composite curve for heat exchanger when Comp.1 has an outlet pressure of 1 bar.*

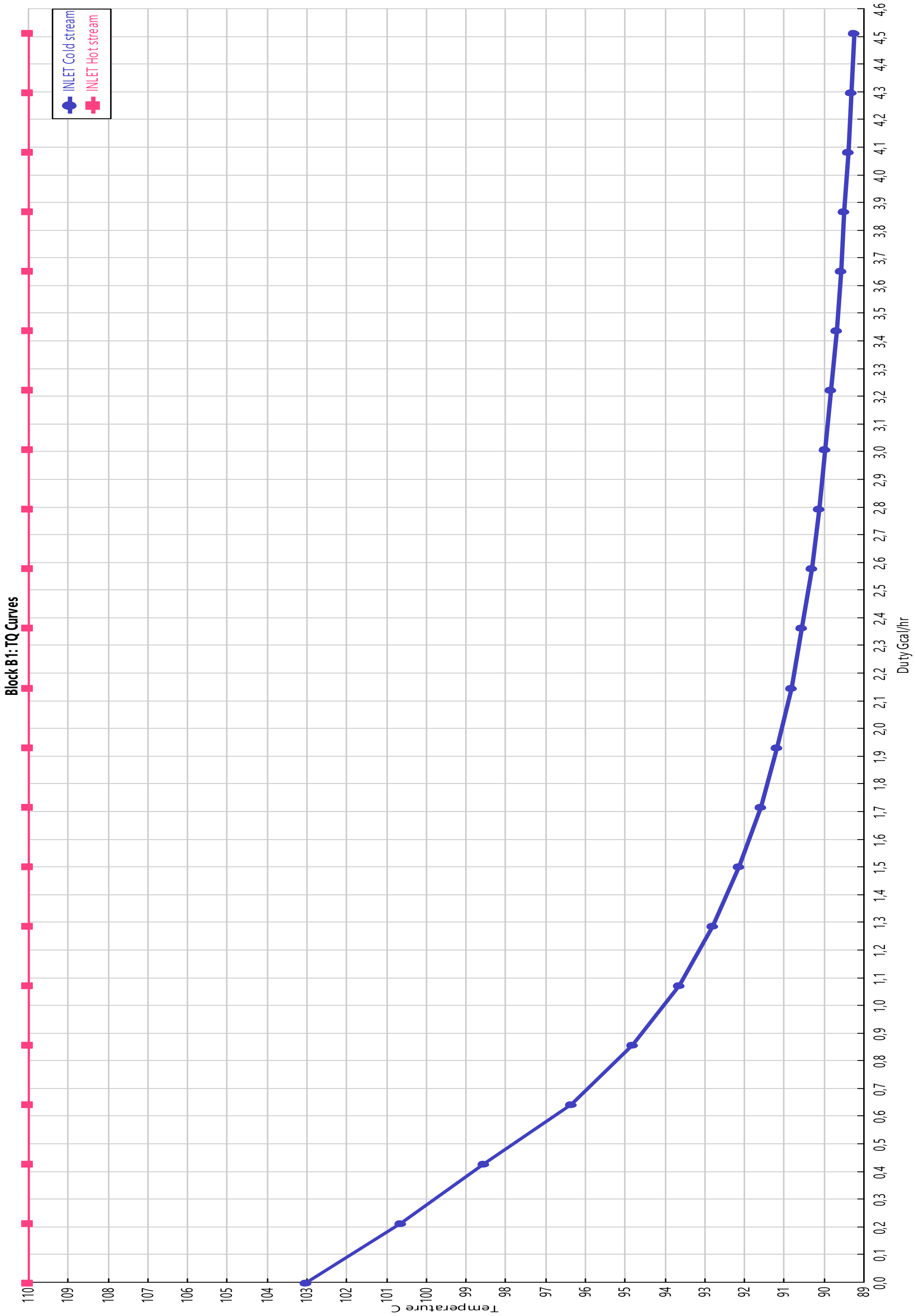

*Figure 31. Cold and hot composite curve for Evap. 1, when Comp.1 has an outlet pressure of 1 bar.*

