Review of Treatment Technologies for Mine Water and Reverse Osmosis Brines

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Prepared by

Nicholas du Preez
Jasper Christie
Frank Crundwell

Confidential

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CRUNDWELL MANAGEMENT SOLUTIONS (PTY) LTD, t/a CM SOLUTIONS (PTY) LTD

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Building T5, Pinelands Office Park
Modderfontein, 1609

PO Box 1286,
Parklands, 2121, South Africa

Tel: + 27 (0) 11 608 0019

Email: consultants@cm-solutions.co.za
Web: www.cm-solutions.co.za

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EXECUTIVE SUMMARY

The treatment of reverse osmosis brines is an important topic for Coaltech's Environmental research programme. For this reason, four reverse osmosis brine treatment pilot plants were tested. Sigrotec commissioned their HybridICE^{TM} process, and Prentec commissioned their EFC pilot plant at Optimum Colliery; PROXA developed a permanent plant at New Vaal Colliery, and Salttech tested their DyVaR using a portable unit situated at eMalahleni Water Reclamation Plant (EWRP).

In late 2014, CM Solutions was appointed to provide an independent review of these pilot plants. However, early in the review process PROXA declined to participate. Therefore, the study focused on the remaining three pilot plants. From 2014 through to early-2017 the Sigrotec and Prentec pilot plants were operated, modified and tested. Unfortunately, due to various issues, limited formal test work was performed with these pilot plants. Salttech were able to perform a much more structured formal test on the EWRP stage 3 reject.

The objective of this report is to present the available information collected from these pilot plants. In addition, to supplement the limited data collected, a literature review of the available technologies has also been compiled to give the reader background to the available technologies and provide some context to the pilot plants. Several technologies were reviewed in the literature review, including reverse osmosis, high-pressure reverse osmosis, forward osmosis, electrodialysis, traditional evaporators, and each of the technologies underlying the pilot plants. The following table shows the typical efficiencies, limitations and energy requirements for each of the technologies. The literature review provides additional information on feed, exit concentrations, reagents used, cost drivers, and costs (where available). The energy requirements quoted here are those reported in literature, not from pilot plants. None of the pilot plants were designed for optimal power usage, therefore the usages are typically orders-of-magnitude too high.

Technology	Efficiency	Limitations	Energy requirement
	[%]	[-]	[kWh/m^3]
Reverse osmosis	~50%	< 70,000 mg/L	2-6
High-pressure reverse osmosis	~50%	< 120,000 mg/L	3-9
Forward osmosis	>95%	< 200,000 mg/L	0.1-13
Electrodialysis	~50-85%	< 200,000 mg/L	7-15
Traditional evaporators	99%	< 250,000 mg/L	16-26
Salttech's DyVaR	~88%+	-	~45
Eutectic freeze crystallisation	~98%	-	44-69
Sigrotec's HybridICE^{TM}	~96%	-	30-100

The results of this study show that all pilot plants were able to successfully treat the brines and produce near zero-liquid discharges and relatively pure ice/condensate. In addition, the technologies tested have much more flexibility in terms of feed limitations compared to the other technologies considered. However, all of the pilot plants technologies cost much more (both in terms of $/m^3 and kWh/m^3) than reverse osmosis or high-pressure reverse osmosis. Therefore, while technically viable and excellent options for concentrated brines, these technologies are not economically appropriate to treat mine waters directly.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1 INTRODUCTION

Currently, it is standard practice to treat mine waters via reverse osmosis treatment (RO). This process recovers in excess of 90% of the mine water. Often, the mine water goes through three stages of RO treatment, each stage treating the concentrated brine from the previous stage. However, beyond three stages, it becomes technically more difficult uneconomical to further treat the resulting brines via these methods. To date, these brines are typically stored in brine dams and either treated via high-pressure reverse osmosis or natural evaporation. However, many sites continue to have issues with final treatment and storage space for these brine solutions.

As part of the Coaltech's Environmental research programme, four reverse osmosis brine treatment pilot plants were tested. Two were situated at Optimum Colliery, one at New Vaal Colliery, and the final one (tested in 2019) was at eMalahleni Water Reclamation Plant (EWRP). These pilot plants were:

- Sigrotec's HybridICE^{TM} plant (Optimum);
- Prentec's brine treatment plant (Optimum);
- PROXA's brine treatment plant (New Vaal); and,
- Salttech's DyVaR pilot plant (EWRP).

In 2014, CM Solutions was appointed to provide an independent review of these pilot plants. However, early in the review process PROXA declined to participate. Therefore, the study focused on the remaining three pilot plants.

1.1 Brief history of study

This study has been ongoing for many years. This is largely due to the wide timespan over which the various pilot plants were commissioned and operated. The following presents a summary of the key events:

- 2013/4:
  - HybridICE^{TM} demo plant commissioned
  - Various feeds tested (incl. EWRP) during this time
  - CM Solutions appointed in Q4, 2014
  - During 5-7 Dec 2014 – Attempted trial run of HybridICE
- 2015:
  - HybridICE plant mothballed early 2015
  - Prentec demo plant commissioned early in 2015
  - Prentec continued to operate pilot plant with various regular upgrades
- 2016
  - Prentec plant shut down early 2016 while waiting for various upgrades
  - CM Solutions study put on hold shortly after shutdown due to limited data
  - Prentec restarted plant at the Q4, 2016
- 2017:
  - A refrigerant loss in February 2017 forced the Prentec plant to shut down again
- 2018/9:
  - CM Solutions study reinstated Q4, 2018 with primary focus to document plants at Optimum Colliery
  - Study expanded in Q2, 2019 to include DyVaR pilot plant
  - DyVaR pilot plant commissioned & trial run from 18th to 26th July 2019

1.2 Scope of the study

The original scope of the study intended to consider the following aspects of each pilot plant:

- Production & productivity;
- Design;
- Plant operability & stability;
- Product quality & efficiency;
- Technology scale-up & replication; and,
- Costs.

These aspects were to be reviewed through a combination of site visits by CM Solutions personnel and data supplied by the each of the vendors. Unfortunately, the due to various issues experienced on the pilot plants, limited data was collected or made available for the review. Due to this, the depth to which each of these aspects can be considered was drastically limited.

1.3 Objective of study

Given the limitations discussed in the previous section, the focus of the study shifted from a comparative study to one focussed on documentation of the history, data, and other available information for each pilot plant. To compensate for the lack of pilot plant operating data, a literature survey section has been included which provides published performance data.

In addition, CM Solutions is currently trying to collect operational data from other sites where Sigrotec and Prentec have commissioned similar plants. When available and collated, these data will be added to this report as an addendum.

1.4 Outline of report

The next section of the report will present information on the various mine water and brine treatment technologies currently available in literature. This survey will consider reverse osmosis (RO), high pressure reverse osmosis (HPRO), forward osmosis (FO), electrodialysis (ED), traditional brine concentrators, DyVaR, eutectic freeze crystallization (EFC), and HybridICE^{TM}. For each of these technologies, the following will be presented:

- Description;
- Considerations;
- Current state of technology; and,
- Evaluation.

Following this literature survey, a discussion of each pilot plant will be presented. For each pilot plant the following will be covered:

- Pilot plant description and flowsheet;
- Available design specifications; and,
- Available commissioning and operational data.

After the pilot plants have been presented, the report will present conclusions and recommendations, references and appendices.

2 LITERATURE SURVEY

Various treatment technologies are available for treating mine and brine waters. Table 2.1 below shows the treatment options that are most commonly implemented. The purpose of this section is to provide a holistic overview of possible treatment options that could be considered feasible for treating RO concentrates (also known as RO reject or RO brine). This section aims to give a brief introduction to each technology, highlight industrial applications (should they exist) and to provide details on costs, energy requirements and limitations, as reported in literature. Reverse osmosis has been included since it provides context for the other technologies and since it can still (at least partly) be used to treat the RO concentrates considered in this study.

Table 2.1: List of commonly implemented brine treatment technologies

Treatment technology	Reference source(s)
Reverse osmosis	(Panagopoulos, Haralambous, & Loizidou, 2019), (Kaplan, Mamrosh, Salih, & Dastgheib, 2017)
High pressure reverse osmosis	(Panagopoulos, Haralambous, & Loizidou, 2019)
Forward osmosis	(Panagopoulos, Haralambous, & Loizidou, 2019), (Eyvaz, Arslan, Imer, Yuksel, & Koyuncu, 2018), (Martin, Kolliopoulos, & Papangelakis, 2019), (Kaplan, Mamrosh, Salih, & Dastgheib, 2017)
Electrodialysis	(Panagopoulos, Haralambous, & Loizidou, 2019), (Kaplan, Mamrosh, Salih, & Dastgheib, 2017), (Al-Amshawee, et al., 2020), (Strathmann, Grabowski, & Eigenberger, 2006)
Traditional brine concentrators	(Panagopoulos, Haralambous, & Loizidou, 2019), (Spellman, 2016), (Kaplan, Mamrosh, Salih, & Dastgheib, 2017)
DyVaR	(Salttech, 2019)
Eutectic freeze crystallization	(Panagopoulos, Haralambous, & Loizidou, 2019), (Randall & Nathoo, A succinct review of the treatment of Reverse Osmosis brines using Freeze Crystallization, 2015), (Randall, Nathoo, & Lewis, A case study for treating a reverse osmosis brine using Eutectic Freeze Crystallization—Approaching a zero waste process, 2011), (Randall, Zinn, & Lewis, Treatment of textile wastewaters using Eutectic Freeze Crystallization, 2014),
HybridICE™	(Adeniyi A. , Maree, Mbaya, Popoola, & Mtombeni, 2014), (Adeniyi A. , Maree, Mbaya, & Popoola, 2013), (Mtombeni, et al.)

For the purposes of this discussion, these technologies have been categorised as either "membrane" or "thermal" treatment technologies. Membrane technologies are reliant on physical separation using semi-permeable or ion-selective membranes, while thermal technologies depend on the change in temperature of the brine water to separate fresh water from the process stream.

2.1 Membrane treatment options

2.1.1 Reverse osmosis (RO) and high-pressure reverse osmosis (HPRO)

Description

During RO, two compartments, one containing a higher salt (impurity) concentration, are separated by a semi-permeable membrane. An external hydraulic pressure is applied to the compartment containing the higher salt concentration as to overcome the difference in osmotic pressure between the two solutions, thus forcing water molecules to migrate through the semi-permeable membrane to the compartment with a lower salt concentration. This migration results in the production of a low-impurity water stream and a concentrated brine solution. The impurity is concentrated through volume reduction.

The typical operating pressure of RO modules less than 82 bar. Applications where this pressure is exceeded (operating between 82-150 bar) are typically referred to as HPRO (sometimes ultra-high pressure when operating pressures are greater than 120 bar). These systems can treat brines at higher concentrations, but the water recovery and typical freshwater production rates are generally lower than that of regular RO.

Considerations

The low energy requirement of RO makes it an appealing technology for RO concentrate treatment, but the technology is heavily reliant on pre-treatment processes, which can increase the operating cost of the technology. The performance of RO is sensitive to the inlet salt concentrations of the brine water, since increased concentrations reduce permeate flow and increases the passage of salt through the membrane.

