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Treatment of Spent Cation Exchange Regenerant with Eutectic Freeze Crystallisation



Feasibility Study for Demin Water Plant Botlek



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Summary

The goal of the study was to determine the technical and economic feasibility of Eutectic Freeze crystallisation (EFC) to treat the spent cation exchange (CIEX) regenerant at demin water plant Botlek (DWP Botlek). DWP Botlek is the largest demineralised water production plant in the Netherlands that applies CIEX for hardness removal from its source water.

For the technical assessment, a semi-industrial EFC pilot plant was installed at DWP Botlek and series of pilot tests were performed to study the EFC process performance. The pilot tests were performed in two phases, phase 1 involved the operation of the pilot unit in discontinuous mode (few hours each day) and phase 2 involved operation of the pilot unit in continuously mode (multiple days). In phase 1 the crystalliser was fed sequentially with two types of start solutions: (i) synthetic saline solution that contained approximately 20 wt% NaCl in the spent CIEX regenerant of DWP Botlek and (ii) start solution that contained multiple salts (4.9 wt% NaCl, 12.6 wt% CaCl₂ and 3.2 wt% MgCl₂). In phase 2 only the multicomponent start solution that contained 4.9 wt% NaCl, 12.6 wt% CaCl₂ and 3.2 wt% MgCl₂ was used. The main purpose of the pilot tests was to determine the influence of key variables on heat transfer and the quality of products, and eventually to achieve steady state operation.

We have noticed that when the solution produced by dissolving 20 wt% NaCl in spent CIEX regenerant was used during phase 1 of the pilot tests, the cooling plates scaled rapidly and the scale hampered the heat exchange in the crystalliser. However, when we replaced the start solution with the multicomponent solution the scaling of the plates significantly reduced and a higher total heat transfer in the crystalliser was achieved. Moreover, we have noticed that the eutectic temperature of the process stream gradually shifted to lower values during the continuous experiments of phase 2. This “freezing point depression” can be attributed to the gradual accumulation of Ca and Mg ions in the process stream. It must be noted that the system was not bled during these tests. Furthermore, it was noticed that the washing of ice and salt crystals dramatically improves the quality of the products.

Heat loss was the major challenge during the pilot testing. Melting of ice on the belt filter and during the transport from the settler to belt filter disturbed the tests. When cooling power is constant, melting of ice due to causes such as the higher atmospheric temperature, heat of the vacuum pumps etc. dilutes the process stream. This is unwanted for process efficiency and therefore should be a point of focus for further optimisation.

The results of the EFC pilot at DWP Botlek has been used to conduct an economic comparison of two alternative scenarios for a theoretical case in which the disposal of salt load to surface water is restricted. The two scenario's compared were:

- Scenario 1: Reverse Osmosis – Evaporation – Crystallisation
- Scenario 2: Reverse Osmosis – Eutectic Freeze Crystallisation – Crystallisation

Scenario 1 is the current state of the art scenario for this type of application. In scenario 2 the EFC is incorporated to reduce the flow of water to the crystalliser and to recover part of the NaCl as salt to reduce the volume of remaining salt that has to be disposed.

As indicated above EFC energy consumption should be optimised. A full scale design of an EFC installation similar to the pilot as used on DWP Botlek would require an energy requirement of approximately 62 kWh/ton feed. This includes precooling of the feed water to the EFC installation from 20 °C to 2 °C. Examples of easy achievable improvements are:

- Use of state of the art cooling machines with higher Energy Efficiency Ratio (EER) and lower cooling water consumption;
- Better designed filter belts to minimize heat input by warm air going through the ice and salt cakes and to minimize water consumption for cooling of the vacuum pumps;
- Reuse of cold streams (melting ice and/or cold salt slurry) to cool the feed water or to cool the cooling machine (and thus improve its efficiency).

Advanced heat integration by cooling the compressor and refrigerant condensate cooling will reduce the energy consumption for EFC to 30 – 35 kWh/ton feed.

The results of the “base case” economic comparison indicate that application of EFC in scenario 2 to treat spent CIEX regenerant is less expensive compared to the treatment process without EFC in scenario 1. Although the Capex and related yearly depreciation is higher the overall Opex is lower, mainly due to the lower disposal costs for the residual mixed salt. It should be noted however that the difference in Capex between the two scenarios is within the range of accuracy ($\pm 25\%$) of this conceptual design cost estimate. This leads to the conclusion that the costs for both treatment scenarios are at the same level.

Sensitivity analysis on the cost component in the economic comparison with the highest impact on the Opex, the total depreciation, shows that the estimated equipment costs for the EFC system can increase approximately 17% to obtain the break-even point for total Opex at the applied depreciation terms of 15 years and interest rate of 8%.

The sensitivity analysis on the disposal costs for the remaining mixed salt shows that these costs can decrease to € 65/tonne (base case € 150/tonne) to obtain the break-even point in total Opex.

It is encouraging that a newly commercialized technology such as EFC can already be very competitive, while it is still at the start of its learning curve and manufacturing cost down curve. Also the chloride system in this project is probably very challenging for any technology, while at the same time for EFC it is thermodynamically very unfavourable, due to the very low temperature required and the crystallization energy generated for this system. E.g. sulphate rich water streams reach the eutectic freezing point often already at higher temperatures and hence EFC is even more competitive compared to evaporative technologies.

Furthermore, EFC is especially suitable in areas where evaporative technologies struggle to perform, e.g. highly corrosive conditions and/or salts systems with high scaling and fouling tendencies. Under these circumstances EFC can treat systems that are very difficult to treat with conventional technologies.

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1 Introduction

1.1 Background

The disposal of aqueous waste streams with high salt content, such as those produced during membrane filtration or regeneration of industrial ion exchange (IEX) columns, is a growing challenge. Traditional disposal options include discharge to sea or other surface water bodies, discharge to sewer, deep well injection, land application or storage in evaporation ponds. However, these disposal options are often restricted because of unavailability, cost of transportation, environmental impact, regulatory requirements and/or public perception. The need is to find efficient, cost-effective and sustainable management options which does not simply shift a water quality problem from one area or one user to another.

One way of managing the waste streams with high salt concentration is to consider them a source of salt and water (Kim, 2011). Selective salt recovery and subsequent use or sale may offset the high operational costs that are typically associated with high recovery Zero Liquid Discharge (ZLD) processes (Kim, 2011). Moreover, reclamation of water from waste streams results in the reduction of the waste volume, eventually leading to cost savings in waste disposal.

Eutectic Freeze Crystallisation (EFC) is a promising technique that can retrieve salt and water in pure form from (concentrated) salt laden solutions, at a relatively low energy demand compared to conventional evaporation based separation processes (Van der Ham, 1999). The energy required to separate water as ice is significantly lower than that required to separate it as vapours (i.e. by evaporation), indicated by the fact that the heat of fusion of ice (6.01 kJ/mol) is much lower than the heat of vaporisation of water (40.65 kJ/mol) (Van der Ham, 1999; Nathoo et al., 2009).

Figure 1-1 presents a schematic representation of (continuous) salt and ice recovery by EFC. The process stream with dissolved salts enter the crystalliser (maintained at eutectic temperature) where heat is removed. From the crystalliser the process stream enters a separation unit where ice and salt are separated by (the force of) gravity. The flow from the bottom of the gravity separator (salt slurry) is fed to a salt slurry dewatering chamber, and the overflow of the gravity separator (ice slurry) is fed to a separate dewatering chamber. The dewatered ice and salt crystals are collected for further processing (if needed) and the supernatants, containing dissolved salts, are recycled back to the crystalliser.

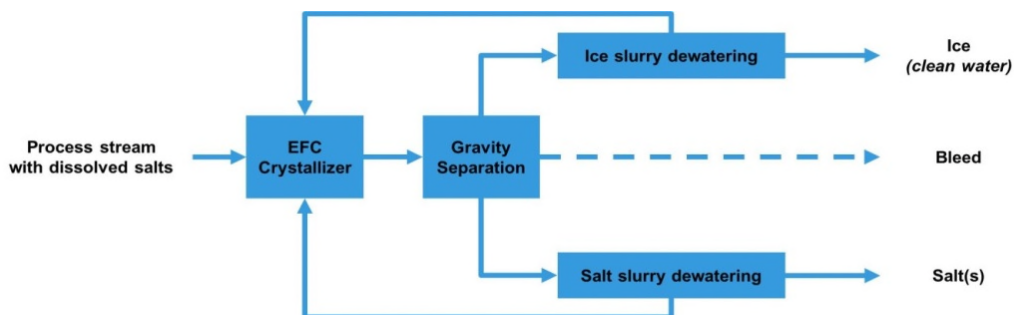


FIGURE 1-1 SCHEMATIC REPRESENTATION OF SALT AND ICE RECOVERY BY EFC.

The principle of EFC can be described using the phase diagram of a binary salt-water system (Figure 1-2). The basis of EFC is the existence of eutectic point. The eutectic point is a characteristic point in the phase diagram of any salt-water mixture where an equilibrium exists between ice, salt and the solution with a specific concentration. This specific concentration is called eutectic concentration and the temperature at which the equilibrium is achieved is called eutectic temperature. In multi-component mixtures more than one eutectic points may exist. When an unsaturated solution with a concentration lower than eutectic concentration (A) is cooled down below its freezing point, ice crystals start to form (B) by following the ice line. Further cooling decreases the temperature and increases the concentration of salt in the solution with the formation of ice crystals along the ice line (B to C). At point C (eutectic point), the concentration of salt reaches saturation and further cooling will result in the formation of ice and salt crystals simultaneously. Similarly, starting with a solution having a higher concentration than eutectic concentration will first result in the crystallisation of salt and the system will reach to the eutectic point (C) by following the salt solubility line (Genceli, 2008).

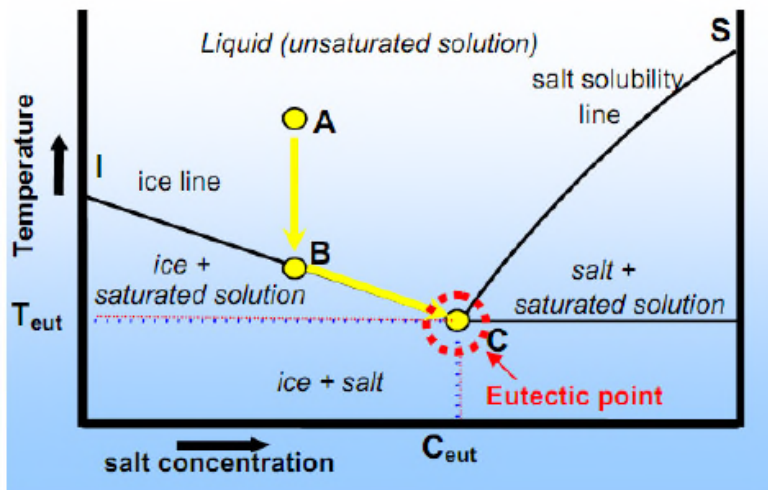


FIGURE 1-2 PHASE DIAGRAM OF A BINARY SALT-WATER SYSTEM AT LOW TEMPERATURE (GENCELI, 2008).

Cation exchange (CIEX) is a widely used hardness removal technique in water treatment. In this process multivalent cations, such as calcium (Ca^{+2}) and magnesium (Mg^{+2}), are removed from water by exchange with sodium ions (Na^{+}). When exhausted, the CIEX resin needs regeneration which is usually performed with 9 to 10 wt% NaCl solution, also known as the regenerant. The spent regenerant usually contains a mixture of Na, Ca, Mg and Cl ions, having a total salt concentration ranging from 2 to 4 wt%. Since most of the hardness (Ca, Mg) stripped-off from the resin is discharged in the first half of the regeneration, the volume of spent regenerant produced in the latter half of the regeneration process is usually more concentrated in Na and Cl ions. This part of the spent regenerant can be collected and treated by EFC to recover NaCl and water.

The Demin Water Plant Botlek (DWP Botlek) of Evides Industriewater is the largest demineralised water production plant in the Netherlands that applies CIEX for Hardness removal from its source water. The eutectic temperature and eutectic concentration of a binary H_2O -NaCl mixture is -21.1 °C and 23.2 wt% (Figure 1-3; Sterner et al.1988; Bodnar, 1993). However, the eutectic point for the spent CIEX regenerant produced at DWP Botlek was unknown because of the presence of additional ions such as Ca, Mg, etc. A semi-industrial EFC pilot setup was installed at DWP Botlek and operated for several months to realize stable operation of the pilot unit under eutectic conditions.

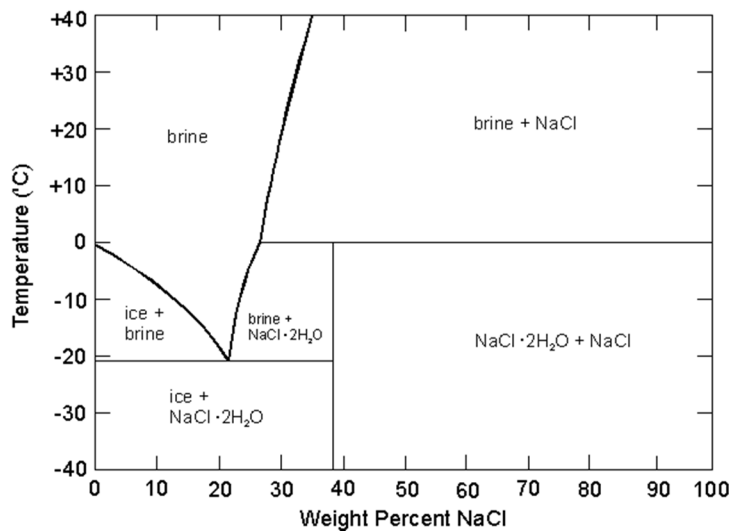


FIGURE 1-3 PHASE DIAGRAM OF BINARY H₂O-NaCl SYSTEM.

1.2 Scope and objectives of the study

The overall goal of the study was to investigate the technical and economic feasibility of EFC to treat the (NaCl concentrated part of the) spent CIEX regenerant at DWP Botlek.

A semi-industrial EFC pilot setup was installed at DWP Botlek to investigate the technical feasibility. Pilot tests evaluated the process performance in terms of heat transfer in the crystalliser, scaling of the heat exchangers, heat loss in the system, and the quantitative and qualitative recovery of NaCl and ice.

The economic feasibility of the EFC technology was determined in comparison with alternative treatment scenarios for spent CIEX regenerant.

1.3 Reading guide

Chapter 1 describes the background and sets the scope of this research. Chapter 2 describes materials and methods of the pilot study. Section 3 provides the results and discussion on the pilot tests. Section 4 focuses on the feasibility of EFC at DWP Botlek. Finally, section 5 describes the main conclusions from the study and gives recommendations for further research.