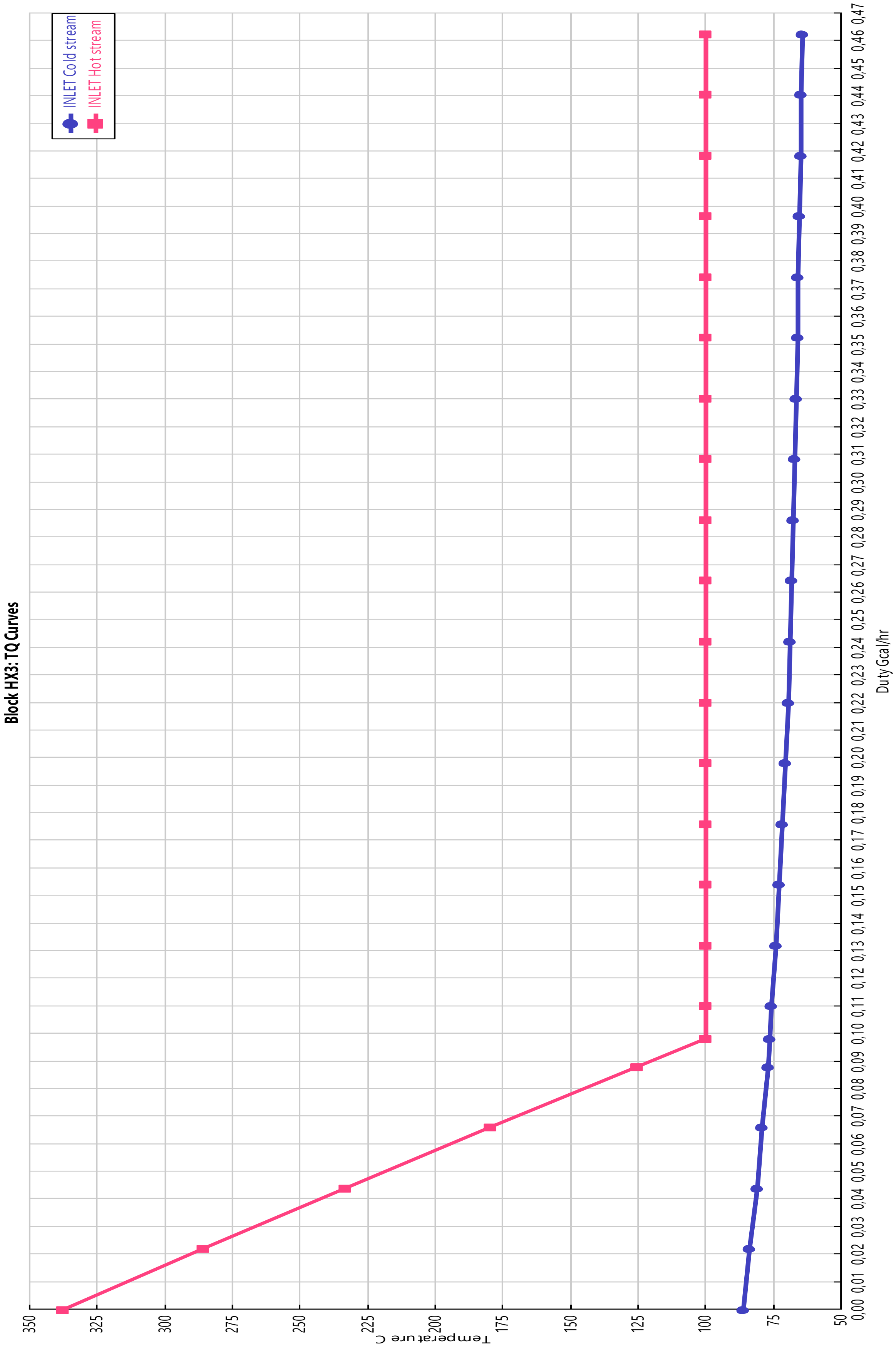

*Figure 32. Cold and hot composite curve for Evap. 2, when Comp.1 has an outlet pressure of 1 bar.*

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