Current state of technology

RO is an established technology, with wide adoption in water treatment and desalination. Membrane technology has been used for water treatment since the 1960s but is still rapidly developing to new applications. Recent developments in acid-stable RO technology have established the technology as a viable option for processing acidic mine waters. RO has been successfully implemented for treating low-TDS brines and industrial waters, as well as sea water, but struggles to effectively treat high-TDS brines or operate in caustic environments. The major difference between applications in conventional water treatment, desalination, and industrial brine water treatment is that the concentration of major salts such as Na, Ca and Mg are significantly higher in brine waters. At higher salt concentrations, higher pressures are required, and scaling, fouling and corrosion all become major challenges. Scaling is especially prevalent in the presence of divalent ions such as Ca and Mg. Table 2.2 summarises the operational parameters for RO and HPRO.

Table 2.2: Summary of RO and HPRO operational parameters

Attribute	Unit	Value	
		RO	HPRO
Typical feed concentrations	[mg/L]	-	-
Typical exit concentrations	[mg/L]	-	-
Typical removal efficiencies	[%]	50%	50%
Limitations	[mg/L]	< ~70,000	< ~120,000
Reagents used		Anti-scalants	Anti-scalants
Primary cost driver		Chemical, Energy	Chemical, Energy
Typical cost	[\$/m^3]	0.75	0.79
Energy requirement	[kWh/m^3]	2-6	3-9
Waste product		Concentrated brine	Concentrated brine

Evaluation

Considering the current state of the technology and the available information from literature, it is expected that water recoveries would be low and that the chemical costs to mitigate the fouling effects of RO concentrate on the membranes would be high. The technology is thought that HPRO is not suited for treating RO brine at the time. However, the technology is still developing, and it may become an option in the future.

2.1.2 Forward osmosis (FO)

Description

Forward osmosis is based on the principle of osmotic pressure gradients, rather than relying on an external hydraulic pressure to promote the transfer of water molecules across a semi-permeable membrane. During FO, a highly concentrated "draw solution" is circulated on one side of a semi-permeable membrane to promote the transfer of water molecules from a less saline brine solution to the draw solution. This results in the formation of a concentrated brine solution and a diluted draw solution. Fresh water is separated from the draw solution in a second step using either thermal, membrane or chemical separation, and the draw solution is recycled to the first step.

Considerations

For the effective operation of forward osmosis, the draw solution must be inexpensive, commercially available, safe to use, provide a high flux of water and have a low fouling potential. Various draw solutions, including organic solutes and inorganic salts, have been investigated. No ideal draw solution has been identified yet.

While FO requires much less energy during the first osmosis step because it doesn't rely on an external pressure, the energy requirement of the second step may be of potential concern to the process. The first step typically requires 0.1 – 0.85 kWh/m^3, but the overall energy requirement can be as high as 13 kWh/m^3.

Current state of technology

The number of annual research publications relating to FO have increased 50-fold over the last decade. The technology has been investigated as a method of desalination for approximately four decades and, more recently, as a method of treating industrial and brine waters. Research is ongoing to improve draw solutions, as well as modifying membrane surfaces to mitigate fouling and improve water flux through the membrane. FO is still widely regarded as an emerging technology, but there are some commercially available applications.

Table 2.3: Summary of FO operational parameters

Attribute	Unit	Value
Typical feed concentrations	[mg/L]	65,000
Typical exit concentrations	[mg/L]	-
Typical removal efficiencies	[%]	98
Limitations	[mg/L]	< ~200,000
Reagents used		Atni-scalants
Primary cost driver		Chemical, Energy
Typical cost	[\$/m^3]	0.63
Energy requirement	[kWh/m^3]	0.1 – 13
Waste product		Concentrated brine

Evaluation

Based on the available information, FO can be a feasible solution to treating RO concentrate, considering the high water recoveries and low operating costs. However, since the technology is still in development, further research regarding an appropriate draw solution and membrane would be required. Another factor that would have to be considered is the energy consumption of the draw solution recovery step.

2.1.3 Electrodialysis (ED)

Description

ED is based on the transfer of cations and anions from the brine solution in opposite directions through a series of alternating cation exchange membranes and anion exchange membranes (can be up to 300-500 individual cells). By applying an external voltage, the electromigration of cations in solution to the negatively charged cathode and anions in solution to the positively charged anode is promoted. The cations permeate the cation exchange membranes but are retained by the anion exchange membranes. The converse is true for the anions. As ions migrate from the compartments to which brine water is fed, a fresh-water stream is produced, and the ions accumulate in alternating compartments, from which a concentrated brine is produced.

Considerations

ED is an attractive membrane technology, since it does not require any pre-treatment steps. Compared to RO, longer membrane lifetimes and improved water recovery rates are expected. ED systems are also easier to maintain and do not require additional chemicals since scaling and fouling on the membranes can be maintained by periodically reversing the voltage across the cells.

While good water recoveries are reported for low-TDS brines, there is a notable decrease in recovery when high-TDS brines are treated. Furthermore, the energy consumption of the technology increases as the salinity of the feed solution increases.

Current state of technology

ED is a commercially available technology and has been implemented for the treatment of industrial wastewater, brackish water, municipal wastewater and pharmaceutical waste for more than 60 years.

Table 2.4: Summary of ED operational parameters

Attribute	Unit	Value
Typical feed concentrations	[mg/L]	107,000 – 195,000
Typical exit concentrations	[mg/L]	240 – 2,700
Typical removal efficiencies	[%]	50-86
Limitations	[mg/L]	< ~200,000
Reagents used		None
Primary cost driver		Energy
Typical cost	[$/m^3]	0.85
Energy requirement	[kWh/m^3]	7-15
Waste product		Concentrated brine

Evaluation

ED is likely to be feasible for treating RO concentrate, considering the low treatment cost and high recovery that can be achieved. Before adopting the technology, the energy consumption and water recovery at a high TDS would have to be considered, since the technology is sensitive to the salinity of the feed solution.

2.2 Thermal treatment options

2.2.1 Traditional brine concentrators (BC)

Description

Brine concentrators, also known as thermal evaporator compressor systems, are evaporative concentrators that reduce the high energy requirements associated with evaporating water by implementing integrated heat transfer.

Initially, the temperature of the brine water is increased to its boiling point via a heat exchanger, after which it is fed to a concentrator. Concentrators are typically falling-film or plate-type evaporators. In the concentrator a portion of the water is evaporated, and a concentrated brine is collected (of which a portion is recycled to the concentrator).

The evaporated water is then compressed in such a manner that it elevates the boiling point of the collected water enough that it can be used as steam in the concentrator to allow for the evaporation of the brine being fed to the concentrator. The water condenses and is then pumped through the initial heat exchanger to heat the brine to its boiling point before being removed from the process as fresh water.

Due to the inherent inefficiency of the compressor, mechanical vapour recompression is often used. This is where some of the energy introduced to the system is lost as heat, which allows the collected water vapour to be superheated. Because of this, it is often not necessary to provide the system with additional energy for heating.

Typically, the energy requirement to evaporate a cubic meter of water via the vapor compression approach is a tenth of what it would be via normal heating.

Considerations

Brine concentrators have been successfully implemented to treat a wide range of concentrated brine water streams, often achieving freshwater recoveries in excess of 90% for brine up to 250,000 mg/L TDS. The technology is robust and versatile.

Brine concentrators are essentially evaporators that are optimised to reduce the energy requirement of the process. Therefore, it is important to consider that the energy requirements for treating brine water can be sizable if the energy usage throughout the process isn’t integrated efficiently.

Despite the optimisation, the energy consumption of brine concentrators is still comparatively high to that of membrane technologies.

Brine concentrators are highly susceptible to scaling and corrosion and therefore require expensive, and often exotic, materials of construction. Capital costs for brine concentrators are therefore a major disadvantage to their adoption. Scaling and fouling are effectively mitigated in these processes by circulating a calcium sulphate slurry through the concentrators. This promotes the preferential deposition of calcium and silica on the calcium sulphate crystalsrather than onto the surfaces of the equipment.

Current state of technology

Brine concentrators are commercially available and have been successfully implemented for the treatment of industrial wastewater. There are more than 75 brine concentrators operational across the globe, of which approximately 12 are implemented to treat RO concentrate.

Table 2.5: Summary of BC operational parameters

Attribute	Unit	Value
Typical feed concentrations	[mg/L]	-
Typical exit concentrations	[mg/L]	-
Typical removal efficiencies	[%]	99
Limitations	[mg/L]	< ~250,000
Reagents used		$CaSO_4$*
Primary cost driver		Energy
Typical cost	[$/m^3]	1.11
Energy requirement	[kWh/m^3]	15.9-26
Waste product		Concentrated brine

Evaluation

Based on the available information from literature, brine concentrators are a feasible option for treating RO concentrate.

2.2.2 Dynamic vapour recovery (DyVaR)

Description

DyVaR is a proprietary technology developed by Salttech and is analogous to typical brine concentrators in its basic function. The key difference between brine concentrators and DyVaR is that the design enables a wider operational range (see Figure 2.1). The temperature of the feed brine water is increased via a heat exchanger as part of a pre-heating step, before it is combined with a recirculated brine concentrate. The recirculating concentrate stream is heated to its boiling point before it enters a cyclone-type separation unit which allows water vapour to be separated from the recirculating stream. The concentrated brine is recirculated back to the heat exchanger and is then reintroduced to the separation unit.

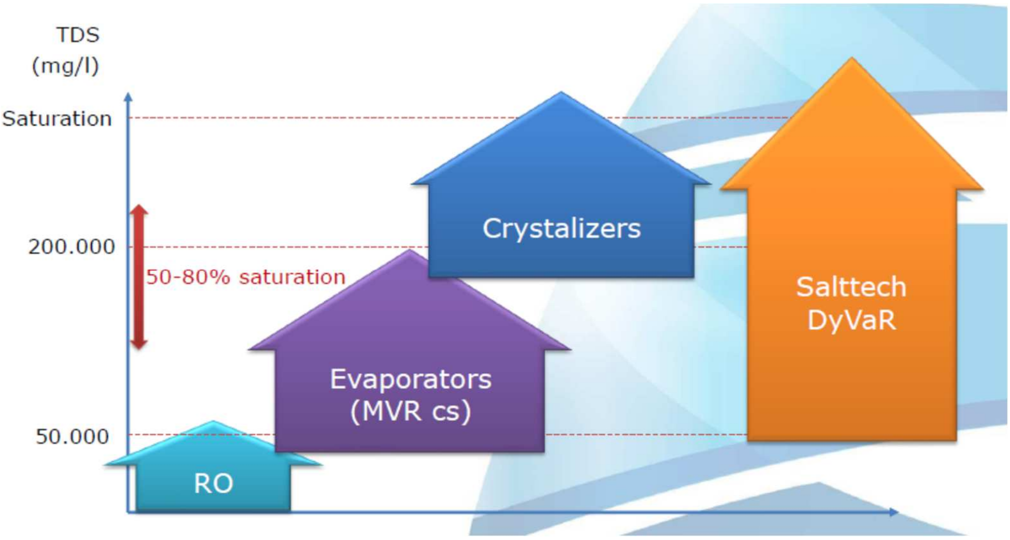

Figure 2.1: DyVaR operational range (shown on the Y-axis).