2 Pilot tests: Materials and methods

2.1 The pilot scale EFC setup

The EFC installation used in this study was a skid mounted machinery designed to process (semi-industrial) saline solutions at their eutectic point. The installation was constructed by EFC separations B.V. The setup was split in two main sections, namely the crystalliser-settler unit and the filtration unit (Figure 2-1). In the crystalliser-settler unit (Figure 2-2), the ice and salt slurries were produced. In the filtration unit (Figure 2-3), the ice and salt crystals were separated from the accompanying mother liquor by vacuum belt filtration. Figure 2-4 presents the process scheme of the EFC pilot plant.

The crystalliser-settler unit included the following equipment:

- A cooling machine (Tamson Centaur Cooler Unit TLC 50-120) with adjustable cooling capacity and temperature control of the heat transfer fluid. The cooling machine was designed with a primary and secondary cooling circuit. The primary cooling circuit used R404a as refrigerant in a classical vapour recompression cycle. The secondary cooling circuit was coupled with the primary circuit. Freezium, the heat transfer fluid, was circulated through the evaporator to absorb the heat. The production capacity was dependent on the cooling capacity of the cooling machine.
- A 400-L crystalliser (EFC Separations B.V.) which contained the heat exchangers. In the heat exchangers the heat transfer fluid was pumped to extract the heat from the solution.
- A scraper system (EFC Separations B.V.) with advanced rotating scrapers driven by an electrical motor. Once the ice and salt were formed in the crystalliser, a scale layer will start forming on the heat exchangers. This was intended to be scraped off with the advanced scraping system.
- A settling tank (EFC Separations B.V.) to separate the ice crystals from the salt slurry.
- A hose pump (Watson-Marlow 620 DuN) with adjustable flow to feed the crystalliser.
- A hose pump (Watson-Marlow 620 DuN) with adjustable flow to recirculate salt slurry from the settler to the crystalliser.
- A bleed pump (Watson-Marlow 620 DuN) .
- A hose pump (Bredel SPX-15) with adjustable flow to transport the salt slurry from the crystalliser unit to the separation unit.
- A progressing cavity pump (mono pump) (Bedu BW-035) with adjustable flow to transport the ice slurry from the crystalliser unit to the filtration unit.
- A process feed buffer vessel.
- An additional cooling machine to lower the temperature of the process feed buffer
- Start solution vessel.

The filtration unit included the following equipment:

- Pannevis RT type vacuum belt filter (1 m × 0.1 m filtration surface).
- Pannevis RT type vacuum belt filter (2 m × 0.1 m filtration surface).

Vacuum was applied under the product cake in each belt to draw the adhering mother liquor from the ice and salt crystals. The mother liquor was collected in vacuum separators/filtrate receivers and then pumped with hose pumps to the buffer vessel.

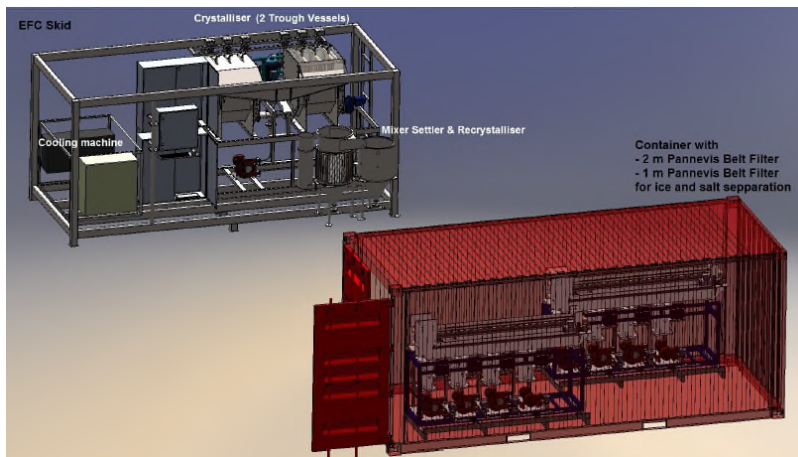


FIGURE 2-1 PILOT SCALE EFC SETUP



FIGURE 2-2 THE CRYSTALLISER-SETTLER UNIT



FIGURE 2-3 ONE OF THE SEPARATION UNITS

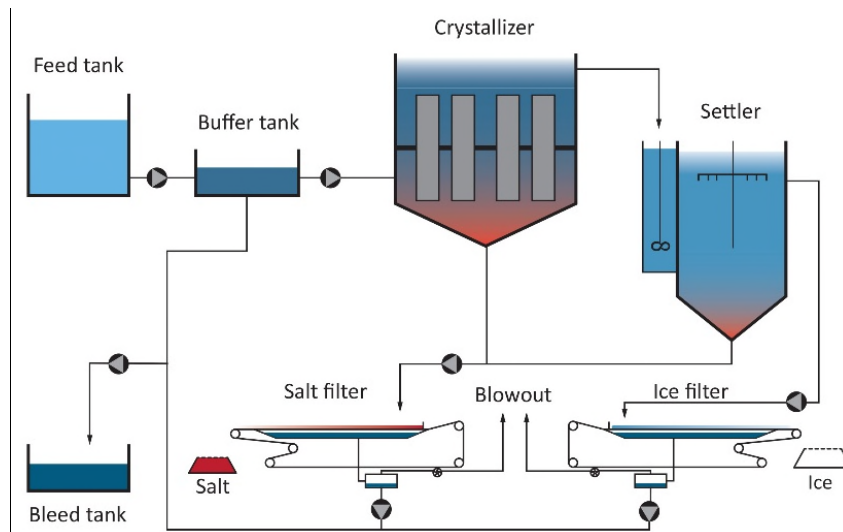


FIGURE 2-4 PROCESS SCHEME OF THE EFC PILOT SETUP

2.2 DWP Botlek: The pilot testing site

Demi water plant Botlek produces approximately 1,400 m³/h of demi water with a conductivity of < 0.06 μS/cm and TOC < 10 ppb. It uses fresh water from Brielse Meer as its raw water. The water from the Brielse Meer has a typical turbidity of 2 to 10 NTU, a typical conductivity of 500 to 850 μS/cm and approximate total hardness of 80 mg/L Ca. Figure 2-5 shows the process scheme of DWP Botlek. The first step in the demineralization process is the pre-treatment of water to remove suspended solids. Coagulation and flocculation of the suspended solids is carried out by dosing ferric chloride (FeCl₃). The water is then treated by dissolved air flotation (DAF) and filtration (anthracite/sand). The pre-treated water is then pumped to the softening section, where hardness removal takes place. The softening section consists of 8 CIEX vessels, filled with strong acidic CIEX resins, which is regenerated using 10 wt% NaCl solution as regenerant. The regenerant is produced by dissolving industrial grade NaCl in softened water from the softening section. After regeneration the salinity of the spent regenerant drops to approximately 2 wt%. The major ions in the spent regenerant are Na, Ca, Mg and Cl and relatively low(er) levels of potassium (K), sulphate (SO₄), copper (Cu), nickel (Ni) and iron (Fe). Table 2-1 presents the composition of two spent CIEX regenerant samples, collected on different dates, and at different point of time during the regeneration process. This provides an idea about how the composition of spent CIEX regenerant varies during the regeneration process

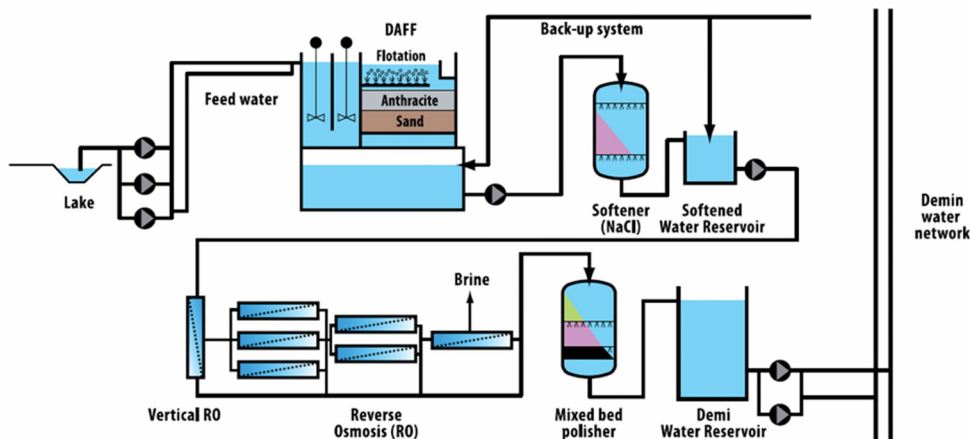


FIGURE 2-5 PROCESS SCHEME OF DWP BOTLEK

TABLE 2-1 COMPOSITION OF SPENT CIEX REGENERANT AT DWP BOTLEK

Parameter	unit	Sample of 26-6-2013	Sample of 1-10-2015
Chloride	mg/L Cl	41,000	12,500
Sulphate	mg/L SO ₄	< 200	86
Silicate	mg/L SiO ₂	-	5.68
Nitrate	mg/L NO ₃	< 100	3.2
o-phosphate	mg/L P	-	< 0.003
Potassium	mg/L K	426.5	-
Sodium	mg/L Na	5,953	3,400
Calcium	mg/L Ca	12,500	2,800
Magnesium	mg/L Mg	2,692	510
Strontium	mg/L Sr	86	18
Iron	µg/L Fe	5,125	< 250
Manganese	µg/L Mn	57.7	< 250
Aluminium	µg/L Al	< 100	260
Antimony	µg/L Sb	< 2	< 25
Arsenic	µg/L As	< 50	< 25
Barium	µg/L Ba	8,426	< 125
Boron	µg/L B	< 500	< 125
Cadmium	µg/L Cd	0.8	< 2.5
Copper	µg/L Cu	< 50	< 125
Lead	µg/L Pb	< 1	< 25
Nickel	µg/L Ni	188.3	< 25
Selenium	µg/L Se	< 50	< 25
Zinc	µg/L Zn	131.2	< 125
Rubidium	µg/L Rb	265	-
Lithium	µg/L Li	220	-

- refers to unavailability of data

Figure 2-6 shows typical variation in the concentration of Na, Ca and Mg during the 20 to 55 minutes after the start of regeneration of CIEX at DWP Botlek. Calculation has shown that most of the unused NaCl can be collected in the period from 27 - 54 minutes.

After softening, the softened water is treated by reverse osmosis (RO) to remove approximately 95% of the salinity. In order to achieve an acceptable removal of bicarbonate (HCO₃), caustic soda (NaOH) is dosed upstream of the RO. The remaining salinity in the reverse osmosis permeate is removed by mixed bed IEX (strong acidic CIEX resins and strong basic ALEX resins). The effluent of the mixed bed polisher is the demin water produced at DWP Botlek.

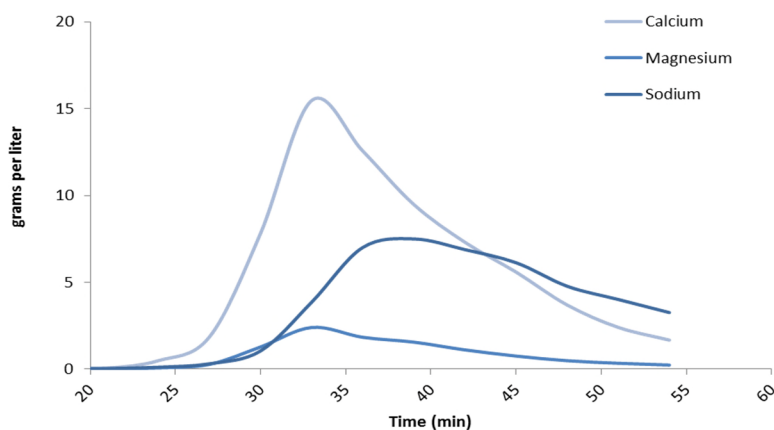


FIGURE 2-6 COMPOSITION OF SPENT CIEX REGENERANT FROM 20 TO 54 MIN OF REGENERATION PROCESS

2.3 Pilot tests

From the 1 July to 26 October 2015 the pilot unit was installed and started-up at the DWP Botlek site. Various measuring instruments of the installation (e.g. temperature sensors, pumps, flow meters etc.) were calibrated. The supply of compressed air was arranged for the belt filters and the pilot setup was insulated. Moreover, the researchers and process technologists from KWR and Evides Industriewater received training from the experts of EFC Separations on the operation of the pilot unit.

After the start-up, the pilot trials were carried out in two phases. In phase 1 the pilot setup was operated discontinuously, for a short duration during normal working hours (few hours each day). In phase 2 the pilot setup was operated continuously, first for 48 hours and later for 100 hours. Below are more details regarding the materials and methods used during pilot tests.

Phase 1: Discontinuous EFC pilot operation

From 27 October 2015 to 12 April 2016 discontinuous tests were carried out with the EFC pilot setup at Botlek. The main purpose of these tests was to determine the influence of the cooling machine set-point, flow of cooling liquid through the cooling plates in the crystalliser, scrapping speed in the crystalliser, recycle flow from the settler to the crystalliser etc. on the total heat exchange in the crystalliser. The scaling on the heat exchangers was monitored by a conjunction of torque of the scrappers, intensity of scrapping sound and the vibration of the crystalliser. Appendix I includes the full details of various settings tested during each day.

During the tests performed from 27 October to 24 November 2015 the crystalliser was fed with a synthetic saline solution that was prepared by dissolving approximately 20% NaCl (Broxozout 6-15, Boom The Netherlands) in the spent CIEX regenerant (Table 2-2). It was soon observed that the cooling plates in the crystalliser were scaled rapidly. Therefore, after 24 November 2016 the start solution was changed by introducing Ca and Mg ions (as non-crystallizing components) in the solution (Table 2-3). This was done to prevent scaling of the heat exchangers during the experiments (Pronk, 2006; De Graaf, 2012).

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Calcium chloride-2-hydrate, lab grade, Boom The Netherlands) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Magnesium chloride-6-hydrate, lab grade, Boom The Netherlands) were used to increase the Ca and Mg content in the start solution.

