Industrial Application of Eutectic Freeze Crystallization

A Thesis submitted to the

UNIVERSITY OF CAPE TOWN

In Fulfilment of the Requirements for the Degree

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

By

Rineshkumar Bharat Jivanji

Department of Chemical Engineering

University of Cape Town

Rondebsoch

7700

South Africa

February 2011

Declaration

I know the meaning of plagiarism and declare that all work in the dissertation, save for that which is properly acknowledged, is my own.

Signature:_____ Date:22nd May 2011

Synopsis

South African industries are currently generating increasing quantities of hypersaline brine streams. These wastewater streams need to be processed in an ecologically friendly and economically favourable method to produce both purified water and salts. Currently, the most widely implemented brine treatment strategies in South Africa are discharges to evaporation ponds and Evaporative Crystallization (EC). Limitations of these and other conventional methods include high energy requirements, environmental repercussions, large land requirements, impure salt and water products and a remaining, even more concentrated, brine stream.

Eutectic Freeze Crystallization (EFC) offers an innovative solution to the purification of wastewater streams. EFC has proved to be both economically and ecologically viable for certain single salt-water systems. In this study, four case study brines were chosen to broadly represent a South African industrial brine. Comprehensive brine analysis revealed that the brines varied in concentrations between 18,800 - 187,000mg/l, with dominant ions of Na^{+}, Ca^{2+}, K^{+}, CO_3^{2-}, SO_4^{2-} and Cl^{-} accounting for more than 98% of the Total Dissolved Solids (TDS) in the brines.

This report focused on the energy requirements of the EFC process and a direct preliminary operating cost comparison with the energy requirements of EC. Calculated operating costs for the EFC process varied between R29/m^3 and R31/m^3, with the cost to treat a brine increasing with increasing TDS. The calculated operating costs for the EC process were reasonably high, varying between R135/m^3 and R138/m^3. Even if the operating costs for the EC process were overestimated the large difference in operating costs for the two processes showed favourable cost savings for the EFC process, which excluded the revenue generated from the re-sale of pure salts from the EFC process.

EC is a well established process whereas EFC had the potential to incorporate heat integration using the ice slurry generated to pre-cool the feed brine and to condense a fraction of the refrigerant in the condenser of the refrigeration cycle. Heat integration options were highly brine dependent with operating cost savings ranging between 13% and 24%.

The capital cost comparison for the two processes were based on the method employed by (Vaessen 2003). As expected, the capital costs for the EFC process, a relatively new process, were much higher than the already well established multi-effect EC process. Calculated capital costs varied between R16 million and R22million, which were on average five times higher than that of the EC process. Capital costs for the EFC process are expected to decrease with the potential for improvements in the EFC process outweighing the well established EC process. The total cumulative costs (operating + capital costs) over a 10 year period showed a large cost savings for the EFC process over the EC process after just two years.

This study focused on a thermodynamic model for both the EFC and EC processes, with operating costs based solely on energy consumption of the major units. It is recommended that once sufficient kinetic work is carried out, that a more refined model, which includes both thermodynamics and kinetics, be proposed. Operating costs should incorporate all units and capital costs be determined on a South African scale and not that of the method employed by

(Vaessen 2003). In conclusion, it must be noted that EFC may not be the best hypersaline brine treatment method and that an integration of various brine treatment methods needs to be considered to help alleviate the stresses associated with South African industrial waste water streams.

Acknowledgements

I would first like to thank God for always opening the right doors to lead me to where I have come. The experiences, mistakes and achievements I have learnt from are credit to you.

I would like to thank my supervisors, Professor Alison Lewis and Mr Jeeten Nathoo for their supervision during this project. Your help and guidance has taught me a great deal.

Thanks must be given to the members of the Crystallization and Precipitation Unit for their continual support, which has certainly made the past two years a really enjoyable experience. I would like to thank the unit for their support for funding this project.

Special thanks must be given to Dr Mike Dry for his support and willingness to help me with my simulation whenever I was stuck.

To my parents and my siblings, your support and belief in me over my growing years cannot be ever repaid and only God knows how thankful I am. To my closest family, thank you for your support, patience and understanding through my university career, especially Ketanbhai, your kindness and support was greatly appreciated.

Lastly to my close friends, Melisha, Mariam, Mitesh, Muhammad and Nabeel, through the past six years you have been by my side, Thank You.

Table of Contents

List of Figures

List of Tables

Chapter 1: General Introduction

The total combined projected brine production rates for coal and gold mining is expected to be in the region of 15000m^3/day in the next 20 years (Figure 1).

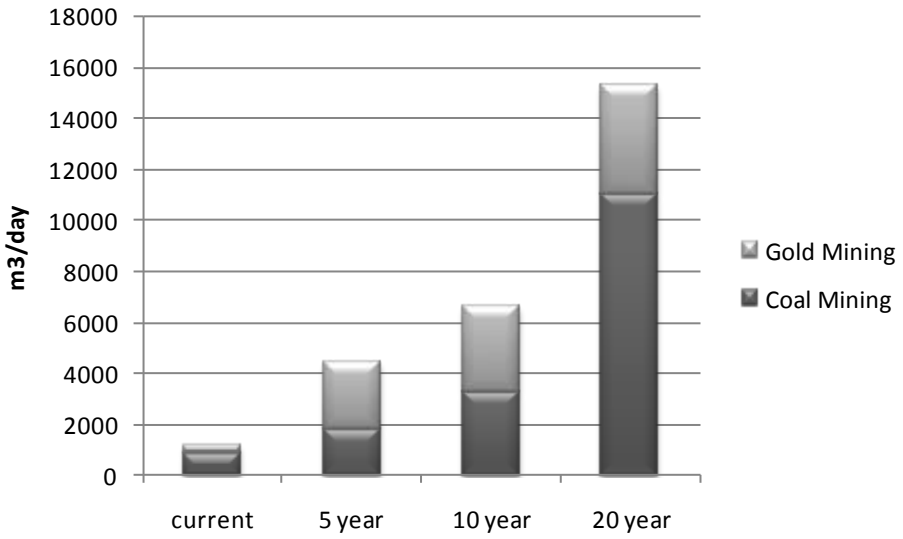


Figure 1: Projected Brine Generation for South African Industries (van der Merwe et al. 2009)

There are currently two major problems currently facing South African water users, firstly: the declining availability of sufficient quantities of water and secondly: the deterioration of the quality of available water (Buckley 2005). South African industries have looked at various water recycling technologies to reduce their fresh water consumption such as desalination, inorganic precipitation, ion exchange and membrane treatments. These treatment methods inevitably produce large quantities of concentrated inorganic brines which subsequently need to be disposed of or treated in an environmentally sustainable manner.

Conventionally, salts are separated from these hypersaline brines by evaporative or cooling crystallization, producing purified water. Evaporative crystallization is costly due to its high energy consumptions as a result of the high heat of vaporization of water. Furthermore, it has the added disadvantage in that it frequently produces a mixed salt product. Consequently the disposal of these mixed salt products to waste landfill sites is uneconomical and is becoming increasingly unsustainable due to the reduced availability of land for the rising brine production rates. The recovery of both water and reusable salts from these industrial process streams is ideal as it will help reduce the environmental impact of disposal of the salts and allow large quantities of process waste streams to be treated in both an ecological and economical manner.

Eutectic Freeze Crystallization (EFC) provides an innovative solution to treating brines and concentrates which produces purified water and pure salts. The principal behind EFC is that a reduction in temperature of a brine stream to conditions where both ice and salt will crystallize out. This will result in the ice and salt crystals being subsequently separated out based on the density difference between them.

From an energy efficiency perspective, due to the fact that the heat of fusion for the formation of ice is six times lower than the heat of vaporisation of water, EFC has been proven to be very

energy efficient, requiring less energy than alternative methods of separation such as evaporative crystallization (van Der Ham 1999). However, this principle has only been applied to certain single salt-water systems. The current study focused on expanding on this principle and its applicability to sequential salt separation in multi-component complex hypersaline brines that are broadly representative of South African industrial brines. The applicability of EFC for the treatment of the hypersaline brines was investigated within the context of its relative energy requirements, operating costs and capital costs and compared to evaporative crystallization. The potential of heat recovery within the EFC process was also evaluated.

1.1 Objectives

The objectives of this study were firstly to obtain an estimate of the operating and capital costs for an EFC process to treat a South African industrial brine. Furthermore, the operating and capital costs were compared to the costs of a comparable, current brine treatment process - Evaporative Crystallization (EC), albeit that the cost of salt disposal for the EC process is not taken into account, which would further add to the operating costs of the EC process.

To calculate the operating and capital costs, both processes were thermodynamically modelled to estimate energy requirements for the two processes. The operating costs were determined solely on energy requirements for both processes (i.e. the cost of electricity for the refrigeration cycle in EFC and the cost of steam for the EC process) with the costs of pure salt resale and disposal not taken into account.

1.2 Hypotheses

The heat of fusion of water is approximately six times less than the heat of evaporation of water. Hence it follows that EFC would be more energy efficient than EC for treating multi-component complex hypersaline brine; making it more economically viable than the conventional evaporative crystallization route.

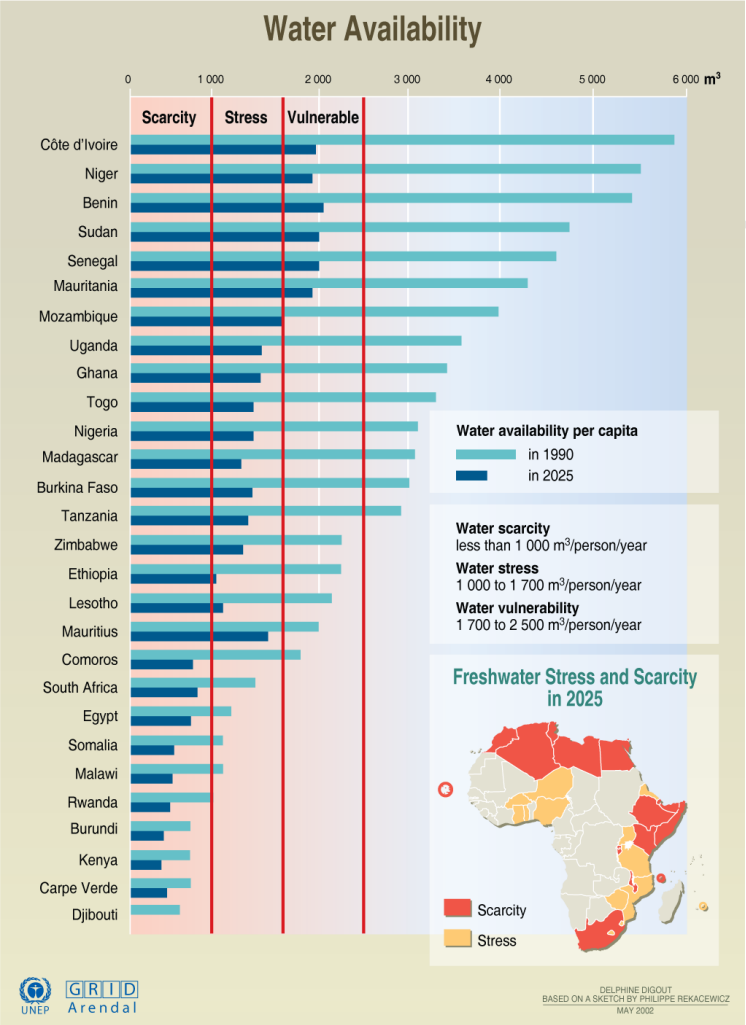
1.3 Scope of study

This study was based on four case study brines with varying concentrations which are broadly representative of South African industrial brines. The project focuses on the thermodynamic modelling of each of the case study brines to calculate the energy requirements for the EFC & EC processes and hence, the associated economics. A comparison between the two treatment processes was carried out and conclusions were drawn on the advantages of using a novel EFC process over the EC process.

Chapter 2: Literature Review

2.1 Current Brine Status

South Africa is classed as a semi-arid region, with climatic conditions varying from desert and semi-desert to sub-humid. The country's water resources are, in global terms, scarce and extremely limited (GCIS 2009). The average rainfall in South Africa is about 500mm per annum which is significantly less than the average worldly annual rainfall of 800mm. Figure 2 highlights the predicted water availability statuses of African countries in 2025 (Rekacewicz 2002).



Source: United Nations Economic Commission for Africa (UNECA), Addis Abeba ; Global Environment Outlook 2000 (GEO), UNEP, Earthscan, London, 1999.

Figure 2: Water availability in Africa (Rekacewicz 2002)

According to Figure 2, South Africa's 2025 water availability per capita is classified as scarce. Other countries with similar classifications have climates which are primarily desertous. South Africa depends mainly on surface-water resources for the urban, industrial and irrigation water supplies in the country (GCIS 2009).Figure 3 shows the major consumers of water in South Africa per capita.

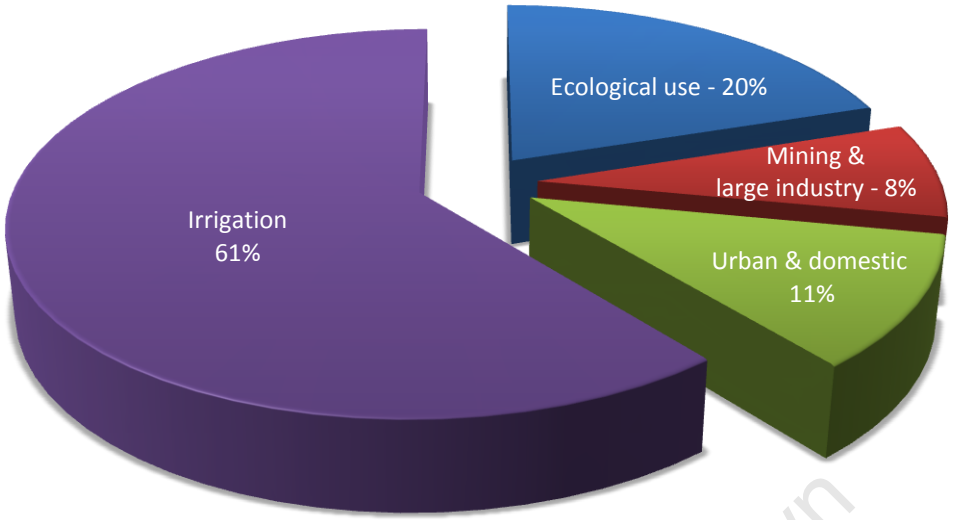


Figure 3: South Africa's water consumption per sector (DWAF 2004)

Although the industrial, mining and power generation sectors account for 8% of South Africa's total water consumption, the wastewater produced from these sectors can, if polluted and disposed of incorrectly, have negative impacts on current surface water reserves. Stricter environmental regulations have forced many industrial sectors, particularly the mining sector, to control wastewater disposal by exploring current and novel treatment methods. Due to the extensive water use in a multitude of process operations, the effluent water is, in most cases, a complex, multi-component stream containing amongst other elements, solid, organic and toxic elements. Consequently, the treatment of these effluent streams to recover recyclable water further concentrates these streams resulting in complex hypersaline brines.

Industrial sectors close to the sea have the option of disposing brines into the marine environment; however this too is under increasing constraints. The majority of industries generating large quantities of brine are further inland and disposal to the marine environment is not a viable option. Table 1 below highlights the amount of brine and salt generated by various sectors in South Africa including the amounts disposed to the marine environment.

Table 1: Brine and salt production rate for various South African Sectors (van der Merwe et al. 2009)

Sector	Total effluent			Salt load to environment		
	Total effluent [kl/day]	Total excl marine [kl/day]	Portion excl marine [%]	Total salt [t/day[]	Total salt excl marine [t/day]	Portion excl marine [%]
Paper & Pulp/Wood	272001	89001	16.6	1440	80	7.6
General Packaging	1950	1950	0.4	2	2	0.2
Steel/metals processing	30500	30500	5.7	72	72	6.8
Petroleum	83900	69100	12.9	354	300	28.3
Chemical	13070	11070	2.1	51	44	4.2
Power Generation	132000	132000	24.7	158	158	14.9
Mines	145025	145025	27.1	350	350	33.1
Chemical suppliers	528	528	0.1	0	0	0.0
Dairy	2700	2700	0.5	4	4	0.4
Sugar	8100	3900	0.7	10	2	0.2
Canning	2200	2200	0.4	1	1	0.1
General food	13970	10970	2.1	11	5	0.5
Pharmaceutical & personal care	1430	1430	0.3	1	1	0.1
Animal Nutrition	1205	1205	0.2	1	1	0.1
Poultry & Meat	12100	12100	2.3	8	9	0.8
Beverage	14670	14670	2.7	11	11	1.0
Textile	6000	6000	1.1	13	13	1.2
Waste management	190	190	0.0	5	5	0.5
Fish Processing	220700	200	0.0	7921	1	0.1
Totals	**962239**	**534739**	**100**	**10413**	**1059**	**100**

From Table 1, the largest contributors to brine production (excluding marine disposal) are the mining (27.1%), power generation (24.7%), paper & pulp/wood (16.6%) and petrochemical (12.9%) industries. These industries account for 81.3% of the 535 000 kl of brine being produced daily. These brines are either treated in the appropriate manner or are being disposed of to surface waters. Major sources of pollution of surface waters are agricultural drainage and wash-off (irrigation return flows, fertilisers, pesticides and runoff from feedlots), urban wash-off and effluent return flows (bacteriological contamination, salts and nutrients), industries (chemical substances), mining (acids and salts) and areas with insufficient sanitation services (microbial contamination) (DWAF 2004).

Recovery of water from the brines is important; however recovery of the salts is fast becoming just as important. Highly concentrated brines and mixed salt products cannot be disposed of indefinitely and have to be treated in a correct, sustainable manner. Various disposal strategies, including innovative approaches, will be discussed in the next section.

2.2 Current Brine Management Strategies

Commonly employed brine management strategies worldwide include (van der Merwe et al. 2009):

- Evaporative (mechanical) crystallization
- Discharge to evaporation ponds
- Disposal to surface water bodies and sewers
- Land application and irrigation

However, in South Africa, discharges to surface water and sewers, as well as irrigation are not practical options, except for the smallest applications, which require very dilute brines (van der Merwe et al. 2009).

More recent brine management strategies include:

- Wind Aided Intensified Evaporation, WAIV enhanced evaporation
- Dewvaporation
- Extractive Crystallization
- Ion Exchange
- Freeze Crystallization

Many of the more recent forms of brine treatment techniques, namely Dewvaporation and WAIV, are currently at the pilot plant stage with no industrial scale plants having yet being developed (Brandhuber et al. 2008).The following sections will highlight the main advantages and disadvantages of each of these brine management strategies. Furthermore, a summary of the total cost of implementing five such strategies for treating a 1000m^3/day brine will be presented according to van der Merwe et al. (2009). A cost comparison between extractive crystallization and evaporation crystallization has been shown by Zijlema et al. (2000) and will be discussed in Section 2.2.5.

2.2.1 Evaporative Crystallization

The most common saline separation method used in industry is Evaporative Crystallization (EC); in which the aqueous salt solution is heated causing the water to evaporate and the salt to crystallize out. In this process, the majority of the energy is used to heat the water and convert it to its pure state by a phase change from water to steam, allowing it to be physically separated from the salt (Hartmann 2006). The solution becomes more concentrated as more water is evaporated off, resulting in a boiling point elevation. The increase in boiling point consequently increases the energy required to evaporate the water. Major disadvantages of EC include (van der Merwe et al. 2009):

- High capital cost resulting from the use of exotic materials due to corrosion and erosion problems
- In most cases a mixed salt product is produced, which needs to be disposed of at an additional cost
- High maintenance
- Skilled labour
- High operating costs.

A summary of the costs to install a plant with a 20 year project life for a 1000m^3/day brine is presented in Table 2.

Table 2: Estimated costs for an evaporative crystallization plant (van der Merwe et al. 2009)

Capital cost estimate [Rm]	Operating cost estimate over 20yr project life [Rm]	Total cost over 20yr project life [Rm]
180	267	447

The work carried out by van der Merwe et al. (2009) for cost estimation does not take into account the final store of the salt product and a cost of disposal for the purge stream for the crystallizer. These two factors would both increase the final capital costs.

2.2.2 Solar Evaporation

Solar evaporation is well established and is the preferred disposal method in arid and sparsely populated areas. Evaporation ponds may be lined or unlined. However, 'unlined' is not a feasible option due to groundwater contamination even in arid areas. Disadvantages of evaporation ponds (van der Merwe et al. 2009) include:

- High disposal and low evaporation rates which increases land requirements rapidly
- Prevention of groundwater contamination requires liners of synthetic membranes such as PVC, further adding to costs
- Seepage from damaged lining or poorly constructed ponds can contaminate groundwater
- Wildlife protection and management is an additional supervisory cost

A survey by (Mickley 2001)showed that only 6% of the installations in the United States of America used this method of concentrate disposal up to 1993 and only 2% after 1993. The decrease could be due to the large land requirements of this method. A study carried out by van der Merwe et al. (2009) evaluated the costs to implement an evaporation pond over a 20 year period for a 1000m^3/day brine. The results are presented in Table 3.

Table 3: Estimated costs for an evaporation pond (van der Merwe et al. 2009)

Capital cost estimate [Rm]	Operating cost estimate over 20yr project life [Rm]	Total cost over 20yr project life [Rm]
150-230	1.2	151-230

The study was based on a 38.2ha double lined surface area, which may not have seemed practical but did provide a basis for comparison. The more recent methods of brine disposal, which use the principle of evaporation, discussed in the next section have both arisen from the need to improve efficiencies of evaporative ponds and reduce the large surface areas required.

2.2.3 WAIV Enhanced Evaporation

WAIV, wind aided intensified evaporation, builds on the idea of using solar energy to evaporate water, by, increasing the evaporation rate. Specific materials are chosen which are hydrophilic enough to allow the water to spread on the material but at the same time not too hydrophilic as to reduce the effective vapour pressure. By deploying such surfaces in arrays with large lateral dimensions, significant height and with minimal depths (e.g. 3-4 m); the wind can be exploited while it is still less than saturated with vapour (Gilron et al. 2003). The material needed to

construct the WAIV unit can work out expensive on comparison to evaporation ponds even though they require less surface areas.

Figure 4: WAIV unit (van der Merwe et al., 2008))

A WAIV unit was constructed with hydrophilic materials and wetting methods that allowed increasing the evaporative capacity per area foot-print by a factor of ten or more (Gilron et al. 2003). A summary of the costs of installing WAIV units to treat a 1000m^3/day brine are shown in Table 4.

Table 4: Estimated costs for a WAIV unit (van der Merwe et al. 2009)

Capital cost estimate [Rm]	Operating cost estimate over 20yr project life [Rm]	Total cost over 20yr project life [Rm]
100	30.5	130.5

Although the WAIV plant may only require 1.9ha of double lined surface area, a final salt store of 9.2ha is also required. Additionally, the WAIV units need to be spaced out further increasing the overall surface area. The WAIV technology may present greater advantages over solar evaporation but both have shortcomings in that the water is not recovered and is lost to the atmosphere and smaller, yet highly concentrated brine volumes still remain.

2.2.4 Dewvaporation

The Dewvaporation process is a patented technology that uses a humidification/dehumidification cycle to purify water (van der Merwe et al. 2009). A simplified diagram is shown in Figure 5 to highlight the process.

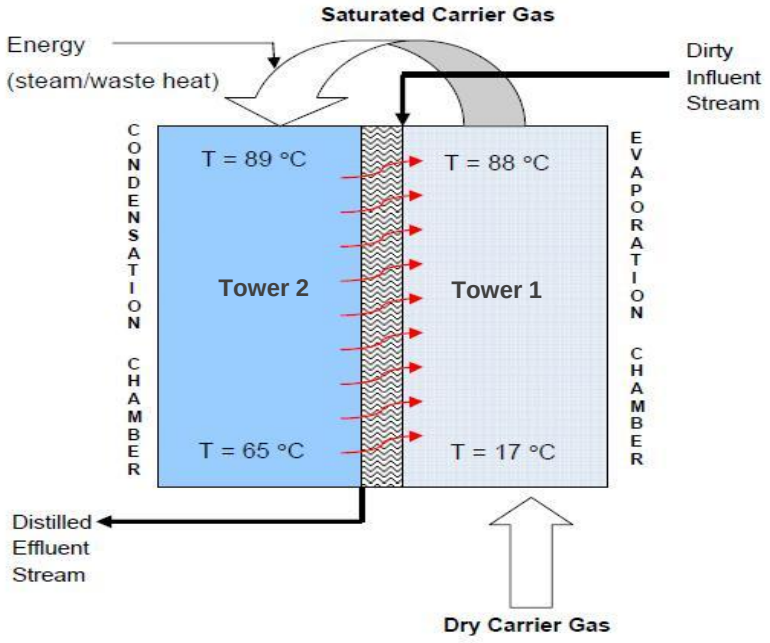


Figure 5: The Dewvaporation process (van der Merwe et al. 2009)

The Dewvaporation tower is primarily made up of two chambers with an internal heat exchanger. The first tower is for the evaporation of the brine, which is dribbled on the side of the wall, into a dry air stream that is passed up from the bottom. The heat that is transferred to the dry air stream increases its temperature, thereby increasing the water carrying capacity of the air. The air stream is then further heated upon leaving the tower and returned into the second chamber. Heating the air stream laden with water, increases the stream temperature providing the driving force for heat transfer into the first chamber. As the stream temperature decreases in the second chamber, the water condenses out on the wall opposite to the heat transfer wall. The process does not have any moving parts and corrosion of materials can be avoided by using plastics. The process produces a purified water stream and a concentrated brine stream that still needs to be treated. Other disadvantages include (van der Merwe et al. 2009):

- There is no evidence of the overall efficiency claimed by the technology suppliers being reached.
- Scaling on heat transfer surfaces may significantly reduce the overall efficiencies
- Ambient air temperature and humidity may limit effectiveness of the process significantly

A summary of the costs of installing a Dewvaporation plant to treat a 1000m^3/day brine has been presented in Table 5.

Table 5: Estimated costs for a Dewvaporation plant (van der Merwe et al. 2009)

Capital cost estimate [Rm]	Operating cost estimate over 20yr project life [Rm]	Total cost over 20yr project life [Rm]
44	84	128

2.2.5 Extractive Crystallization

Extractive Crystallization (antisolvent crystallization) is an alternative technique to process the brine solution. This technique is illustrated using a NaCl brine in Figure 6 and involves the introduction of a new component (antisolvent – i.e. an Amine), in which the solute (NaCl) is insoluble.

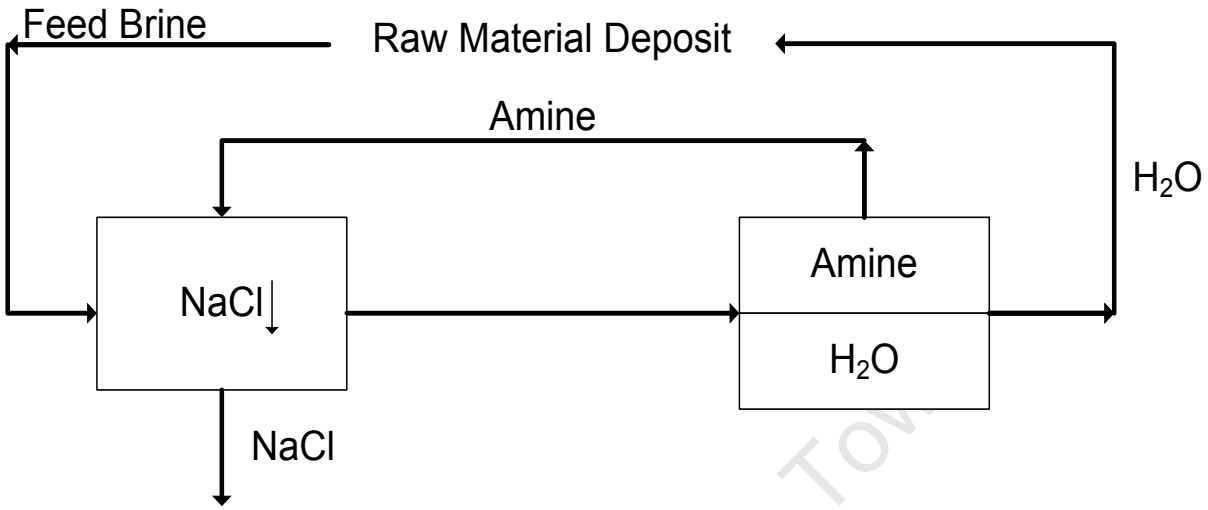


Figure 6: Extractive crystallization flowsheet

The introduction of the antisolvent causes a sudden decrease in the solubility of the solute (NaCl) causing it to crystallize out and subsequently requires separation of the solid and liquid phases. The water/antisolvent mixture can be separated by varying the temperature of the mixture and allowing the antisolvent to be re-used (van Der Ham 1999).

Applying extractive crystallization to treat an industrial brine is difficult due to the number of different dissolved ions present in the brine. The different salts need to be insoluble in the antisolvent to precipitate all the salts, consequently producing a mixed salt product that needs further treatment. A further option could be to use a number of antisolvents to selectively precipitate out certain salts. However this will incur further operating and capital costs.

Zijlema et al. (2000) looked at the applicability of antisolvent crystallization to the production of NaCl as compared to Evaporative Crystallization. They found that the major operating costs were in fact 9-20% higher for antisolvent crystallization. Estimated fixed capital costs were 8-55% higher, depending on the anti-solvent crystallization process configuration that was chosen. Extractive crystallization has a major shortcoming in that either the water or crystallized product is contaminated with anti-solvent, which subsequently will increase the operating costs. Thus, its application to treating an industrial wastewater stream is limited.

2.2.6 Ion Exchange Resins

In water purification, ion exchange resins are polymers laden with H^+ and OH^- ions. A stream is passed over a first resin which will bind with certain cations (Na^+, Ca^{2+}) more readily than with the H^+ ions, displacing them from the resin. The stream is then passed over the second resin where the OH^- ions are displaced and then allowed to react with H^+ ions forming water. The resins are regenerated with a strong acid (e.g. HCl for cation removal) and a strong base (e.g. NaOH for anion removal). Ion exchange has advantages of low running costs. Very little energy is required, the regeneration chemicals are cheap for small applications and if well maintained

resin beds can last for many years before replacement is needed (Alchin 1998). However, disadvantages include significant fouling and contamination of the resins which include (Alchin 1998):

- Calcium sulphate fouling
- Iron fouling
- Adsorption of organic matter
- Organic contamination from the resin
- Bacterial contamination and
- Chlorine contamination

Ion exchange may also produce a highly mineral free stream but at the expense of a smaller concentrated water stream during regeneration of the resin resulting in none of the salts being recovered.

2.2.7 Freeze Crystallization

Freeze Crystallization (FC) is a method used in the food industry for the concentrating of juices and beverages. Freeze Crystallization started off as a desalination technique but was not implemented due to the unavailability of large scale washing equipment (van Der Ham 1999). Freeze crystallization can be used to separate water from organic chemicals as well as a wide range of materials such as water from seawater, brines or organic waste (Conlon 1992). Due to the problems and inefficiencies associated with evaporative systems, freeze desalination has once again being investigated. Table 6 summarizes the costs of installing a 1000m^3/day freeze desalination plant.

Table 6 Estimated costs for a freeze desalination plant (van der Merwe et al. 2009)

Capital cost estimate [Rm]	Operating cost estimate over 20yr project life [Rm]	Total cost over 20yr project life [Rm]
147.8	90.9	238.7

The costs that have been calculated were based on relatively inefficient ice making equipment and includes a WAIV evaporation pond for disposing off the final brine.