As with brine concentrators, the water vapour is compressed and utilised to provide heat to both the recirculating brine and the brine water fed to the process. After the compressed water vapour condenses, it is removed as fresh water from the system.

A portion of the recirculating concentrated brine is removed as a waste product from the system, see Figure 2.2.

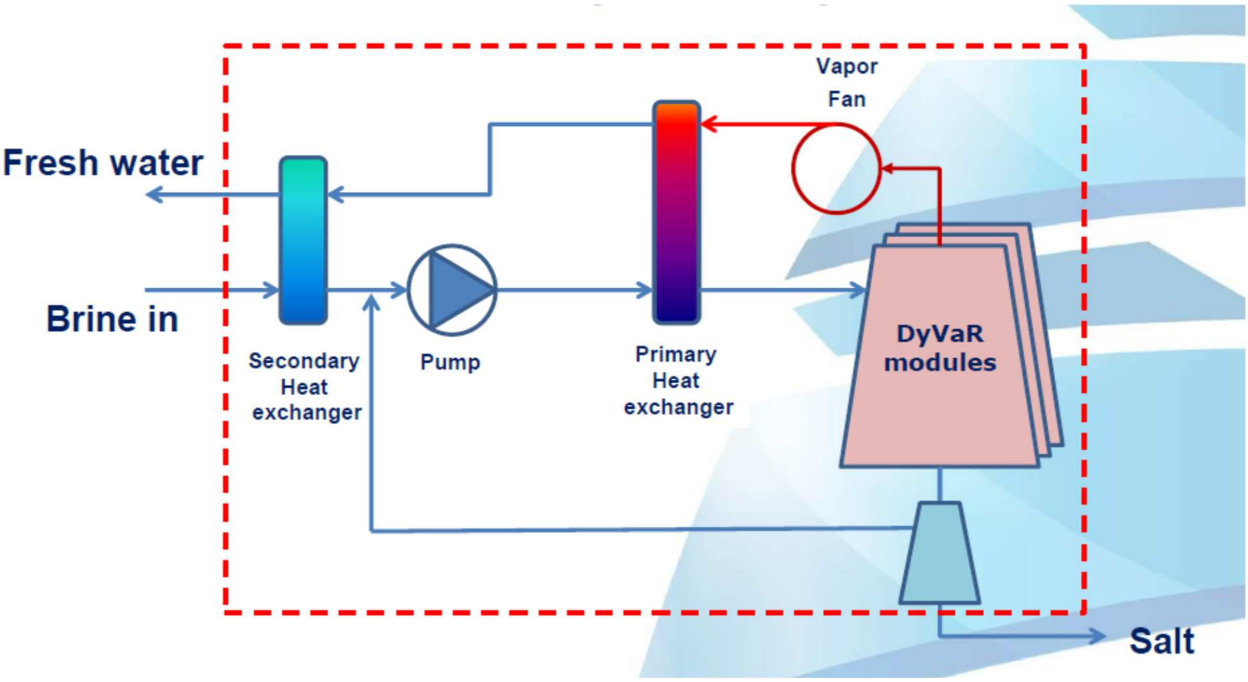

Figure 2.2: Typical DyVaR flowsheet

Variability in the influent TDS is handled in the process by controlling the rate of concentrated brine removal from the circuit.

The DyVaR is built as modular units: each DyVaR "pot" consists of a single cyclone that can process 50 L/h. A DyVaR "set" consists of 10 pots with a capacity of 500 L/h. The next level of scale is a DyVaR "string" that consists of 30 pots with a capacity of 1500 L/h. The influent is injected into a set or string via a side manifold which splits the feed to each of the pots in operation.

Considerations

The DyVaR technology has advantages when compared to that of typical brine concentrators. The first advantage is that the process units are fabricated from polymers rather than exotic construction materials. The benefits of constructing the process units from polymer are that the units are corrosion resistant, do not require chemical additives to mitigate corrosion and the material is relatively inexpensive compared to complex alloys and titanium.

The second advantage is that the cyclone technology prevents scaling deposits from forming inside the operating units.

The final advantage is the modular design. The process is constructed as a series of bucket-sized cyclones, each capable of treating 50 L/h of brine water. This implies that the technology can be scaled by simply increasing the number of cyclones. While is no benefit of scale for the separator portion of the design, there is still a benefit when sizing the heat exchanger systems.

Table 2.6: Summary of DyVaR operational parameters

Attribute	Unit	Value
Typical feed concentrations	[mg/L]	8,000 – 300,000
Typical exit concentrations	[mg/L]	< 200
Typical removal efficiencies	[%]	88
Limitations		-
Reagents used		None
Primary cost driver		Energy
Typical cost	[\$/m^3]	-
Energy requirement	[kWh/m^3]	45
Waste product		Concentrated brine

Current state of technology

The DyVaR process is a commercially available technology marketed by Salttech.

Evaluation

The DyVaR process can treat brine water over a wide range of inlet concentrations at a specific energy consumption (SEC) values comparable to that of brine concentrators, producing a reasonably pure water effluent at a high recovery rate. Considering that the capital cost is likely to be lower than that of typical brine concentrators, operational challenges are inherently mitigated, and the technology is readily scalable, the DyVaR process appears to be an ideal selection for treating brine water.

2.2.3 Eutectic freeze crystallization (EFC)

Description

EFC concentrates brine water by lowering the temperature in such a manner that ice and salt crystalizes from the brine water. Since ice is less dense than water, and salts have a higher density than water, physical separation of the salt and ice becomes possible.

EFC is based on the principle of the eutectic point – the temperature and solution concentration at which an equilibrium exists between the ice, salt and solution concentrations. Each compound has a different eutectic point, which makes the stage-wise separation of different components possible. This implies that the process could be implemented to produce high-purity salts from brine water.

Considerations

Due to the low operating temperatures of EFC, the scaling and fouling potential in the equipment is greatly reduced. No additional chemical additives are required to maintain the process.

EFC allows for the production of clean water through the production of pure ice crystals, as well as either a very concentrated brine solution or a pure salt. Water recovery can theoretically be 100%. If pure salts are produced, it could potentially be viewed as a saleable product. While the technology has been proven at lab-scale and a number of vendors have working designs, research is still ongoing for applications with multicomponent brine solutions.

The technology comes at a high capital cost. Energy is the primary cost driver of the technology with a specific energy consumption between 43.8 – 68.5 kWh/m^3, despite the lower specific energy requirement of freezing water compared to evaporating water. This specific energy consumption is higher than that of the integrated evaporator technologies (brine concentrator and DyVaR)

Current state of the technology

EFC processes are commercially available, but the technology is still regarded as an emerging technology. In South Africa, the Eskom Research and Innovation Centre in Rosherville houses a large-scale EFC process. Table 2.7 shows the summary of the typical EFC operational parameters.

Table 2.7: Summary of EFC operational parameters

Attribute	Unit	Value
Typical feed concentrations	[mg/L]	-
Typical exit concentrations	[mg/L]	-
Typical removal efficiencies	[%]	98
Limitations		-
Reagents used		None
Primary cost driver		Energy
Typical cost	[\$/m^3]	1.42
Energy requirement	[kWh/m^3]	43.8 - 68.5
Waste product		Concentrated brine or salt

Evaluation

The high capital cost and energy requirements of the EFC process poses a major challenge to its adoption but considering the low operating and maintenance costs it may be a feasible option for treating brine water. The technology becomes especially attractive if the potential exists for generating a salt product from the brine water that is salable.

2.2.4 HybridICE^{TM}

Description

The HybridICE^{TM} system is a freeze desalination process that cools the brine water down sufficiently to form ice crystals without reaching the eutectic point of any of the impurities in the brine solution. This results in the formation of a brine slurry containing ice crystals. The cooling is done with a refrigeration circuit, typically using R404A refrigerant.

During the formation of ice crystals, impurities are largely rejected (minimal entrainment with the ice occurs) and remain in the brine solution. One of the challenges faced by freeze desalination processes is the separation of the ice crystals from the brine which usually required washing the ice with fresh water. However, the HybridICE^{TM} system does make use of washing. Instead, it relies on the re-melted water to wash the remaining ice crystals.the ice is separated from the brine solution through a special “HybridICE^{TM} Filter”. This filter is designed as a vertical column to which the brine slurry is introduced from the bottom. An ice column builds to a height that is sufficient for it to be removed by a scraper. The brine solution exits the column through a filter medium and is pumped out. The “HybridICE^{TM} Filter” produces a freshwater stream and a concentrated brine solution. Water is further recovered from the concentrated brine solution through vacuum evaporation, which could allow for the removal of contaminant salts as solid products.

Integral to the efficient operation of the HybridICE^{TM} process is its utilisation of waste heat from the refrigeration cycle for recovering water through vacuum evaporation, as well as using ice and concentrated brine to cool the inlet brine solutions.

Considerations

Due to the low operating temperatures of the process, the scaling and fouling potential in the equipment is greatly reduced. This also means that additional chemical additives are not required.

The freeze crystallisation process produces highly pure water and, if coupled with the vacuum evaporator, solid waste products that simplify disposal.

Energy is the primary cost driver of the technology. During the initial iterations of the technology, the SEC was in the order of 100 kWh/m^3. With some optimisation, the SEC has been reduced to SECs approximately to 40 kWh/m^3.

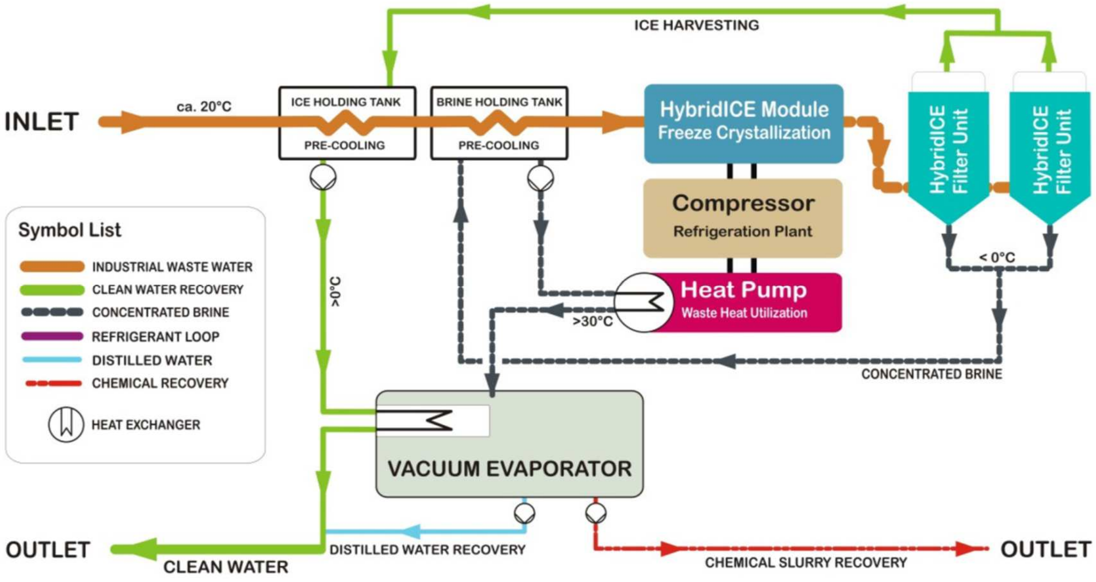

Figure 2.3: Typical HybriICE™ flowsheet.