TABLE 2-2 COMPOSITION OF THE START SOLUTION USED IN PHASE 1 FROM 27 OCTOBER TO 24 NOVEMBER 2015 (20 WT% NaCl IN SPENT CIEX REGENERANT)

Parameter	unit	Sample of 01-10-2015	Sample of 22-10-2015
Sodium	mg/L Na	74,000	83,000
Calcium	mg/L Ca	2,200	1,700
Magnesium	mg/L Mg	380	280

TABLE 2-3 COMPOSITION OF THE START SOLUTION USED IN PHASE 1 AFTER 24 NOVEMBER 2015, AND DURING 48-H AND 100-H CONTINUOUS TRIALS

Parameter	Unit	Sample 1	Sample 2
Sodium	mg/L Na	49,420	54,000
Calcium	mg/L Ca	41,990	40,000
Magnesium	mg/L Mg	7,756	6,600
Chloride	mg/L Cl	169,900	175,000

Phase 2: Continuous EFC pilot operation

The EFC pilot plant was operated continuously for 48 hours (from 19 to 21 April 2016) and for 100 hours (from 9 May to 13 May 2016). The main aim of the continuous runs was to achieve steady operation of the EFC pilot plant in the production mode under eutectic condition. It is well-known that EFC is (economically) most feasible when the concentration of the salt to be recovered is close to the eutectic concentration. However, the concentration of NaCl in the spent CIEX regenerant available at Botlek was very low (2-4 wt%). Instead of pre-concentrating the spent regenerant by techniques like Forward Osmosis (FO), Reverse Osmosis (RO), Freeze Crystallisation (FC) etc. it was decided within the project group to use a synthetic start solution having higher concentration of dissolved salts. Therefore, a synthetic stream was produced at the pilot testing site which was approximately 7 times more concentrated in terms of NaCl, 11 times more concentrated in terms of CaCl₂ and 13 times more concentrated in terms of MgCl₂ compared to the spent CIEX regenerate that was produced at DWP Botlek (Table 2-3, Table 2-4).

TABLE 2-4 COMPARISON OF SPENT CIEX REGENERANT AND THE SYNTHETIC START SOLUTION USED IN THE CONTINUOUS TRIALS

Parameter	Spent CIEX regenerant	Start solution of long-term tests	Concentration factor
	wt%	wt%	-
NaCl	2.1	14.9	7
CaCl ₂	1.2	12.6	11
MgCl ₂	0.3	3.2	13

The continuous trials were conducted in several work shifts. Each shift continued for 8-12 hours. At least 2 operators were available at DWP Botlek during each shift. The test started by filling the start solution vessel, the buffer vessel, the crystalliser and the settler with the start solution (Table 2-3). As soon as the crystalliser was filled with the start solution, stirring was started and the start solution was circulated between the crystalliser, the settler and the feed tank to homogenize the quality. Subsequently, the cooling machine was started. When the solution was cooled in the crystalliser, ice started forming first. Therefore the ice belt filter and the ice slurry pump were started first. Later on, when the

system reached at eutectic condition, the salt belt filter and the salt slurry pump were also started. The ice slurry was transported from the top of the crystalliser to the settler. From the settler it is pumped to the vacuum belt filter for separation. The produced ice was weighed and then discharged. The filtrate of the ice belt filter was returned to the process stream buffer vessel. The salt slurry was pumped from the bottom of the crystalliser to a different vacuum belt filter for separation. The salt was also weighed and then discharged. The filtrate from the salt filter was returned to the process stream buffer vessel. As the salt and ice were removed the volume of process stream decreased in time. In order to maintain the level of the process stream buffer, fresh start solution was pumped to the process stream buffer tank whenever required.

Samples were regularly collected during the continuous trials and analysed for determination of Na, Ca, Mg and Cl at Aqualab Zuid. Samples were collected (in most instances) 1 hour after a new setting was placed. Following is the list of various streams that were sampled during long term continuous trials.

- Process stream (from the process stream buffer)
- Ice slurry
- Salt slurry
- Ice
- Salt
- Filtrate of ice filter
- Filtrate of salt filter

Appendix II includes the overview of the settings applied during the complete 48-h operation of the pilot scale unit. The text in red indicates change in setting(s) during the run. The main operational parameters that were varied during the 48-h test were the cooling machine set-point, flow of the cooling liquid in the heat exchangers, the feed flow to the crystalliser and the flow of ice slurry to the belt filter. As there was only one pump that delivered the flow of coolant to both the crystalliser and the pre-cooler, the variation in the coolant flow through the heat exchangers in the crystalliser also influenced the coolant flow through the pre-cooler.

For 100-h trial additional cooling capacity was integrated in the system by adding an extra cooling machine in order to cool the process stream buffer. The data from last 10 hours of the 100-h test is discussed in this report. Appendix III includes an overview of the settings tested during last 10 hours of the test.

Washing of ice and salt

Washing of products was not performed as part of the continuous cycle because the pilot installation was not equipped with the washing step. Nevertheless, one test was performed on small scale (batch scale), using a Buchner flask and vacuum pump. The aim was to determine the influence of washing of the products (ice and salt). For the test ice and salt slurries were extracted from the crystalliser, filtered through Buchner filter, and subsequently washed in 2 steps. Demi water, just above the freezing point, was used for washing the ice crystals. The washing of the salt was performed with a 20 wt% NaCl solution. Samples of the washing liquids, ice, salt and filtrates were collected and sent to Aqualab Zuid for the analysis of Na, Ca, Mg and Cl.

3 Pilot tests: Results and discussion

3.1 Phase 1: Discontinuous EFC pilot operation

In this phase the EFC installation was operated during the normal working hours (no overnight tests). Short term trials were carried out to investigate the highest achievable total heat exchange without encountering the scaling of cooling plates. During the tests performed from 27 October to 24 November 2015 the crystalliser was fed with a synthetic saline solution that was prepared by dissolving approximately 20 wt% NaCl in the spent CIEX regenerant (Table 2-2). In general, it was noticed that the cooling plates were scaled rapidly (within 45 min to 2 hours). With scaling of the cooling plates the torque of the scrapers increased rapidly and the total heat exchange gradually decreased. For example, Figure 3-1 shows the temperature profile of the crystalliser during the test performed on 11 November 2016 and Figure 3-2 shows the torque, total heat exchange and ΔT (the temperature difference between the cooling liquid entering the heat exchangers and the average temperature of the process stream in the crystalliser) during this test. It can be seen in Figure 3-1 that at approximately $-21.3\text{ }^{\circ}\text{C}$ the system reached eutectic point and the temperature in the crystalliser became stable, however only for a short duration. Figure 3-2 shows that the torque rapidly increased in few minutes after the system reached eutectic point. The rapid increase in torque was an indication of ice scaling on the plates. Also, a heavy ticking noise from the crystalliser was noticed together with the rising torque. The scaling of the plates resulted in the decrease of the total heat exchange in the crystalliser, eventually leading to gradual lowering of the solution temperature in the crystalliser. Another example is provided as Figure 3-3 which shows the torque, total heat exchange and ΔT during the test performed on 18 November 2015. Again, a rapid increase in torque and gradual lowering of heat exchange due to scaling of the cooling plates can be observed.

A scale layer forms when solid particles (either salt or ice) adhere to the surface of the heat exchanger. The scale hampers the heat transfer due to its thermal resistance. Decrease in heat transfer is generally undesired in EFC because it directly influences the energy efficiency of the system. To prevent the scaling of the cooling plates, scrapers were available that continuously removed scaling from the surface of the plates. However, the scaling was so severe that even increasing the scrapping speed from 35 RPM to 45 RPM in one of the tests was not much effective. Therefore, actions, such as increasing the temperature of the cooling machine or decreasing the flow of cooling liquid had to be taken to melt away the scale from the cooling plates.

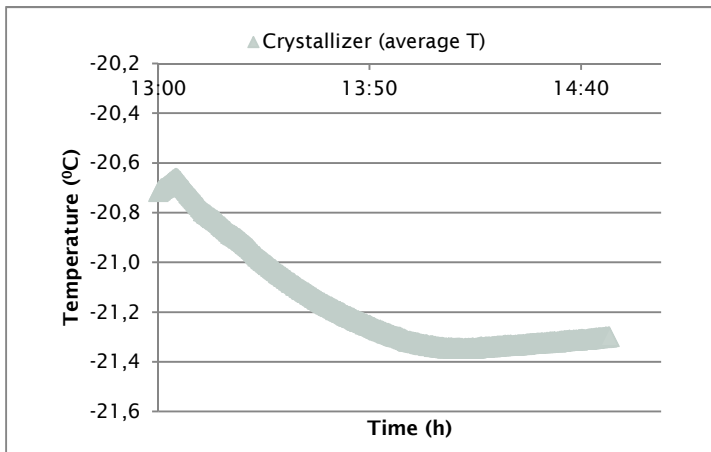


FIGURE 3-1 TEMPERATURE PROFILE OF CRYSTALLISER DURING SHORT TERM TEST OF 11 NOVEMBER 2015

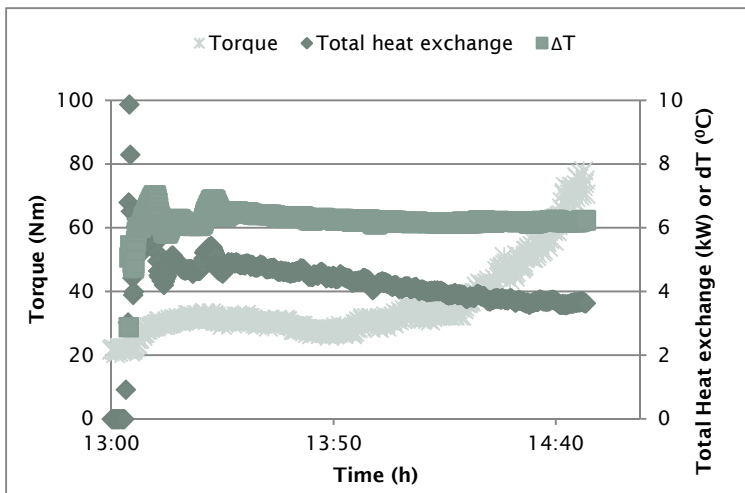


FIGURE 3-2 TORQUE, TOTAL HEAT EXCHANGE AND ΔT IN THE CRYSTALLISER DURING SHORT TERM TEST OF 11 NOVEMBER 2015

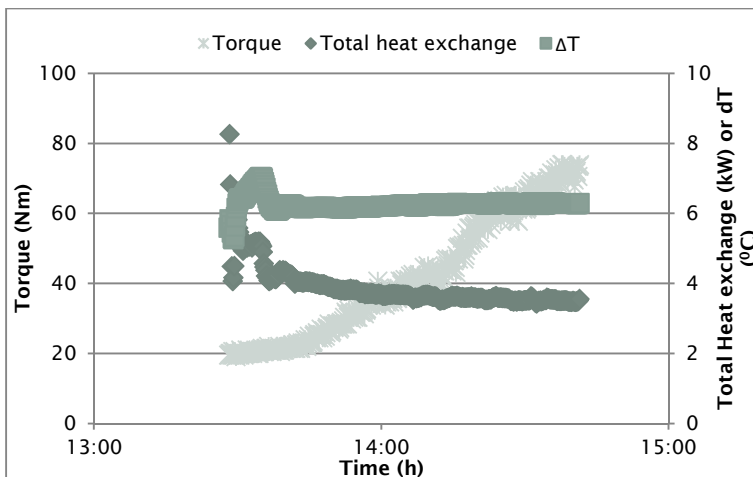


FIGURE 3-3 TORQUE, TOTAL HEAT EXCHANGE AND ΔT IN THE CRYSTALLISER DURING SHORT TERM TEST OF 18 NOVEMBER 2015

The short term tests performed from 8 March 2016 to 12 April 2016 were carried out with a different start solution (14.9% NaCl, 12.6% CaCl₂, 3.2% MgCl₂). Now the solution contained significant concentrations of Ca and Mg, besides the Na and Cl. This was done to prevent scaling of the heat exchangers during the experiments. This step was taken based on the results of De Graaf, 2012 who reported a significant decrease in scaling when non-crystallizing salts were added in the start solution. With the new recipe of the start solution the scaling of heat exchangers was noticeably reduced. And the pilot plant could be operated for a longer period. Figure 3-4 presents the results of torque, total heat exchange and ΔT during the test performed on 12 April 2016. It can be seen that the parameters remained stable for more than 4 hours after the system reached eutectic conditions (around 11:00 h). Moreover, a significantly higher heat exchange (around 4.3 kW at ΔT of 7.9 °C) was achieved.

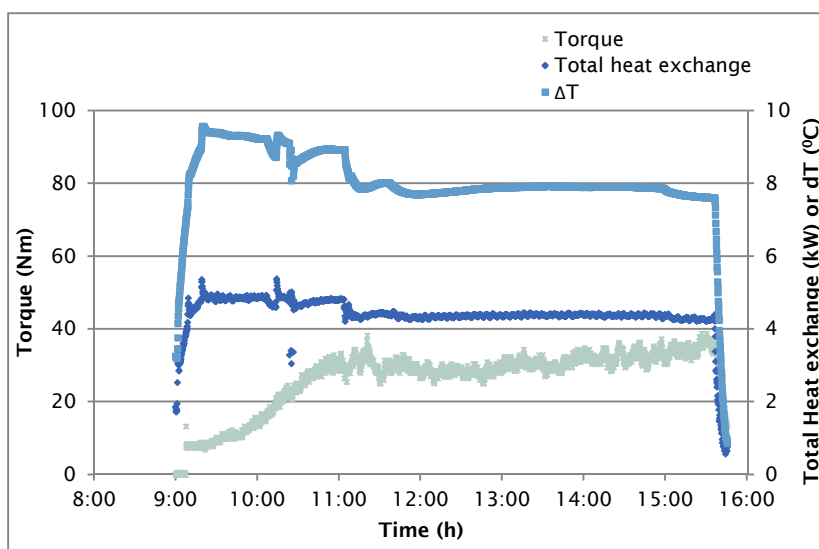


FIGURE 3-4 TORQUE, TOTAL HEAT EXCHANGE AND ΔT IN THE CRYSTALLISER DURING SHORT TERM TEST PERFORMED ON 12 APRIL 2016

3.2 Phase 2: Continuous EFC pilot operation

48-h trial

The EFC pilot plant was continuously operated for 48 hours using the start solution composition of which is presented in Table 2-3. As the start solution was a multi-component stream (NaCl, CaCl₂, MgCl₂), the eutectic temperature for the crystallisation of NaCl was found to be around -26 °C, based on the observation that the temperature in the crystalliser remained stable for multiple hours (Figure 3-5). The temperature in the crystalliser gradually decreased during the test duration, i.e. the eutectic temperature was gradually shifting to lower values. This was probably due to the accumulation of Ca and Mg ions in the process stream. Table 3-1 shows the variation in the composition of process stream during the test. It is evident that the concentration of NaCl in the solution decreased, and on the other hand concentration of CaCl₂ and MgCl₂ increased.