2.2.8 Eutectic Freeze Crystallization

Eutectic Freeze Crystallization (EFC) first emerged from the continued research in freeze crystallization and the first literature was published in the 1970s (Swenne 1983; Barduhn & Manudhane 1979; Stepakoff et al. 1974). EFC, however, involves the formation of two solid phases whereas FC produces only one solid phase.

The EFC process for a binary system has been compared to the evaporative crystallization process by both van Der Ham (1999) and Vaessen (2003). van Der Ham (1999) showed that for a KNO_3 waste stream EFC had an operating cost savings of 55%, however the investment costs were much higher (about 86% higher) than that of evaporative crystallization. Vaessen (2003) showed that the energy costs saving for the EFC process was about 69% and also observed a much higher investment cost for the EFC process by about 5 times.

Conventional techniques for salt separation have disadvantages such as the high energy requirements in evaporative crystallization, the limited yield in cooling crystallization and a

limited operating range for reverse osmosis. These techniques recover part of the water but still form a concentrated brine solution or a single solid phase. Thus, separation of a multi-component complex hypersaline solution using these methods will result in crystallization of all salts in one solid phase.

2.2.9 Summary of Brine Treatment Strategies

Figure 7 classes the various hypersaline brine treatment strategies discussed before, in terms of product recovery. Included in the diagram are the relative operating and capital costs for treating a 1000m^3/day brine. The costs for the anti-solvent crystallization process are estimated using the percentage costs relative to the evaporative crystallization process.

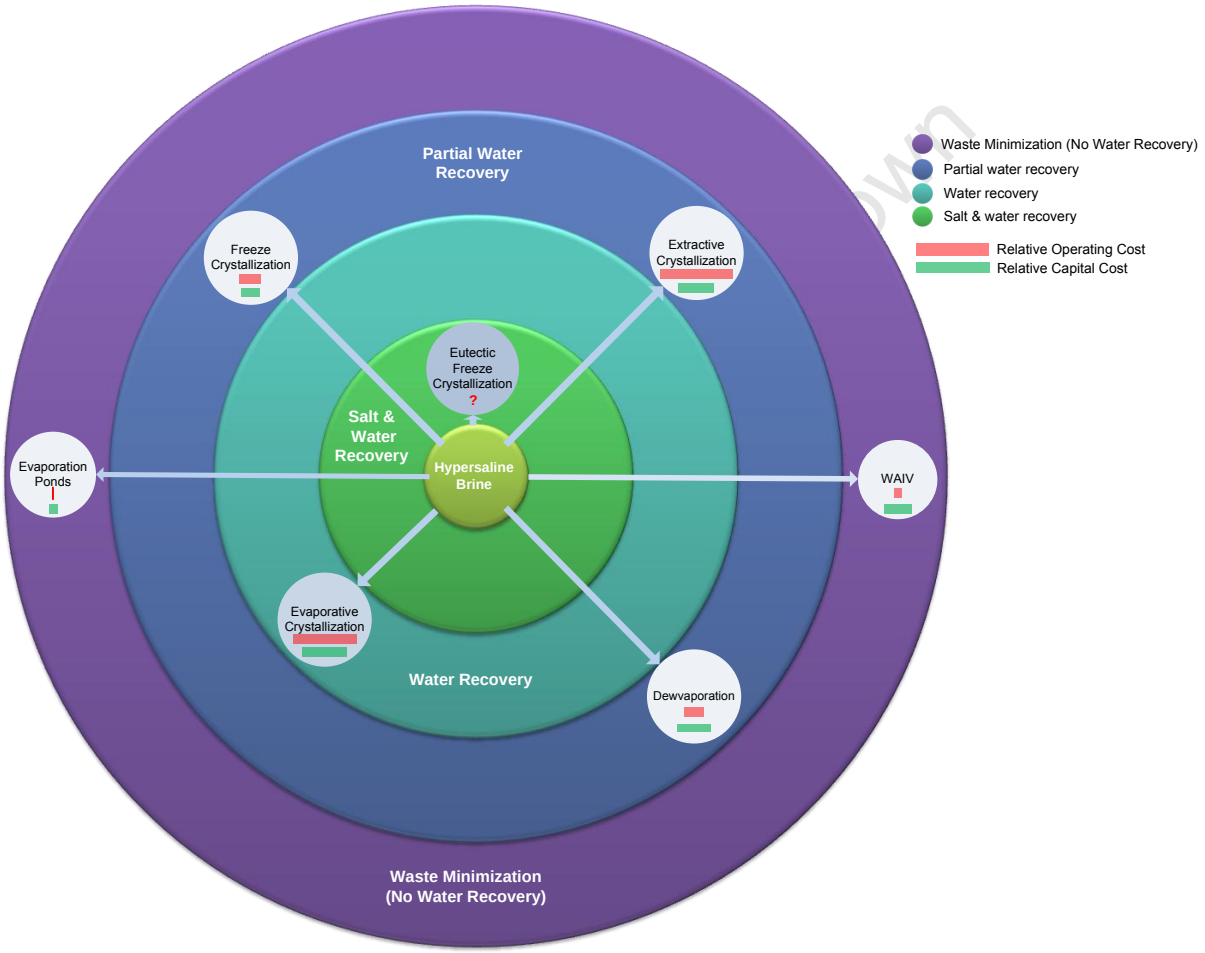


Figure 7: Summary of brine treatment strategies

The outer tier in brine treatment strategy diagram represents those processes that only minimize the waste stream. Two processes fall under this class; evaporation ponds and WAIV units. These two processes separate the water but it is lost to the environment and hence is not available for re-use within the process at large. The second tier describes processes that recover part of the water but still produce a concentrated multi-component brine stream that needs to be further treated, consequently increasing the operating costs. Evaporative crystallization recovers most of the water and produces a mixed salt product that needs to be further treated/disposed of, also incurring additional mixed salt disposal costs. The EFC process has the

potential to produce both pure water and recoverable salts, thus making it the most attractive brine treatment option and will be discussed in detail in the following chapter.

2.3 Eutectic Freeze Crystallization

Eutectic Freeze Crystallization (EFC) provides an innovative approach to treating brines and concentrates that can produce purified water and pure salts. The binary phase diagram below (Figure 8) is used to illustrate the principle of EFC. The phase diagram is made up of four distinct regions:

1) A liquid phase: unsaturated solution
2) A liquid–solid phase: ice and unsaturated solution
3) A liquid–solid phase: salt and saturated solution
4) A solid phase: ice and salt

The binary phase diagram is made up of an ice solubility line and a salt solubility line which respectively show the equilibrium between the ice/salt and the saturated solution at various temperatures. These two intersect at a specific temperature and weight fraction of salt, termed the eutectic point, where two solids are in equilibrium with a single liquid phase and vapour phase. In the region below the eutectic temperature two solid phases exist, ice and salt. Whilst pure water freezes at 0°C, the addition of salt to water affects the freezing point by either elevating or depressing it.

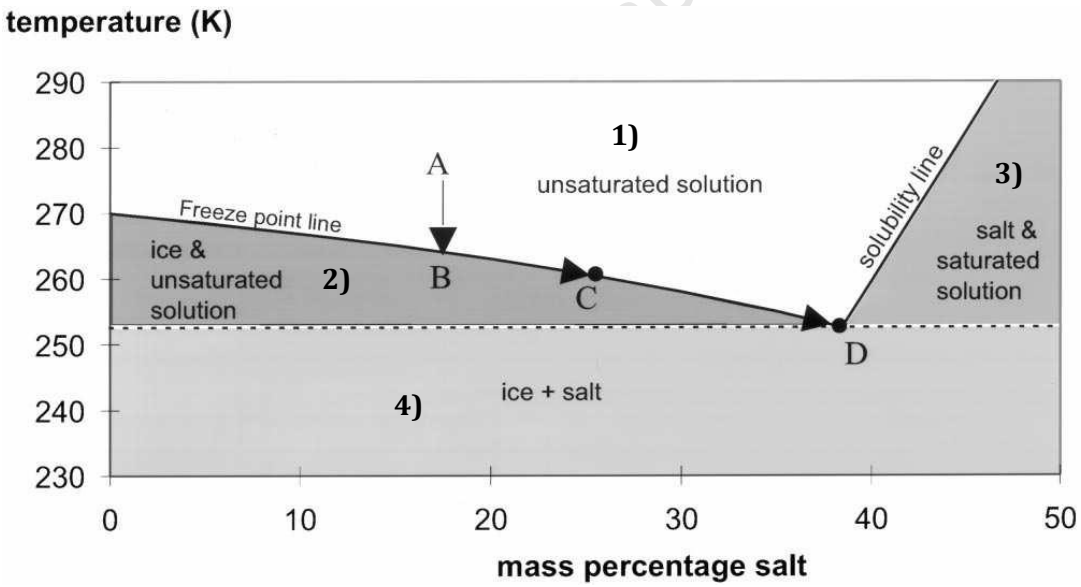


Figure 8: Salt- Water Phase Diagram (van Der Ham 1999)

A feed stream with composition 'A' enters the crystallizer which is maintained just below its eutectic temperature. As heat is removed from the stream, it is cooled from point A to point B, located on the ice freezing point line. At this point ice will begin to crystallize out. As the solution is cooled further the concentration of the brine moves along the solubility line from point B to C, producing more ice and finally to the eutectic temperature and composition at point D. At the eutectic point, further cooling results in the simultaneous crystallization of pure ice and salt. Due to the density difference between the ice and salt crystals they can be separated by allowing the ice to float to the top and the salt to sink to the bottom. For a more concentrated feed solution, point A would be located on the right of the eutectic point and upon

cooling, the system will reach the salt solubility line resulting the salt in crystallizing out first as opposed to the ice.

For a ternary system (i.e. two salts and water), the phase diagram resembles that shown in Figure 9.

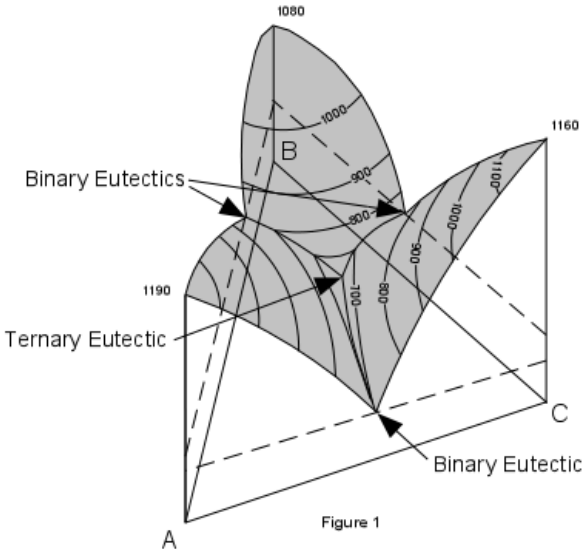


Figure 9: Ternary Phase Diagram (Nelson 2002)

In the ternary phase diagram, two components form a binary eutectic line as opposed to a single binary eutectic point. The three binary lines intersect at a ternary eutectic point. As reading off a specific concentration and temperature can be difficult, an alternative method of presenting a ternary system is shown in the next section. A Na_2SO_4 – H_2O binary system will first be introduced followed by the introduction of the ternary system which includes $MgSO_4$.

2.3.1 Binary system – Na_2SO_4-H_2O

The Na_2SO_4-H_2O binary phase diagram is presented in Figure 10. Na_2SO_4 exists in two hydrated forms between the temperature range -25° to 60°C.

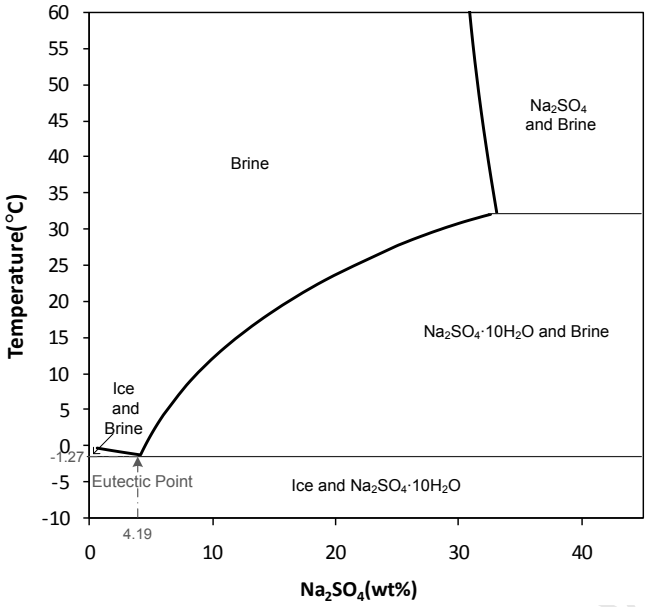


Figure 10: Na_2SO_4-H_2O eutectic phase diagram as calculated from the UNIQUAC model (Thomsen 2007)

The phase diagram above shows the stability of the different sodium sulphate salts as a function of concentration and temperature. The eutectic point of the Na_2SO_4 – H_2O system is at a temperature of -1.27°C and a salt weight percentage of 4.19%. A ternary phase diagram with $MgSO_4$ added as the second salt is shown in Figure 11.

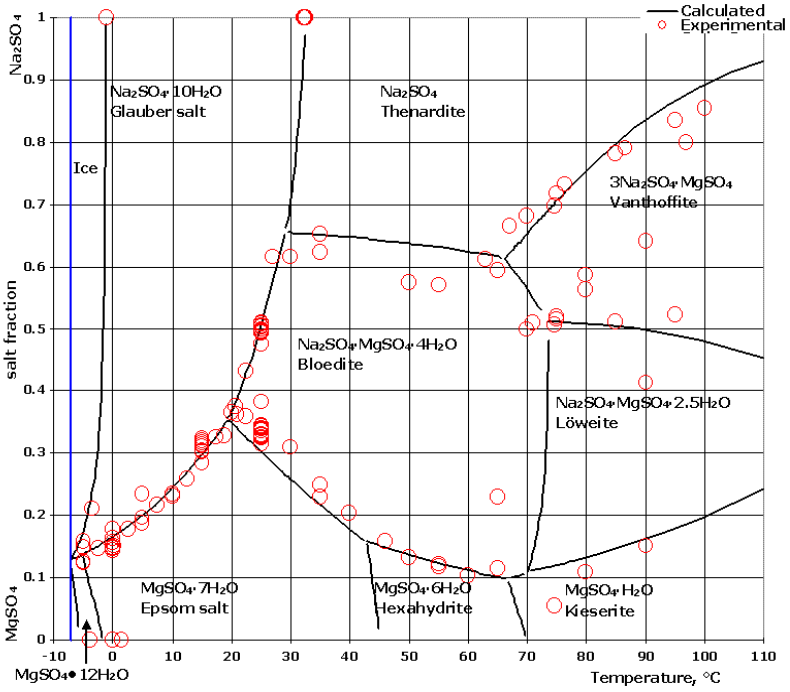


Figure 11: Ternary Phase diagram of $MgSO_4$-Na_2SO_4-H_2O system (Thomsen 2007)

This ternary phase diagram is presented in a 2-dimensional format as compared to the previous 3-dimensional ternary phase diagram shown earlier (Figure 9). The temperature is located on the x-axis with a salt fraction on the y-axis. Lewis et al. (2010) reported that using a binary

phase diagram to model a ternary system was not sufficient, as the ternary eutectic point of the $MgSO_4$-Na_2SO_4-H_2O system was -7°C as opposed to the binary eutectic of -1°C of the Na_2SO_4-H_2O system and -3.9°C of the $MgSO_4$-H_2O system. These differences would affect operating conditions, energy requirements and consequently operating costs.

Generating a phase diagram for a complex multi-component brine is difficult due to the lack of experimental solubility data at low temperatures. Furthermore, depicting and understanding a phase diagram with more than three components becomes much more difficult. Consequently using aqueous thermodynamic modelling software to model complex, multi-component hypersaline brines at low temperatures has proved to be very useful.

2.3.2 Aqueous Thermodynamic Modelling

Lewis et al. (2010) tested two modelling software programs, namely, MINTEQ and OLI Stream Analyzer. MINTEQ (Gustafsson 2007) is an equilibrium speciation model that can be used to calculate the equilibrium composition of dilute aqueous solutions in the laboratory or in natural aqueous systems. The OLI software uses a speciation-based thermodynamic model to calculate speciation and chemical equilibria as well as phase equilibria for multi-component aqueous systems (Lewis, Nathoo, Reddy, et al. 2010). It was found that MINTEQ could not model streams below 0°C whereas OLI Stream Analyzer can successfully model temperatures as low as -200°C.

2.3.3 Binary eutectic freeze crystallization process

Eutectic freeze crystallization utilizes the unique property of water in that the solid phase (ice) density is less than its liquid phase density. The density difference between the salt and ice crystals is generally of the order of magnitude of one kilogramme per litre (van Der Ham 1999). The salt and water crystals can thus be physically separated by gravity and isolated. The unit operation of a single salt-water EFC process is depicted in Figure 12:

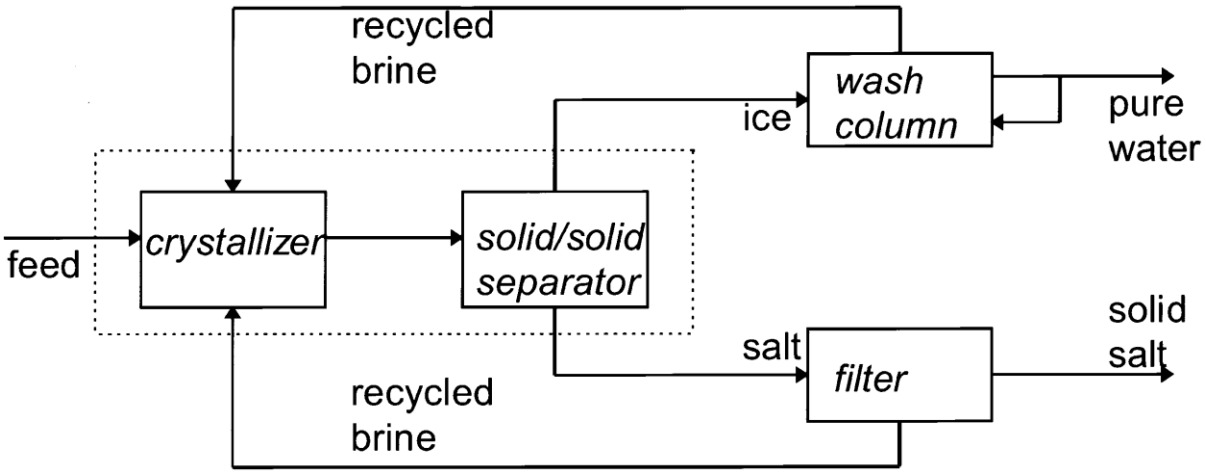


Figure 12: Flow Diagram for Binary Eutectic Freeze Crystallization (van Der Ham 1999)

A Eutectic Freeze Crystallization process generally has two particle processes occurring simultaneously, nucleation and growth. Hence, EFC equipment essentially has two stages for nucleation and growth of ice and salt. However, the density difference of ice and salt allows the incorporation of the ripening tank and settling vessel into one single reactor. The performance of the wash column and the filter depend a great deal on the performance of the crystallizer. The need to develop an efficient and reliable crystallizer, along with the savings on investment costs

of a solid-solid separator, has led to the proposition of two types of reactors for EFC, the cooled disk column crystallizer and the scraped cooled wall crystallizer.

The **Cooled Disk Column Crystallizer (CDCC)** (van Der Ham 1999) has disks which provide the cooling in the reactor. The refrigerant flows through the disks, which are wiped clean to improve heat transfer and prevent scaling. The disks are evenly spaced out and have orifices which allow liquids and solids to freely flow between compartments. An important advantage of the CDCC design is relative ease in scaling up the reactor. As long as the distances between the disks are kept constant, increasing the volume of the reactor increases the area available for cooling in a 1:1 ratio.

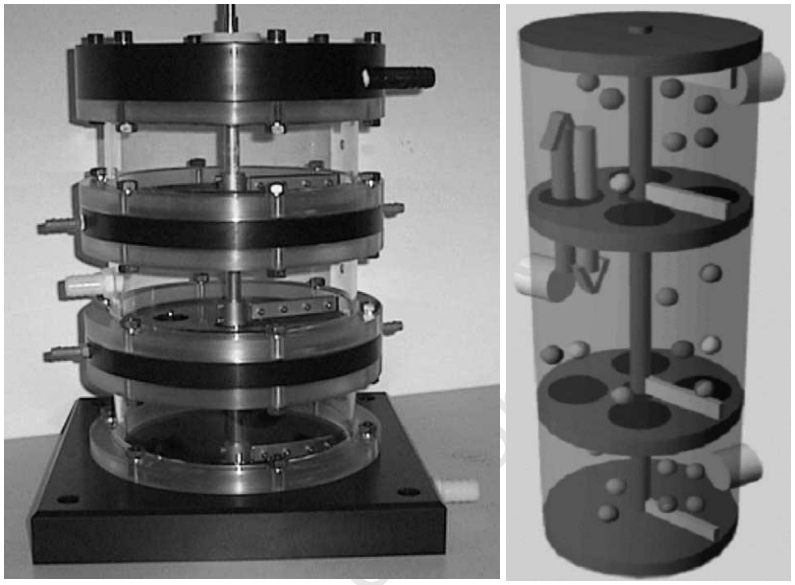


Figure 13: The Cooled Disk Column Crystallizer (van Der Ham 1999)

The second, updated crystallizer design proposal by TU Delft is the **Scraped Cooled Wall Crystallizer (SCWC)** which was proposed as an alternative over the CDCC. The SCWC is fundamentally a jacketed vessel with rotating scrapers on the walls of the reactor. The Teflon scrapers prevent ice formation on the walls and increase the heat transfer of the crystallizer. Figure 14 below shows the top section and a cross section of the jacketed wall of the SCWC. An inner cooled cylinder is placed in the centre of the reactor to increase the cooling capacity of the crystallizer. A spiral shaped path ensures an even distribution of the coolant flow throughout each jacket (Vaessen 2003). The top and bottom of the SCWC are conical in shape for efficient solid collection towards the product outlets.

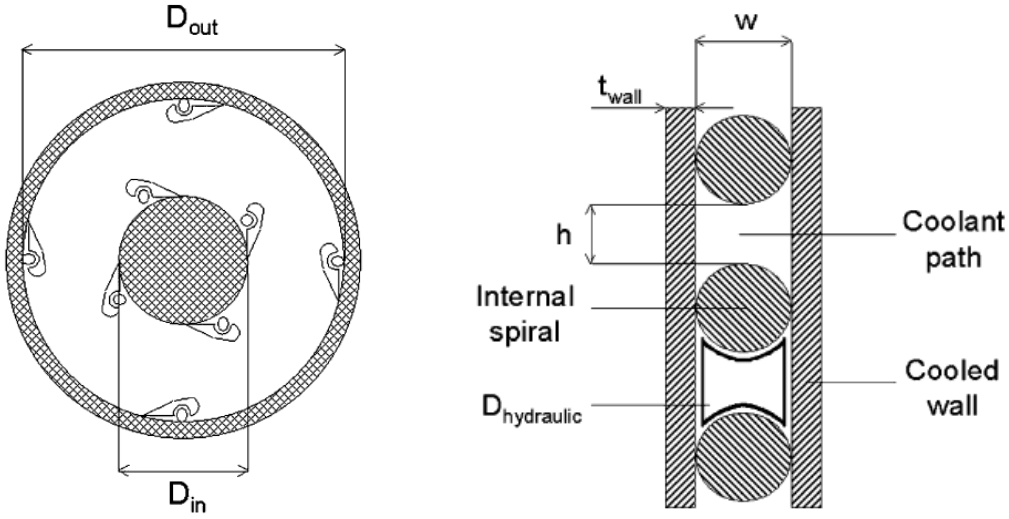


Figure 14: Top View and Cross-section of Jacketed Wall in the SCWC (Vaessen 2003)

Vaessen (2003) compared the performance and investment costs of the CDCC and the SCWC. It was found that the overall performance of both crystallizers were very similar with the only major differences being the gravity separation efficiency and heat transfer area per unit volume between the two crystallizers. The SCWC had a higher gravity separation efficiency due to the geometry of the vessel and the significantly larger settling area. The SCWC had a slightly higher heat transfer area per unit volume.

2.3.4 Kinetics of the EFC process

Previous EFC experimental work on industrial brines was carried out in batch mode either in jacketed reactors or in a 12l SCWC (Reddy et al. 2010). The experimental work was aimed at verifying the eutectic point along with establishing the product purity and yield. Kinetic work was also extended to the investigation of the metastable zone width (Lewis, Nathoo, Reddy, et al. 2010). The key findings of these studies are highlighted below.

Eutectic Point, Purity and Yield

Reddy et al. 2010 and Lewis, Nathoo, Thomsen, et al. 2010 both showed the applicability of EFC for the treatment of an industrial brine, through experiments ranging from binary systems to synthetic industrial brines. The following results were observed:

- The eutectic temperature and concentration of the binary Na_2SO_4–H_2O (5wt% Na_2SO_4) system was experimentally determined to be -1.24°C and approximately 4wt%, which is in good agreement with literature (-1.27°C & 4.19wt% - (Thomsen 2007)).
- The presence of low concentrations of F, Cl, K, Li, Mg, Ca,NO_3 and NH_4 impurities in a Na_2SO_4–water system depresses the eutectic point of $Na_2SO_4 \cdot 10H_2O$ crystallisation from -1.24 to -2.22°C.
- Both ice and $Na_2SO_4 \cdot 10H_2O$ crystals were produced from synthetic streams, as well as a sodium sulphate stream containing NaCl.
- A recovery of >90% pure $Na_2SO_4 \cdot 10H_2O$ crystals was obtained from a concentrated NaCl stream prior to any sodium chloride crystals being produced, this has great implications for possible sequential removal of salts from a brine.

Metastable Zone

The metastable zone width (MSZW) describes the maximum supercooling or supersatutation permissible for stable operation without spontaneous nucleation in a batch or semi-batch crystallizer (Trifkovic et al. 2009). Nucleation can be divided into primary (spontaneous) or secondary nucleation. Primary nucleation occurs where no parent material is present whereas, secondary nucleation occurs when a parent material is present for nucleation to take place on. The different regions of supersaturation are presented in Figure 15. Below the ice solubility line is a supersaturated region where nucleation can occur.

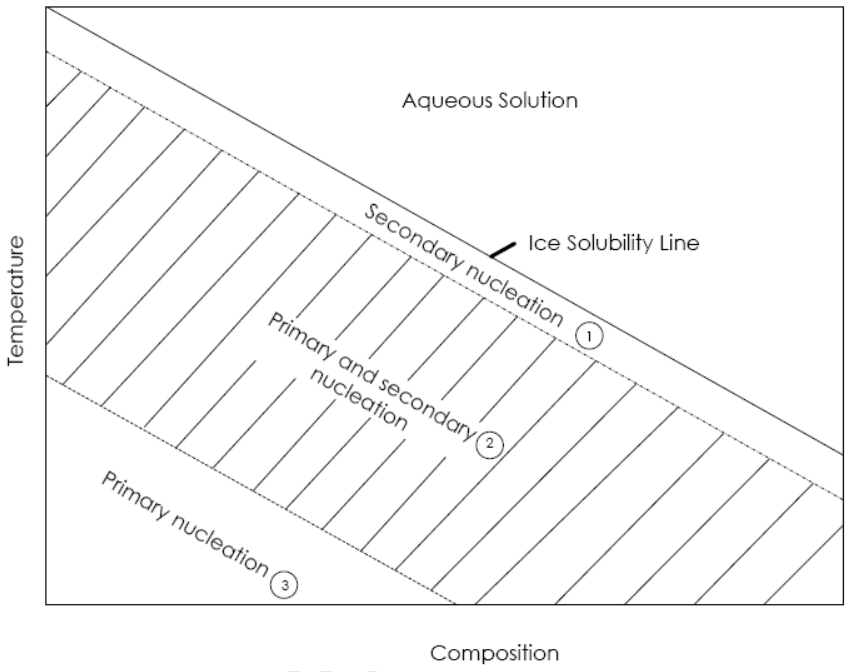


Figure 15: Nucleation regions in a supersaturated solution (Randall et al. 2009)

Determining the lower limit of the MSZ aids the choice of operating temperatures for the crystallizers when seeding the supersaturated solution. Seeding with both salt and ice crystals results in two distinct solid phases (van Der Ham 1999). Randall et al. (2009) have shown that when seeding a ternary Na_2SO_4- $MgSO_4$-H_2O system with $Na_2SO_4 \cdot 10H_2O$, a salt purity of 95% and yield of 57% for $Na_2SO_4 \cdot 10H_2O$ was obtained. The low yield was attributed to the high temperatures (25°C) that the washing took place. Hence, by operating within the MSZW the preferred crystallization product can be controlled and even manipulated by seeding (Region 1 and 2).

2.4 Energy Requirements of the EFC process

The temperature at which a crystal nucleates is termed the nucleation temperature. When a system is cooled, there is a steady decrease in the temperature profile up until the nucleation temperature is reached. For a dilute system, once the first ice crystal forms there is an increase in temperature. The observed sudden increase in temperature is as a result of the release of crystallization heat (Vaessen et al. 2000). The energy released from the number of ice crystals formed, together with the volume of the system determines the magnitude of this increase in temperature.

The heat of fusion of ice is 6.01 kJ/mol whilst the heat of evaporation of water is 40.65 kJ/mol and hence, the phase change of water to ice at 0°C requires only a sixth of the energy required to convert water to steam at 100°C. EFC can theoretically achieve a 100% conversion to pure water and pure salt while keeping energy requirements low (Vaessen 2003).

Due to high energy consumption as well as inadequate yield and product quality for an EC process, EFC has been shown to be a greatly viable alternative to EC for certain salt-water separations (van Der Ham 1999). The energy efficiency and economic comparison of using EFC over other conventional techniques has only been proven for certain binary systems and certain single salt extractions from multi-component complex hypersaline brines (van Der Ham 1999). The results showed that EFC has an energy reduction of up to 70% for a 17wt% $CuSO_4$ solution.

As each particular salt has its own unique freezing point temperature, EFC allows the possibility of sequential salt separations yielding pure salts and pure water. In multi-component complex hypersaline solutions multiple salts can be obtained in their pure form. Controlling the temperatures at which the salts crystallize out is of great importance with regard to reactor design and choice of cooling options. There are a number of options for removing the heat for an EFC process and these will be discussed in the following section.

2.4.1 Cooling Options

Direct Cooling

Early researchers (Swenne 1983; Barduhn & Manudhane 1979; Stepakoff et al. 1974) all used a direct cooling approach to heat removal which involves direct contact between the refrigerant and the brine, in order to reduce the temperature of a solution to its eutectic temperature. The volatile liquid refrigerant absorbs the heat from the solution and evaporates in the mixture to provide the required cooling. This method has two setbacks: firstly, the crystallizer has to be pressurized and the evaporation rate of the refrigerant has to be well controlled. Secondly, the refrigerant is carried to all parts of the process and could potentially contaminate the salt and ice produced, requiring a further processing step in order to be separated from the products.

Indirect Cooling

Using indirect cooling in which the refrigerant does not come into contact with the solution has been proven to be successful for Eutectic Freeze Crystallization (van Der Ham 1999). Indirect cooling is achieved by using a jacketed reactor, where the refrigerant and the crystallizer contents are separated by a heat transfer medium (wall) allowing the refrigerant to absorb the heat. As scaling tends to occur on the heat transfer surface in the indirect crystallization process, scrapers are required to minimize scale formation on the heat transfer surface.