Current state of technology

The HybridICE™ process is commercially available and is currently marketed by Sigrotec. Table 2.8 shows the operation parameters for the HybridICE™ process.

Table 2.8: Summary of HybridICE™ operational parameters

Attribute	Unit	Value
Typical feed concentrations	[mg/L]	-
Typical exit concentrations	[mg/L]	-
Typical removal efficiencies	[%]	96
Limitations		-
Reagents used		None
Primary cost driver		Energy
Typical cost	[$/m^3]	4-6
Energy requirement	[kWh/m^3]	30-100
Waste product		Concentrated brine

Evaluation

The HybridICE™ process can produce pure water at high recovery rates, as well as solid waste streams that allow for easy disposal. No information is available regarding the capital cost of the technology, but low maintenance costs are to be expected.

No chemical additives are needed, and the SEC of the process is similar to that of BC, DyVaR and EFC, which makes HybridICE™ worth considering as a possible treatment option for RO concentrate.

3 PILOT PLANT ASSESSMENTS

This section presents the available information for each of the pilot plants considered in this study.

3.1 Sigrotec's HybridICE^{TM}

3.1.1 Pilot plant description

A typical HybridICE^{TM} process was described in Section 2.2.4. It is similar to an EFC process, except that excess heat generated by the refrigeration circuit powers an additional vacuum evaporation step. The following description outlines the specific detailsof the pilot plant, shown in Figure 3.1, that was implemented at Optimum Colliery.

The Optimum Colliery circuit consisted of three cooling modules. The raw feed to the process was fed into the first process holding tank (3.6 m^3) with an option to feed it via the ice holding tanks for pre-cooling of the raw feed. The temperature of this first module was maintained at the target temperature (approximately -2°C) by cooling with the first refrigeration circuit. The overflow from this first module is fed into the second process holding tank (3.6 m^3). Solution from this stage was then sent to the second cooling circuit where ice was expected to begin forming. The chilled slurry (ice and concentrated brine) from the second stage cooling was fed to the first ice filter module where clean ice was removed from the concentrated brine slurry. The concentrated brine solution remaining after the ice had been removed was then recycled to the first holding tank. The overflow from the second module fed into the third process holding tank (3.6 m^3). Solution from this stage was then fed into the third cooling circuit where the chilled slurry was fed to the other ice filter module where ice was removed, and the remaining concentrate returned to the first module as well.

Each of the holding tank modules had the facility to remove any precipitated solids. It was possible to control the temperature profile down these modules by adjusting overflow rates and concentrated brine addition. This would make it possible to selectively precipitate different solids (with similar saturation concentrations at the module temperature) in each module.

Bleeds of the concentrated brine solutions from both of the ice filter modules could also be sent to the vacuum evaporator section of the process. This section made use of the heat generated by the compressor (as part of the refrigeration loop) to heat these brine solutions under a vacuum, thus evaporating the remaining water and generating a salt discharge. Three of these evaporators were operated in parallel at Optimum Colliery.

The operation of the HybridICE^{TM} ice filters were particularly noteworthy as they provided an elegant and effective separation of ice from brine solution. The partially frozen brine slurry was fed from the bottom, into the inner tube of the filter. This tube is perforated to allow the brine solution to pass through while preventing the majority of the ice particles from passing through. Thus, the ice builds up in this inner perforated tube while the brine flows into the outer chamber of the filter where it drains away and is fed back to the holding tanks. As ice level builds in the tube and brine drains away the brine is replaced with air at ambient temperatures. This causes a small amount of the surface ice to remelt and drain away. Although this small amount of melting reduces the ice production slightly, the partial remelting helps to further purify the ice since it drains away much of the brine solution that was on the surface of the ice.

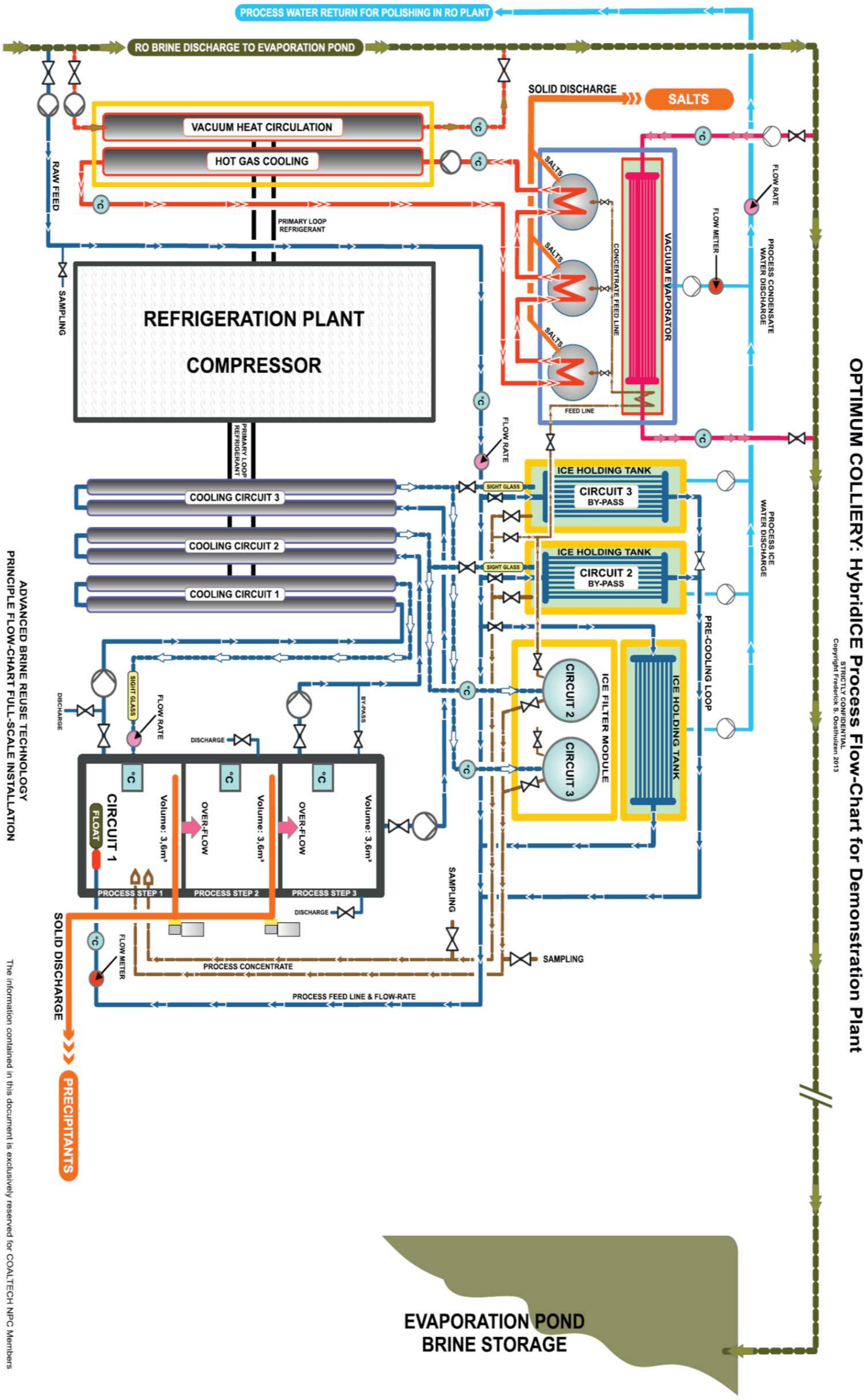

Figure 3.1: Optimum Colliery HybriICE™ flowsheet

3.1.2 Pilot plant design specifications

The following design values are based off calculations shown in Section 6.1 (mass and energy balance for the HybridICE^{TM} process). The values presented here were used as a basis for the pilot plant design, however, since the objective was to demonstrate the HybridICE^{TM} process using other brine solutions, the plant equipment was over-designed

Typical pilot plant feed

The design feed is expected to be stage 3 reject from the Optimum Colliery RO plant:

- Raw feed flow = 50 m^3/day (2.1 m^3/h)
- Expected TDS = 20,000 mg/L
- Expected feed temperature = 18^oC

Ice removal circuit

Two "HIF 5000" filters were commissioned for the pilot plant – one linked to the circuit 2 chiller, and one linked to the circuit 3 chiller. Based on the design feed rate, expected TDS and an overall concentration factor (CF) of 6.67 (85% recovery of water as ice) the filters are expected to produce about 22 m^3/d or 1 m^3/h water from ice.

Vacuum evaporation circuit

Based on the expected available process waste heat (~3,100 kWh) from the refrigeration circuit, about 4.5 m^3/d of condensate production can be processed. Three evaporation units that operate in parallel have been commissioned to handle this flow.

Concentrated salt/brine removal

Based on the design values quoted above, 42.5 m^3/d (85% of the feed) will be recovered as ice, and 4.5 m^3/d (9% of the feed) will be recovered as condensate. Therefore, it is expected that 3.0 m^3/d of ultra-concentrated brine slurry will need to be removed from the circuit.

Although not included in this pilot plant design, this brine slurry could be filtered to remove precipitated salts and the remaining brine solution returned into the first process holding tank, along with the concentrated brine from the ice filters. This would make the pilot plant effectively a zero liquid discharge process.

Refrigeration loop

The refrigeration loop was based on a 60 kW (Bitzer) NH_3 compressor. Each of the cooling circuits was operated in parallel to one another. Since this plant was designed as a demonstration plant, the compressor was sized to enable the cooling of larger, higher concentration brines. For this reason, the expected stage 3 reject brines from Optimum's water treatment plant (~20 g/L TDS) were on the lower end of the design range, limiting the minimum brine concentration that could be fed to the plant. As is shown in Section 6.1, with the expected stage 3 reject brine the compressor needed to be turned down to about 30-50% of its design output.

3.1.3 December 2014 trial

In early December 2014 a formalised trial, including sampling was attempted. However, this trial proved problematic from the start as during this time the water treatment plant could not supply stage 3 reject for treatment, so stage 2 reject was treated. The daily average TDS values measured during the four days of operation are given in Table 3.1. The

(RO) stage 2 reject typically only consisted of about 10 g/L TDS compared to the expected 20-30 g/L TDS from stage 3 (RO) reject.

Table 3.1: Total dissolved solids during the attempted trial

Date	Stage 3 brine	Vacuum evaporation condensate	Circuit 2 ice filter	Circuit 3 ice filter
	[g/L]	[g/L]	[g/L]	[g/L]
5/12/2014	9.87	2.00	14.55	18.00
6/12/2014	10.67	1.92	13.37	11.06
7/12/2014	5.32	1.58	8.11	5.37
8/12/2014	9.76	1.75	6.52	2.04

As discussed previously, the pilot plant compressor could not be turned down enough to prevent icing up of the cooling systems at stage 2 reject concentrations. This slowed down ice removal and therefore it took a few days to build up the internal recirculating brine concentrations to prevent this icing up from occurring. In addition, since the ice production was initially slow, the filters were not able to function optimally. This can be seen by the high TDS values on the 5th and 6th of December 2014. Once the concentrations were higher, the ice formed more in the slurry rather than on the chilling surface. This meant that a better separation between the ice and the remaining concentrated brine slurry could be achieved.