Approximately 190 kg of ice and 0.6 kg of salt was separated from the respective slurries on the belt filters in 48-h. The melting of ice on the belt filter was noticed frequently during the test because of the higher temperature of the surroundings. Moreover, it was noticed that a significant amount of ice melted while transportation of the ice slurry from the settler to the ice filter. Moreover, due to the heat of vacuum pumps the filtrates of both belt filters were heated. As a result, the temperature of the process stream buffer was higher compared to

the crystalliser. It can be seen in Figure 3-5 that throughout the 48-h test the temperature of the process stream buffer remained 6-7 °C higher compared to the average temperature in the crystalliser. It means that a significant amount of cooling power was used in cooling the feed solution instead of crystallizing ice and salt. An option to minimize the energy consumption in EFC would be to reduce the heat loss over the filtration unit, by placing the belt filters in the enclosed cooled area and by reducing the length of the hoses that return the filtrate to the buffer vessel. A higher flow of the streams through hoses and pipes would also reduce the time that the fluid spends in the warm environment, thus losing cold. The vacuum flow through the cake can be regulated as well, mitigating warm air to be transported through the ice cake.

Figure 3-6 shows the total heat exchange, torque and ΔT in the crystalliser. In general, a stable total heat exchange of 4.3-4.5 kW could be maintained at ΔT of 7-8 °C during most of the test duration. During the 48-h trial, set points of the cooling machine and coolant flow through the heat exchangers were varied to achieve higher values of total heat exchange in the crystalliser. The highest total heat exchange achieved during the 48-h test was 5.1 kW, however for a short duration. This was achieved when the cooling machine was set at the lowest set point of the 48-h test, i.e. -38 °C, and the flow of the cooling liquid through the heat exchangers was the highest of the 48-h test, i.e. 12 L/min. However, the crystalliser could not be operated for long with these settings because of increasing torque and ticking sound which represented scaling of the plates. At torque of > 90 nm the crystalliser started producing loud scrapping sound and therefore the flow of the cooling liquid in the heat exchangers was decreased to melt away the scaling.

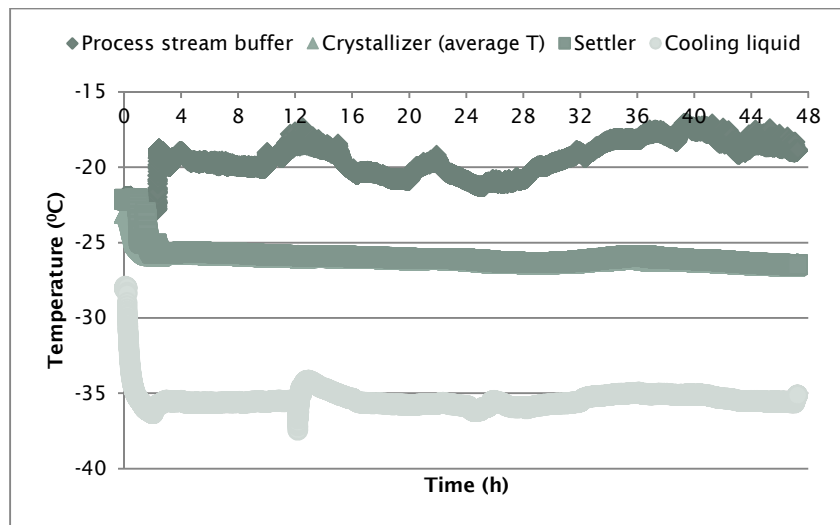


FIGURE 3-5 TEMPERATURE PROFILE OF PROCESS STREAM BUFFER, CRYSTALLISER, SETTLER AND THE COOLING LIQUID DURING 48-H TRIAL

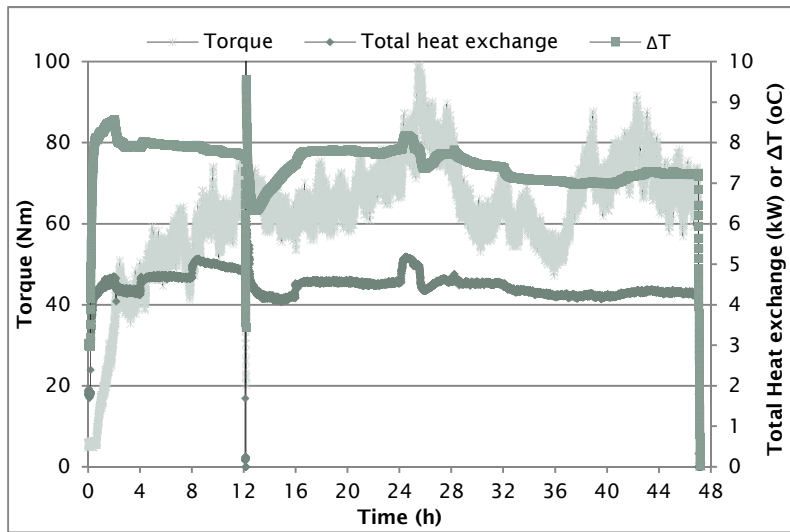


FIGURE 3-6 TORQUE, TOTAL HEAT EXCHANGE AND ΔT IN THE CRYSTALLISER

TABLE 3-1 QUALITY OF PROCESS STREAM DURING 48-H TEST

Test duration (h)	Process stream buffer		
	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%
0	12.6	11.6	3.0
4	12.7	11.6	3.0
8	12.7	11.7	3.1
12	12.6	11.8	3.1
16	12.0	12.3	3.2
20	12.6	12.2	3.2
24	12.1	12.1	3.1
28	12.0	12.3	3.2
32	11.9	12.5	3.2
36	11.9	12.3	3.2
40	11.6	12.1	3.1
44	11.7	12.4	3.2

Table 3-2 presents the composition of ice slurry, ice and the filtrate of ice filter. It can be seen that at various instances the ice slurry and the ice filtrate were similar in composition. This shows that a significant amount of ice was melting on the belt filter, e.g. at 4 h, 8 h, 20 h etc. In ideal situation, if there was no melting of ice on the belt filter, the filtrate would have been more concentrated compared to the ice slurry. At 44 h it was visually noticed that the ice cake was thick and the melting was relatively lower. However, in Table 3-2 it is not reflected, i.e. the filtrate at 44 h is not significantly concentrated compared to the ice slurry. It should be noted that the ice was not washed during the 48-h test because continuous washing was not integrated in the pilot setup.

TABLE 3-2 QUALITY OF ICE SLURRY, ICE AND FILTRATE OF ICE FILTER DURING 48-H TEST

Test duration (h)	Ice slurry			Ice			Ice belt filtrate		
	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%
0	-	-	-	-	-	-	-	-	-
4	12.5	11.5	3.0	4.0	3.3	0.9	12.6	11.5	3.0
8	12.7	11.6	3.0	5.6	3.8	1.0	12.6	11.7	3.0
12	12.4	11.7	3.1	7.1	2.2	0.6	13.5	12.8	3.3
16	12.4	11.8	3.1	-	-	-	12.5	12.0	3.1
20	12.6	12.4	3.2	-	-	-	12.6	12.2	3.2
24	11.8	11.9	3.1	-	-	-	12.1	12.2	3.2
28	12.3	12.8	3.3	-	-	-	12.0	12.6	3.3
32	12.0	12.6	3.3	-	-	-	12.2	12.9	3.3
36	12.1	12.4	3.2	-	-	-	11.9	12.4	3.2
40	11.8	12.3	3.2	5.3	3.4	0.9	11.8	12.3	3.2
44	11.4	12.1	3.1	3.9	2.8	0.7	11.9	12.8	3.3

- Refers to unavailability of data

Table 3-3 shows the composition of salt slurry, salt and salt filtrate during 48-h test. It can be seen that the wt% of NaCl in the salt collected from the belt filter was much higher compared to CaCl₂ and MgCl₂, confirming the fact that NaCl was the main salt that was crystallised. As the salt was not washed, small concentrations of the mother liquor was entrapped between the crystals.. As indicated in the phase diagram, NaCl·2H₂O is formed at eutectic crystallisation instead of pure NaCl crystals. At 0.1 °C the re-crystallisation to the anhydrate takes places, which is the desired product in the process. However, the salt samples collected during pilot testing were not heated to re-crystallise anhydrous NaCl.

TABLE 3-3 QUALITY OF SALT SLURRY, SALT AND FILTRATE OF SALT FILTER DURING 48-H TEST

Test duration (h)	Salt slurry			Salt			Salt belt filtrate		
	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%
0	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-
8	12.7	11.8	3.1	48.2	0.9	0.2	13.0	11.9	3.1
12	13.0	12.1	3.1	69.9	0.4	0.1	12.8	12.0	3.1
16	13.5	12.7	3.3	63.8	0.7	0.2	12.6	12.0	3.1
20	12.5	12.4	3.2	74.1	0.4	0.1	12.5	12.3	3.2
24	10.7	10.7	2.8	70.6	0.4	0.1	12.3	12.3	3.2
28	12.7	13.0	3.4	69.5	0.7	0.2	12.3	12.7	3.3
32	12.0	12.6	3.3	-	-	-	12.1	12.6	3.3
36	12.2	12.6	3.3	-	-	-	12.2	12.6	3.3
40	12.1	12.7	3.3	74.9	0.7	0.6	12.3	12.6	3.3
44	12.1	12.7	3.3	75.8	0.6	0.2	11.9	12.7	3.3

- Refers to unavailability of data

100-h trial

The EFC pilot plant was operated for 100 hours using a start solution with similar composition as 48-h trial. Figure 3-7 presents the temperature profile of the crystalliser, settler, process feed buffer and the cooling liquid. In-line with the 48-h trial, the eutectic condition was achieved around -26 °C. Only the results of last 10 hours have been discussed

here. During the last 10 hours the process was stable, as can be seen in Figure 3-7. During this period approximately 110 kg of ice and 0.4 kg of salt was produced on the belt filters. Throughout the last 10 hours the temperature of the process stream buffer remained 3-4 °C higher compared to the average temperature in the crystalliser. Compared to the 48-h trial the buffer was 3-4 °C lower in temperature than the average temperature in the crystalliser. This was because of the fact that the buffer was cooled in this experiment with an extra cooling machine. This cooling of the buffer p resulted in higher rate of ice and salt production on the belt filters, but other factors might also have played a role. For example, in the last 10 hours of the 100-h test the smaller belt filter (RT 0.1×1 m) was used for ice separation. In the 48-h test the larger belt filter was used for ice filtration. This resulted in less melting of ice compared to the 48-h test. Moreover, in these 10 hours the flow of coolant in the heat exchangers of the crystalliser was 13.5 L/min, unlike the 48-h test where the maximum applied coolant flow was 12 L/min. Furthermore, feed flow and the recycle flow from the settler to the crystalliser was significantly lower compared to the 48-h test, resulting in a much longer residence time of the process stream in the crystalliser.

Figure 3-8 shows the torque, ΔT and the total heat exchange in the crystalliser during last 10 hours of the 100-h trial. The ΔT was in the similar range (± 1 °C) to the 48-h test. The torque was much higher compared to the 48- trial. Moreover, the crystalliser could be operated at a higher heat exchange and higher torque compared to 48-h test.

Table 3-4 presents the composition of ice slurry, ice and ice belt filtrate sampled during the last 10 hours of the 100-h test. Table 3-5 presents the composition of salt slurry, salt and salt belt filtrate. In general, the quality of produced ice and salt was comparable to the products obtained during the 48-h test. However, the concentration of CaCl_2 and MgCl_2 in the products obtained during 48-h test was higher.

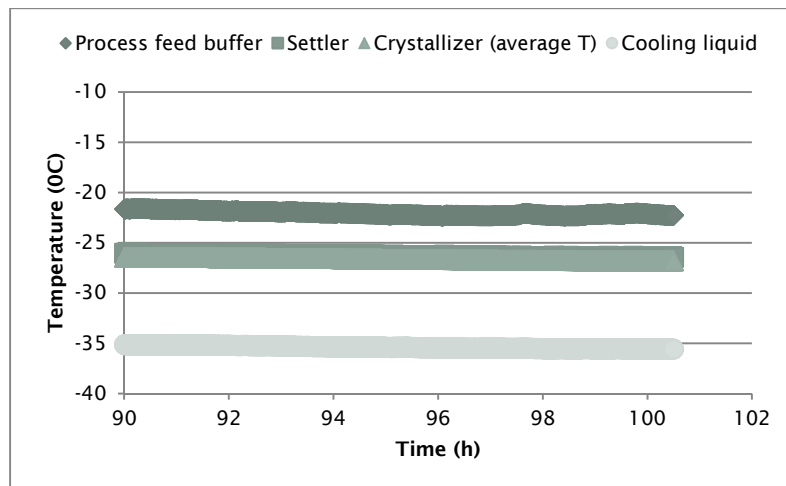


FIGURE 3-7 TEMPERATURE PROFILE OF PROCESS STREAM BUFFER, CRYSTALLISER, SETTLER AND THE COOLING LIQUID DURING LAST 10 HOURS OF THE 100-H TRIAL

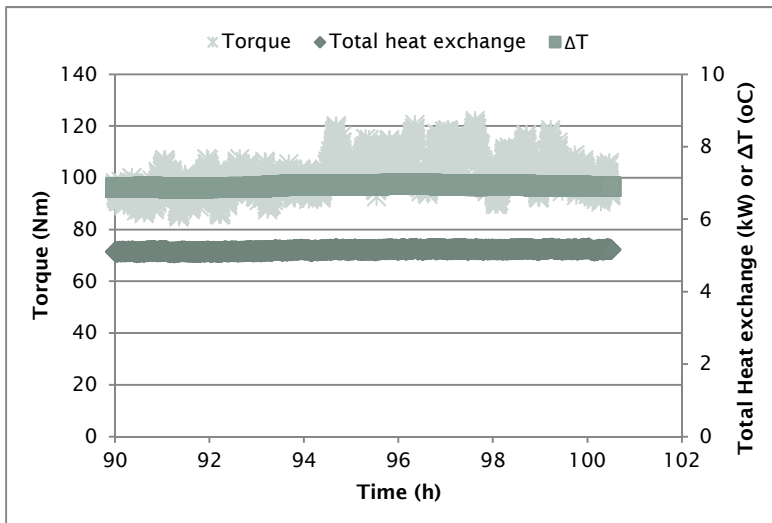


FIGURE 3-8 TORQUE, TOTAL HEAT EXCHANGE AND ΔT IN THE CRYSTALLISER

TABLE 3-4 QUALITY OF ICE SLURRY, ICE AND FILTRATE OF ICE FILTER DURING 100-H TEST

Test duration (h)	Ice slurry			Ice			Ice belt filtrate		
	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%
96	12.0	11.8	3.0	4.6	1.1	0.3	12.3	12.3	3.1
97	12.1	12.0	3.0	6.5	1.6	0.4	12.4	12.4	3.2
99	11.9	12.0	3.1	5.5	1.3	0.3	12.2	12.4	3.1

TABLE 3-5 QUALITY OF SALT SLURRY, SALT AND FILTRATE OF SALT FILTER DURING 100-H TEST

Test duration (h)	Salt slurry			Salt			Salt belt filtrate		
	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%	NaCl wt%	CaCl ₂ wt%	MgCl ₂ wt%
96	13.1	12.3	3.1	67.7	0.11	0.03	12.9	12.7	3.2
97	12.0	12.3	3.1	72.6	0.13	0.03	12.4	12.2	3.1
99	12.3	12.2	3.1	65.9	0.17	0.04	12.2	12.5	3.2

During the 100-h continuous operation at some points in the process the solid fraction in the solution was determined. This was done by sampling the solid / liquid mixture and directly filtering it through the Buchner filter. Dividing the mass of the solid by the mass of the initial solution, the solid fraction was determined. Table 3-6 shows the percentage of solids in the ice slurry at three points in the process. It can be seen that the solids content significantly decreased when the ice slurry reached the belt filter. This indicates a loss of heat during the transportation of slurry to the belt filter which reduced the overall ice production in the process.