2.4.2 Refrigeration Cycle

A detailed understanding of the refrigeration cycle is needed when applying it to EFC. Basic understanding of the process will also aid in heat recovery and optimisation of the process to minimize operating costs. The refrigeration cycle is modelled to obtain indirect cooling and determine the link between the cooling duty required, the work done by the compressor and the cost of providing the required electricity to the compressor for the required work input.

The Rankine refrigeration cycle uses work to pump heat from a region of high temperature to a region of low temperature. The refrigeration cycle comprises of a compressor and turbine which operate isentropically. The work recovered in the turbine of the refrigeration cycle is relatively small and consequently, the design and operation of the cycle can be simplified by replacing the turbine with an expansion valve. As a result the refrigerant does not undergo an isentropic expansion but rather it now undergoes a Joule-Thompson expansion. This cycle is commonly referred to as the vapour-compression refrigeration cycle and is shown in Figure 16.

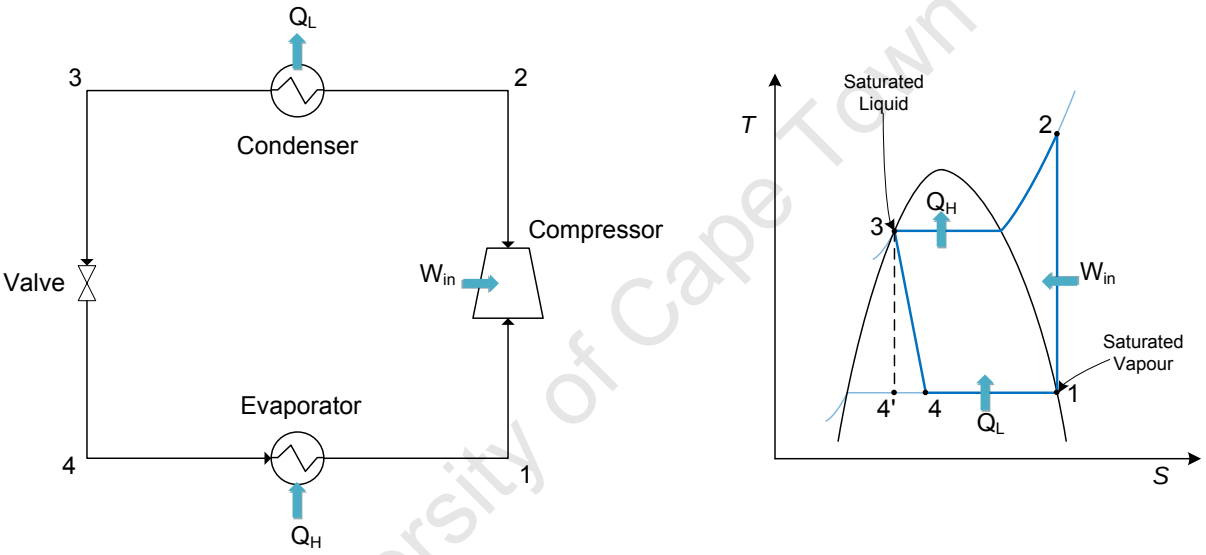


Figure 16: Vapour-Compression Cycle **(Mei et al. 2007)**

Looking at the temperature – entropy graph in Figure 16; the left side of the curve represents a saturated liquid whilst the right side of the curve represents a saturated vapour. The two lines meet at the critical point and within them the component is both liquid and vapour

Starting at point 1 in the refrigeration cycle, where the component is a saturated vapour, the component enters the compressor and is isentropically pressurized to point 2. The refrigerant is then cooled isobarically from point 2 to point 3, a saturated liquid. The saturated liquid is then passed over an expansion valve, where the pressure and temperature are decreased isenthalpically. Finally at point 4, the refrigerant is in the vapour-liquid phase and heat is given off to vaporize the remaining liquid. This operation occurs at constant temperature and pressure until the refrigerant is a saturated gas, back at point 1. A summary of this process is shown in Table 7.

Table 7: Summary of Stages in Vapour Compression Cycle (Sandler 1999)

Point	State	Path to Next Point	T	P	Entropy ($\hat{S}$)	Enthalpy ($\hat{H}$)
1	Saturated Vapour	Isentropic	$T_1 = T_4$	$P_1 = P_4$	$\hat{S}_1 = \hat{S}_2$	$\hat{H}_1$
2	Superheated Vapour	Isobaric Heating	T_2	$P_2 = P_3$	$\hat{S}_2 = \hat{S}_1$	$\hat{H}_2$
3	Saturated liquid	Isenthalpic	T_3	$P_3 = P_2$	$\hat{S}_3$	$\hat{H}_3 = \hat{H}_4$
4	Vapour-liquid mixture	Isobaric Heating	$T_4 = T_1$	$P_4 = P_1$	$\hat{S}_4$	$\hat{H}_4$

The Coefficient of Performance (C.O.P) of the vapour-compression refrigeration cycle is defined below.

$$C.O.P = \frac{Q_L}{W_{in}} \qquad \textbf{Equation 1}$$

Where: Q_L = the heat absorbed by the refrigerant from the crystallizer
W_{in} = the work duty of the compressor

The work done by the compressor (W_{in}) is much less than the heat absorbed by the refrigerant (Q_L) in an ideal refrigeration cycle. However, in reality, compressors have an efficiency of 70% (Turton et al. 1998) which in turn reduces the co-efficient of performance by 70%. Other researchers report compressor efficiencies as high as 80% (Zijlema et al. 2000).

The driving force for heat transfer from the crystallizer to the coolant is the temperature difference between the bulk phase and the refrigerant. As the extent of scaling is dependent on the level of supersaturation, the temperature difference must not be too large, as very large differences will promote scale formation on the heat transfer surface and will also result in poor crystal shape and/or size (van Der Ham 1999) impacting downstream processes, such as filtration. However, if the temperature difference is too low a larger surface area for cooling is required and the kinetics of the process are slow. Hence an optimum temperature difference needs to be chosen.

2.4.3 Heat Recovery within the EFC Process

The ice produced in the EFC process can be utilised to reduce the utility requirement in other areas of the process. The crystallizer and the condenser in the refrigeration cycle are such areas and both require a significant amount of cooling. van Der Ham (1999) has investigated the use of ice in heat exchangers in these areas. The ice produced can be melted and the heat absorbed can be used to pre-cool the feed to the crystallizer as shown in Figure 17.

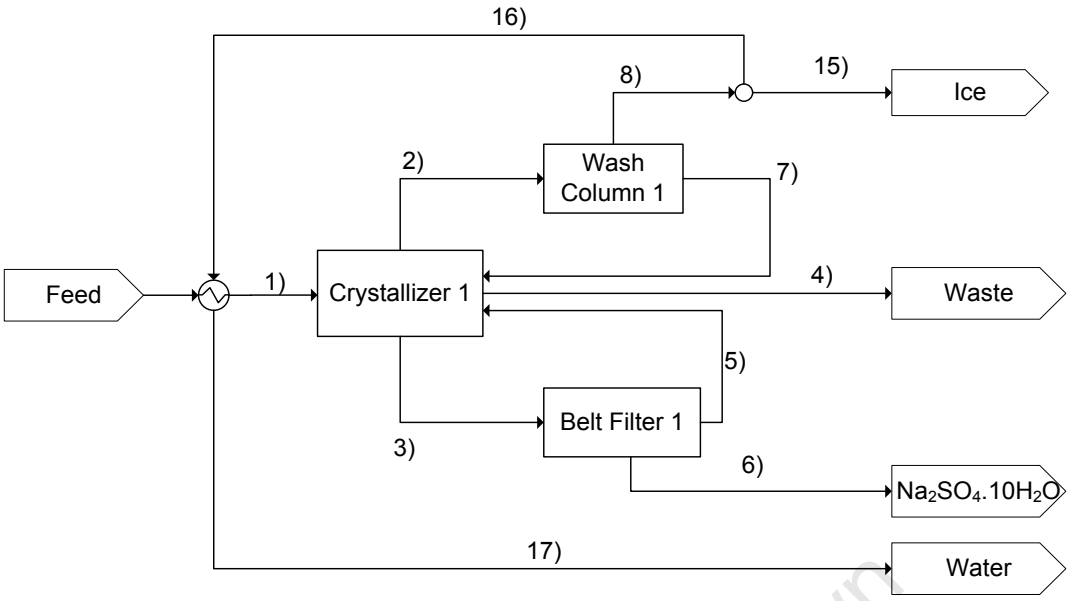


Figure 17: Ice used to pre-cool feed in EFC process (van Der Ham 1999)

The second option considered was to use the ice to cool the condenser in a two stage refrigeration cycle. A portion of the refrigerant is condensed with the ice whilst the rest is condensed in a second condenser with cooling water. The overall performance of the refrigeration cycle is improved, as the second stage operates at a lower temperature and pressure and resulting in a reduced compressor duty.

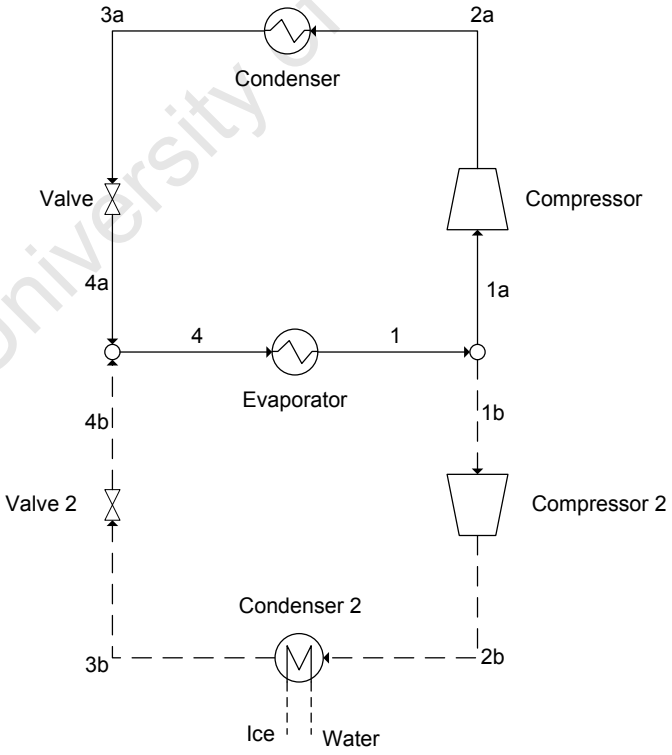


Figure 18: Two stage refrigeration cycle (van Der Ham 1999)

Previous studies have focused on binary saltwater systems and hence there is a need to establish the recovery of heat for using EFC for a multi-component complex hypersaline system.

The cooling capacity of ice only allows streams to be cooled down to 10°C due to the minimum temperature difference between streams when crossed. In the application of EFC to an industrial brine, multiple crystallizers will be operating at different temperatures with refrigeration cycles for each crystallizer. Using the ice product as utility will only be effective in pre-cooling the feed to the first crystallizer and with any remainder ice product in the condensers of the refrigeration cycles.

2.5 Cost Evaluation

Currently the two main treatments methods for treating hypersaline wastewater streams are Evaporative Crystallization and Evaporative Ponds. Figure 19 summarizes the estimated costs for the various treatment methods mentioned earlier.

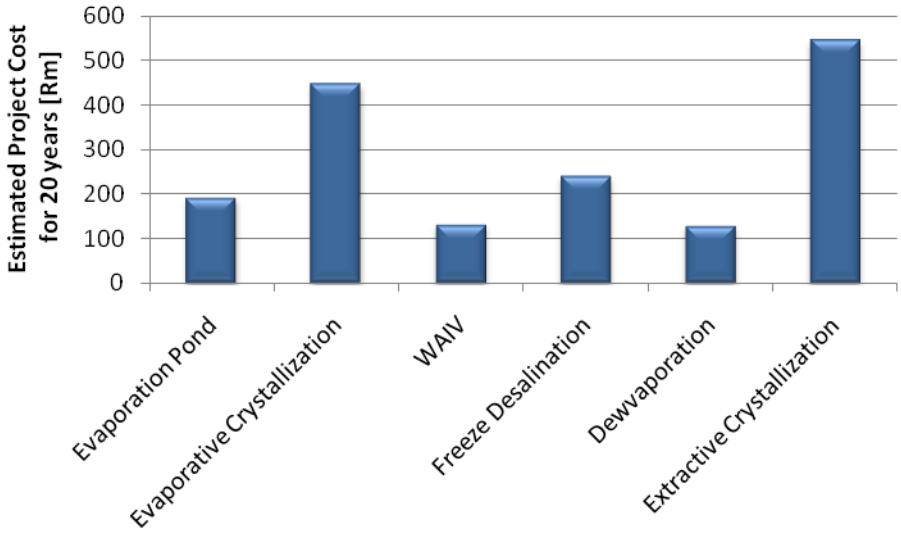


Figure 19: Estimated costs for 20 year project life (van der Merwe et al. 2009)

Dewvaporation and WAIV technology show high cost savings over a 20 year period. These two treatments, along with freeze desalination, are relatively novel techniques with WAIV and Dewvaporation at the pilot plant stage (Brandhuber et al. 2008).The estimated costs for extractive crystallization were based on the work carried out by Zijlema et al. (2000). Aside from evaporative crystallization, all the other processes listed above produce a concentrated brine solution. When treating a hypersaline brine with EC, a mixed salt product is still produced which needs to be disposed of efficiently.

The evaporative crystallization process can be thermodynamically modelled to determine energy requirements and subsequently operating costs. Increased research has led to the proposal of many crystallizers for evaporative crystallization. The most widely used type of crystallizer, especially for vacuum evaporation, is the Forced Circulation Crystallizer (FCC) (Vaessen 2003). The FCC is generally less expensive compared to other crystallizers. Hence in this study a multiple effect EC process was compared to the EFC process from an operating and capital cost perspective.

2.5.1 Operating Cost Estimation

A comparison of operating costs for both processes, Eutectic Freeze Crystallization and Evaporative Crystallization, will be drawn up. The basis for determining the respective operating costs is that the major energy requirements in the EFC process are based on the compressor duties of the refrigeration cycles. The large compressor duties will incur electricity costs for the process with the only other utility requirement being cooling water for the condenser of the refrigeration cycles.

For an Evaporative Crystallization process the steam requirement is the major operating cost utility and the cost of running the EC process will be determined on the current cost of Low Pressure Steam produced off site.

As mentioned before, Evaporative crystallization produces a mixed salt product, whereas EFC has the potential to produce multiple pure salts through selective seeding. Although the potential income generated from the sale of salt is not included in the operating costs presented, the import amounts and prices for various salts for the 2006 year are listed in Table 8 for reference.

Table 8: Various imported raw materials Jan – Dec 2006 (van der Merwe et al. 2009)

Product	Quantity Imported [t]	Value of imported product [R'000]	Unit value of product imported [R/t]
Gypsum	3703	2,408	650
Chlorine	38	0	8.8
Magnesium hydroxide	2,001	968	484
Ferric oxide	81,970	13,701	167
Calcium chloride	6,219	3,525	567
Calcium carbonate			
Magnesium chloride	1,266	535	423
Magnesium sulphate	6,006	8,269	1,377
Potassium chloride	1,576	77	49
Mono ammonium phosphate fertiliser	526	103	196
Sodium chloride	4,592	4,936	1,075
Sulphur	295,453	681,000	2,305
Sodium sulphate	7,671	16,310	2,126
Potassium nitrate	79,737	20,603	258
Sodium nitrate	4,913	2,632	536

Table 8 shows an opportunity for generating salts such as sodium sulphate, sodium chloride and magnesium sulphate. However, it is anticipated that recovery of by-products should generally not be viewed as the prime driving force for cost recovery or making such projects economically viable, but rather to eliminate a long term liability from sludge/brine (van der Merwe et al. 2009). Table 8 is used to highlight the possibility of marketing salt by-products from an EFC process.

2.5.2 Capital Cost Estimation

Economic evaluations for the EFC process for binary systems and salt-water systems have been proposed with basic capital cost estimations. Vaessen (2003) conducted a basic economic evaluation on a ternary synthetic KNO_3 – HNO_3 – Water industrial brine. There is currently no industrial scale EFC process and the capital cost estimation has been based on work proposed by Vaessen (2003) and van Der Ham (1999). Sample calculations are presented in the Appendix (Section 10.1, page a). The majority of the unit operations for both the EFC and EC process adopt a size adjustment approach to the estimated investment costs.

When looking at the binary process flowsheet for the EFC process, Figure 12, the major pieces of equipment are the:

- Crystallizer
- Wash Column
- Belt filter
- Cooling equipment – Refrigeration system

For the crystallizer, two different crystallizers have been looked at in Chapter 2.3.3, the SCWC and the CDCC. The investment costs for the two reactors are summarised in the Table 9 below.

Table 9: Reference Investment Costs for SCWC and CDCC (Vaessen 2003)

Crystallizer Type	Area [m^2]	Investment[k€]	I/A [k€/m^2]
Scraped Cooled Walled Crystallizer	30	86	2.9
Cooled Disk Column Crystallizer	32	292	9.1

As mentioned before, although the SCWC and CDCC are very similar in performance, the SCWC has a slightly higher heat transfer area and gravity separation efficiency. Additionally, the SCWC has a lower investment cost per unit area than the CDCC of up to three times.

Various types of equipment are available for solid/liquid separation depending on the specific application. For the recovery of salt from entrained filtrate, van Der Ham (1999) models the EFC process with centrifuges while Vaessen (2003) uses belt filters. However counter-current washing and drying can be incorporated into a belt filter. Vaessen (2003) uses reciprocating tray vacuum belt filters which were quoted by Outokumpu-Royal Pannevis.

Table 10: Reference Price of Reciprocating Tray Belt Filters (Vaessen 2003)

	$V_{Salt\ Slurry}$ [m^3/hr]	I(k€)
Reference Belt Filter	2.3	140

The ice crystals that are produced in the EFC crystallizer are sent to a hydraulic wash column (HWC). Both van Der Ham (1999) and Vaessen (2003) use TNO hydraulic wash columns. The reference and maximum size wash columns are given in Table 11.

Table 11: Reference Price and Maximum Dimensions of hydraulic wash columns (Vaessen 2003)

	D [mm]	m_{ice} [kg/s]	m_{ice}/A [kg/m^2s]	I(k€)	f
Reference HWC	550	0.64	2.7	70	0.55
Maximum HWC	1200	3.0	2.7	108	-

The capacity of the wash column was determined by its diameter, considering the throughput in kg/m^2s should maximally have a constant value of 2.7 kg/m^2s (Vaessen 2003). The scaled investment cost was given by the following formula:

$$I_{HWC} = \left(\frac{D_{HWC}}{D_{HWC,1}}\right)^{f} \cdot I_{HWC,1} \qquad \textbf{Equation 2}$$

A scale factor (*f*) of 0.55 was used to scale the diameter of the wash column to estimate the appropriate investment cost.

Cooling of the EFC process is achieved through indirect cooling in the form of a refrigeration cycle. van Der Ham (1999) priced a cooling unit per kW of cooling power from a Dutch literature reference. However, Vaessen (2003) obtained prices for 0.83MW and 12.1MW single stage cooling units from an industrial supplier. Table 12 summarizes the reference costs that were used.

Table 12: Reference price of Cooling Equipment (Vaessen 2003)

	Q_{cryst} [kW]	I [k€]	*F*
Cooling Equipment	830	280	0.9

The investment costs for a refrigeration cycle with a different cooling power is estimated using a similar formula to Equation 2, where the cooling power was used to scale the costs.

$$I_{Cooling\ Equipment} = \left(\frac{P_{Cool}}{P_{Cool,1}}\right)^{f} \cdot I_{CoolingEquipment,1} \qquad \textbf{Equation 3}$$

A two-stage refrigeration cycle has additional units, namely a heat exchanger and compressor. The second loop of the two-stage refrigeration cycle is by no means an ordinary cooling cycle. Thus, the costs of a two-stage refrigeration cycle were assumed to be double that of a single stage refrigeration cycle, as all units are doubled (compressor, condenser, valve and piping) aside from the evaporator.

The evaporative crystallization process was modelled using plate evaporators and a Forced Circulation Crystallizer (FCC) for the crystallization step. As mentioned before in Chapter 2.5, the FCC is considered less expensive and the investment costs for a reference crystallizer are highlighted in Table 13.

Table 13: Reference price of forced circulation crystallizer (FCC) (Vaessen 2003)

Crystallizer Type	V_{cryst} [m^3]	$P_{evaporation}$ [kW]	I [k€]	*f*
Reference FCC	1.5	1570	147	0.7

The investment cost for a similar crystallizer was scaled according to Equation 4:

$$I_{FCC} = \left(\frac{V_{Cryst}}{V_{Cryst,1}}\right)^{f} \cdot I_{FCC,1}$$ **Equation 4**

In the EC process, when no crystallization takes place, plate evaporators were used to model the process. Plate condensers were used when the product steam is condensed. Vaessen (2003) reported investment costs quoted by Alfa Laval along with a quoted scaling factor of 0.52. The investment costs are shown in Table 14.

Table 14: Reference costs for plate condensers and evaporators (Vaessen 2003)

Equipment	Q_{duty} [kW]	$U_{evap/cond}$ [kW/m²]	A [m²]	I [k€]	*f*
Reference plate evaporator	1500	25	60	39	0.52
Reference plate condenser	400	36	11	7.5	0.52

The specific heat flux for the evaporator and condenser were assumed to be 25 and 36 kW/m² respectively. As the EC process produces a mixed salt crystal product, the separation step from the liquor was modelled using a belt filter. The investment costs for this step were calculated in the same manner as the investment costs for the belt filters in the EFC process. The ancillaries of both the EFC and EC processes were estimated at 10% of the total capital cost (Vaessen 2003).

Chapter 3: Experimental Program

3.1 Case Studies

Four case study brines were chosen based on their composition being broadly representative of a South African Industrial Brine. Ideally the case study brines would have come from the industries that contribute the most to brine production in South Africa as mentioned earlier in Chapter 2.1. Table 15 below, has been modified to only include the major brine producing industries; the mining, petrochemical, power generation and paper & pulp/wood industries. Disposal to the marine environment has also been omitted from this table.

Table 15: Modified Brine and Salt Production Rates Table (van der Merwe et al. 2009)

	Total effluent excl marine		Salt load to environment excl marine	
	Total	Portion	Total salt	Portion
	kl/day	% of total	t/day	% of total
Paper & Pulp/Wood	89001	16.6	80	7.6
Petroleum	69100	12.9	300	28.3
Power Generation	132000	24.7	158	14.9
Mines	145025	27.1	350	33.1
Total	534739		1059	

*For full table please refer to Chapter 2.1 Table 1

A case study brine from the paper & pulp/wood industry could not be obtained within the timeframe of this study and thus only the other three industries were considered. The salt load from the paper & pulp/wood industry was fairly low (7.6%) when compared to the other three industries, in spite of the high effluent load (16.6%). This indicates a more dilute brine, whereas the mining and petrochemical industry brines have a significantly higher concentration. A second mining brine was included as a case study and the four case studies were chosen from the following industries:

Case Study 1: Platinum Mine (PM)
Case Study 2: Coal Mine (CM)
Case Study 3: Petrochemical Plant (PC)
Case Study 4: Power Generation Plant (PG)

3.2 EFC Protocol for Evaluating a Brine

A general protocol has been setup for evaluating the applicability of using EFC to treat a brine which begins with a comprehensive brine analysis, including thermodynamic modelling, experimental studies and concludes with operating and capital costs. For this study the experimental studies were not taken into account. The operating and capital costs will be compared to a triple effect evaporative crystallization process. Figure 20 provides an outline of the general protocol that has been adopted.

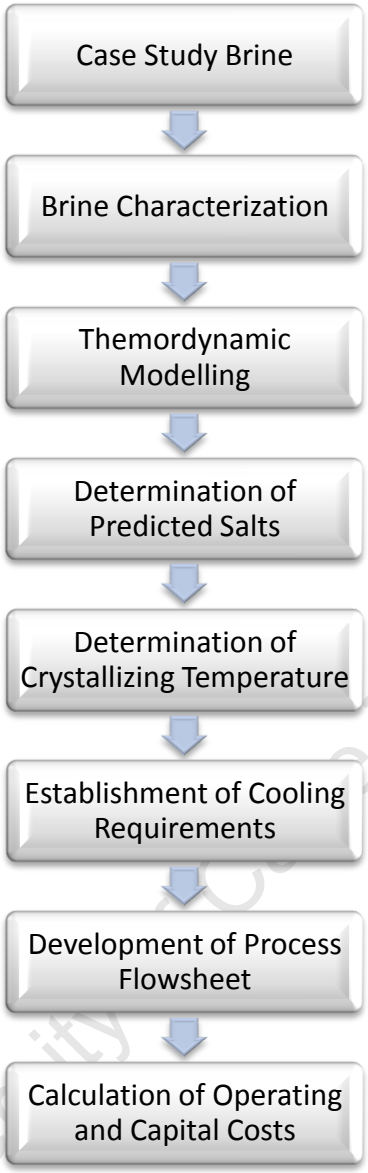


Figure 20: EFC case study protocol

The four case study brines were put through the same protocol, starting with brine characterization. Once the chemical analysis to determine the various impurities present and their concentrations was complete, the thermodynamic modelling was used to predict which sequence the salts would crystallize out and at what temperatures crystallization would take place.

Using this information a process flowsheet was developed and the energy requirements of the process calculated along with the operating costs which were based on the energy requirements. Finally the capital costs were calculated for each of the case study brines. The next few sections will expand on each of the steps in the protocol in more detail. A basis of 1l/hr was used for the thermodynamic modelling. However, when costing the EFC and EC process a basis of 300 m^3/day was used as this is more representative of the brine flow in the mining industry.

3.3 Brine Characterization

As the exact compositions of the case study brines were unknown, determining what impurities were in the brine was key to the EFC protocol. The thermodynamic modelling, process modelling and costing calculations all stem from the analysis and a complete and thorough brine analysis is needed to produce optimal results. Analysis of the brines was based on the work completed by Zibi (2010). The different parameters that were measured are presented in Figure 21.

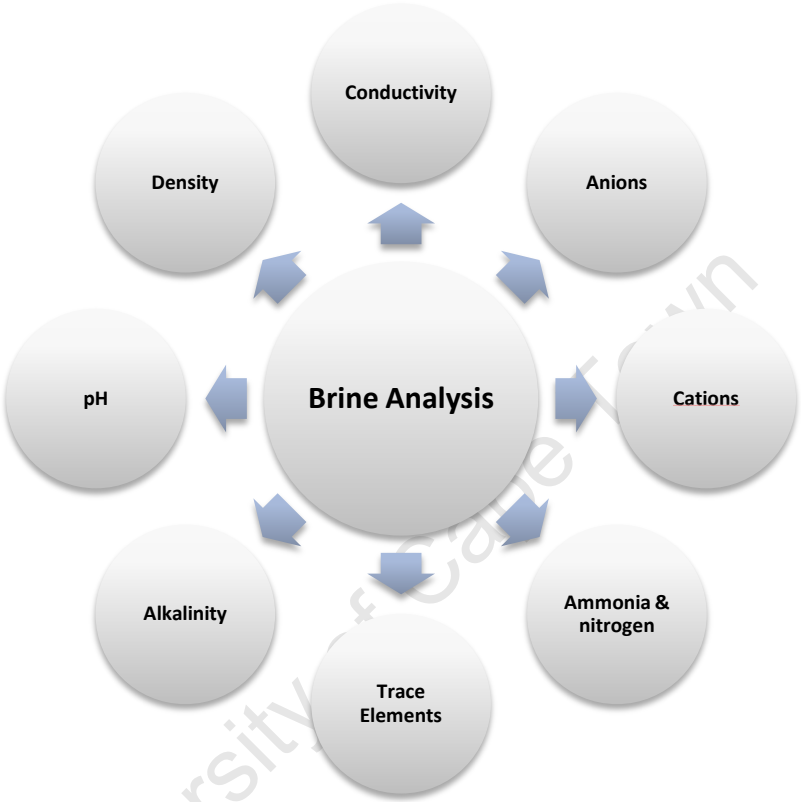


Figure 21: A schematic of a strategy of analysing an inorganic industrial brine (Zibi 2010)

The characterization will be broken up into two major categories; general analysis and major and trace elements analysis. Firstly, the general properties of the brine needed to be determined, with the three main properties being:

- pH
- Electrical conductivity and
- Density

The Total Dissolved Solids (TDS) of each of the case study brines was reported, which is defined as the sum of all the measured components present in the brine, specifically, the sum of cations, anions, and total nitrogen in the system.

The major and trace elemental analysis was divided into five categories:

- Anion analysis
- Cation analysis
- Ammonia & nitrogen analysis

- Trace elements analysis and
- Alkalinity

The Ion Chromatography analysis determined the **anions** present in the brine. The analysis gave the concentration of Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-} and Ac^{2-} ions.

The **cation** and **trace elemental** analysis was carried out using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) or Inductively Coupled Atomic Emission Spectroscopy (ICP-AES)**.** This method can measure the concentration of the following elements, Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Se, Si, Sr, Ti, V and Zn. The ICP-MS is capable of reporting trace elements concentration in the working range of mid ppb's to 1000ppm.

An undigested and digested sample of the brine underwent an acid titration to determine the total organic nitrogen and the **ammonia nitrogen**. This method is called the Total Kjeldahl Nitrogen.

The **alkalinity** of a sample which indicates the concentration of CO_3^{2-} present in the brines was measured using the Gran Titration method.

Before commencing a thermodynamic analysis of the brine, an anion-cation balance was carried out. Carvalho (2006) reports an allowable imbalance of not more than 10%. If there is an imbalance the dominant species from either the anions or cations was added to balance the stream. At this stage if the imbalance was more than the tolerable 10% then it was assumed that the brine characterization step was incomplete as it did not account for the charge imbalance.

3.4 Thermodynamic Analysis

Once a complete analysis of the brine was completed, a thermodynamic model could be setup in Oli Stream Analyzer® 3.0.10. As mentioned before (Lewis, Nathoo, Reddy, et al. 2010) endorsed the use of Oli Stream Analyzer over other aqueous thermodynamic modelling programs.

The Helgeson-Kirkham-Flowers Equation of state was used as the thermodynamic property model. The built in model also integrated the Bromley-Meissner, Pitzer, Helgeson and Bromley-Zematis equations for calculations of the activity calculations (Berthold, 2001). The OLI software also incorporated a Mixed Solvent Electrolyte (MSE) database, which used the Helgeson direct method and has the capability of successfully modelling temperatures as low as -200°C (Lewis, Nathoo, Reddy, et al. 2010).

The evaluation of the following formula was critical to the thermodynamic modelling and hence, Oli Stream Analyzer.

$$\Delta_R \bar{G}^\circ = -RT \ln K \qquad \textbf{Equation 5}$$

Every thermodynamic property is composed of two parts. The first is the standard state property which is temperature and pressure dependant. The second, is the excess property which is a function, of temperature, pressure and concentration.

Partial Molal Gibbs Free Energy $$\bar{G}_i = \bar{G}_i^\circ + \bar{G}_i^E \qquad \textbf{Equation 6}$$

Partial Molal Enthalpy	$\bar{H}_i = \bar{H}_i^{\circ} + \bar{H}_i^E$	**Equation 7**
Partial Molal Entropy	$\bar{S}_i = \bar{S}_i^{\circ} + \bar{S}_i^E$	**Equation 8**
Partial Molal Heat Capacity	$\bar{C}p_i = \bar{C}p_i^{\circ} + \bar{C}p_i^E$	**Equation 9**
Partial Molal Volume	$\bar{V}_i = \bar{V}_i^{\circ} + \bar{V}_i^E$	**Equation 10**

Standard state properties can be represented by equations of state, and as mentioned before, the Helgeson-Kirkham-Flowers equation of state was used. The excess properties were calculated using Bromley-Meissner, Pitzer and Helgeson equations.