The trial ended early due to feed supply issues. However, the trend in TDS levels for both ice products and the evaporator condensate show a strong decreasing trend to acceptable levels.

Due to the commissioning of new plants, further plant trials could not be arranged and in early 2015 Sigrotec mothballed the HybridICE^{TM} pilot plant.

3.1.4 Previous operation

The pilot plant was commissioned in 2013 and was tested on several RO brines from various water treatment operations, including samples from the Navigation Colliery water treatment plant and the eMalahleni Water Reclamation Plant. Although these runs appeared to be successful, no data was collected, therefore the performance of the technology cannot be quantified.

However, some pictures were taken of the plant during these runs and some of these are included here. Figure 3.2 shows the three holding tanks, Figure 3.3 shows the ice filters after successfully generating large amounts of ice from brine, and Figure 3.4 shows the vacuum evaporators and the evaporator condensate tank.

Figure 3.2: Optimum Colliery HybriICE™ holding tank modules

Figure 3.3: Optimum Colliery HybriICE™ ice filters

Figure 3.4: Optimum Colliery HybriICE™ vacuum evaporators and condensate tank

3.2 Prentec's EFC process

3.2.1 Pilot plant description

Fresh feed (stage 3 reject) is fed to the brine tank. Before feeding this brine solution into the main crystalliser recirculating loop it is cooled to about 4°C via the feed pre-cooler unit (this unit cools the stream down to ~6°C using ice melt) and via the super heater unit (this unit cools the stream down using the main refrigerant). The solution within the crystalliser is recirculated from the lower part of the unit and fed back into the top of the crystalliser using a recirculation pump at 15 t/h. Generated ice is removed via the scraper system and vacuum filter into the ice melt tank. This melted ice is sent to the product storage after being used to cool the fresh brine feed.

The refrigeration circuit consists of two parts, a trim circuit and a main circuit. The main circuit consists of the main condenser, receiver and crystalliser. It is responsible for directly cooling the brine slurry within crystalliser and partially pre-cooling the brine feed (in the super heater unit). The trim circuit consists of its own condenser, receiver and evaporator. This circuit extracts the heat from main circuit to enable it to operate more efficiently than it would if its condenser operated at higher temperatures. This trim circuit is then cooled using cooling water fed into the trim condenser at 20^{o}C (increasing to ~24^{o}C).

The commissioned pilot plant can be seen below in Figure 3.5. Figure 3.6 shows the design flowsheet for the Prentec EFC process commissioned at Optimum Colliery.

Figure 3.5: Optimum Colliery Prentec EFC pilot plant

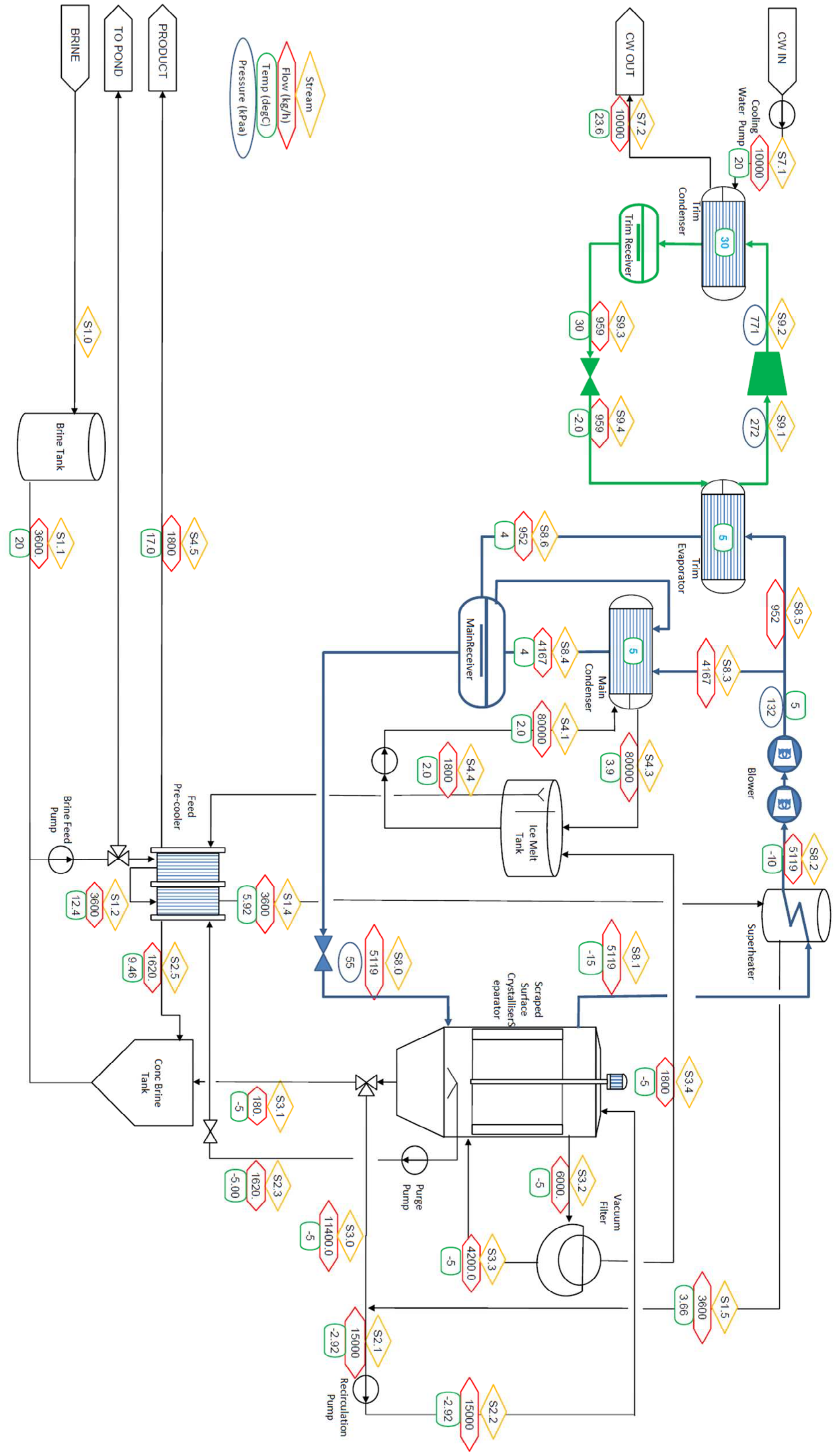

Figure 3.6: Optimum Colliery (Original) Prentec EFC flowsheet

3.2.2 Pilot plant design specifications

The following design values are based off calculations shown in Section 6.2 (mass and energy balance for the Prentec EFC process). The values presented here are Version 9, Revision D.

Typical pilot plant feed

The design feed is expected to be stage 3 reject from the Optimum Colliery RO plant. As discussed in the plant description, the pilot plant operates in two steps: the first step treats fresh stage 3 reject, and the second step treats the concentrated brine left over from the first step. The following design parameters were initially assumed:

- Fresh feed to plant = 25.2 t/d
- Overall water recovery = 95%
- Step 1:
    - Feed flow = 3,600 kg/h
    - Recirculating flow = 15,000 kg/h
    - Step duration = 7.0 hours
    - Expected feed temperature = 20°C
- Step 2:
    - Feed flow = 777.8 kg/h
    - Recirculating flow = 15,000 kg/h
    - Step duration = 16.2 hours
    - Expected feed temperature = 20°C

Ice removal circuit

The ice is removed using a scraper system (that underwent significant development during the operation of the pilot plant) into the ice melt tank. The following design figures for ice production were expected:

- Step 1:
    - Ice recovery = 50%
    - Ice production = 1,800 kg/h
    - 23.8 kW/t-ice
- Step 2:
    - Ice recovery = 90%
    - Ice production = 700 kg/h
    - 41.2 kW/t-ice

Refrigeration circuit

- Step 1:
    - Bulk temperature = -5°C
    - Refrigerant (main) flow = 5,119 kg/h
    - Refrigerant (trim) flow = 959 kg/h
    - Stage $^{\#}1$ (main) = 23.18 kW
    - Stage $^{\#}2$ (main) = 6.44 kW
    - Stage $^{\#}3$ (trim) = 13.16 kW
    - Overall COP = 6.9
- Step 2:
    - Bulk temperature = -20°C
    - Refrigerant (main) flow = 2,088 kg/h

- Refrigerant (trim) flow = 187 kg/h
- Stage #1 (main) = 19.09 kW
- Stage #2 (main) = 7.19 kW
- Stage #3 (trim) = 2.57 kW
- COP = 2.9

Main circuit refrigerant was R236FA and the trim circuit used R134.

3.2.3 Commissioning and operation

Due to the continuous improvement of the operation, the Prentec EFC process was never formally trialled. However, several shorter runs were performed by Prentec. This section presents a chronological summary of these runs.

Pilot plant commissioning

During early 2015 (March – May) the pilot plant commissioned. During this time there were a number of issues that needed to be resolved (Prentec, Brine Treatment Demonstration Plant (J1410 - Prog 1), 2015). Some of these included:

- Issues with motor overheating due to the startup bypass on the blower which needed to be modified.
- Initially the temperature bottomed out before freezing was achieved. While the main refrigeration circuit worked as expected, the trim refrigeration circuit control required further refinement.
- Further refinements to trim evaporator were required to ensure the correct operation of the trim refrigeration circuit.
- After these changes were made, lagging was added, and further refrigeration circuit refinements were made.
- After these changes the plant was restarted and ice was formed (6 May).
- After this ice was formed on a more regular basis, however issues with level control and ice removal/transfer needed to be resolved.
- In response to these issues new automated level control of crystalliser was implemented.
- A linear screen was installed but didn’t prove effective with the fine ice.

During this period, ice production reached 856 kg/h (~50% of the design ‘step 1’ production rate). It was identified that the scrapers were operating effectively, the torque on the scraper drive was minimally affected by the load. However, the ice produced was too fine due to the low production rates and the high scraper speeds.

The best result achieved during this period was a concentration factor of 6.9 (29 mS/cm down to 4.2 mS/cm). Several improvements were recommended with associated costs.

Continuous improvement

In September 2015 Prentec provided additional feedback on new runs that had been performed post-May 2015 (Prentec, Brine Treatment Demonstration Plant (J1410 - Prog2), 2015). During this time mechanical modifications were implemented to resolve ice removal and dewatering bottlenecks. Figure 3.7 shows the first ice formation after these changes (Prentec, Brine Treatment Demonstration Plant (J1410 - Prog2), 2015). Prentec reported that while the ice production was improved, the quality of the ice was not at the required levels since the conductivity was 12.8 mS/cm.

Figure 3.7: First ice production with new ice removal and dewatering equipment

A possible cause for the higher conductivity in the ice suggested (by Prentec) was the recirculation system. This system allowed precipitating salts to come into contact with ice crystals, resulting in entrainment. In addition, the salt particles could get too large, which would also be entrained with ice. A possible remedy might be to wash the ice. Further bench-scale research on this washing was recommended.