TABLE 3-6 PERCENTAGE OF SOLIDS IN THE ICE SLURRY AT 3 POINTS IN THE EFC LOOP

Test duration (h)	Solids content at settler inlet	Solids content at settler outlet	Solids content at ice filter inlet
	%	%	%
90	16.4	14.0	8.9
91	16.5	14.9	10.5
92	16.9	15.9	11.2
93	15.8	15.7	11.4
94	18.5	18.0	12.7
95	18.4	18.2	12.9
96	18.9	18.6	12.5

Ice and salt washing

In this study although the continuous washing of ice and salt could not be realized within the pilot setup, small scale (batch tests) were carried out to determine the influence of washing on the product purity. Figure 3-9 shows the results of a test in which ice slurry was extracted from the top of the crystalliser and filtered immediately by the help of a Buchner filter. Afterwards the ice retained on the filter was washed in 2 steps with demi-water. It can be seen that washing of ice improved the quality and after the first round of washing the wt% of NaCl, CaCl₂ and MgCl₂ decreased to <1%, which was according to previous work (Vaessen, 2003). Critical factor is the temperature of the washing liquid. If the washing liquid is warmer compared to the ice temperature, a reduction in the quantity of recovered ice due to melting will take place.

Figure 3-10 presents the results of a salt washing test in which the salt slurry was extracted from the bottom of the crystalliser and filtered immediately. Subsequently, the salt retained on the filter was washed using a 20% solution of NaCl. It can be seen that the CaCl₂ and MgCl₂ concentration decreased with each washing. The wash liquid had a lower concentration of these salts therefore it dissolved them from the crystals, eventually leading to purer NaCl.

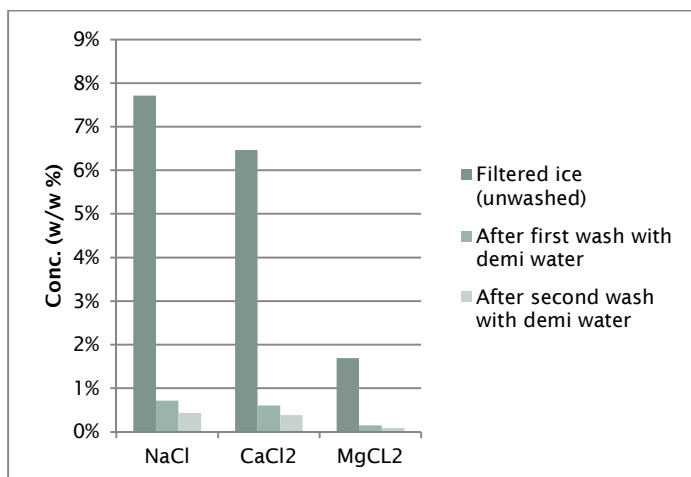


FIGURE 3-9 QUALITY OF ICE AS A FUNCTION OF WASHING WITH DEMI WATER AT SMALL SCALE BY BUCHNER FILTER

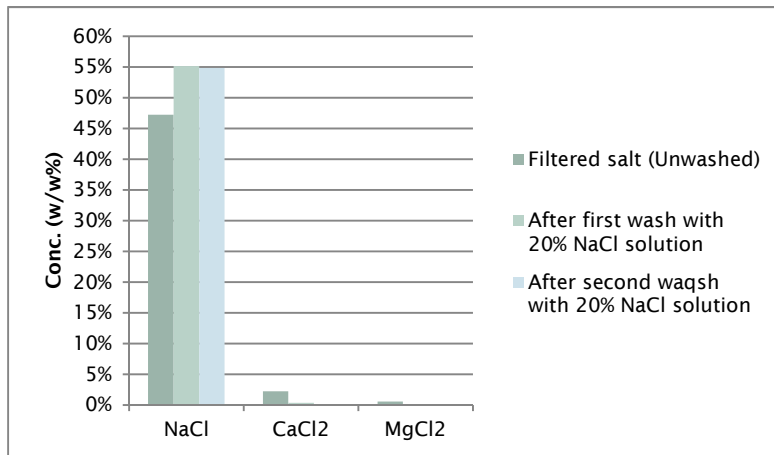


FIGURE 3-10 QUALITY OF SALT AS A FUNCTION OF WASHING WITH SATURATED NaCl SOLUTION AT SMALL SCALE WITH BUCHNER FILTER

4 Feasibility of EFC for treatment of CIEX spent regenerant

4.1 Introduction

In this chapter the economic feasibility of the EFC technology will be determined in comparison with a state of the art treatment scenario with reverse osmosis and evaporation/crystallisation to treat CIEX spent regenerant. To make a fair comparison between the different treatment options originally the following cases were considered for the economic evaluation:

1. Legal restrictions on disposal of moderate to high saline waste water streams (salt concentration > 0.5 wt%) from an CIEX-plant. In this case the high salt load of the spent CIEX regenerant is not allowed to be disposed to surface water. The salt load has to be disposed through disposal to e.g. a land fill.
2. Legal requirements for zero liquid discharge (ZLD) for all the waste streams of the water treatment plant. This requires that all the waste water of the plant has to be reused and the salt has to be disposed through disposal to e.g. a land fill.

Obtaining the data (for capacities as well as composition) of all waste water streams from the DWP Botlek site would be a comprehensive and very time consuming activity, which was not part of this research. Therefore it has been decided not to incorporate this case (2) ZLD for all waste streams in the feasibility study.

In the economic feasibility for the case (1) with restrictions in the salt load to surface water the following treatment scenarios are compared:

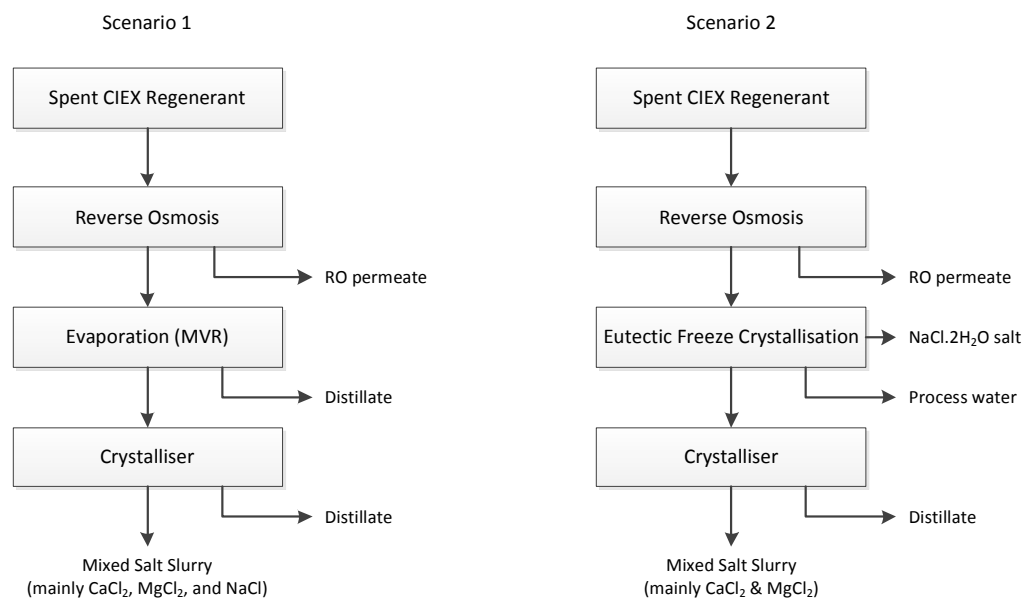


FIGURE 4-1 FLOW DIAGRAM OF BOTH SCENARIO'S.

The periodic batches of CEIX spent regenerant are buffered to obtain a constant flow to the reverse osmosis system. In the reverse osmosis system the process stream is concentrated twice by permeation of water through the reverse osmosis membranes.

In scenario 1 the concentrate of the reverse osmosis system is fed to the evaporation crystallisation system in which first the stream is concentrated with Mechanical Vapour Recompression (MVR) up to the saturation point by thermal evaporation. The almost saturated concentrate stream of the MVR is fed to the crystallisation system in which more water is evaporated and salts (NaCl, CaCl₂ and MgCl₂) will precipitate. The precipitated salt mixture is collected and disposed.

In scenario 2 the RO concentrate is fed to the EFC system, in which water is removed and sodium chloride (as NaCl·2H₂O) precipitates by cooling down the solution. The sodium chloride is collected and washed and can be reused to prepare fresh regenerant solution. As the remaining liquid from the EFC is already highly concentrated the MVR step is not required in scenario 2. This residual stream is fed to the crystallisation system to obtain a “dry” residual salt mixture that will be disposed. In the next paragraphs the different treatment processes are discussed in more detail.

4.2 Composition of spent regenerant as feed to the EFC plant

The regeneration of an CIEX filter consists of a number of steps;

- At the start of the regeneration the IX filter is rinsed to expand the filter bed and to remove any suspended matter trapped in the resin bed. The water displaced during the backwash has the salinity (< 0,5 wt%) of the feed water (at DWP Botlek feed water is Brielse Meer water) and can be discharged to surface water. There is no data available on the concentration of suspended matter.
- The next step is the introduction of the fresh regenerant into the filter, which is a 9-10% NaCl salt solution, also called brine. The water displaced during the brine injection still has the low salinity (< 0,5 wt%) and can be discharged to surface water.
- The next step after the injection of the brine is a fast flush with feed water. In this phase the salinity of the water (spent regenerant) leaving the filter will increase rapidly to a TDS of approximately 60 g/L. Calculations has shown that most of the unused sodium chloride can be collected in the period from 27 - 54 minutes after start of the regeneration. In the first part of this period the sodium concentration increase from 1 to 7.5 g/L and in the second part decreases to approximately 3 g/L (see Figure 4-2).

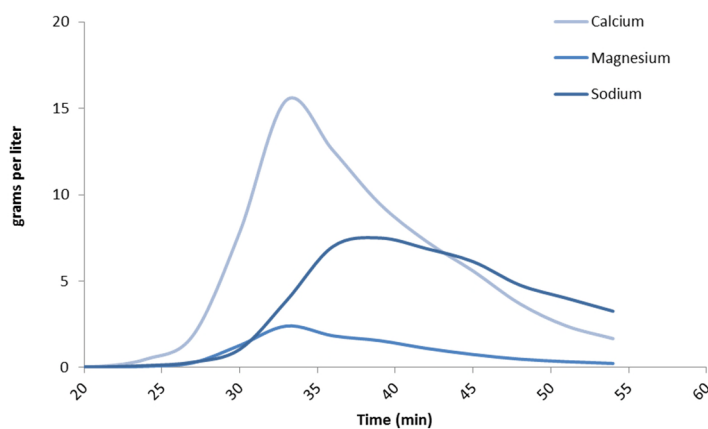


FIGURE 4-2 COMPOSITION OF SPENT CIEX REGENERANT FROM 20 TO 54 MIN OF REGENERATION PROCESS.

The total water volume collected from one CIEX vessel at DWP Botlek in this time period is 36 m³ per regeneration cycle and has a typical composition as indicated in Table 4-1.

TABLE 4-1 QUALITY OF SPENT REGENERANT COLLECTED FROM 27 - 54 MINUTES

Cations	Unit	Concentration	Anions	Unit	Concentration
Calcium	mg/L Ca	7,200	Bicarbonate	mg/L HCO ₃	157
Magnesium	mg/L Mg	1,170	Sulphate	mg/L SO ₄	58
Sodium	mg/L Na	4,790	Chloride	mg/L Cl	23,400
Potassium	mg/L K	3	Nitrate	mg/L NO ₃	10
Others					
TDS	mg/L	36,800	pH	-	8.2

At DWP Botlek a total of 8 CIEX vessels are installed and each filter is regenerated approximately 270 times a year. Based on the number of regenerations of each IX filter of DWP Botlek the total amount of spent regenerant produced will be approximately 9 - 10 m³/h on average.

4.3 Pre-concentration with Reverse Osmosis

As the spent regenerant of DWP Botlek is not highly concentrated (the TDS is in the range of seawater; 35-40 g/L) the performance of the total plant to treat spent regenerant can be improved substantially with the implementation of a pre-concentration step like a seawater reverse osmosis (SWRO) system. This will be a single stage SWRO of which the recovery is limited to 50% by the maximum feed pressure of such systems of 70 bar. It is assumed that a pretreatment is not required as the first rinse water containing suspended solids is not collected.

The design of the SWRO has been calculated with the design software ROSA (version 9.0.0, configDB u399339_282) from DOW. The results of the Rosa calculation are given in Appendix IV. The equipment costs for the reverse osmosis system has been supplied by Hatenboer Water (Jan Arie de Ruijter, personal communication 2016).

The energy consumption of the SWRO without energy recovery will be approx. 4.3 kWh/m³ product (calculated with ROSA). With an Energy Recovery Inc. PX-30 energy recovery system this will be around 2.6 kWh/m³ (calculated with the PX Power Model Selector tool, version 80068-01-8).

As can be seen in Table 4-1 the calcium concentration is rather high in the feed water and some bicarbonate is present. The calculated saturation index of calcite (calculated with ROSA) in the SWRO concentrate is positive. To prevent scaling small dosages of an acid and an anti scalant are required. The required dosages are calculated with the design software Membrane Master 4 (version 1.23, dll V1.8.7) from Genesys RO. The results of the Membrane Master 4 calculation are given in Appendix V.

4.4 Eutectic Freeze Crystallisation

The results of the pilot study at DWP Botlek will be the starting point for the process conditions of the EFC installation. However the auxiliary equipment of the EFC pilot, amongst others the cooling machine and the vacuum belt filters was not the most efficient equipment available and significant improvements of the performance of that equipment will be possible with proper heat integration in an improved design of the EFC installation. Examples of easy achievable improvements are:

- Use of state of the art cooling machines with higher Energy Efficiency Ratio (EER) and lower cooling water consumption;
- Better designed filter belts to minimize heat input by warm air going through the ice and salt cakes and to minimize water consumption for cooling of the vacuum pumps;
- Reuse of cold streams (melting ice and/or cold salt slurry) to cool the feed water or to cool the cooling machine (and thus improve its efficiency).