Barduhn & Manudhane (1979) investigated the eutectic temperatures of a synthetic aqueous mixture consisting of seven ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and HCO_3^-) and found that the EFC process will operate and be economically viable if the eutectic temperatures are no lower than -25°C. A temperature survey from 25°C to -25°C was carried out to predict which salts crystallize out and the temperatures at which these salts crystallize out.

3.5 Process Flowsheet Development

A process flowsheet was proposed based on the key operating parameters deduced from thermodynamic modelling analysis. The number of different salts that precipitated out and the temperatures at which the individual salts precipitated out aided in determining the operating sequence and temperatures of the crystallizers. The energy requirement of the successive crystallizers was calculated in order to determine the total cooling requirement of the EFC process. The salts and ice produced were separated from the liquid stream using belt filters and wash columns respectively.

Aspen Plus 7.1 ® was chosen to model the process and calculate energy requirements of the crystallizers. Aspen Plus software has been used extensively for steady-state modelling in a range of chemical engineering fields. Aspen Plus was considered to be very robust when modelling petrochemical plants. It has also been shown to accurately model hydrometallurgical plants (Bhikha 2009) and waste incineration plants (Cimini et al. 2005) as well.

Aspen Plus was used by Zheng & Furimsky (2003) to model the energy requirements of a cogeneration plant. The Aspen model of the cogeneration plant was in good agreement with actual plant data. The applicability of Aspen to model aqueous electrolyte systems at low temperatures was compared to that of Oli Stream Analyzer. The component database in Aspen was limited when compared to the Oli Database, and did not include some of the more uncommon hydrated salts. One common hydrated salt that was not found in the Aspen database was the hydrated salt of sodium chloride, Hydrohalite ($NaCl{\cdot}2H_2O$). To calculate the energy requirements of the process four main properties are required in Aspen:

- Heat of Formation (ΔH_f)
- Gibbs Free Energy (ΔG_f)
- Solid Heat Capacity (Cp)

- Solid Molar Volume

The first two values, ΔH_f and ΔG_f, were not readily available at first and thus the Mostafa method (Mostafa et al. 1996; Mostafa et al. 1995) was used to estimate these values. At a later stage of the studies these values were obtained through correspondence with (Thomsen 2008). Table 16 highlights the values used for the Mostafa method.

Table 16: Mostafa Functional Groups

Functional Group	Mostafa Group Number	Quantity
Na^+	1127	1
Cl^-	1305	1
H_2O	1803	2

Table 17 highlights the accuracy of the Mostafa method that was used to actual values that were sourced.

Table 17: Predicted and actual ΔH_f and ΔG_f of $NaCl \cdot 2H_2O$

	Predicted	Actual (Thomsen, 2008)	Percentage Difference
ΔHf	-9.58E+08	-9.92E+08	3%
ΔGf	-8.23E+08	-8.59E+08	4%

As the model was fully thermodynamic, the equilibrium reaction for $NaCl \cdot 2H_2O$ was taken into account.

$$Na^+ + Cl^- + 2H_2O \leftrightarrow NaCl \cdot 2H_2O \qquad \textbf{Equation 11}$$

Aspen Plus models any salt equilibrium reaction in the form shown in Equation 12 (T in Kelvin).

$$\mathrm{Ln}\, Ksp = A + \frac{B}{T} + \mathrm{C} \cdot \ln T + D \cdot T \qquad \textbf{Equation 12}$$

Thus to model Equation 11 correctly, the equilibrium constants A, B, C & D were required. However, despite an extended search, these values could not be found. Consequently these values were not inputted into Aspen Plus, resulting in the equilibrium constants being calculated by Aspen Plus from the reference state Gibbs free energies of the participating components.

The ELECNRTL (Electrolyte Non-Random Two Liquid) property method was chosen to model the process. With only binary parameters, the equation satisfactorily represents physical interactions of true species in aqueous single electrolyte systems and multicomponent electrolyte systems over wide ranges of concentrations and temperatures (Aspen 2009).

The crystallizer in the process was modelled as a 'heater' block in Aspen Plus. This block takes into account the thermodynamic equilibrium reactions.

The process was modelled based solely on thermodynamics, thus a heater block was chosen to model the process and not as a crystallizer block. As the model was used to calculate the energy requirements of the process, the separation between the two solid phases and the liquid phase within the crystallizer was assumed to be perfect with no salt entrained in the ice and vice versa.

3.6 Refrigeration Cycle

The cooling requirements for each crystallizer were to be achieved through indirect cooling, in the form of refrigeration cycles. The refrigerant chosen to model the refrigeration cycle was ammonia. Based on the cooling requirements, the compressor duties for the different refrigeration cycles were calculated. Smith & Varbanov (2005) assume compressor isentropic and mechanical efficiencies of 85% and 95% respectively. In this study a combined efficiency of 75% was used. A minimum temperature difference of 10°C between the refrigerant and crystallizer was selected, thus the following operating pressures and temperatures shown in Table 18 were selected for the refrigeration cycle.

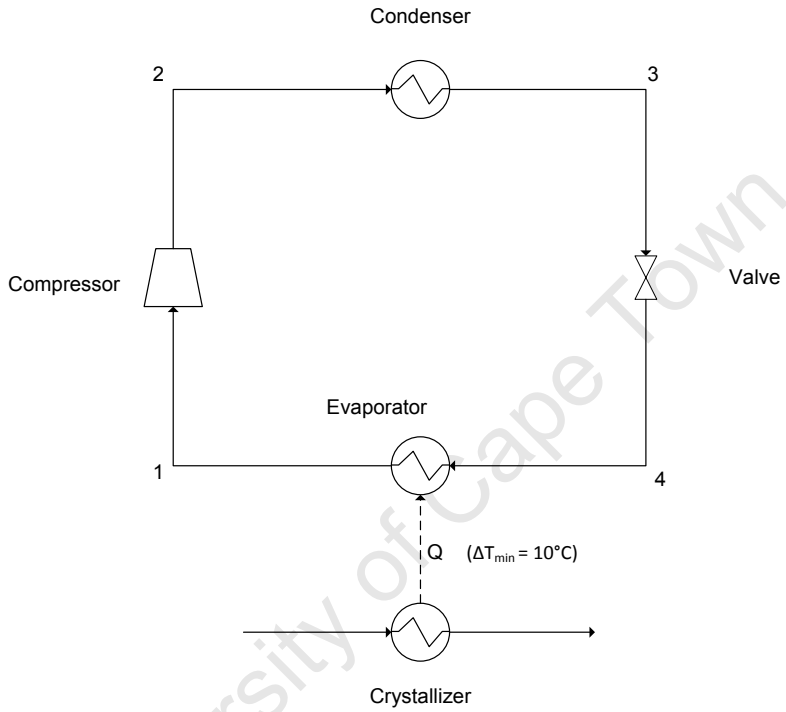


Figure 22: Refrigeration Cycle used for modelling EFC process

Table 18: Operating Conditions for Refrigeration Cycle

Stream	T(°C)	P(bar)	Phase
1	-33.3	1	Vapour
2	165	13.4	Vapour
3	35	13.4	Liquid
4	-33.3	1	Liquid/Vapour

The single stage refrigeration cycle operated at two pressures. The maximum pressure of 13.4bar was chosen to ensure cooling water at 25°C could be used as a utility in the condenser. Any lower operating pressure would require a special coolant to ensure the minimum temperature approach of 10°C was not affected, which would consequently increase the operating costs of the process. The final crystallizer for most case study brines did not operate at a temperature less than -23°C, thus the evaporator in the refrigeration cycle operated at a

temperature of -33°C, which corresponded to a minimum pressure of 1bar. If a case study brine did operate at a temperature more than -23°C, then the minimum pressure of the refrigeration cycle would need to be altered.

In the two stage refrigeration cycle, ice slurry was used to condense the refrigerant. It was assumed that the ice slurry exiting the wash column would be at 0°C with a solids mass fraction of 0.40. Using the minimum temperature approach, the minimum temperature the refrigerant could be cooled down to in the condenser (stream 3, Table 18) was 10°C which corresponded to a pressure of around 6.1bar.

The evaporative crystallization process was modelled as a triple-effect evaporation process, where steam produced from the preceding evaporators was used as a utility in the subsequent evaporators as shown in Figure 23.

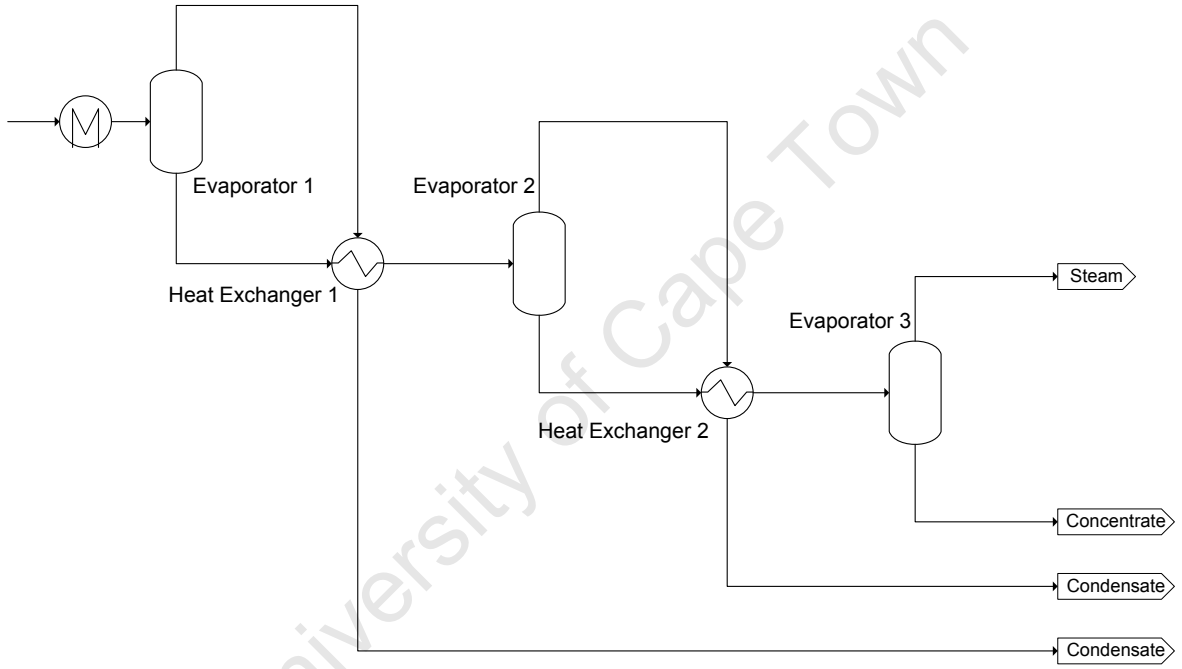


Figure 23: Evaporative Crystallization Flowsheet

The first evaporator would require steam to partially evaporate the brine. The utilization of steam produced in the first two evaporators significantly reduced the steam requirement of the EC process. Subsequent evaporators needed to be operated at decreased pressures in order to ensure the minimum temperature approach is maintained to allow for heat transfer.

3.7 Costing

Operating costs for both the EFC and EC process were based on the energy requirements of the processes. For the EFC process, the major energy requirement for the process was based on the electricity costs to power the compressor of the refrigeration system used to cool the crystallizers. Electricity for running the compressor was costed at R0.49/kWh (Eskom Holdings LTD 2008) from Eskom, South Africa's national electricity supplier. Minor costs for running the separation equipment were not taken into account when compared to evaporative crystallization, as both processes required similar separation equipment. The cooling water for

the condensers in the refrigeration cycles was not accounted for as it was assumed cooling water was readily available, along with the fact that the process itself produced pure water.

The major energy requirements, and hence costs, for the Evaporative Crystallization process was the steam costs in the first evaporator. Pressured steam (350kPa) was used at a cost of R270/ton.

A basic capital cost calculation was carried out for the two processes as outlined in (Vaessen 2003). The crystallizer cost was based on the scraped cool walled crystallizer (SCWC), with the biggest SCWC having a maximum cooling capacity of 160kW. Thus depending on the cooling requirement for the crystallizers, multiple crystallizers operating in parallel were employed.

The cost of reciprocating belt filters were approximated by scaling the values quoted by Vaessen (2003), where a 2.3m^3/hr slurry had an investment cost of €140,000 and a 2.2 m^2 filter surface area. The wash columns and cooling equipment were scaled according to their diameters and cooling power required respectively as shown in Section 27.

For the evaporative crystallization process plate evaporators, plate condensers and the forced circulation crystallizer were scaled according to the heating duty to estimate capital costs as shown in Section 27.

A comparison between the two processes was drawn up for operating costs and capital costs. A sum of the total operating costs and capital costs for successive years were shown.

3.8 Heat Recovery

The EFC process has the potential to utilize the ice product produced to lower the energy input by heat integration and hence reduce the costs of the process. As mentioned before, the ice can be used in two main areas to reduce the operating costs of the process; to pre-cool the feed before entering the first crystallizer or in the condenser of a two-stage refrigeration cycle. Each of these options was investigated and depending on the amount of ice produced a combination of both options was also considered.

Chapter 4: Brine Characterization

Brine characterization is an integral part of evaluating the applicability of any process technology for a particular brine. It informs which brine treatment route should be taken and process operating conditions that should be selected. Four case study brines were analysed to obtain an indication of the main constituents and the impurities that are present in the brine stream from the various processing applications. The four brines studied were:

Case Study 1: Platinum Mine (PM)
Case Study 2: Coal Mine (CM)
Case Study 3: Petrochemical Plant (PC)
Case Study 4: Power Generation Plant (PG)

4.1 Measurement of General Parameters

The measurements obtained for pH, density, conductivity and the Total Dissolved Solids (TDS) for all four case study brines are presented in Table 19.

Table 19: General measurements for four case study brines

Component	Units	PM	CM	PC	PG
pH		9.80	7.28	7.00	7.26
Conductivity	mS/cm	141	19.6	68	20
Density	g/cm^3	1.15	1.02	1.06	1.01
TDS	mg/L	191,801	28,960	67,114	18,875

The pH values of the brines were all in the region of pH 7 with the exception of the PM brine which has a pH of 9.80. The variation of conductivity and density between the four case study brines can be explained by the TDS of the brines. A higher TDS relates to a higher number of dissolved anions and cations in the brine accounting for a higher conductivity. In the same respect, a higher TDS increases the density of the brine stream.

4.2 Major and Trace Elemental Analysis

4.2.1 Cation Analysis

The cation analysis was carried out using ICP-MS/AES measurement technique, which yielded the following results presented in Table 20 for the case study brines.

Table 20: Cation Analysis for case study brines

Component	Units	PM	CM	PC	PG
NH_4	mg/L	18	86	54	-
Na	mg/L	70297	5796	21149	5,400
Mg	mg/L	-	170	208	41
Si	mg/L	251	-	44	-
K	mg/L	110	3871	2161	300
Ca	mg/L	5	1058	707	390
Cd	mg/L	2	-	-	-
Ni	mg/L	9	-	1	-

The cation that was present in the highest concentration in all four case study brines was the sodium ion, Na^+. Other cations that were common were the calcium and potassium ions. These three cations made up more than 97.5% (99.6%, 97.7%, 98.7% & 99.3% respectively) of the cations present in the brine.

As mentioned before the pH of the PM brine was higher than the other case study brines. The high pH and Na content is due to the caustic soda (NaOH) added to neutralize the streams. Zibi (2010) reports the use of caustic soda to precipitate non-recovered base metals in the platinum mining industry.

4.2.2 Anion Analysis

Ion chromatography was used to determine which anions were present in the brine stream and at what concentration. The anion analysis for the four case study brines are presented in Table 21.

Table 21: Anion analysis for case study brines

Component	Units	PM	CM	PC	PG
CO_3	mg/L	32821	-	390	-
HCO_3	mg/L	-	151	-	-
PO_4	mg/L	475	5	55	-
SO_4	mg/L	37363	15565	29920	8,690
NO_3	mg/L	2175	741	785	30
NO_2	mg/L	-	-	395	-
Cl	mg/L	46963	1504	11135	4,010
Br	mg/L	988	-	85	-
F	mg/L	-	14	-	14

Major anions present in the four case study brines were the sulphate (SO_4^{2-}) and chloride (Cl^-) ions. For the three case study brines (CM, PC and PG) these two anions contributed more than 95% of the total anions present in the case study brines. The PM brine had a third major anion present, the carbonate ion (CO_3^{2-}), and together with Cl^- and SO_4^{2-}, they made up 97% of the anions present in the brine.

4.3 Complete Analysis

The full brine analysis for the four case study brines is presented in Table 22. This includes the general, cation and anion analyses for all the case study brines.

Table 22: Full brine analysis for case study brines

Component	Units	PM	CM	PC	PG
pH		9.80	7.28	7.00	7.26
Conductivity	mS/cm	141	19.6	68	20
Density	g/cm3	1.15	1.02	1.06	1.01
CO_3	mg/L	32821	-	390	-
TKN as N	mg/L	238	-	25	1
NH_3 (by FSA)	mg/L	86	-	-	-
NH_4 (by FSA)	mg/L	18	86	54	-
HCO_3	mg/L	-	151	-	-
PO_4	mg/L	475	5	55	-
SO_4	mg/L	37363	15565	29920	8,690
NO_3	mg/L	2175	741	785	30
NO_2	mg/L	-	-	395	-
Cl	mg/L	46963	1504	11135	4,010
Br	mg/L	988	-	85	-
F	mg/L	-	14	-	14
Na	mg/L	70297	5796	21149	5,400
Mg	mg/L	-	170	208	41
Si	mg/L	251	-	44	-
K	mg/L	110	3871	2161	300
Ca	mg/L	5	1058	707	390
Cd	mg/L	2	-	-	-
Ni	mg/L	9	-	1	-
TDS	mg/L	191 801	28 960	67 114	18 875

The Platinum Mine case study brine had the greatest range of dissolved species in it. This brine was the most concentrated brine of the four case studies with a TDS of 191800mg/L. The Petrochemical brine showed a great variety of dissolved elements, but was less concentrated than the PM brine. The last two case study brines were similar in dissolved species and had a low concentration compared to the PM and PC brines. Understanding the processing steps that lead to the formation of these brines can help understand the differences in compositions and concentrations of the brines. However, this information was not readily available from the different industries and each of the case study brines had to be modeled on the brine characterizations carried out, with the results presented above.

4.4 Ion Imbalance

In reality, the brine as a whole is neutral and the negative charges of the anions are complemented with positive charges of the cations on a molar basis. However, in the brine characterization steps, a result of factors such as limitations in the analytical techniques and dilution errors, the cations and anions measured may not balance. Moreover, not accounting for every species in the brine characterization steps is a large contributor to ion imbalances and hence errors in brine characterization. A simple check to verify the accuracy of the brine

characterization step is to perform an anion-cation balance. Table 23 presents the percentage imbalance for the four case study brines.

Table 23: Percentage ion imbalance of case study brines

	PM	CM	PC	PG
Cation Charge	3.062	0.423	1.031	0.265
Anion Charge	-3.259	-0.382	-0.974	-0.295
Imbalance	-0.197	0.041	0.057	-0.030
% Imbalance	3.112	5.084	2.822	5.323

As mentioned before in Chapter 3.4 (pg 34) an acceptable imbalance in the order of 10%, and hence all four brines with calculated imbalances of less than 6% are within the acceptable levels.

4.5 Identification of the Dominant Ions in the Brines Investigated

The four case study brines had a wide range of elements dissolved in them, with some elements at relatively low concentrations compared to others. Inclusion of the trace elements did have an impact on the convergence of the model and resulted in extended simulation times for convergence. For this reason and the fact that the dominant ions made up more than 98% of the ions present in the brine, the case study brines were simplified to only include the dominant ions as a good representation of the actual brines. The dominant ions present in each of the brines are summarized in the Table 24.

Table 24: Case study dominant ions

Component	Units	PM	CM	PC	PG
CO_3	mg/L	32821	-	390	-
SO_4	mg/L	37363	15565	29920	8690
Cl	mg/L	46963	1504	11135	4010
NO_3	mg/L	-	741	785	-
Na	mg/L	70297	5796	21149	5400
K	mg/L	-	3871	2161	300
Ca	mg/L	-	1058	707	390

There were three ions which were common to all four case study brines; these were the Na^+, Cl^- and SO_4^{2-} ions. An ion balancing exercise was carried out on the stream based on the dominant ions in order to validate the abovementioned assumption and to ensure that the minimum imbalance was not exceeded. Table 25 shows the percentage ion imbalance in using the dominant ion approach for the four case study brines.

Table 25: Percentage imbalance on dominant ion case study brines

	PM	CM	PC	PG
Cation Charge	3.058	0.404	1.010	0.262
Anion Charge	-3.196	-0.378	-0.963	-0.294
Imbalance	-0.139	0.025	0.048	-0.032
% Imbalance	2.217	3.258	2.423	5.757
Make-Up Ion (amount – [mg/l])	Na^+ (3188)	SO_4^{2-} (1224)	SO_4^{2-} (2296)	Na^+ (736)

As can be seen, selecting the dominant ions did not negatively impact the ion imbalance. On the contrary, the ion imbalance accountability improved for the first three brines. The accurately characterized brines were then put through a thermodynamic modeling exercise as detailed in the subsequent sections of this dissertation.

Chapter 5: Thermodynamic Analyses and Operating Cost Estimations

The thermodynamic analysis was carried out in order to determine the energy requirements for the EFC process. To calculate the energy requirements, and subsequently operating costs, a number of steps have to be carried out first which will be highlighted in the following sections.

5.1 Temperature survey

The first part of the thermodynamic analysis was carried out in Oli Stream Analyzer® to perform temperature surveys on the ion balanced case study brines. The ion imbalances were discussed in the previous chapter and this chapter will focus on the temperature surveys of the case study brines. The temperature surveys were carried out from 25°C to -25°C. The thermodynamic modelling software uses chemical and phase equilibria to predict:

- the salts that will crystallize out and in what sequence
- the temperature at which crystallization takes place and
- the yield of each salt and ice that will form

A basis of 1litre of brine was used for the temperature surveys that were carried out for the case study brines. The temperature surveys will be discussed separately for each of the case study brines.

5.1.1 PM case study

As mentioned before , the PM case study brine was the most concentrated brine of the four brines investigated. The major ions present in the brine are listed in Table 26:

Table 26: PM case study brine – dominant ions

Component	Units	PM
Na^+	mg/L	70297
Cl^-	mg/L	46963
SO_4^{2-}	mg/L	37363
CO_3^{2-}	mg/L	32821

The result of temperature survey of the PM brine is shown in Figure 24. The temperature is shown on the x-axis whilst the, salt recovery (kg) is shown on the primary y-axis and the ice recovery (kg) shown on the secondary y-axis.

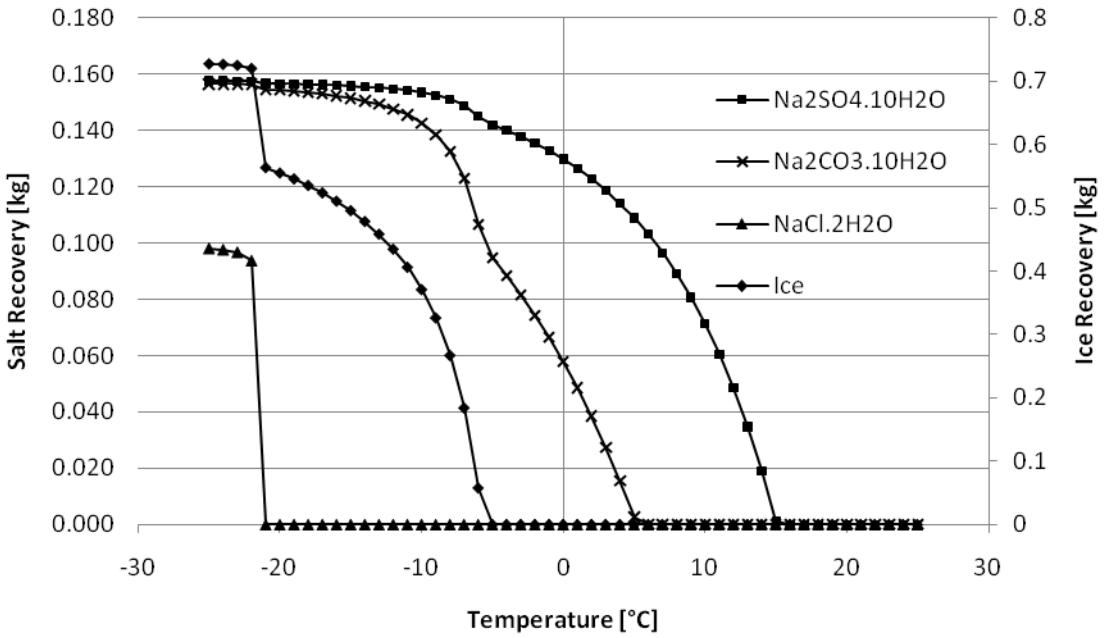


Figure 24: Thermodynamically predicted salt and ice crystallization temperatures for PM brine

From the results it is evident that the first species that is predicted to crystallize out is $Na_2SO_4 \cdot 10H_2O$ (Glauber salt) at 15°C, followed by $Na_2CO_3 \cdot 10H_2O$ (washing soda) at 5°C. The reason for the salt crystallizing out first as opposed to the ice is that when considering a binary phase diagram, if a solution is highly concentrated, the system will approach the salt solubility line first (see chapter 2.3) resulting in the salt crystallizing out first. After a further reduction in temperature, the solution will reach the eutectic point at which both salt and ice crystallization takes place. Similarly for the PM brine, two salts crystallized out before ice crystallization, indicating that it is a highly concentrated brine. As can be expected the large concentration of ions present in the brine depressed the freezing point of the ice from 0°C to -5°C. There was an increase in the amount of both $Na_2SO_4 \cdot 10H_2O$ and $Na_2CO_3 \cdot 10H_2O$ when ice crystals were first formed. This increase in salt yield is attributed to the removal of the ice, which is the solvent, thereby increasing the concentration of the brine up to and beyond the saturation limit of the salts. The last component to crystallize out was the $NaCl \cdot 2H_2O$ (Hydrohalite) salt, crystallizing out at -23°C. Table 27 highlights the recoveries of the various products obtained from the temperature survey modelling exercise on the PM brine. The temperatures at which the salts first crystallize out are shown along with the final product recoveries at -25°C.

Table 27: Product recovery from the PM brine (basis = 1l)

Product	Molar Mass	Crystallizing Temperature (°C)	Amount at -25°C (mol)	Amount at -25°C (kg)
$Na_2SO_4 \cdot 10H_2O$	322.20	15	0.49	0.16
$Na_2CO_3 \cdot 10H_2O$	286.14	5	0.55	0.16
Ice	18.02	-5	40.34	0.73
$NaCl \cdot 2H_2O$	94.47	-23	1.04	0.10

5.1.2 CM case study

The CM case study brine had a TDS of 28900 mg/L, which was about six times less than the TDS of the PM brine. The major ions present in the CM brine are highlighted in Table 28 below.

Table 28: CM case study brine – dominant ions

Component	Units	CM
Na^+	mg/L	5796
K^+	mg/L	3871
Ca^{2+}	mg/L	1058
Cl^-	mg/L	1504
SO_4^{2-}	mg/L	15565
NO_3^-	mg/L	741

These six dominant ions accounted for 99% of the total dissolved ions in the CM case study brine. The temperature survey of the CM brine is shown in Figure 25. The reduction in solution temperature is from right to left on the x-axis. Salt recovery (kg) is shown on the primary y-axis with the ice recovery (kg) shown on the secondary y-axis.

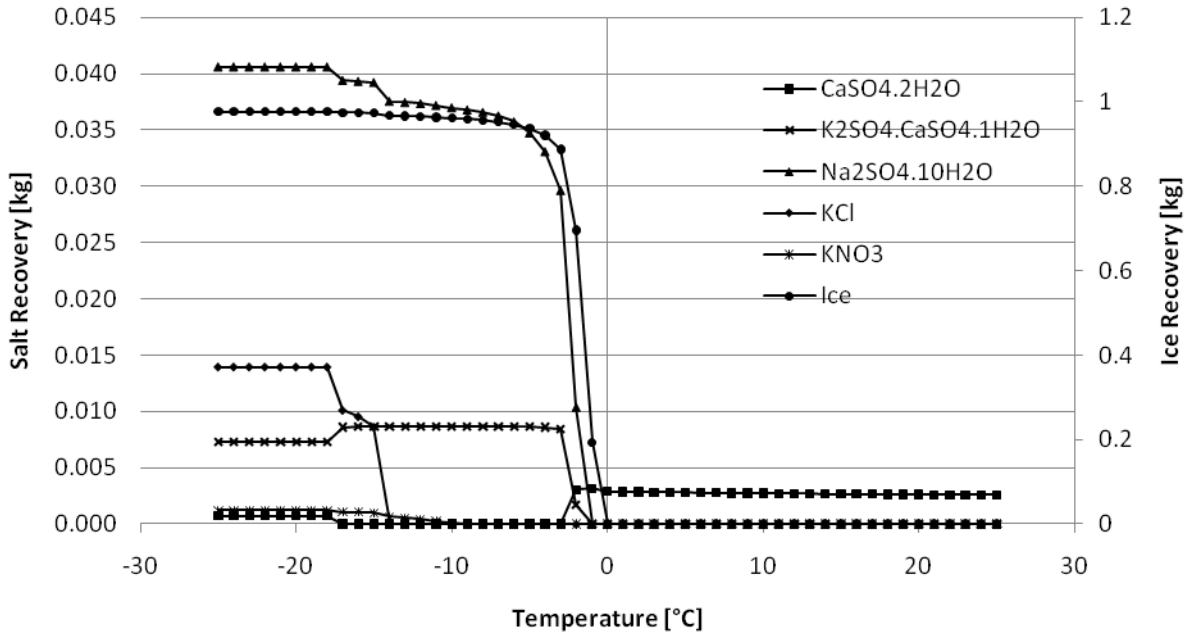


Figure 25: Thermodynamically predicted salt and ice crystallization temperatures for CM brine

Figure 25 shows that the brine is already saturated with respect to calcium sulphate at 25°C and that the first component to crystallize out is ice at -1°C. On further reduction in temperature to -2°C, three changes occur. Below -2°C, the Ca ion favours the formation of the double salt, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$, instead of the $CaSO_4 \cdot 2H_2O$ salt. In addition to the double salt, a second salt crystallizes out at -2°C, $Na_2SO_4 \cdot 10H_2O$. Further reduction in temperature down to -10°C shows the crystallization of KNO_3. The final salt to crystallize out is KCl at a temperature of -15°C. Table 29 highlights the recoveries of the various products with a reduction in temperature.

Table 29: Product recovery from the CM brine (basis = 1l)

Product	Molar Mass	Crystallizing Temperature (°C)	Amount at -25°C (mol)	Amount at -25°C (kg)
$CaSO_4.2H_2O$	172.17	present	0.00	0.00
Ice	18.02	-1	54.22	0.98
$Na_2SO_4.10H_2O$	322.20	-2	0.13	0.04
$K_2SO_4.CaSO_4.H_2O$	328.42	-2	0.02	0.01
KNO_3	101	-10	0.01	0.00
KCl	74.55	-15	0.04	0.00

5.1.3 PC case study

The petrochemical brine was the second most concentrated brine of the four case study brines. The major ions present in the brine are listed in Table 30 with their concentrations in mg/L.