Pilot plant shutdown

The pilot was operated for the rest of 2015 (Prentec, Brine Treatment Demonstration Plant (J1410 - Prog3), 2016). During this run a number of additional improvements were made to the plant:

- The trim condenser was modified to handle the higher ambient temperatures experienced during summer.
- The feed pre-cooler required cleaning due to scaling and it was further recommended that this be done on a regular basis.
- Barrel fatigue was noted, and the cause identified as the shudder in the scraper. Possible way to correct this were considered.
- Issues with the refrigerant evaporator were noted, a refrigeration recirculation pump was suggested to correct this issue.
- It was then suggested that the plant be shut down until these operational issues could be resolved – all requiring further funding from Coaltech.

In January 2016 the plant was mothballed for the first time

Restart and final shutdown

In late 2016 the plant was restarted and operating normally by the end of the year. During this time the following improvements were made:

- Trim circuit was upgraded to more effectively remove excess heat
- Refrigerant circulation pump was installed

Further improvements suggested were:

- Installation of a new scraper system.
- Installation of a new rotary wash valve.

However, in February 2016 the refrigerant charge was lost. Replacing it would cost R270,000 and take many weeks for delivery. Primarily for this reason, the plant was shut down and mothballed shortly after this.

3.3 Salttech's DyVaR

The DyVaR technology was trialed by Tecroveer at eMalahleni Water Reclamation Plant (EWRP) from the 18th to the 26th July 2019. The tests were performed on the stage 3 reject brines and an artificially generated mixed brine.

3.3.1 Pilot plant description

The pilot plant consisted of a single module (pot), as shown in Figure 3.8. For each run EWRP stage 3 reject effluent was fed to the pilot plant from the IBC shown in the figure. This effluent fed into the pilot plant buffer tank via gravity from where it was combined with returning concentrate brine solution and then pumped into the DyVaR unit. The concentrated brine solution was then recycled to the buffer tank for the duration of each run, while condensate was discharged at a constant flowrate through the condensate outlet. As mentioned previously, this single module/pot can produce 50 L/h of clean water.

Figure 3.8: EWRP DyVaR pilot plant

3.3.2 Pilot plant set up

Brine feed solutions

EWRP supplied approximately 2000 L of stage 3 reject effluent. Table 3.2 shows the properties and major component compositions of the stage 3 reject effluent as given in Appendix A (Tecroveer, 2019). It shows the brine consists largely of sodium, calcium and potassium sulfates and chlorides.

Table 3.2: EWRP stage 3 reject effluent composition

Attribute	Unit	Value
Conductivity	[mS/cm]	27.17
pH	[-]	8.24
TDS	[mg/L]	24,530
Sodium	[mg/L]	8,084
Calcium	[mg/L]	1,291
Potassium	[mg/L]	1,212
Chlorides	[mg/L]	2,068
Sulfates	[mg/L]	13,359

In addition to the test run using the stage 3 reject effluent, an additional run was performed using a concentrated brine mix that was generated by blending some of the saturated brines from the original trial. The objective of this run was to observe the performance of the unit on a brine with a higher concentration. Table 3.3 shows the mixed brine influent composition used for the second test run as given in Appendix A (Tecroveer, 2019).

Table 3.3: Mixed brine influent composition

Attribute	Unit	Value
Conductivity	[mS/cm]	68.10
pH	[-]	7.03
TDS	[mg/L]	76,864
Sodium	[mg/L]	19,062
Calcium	[mg/L]	844
Potassium	[mg/L]	4,119
Chlorides	[mg/L]	8,883
Sulfates	[mg/L]	37,494

Each brine solution was processed with the DyVaR unit. The concentrate and condensate samples were collected during the runs for analysis, and the concentrates recycled until the end of the run. The stage 3 reject was processed until approximately 88% of the water was recovered as condensate. The mixed brine was processed until about 54% of the water was recovered as condensate.

An alternative way of describing the volume reduction of the brine is to refer to concentration factor (CF). This is defined as the original volume divided by the final volume. Therefore, if a volume of 1000 L is reduced to 125 L, then the CF is 8. This is also equivalent to an 87.5% reduction in volume.

3.3.3 Trial results

Treatment of stage 3 reject

For the set of runs stage 3 reject effluent was used to fill the feed buffer tank. This was then fed to the DyVaR unit. Any condensate generated was sampled and removed from the process. The concentrate produced was also sampled and then recycled back to the feed buffer tank.

Table 3.4 shows the analysis results for concentrate samples taken during the runs where the brine was concentrated up to a CF of 8.5 (Tecroveer, 2019).

Table 3.4: EWRP stage 3 reject concentrate trial compositions

Attribute	Unit	Stage 3 reject	CF 5	CF 7	CF 8.5
Water recovery	[%]	-	80.0%	85.7%	88.2%
Conductivity	[mS/cm]	27.17	84.1	107.2	106.4
pH	[-]	8.24	6.58	6.03	6.02
Alkalinity as $CaCO_3$	[mg/L]	162	80	80	78
TDS	[mg/L]	24,530	97,914	136,796	154,016
Sodium	[mg/L]	8,084	27,072	36,915	42,457
Calcium	[mg/L]	1,291	615	579	644
Potassium	[mg/L]	1,212	3,962	5,859	6,400
Chlorides	[mg/L]	2,068	12,686	12,965	13,408
Sulfates	[mg/L]	13,359	51,155	75,154	82,077

As the CF increases, each the parameters increases, however not by the same amount that the volume decreases. This indicates that small amounts of the impurities are reporting to the condensate. At CF 8.5, many of the parameters have a ratio relative to their feed composition of about 6. The TDS, for example, increases by about 6 times, from 24 g/L to 154 g/L. Therefore, based on CF 8.5, the recovery of dissolved solids to the concentrate is 74%. Considering the high water-removal ratio, losses to the condensate should be considered acceptable.

Table 3.5 shows the analytical results for condensate samples taken during the run (Tecroveer, 2019). For reference, the limits from SANS 241:2015 (drinking water) and stage 3 reject effluent compositions are also included in the table. All the required parameters for these condensates are well within the required SANS 241:2015 drink water limits.

Table 3.5: EWRP stage 3 reject trial condensate compositions

Attribute	Unit	SANS 241:2015	Stage 3 reject	CF 7	CF 8
Water recovery	[%]	-	-	85.7%	87.5%
Conductivity	[mS/cm]	< 170	27.17	0.274	0.234
pH	[-]	5 – 9.7	8.24	8.98	9.10
Alkalinity as $CaCO_3$	[mg/L]	-	162	100	115
TDS	[mg/L]	< 1,200	24,530	158	194
Sodium	[mg/L]	< 200	8,084	12.3	39.3
Calcium	[mg/L]	-	1,291	3.71	4.81
Potassium	[mg/L]	-	1,212	0.87	11
Chlorides	[mg/L]	< 300	2,068	8.85	12.8
Sulfates	[mg/L]	< 250	13,359	13.2	4.61

Treatment of mixed brine

To further test the efficacy of the DyVaR system with more concentrated brines, a blend of previously generated concentrate combined with stage 3 reject effluent was generated. This mixed brine solution is approximately equivalent to a stage 3 reject concentrate with a CF of 3.13 (~68% volume reduction). Table 3.6 shows the concentrate compositions produced after reducing the original mixed brine volume by 50% (CF 2) and by 54.5% (CF 2.2) compared to the original composition (for reference). The concentration of this brine was stopped at CF 2.2 due to the turbidity of the brine.

Table 3.6: Mixed brine trial concentrate compositions

Attribute	Unit	Mixed brine	CF 2	CF 2.2
Water recovery	[%]	-	50%	54.5%
Conductivity	[mS/cm]	68.10	110.3	115.1
pH	[-]	7.03	5.7	5.62
TDS	[mg/L]	76,864	130,724	145,406
Sodium	[mg/L]	19,062	33,354	35,497
Calcium	[mg/L]	844	1,344	605
Potassium	[mg/L]	4,119	7,508	7,999
Chlorides	[mg/L]	8,883	16,518	19,346
Sulfates	[mg/L]	37,494	69,572	70,640

As with the stage 3 reject concentrates, the concentration of the mixed brine also results in some losses to the condensate. For TDS, the reduction ratio is 1.1-times (76 g/L – 145 g/L), with 86% recovery to the concentrate stream.

Table 3.7 shows the condensate compositions produced when reducing the mixed brine solution by 50% and 54.5%; For reference the limits from SANS 241:2015 (drinking water) and original mixed brine influent compositions are also included in the table. These data show that even when processing a much more concentrated feed brine solution, the condensates produced are still within the SANS 241:2015 specified ranges for drinking water.

Table 3.7: Mixed brine trial condensate compositions

Attribute	Unit	SANS 241:2015	Mixed brine	CF 2	CF 2.2
Water recovery	[%]	-	-	50%	54.5%
Conductivity	[mS/cm]	< 170	68.10	0.167	0.180
pH	[-]	6.0-9.7	7.03	9.04	9.09
TDS	[mg/L]	< 1,200	76,864	112	114
Sodium	[mg/L]	< 200	19,062	7.56	7.67
Calcium	[mg/L]	-	844	1.65	1.63
Potassium	[mg/L]	-	4,119	0.35	0.38
Chlorides	[mg/L]	< 300	8,883	2.78	1.00
Sulfates	[mg/L]	< 250	37,494	5.66	2.16

Removal of bacteria

Table 3.8 shows the bacteriological analysis performed on two condensates produced during the trial runs. Both condensates are within the required limits for each criterion measured.

Table 3.8: Bacteriological analysis of selected condensate samples

Attribute	Unit	SANS 241:2015	Stage 3 reject condensate CF 7	Mixed brine condensate CF 2.2
Total coliform bacteria	[count/100 mL]	< 10	Nil	Nil
Faecal coliform	[count/100 mL]	Nil	Nil	Nil
Heterotrophic plate count	[count/mL]	< 1,000	30	41

Removal of metals

The stage 3 reject effluent and the mixed brine feed contained small amounts of a number of metals, including zinc, aluminium, arsenic, nickel, cobalt, selenium, and antimony. It was observed that the condensates for both sets of the influent had metal levels below the specified SANS 241:2015 limits. A complete listing of the amounts of each metal in each sample can be found in Appendix A of the DyVaR pilot plant report (Tecroveer, 2019).

Form of salt produced

The main salt produced during the pilot plant trials was sodium sulfate. It has been indicated that the anhydrous form of this salt is produced since the evaporation unit operates at the saturation point. Therefore, as the solution enters the unit, it crystalizes immediately. This was shown in "Figure 7, b)" the of the DyVaR pilot plant report (Tecroveer, 2019). It is shown again below in Figure 3.9 for the reader convenience.

a) Precipitated salts observed before brine has cooled down completely

b) Additional salts precipitated after brine cooled down to room temperature

Figure 7: Solids (stage 3 reject brine CF 8) showing precipitated salts

Figure 3.9: CF 8 reject brine and associated precipitated salts

4 CONCLUSIONS & RECOMMENDATIONS

In this study three different technologies for the treatment of mine waters and reverse osmosis brines were considered by CM Solutions. The technologies in question were the HybridICE^{TM} process from Sigrotec, a eutectic freeze crystallisation process from Prentec, and the DyVaR process from Salttech.

Based on the available information, the selected technologies were among the most appropriate technologies for treating RO concentrate. While more conventional brine concentrators could also be considered feasible, the DyVaR process is more advantageous and it therefore makes sense to exclude the conventional technology from consideration.