The design of the EFC plant (including energy and water consumption) and the required equipment costs has been supplied by EFC Separations (Ben Brocades, personal communication 2016). A full scale design of an EFC installation similar to the pilot as used on DWP Botlek would require an energy requirement of approximately 62 kWh/ton feed. This includes precooling of the feed water to the EFC installation from 20 °C to 2 °C. Advanced heat integration by cooling the compressor and refrigerant condensate cooling will reduce the energy consumption to 30 – 35 kWh/ton feed.

4.5 Evaporation Crystallisation

In treatment scenario 1 with just RO as pre-concentration step the evaporation crystalliser will be fed with the concentrate of the RO system. This concentrate has a TDS of 75 – 80 g/L (approximately twice the TDS of seawater). Before crystallisation will occur most of the water has to be removed with the MVR. In the consecutive crystalliser all the dissolved ions will precipitate as a mixture of predominantly NaCl, CaCl₂ and MgCl₂.

In treatment scenario 2 with EFC after the RO the remaining stream, the so-called mother liquor, from the EFC is already highly concentrated. The water content is reduced with a factor of approximately 8 – 10. This stream can be fed directly to the crystalliser. Because less water has to be evaporated the energy consumption will be reduced significantly. In the crystalliser all the dissolved ions will precipitate as a mixture of predominantly CaCl₂ and MgCl₂ with a relative small amount of NaCl. The mixed salt residues have to be disposed to for instance a landfill.

Design and cost data for the MVR and crystalliser systems have been supplied by EFC Separations (Ben Brocades, personal communication 2017). The energy consumption of the MVR will be approximately 40 kWh/ton feed, and for the crystalliser approximately 50 kWh/ton feed. The equipment costs for an evaporator crystalliser installation are rather high and below a feed capacity of less than 10 ton/h costs are hardly influenced by the feed capacity. From the total equipment costs (M€ 5 at feed 5 ton/h) the costs for the MVR are around 60% and the crystalliser represent approximately 40% of the costs.

4.6 Overview of the two scenarios

In Figure 4-3 on the next page the process flow diagram is given for both scenarios. In this diagram also the water mass balance is shown, including the salt streams

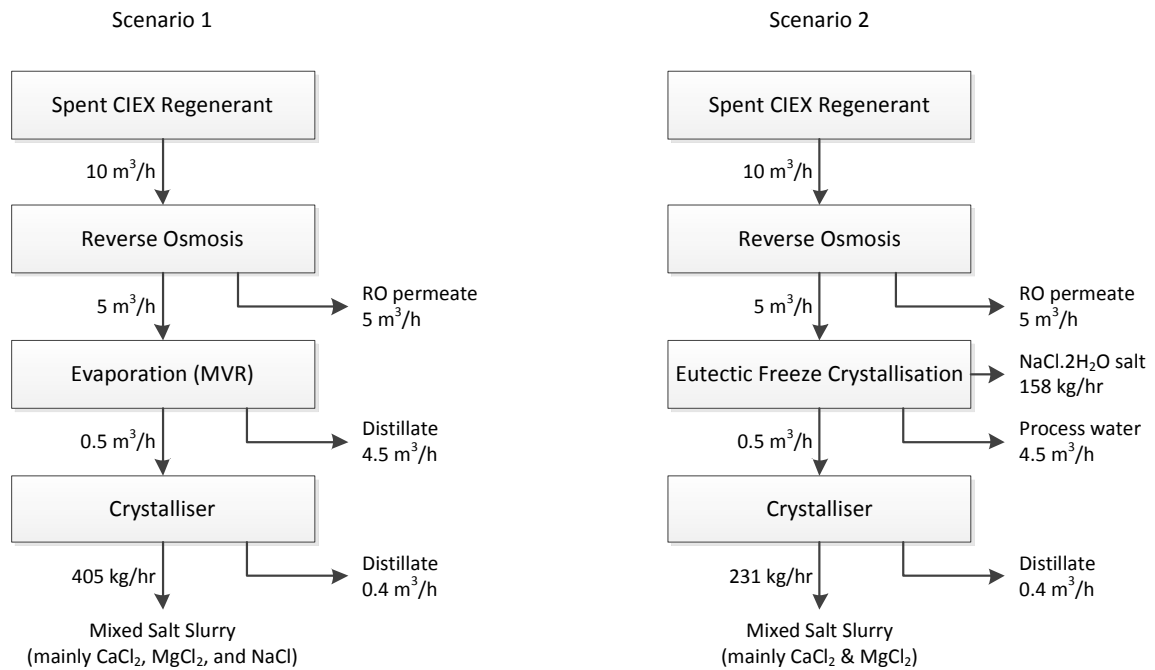


FIGURE 4-3 PROCESS FLOW DIAGRAM WITH MASS BALANCE OF BOTH SCENARIO'S.

4.7 Economic comparison

The economic comparison for the “base case” according the above mentioned design basis is based on Capex and Opex calculations. The degree of accuracy of the cost estimate (Conceptual Design Estimate) in this study is plus or minus 25 percent.

Capex calculation

For the equipment cost data from suppliers is obtained for the specific capacity of the treatment processes. To obtain the investment cost (Capex) the equipment costs are multiplied with a cost factor. In this study a typical cost factor of 1.5 is used for amongst others site preparation, integration, commissioning and general requirements. The cost factor of 1.5 is applicable for greenfield projects (building from scratch). For brownfield project (installing completely ‘new production line’ at an existing location utilising already available facilities) a much higher costs factor (up to 3.0) can be applicable.

The equipment costs for the reverse osmosis system, including the energy recovery device, (used in both scenario's) are rather low (k€ 117) compared to the costs of the evaporator (k€ 3.000) and crystalliser (k€ 2.000).

The additional equipment costs for the EFC installation (k€ 3.500) in scenario 2 is higher than the savings in the equipment costs for the evaporator installation (k€ 3.000). Therefore the total Capex for scenario 2 is higher than the total Capex for scenario 1.

In Table 4-2 the total Capex for the two scenario's is summarised. More details about the Capex calculations are given in Appendix IV, table VII.1.

TABLE 4-2 CAPEX COSTS IN K€

Equipment costs	Scenario 1: RO-MVR-Cryst	Scenario 2: RO-EFC-Cryst.
SWRO with energy recovery	117	117
EFC	-	3.500
MVR	3.000	-
Crystalliser	2.000	2.000
Total Equipment costs	5.117	5.667
Total Capex ^{*)}	7.675	8.425

*) Capex = Equipment cost * Cost factor

Opex calculation

The following costs are included in the Opex calculations:

- Depreciation (period and interest rate)
- Energy
- Chemicals
- Cooling water
- Labour/Maintenance
- Waste (residual salt) disposal

Depreciation of the equipment has been calculated over a period of 15 years. For membranes a lifetime (depreciation period) of 5 years has been applied. The interest rate used is 8%. This results in a yearly depreciation of 11.68% for the equipment and 25.05% for the membranes.

As indicated in chapter 4.3 small dosages of hydrochloric acid (10 mg/L) and anti scalant (1 mg/L) are required to prevent scaling in the SWRO system. The unit costs used for hydrochloric acid is € 200/tonne 30% HCl and for antiscalant is € 5/kg product as supplied.

The costs used for energy is € 0.10/kWh. For labour and maintenance an average value of 2.5% of the equipment cost has been used. The remaining salt slurry from both scenario's has to be disposed to for instance a landfill. The costs for disposal of the salt are estimated at € 150/tonne.

The following revenues are taken into account:

- Reuse of fresh water (RO permeate, EFC ice, evaporator water)
- Recovered NaCl salt at € 50/tonne

In both scenario's a number of water streams are produced which can be reused.

- At a recovery of 50% the SWRO system will produce approximately 5 m³/h of RO permeate. The unit costs for RO permeate are estimated to be € 0.50/m³.
- In scenario 2 the EFC system will produce approximately 4.5 m³/h of fresh water at an estimated unit cost of € 0.25/m³.
- The MVR and the crystalliser will produce distillate (demin water). In scenario 1 this will be approximately 4.9 m³/h and in scenario 2 this will be 0.4 m³/h. The revenue for demin water is estimated to be € 0.50/m³.

The EFC system produces approximately 100 kg/h of sodium chloride salt of relative good quality which can be reused to prepare fresh regenerant solution for the CIEX system. This reduces the amount of NaCl to be purchased. The unit cost for NaCl salt used is € 50/tonne.

In Table 4-3 the total Opex for the two scenario's is summarised. A more detailed Opex calculation is given in Appendix VI, table VI.1.

TABLE 4-3 OPEX COSTS (IN BLACK) AND REVENUES (IN RED) IN K€/YEAR

Process step	Opex component	Scenario 1:	Scenario 2:
		RO – MVR – Cryst	RO – EFC – Cryst.
Seawater Reverse Osmosis with ERI energy recovery	Depreciation	21.8	21.8
	Energy	11.4	11.4
	Chemicals	1.0	1.0
	Labour/Maintenance	2.9	2.9
	RO permeate	-21.9	-21.9
Eutectic Freeze Crystallisation	Depreciation	-	613.4
	Energy	-	153.3
	Cooling Water	-	26.3
	Labour/Maintenance	-	87.5
	Process water	-	- 9.9
	NaCl salt	-	- 42.7
MVR	Depreciation	525.7	-
	Energy	157.7	-
	Labour/Maintenance	75.0	-
	Demin water	-19.7	-
Crystalliser	Depreciation	350.5	350.5
	Energy	21.9	21.9
	Labour/Maintenance	50.0	50.0
	Demin water	- 1.8	- 1.8
Salt disposal		531.7	324.8
	Total Depreciation	898.0	985.6
	Total other costs/revenues	808.2	602.9
	Total Opex	1,706.2	1,588.5

Summary Capex and Opex

As can be seen in Table 4-2 the Capex for scenario 2 with EFC (M€ 8.425) is higher than the Capex for scenario 1 without EFC (M€ 7.675). This is due to the fact that an EFC installation for 5 m³/h feed water is more expensive than an MVR for the same feed capacity. As a result of the higher Capex also the depreciation costs (see Table 4-3) are higher for scenario 2 (k€ 986) than the depreciation for scenario 1 (k€ 898). The higher Capex also results in higher costs for labour and maintenance of the installations.

However the difference in Capex between the scenarios is within the range of accuracy ($\pm 25\%$) of the cost estimate.

In scenario 2 the annual costs for energy consumption of the total system and for the disposal costs of the remaining salt stream are reduced significantly, respectively approximately 20% and approximately 40% (as can be seen in Table 4-3). These reductions compensate for the additional costs for depreciation and for labour and maintenance.

As a result the total Opex (depreciation, chemicals, energy, labour/maintenance, revenues) for scenario 2 with EFC (k€ 1,589) are lower than the Opex for scenario 1 without EFC (k€ 1,706).

Based on the results of this “base case” economic comparison it is concluded that application of EFC in scenario 2 to treat spent CIEX regenerant is equally expensive compared to the treatment process without EFC in scenario 1.

Sensitivity analysis

The two cost components in the economic comparison with the highest impact on the Opex are:

- the Capex/depreciation for the MVR/crystalliser and EFC equipment. The depreciation costs account for the largest part of the total Opex. For scenario 1 without EFC the total depreciation costs are 53% of the total Opex and for scenario 2 with EFC it is nearly 62%;
- the costs for disposal of the remaining salt stream, with 31% respectively 20% of the total Opex;

In the base case comparison the equipment cost for the EFC system with a feed capacity of 5 m³/h was estimated by EFC Separations at 3.5 million euros. Variation of the Capex of the EFC system shows that the equipment costs of the EFC system can increase to approximately 4.1 million euro to obtain the break-even point for total Opex at the applied depreciation terms of 15 years and interest rate of 8% (see Figure 4-4).

Variation in the costs for disposal of the remaining salt is shown in Figure 4-5. The break-even point in total Opex is obtained at a disposal cost for the remaining salt at approximately € 65/tonne.

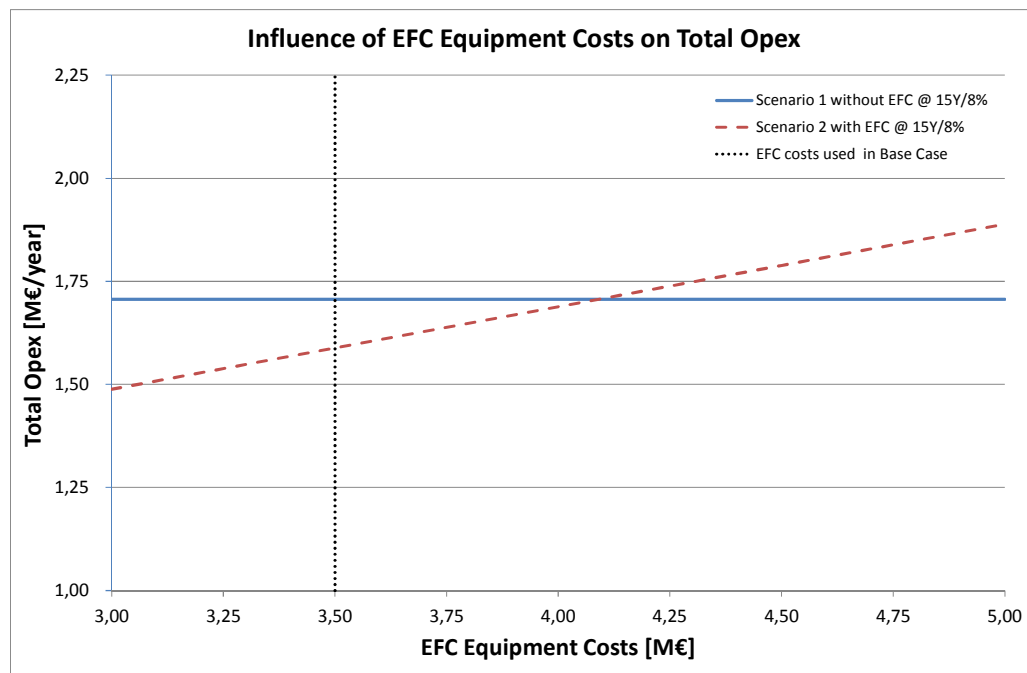


FIGURE 4-4 SENSITIVITY ANALYSIS OF EQUIPMENT COSTS EFC SYSTEM ON TOTAL OPEX.