Table 30: PC case study brine – dominant ions

Component	Units	PC
Na^+	mg/L	21149
K^+	mg/L	2161
Ca^{2+}	mg/L	707
NO_3^-	mg/L	785
Cl^-	mg/L	11135
SO_4^{2-}	mg/L	29920

These 6 dominant ions accounted for more than 98% of the TDS in the PC brine. The temperature survey of the PC brine is shown in Figure 26. The temperature is shown on the x-axis whilst the salt recovery (kg) is shown on the primary y-axis and the ice recovery (kg) shown on the secondary y-axis.

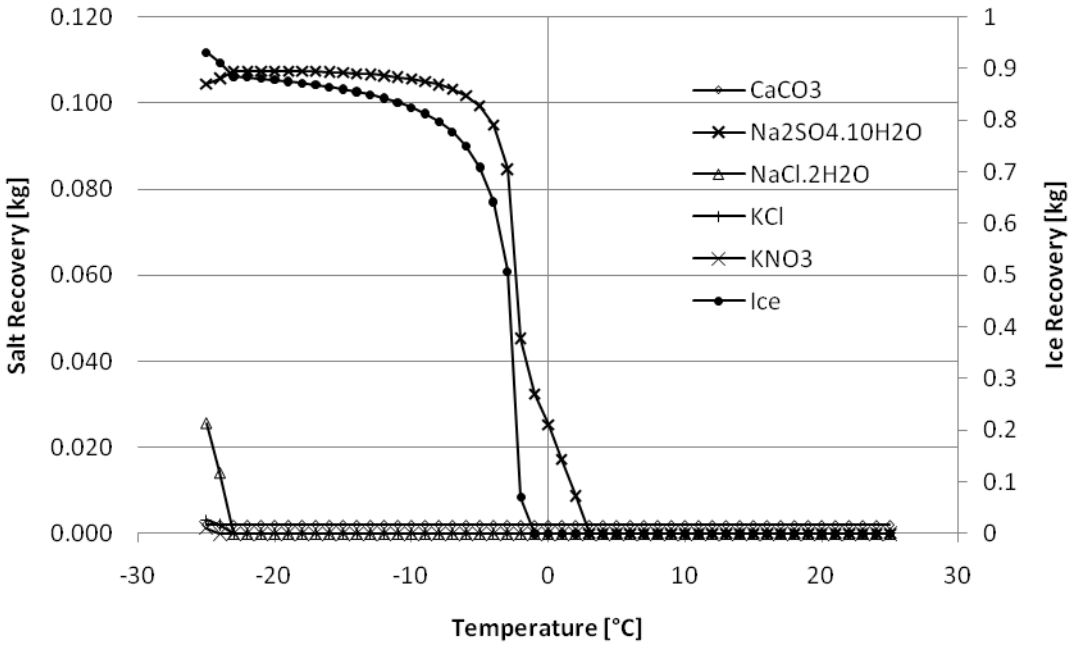


Figure 26: Thermodynamically predicted salt and ice crystallization temperatures for PC brine

The results show that the brine is already saturated with respect to $CaCO_3$ at 25°C. Hence, the first species to crystallize out was $Na_2SO_4 \cdot 10H_2O$, at 2°C. As previously mentioned, with a concentrated solution, the salt crystallizes out first as can be seen in both the PC and PM case study brines. The freezing point of ice in the PC brine was only depressed to -2°C, which is slightly higher than the more concentrated PM brine (-5°C). Below -24°C, a few salts crystallized out, but the exact amounts and temperatures which crystallization took place cannot be seen clearly in Figure 26 and are listed in Table 31.

Table 31: Product recovery from the PC brine (basis = 1l)

Product	Molar Mass	Crystallizing Temperature (°C)	Amount at -25°C (mol)	Amount at -25°C (kg)
$CaCO_3$	100.09	Already Present	0.006	0.001
$Na_2SO_4 \cdot 10H_2O$	322.20	2	0.324	0.104
Ice	18.02	-2	51.701	0.932
$NaCl \cdot 2H_2O$	94.47	-24	0.271	0.026
KCl	74.55	-24	0.043	0.003
KNO_3	101.10	-25	0.013	0.001

The $NaCl \cdot 2H_2O$ and KCl crystallize out at -24°C, followed by KNO_3 at -25°C. No further salts were formed below this temperature. There was a very low recovery of the $CaCO_3$ and KNO_3 salts, due to the low concentrations of the Ca^{2+} and NO_3^- ions present in the PC brine.

5.1.4 Temperature survey PG case study

The power generation brine was the most dilute brine of the four case study brines, with a TDS of 18875mg/l. The major ions present in the brine are listed in Table 32 with their concentrations in mg/L.

Table 32: PG case study brine – dominant ions

Component	Units	PG
Na^+	mg/L	5 400
K^+	mg/L	300
Ca^{2+}	mg/L	390
Cl^-	mg/L	4 010
SO_4^{2-}	mg/L	8 690

The dominant ions presented in Table 32 were chosen as the five ions that made up 99% of the total dissolved ions in the original brine. The results of the temperature survey of the PC brine are shown in Figure 27. The temperature is shown on the x-axis whilst the salt recovery (kg) is shown on the primary y-axis and the ice recovery (kg) shown on the secondary y-axis.

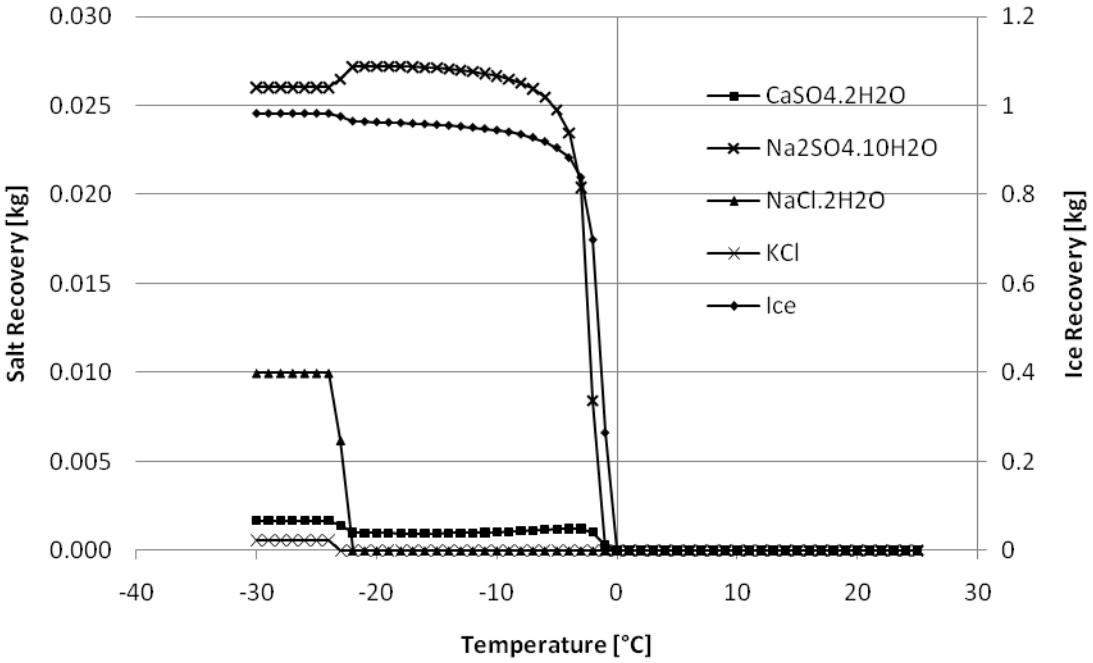


Figure 27: Thermodynamically predicted salt and ice crystallization temperatures for PG brine

As expected, due to the power generation brine being dilute, ice crystallized out first at -1°C, along with the $CaSO_4 \cdot 2H_2O$ salt. However, the amount of $CaSO_4 \cdot 2H_2O$ that was crystallized was negligible, even at -25°C as shown in Table 33. The next salt to crystallize out as the temperature was lowered was $NaSO_4 \cdot 10H_2O$ at -2°C. The final two salts, $NaCl \cdot 2H_2O$ and KCl, both crystallized out at much lower temperatures of -22.5°C and -23°C respectively. Table 33 highlights the various salt and ice recoveries and temperatures of crystallization.

Table 33: Product recovery from the PG brine (basis = 1l)

Product	Molar Mass	Crystallizing Temperature (°C)	Amount at -25°C (mol)	Amount at -25°C (kg)
Ice	18.02	-1	54.471	0.981
$CaSO_4 \cdot 2H_2O$	172.17	-1	0.010	0.002
$NaSO_4 \cdot 10H_2O$	322.20	-2	0.081	0.026
$NaCl \cdot 2H_2O$	94.47	-22.5	0.105	0.010
KCl	74.55	-23	0.008	0.001

5.1.5 Summary of Temperature Surveys

From the four different temperature surveys, various salts were predicted to crystallize out under reduced temperatures. The different salts for the different brines are summarized in Table 36.

Table 34: Predicted salts produced from the various case study brines using EFC

Dominant Products	PM	CM	PC	PG
Ice	✓	✓	✓	✓
$CaSO_4 \cdot 2H_2O$		✓		✓
$CaCO_3$			✓	
KCl		✓	✓	✓
$K_2SO_4 \cdot CaSO_4 \cdot H_2O$		✓		
KNO_3			✓	
$Na_2CO_3 \cdot 10H_2O$	✓			
$NaCl \cdot 2H_2O$	✓		✓	✓
$NaSO_4 \cdot 10H_2O$	✓	✓	✓	✓

For all four brines there was one common salt, $NaSO_4 \cdot 10H_2O$, and incidentally, this salt had the greatest recovery in all four case study brines. Other salts that were common were the KCl and $NaCl \cdot 2H_2O$ salts. If the full analysis for each of the case study brines was considered, the number of salts crystallized out and the number of salts common to each of the case studies would increase. However, the amounts of these minor salts that would be crystallized out would be insignificant compared to the amount of dominant salts that would be crystallized out.

5.2 EFC Operating Costs

Having ascertained the salts that are predicted to crystallize out, and the respective crystallization temperatures, the next stage of the thermodynamic analysis was to propose a process flowsheet for the EFC process. The different units chosen are first discussed with any assumptions associated with them after which the proposed flow diagrams for each of the case study brines are presented along with estimated operating costs.

For a binary system, the crystallizer would be operated within the Metastable Zone Width (MSZW), below the eutectic temperature such that both the ice and salt crystallize out and separated according to the density difference of the two products. On the other hand, for a multi-component hypersaline brine, the process is slightly more complicated as there is more than one salt crystallizing out. For each of the case study brines, the crystallizing temperatures were chosen to maximise salt and ice product yields before the second salt crystallized out. It must be noted that as the model is purely thermodynamic, in practice two salts with similar eutectic temperatures could crystallize out at the same time based on their respective kinetics resulting in the possibility of producing a mixed salt product. For this, selective salt formation through strategic seeding could be used to overcome two or more salts crystallizing out at the same temperature. This would allow the first salt to be formed in the first crystallizer followed by the second salt in the second crystallizer, avoiding a mixed salt product to be formed.

The thermodynamic simulation of the EFC process was carried out using Aspen Plus 7.1® due to its ability to successfully model process flowsheets. The first unit operation, the scraped cool walled crystallizer, serves two functions: to provide cooling to the brine stream and to separate the ice and salt products. The salt and ice were taken off from the bottom and top of the crystallizer respectively and were then sent to a belt filter or a wash column in order to remove the entrained brine, which produced pure ice and salt. For the ice filtration, a hydraulic wash column was used to produce the pure ice product. A belt filter was used to separate the salt from the brine concentrate. The other major unit in the EFC process was the cooling equipment which supplies indirect cooling to the crystallizers. The refrigeration cycle was also modelled in Aspen Plus 7.1® to determine the energy requirements of the EFC process.

5.2.1 Temperature Survey – Aspen

The respective salt & ice yields produced over a temperature survey for the PM Case Study brine was selected to compare the results of the temperature surveys obtained using Aspen Plus 7.1® and Oli Stream Analyzer®. The temperature survey is shown in Figure 28 below for a 300m^3/day brine flowrate.

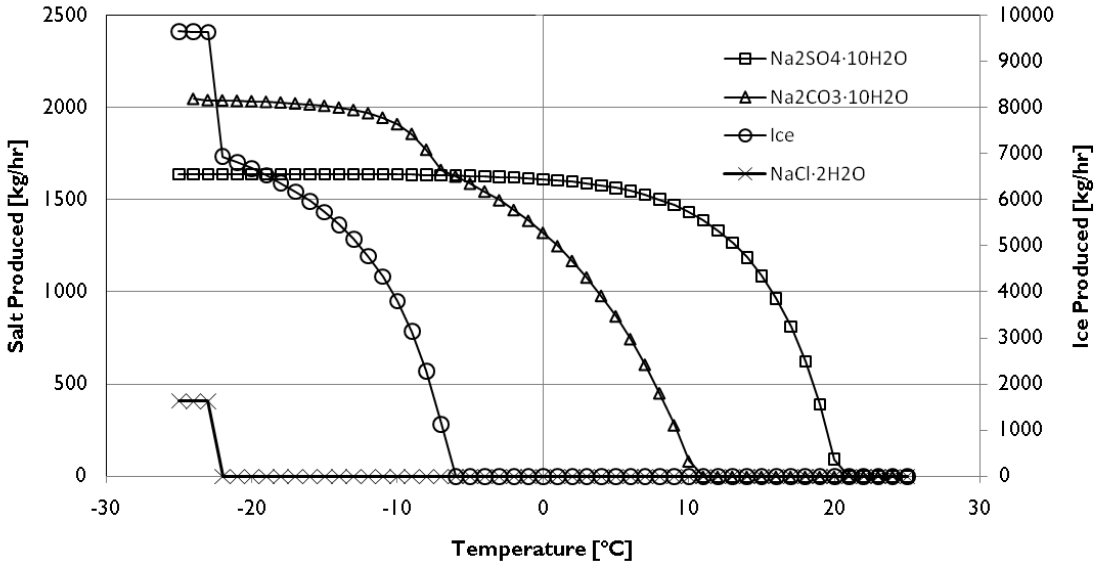


Figure 28: Temperature Survey of PM Case Study using Aspen Plus 7.1®

The comparison between the two thermodynamic modelling packages showed similar product recoveries and compositions; however the temperatures at which the first two salts crystallize out were slightly higher for the temperature survey in Aspen Plus. This minor difference is not expected to significantly affect the energy requirements of the overall process and can be attributed to the different property methods that the two programs use as well as the manual input of the $NaCl{\cdot}2H_2O$ salt into Aspen Plus 7.1®.

5.2.2 Development of a flowsheet for the PM Case Study

The operating temperature for the first crystallizer of the PM Case study brine was chosen to be 12°C to maximise $Na_2SO_4{\cdot}10H_2O$ recovery before the crystallization of $Na_2CO_3{\cdot}10H_2O$. The second crystallizer was chosen to operate at -12°C to maximise salt and ice recovery, while at the same time ensuring there is enough brine in the final crystallizer to enable gravitational separation between the ice and $NaCl{\cdot}2H_2O$. The final crystallizer was operated at -23°C producing ice, $NaCl{\cdot}2H_2O$ and a small waste stream. The full flowsheet for the PM case study brine is presented in Figure 29.

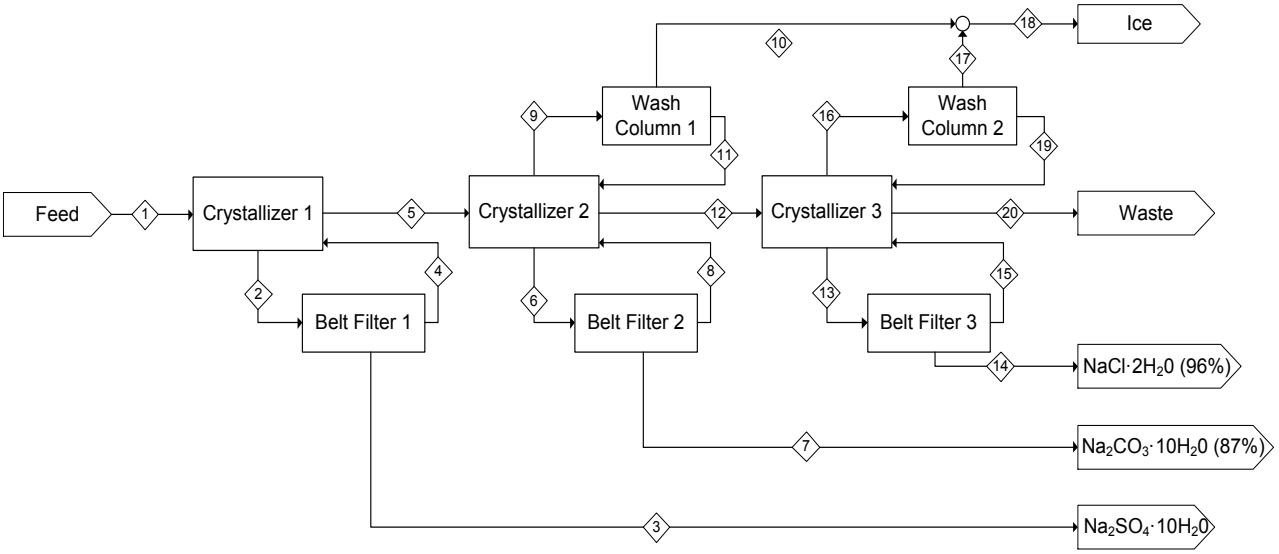


Figure 29: Proposed flowsheet for PM case study brine

The first crystallizer only produces $Na_2SO_4 \cdot 10H_2O$ and this was sent to a belt filter to recover the salt from the liquor stream. Any ice produced in the subsequent crystallizers was sent to wash columns and the salt products were sent to belt filters. Table 35 highlights the recoveries of ice and salt products along with the cooling duties of the three crystallizers.

Table 35: Crystallizer cooling duties and product flowrates for 300m³/day PM case study brine

Unit	Duty [kW]	Salt Produced [kg/hr]			Ice Produced [kg/hr]
		$Na_2SO_4 \cdot 10H_2O$	$Na_2CO_3 \cdot 10H_2O$	$NaCl \cdot 2H_2O$	
Crystallizer 1 (12°C)	-306	1330	0	0	0
Crystallizer 2 (-12°C)	-846	304	1990	0	4770
Crystallizer 3 (-23°C)	-531	1.01	60.0	1630	4870

When either ice or salt crystals are formed there is a release of energy, the enthalpy of crystallization (ΔH^{cryst}), and this requires cooling to sustain the low temperature. The second crystallizer produced a mixed salt product that had an 87 wt% $Na_2CO_3 \cdot 10H_2O$ content, with the remainder in the form of $Na_2SO_4 \cdot 10H_2O$. The large energy requirement of the second crystallizer was due to the formation of ice crystals. The total cooling requirement for the process is presented in Figure 30.

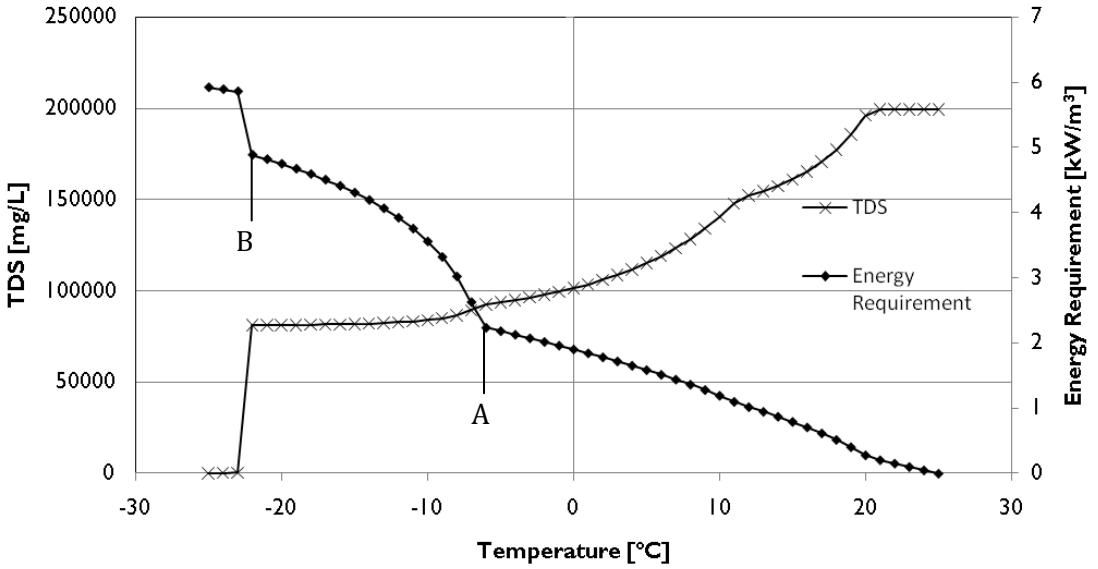


Figure 30: Cumulative cooling requirements for PM case study brine

The graph above shows a steady increase in cooling requirement per m^3 of brine treated, as the temperature of the brine is decreased. Included in the graph is the TDS of the brine. At about -5°C (point A), when the ice starts to crystallize out there is a significant increase in the cooling requirements to overcome the heat released by the heat of fusion when the ice crystals are formed. There was also a sharp increase in the cooling requirements at about -23°C (point B) where $NaCl{\cdot}2H_2O$ crystallizes out along with an additional increase in ice formation as shown previously in Figure 28.

The corresponding compressor duties for the cooling systems used to cool the crystallizers are summarised in Table 36.

Table 36: Compressor duties & associated operating costs for treating PM case study brine using EFC

Unit	Crystallizer Duty [kW]	Compressor Duty [kW]	Cost / day [R/day]	Cost / m^3 of Brine [R/m^3]
Crystallizer 1 (12°C)	-306	156	R 1720	R 5.75
Crystallizer 2 (-12°C)	-846	432	R 4770	R 15.91
Crystallizer 3 (-24°C)	-531	271	R 3000	R 9.99
Total operating costs for PM Brine (300m^3/day)			**R 9490/day**	**R 31.64/m^3**

The operating costs for treating 300m^3/day of the PM case study brine were calculated from the electricity cost of running the compressors. Hence, the total cost for treating the PM case study brine was calculated to be R31.64/m^3 of feed brine.

5.2.3 CM Case Study

There was a greater variety of major ions present in the CM case study brine which consequently led to more salt products being formed. The different salts, along with the low TDS, led to a more complex flowsheet. Four crystallizers were chosen to operate within a temperature range of -2°C to -15°C. The double salt $K_2SO_4{\cdot}CaSO_4{\cdot}H_2O$ that was predicted by Oli

Stream Analyzer®, was not present in the Aspen database but the simulation predicted the simultaneous crystallization of the two salts separately. A large portion of $CaSO_4 \cdot 2H_2O$ was removed before the double salt crystallizing temperature was reached and could explain the favoured formation of the two salts separately.

Aspen Plus 7.1® and Oli Stream Analyzer® predicted that the $CaSO_4 \cdot 2H_2O$ salt would be present in the brine at ambient conditions and hence a belt filter was to be used to recover the salt. The selected operating temperature for the first crystallizer was chosen to be -2°C before any $Na_2SO_4 \cdot 10H_2O$ salt crystallizes out. The second crystallizers selected operating temperature is -5°C, so as to maximise the $Na_2SO_4 \cdot 10H_2O$ and ice recovery. Below -5°C, $Na_2SO_4 \cdot 10H_2O$ crystallizes along with K_2SO_4 and KNO_3 and thus the third crystallizers operating temperature is selected to be -12°C, with the fourth crystallizer producing the final salt, KCl, at -15°C. The full flowsheet is presented in Figure 31.

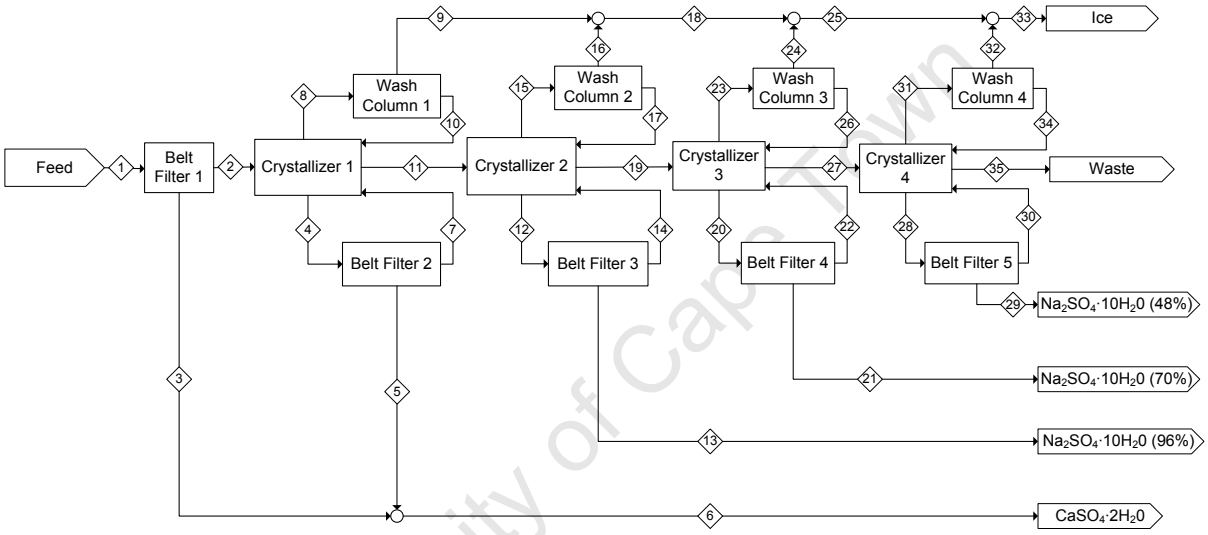


Figure 31: Proposed flowsheet for CM case study brine

$CaSO_4 \cdot 2H_2O$ is recovered from the feed brine and filtered from the first crystallizer producing 40.9 kg/hr of salt product. A large amount of ice is produced in the first crystallizer which accounts for the high cooling requirements of the crystallizer when overcoming the heat of crystallization. Table 37 highlights the crystallizer operating temperatures, cooling duties and product flowrates.

Table 37: Crystallizer cooling duties and product flowrates for 300m³/day CM case study brine

	Duty [kW]	Salt Produced [kg/hr]					Ice Produced [kg/hr]
		$CaSO_4 \cdot 2H_2O$	$Na_2SO_4 \cdot 10H_2O$	KNO_3	K_2SO_4	KCl	
Filter 1		25.2	0	0	0	0	0
Crystallizer 1 (-2°C)	-1070	15.7	0	0	0	0	7450
Crystallizer 2 (-5°C)	-371	10.7	286	0	0	0	3700
Crystallizer 3 (-12°C)	-101	2.15	178	6	70	0	863
Crystallizer 4 (-15°C)	-7.25	0	9	5	0	5	60

Further cooling in the second crystallizer to -5°C increases the amount of ice that crystallizes out. The amount of ice formed in the second crystallizer is about half that of the first crystallizer.

The duty of the second crystallizer does not follow the same trend and is in fact much less than half the duty of the first crystallizer. This smaller duty can be attributed to the lower temperature difference between the entering and exiting streams (27°C as opposed to 3°) and also the significantly smaller flowrate entering the second crystallizer.

A mixed salt product of $Na_2SO_4 \cdot 10H_2O$ and $CaSO_4 \cdot 2H_2O$ is produced in the second crystallizer with a 96% purity of $Na_2SO_4 \cdot 10H_2O$. The third crystallizer, operating at -12°C, produces four different types of salt with a dominant salt, $Na_2SO_4 \cdot 10H_2O$, with a purity of about 70%. The final crystallizer, operating at -15°C, has a low cooling duty and produces a fifth salt KCl, along with $Na_2SO_4 \cdot 10H_2O$ and KNO_3. The corresponding compressor duties for the crystallizers are summarised in Table 38 below.

Table 38: Compressor duties and associated operating costs for treating CM case study brine

Unit	Crystallizer Duty [kW]	Compressor Duty [kW]	Cost / day [R/day]	Cost / m^3 of Brine [R/m^3]
Crystallizer 1 (-2°C)	-1070	410	R 6050	R 20.16
Crystallizer 2(-5°C)	-371	142	R 2090	R 6.98
Crystallizer 3 (-12°C)	-101	38	R 569	R 1.90
Crystallizer 4 (-15°C)	-7.25	3	R 41	R 0.14
Total operating costs for CM Brine (300m^3/day)			**R 8750/day**	**R 29.17/m^3**

The crystallizer and compressor duties decrease for subsequent crystallizers due to the large amount of ice that was crystallized in the first two crystallizers. The total cost for treating the CM case study brine was calculated to be R29.17/m^3.

5.2.4 PC Case Study

The PC case study brine had a variety of major ions present with five different salts predicted to crystallize out. $CaCO_3$ was predicted to be present at 25°C by both modelling software tools and a belt filter was used to separate the salt from the feed stream. The high TDS of the PC brine results in the $Na_2SO_4 \cdot 10H_2O$ crystallizing out before any ice is formed. The operating temperature of the first crystallizer was selected to be 0°C in order to recover as much of the $Na_2SO_4 \cdot 10H_2O$ as possible. The $Na_2SO_4 \cdot 10H_2O$ was filtered on a belt filter before the remaining effluent was sent to the second crystallizer operating at -15°C. This temperature was chosen to ensure a high recovery of $Na_2SO_4 \cdot 10H_2O$ and ice, while at the same time allowing a reasonable liquid flowrate for the third and final crystallizer. The full proposed flowsheet for the PC case study brine is presented in Figure 32.

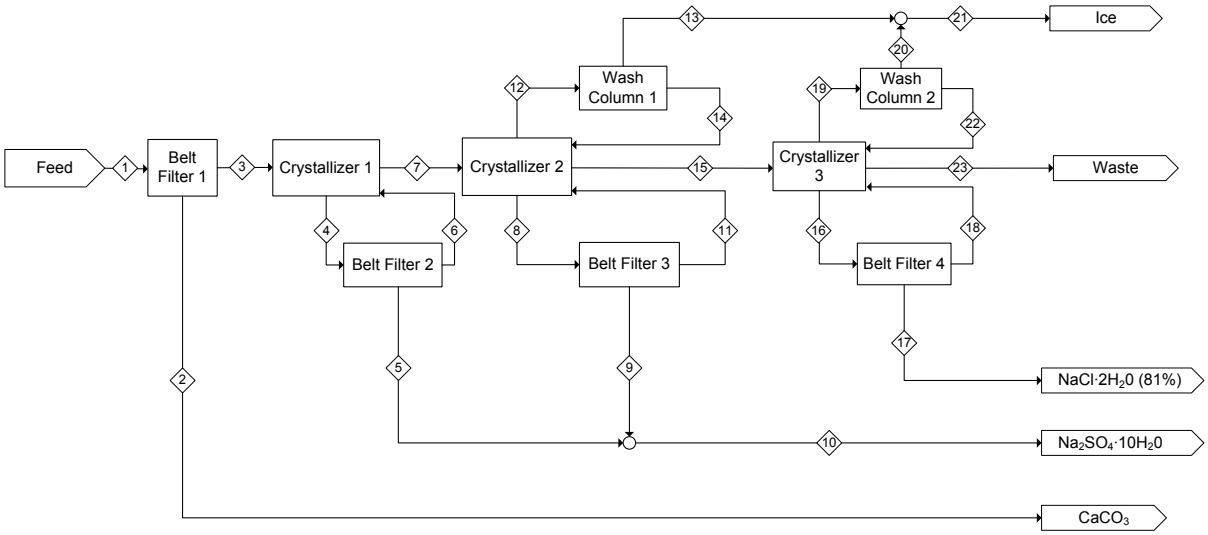


Figure 32: Proposed flowsheet for PC case study brine

The third crystallizer is operated at -26°C where three different salts crystallize out. $NaCl{\cdot}2H_2O$ was the major salt formed at this temperature resulting a 81% purity of the salt stream. The various product recoveries and crystallizer cooling duties are presented in Table 39.