Regarding membrane technologies, RO and HPRO are not feasible due to the challenges that the technologies face with high-TDS brines and divalent ions that are commonly present in RO concentrate. FO is still a developing technology which may become feasible in the future. ED may be another option to consider for the treatment of RO concentrate due to its low operating cost and energy requirements, as well as its capability to handle high-TDS brines. A study would have to be conducted to determine the water recovery and energy consumption with the RO concentrate in question.

It is important to note that while the reviewed technologies are excellent options for RO brines, they are not appropriate for directly treat low-TDS mine water. This is not due physical/technological limitations, but rather due to the capital and operating costs (energy is the primary operating cost). The energy costs alone range from five to ten times more expensive than RO.

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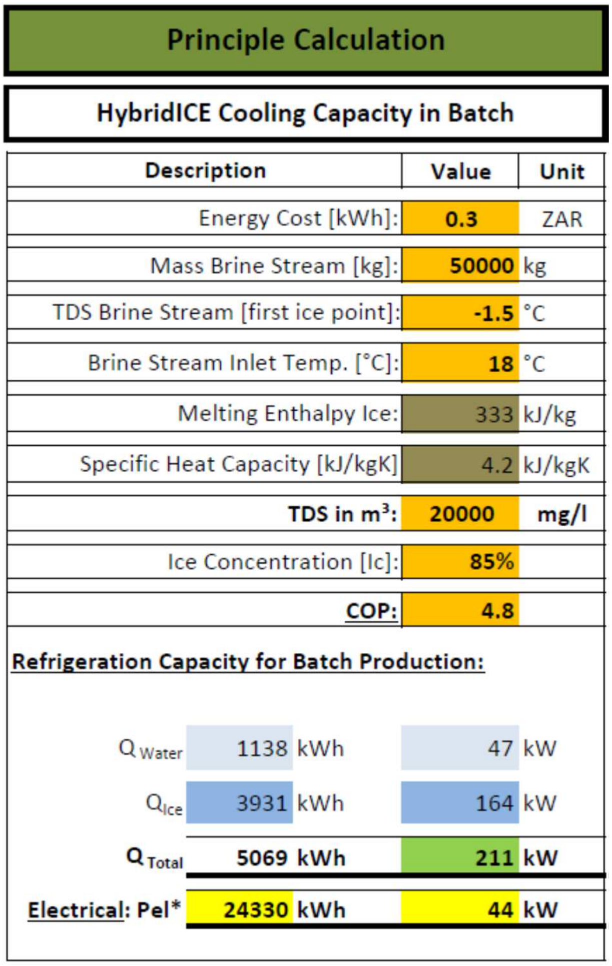
6 APPENDICES

This section presents information/summary/review for each of the pilot plants considered in this study.

6.1 Energy and mass balance for HybridICE^{TM} process

The following figures show the mass and energy balance calculations provided by Sigrotec. Included in these calculations are an estimate of the treatment costs based on estimated compressor and electrical requirements.



Principle Calculation

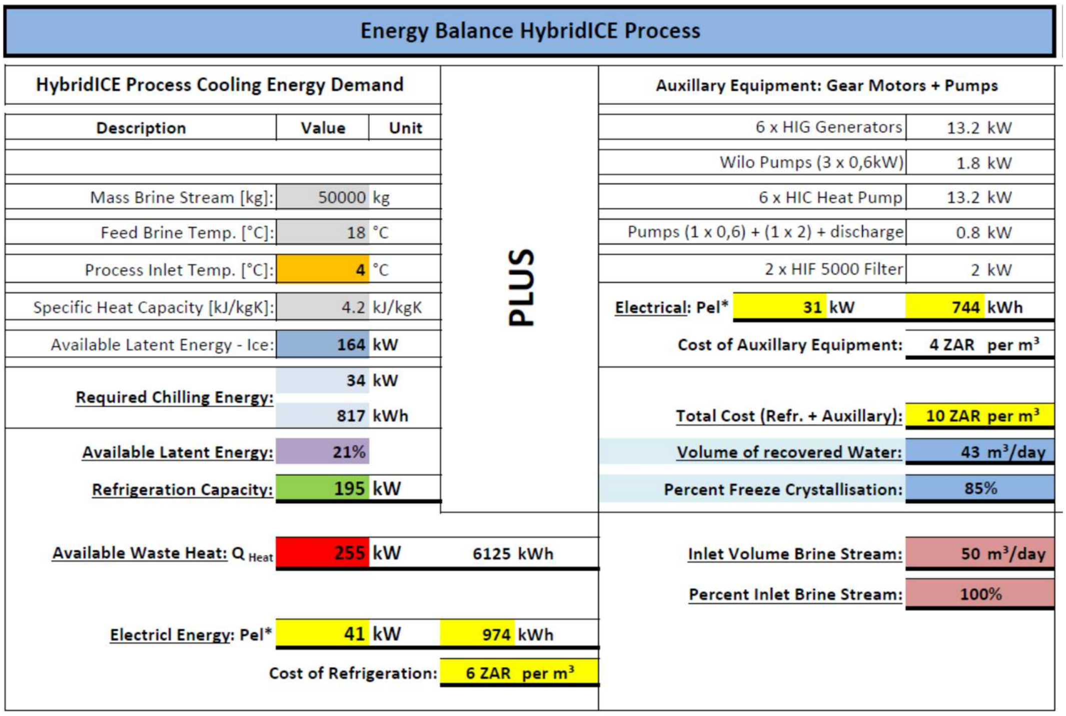
HybridICE Cooling Capacity in Batch

Description	**Value**	**Unit**
Energy Cost [kWh]:	**0.3**	ZAR
Mass Brine Stream [kg]:	**50000**	kg
TDS Brine Stream [first ice point]:	**-1.5**	°C
Brine Stream Inlet Temp. [°C]:	**18**	°C
Melting Enthalpy Ice:	333	kJ/kg
Specific Heat Capacity [kJ/kgK]	4.2	kJ/kgK
TDS in m^3:	**20000**	**mg/l**
Ice Concentration [Ic]:	**85%**	
COP:	**4.8**	

Refrigeration Capacity for Batch Production:

Q_{Water}	1138	kWh	47	kW
Q_{Ice}	3931	kWh	164	kW
Q_{Total}	**5069**	**kWh**	**211**	**kW**
Electrical: Pel*	**24330**	**kWh**	**44**	**kW**

Figure 6.1: HybridICE™ – Principle Calculation



Energy Balance HybridICE Process

HybridICE Process Cooling Energy Demand

Description	Value	Unit
Mass Brine Stream [kg]:	50000	kg
Feed Brine Temp. [°C]:	18	°C
Process Inlet Temp. [°C]:	4	°C
Specific Heat Capacity [kJ/kgK]:	4.2	kJ/kgK
Available Latent Energy - Ice:	164	kW
Required Chilling Energy:	34	kW
	817	kWh
Available Latent Energy:	21%	
Refrigeration Capacity:	195	kW

PLUS

Auxillary Equipment: Gear Motors + Pumps

6 x HIG Generators	13.2 kW
Wilo Pumps (3 x 0,6kW)	1.8 kW
6 x HIC Heat Pump	13.2 kW
Pumps (1 x 0,6) + (1 x 2) + discharge	0.8 kW
2 x HIF 5000 Filter	2 kW
Electrical: Pel*	**31 kW** / **744 kWh**
Cost of Auxillary Equipment:	**4 ZAR per m^3**
Total Cost (Refr. + Auxillary):	**10 ZAR per m^3**
Volume of recovered Water:	**43 m^3/day**
Percent Freeze Crystallisation:	**85%**

Available Waste Heat: Q$_{Heat}$ **255** kW **6125 kWh**

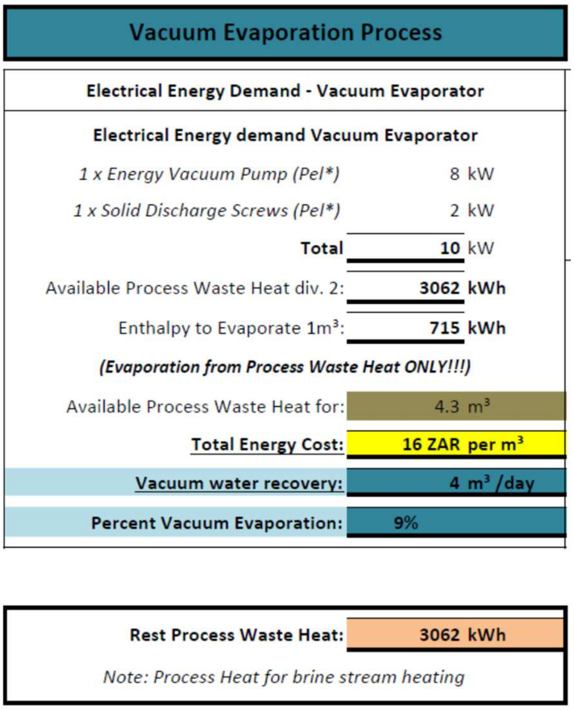
Electricl Energy: Pel* **41** kW **974** kWh

Cost of Refrigeration: **6 ZAR per m^3**

Inlet Volume Brine Stream: **50 m^3/day**

Percent Inlet Brine Stream: **100%**

Figure 6.2: HybridICE™ – Energy Balance



Vacuum Evaporation Process

Electrical Energy Demand - Vacuum Evaporator

Electrical Energy demand Vacuum Evaporator

1 x Energy Vacuum Pump (Pel)*	8 kW
1 x Solid Discharge Screws (Pel)*	2 kW
Total	**10** kW
Available Process Waste Heat div. 2:	**3062 kWh**
Enthalpy to Evaporate 1m^3:	**715 kWh**

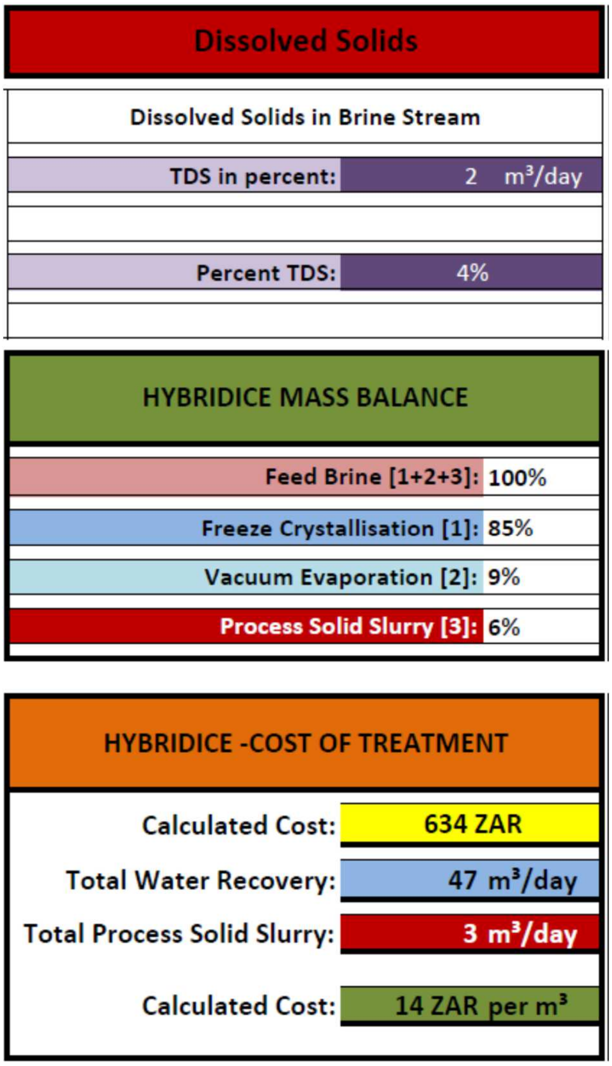
(Evaporation from Process Waste Heat ONLY!!!)