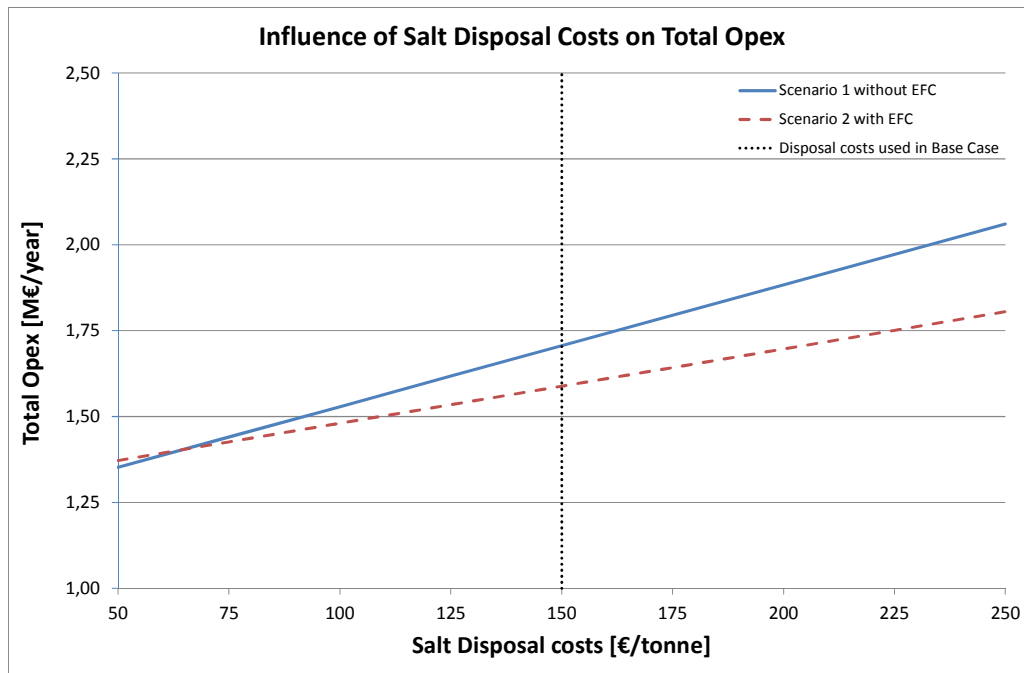


FIGURE 4-5 SENSITIVITY ANALYSIS OF SALT DISPOSAL COSTS ON TOTAL OPEX.

5 Conclusions and recommendations

Conclusions

Following are the main conclusions from this study:

- The eutectic temperature for the crystallisation of NaCl from the original spent CIEX regenerant of DWP Botlek remained unknown in this study because the stream was too dilute. Achieving the eutectic point at pilot scale required a long freeze crystallisation period or concentration by other means which could not be carried out in this study due to time limitation.
- The eutectic temperature of the feed solution produced by adding 20 wt% NaCl in spent CIEX regenerant was $-21.3\text{ }^{\circ}\text{C}$, slightly lower than the binary H_2O -NaCl mixture, and the eutectic temperature of the feed solution produced by dissolving 14.9 wt% NaCl, 12.6 wt% CaCl_2 and 3.2 wt% MgCl_2 in spent CIEX regenerant was $-26\text{ }^{\circ}\text{C}$, significantly lower than the binary H_2O -NaCl mixture. It means that the presence of “impurities”, in this case Ca and Mg, depresses the eutectic temperature of NaCl crystallisation.
- When the solution produced by dissolving 20 wt% NaCl in spent CIEX regenerant was used, the cooling plates scaled rapidly and the scale hampered the heat exchange in the crystalliser. However, scaling of the plates was significantly reduced when a different start solution, containing 4.9 wt% NaCl, 12.6 wt% CaCl_2 and 3.2 wt% MgCl_2 , was used in the tests. In the latter case a higher total heat exchange in the crystalliser was achieved.
- The temperature in the crystalliser gradually decreased during the continuous tests, i.e. the eutectic temperature was gradually shifting to lower values. This was due to the accumulation of Ca and Mg ions in the process stream because a bleed stream was not applied to the system during the tests
- Heat loss was noted as the major challenge during the pilot testing. Melting of ice on the belt filter was noticed during the tests. A significant amount of ice melted while transportation of the ice slurry from the settler to the ice filter. In addition ice melted due to the large amount of warm air going through the ice cake in the filter belt. Moreover, due to the heat of vacuum pumps the filtrates of both belt filters were heated. As a result, the temperature of the process stream buffer remained much higher compared to the crystalliser.
- Washing of ice and salt crystals, performed on small scale (in batch mode), improved the quality of the products, as expected based on the results of previous studies.
- The results of the “base case” economic comparison indicate that application of EFC in scenario 2 to treat spent CIEX regenerant is equally expensive compared to the treatment process without EFC in scenario 1. Although the Capex and related yearly depreciation is higher the overall Opex is lower, mainly due to the lower disposal costs for the residual mixed salt.
- It should be noted that the difference in Capex between the two scenarios is within the range of accuracy ($\pm 25\%$) of the cost estimate.
- Sensitivity analysis on the cost component in the economic comparison with the highest impact on the Opex, the total depreciation, shows that the estimated equipment costs for the EFC system can be approximately 17% higher than the actual estimated costs to obtain the break-even point in total Opex.
- The sensitivity analysis on the disposal costs for the remaining salt shows that a reduction of these costs to € 65/tonne (base case € 150/tonne) is required to obtain the break-even point in total Opex.

Recommendations

The EFC installation used for pilot tests at DWP Botlek was an experimental setup and the auxiliary equipment of the EFC pilot was not the most efficient equipment. Significant improvements of that equipment can be possible with proper heat integration in an improved design of the EFC installation. Examples of easy achievable improvements are:

- State of the art cooling machines with higher Energy Efficiency Ratio (EER).
- Energy consumption of the EFC process is highly dependent on the amounts of ice that are being produced, because ice formation has the highest energy expenditure relative to the rest. Using a performant refrigeration system with a high COP, designed to operate at the desired temperature, will reduce the overall electrical energy consumption.
- For the pilot setup used at Botlek, one possibility of minimizing the energy consumption would be to reduce the heat loss over the filtration units. This can be achieved by improved sizing of the vacuum filter belts to minimize heat input by warm air going through the ice and salt cakes and by placing the belt filters in an enclosed cooled area, and by reducing the length of the hoses that return the filtrate to the buffer vessel. A higher flow of the streams through hoses and pipes would also reduce the time that the fluid spends in the warm environment, thus losing cold. The vacuum flow through the cake can be regulated as well, therefore less warm air would be sucked through the ice cake.
- Overall, for a full scale unit, several heat integration methods can be implemented. Using the ice to cool the feed to the crystalliser and to cool the condenser of the cooling machine are the two main energy saving methods. The lower the temperature of the cooling water for the condenser, the lower the condensation temperature thus the higher the EEP of the cooling machine would be. Best case would be to use condensers that can be cooled with slurry ice, as the melting enthalpy of ice is higher than the heat capacity of water, therefore the cooling is faster and more efficient. 1 kg of ice/h would carry 0.09 kW/h whereas 1 kg water/h with a $\Delta T = 20\text{K}$ would carry 0.02 kW/kg. Even though the energy conduction would be lower by using slurry ice in the condenser, the complexity of the system will increase, therefore a trade-off has to be made.

References

Bodnar, R.J. 1993. Revised equation and table for determining the freezing point depression of H₂O-NaCl solutions. *Geochemica et Cosmochimica Acta*. 57, 683-684.

De Graaff, 2012. MSc thesis.

Genceli, F.E., 2008. Scaling-Up Eutectic Freeze Crystallization.

<http://www.un.org/waterforlifedecade/scarcity.shtml>.

Kim, D. H. (2011). "A review of desalting process techniques and economic analysis of the recovery of salts from retentates." *Desalination* 270(1-3): 1-8.

M.M. Seckler, D. Verdoes, G.J. Witkamp, Application of eutectic freeze crystallization to process streams and wastewater purification, in, 2003.

Nathoo, J. Jivanji, R., Lewis, A.E. 2009. Freezing your brines off: eutectic freeze crystallization for brine treatment, in: International mine water conference, South Africa 2009.

Pronk, P., 2006. Fluidized bed heat exchangers to prevent fouling in ice slurry systems and industrial crystallizers.

Rodriguez Pascual, M., 2009. Physical Aspects of Scraped Heat Exchanger Crystallizers: An Application in Eutectic Freeze Crystallization.

S.T. Reddy, A.E. Lewis, G.J. Witkamp, H.J.M. Kramer, J. van Spronsen, Recovery of Na₂SO₄ · 10H₂O from a reverse osmosis retentate by eutectic freeze crystallisation technology, *Chemical Engineering Research and Design*, 88 (2010) 1153-1157.

Sterner, S.M., Hall, D.L. and Bodnar, R.J. (1988). Synthetic fluid inclusions. V. Solubility relations in the system NaCl-KCl-H₂O under vapor saturated conditions. *Geochemica et Cosmochimica Acta*, 52, 989-1005.

Tempel, W.M. Van der, 2012. Eutectic Freeze Crystallization: Separation of salt and ice.

United Nations, 2016.

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

Van der Ham, F. 1999. Eutectic Freeze Crystallization. PhD thesis submitted to TU Delft. pp 122

Van der Ham, F., Witkamp, G.J., De Graauw, J., Van Rosmalen, G.M., 1999. Eutectic freeze crystallization simultaneous formation and separation of two solid phases. *Journal of crystal growth* 198, 744-748.

Brocades (2016). Personal communication from Ben Brocades (EFC Separations) to Hans Huiting, dd. Dec. 22, 2016 concerning the capex and opex of EFC.

Brocades (2017). Email communication from Ben Brocades (EFC Separations) to Edwin Beerendonk, dd. May 11, 2017 concerning the capex of evaporation crystalliser.

Ruijter (2016). Personal communication from Jan Arie de Ruijter (Hatenboer Water) to Hans Huiting, dd. Nov. 24, 2016

Appendix I Settings during short term trials

Trial. No.	Date	Cooling machine	Freezium flow	Precooler flow	feed flow crystalliser	set points							
						salt slurry recycle	Total flow	Ice slurry flow	Salt slurry flow	Bleed flow	Stirrer settler	Stirrer mixer	Scraping speed
		TIC-300 SP	FV-300 - 360	FL-212	pump1	pump 4	pump 1 + 4	Mono pump	pump 2	pump 3	M500	M501	SC-400
		°C	L/min	L/min	L/min	L/min	L/min	L/min	L/min	L/min	RPM		RPM
1	27-okt	-30.0	10	4.4	2.5	5.0	7.5	2.5	0.5	0.0	17	13	35
2	27-okt	-30.0	11	3.6	2.5	5.0	7.5	2.5	0.5	0.0	17	13	35
3	28-okt	-29.5	9	4	2.5	3.0	5.5	2.5	0.0	0.0	17	13	35
4	28-okt	-29.5	9	4	2.5	3.0	5.5	2.5	0.0	0.0	17	13	45
5	29-okt	-29	9	4	2.5	2.0	4.5	2.5	0.0	0.0	17	13	35
6	30-okt	-29.5	9	4	2.5	1.0	3.5	2.5	0.0	0.0	17	13	25
7	3-nov	-29.5	9	4	4.0	1.0	5.0	4.0	0.0	0.0	17	13	35
8	3-nov	-29	9	4	4	1	5.0	4	0	0	17	13	35
9	6-nov	-29.5	9	4	4.0	1.0	5.0	4.0	0.0	0.0	17	13	35
10	11-nov	-31.0	11	4	4.0	1.0	5.0	4.0	0.0	0.0	17	13	35
11	11-nov	-29.5	9	4	4.0	1.0	5.0	4.0	0.0	0.0	17	13	35
12	17-nov	-29.5	10	4	4.0	1.0	5.0	4.0	0.0	0.0	17	13	35
13	18-nov	-29.5	10	4	4.0	1.0	5.0	4.0	0.0	0.0	17	13	35
14	18-nov	-29.5	11	4	4.0	1.0	5.0	4.0	0.0	0.0	17	13	35
15	19-nov	-29.0	10	4	4.0	1.0	5.0	4.0	0.0	0.0	17	13	35
16	24-nov	-29.0	10	4	4.0	1.0	5.0	4.0	0	0	17	13	35
17	24-nov	-29.0	10	4	5.0	1.0	6.0	5.0	0	0	17	13	35
18	8-mrt	-31.0	10	3.3	4.3	3.0	7.3	-	0.0	0.0	10	10	35
19	10-mrt	-33	10	4	4.3	3.0	7.3	-	-	0.0	17	13	25
20	23-mrt	-	-	-	-	-	-	-	0.0	0.0	-	-	-
21	30-mrt	-35.0	10	4.3	4.9	6.0	10.9	-	0.0	0.0	15	13	25
22	5-apr	-35.0	10	4	4.8	3.0	7.8	-	0.0	0.0	0	13	25
23	6-apr	-	-	-	-	-	0.0	-	0.0	0.0	-	-	-
24	12-apr	-38.0	10	0	4.3	3.5	7.8	-	0.0	0.0	10	13	30