Table 39: Crystallizer cooling duties and product flowrates for 300m³/day PC case study brine

Unit	Duty [kW]	Salt Produced [kg/hr]					Ice Produced [kg/hr]
		$CaCO_3$	$Na_2SO_4{\cdot}10H_2O$	$NaCl{\cdot}2H_2O$	KCl	KNO_3	
Filter 1		7.95	0	0	0	0	0
Crystallizer 1 (0°C)	-446	0.13	1260	0	0	0	0
Crystallizer 2 (-15°C)	-1090	0.05	92	0	0	0	10500
Crystallizer 3 (-26°C)	-76	0	0.12	178	37	5	679

The largest cooling duty is in the second crystallizer, which was expected due to the large $Na_2SO_4{\cdot}10H_2O$ and ice recovery in the crystallizer. There was a small cooling duty for the final crystallizer as the brine volume being fed to the crystallizer is significantly reduced. The corresponding compressor duties of the cooling systems for the crystallizers are presented in Table 40.

Table 40: Compressor duties and associated operating costs for treating PC case study brine

Unit	Crystallizer Duty [kW]	Compressor Duty [kW]	Cost / day [R/day]	Cost / m3 of Brine [R/m3]
Crystallizer 1 (0°C)	-446	228	R 2520	R 8.39
Crystallizer 2 (-15°C)	-1095	559	R 6180	R 20.59
Crystallizer 3 (-26°C)	-76.5	39	R 431	R 1.44
Total operating costs for PC Brine (300m³/day)			**R9120/day**	**R 30.41/m³**

The operating costs for treating 300m³/day of PC case study brine based on the energy requirements of the compressors was calculated to be R30.41/m³.

5.2.5 PG Case Study

The PG case study brine was the most dilute of the four case study brines, which resulted in a large amount of ice being formed. Ice and $CaSO_4 \cdot 2H_2O$ first crystallize out at -1°C, followed by $Na_2SO_4 \cdot 10H_2O$ at -2°C. It was decided that operating a crystallizer at -1°C to recover the $CaSO_4 \cdot 2H_2O$ salt alone would not be feasible due to the close crystallizing temperatures of the two salts along with the very low recovery of $CaSO_4 \cdot 2H_2O$ at -1°C. The full flowsheet for treating the PG case study brine is presented in Figure 33.

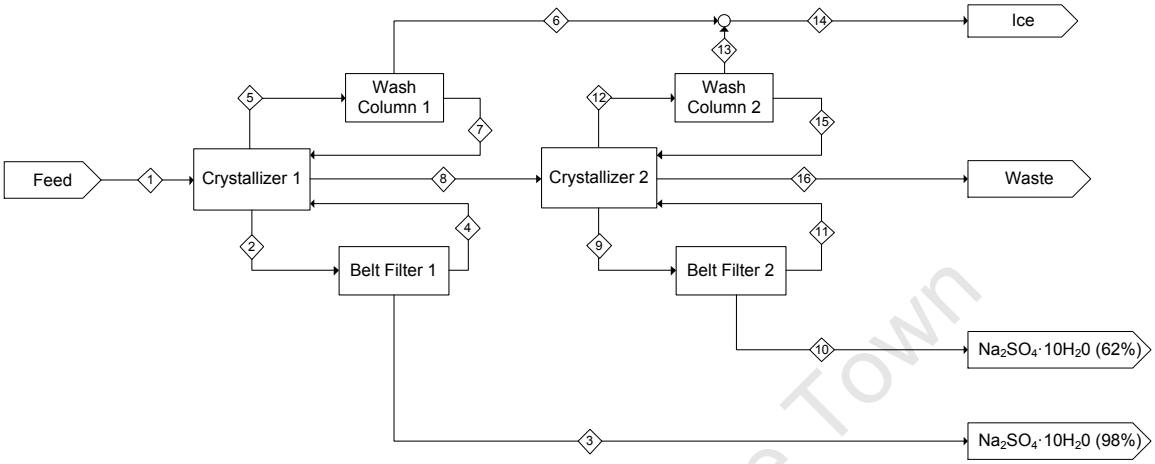


Figure 33: Proposed flowsheet for PG case study brine

The operating temperature of the first crystallizer was selected in order to maximise $Na_2SO_4 \cdot 10H_2O$ recovery. However, as the PG case study brine was so dilute, a large amount of ice was produced in the first crystallizer and thus an operating temperature of -5°C was selected. The second crystallizer was operated at -26°C to recover KCl and $NaCl \cdot 2H_2O$.

Table 41: Crystallizer cooling duties and product flowrates for 300m³/day PG case study brine

Unit	Duty [kW]	Salt Produced [kg/hr]				Ice Produced [kg/hr]
		$CaSO_4 \cdot 2H_2O$	$Na_2SO_4 \cdot 10H_2O$	$NaCl \cdot 2H_2O$	KCl	
Crystallizer 1 (-5°C)	-1440	4	230	0	0	11000
Crystallizer 2 (-26°C)	-125	0	125	72	4	1050

The first crystallizer has a very large cooling duty and produces a salt stream with a $Na_2SO_4 \cdot 10H_2O$ purity of 98%. The second crystallizer has a lower cooling duty and produces a variety of salts, with the major salt $Na_2SO_4 \cdot 10H_2O$, with a purity of only 62%.

Table 42: Compressor duties and associated operating costs for treating PG case study brine

Unit	Crystallizer Duty [kW]	Compressor Duty [kW]	Cost / day [R/day]	Cost / m3 of Brine [R/m3]
Crystallizer 1 (-5°C)	-1440	736	R 8130	R 27.10
Crystallizer 2 (-26°C)	-125	64	R 707	R 2.36
Total operating costs for PG Brine (300m³/day)			**R 8840/day**	**R 29.46/m³**

The operating costs for treating 300m³/day of the PG case study brine were calculated to be R29.46/m³.

The waste streams produced by EFC for the four case study brines are presented in Table 43 along with the feed flowrates of the case study brines.

Table 43: Brine waste streams produced from the EFC process

	PM		CM		PC		PG	
Component	**Feed Stream [kg/hr]**	**Waste Stream [kg/hr]**	**Feed Stream [kg/hr]**	**Waste Stream [kg/hr]**	**Feed Stream [kg/hr]**	**Waste Stream [kg/hr]**	**Feed Stream [kg/hr]**	**Waste Stream [kg/hr]**
Water	12500	6.22	125	125	12300	271	12400	100
Na^+	961	0.67	73	5.35	264	28	77	8
K^+	-	-	48.6	10.6	27	6.15	3.75	1.91
Ca^{2+}	-	-	7	0.80	5.65	5.58	4.88	3.83
Cl^-	614	1	19	17	139	55	50	21
SO_4^{2-}	488	0	197	1.43	403	0	109	0
CO_3^{2-}	429	0	-	-	0	0	-	-
NO_3^-	-	-	9.3	2.77	9.81	7.05	-	-
Total [kg/hr]	**14967**	**7.93**	**163**	**163**	**13147**	**372**	**12669**	**136**

The four case study brines showed a reduction in brine flowrates of about 97% when treated using EFC. In the PM case study there was a complete recovery of the SO_4^{2-} and CO_3^{2-} ions. The PC and PG case study brines also showed a 100% recovery of the SO_4^{2-} ion.

Figure 34 summarizes the operating costs for daily treatment of the four case study brines.

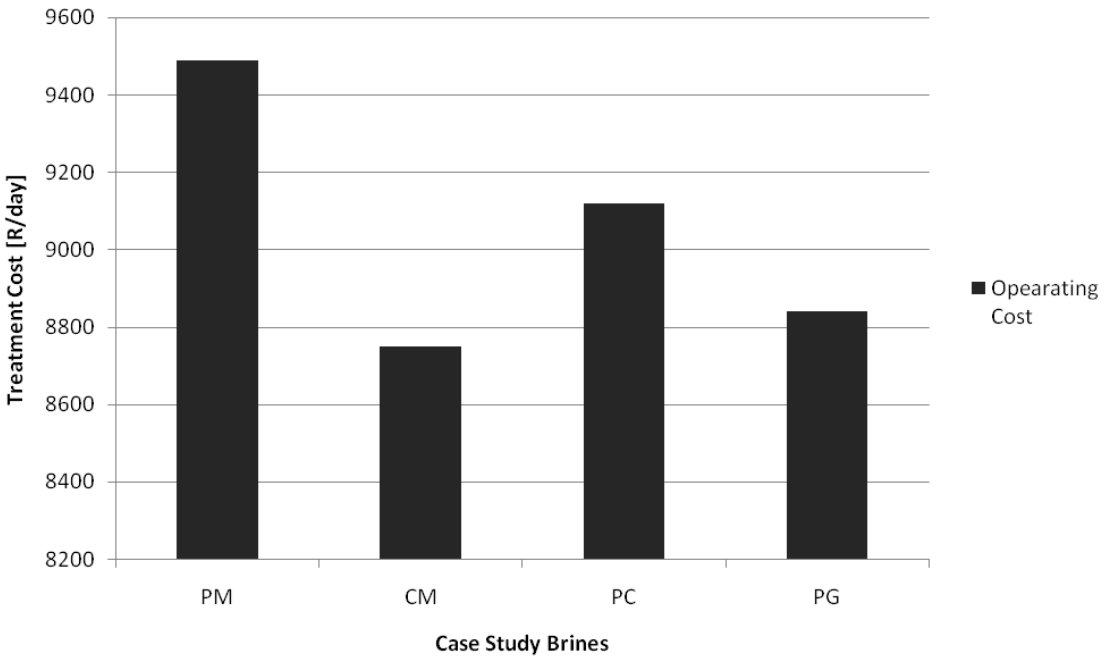


Figure 34: Comparison of operating costs for the four case study brines

The operating costs to treat the case study brines varied with concentration as seen in Figure 34. The differences in operating costs were not that vast but it can be deduced that the more

concentrated brines had higher operating costs. This can be explained with the standard enthalpy of formation of the various salts and that of ice.

Table 44: Solid heats of formation for common salts and water (Perry & Green 1997)

Compound	Solid Enthalpy of Formation (kJ/kmol)
Water	-291
NaCl	-411
$NaCl.2H_2O$[a]	-992
Na_2SO_4	-1381
$Na_2SO_4.10H_2O$	-4321
$CaSO_4$	-1416
$CaSO_4.2H_2O$	-2004

a – (Thomsen, 2008)

Table 44 shows that the standard enthalpy of the crystallizing salts are much higher than that of water. The more concentrated the brine, the larger is the amount of energy released when salt crystallization takes place and subsequently the larger the cost to provide cooling to remove the heat produced. The ions present in the feed brine determine which salts will form and thus determine the energy needed to form those salts. As mentioned before, the resale of the salt products was not taken into account in this study and would reduce the total costs for treating the case study brines with EFC.

5.3 Evaporative Crystallization

Simulations of the evaporative crystallization (EC) process were setup in Aspen Plus 7.1® to calculate the operating costs to treat the case study brines. In order to compare the EFC process to EC process, similar assumptions were made to model both processes. The simulations were based on the major ions present in the case study brines and the operating costs for the EC process were based solely on the energy requirements. The EC process flowsheets for each of the case study brines were very similar. The brine was fed to a first evaporator where about a third of the water was evaporated off. Saturated stream (350kPa) was used as utility in the first evaporator. A general flow diagram is shown in Figure 35.

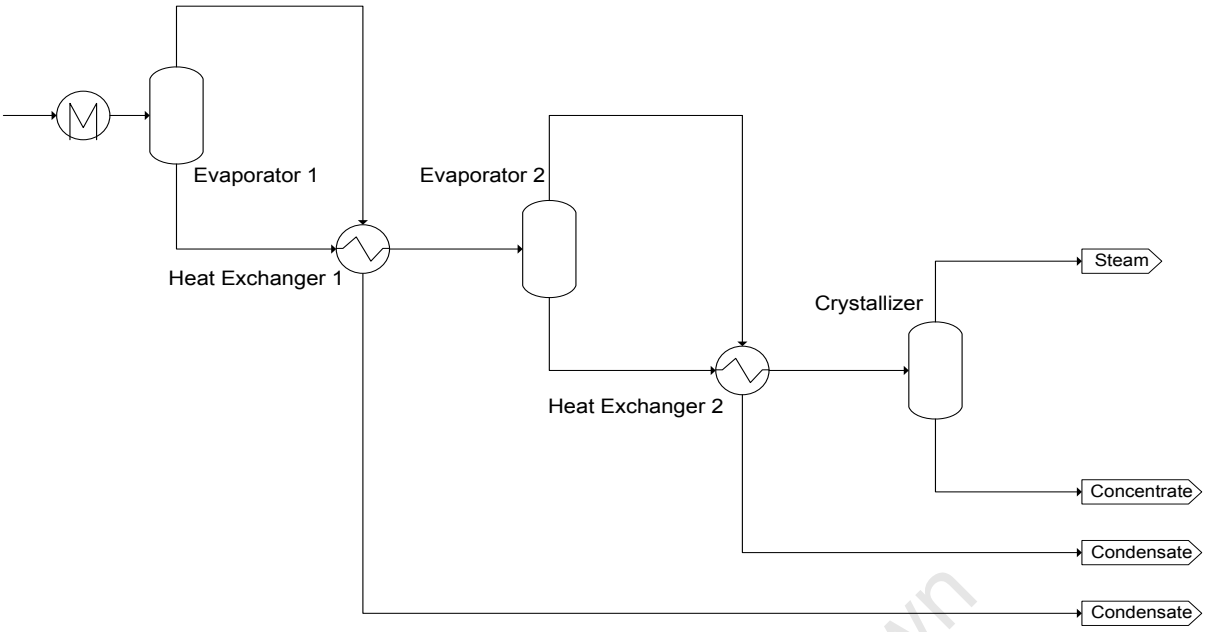


Figure 35: Flow diagram for the EC process

The steam that was produced in the first crystallizer was then used as utility in a second flash column operating at a lower pressure. This step was repeated for the third evaporator operating at an even lower pressure, where the steam produced in the second evaporator was used as utility. The operating pressures of the last two evaporators were chosen such that there was a minimum temperature difference of 10°C between the condensing steam and the evaporator. The EC product recoveries, energy requirements and operating costs for the four case study brines are presented in Table 45.

Table 45: Summary of Evaporative Crystallization process

	PM	CM	PC	PG
Water Recovery [wt%]	95.1	95.3	97.9	98.7
Mixed Salt Product [kg/hr]	2280	238	689	183
Duty [kW]	3800	3880	3900	3890
Utility Requirement [kg/hr]	6280	6360	6390	6370
Operating Cost [R/day]	40,700	41,200	41,400	41,200
Operating Cost [R/m^3]	**136**	**137**	**138**	**137**

There was a high water recovery in all four case study brines, ranging from 95 – 98%. A large mixed salt product was formed in the PM case study brine due to the high TDS of the brine. The steam requirements for the first evaporator are used to calculate the operating costs for the EC process, with all four case study brines requiring around 6300 kg/hr. The operating costs for treating the case study brines were between R136/m^3 and R138/m^3.

5.4 Comparison of Estimated Operating Costs for EFC and EC processes

The operating costs of the two processes are summarised in Figure 36 for the chosen case study brines.

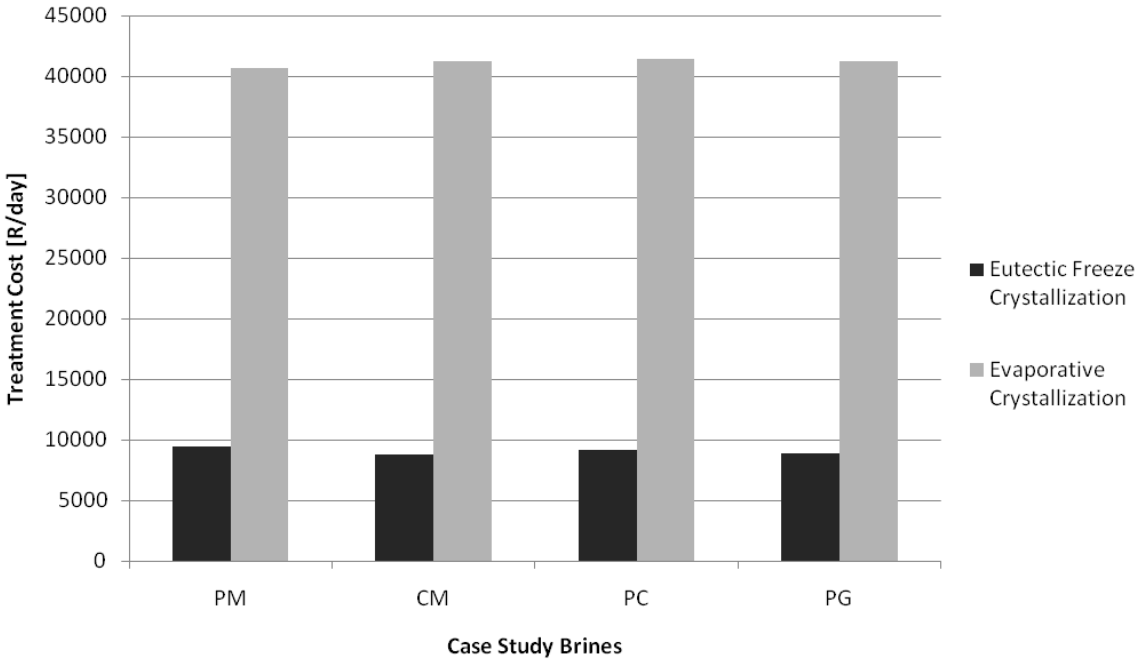


Figure 36: Operating cost comparison for Eutectic Freeze Crystallization and Triple Effect Crystallization (Basis = 300m³/day)

When comparing the operating costs of the two processes, EFC based on the compressor duties of the cooling equipment and EC based on the steam requirements of the first evaporative crystallization process, it can be seen that there is a large cost saving for the EFC process. It is important to note that the operating costs were estimated purely on thermodynamic energy requirements and could change or be refined with actual experimental tests. However, the trend is expected to be the same. The operating costs for the EC process may be high and a more refined model may show a lower operating cost. Nevertheless, even if the EC process has been overestimated, the operating cost of the EFC process is still expected to be lower due to the large difference in the $\Delta H^{vaporization}$ and ΔH^{fusion} of water. EFC also has the potential for heat integration to further reduce the energy requirements and hence the operating costs. This will be discussed further in the next chapter.

Chapter 6: Heat Integration

As the product water leaving the EFC process needs to be in liquid form at a temperature between 15°C - 20°C, the purified ice exiting the wash columns has the potential to be used as a cooling utility within the process. The ice slurry was assumed to have a solids mass fraction of 40% (van Der Ham 1999) and exits the wash columns at a temperature of 0°C. Three main heat integration options were considered in order to utilize this cooling resource:

1. Pre-cooling the feed brine (Feed brine temperature = 25°C)
2. Cooling the condenser of the refrigeration cycle and
3. a combination of the previous two options

Feasibility of this third option above is subject to the availability of additional cooling utility from the ice product remaining from one of the first heat integration options. In the combination of the two options, the ice slurry was first used to pre-cool the feed as shown in Figure 17, after which any remaining ice slurry was used in the two-stage refrigeration cycle. Pre-cooling the feed reduced the crystallizer cooling duty and thus reduced the load on the refrigeration cycle. Any remaining ice slurry could then be used in a two-stage refrigeration cycle for the already lowered crystallizer duty.

In the second option, ice slurry was used to condense a fraction of the refrigerant in a second refrigeration cycle operating at a lower pressure as shown in Figure 18. In certain instances, there was more than enough ice slurry to condense all of the refrigerant and a single stage refrigeration cycle operating at 6.1bar was employed instead of a two-stage refrigeration cycle. Any ice slurry remaining after this was then used in a two-stage refrigeration cycle for a second crystallizer. The results of the heat integration for the four case studies are presented in the following sections.

6.1 PM Case Study

In the PM case study four different options were investigated due to the large amount of ice produced in the process. The total ice slurry produced in the treatment of the PM case study was 9640kg/hr. The four heat integration options are discussed separately and a comparison between the four options presented below.

6.1.1 Option A – Pre-cooling the feed

The first option was to pre-cool the feed entering the first crystallizer. The temperature that the stream was pre-cooled to was 21°C to avoid any scaling within the heat exchanger due to the formation of $Na_2SO_4 \cdot 10H_2O$ at 20°C.

Table 46: Cooling duties for crystallizer 1 for Option A (Basis: 300m³/day of PM Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-306	-244
Compressor Duty [kW]	156	125
Operating Cost [R/m³]	5.75	4.58

Table 46 shows a reduction in cooling duty for crystallizer 1 of about 66kW (21%). This reduction in turn required a small compressor duty and hence a lower operating cost for the

first crystallizer. The summary of operating costs with and without heat integration is presented in Table 47.

Table 47: Summary of operating costs for Option A (Basis: 300m³/day of PM Brine)

	Without Pre- cooling [R]	With Pre-cooling [R]	% Savings
Crystallizer 1	5.70	4.60	
Crystallizer 2	15.90	15.90	
Crystallizer 3	10.00	10.00	
Total	**R31.60**	**R30.50**	**4%**

Pre-cooling of the PM case study brine to 21°C resulted in a total operating cost of R30.5/m³ and a savings of 4%. This low savings is expected because of the limitation in the pre-cooling temperature of the feed brine due to the risk of $Na_2SO_4 \cdot 10H_2O$ scaling below 21°C.

6.1.2 Option B – Single stage refrigeration cycle operating at 6.1bar

The second option that was considered for the PM case study brine was a two-stage refrigeration cycle. However, the ice slurry that was available was able to provide the necessary cooling for the condenser of the cooling cycle to condense all the refrigerant at the reduced pressure. A single stage refrigeration cycle was operated at 6.1bar instead of a two-stage refrigeration cycle for crystallizer 1. The results of the operating conditions for crystallizer 1 are summarised in Table 48.

Table 48: Cooling duties for crystallizer 1 for Option B (Basis: 300m³/day of PM Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-306	-306
Compressor Duty (6.1bar)[kW]	156	89
Operating Cost [R/m3]	5.75	3.26

Using the ice slurry to cool the condenser of the refrigeration cycle at 6.1bar showed a large reduction in compressor duty and consequently the operating cost, which was R3.26/m³ for the first crystallizer. The summarized operating costs for Option B are shown in Table 49.

Table 49: Summary of operating costs for Option B (Basis: 300m³/day of PM Brine)

	Single stage refrigeration cycle (13.4bar) [R]	Single stage refrigeration cycle (6.1bar) [R]	% Savings
Crystallizer 1	5.70	3.30	
Crystallizer 2	15.90	15.90	
Crystallizer 3	10.00	10.00	
Total	**R31.60**	**R29.20**	**8%**

The total operating costs with a refrigeration cycle operating at 6.1bar for crystallizer 1 was R29.2/m³ resulting in a cost savings of 8%. Due to the fact that there was still ice slurry available as a cooling duty, a combination of both Option A & Option B was investigated.

6.1.3 Option C – Single stage refrigeration (6.1bar) and pre-cooling the feed

A combination of the two options presented above was next investigated. First the feed was pre-cooled and any remaining ice slurry was used to provide the cooling duty for the condenser in the refrigeration cycle. There was sufficient ice slurry available after pre-cooling the feed to operate the refrigeration cycle at 6.1bar and not as a two-stage refrigeration cycle. The results of the operating conditions for crystallizer 1 are summarised in Table 50.

Table 50: Cooling duties for crystallizer 1 for Option C (Basis: 300m^3/day of PM Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-306	-244
Compressor Duty (6.1bar)[kW]	156	71
Operating Cost [R/m3]	5.75	2.60

The resulting compressor duty was 71kW (23%), less than half of that before heat integration was applied. The resulting operating costs for the PM case study brine are summarized in Table 51.

Table 51: Summary of operating costs for Option C (Basis: 300m^3/day of PM Brine)

	Without Pre-cooling & single stage refrigeration cycle @ 6.1bar [R]	With Pre-cooling & single stage refrigeration cycle @ 6.1bar [R]	% Savings
Crystallizer 1	5.70	2.60	
Crystallizer 2	15.90	15.90	
Crystallizer 3	10.00	10.00	
Total	**R31.60**	**R28.50**	**10%**

Using the ice slurry to pre-cool the brine and to condense the refrigerant resulted in an operating cost of R28.5/m^3 and cost savings of 10% to treat the PM case study brine. The amount of ice used in Option C was ~6500kg/hr, which still left 3140kg/hr of ice slurry for cooling purposes. This ice slurry could be used in the refrigeration cycles of the other crystallizers as described in Option D below.

6.1.4 Option D – Two-stage Refrigeration (crystallizer 3) combined with option C

The final heat integration option was to use the remaining ice slurry from Option C to condense a fraction of the refrigerant in a two-stage refrigeration cycle for the third crystallizer. Due to the fact that the cooling duty of the second crystallizer (846kW) was larger than the third crystallizer (531kW) & that the third crystallizer was operated at a much lower temperature, it was decided to use the ice slurry for the third crystallizer. Table 52 summarizes the operating conditions for both crystallizers before and after heat integration.

Table 52: Cooling duties for crystallizers 1 & 3 for Option D (Basis: 300m³/day of PM Brine)

		Before Heat Integration	After Heat Integration
Crystallizer 1	**Crystallizer Duty [kW]**	-306	-244
	Compressor Duty [kW]	156	71
	Operating Cost [R/m³]	5.75	2.60
Crystallizer 3	**Crystallizer Duty [kW]**	-531	-531
	Compressor Duty [kW]	271	199
	Compressor Duty 2nd Stage [kW]	0	41
	Operating Cost [R/m³]	9.99	8.83

The ice slurry used to condense a fraction of the refrigerant in the two-stage refrigeration cycle of the third crystallizer reduced the operating costs by R1.16/m³ for crystallizer 3. The full operating costs for the PM case study brine are presented in Table 53.

Table 53: Summary of operating costs for Option D (Basis: 300m³/day of PM Brine)

	Without Pre-cooling & single stage refrigeration cycle @ 6.1bar & 2-Stage refrigeration cycle [R]	With Pre-cooling, single stage refrigeration cycle @ 6.1bar & 2-Stage refrigeration cycle [R]	% Savings
Crystallizer 1	5.70	2.60	
Crystallizer 2	15.90	15.90	
Crystallizer 3	10.00	8.80	
Total	**R31.60**	**R27.30**	**13.6%**

The total operating costs for implementing option D as a heat integration method for the PM case study brine was R27.30/m³ with all the ice slurry being utilized, resulting in an operating cost savings of 13.6%. Table 54 highlights the various heat integration options for treating the PM brine and the associated costs and savings.

Table 54: Summary of heat integration options to treat PM case study brine

	Heat Integration Option	Cost [R/m³]	Savings [%]	Ice Slurry Remaining [kg/hr]
	No Heat Integration	31.60		9643
A	Pre-Cooling of Feed	30.50	3.68	8520
B	Single Stage @ 6.1bar	29.20	7.85	2900
C	Pre-Cooling of Feed & Refrigeration Cycle @ 6.1bar	28.50	9.94	3144
D	Pre-Cooling of Feed & Refrigeration Cycle @ 6.1bar (Crystallizer 1) & 2-Stage Refrigeration Cycle (Crystallizer 3)	27.30	13.60	0

The ice slurry remaining for Option C was greater than that of Option B due to the lowered crystallizer duty and hence a lower cooling duty at 6bar. The most effective heat integration option was Option D where all the ice slurry was utilized. The savings obtained from Option D was 13.6%, reducing the total operating costs for treating the PM brine to R27.30/m³.

6.2 CM Case Study

The CM case study brine was very dilute consequently generating about 12000kg/hr of ice slurry that could be used for heat integration. As the brine was dilute, a large amount of ice was produced in the first crystallizer, requiring a large cooling duty. This in turn limited the options available for heat integration with three options being considered as a large fraction of the ice product was used in pre-cooling the brine. Each option will be discussed separately followed by a comparison between all three.

6.2.1 Option A – Pre-cooling the feed

The first option that was investigated was the pre-cooling of the brine stream before it entered the first crystallizer operating at -2°C. Ice was only available at 0°C and the minimum temperature approach of 10°C was used. Table 55 highlights various key operating parameters for crystallizer 1 before and after pre-cooling of the brine.

Table 55: Cooling duties for crystallizer 1 for Option A (Basis: 300m^3/day of CM Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-1072	-857
Compressor Duty [kW]	548	438
Operating Cost [R/m^3]	20.16	16.10

Heat integration by pre-cooling of the brine resulted in a 215kW reduction in the crystallizer cooling requirement. This is equivalent to about one fifth of the original cooling requirement. Table 56 summarizes the operating costs for the three crystallizers used to treat the CM case study brine before and after pre-cooling.

Table 56: Summary of operating costs for Option A (Basis: 300m^3/day of CM Brine)

	Without Pre-cooler [R]	With Pre-cooler [R]	% Savings
Crystallizer 1	20.20	16.10	
Crystallizer 2	7.00	7.00	
Crystallizer 3	1.90	1.90	
Total	**R29.00**	**R25.00**	**14%**

Pre-cooling the brine resulted in an operating cost of R25/m^3 of brine amounting in a 14% saving as compared to operating without pre-cooling.

6.2.2 Option B – Two-Stage Refrigeration Cycle

Option B of heat integration for the CM case study looked at the incorporation of a two-stage refrigeration cycle for cooling the first crystallizer. Table 57 highlights various key operating parameters for the first crystallizer.

Table 57: Cooling duties for crystallizer 1 for Option B (Basis: 300m^3/day of CM Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-1072	-1072
Compressor Duty [kW]	548	268
Compressor Duty 2nd Stage [kW]	0	159
Operating Cost [R/m^3]	20.16	15.71

The large cooling requirement of the first crystallizer led to the entire ice slurry product being used to cool a portion of the refrigerant. This led to a reduced operating cost of R15.71/m^3 for the first crystallizer. The total savings achieved when using a two-stage refrigeration cycle is shown in Table 58.

Table 58: Summary of operating costs for Option B (Basis: 300m^3/day of CM Brine)

	Single Stage Refrigeration Cycle [R]	Two-Stage Refrigeration Cycle [R]	% Savings
Crystallizer 1	20.20	15.70	
Crystallizer 2	7.00	7.00	
Crystallizer 3	1.90	1.90	
Total	**R29.00**	**R24.60**	**15%**

In summary, using a two-stage refrigeration cycle reduced the calculated operating costs to R24.6/m^3, achieving a 15% savings on the operating costs to treat the CM case study brine.

6.2.3 Option C – Pre-cooling feed and Two-stage Refrigeration Cycle

In Option B the entire ice slurry product was used as a cooling utility for the condenser of the second stage of the refrigeration cycle leading to a higher cost savings than for Option A. The operating costs for option B could be further reduced when combining the previous two options. First the brine would be pre-cooled, reducing the cooling duty, after which a two stage refrigeration cycle could be used for the first crystallizer. The operating parameters are summarized in Table 59.

Table 59: Cooling duties for crystallizer 1 for Option C (Basis: 300m^3/day of CM Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-1072	-857
Compressor Duty [kW]	548	248
Compressor Duty 2nd Stage [kW]	0	107
Operating Cost [R/m^3]	20.16	13.09

Pre-cooling of the feed reduced the duty for the first crystallizer by 215kW, reducing the required compressor duty of the cooling cycle. The remaining ice slurry cooling utility was then used in a two-stage refrigeration cycle consequently reducing the operating costs of Crystallizer 1 to R13.09/m^3. The total savings for Option C are summarized in Table 60.