Available Process Waste Heat for:	4.3 m^3
Total Energy Cost:	**16 ZAR per m^3**
Vacuum water recovery:	**4 m^3 /day**
Percent Vacuum Evaporation:	**9%**

Rest Process Waste Heat: **3062 kWh**

Note: Process Heat for brine stream heating

Figure 6.3: HybridICE™ – Vacuum Evaporation Process



Dissolved Solids

Dissolved Solids in Brine Stream

TDS in percent:	2 m³/day
Percent TDS:	4%

HYBRIDICE MASS BALANCE

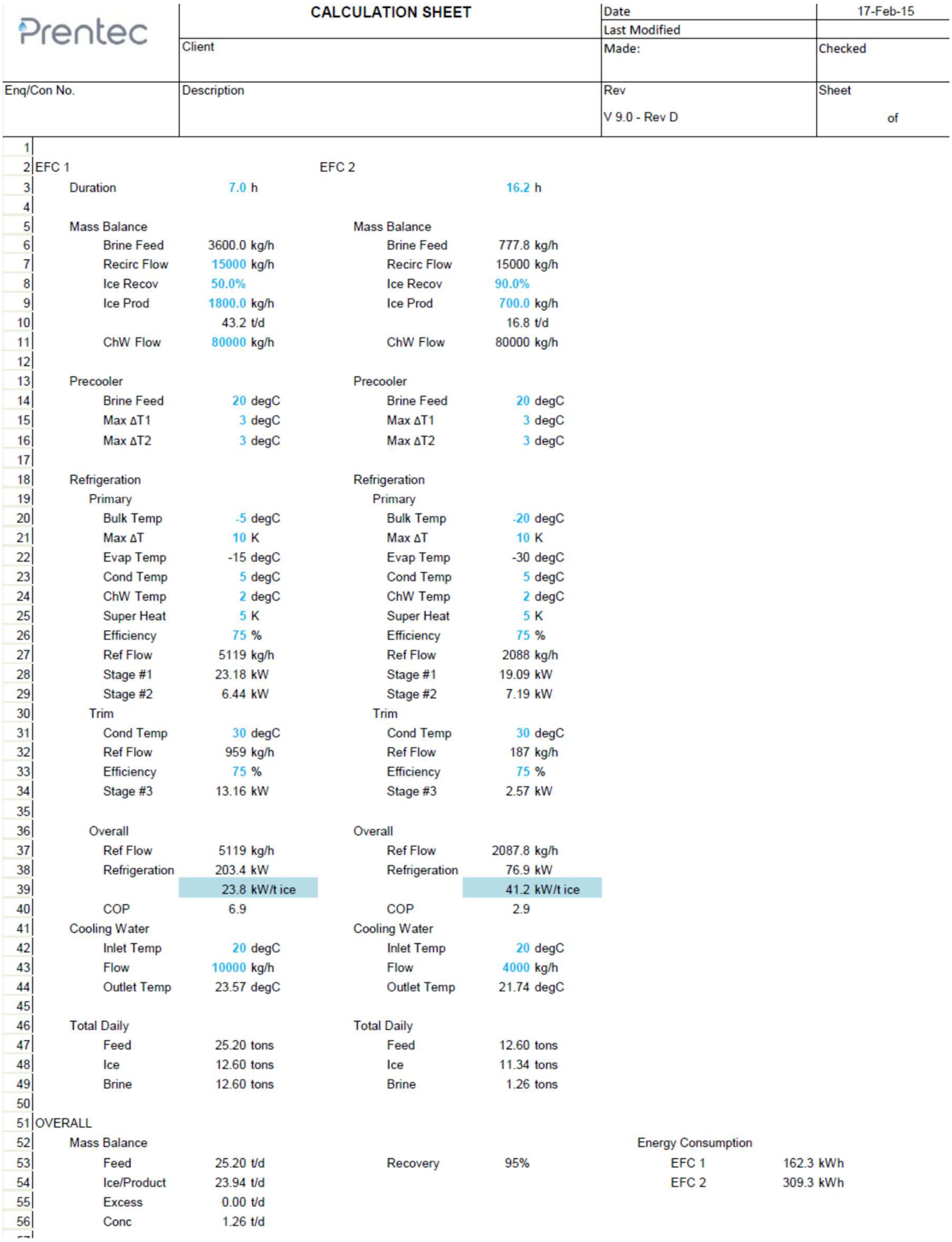
Feed Brine [1+2+3]:	100%
Freeze Crystallisation [1]:	85%
Vacuum Evaporation [2]:	9%
Process Solid Slurry [3]:	6%

HYBRIDICE -COST OF TREATMENT

Calculated Cost:	634 ZAR
Total Water Recovery:	47 m³/day
Total Process Solid Slurry:	3 m³/day
Calculated Cost:	14 ZAR per m³

Figure 6.4: HybridICETM – Additional calculations

6.2 Energy and mass balance for Prentec EFC process



Prentec

CALCULATION SHEET

Client		Date	17-Feb-15
		Last Modified	
		Made:	Checked
Enq/Con No.	Description	Rev V 9.0 - Rev D	Sheet of

#	EFC 1		EFC 2			
1						
2	EFC 1		EFC 2			
3	Duration	7.0 h		16.2 h		
4						
5	Mass Balance		Mass Balance			
6	Brine Feed	3600.0 kg/h	Brine Feed	777.8 kg/h		
7	Recirc Flow	15000 kg/h	Recirc Flow	15000 kg/h		
8	Ice Recov	50.0%	Ice Recov	90.0%		
9	Ice Prod	1800.0 kg/h	Ice Prod	700.0 kg/h		
10		43.2 t/d		16.8 t/d		
11	ChW Flow	80000 kg/h	ChW Flow	80000 kg/h		
12						
13	Precooler		Precooler			
14	Brine Feed	20 degC	Brine Feed	20 degC		
15	Max ΔT1	3 degC	Max ΔT1	3 degC		
16	Max ΔT2	3 degC	Max ΔT2	3 degC		
17						
18	Refrigeration		Refrigeration			
19	Primary		Primary			
20	Bulk Temp	-5 degC	Bulk Temp	-20 degC		
21	Max ΔT	10 K	Max ΔT	10 K		
22	Evap Temp	-15 degC	Evap Temp	-30 degC		
23	Cond Temp	5 degC	Cond Temp	5 degC		
24	ChW Temp	2 degC	ChW Temp	2 degC		
25	Super Heat	5 K	Super Heat	5 K		
26	Efficiency	75 %	Efficiency	75 %		
27	Ref Flow	5119 kg/h	Ref Flow	2088 kg/h		
28	Stage #1	23.18 kW	Stage #1	19.09 kW		
29	Stage #2	6.44 kW	Stage #2	7.19 kW		
30	Trim		Trim			
31	Cond Temp	30 degC	Cond Temp	30 degC		
32	Ref Flow	959 kg/h	Ref Flow	187 kg/h		
33	Efficiency	75 %	Efficiency	75 %		
34	Stage #3	13.16 kW	Stage #3	2.57 kW		
35						
36	Overall		Overall			
37	Ref Flow	5119 kg/h	Ref Flow	2087.8 kg/h		
38	Refrigeration	203.4 kW	Refrigeration	76.9 kW		
39		23.8 kW/t ice		41.2 kW/t ice		
40	COP	6.9	COP	2.9		
41	Cooling Water		Cooling Water			
42	Inlet Temp	20 degC	Inlet Temp	20 degC		
43	Flow	10000 kg/h	Flow	4000 kg/h		
44	Outlet Temp	23.57 degC	Outlet Temp	21.74 degC		
45						
46	Total Daily		Total Daily			
47	Feed	25.20 tons	Feed	12.60 tons		
48	Ice	12.60 tons	Ice	11.34 tons		
49	Brine	12.60 tons	Brine	1.26 tons		
50						
51	OVERALL					
52	Mass Balance				Energy Consumption	
53	Feed	25.20 t/d	Recovery	95%	EFC 1	162.3 kWh
54	Ice/Product	23.94 t/d			EFC 2	309.3 kWh
55	Excess	0.00 t/d				
56	Conc	1.26 t/d				

Figure 6.5: Prentec EFC process design mass and energy balance

6.3 SANS 241:2015

Analyses in mg/ℓ (Unless specified otherwise)	Risk	SANS 241 : 2015 Limits
pH - Value @ 25 °C	Operational	≥5 to ≤ 9.7
Electrical Conductivity in mS/m @ 25°C	Aesthetic	≤170
Total Dissolved Solids @ 180°C	Aesthetic	≤1200
Colour in PtCo Units	Aesthetic	≤15
Turbidity in N.T.U	Operational/Aesthetic	≤1 / ≤5
Total Alkalinity as $CaCO_3$	---	---
Langelier Index at 25°C	---	---
Chloride as Cl	Aesthetic	≤300
Sulphate as SO_4	Acute health/Aesthetic	≤500 / ≤250
Fluoride as F	Chronic health	≤1.5
Nitrate as N	Acute health	≤11
Nitrite as N	Acute health	≤0.9
Combined Nitrate & Nitrite	Acute health	≤1
Silica as SiO_2	---	---
Total Organic Carbon as C	Chronic health	≤10
E. coli / (100 mℓ)	Acute health	Not detected
Free and Saline Ammonia as N	Aesthetic	≤1.5
Sodium as Na	Aesthetic	≤200
Potassium as K	---	---
Calcium as Ca	---	---
Magnesium as Mg	---	---
Aluminium as Al (µg/ℓ)	Operational	≤300
Antimony as Sb (µg/ℓ)	Chronic health	≤20
Arsenic as As (µg/ℓ)	Chronic health	≤10
Barium as Ba (µg/ℓ)	Chronic health	≤700
Boron as B (µg/ℓ)	Chronic health	≤2400
Cadmium as Cd (µg/ℓ)	Chronic health	≤3
Total Chromium as Cr (µg/ℓ)	Chronic health	≤50
Copper as Cu (µg/ℓ)	Chronic health	≤2000
Iron as Fe (µg/ℓ)	Chronic health/Aesthetic	≤ 2000 / ≤300
Lead as Pb (µg/ℓ)	Chronic health	≤10
Manganese as Mn (µg/ℓ)	Chronic health/Aesthetic	≤ 400 / ≤100
Mercury as Hg (µg/ℓ)	Chronic health	≤6
Nickel as Ni (µg/ℓ)	Chronic health	≤70
Selenium as Se (µg/ℓ)	Chronic health	≤40
Uranium as U (µg/ℓ)	Chronic health	≤ 30
Zinc as Zn	Aesthetic	≤5

Figure 6.6: SANS 241:2015

(Technologies, 2015)