Table 60: Summary of operating costs for Option C (Basis: 300m^3/day of CM Brine)

	Without Pre-cooling the feed & single stage refrigeration cycle [R]	Pre-cooling the feed & two-stage refrigeration cycle [R]	% Savings
Crystallizer 1	20.20	13.10	
Crystallizer 2	7.00	7.00	
Crystallizer 3	1.90	1.90	
Total	**R29.00**	**R22.00**	**24%**

Using the combination of pre-cooling the feed and using a two-stage refrigeration cycle led to a reduced operating cost to treat the CM case study brine of R22.00/m^3. The summary of the various options investigated and the achieved savings are presented in Table 61.

Table 61: Summary of heat integration options to treat CM case study brine

	Heat Integration Option	Cost [R/m3]	Savings [%]	Ice Slurry Remaining [kg/hr]
	No Heat Integration	29.00		12075
A	Pre-Cooling of Feed	25.00	14.00	8165
B	2 Stage Refrigeration Cycle	24.60	15.30	0
C	Pre-Cooling of Feed & 2-Stage Refrigeration Cycle	22.00	24.30	0

Included in Table 61 is the remaining ice slurry available after each heat integration option is investigated. The first two options showed a similar operating cost of about R25/m^3 with the first option only using a third of the ice slurry available. The final option to pre-cool the feed brine and use a two-stage refrigeration cycle showed the greatest savings amounting to a 24% reduction in operating costs.

6.3 PC Case Study

The PC case study brine was a concentrated brine relative to the other case study brines and as such the salt crystallized out before the ice. The total ice slurry cooling utility available for heat integration was 11200kg/hr. Four different options were investigated for the PC case study starting with the pre-cooling of the brine as shown below.

6.3.1 Option A – Pre-cooling the feed

Based on the aqueous thermodynamic modelling exercise, the temperature at which the first salt crystallized out from the PC case study brine was predicted to be 14°C. Consequently, the brine was pre-cooled to 15°C using the ice slurry as a cooling utility in order to avoid any scale formation in the heat exchanger used for pre-cooling. The cooling duties for the first crystallizer are summarized in Table 62.

Table 62: Cooling duties for crystallizer 1 for Option A (Basis: 300m^3/day of PC Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-446	-305
Compressor Duty [kW]	228	156
Operating Cost [R/m^3]	8.39	5.74

Pre-cooling the brine to 15°C showed a reduction in the duty of crystallizer 1 of 140kW. This reduction in turn resulted in a lower compressor duty for the cooling cycle and hence a lower operating cost for crystallizer 1, of R5.74/m^3. A summary of the cost savings for Option A are summarized in Table 63.

Table 63: Summary of operating costs for Option A (Basis: 300m³/day of PC Brine)

	Without Pre-cooling [R]	With Pre-cooling [R]	% Savings
Crystallizer 1	8.40	5.70	
Crystallizer 2	20.60	20.60	
Crystallizer 3	1.40	1.40	
Total	**R30.40**	**R27.80**	**9%**

The total calculated operating costs for treating the PC case study brine with pre-cooling was R27.80/m³, amounting to a savings of 9%. The next option that was investigated was to use the ice slurry as a cooling utility in the condenser of the refrigeration cycle.

6.3.2 Option B – Single stage refrigeration cycle operating at 6.1bar

The large ice slurry product that was available for heat integration for the relatively small crystallizer cooling duty enabled the entire refrigerant to be condensed in the cooling cycle at 6.1bar for the first crystallizer. Table 64 summarizes the cooling duties for the first crystallizer.

Table 64: Cooling duties for crystallizer 1 for Option B (Basis: 300m³/day of PC Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-446	-446
Compressor Duty (6.1bar)[kW]	228	130
Operating Cost [R/m³]	8.39	4.77

The compressor duty to compress the refrigerant to 6.1bar was calculated to be 130kW. This led to an operating cost of R4.77/m³ for the first crystallizer. The total operating cost to treat the PC case study brine with the second heat integration option is summarized in Table 65.

Table 65: Summary of operating costs for Option B (Basis: 300m³/day of PC Brine)

	Single stage refrigeration cycle (13.4bar) [R]	Single stage refrigeration cycle (6.1bar) [R]	% Savings
Crystallizer 1	8.40	4.80	
Crystallizer 2	20.60	20.60	
Crystallizer 3	1.40	1.40	
Total	**R30.40**	**R26.80**	**12%**

Condensing the refrigerant at 6.1bar with the ice slurry led to a total operating cost of R26.8./m³ amounting to a 12% savings in the operating cost.

6.3.3 Option C – Pre-cooling the feed & single stage refrigeration cycle (6.1bar)

The third heat integration option that was investigated to treat the PC case study brine was a combination of pre-cooling the feed brine and using the remaining ice in a two-stage refrigeration cycle. Once again, there was sufficient ice slurry to condense the refrigerant in a single stage refrigeration cycle operating at 6.1bar. Table 66 highlights the cooling duties for the third heat integration option.

Table 66: Cooling duties for crystallizer 1 for Option C (Basis: 300m³/day of PC Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-446	-305
Compressor Duty (6.1bar)[kW]	228	89
Operating Cost [R/m³]	8.39	3.26

Pre-cooling the feed brine reduced the cooling duty of the first crystallize to 305kW. The reduced crystallizer duty and the single stage refrigeration cycle operating at 6.1bar reduced the compressor duty to 88.6kW, about a third of that before heat integration. Table 67 summarizes the operating costs to treat the PC case study brine with heat integration option C.

Table 67: Summary of operating costs for Option C (Basis: 300m³/day of PC Brine)

	Without Pre-cooling & single stage refrigeration cycle @ 6.1bar [R]	With Pre-cooling & single stage refrigeration cycle @ 6.1bar [R]	% Savings
Crystallizer 1	8.40	3.30	
Crystallizer 2	20.60	20.60	
Crystallizer 3	1.40	1.40	
Total	**R30.40**	**R25.30**	**17%**

The calculated operating cost for the first crystallizer was R3.30/m³, resulting in R5.1/m³ saving in the total operating cost. A savings of 17% was achieved when employing the third heat integration option, with the added advantage of 1920kg/hr of ice slurry still available, which was used in Option D.

6.3.4 Option D – Pre-cooling the feed & single stage refrigeration cycle (6.1bar) for crystallizer 1 and 3

The final heat integration option investigated using the remaining ice slurry from Option C for the refrigeration cycle of the third crystallizer. The brine was first pre-cooled with the ice slurry cooling utility after which the remaining ice slurry was used as a cooling utility in the condensers of the refrigeration cycles for either the first or the third crystallizers. The latter option was chosen as the entire refrigerant could be condensed in a single stage refrigeration cycle operating at 6.1bar, saving on investment costs for additional equipment for a two stage refrigeration cycle. The cooling duties for the two crystallizers are summarized in Table 68.

Table 68: Cooling duties for crystallizer 1 & 3 for Option D (Basis: 300m³/day of PC Brine)

		Before Heat Integration	After Heat Integration
Crystallizer 1	Crystallizer Duty [kW]	-446	-305
	Compressor Duty [kW]	228	89
	Operating Cost [R/m³]	8.39	3.26
Crystallizer 3	Crystallizer Duty [kW]	-76	-76
	Compressor Duty [kW]	39	22
	Operating Cost [R/m³]	1.44	0.82

The compressor duty for the refrigeration cycle for the third crystallizer was reduced to 22kW from 39kW, resulting in a operating cost of R0.82/m³ for the third crystallizer. The very low

operating costs for the third crystallizer was due to a large portion of the water being removed in the first two crystallizers, resulting in a small flow to the third crystallizer. Table 69 summarizes the total cost savings for heat integration option D.

Table 69: Summary of operating costs for Option D (Basis: 300m^3/day of PC Brine)

	Without Pre-cooling & single stage refrigeration cycle @ 6.1bar (crystallizer 1 & 3) [R]	With Pre-cooling & single stage refrigeration cycle @ 6.1bar (crystallizer 1 & 3) [R]	% Savings
Crystallizer 1	8.40	3.30	
Crystallizer 2	20.60	20.60	
Crystallizer 3	1.40	0.80	
Total	**R30.40**	**R24.70**	**19%**

The total operating costs when employing heat integration option D was calculated to be R24.70/m^3. The four heat integration options and the associated cost savings are presented in Table 70.

Table 70: Summary of heat integration options to treat PC case study brine

	Heat Integration Option	Cost [R/m3]	Savings [%]	Ice Slurry Remaining [kg/hr]
	No Heat Integration	30.40		11205
A	Pre-Cooling of Feed	27.80	8.71	8652
B	Single Stage (@6bar - crystallizer 1)	26.80	11.90	1361
C	Pre-Cooling of Feed & Single Stage (@6bar - crystallizer 1)	25.30	16.90	1916
D	Pre-Cooling of Feed & Single Stage (@6bar - crystallizer 1 & 3)	24.70	18.90	230

The operating costs to treat the PC case study brine before heat integration was calculated to be R30.40/m^3. The greatest operating cost savings was for option D where a cost savings of 18.9% was achieved. Only 2% of the product ice slurry was not used in heat integration for option D, reducing the operating cost to treat the PC case study brine to R24.7/m^3.

6.4 PG Case Study

The PG case study brine, which was the most dilute of the four case study brines investigated in this study. As with the CM case study, only three heat integration options were investigated. The first crystallizer had a very large cooling duty and thus limited the number of heat integration options.

6.4.1 Option A – Pre-cooling the feed

Option A investigated the option of pre-cooling the feed brine with the ice slurry. Based on the aqueous thermodynamic modelling study, the first salt and ice simultaneously crystallized out at -1°C, allowing the brine to be pre-cooled to 10°C. Table 71 shows the reduction in crystallizer and compressor duties when pre-cooling the brine.

Table 71: Cooling duties for crystallizer 1 for Option A (Basis: 300m³/day of PG Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-1442	-1226
Compressor Duty [kW]	736	626
Operating Cost [R/m³]	27.10	23.05

The crystallizer cooling duty was reduced by 216kW resulting in a reduction of 110kW in the compressor duty. This led to an operating cost of R23.05/m³ for the first crystallizer. The total operating costs are summarized in Table 72.

Table 72: Summary of operating costs for Option A (Basis: 300m³/day of PG Brine)

	Without Pre-cooling [R]	With Pre-cooling [R]	% Savings
Crystallizer 1	27.10	23.10	
Crystallizer 2	2.36	2.36	
Total	**R29.50**	**R25.40**	**14%**

Pre-cooling the feed brine reduced the operating costs for the PG case study brine to R25.40/m³, which amounted to an operating cost savings of 14%.

6.4.2 Option B – Two-stage refrigeration cycle

The second option that was investigated was the use of the ice slurry as a cooling utility in the condenser of the refrigeration cycle. The entire ice slurry was used in the second stage of the refrigeration cycle. A summary of crystallizer 1 operating costs are shown in Table 73.

Table 73: Cooling duties for crystallizer 1 for Option B (Basis: 300m³/day of PG Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-1442	-1442
Compressor Duty [kW]	736	456
Compressor Duty 2nd Stage [kW]	0	159
Operating Cost [R/m³]	27.10	22.65

The compressor duties for the two-stage refrigeration cycle were 120kW less than a single stage refrigeration cycle. This corresponded to a reduction in the operating cost of the first crystallizer of R22.65/m³. The total operating costs are summarized in Table 74.

Table 74: Summary of operating costs for Option B (Basis: 300m³/day of PG Brine)

	Single Stage Refrigeration Cycle [R]	Two-Stage Refrigeration Cycle [R]	% Savings
Crystallizer 1	27.10	22.60	
Crystallizer 2	2.40	2.40	
Total	**R29.50**	**R25.00**	**15%**

The total savings achieved when using the entire ice slurry in a two-stage refrigeration cycle was about 15%. The operating costs to treat the PG brine with a two-stage refrigeration cycle using EFC was R25.00/m³.

6.4.3 Option C – Pre-cooling feed and Two-stage Refrigeration Cycle

The last option looked at first pre-cooling the brine, reducing the compressor duty, and then using the remaining ice slurry in a two-stage refrigeration cycle, further reducing the compressor duty. A summary of the first crystallizers' cooling duties are summarized in Table 75.

Table 75: Cooling duties for crystallizer 1 for Option C (Basis: 300m^3/day of PG Brine)

	Before Heat Integration	After Heat Integration
Crystallizer Duty [kW]	-1442	-1226
Compressor Duty [kW]	736	437
Compressor Duty 2nd Stage [kW]	0	108
Operating Cost [R/m^3]	27.10	20.03

Employing heat integration Option C led to a reduction of 191kW for the compressor duties. This reduction in compressor duty resulted in an operating cost of R20.03/m^3 for the first crystallizer. The summary of the operating costs before and after heat integration option C are shown in Table 76.

Table 76: Summary of operating costs for Option C (Basis: 300m^3/day of PG Brine)

	Without Pre-cooling and Single Stage Refrigeration Cycle [R]	With Pre-cooling and Two Stage Refrigeration Cycle [R]	% Savings
Crystallizer 1	27.10	20.00	
Crystallizer 2	2.40	2.40	
Total	**R29.50**	**R22.40**	**24%**

The total operating costs with heat integration Option C was R22.4/m^3 for the PG case study brine. A summary of the three heat integration options are summarized in Table 77 along with the remaining ice slurry after heat integration.

Table 77: Summary of heat integration options to treat PG case study brine

	Heat Integration Option	Cost [R/m3]	Savings [%]	Ice Slurry Remaining [kg/hr]
	No Heat Integration	29.50		12098
A	Pre-Cooling of Feed	25.40	13.80	8196
B	2 Stage Refrigeration Cycle	25.00	15.10	0
C	Pre-Cooling of Feed & 2 Stage Refrigeration Cycle	22.40	24.00	0

The total ice slurry as a cooling utility available for heat integration was 12100kg/hr with Options B & C utilizing all the cooling utility available. The largest cost savings were for the third option, reducing the operating costs to R22.4/m^3.

A summary of the most cost effective heat integration options for the four case study brines are presented in Table 78.

Table 78: Summary of most cost effective heat integration options for the four case study brines

Case Study	Heat integration option	Cost [R/m3]	Savings [%]
PM	Pre-Cooling of Feed & Refrigeration Cycle @ 6.1bar (crystallizer 1) & 2-Stage Refrigeration Cycle (crystallizer 3)	27.34	13.6
CM	Pre-Cooling of Feed & 2-Stage Refrigeration Cycle	21.97	24.3
PC	Pre-Cooling of Feed & Single Stage (@6bar – crystallizer 1 & 3)	24.66	18.9
PG	Pre-Cooling of Feed & 2 Stage Refrigeration Cycle	22.39	24.0

Figure 37 presents a summary of the operating costs before and after heat integration in R/day.

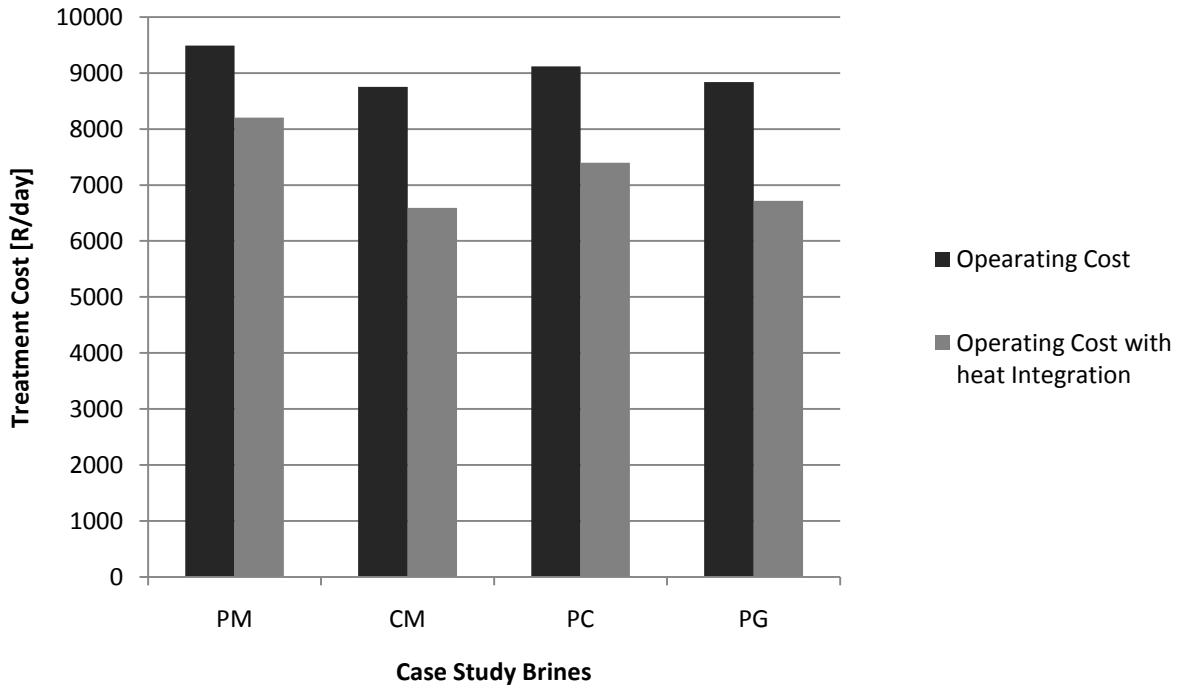


Figure 37: Comparison of operating costs before and after heat integration

The operating costs to treat the cases study brine varied between about R22/m^3 and R27.5/m^3. There was a higher percentage savings for the more dilute brines. The concentrated brines had salts crystallizing out at temperatures greater than 0°C restricting the temperature the brine could be pre-cooled to. Pre-cooling the brine, reduced the crystallizer duty and hence reduced the compressor duty.

Chapter 7: Capital Costs Estimation

The capital costs for the EFC process were calculated based on the empirical method employed by Vaessen (2003) as described in the literature review section in this study. The capital costs for the evaporative crystallization process were also estimated using the method employed by Vaessen (2003), in order to compare the two processes. The capital costs for treating the four case study brines with EFC are presented below followed by the capital costs for the EC process.

7.1 PM Case Study

The estimated capital cost for implementing the EFC process to treat 300m^3/day of the PM case study brine is presented in Table 79.

Table 79: Capital costs for an EFC treatment plant for PM case study brine

Unit	Description	Calculated Cost
Scraped cooled wall crystallizer # 1 operating at 12˚C	Cooling surface area per unit = 32m^2	R 1,561,294
	Cooling capacity per unit = 160kW	
	Number of units required = 1.91	
Scraped cooled wall crystallizer # 2 operating at -12˚C	Cooling surface area per unit = 32m^2	R 4,321,607
	Cooling capacity per unit = 160kW	
	Number of units required = 5.2	
Scraped cooled wall crystallizer # 2 operating at -24˚C	Cooling surface area per unit = 32m^2	R 2,713,565
	Cooling capacity per unit = 160kW	
	Number of units required = 3.32	
Wash column # 1	Diameter = 791mm	R 811,998
Wash column # 2	Diameter = 799mm	R 816,348
Belt filter # 1	Salt flow rate = 2.420m^3/hr	R 1,399,391
Belt filter # 2	Salt flow rate = 3.95 m3/hr	R 2,285,576
Belt filter # 3	Salt flow rate = 2.64 m3/hr	R 1,526,609
Cooling equipment crystallizer # 1	Cooling duty = 306kW	R 1,082,819
Cooling equipment crystallizer # 2	Cooling duty = 846kW	R 2,707,074
Cooling equipment crystallizer # 3	Cooling duty = 531kW	R 1,780,761
Ancillaries	10% of equipment cost	R 2,100,704
Total equipment cost		**R 23,107,747**

The total equipment costs were estimated to be R23million, with the major capital cost contributors being the EFC crystallizers, belt filters and the cooling units. The estimated capital costs for treating the PM case study brine with EC is presented in Table 80.

Table 80: Capital costs for an EC treatment plant for PM case study brine

Unit	Description	Calculated Cost
Plate evaporator 1	Heating duty = 2500kW	R 471,530
Plate evaporator 2	Heating duty = 1360kW	R 344,423
Plate condenser 1	Heating duty = 1250kW	R 328,831
Plate condenser 2	Heating duty = 680kW	R 240,191
Forced circulation crystallizer	Heating duty = 3800kW	R 2,594,740
Ancillaries	10% of equipment cost	R 397,972
Total equipment cost		**R 4,377,687**

The estimated capital costs for the EC process were calculated to be R4.4million. The major cost contributor, as in the case with EFC, was the crystallizer accounting for more than half the total capital costs. The capital costs for the EFC process were much higher than that of the EC process, about five times as much. However, it is important to note that the expected improvements in EC technology will lead to marginal savings. In contrast, EFC is a new technology with future improvements expected, consequently decreasing the capital costs, especially with regards to the EFC reactor.

7.2 CM Case Study

The estimated capital cost for implementing the EFC process to treat 300m^3/day of the CM case study brine is presented in Table 81.

Table 81: Capital costs for an EFC treatment plant for CM case study brine

Unit	Description	Calculated Cost
Scraped cooled wall crystallizer # 1 operating at -2˚C	Cooling surface area per unit = 32m^2	R 5,476,004
	Cooling capacity per unit = 160kW	
	Number of units required = 6.7	
Scraped cooled wall crystallizer # 2 operating at -5˚C	Cooling surface area per unit = 32m^2	R 1,895,510
	Cooling capacity per unit = 160kW	
	Number of units required = 2.3	
Scraped cooled wall crystallizer # 3 operating at -12˚C	Cooling surface area per unit = 32m^2	R 515,411
	Cooling capacity per unit = 160kW	
	Number of units required = 0.63	
Scraped cooled wall crystallizer # 4 operating at -15˚C	Cooling surface area per unit = 32m^2	R 37,007
	Cooling capacity per unit = 160kW	
	Number of units required = 0.04	
Wash column # 1	Diameter = 988mm	R 917,808
Wash column # 2	Diameter = 696mm	R 756,971
Wash column # 3	Diameter = 336mm	R 507,222
Wash column # 4	Diameter = 88.5mm	R 243,473

Belt filter # 1	Salt flow rate = 0.01m^3/hr	R 6,339
Belt filter # 2	Salt flow rate = 0.01 m3/hr	R 3,947
Belt filter # 3	Salt flow rate = 0.52 m3/hr	R 302,935
Belt filter # 4	Salt flow rate = 0.40 m3/hr	R 229,399
Belt filter # 5	Salt flow rate = 0.03 m3/hr	R 16,094
Cooling equipment crystallizer # 1	Cooling duty = 1072kW	R 3,349,939
Cooling equipment crystallizer # 2	Cooling duty = 371kW	R 1,289,356
Cooling equipment crystallizer # 3	Cooling duty = 101kW	R 399,354
Cooling equipment crystallizer # 4	Cooling duty = 7kW	R 37,314
Ancillaries	10% of equipment cost	R 1,598,408
Total equipment cost		**R 17,582,492**

The CM case study brine, which is a more dilute brine than the PM case study brine, had a total equipment cost of R17.6million. The first crystallizer, in which a large amount of ice is formed, is the most expensive piece of equipment due to the large cooling duty. About seven SCWC's are needed to be run in parallel to treat the CM case study brine at -2°C. The cooling systems used for the crystallizers also contribute significantly to the capital costs. The estimated capital costs for treating the CM case study brine with EC is presented in Table 82.

Table 82: Capital costs for an EC treatment plant for CM case study brine

Unit	Description	Calculated Cost
Plate evaporator 1	Heating duty = 2560kW	R 477,436
Plate evaporator 2	Heating duty = 2370kW	R 458,679
Plate condenser 1	Heating duty = 1280kW	R 332,950
Plate condenser 2	Heating duty = 1180kW	R 319,870
Forced circulation crystallizer	Heating duty = 3880kW	R 2,631,230
Ancillaries	10% of equipment cost	R 422,017
Total equipment cost		**R 4,642,182**

The calculated capital cost to treat the CM brine with EC is R4.6million. Once again, the major cost contributor is the forced circulation crystallizer as was with the PM case study brine. The capital costs for treating the CM case study brine using EFC are about four times that for the EC process.

7.3 PC Case Study

The estimated capital cost for using an EFC process to treat 300m^3/day of the PC case study brine is presented in Table 83.

Table 83: Capital costs for an EFC treatment plant for PC case study brine

Unit	Description	Calculated Cost
Scraped cooled wall crystallizer # 1 operating at 0˚C	Cooling surface area per unit = 32m^2	R 2,279,283
	Cooling capacity per unit = 160kW	
	Number of units required = 2.8	
Scraped cooled wall crystallizer # 2 operating at -15˚C	Cooling surface area per unit = 32m^2	R 5,592,410
	Cooling capacity per unit = 160kW	
	Number of units required = 6.8	
Scraped cooled wall crystallizer # 3 operating at -26˚C	Cooling surface area per unit = 32m^2	R 390,408
	Cooling capacity per unit = 160kW	
	Number of units required = 0.48	
Wash column # 1	Diameter = 1170mm	R 1,009,169
Wash column # 2	Diameter = 298mm	R 475,017
Belt filter # 1	Salt flow rate = 0.01m^3/hr	R 4,243
Belt filter # 2	Salt flow rate = 2.28 m3/hr	R 1,321,797
Belt filter # 3	Salt flow rate = 0.17 m3/hr	R 96,329
Belt filter # 4	Salt flow rate = 0.33 m3/hr	R 189,889
Cooling equipment crystallizer # 1	Cooling duty = 446kW	R 1,522,081
Cooling equipment crystallizer # 2	Cooling duty = 1095kW	R 3,413,961
Cooling equipment crystallizer # 3	Cooling duty = 76kW	R 311,018
Ancillaries	10% of equipment cost	R 1,660,561
Total equipment cost		**R 18,266,167**

The total capital cost that is calculated to treat the PC case study brine is about R18million. The production of ice in the second crystallizer resulted in a large cooling duty and consequently a high investment cost for the second crystallizer. The estimated capital costs for treating the PC case study brine with EC is presented in Table 84.

Table 84: Capital costs for an EC treatment plant for PC case study brine

Unit	Description	Calculated Cost
Plate evaporator 1	Heating duty = 2570kW	R 478,942
Plate evaporator 2	Heating duty = 2690kW	R 489,920
Plate condenser 1	Heating duty = 1290kW	R 334,001
Plate condenser 2	Heating duty = 1340kW	R 341,657
Forced circulation crystallizer	Heating duty = 3900kW	R 2,640,795
Ancillaries	10% of equipment cost	R 428,531
Total equipment cost		**R 4,713,845**

The estimated capital cost to treat the PC case study brine is R4.7million, which is about four times less than that of the EFC process. The largest cost contributor to this capital cost is the forced circulation crystallizer with a cost of about R2.6million.

7.4 PG Case Study

The estimated capital cost for implementing the EFC process to treat 300m^3/day of the PG case study brine is presented in Table 85.

Table 85: Capital costs for an EFC treatment plant for PC case study brine

Unit	Description	Calculated Cost
Scraped cooled wall crystallizer # 1 operating at -5˚C	Cooling surface area per unit = 32m^2	R 7,362,281
	Cooling capacity per unit = 160kW	
	Number of units required = 9.0	
Scraped cooled wall crystallizer # 2 operating at -26˚C	Cooling surface area per unit = 32m^2	R 640,116
	Cooling capacity per unit = 160kW	
	Number of units required = 0.8	
Wash column # 1	Diameter = 1200mm	R 1,022,705
Wash column # 2	Diameter = 370mm	R 535,380
Belt filter # 1	Salt flow rate = 0.42m^3/hr	R 243,076
Belt filter # 2	Salt flow rate = 0.34 m3/hr	R 198,701
Cooling equipment crystallizer # 1	Cooling duty = 1440kW	R 4,372,508
Cooling equipment crystallizer # 2	Cooling duty = 125kW	R 485,347
Ancillaries	10% of equipment cost	R 1,486,011
Total equipment cost		**R 16,346,125**

The estimated capital costs for treating the most dilute of the four case study brines, the PG case study, is R16million. As observed for the CM case study, a dilute brine, a large amount of ice is produced in the first crystallizer leading to a large cooling duty, resulting in large equipment and consequently a large investment cost. The large ice production in the first crystallizer

accounts for the large investment costs for the first wash column and the cooling equipment for the first crystallizer. The estimated capital costs for treating the PG case study brine with EC is presented in Table 86.

Table 86: Capital costs for an EC treatment plant for PC case study brine

Unit	Description	Calculated Cost
Plate evaporator 1	Heating duty = 2560kW	R 477,779
Plate evaporator 2	Heating duty = 2380kW	R 459,743
Plate condenser 1	Heating duty = 1280kW	R 333,189
Plate condenser 2	Heating duty = 1190kW	R 320,612
Forced circulation crystallizer	Heating duty = 3890kW	R 2,634,161
Ancillaries	10% of equipment cost	R 422,548
Total equipment cost		**R 4,648,033**

The capital cost for treating the PG case study brine with EC is R4.7million with the crystallizer accounting for a significant percentage of the investment costs. The capital costs for the EC process are less than four times than that of the EFC process.

7.5 Capital cost comparison

There was a variation in capital costs for the EFC process for the four case study brines. Figure 38 shows the variation of capital costs for the four case study brines. As was shown with the operating costs, the capital costs were compared to the TDS of the brines and are shown in Figure 39.

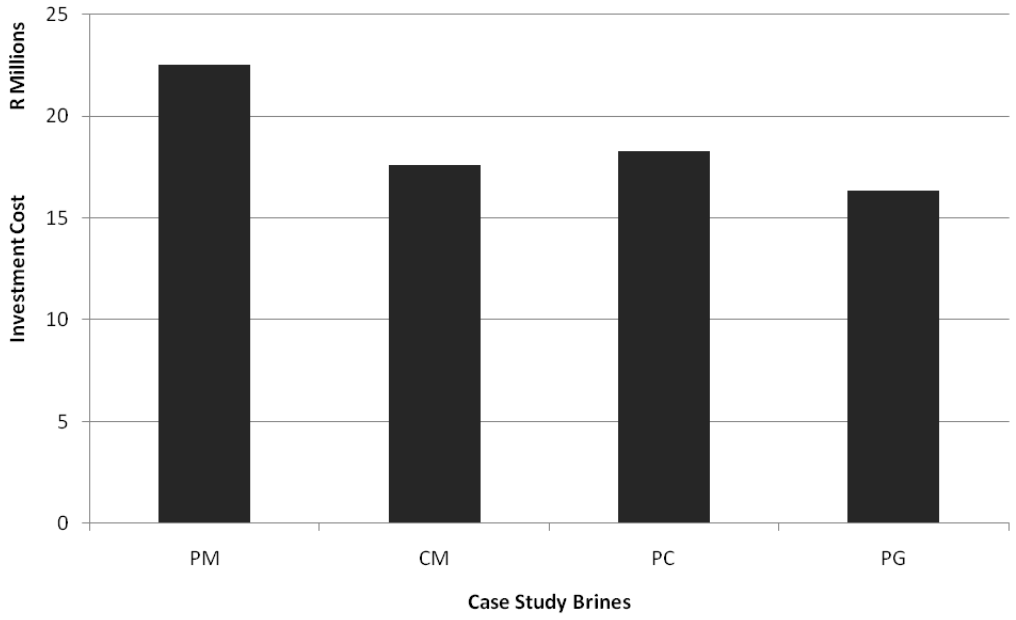


Figure 38: Comparison of EFC capital costs for the four case study brines

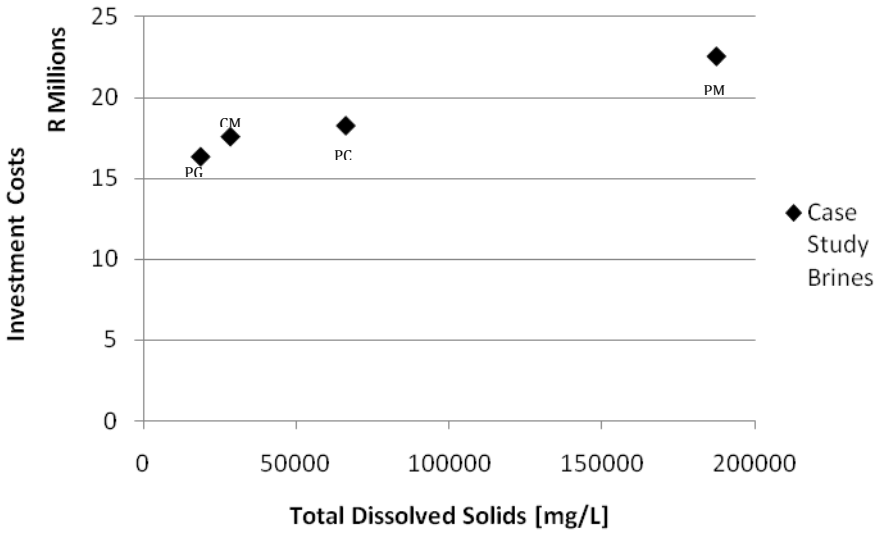


Figure 39: Comparison of EFC capital costs and TDS for the four case study brines

The crystallizers and cooling equipment in the EFC process attribute a large percentage to the capital costs. The capital cost calculations for both the crystallizers and the cooling equipment are based on the respective cooling requirements. The cooling requirements of the EFC process varies with the concentration of the brines and hence attributes to the similar trend that both the operating and capital costs show with concentration. As shown in the graph above; the more concentrated the brine, the higher the investment costs to treat the brine.

Figure 40 compares the capital costs calculated for the EFC and EC process for the four case study brines.

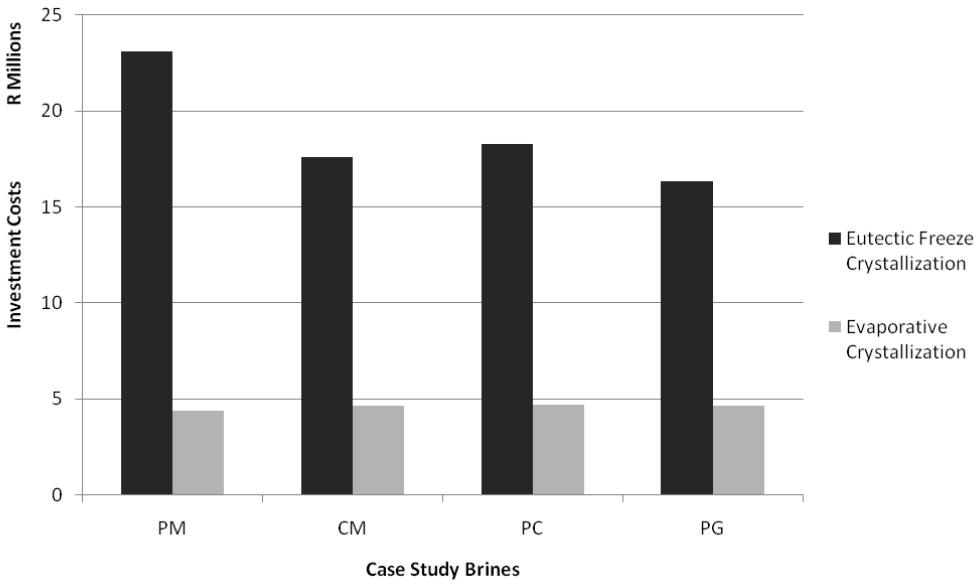


Figure 40: Capital cost comparison for Eutectic Freeze Crystallization and Triple Effect Crystallization

The investment costs for the EFC process with all four case study brines were much higher than that of the EC process. The EC process is a well established process and the investment costs to

treat the four case study brines did not vary as with the EFC process. As the EFC process is relatively new, the accuracy of the capital costs calculated for the investment of a full scale EFC plant can be questioned. The capital costs were based on the use of exotic materials to construct the EFC crystallizer which may not be necessary at low temperatures and hence reduces corrosion rates as compared to the EC process which operates at high temperatures with high corrosion rates. The capital costs were calculated in order to compare them to the capital costs of the EC process.

When heat integration for the EFC process is considered, there was an increase in capital costs for the additional units such as the pre-cooler or a two-stage refrigeration cycle. Figure 41 compares the capital costs for the EFC process with and without heat integration and also includes the capital costs for the EC process.

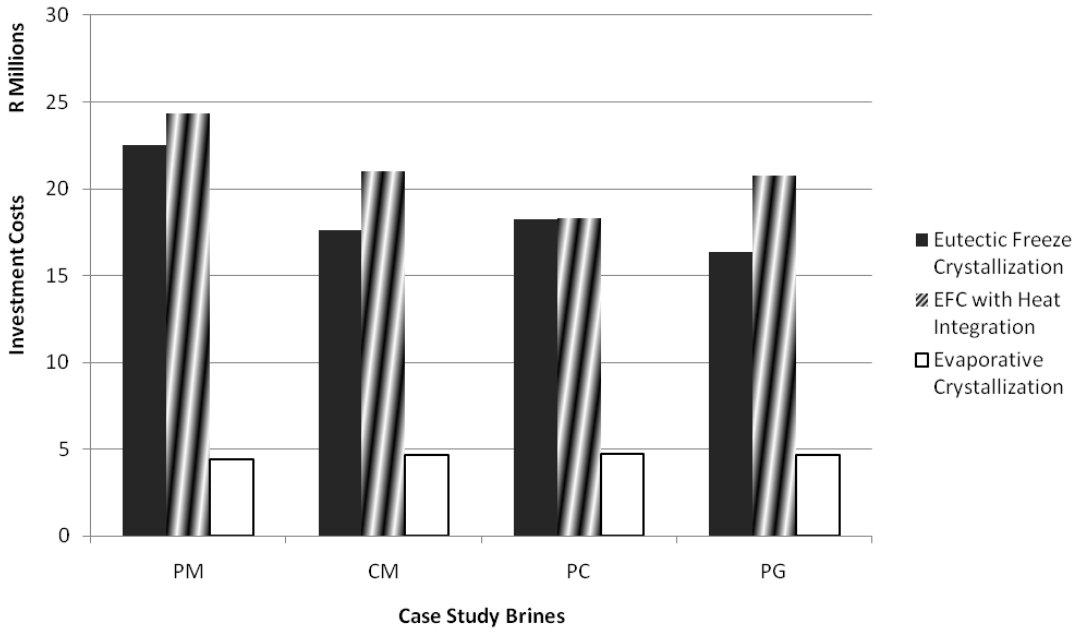


Figure 41: Capital cost comparison including EFC with heat integration

The increase in capital costs is largely dependent on heat integration option selected. Adopting a two stage refrigeration cycle considerably increases the capital costs whereas employing a pre-cooler, in the case of the PC case study, does not increase the capital costs significantly. It is also favourable to employ a single stage refrigeration cycle operating at 6.1bar over a two-stage refrigeration cycle if sufficient ice is available to condense the ammonia.

As mentioned before, the capital costs of the EFC process are much higher than that of the EC process. However, over a period of time, the favourable operating cost savings of the EFC process over the EC process may give a better indication of the feasibility and benefits of the EFC process over other treatment options.

The projected cumulative costs (operating & capital costs) for both the EFC and EC processes to treat the PM case study brine over a period of 10 years with a 10% increase in operating costs were calculated and are presented in Figure 42. The projected cumulative costs to treat the other three case study brines showed similar results and are thus presented in Appendix 10.2.

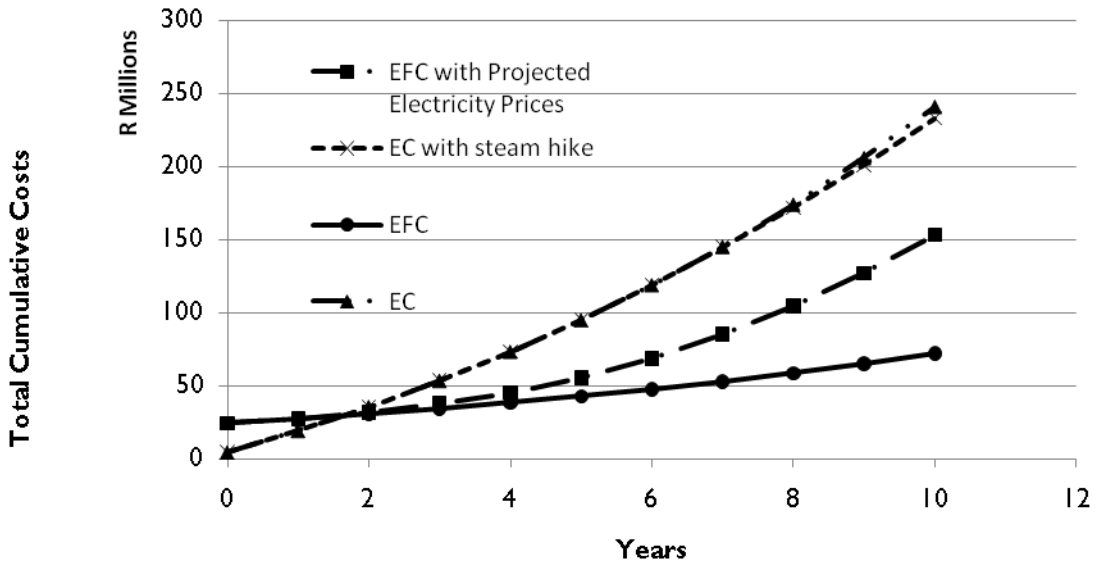


Figure 42: Cumulative costs for the EFC process and the EC processes to treat the PM case study brine

The cumulative costs are based on a 10% inflation in operating costs for both processes. In addition, the projected increase in electricity and steam prices were taken into account for the EFC and the EC processes and are presented in Figure 42. In the first two years the cumulative costs for treating the PM brine with EC are lower than that of EFC. However, the large operating cost savings for the EFC process results in a large cost savings beyond two years. Even with a projected increase in the price of both steam and electricity, the EFC process shows a considerable cost savings over the EC process. The calculations for the projected increases are shown in Appendix 10.2. Steam was assumed to be produced solely from coal, and thus the projected increases in coal prices were taken into account.

It must be reiterated that the cost of mixed salt disposal from the EC process and the income generated from the resale of salts from the EFC process have not been taken into account, which would further enhance the potential of EFC as a competitive hypersaline brine treatment option.

In summary, for the four case study brines investigated, EFC had a larger capital cost but a significantly lower operating cost, which when viewed as a total cost showed EFC to be a significantly more cost effective solution for treating brines.

Chapter 8: Conclusions and Recommendations

8.1 Conclusions

This study investigated the economic feasibility of using Eutectic Freeze Crystallization as an alternative treatment method for hypersaline brines. Four industrial case study brines with compositions that were considered to be broadly representative of a typical South African industrial brine were investigated. The key findings and conclusions from this investigation were as follows:

- Comprehensive brine analysis revealed that the four case study brines had varying concentrations between 18,800 - 187,000mg/l. However, the brines had similar dominant ions (Na^+, Ca^{2+}, K^+, CO_3^{2-}, SO_4^{2-} and Cl^-) and these ions accounted for more than 98% of the Total Dissolved Solids (TDS) in the brines. The variation in the composition of the four brines was attributed to the pre-processing steps involved in the formation of the brines.

- Using Oli Stream Analyzer® software, the aqueous thermodynamic modelling of the four case study brines could be successfully carried out to predict which salts crystallized out, the crystallization temperatures of the salts and ice and the theoretical yields that can be obtained based on thermodynamic solubility. It was found that for the more concentrated brines (PM and PC case study brines), salt crystallized out first and that there was a large depression in the freezing point temperature of water.

- The calculated cost to treat the case study brines with EFC varied between R29/m^3 and R31/m^3 with the cost to treat the more concentrated brines being higher than the cost to treat the dilute brines. For the concentrated brines the heats of crystallization of the various salts produced were higher than the heat of crystallization of the ice leading to the higher operating costs. The cost to treat the case study brines with the EC process were between R135/m^3 and R138/m^3 which was about four times that of the EFC process.

- It was found that when applying heat integration to the EFC process the total savings achieved were brine specific. Pre-cooling the brine with the ice product was the most cost effective option as it reduced the crystallizer duty and consequently reduced the required compressor duty. In general, pre-cooling the brine should first be considered after which using the ice slurry in the condenser of a two-stage refrigeration cycle.

- The capital costs for the EFC process was calculated to be between R16 million and R22million. The major cost contributors to the capital cost were the crystallizers and the cooling units. As expected, the capital costs for a multi-effect EC process was much lower, with calculated costs for all four case study brines to be around R4.5million, which was significantly lower than that of the EFC process. However, as EFC is a new process compared to the already well established EC process, the accuracy of the capital cost estimation is questionable, with the capital costs expected to decrease. When heat integration was considered, the increase in capital costs for the EFC process was highly influenced on the heat integration option considered.

- The projected total cumulative costs (operating & capital costs) over a ten year period with and without the increase in utility costs for both processes revealed that the EFC process broke even and started to show a high cost savings after just over a year of operation. In addition, the cost savings for EFC over EC increased at an increasing rate over a ten year period. Furthermore, it must be reiterated that when the cost of mixed salt disposal for the EC process and the sales of the salt products in the EFC process are taken into account, the economic benefits of the EFC process will be even greater.

8.2 Recommendations

The estimated operating and capital costs for the EFC process and its comparison with EC was purely based on thermodynamic calculations and hence, the following recommendations have been drawn up based on the work that was carried out:

- The thermodynamic model predicted that a mixed salt product would be formed when two or more salts are predicted by thermodynamics to crystallize out, whereas in reality it has been shown (Lewis, Nathoo, Reddy, et al. 2010) that selective seeding can generate highly pure salts. Once sufficient experimental work has been carried out on treating a hypersaline brine with EFC, it is recommended that a more refined model – to include both kinetics and thermodynamics - be built to estimate energy requirements.

- The economic evaluation was based solely on the energy requirements of the major units for both processes and it is recommended that the cost evaluation should include the costs for the minor units as well. In addition, the cost evaluation did not take into account the income generated from the resale of salts. The resale of salts and the cost of a mixed salt disposal should be taken into account when comparing the two processes.

- EFC may not be the only hypersaline brine treatment method and an integration of current and novel methods needs to be evaluated to determine the most ecologic and economic manner to alleviate the stress on South African industrial waste water problems.

Chapter 9: Bibliography

Alchin, D., 1998. *Chemical Processes in New Zealand* 2 ed. N. Z. Chemistry, New Zealand Institute of Chemistry. Available at: http://nzic.org.nz/ChemProcesses/water/index.html.

Aspen, 2009. Aspen Plus V7.1.

Barduhn, A.J. & Manudhane, A., 1979. Temperatures Required for Eutectic Freezing of Natural Waters. *Desalination*, 28, 233-241.

Bhikha, H., 2009. Water Minimisation At Skorpion Zinc.

Brandhuber, H. et al., 2008. A look at conventional and emerging brine disposal and waste minimization technologies. *HDR Waterscapes*, 7-10. Available at: http://www.hdrinc.com/Assets/documents/Publications/Waterscapes/fall2008/BrineDisposal.pdf.

Buckley, C., 2005. Research into the treatment of inorganic brines and concentrates, Water Research Commission Project No. 201.

Carvalho, L., 2006. How to avoid costy water treatment mistakes in industry. In *Ultra Pure Water*. Available at: http://www.waterprofessionals.com/pdfs/avoiding_costly_water_treatment_mistakes_in_CCPP_Projects.pdf.

Cimini, S., Prisciandaro, M. & Barba, D., 2005. Simulation of a waste incineration process with flue-gas cleaning and heat recovery sections using Aspen Plus. *Waste Management*, 25(2), 171-175. Available at: http://www.sciencedirect.com/science/article/B6VFR-4FH4V24-1/2/4d7981d3d338594da5a156e1cdee7af3.

Conlon, W.M., 1992. Recent improvements to the freeze crystallization method of water purification. Available at: http://www.wmconlon.com/wp-content/uploads/papers/IATC92.pdf.

DWAF, 2004. National Water Resource Strategy DWAF. Available at: http://www.dwaf.gov.za/Documents/Policies/NWRS/Default.htm.

Eskom Holdings LTD, 2008. *Eskom - 2008/9 Tariffs and Charges*, Available at: www.eskom.co.za/tariffs.

GCIS, 2009. *South African Year Book 2008/09* 16th. D. Burger, GCIS. Available at: http://www.gcis.gov.za/resource_centre/sa_info/yearbook/2008-09.htm.

Gilron, J. et al., 2003. WAIV -- wind aided intensified evaporation for reduction of desalination brine volume. *Desalination*, 158(1-3), 205-214. Available at: http://www.sciencedirect.com/science/article/B6TFX-49D1YVD-2W/2/523a2589afbecf2dcfa497d71d145486.

Gustafsson, J., 2007. *Visual Minteq Version 2.52*, Stockholm, Sweden.

Hartmann, D., 2006. *Cold, no sweat*, Available at: http://www.delftoutlook.tudelft.nl/info/index2353.html?hoofdstuk=Article&ArtID=2764.

IRP 2010, 2010. Executive Summary of the Draft Integrated Electricity Resource Plan for South Africa - 2010 to 2030. , (October), 13.

International Energy Institution, 1977. World Energy Outlook. *Electronics and Power*, 23(4), 73.

Lewis, A. et al., 2010. Novel Technology for Recovery of Water and Solid Salts from Hypersaline Brines: Eutectic Freeze Crystallization.

Lewis, A.E. et al., 2010. Design of a Eutectic Freeze Crystallization process for multicomponent waste water stream. *Chemical Engineering Research and Design*, 88(9), 1290-1296. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0263876210000377.

Mei, K.Q. et al., 2007. Other Refrigeration Cycles. Available at: http://refrigerationcycleexperiment.blogspot.com/2007/03/theory.html.

Mickley, M., 2001. Mickley, M., 2001. Membrane Concentrate Disposal : Practices and Regulation. Available at: http://www.usbr.gov/pmts/water/media/pdfs/report123.pdf.

Mostafa, A.T. et al., 1996. Prediction of Heat Capacities of Solid Inorganic Salts from Group Contributions. *Industrial & Engineering Chemistry Research*, 35(1), 343-348. Available at: http://dx.doi.org/10.1021/ie9501485.

Mostafa, A.T., Eakman, J.M. & Yarbro, S.L., 1995. Prediction of Standard Heats and Gibbs Free Energies of Formation of Solid Inorganic Salts from Group Contributions. *Industrial & Engineering Chemistry Research*, 34(12), 4577-4582. Available at: http://dx.doi.org/10.1021/ie00039a053.

Nelson, S.A., 2002. Crystallization in Ternary Systems. Available at: http://www.tulane.edu/~sanelson/geol212/ternaryphdiag.htm.

Perry, R.H. & Green, D.W., 1997. *Perry's Chemical Engineers' Handbook* 7th Editio., McGraw-Hill.

Randall, D.G., Nathoo, J. & Lewis, A.E., 2009. Seeding For Selective Salt Recovery During Eutectic Freeze Crystallization. In *Abstracts of the International Mine Water Conference*. Pretoria, South Africa, pp. 639-647.

Reddy, S. et al., 2010. Recovery of Na2SO4·10H2O from a reverse osmosis retentate by eutectic freeze crystallisation technology. *Chemical Engineering Research and Design*, 88(9), 1153-1157. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0263876210000146.

Rekacewicz, P., 2002. Water Availability in Africa. Available at: http://maps.grida.no/go/graphic/water_availability_in_africa.

Sandler, S.I., 1999. *Chemical and Engineering Thermodynamics*, John Wiley & Sons, Inc.

Smith, R. & Varbanov, P., 2005. What's the Price of Steam? *CEP Magazine*. Available at: http://www.aiche.org/uploadedFiles/Energy_Website/Publications/050729_Steam_Smith.pdf.

Stepakoff, G.L. et al., 1974. Development of a eutectic freezing process for brine disposal. *Desalination*, 14, 25-38.

Swenne, D.A., 1983. The Eutectic Crystallisation of NaCl.2H2O and Ice.

Thomsen, K., 2007. *Aqueous electrolytes: Phase diagrams and process simulation/optimization*, Available at: http://www.phasediagram.dk.

Thomsen, K., 2008. *Private Communication*,

Trifkovic, M., Sheikhzadeh, M. & Rohani, S., 2009. Determination of metastable zone width for combined anti-solvent/cooling crystallization. *Journal of Crystal Growth*, 311(14), 3640-3650. Available at: http://www.sciencedirect.com/science/article/B6TJ6-4W7424X-1/2/d53e2de26e519ec0148de574371609b1.

Turton, R. et al., 1998. *Analysis, synthesis and design of chemical processes* 3 ed., Prentice Hall.

Vaessen, R.J., van der Ham, F. & Witkamp, G.J., 2000. Eutectic freeze crystallization using CO2 clathrates. *Annals New York Academy of Sciences*, 912, 483-495.

Vaessen, R.J., 2003. Development of Scraped Eutectic Crystallizers.

Zheng, L. & Furimsky, E., 2003. ASPEN simulation of cogeneration plants. *Energy Conversion and Management*, 44(11), 1845-1851. Available at: http://www.sciencedirect.com/science/article/B6V2P-47DM500-4/2/ec9cf9e0f300f803ebeff76dd365602e.

Zibi, L., 2010. Industrial Brine Characterisation and Modelling.

Zijlema, T.G. et al., 2000. Antisolvent Crystallization as an Alternative to Evaporative Crystallization for the Production of Sodium Chloride. *Industrial & Engineering Chemistry Research*, 39(5), 1330-1337. Available at: http://dx.doi.org/10.1021/ie990221h.

van Der Ham, F., 1999. Eutectic Freeze Crystallization.

van der Merwe, I.W., Lourens, A. & Waygood, C., 2009. An Investigation of Innovative Approaches to Brine Handling.

Chapter 10:Appendix

10.1 Capital Costs

The equations used to calculate the capital costs for both the EFC and EC process will be presented. The method follows that adopted by (Vaessen 2003).

10.1.1 EFC Process

Investment costs for Crystallizers

The heat duties of the Scraped Cooled Wall Crystallizers (SCWC) were used to determine the investment costs for the required number of SCWC's needed. The reference crystallizer is presented in Table 9. Equation 15 summarizes the investment cost calculation.

$$I_{Cryst} = \left(\frac{Q_{Cryst}}{Q_{Ref}}\right) \cdot I_{Ref} \cdot R \qquad \textbf{Equation 13}$$

Where:

Q_{ref} = 160kW
I_{ref} = € 86,000
R = Rand – Euro Exchange Rate (= 9.5)

Investment costs for Wash Columns

The capacity of the wash column is determined by the diameter. The maximum throughput of ice should be 2.7kg/(m^2.s). Therefore if we have the mass flow of the ice we can determine the area and hence the diameter. This is done to ensure that the diameter does not exceed 1200mm (Vaessen 2003). If the diameter does not exceed 1200mm then Equation 2 is used to calculate the required investment cost. If it does exceed 1200mm then the ice flowrate is split and two wash columns were used in parallel (however there was not an instance where this occurred).

Investment costs for Belt Filters

The salt slurry flowrates were used to determine the investment costs for the belt filters. The reference crystallizer is presented in Table 10. Equation 14 summarizes the investment cost calculation.

$$I_{BF} = \left(\frac{V_{BF}}{V_{Ref}}\right) \cdot I_{Ref} \cdot R \qquad \textbf{Equation 14}$$

Where:

V_{ref} = 2.3m^3/hr
I_{ref} = € 140,000
R = Rand – Euro Exchange Rate (= 9.5)

Investment costs for Cooling Equipment
The investment costs for the cooling equipment were calculated based on the required cooling duties of the crystallizers using Equation 3 with the reference cooling equipment summarized in Table 12.

10.1.2 EC Process

Investment costs for Evaporators
The investment costs for the evaporators were calculated based on the required heating duties. The investment costs for the plate evaporators and plate condensers were calculated using Equation 4, with the reference values summarized in Table 14.

Investment costs for Forced Circulation Crystallizer
The investment costs for the crystallizers were calculated based on the required heating duties. The investment costs for the FCC were calculated using Equation 4, with the reference values summarized in Table 13.

10.2 Projected Cost Calculations

$$P_n = P_{n-1} \cdot (1 + i_n) \qquad \textbf{Equation 15}$$

Where:

n = year

i_n = increase for year n

Table 87: Electricity Prices (IRP 2010 2010)

Year	Predicted Electricity Price Increase (%)
2009	31
2010	25
2011	14
2012	24
2013	18
2014	16
2015	4.9
2016	5.9
2017	5.6

Table 88: Steam Prices (International Energy Institution 1977)

Year	Predicted Steam Price Increase (%)
2009	0
2010	0
2011	0
2012	0
2013	0
2014	0
2015	8.33
2016	0
2017	0

It must be noted that the projected steam prices are based on the World Energy Outlook Report which shows the projected increase in steam coal prices. Steam produced in South Africa is predominantly produced from coal and thus the increase in steam coal was used to estimate the increase in steam prices.

10.2.1 CM Case Study

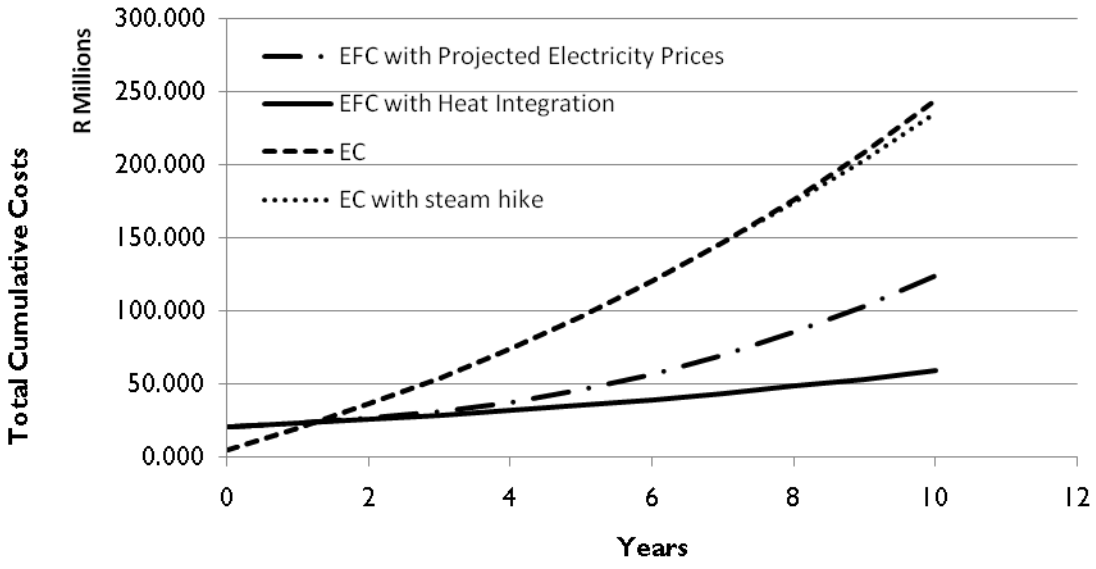


Figure 43: Cumulative costs for the EFC process and the EC processes to treat the CM case study brine

10.2.2 PC Case Study

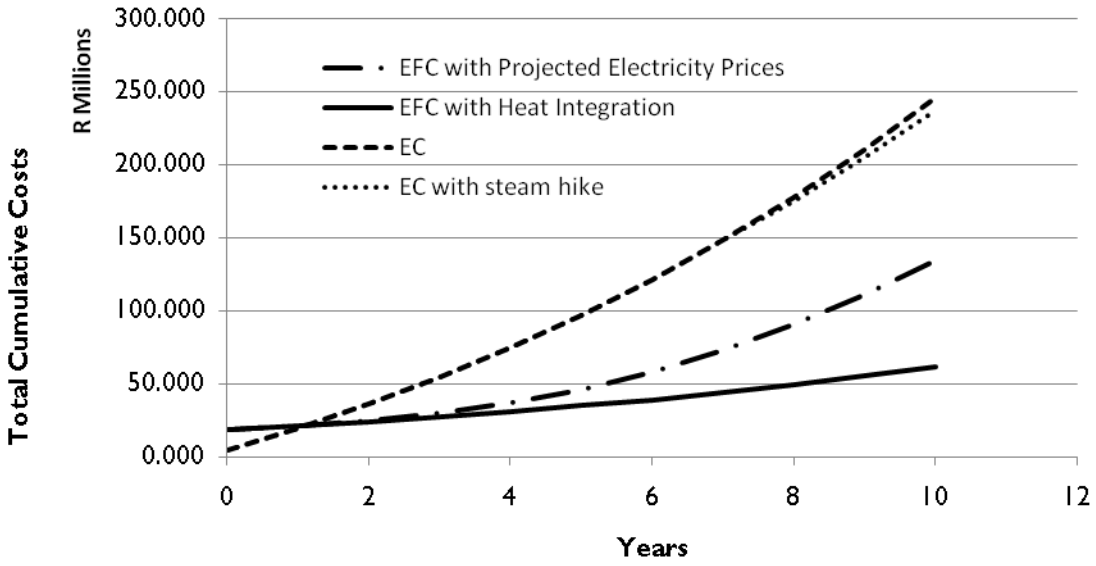


Figure 44: Cumulative costs for the EFC process and the EC processes to treat the PC case study brine

10.2.3 PG Case Study

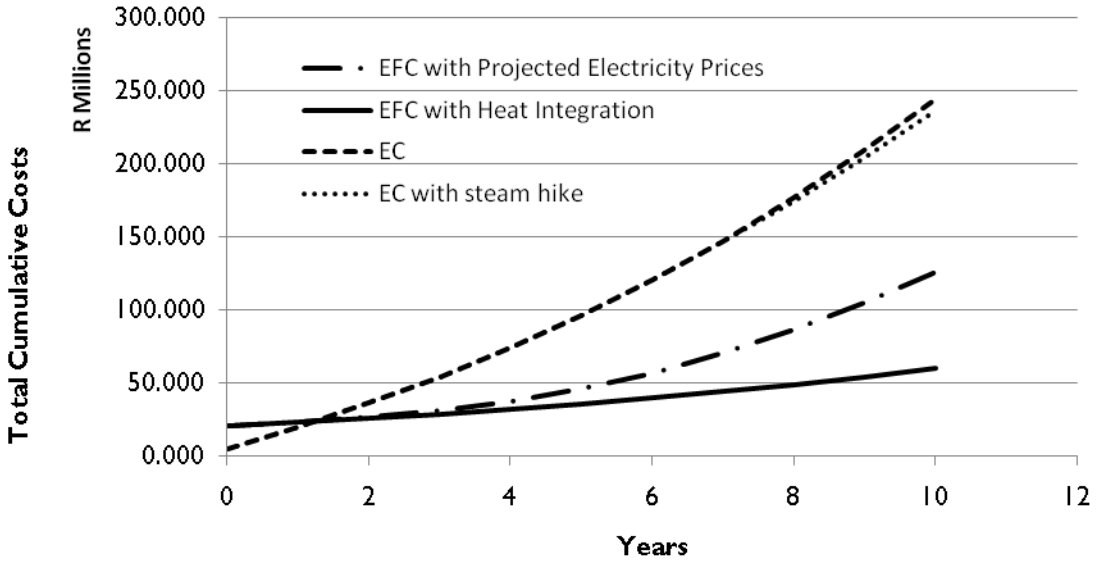


Figure 45: Cumulative costs for the EFC process and the EC processes to treat the PG case study brine