Appendix II Settings during 48-h continuous trial

Date	Time (h)	Set point cooling machine	Avg. coolant Temp. in heat exchangers.	Coolant flow in heat exchangers	Coolant flow in the pre cooler	Feed to crystalliser. Pump 1	Salt slurry recycle from settler to crystalliser. Pump 4	Salt slurry to belt filter. Pump 2	Ice slurry to the belt filter. Pump 2	Scrapper speed	Feed to buffer with fresh start solution	Bleed . Pump 3
		[°C]	[°C]	[L/min]	[L/min]	[L/min]	[L/min]	[Hz]	[Hz]	[Hz]		[L/min]
19-apr-16	0	-36	-34.1	10	5	4.5	3.5	17	17	30	0	0
19-apr-16	1	-36	-33.7	10	1.8	4.4	3.5	0	0	25	0	0
19-apr-16	2	-36	-34.2	10	1.6	4.4	3.5	0	37	25	0	0
19-apr-16	3	-36	-33.6	10	5	4.5	3.5	0	33	25	0	0
19-apr-16	3.3			11	4							
19-apr-16	4	-36	-33.6	11	4	4.5	3.5	25	25	25	0	0
19-apr-16	5	-36	-33.7	11	4	4.5	3.5	25	25	25	0	0
19-apr-16	6	-36	-33.7	11	4	4.5	3.5	25	24.1	25	0	0
19-apr-16	7	-36	-33.7	11	4	4.5	3.5	25	23.7	25	0	0
19-apr-16	8	-36	-33.7	11	4	4.5	3.5	25	23.5	25	0	0
19-apr-16	8.3			12								
19-apr-16	9	-36	-33.7	12	4	4.5	3.5	25	23.5	25	0	0
19-apr-16	10	-36	-33.7	12	4	4.5	3.5	25	23.5	25	0	0
19-apr-16	11	-36	-33.7	12	4	4.5	3.5	25	23.5	25	0.2	0
19-apr-16	12	-36	-33.6	12	4	4.5	3.5	25	23	25	0.5	0
19-apr-16	12.3	-37		10	5							
19-apr-16	13	-37	-32.3	10	5	4.5	3.5	25	23.5	30	0.5	0
19-apr-16	14	-37	-32.8	10	5	4.5	3.5	20	23.9	30	0.5	0
19-apr-16	15	-37	-33.2	10	5	4.5	3.5	20	24	30	0.5	0
19-apr-16	15.3			11	4	5					0.2	
19-apr-16	16	-37	-33.5	11	4	5	3.5	25	28	30	0.2	0
19-apr-16	16.3	-38										
19-apr-16	17	-38	-33.8	11	4	5	3.5	25	27.5	30	0.2	0
20-apr-16	18	-38	-33.8	11	4	5	3.5	25	27.6	30	0.2	0
20-apr-16	19	-38	-33.9	11	4	5	3.5	25	27.5	30	0.2	0
20-apr-16	20	-38	-33.9	11	4	5	3.5	25	27.3	30	0.5	0
20-apr-16	21	-38	-33.9	11	4	5	3.5	25	27.6	30	0.5	0
20-apr-16	22	-38	-33.9	11	4	5	3.5	25	27.6	30	0.2	0
20-apr-16	23	-38	-33.9	11	4	5	3.5	25	27.7	30	0.2	0

Appendix III Settings during last 10 hours of the 100-h continuous trial

Time	Setpoint cooling machine	Average coolant temperature in heat exchangers	Coolant flow in heat exchangers	Coolant flow in pre-cooler	Feed to crystalliser. Pump 1	Salt slurry recycle from settler to crystalliser. Pump 4	Salt slurry to belt filter. Pump 2	Ice slurry to the belt filter. Pump 2	Scrapper speed	Feed to buffer with fresh start solution	Bleed. Pump 3
(h)	[°C]	[°C]	[L/min]	[L/min]	[L/min]	[L/min]	[Hz]	[Hz]	[Hz]		[L/min]
90	-37	-33	13.5	1.6	2.5	1	16	12.8	35	0	0
91	-37	-33.3	13.5	1.6	2.5	1	16	12.8	35	0	0
92	-37	-33.4	13.5	1.6	2.5	1	16	12.8	35	0	0
93	-37	-33.3	13.5	1.6	2.5	1	16	12.6	35	0	0
94	-37	-33.5	13.5	1.6	2.5	1	16	12.7	35	0	0
95	-37	-33.6	13.5	1.6	2.5	1	16	12.7	35	0	0
96	-37	-33.6	13.5	1.6	2.5	1	16	12.7	35	0	0
97	-37	-33.6	13.5	1.5	2.5	1	16	12.9	35	0	0
98	-37	-33.7	13.5	1.5	2.5	1	16	12.5	35	0	0
99	-37	-33.7	13.5	1.5	2.5	1	16	12.5	35	0	0
100	-37	-33.7	13.5	1.5	2.5	1	16	12.5	35	0	0

Appendix IV ROSA calculation for SWRO system

ROSA Detailed Report

Page 1 of 3

Reverse Osmosis System Analysis for FILMTEC™ Membranes
 Project: EFC pre-RO
 Hans Huiting, KWR Watercycle Research Institute

ROSA 9.0.0 ConfigDB u399339_282
 Case: 1
 11/24/2016

Project Information: SWRO as preconcentration before EFC

Case-specific:

System Details

Feed Flow to Stage 1	10.00 m³/h	Pass 1 Permeate Flow	5.00 m³/h	Osmotic Pressure:	
Raw Water Flow to System	10.00 m³/h	Pass 1 Recovery	50.00 %	Feed	22.10 bar
Feed Pressure	69.76 bar	Feed Temperature	15.0 C	Concentrate	45.70 bar
Flow Factor	0.85	Feed TDS	36792.47 mg/l	Average	33.90 bar
Chem. Dose (100% HCl)	5.43 mg/l	Number of Elements	7	Average NDP	34.71 bar
Total Active Area	286.13 M²	Average Pass 1 Flux	17.47 lmh	Power	24.23 kW
Water Classification: Seawater with Conventional pretreatment, SDI < 5				Specific Energy	4.85 kWh/m³

Stage	Element	#PV	#Ele	Feed Flow (m³/h)	Feed Press (bar)	Recirc Flow (m³/h)	Conc Flow (m³/h)	Conc Press (bar)	Perm Flow (m³/h)	Avg Flux (lmh)	Perm Press (bar)	Boost Press (bar)	Perm TDS (mg/l)
1	SW30XHR-440i	1	7	10.00	69.41	0.00	5.00	67.75	5.00	17.47	0.00	0.00	42.45

Pass Streams (mg/l as Ion)						
Name	Feed	Adjusted Feed	Concentrate		Permeate	
			Stage 1	Stage 1	Stage 1	Total
NH4+ + NH3	0.00	0.00	0.00	0.00	0.00	0.00
K	3.00	3.00	5.96	0.04	0.04	0.04
Na	4790.00	4791.81	9573.81	9.83	9.83	9.83
Mg	1170.00	1170.00	2339.18	0.82	0.82	0.82
Ca	7200.00	7200.00	14395.07	4.97	4.97	4.97
Sr	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00
CO3	24.79	16.43	35.36	0.00	0.00	0.00
HCO3	157.00	164.93	324.38	0.53	0.53	0.53
NO3	10.00	10.00	19.83	0.17	0.17	0.17
Cl	23373.00	23378.28	46730.62	26.07	26.07	26.07
F	0.00	0.00	0.00	0.00	0.00	0.00
SO4	58.00	58.00	115.99	0.01	0.01	0.01
SiO2	0.00	0.00	0.00	0.00	0.00	0.00
Boron	0.00	0.00	0.00	0.00	0.00	0.00
CO2	0.60	1.00	2.41	1.34	1.34	1.34
TDS	36785.82	36792.47	73540.23	42.45	42.45	42.45
pH	8.20	8.00	8.16	5.85	5.85	5.85

*Permeate Flux reported by ROSA is calculated based on ACTIVE membrane area. DISCLAIMER: NO WARRANTY, EXPRESSED OR IMPLIED, AND NO WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE, IS GIVEN. Neither FilmTec Corporation nor The Dow Chemical Company assume any obligation or liability for results obtained or damages incurred from the application of this information. Because use conditions and applicable laws may differ from one location to another and may change with time, customer is responsible for determining whether products are appropriate for customer's use. FilmTec Corporation and The Dow Chemical Company assume no liability, if, as a result of customer's use of the ROSA membrane design software, the customer should be sued for alleged infringement of any patent not owned or controlled by the FilmTec Corporation nor The Dow Chemical Company.

ROSA Detailed Report

Reverse Osmosis System Analysis for FILMTEC™ Membranes
 Project: EFC pre-RO
 Hans Huiting, KWR Watercycle Research Institute

ROSA 9.0.0 ConfigDB u399339_282
 Case: 1
 11/24/2016

Design Warnings

-None-

Solubility Warnings

Langelier Saturation Index > 0
 Stiff & Davis Stability Index > 0
 Antiscalants may be required. Consult your antiscalant manufacturer for dosing and maximum allowable system recovery.

Stage Details

Stage	Element	Recovery	Perm Flow (m³/h)	Perm TDS (mg/l)	Feed Flow (m³/h)	Feed TDS (mg/l)	Feed Press (bar)
1		0.10	0.98	22.95	10.00	36792.47	69.41
2		0.10	0.90	27.59	9.02	40805.20	69.06
3		0.10	0.82	33.69	8.11	45345.87	68.76
4		0.10	0.72	41.86	7.30	50409.44	68.50
5		0.09	0.62	52.96	6.58	55933.41	68.27
6		0.09	0.52	68.21	5.95	61779.41	68.07
7		0.08	0.43	89.44	5.43	67736.56	67.90

Permeate Flux reported by ROSA is calculated based on ACTIVE membrane area. DISCLAIMER: NO WARRANTY, EXPRESSED OR IMPLIED, AND NO WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE, IS GIVEN. Neither FilmTec Corporation nor The Dow Chemical Company assume any obligation or liability for results obtained or damages incurred from the application of this information. Because use conditions and applicable laws may differ from one location to another and may change with time, customer is responsible for determining whether products are appropriate for customer's use. FilmTec Corporation and The Dow Chemical Company assume no liability, if, as a result of customer's use of the ROSA membrane design software, the customer should be sued for alleged infringement of any patent not owned or controlled by the FilmTec Corporation nor The Dow Chemical Company.

ROSA Detailed Report

Scaling Calculations

	Raw Water	Adjusted Feed	Concentrate
pH	8.20	8.00	8.16
Langelier Saturation Index	2.33	2.15	2.89
Stiff & Davis Stability Index	1.29	1.12	1.70
Ionic Strength (Molal)	0.93	0.93	1.93
TDS (mg/l)	36785.82	36792.47	73540.23
HCO3	157.00	164.93	324.38
CO2	0.60	1.00	2.41
CO3	24.79	16.43	35.36
CaSO4 (% Saturation)	6.11	6.11	15.81
BaSO4 (% Saturation)	0.00	0.00	0.00
SrSO4 (% Saturation)	0.00	0.00	0.00
CaF2 (% Saturation)	0.00	0.00	0.00
SiO2 (% Saturation)	0.00	0.00	0.00
Mg(OH)2 (% Saturation)	1.01	0.40	1.70

To balance: 1.80 mg/l Na added to feed.

MM4 Report

Water Analysis Data

Component	Feed Water mg/l	Concentrate mg/l
Ca ²⁺	7200.00	14356.80
Mg ²⁺	1170.00	2332.98
Na ⁺	4790.00	9551.26
K ⁺	3.00	5.98
Ba ²⁺	0.00	0.00
Sr ²⁺	0.00	0.00
Fe ³⁺	0.00	0.00
Al ³⁺	0.00	0.00
Mn ²⁺	0.00	0.00
SO ₄ ²⁻	58.00	115.65
Cl ⁻	23403.32	46666.23
F ⁻	0.00	0.00
HCO ₃ ⁻	146.30	291.73
CO ₃ ²⁻	2.78	5.55
CO ₂	1.46	1.46
NO ₃ ⁻	10.00	19.94
SiO ₂	0.00	0.00
PO ₄ ³⁻	0.00	0.00

Operation Details

Permeate Flow	5.0 m ³ /hr
Recovery Rate	50.0 %
Feed Flow	10.0 m ³ /hr
Concentration Factor	2.00
Concentrate Flow	5.0 m ³ /hr
pH Raw Water	8.2
pH Feed Water	7.8
Operating Pressure	70.0 Bar
Operating Temperature	20.0 °C
Operating Time	24.0 hr/day

Water Indices

Index	Feed Water	Concentrate
pH	7.80	7.63
TDS	36788.00	73362.08
Ionic Strength (I)	0.89	1.78
SDSI	1.00	1.38
Alkalinity ppm CaCO ₃	128.80	248.54

Scaling Indices Feed

Scalant Type	Feed Water Untreated (%)	Feed Water Treated (%)
CaCO ₃	117.77	84.84
CaSO ₄	4.47	1.60
BaSO ₄	0.00	0.00
SrSO ₄	0.00	0.00
CaF ₂	0.00	0.00
Ca ₃ (PO ₄) ₂	0.00	0.00
Fe(OH) ₃	0.00	0.00
SiO ₂	0.00	0.00
Al(OH) ₃	0.00	0.00
Mn(OH) ₂	0.00	0.00
Mg(OH) ₂	0.36	0.00

Scaling Indices Concentrate

Scalant Type	Concentrate Untreated (%)	Concentrate Treated (%)
CaCO ₃	128.73	92.73
CaSO ₄	12.84	4.59
BaSO ₄	0.00	0.00
SrSO ₄	0.00	0.00
CaF ₂	0.00	0.00
Ca ₃ (PO ₄) ₂	0.00	0.00
Fe(OH) ₃	0.00	0.00
SiO ₂	0.00	0.00
Al(OH) ₃	0.00	0.00
Mn(OH) ₂	0.00	0.00
Mg(OH) ₂	0.32	0.00

The data used in Genesys Membrane Master 4 is provided in good faith.
The system operation is outside our control and we accept no product liability for consequential results

MM4 Software Version: v1.23 (DLL v1.8.7)

Appendix VI Details of Feasibility study

In table VII.1 the Capex as well as the Opex are given for the 2 scenario's. In table VII.2 the unit costs and revenues used in this study to calculate the Opex are presented. The accuracy of the estimate (Conceptual Design Estimate) in this study is plus or minus 25%.

TABLE VII.1 CAPEX AND OPEX CALCULATION FOR THE TWO SCENARIOS

		Scenario 1: Reverse Osmosis - Evaporation - Crystallisation					Scenario 2: Reverse Osmosis - Eutectic Freeze Crystallisation - Crystallisation				
		parameter	Equipment	Depreciation	Opex	Revenues	parameter	Equipment	Depreciation	Opex	Revenues
Waste Water	m3/h	10					10				
Reverse Osmosis			€ 100.000	€ 17.524			€ 100.000	€ 17.524			
Feed flow	m3/h	10				10					
Recovery		50%				50%					
RO Product (demin water)	m3/h	5				5				€ 21.900	
RO Concentrate	m3/h	5				5					€ 21.900
Membrane Costs			€ 6.667	€ 2.505			€ 6.667	€ 2.505			
Energy Recovery	Yes with ERI		€ 10.000	€ 1.752			€ 10.000	€ 1.752			
Energy cons. with ERI	kWh/m3 product	2,60			€ 11.370	2,60			€ 11.370		
Chem. Hydrochloric Acid	mg/l HCl	10,00			€ 584	10,00			€ 584		
Chem. Anti scalant	mg/l AS	1,00			€ 438	1,00			€ 438		
Maintenance		2,5%			€ 2.917	2,5%			€ 2.917		
EFC							€ 3.500.000	€ 613.355			
Feed flow	m3/h					5					
Concentration factor						10					
Energy Cons./costs	kWh/m3					35			€ 153.300		
Ice water produced	m3/h					4,5				€ 9.855	
NaCl,2H2O Salt produced	kg/h					97,4				€ 42.667	
Cooling/vacuum water	m3/h					12			€ 26.280		
Maintenance						2,5%			€ 87.500		
MVR											
Feed Capacity	m3/h	5	€ 3.000.000	€ 525.733							
Energy Cons./costs	kWh/m3	40			€ 157.680						
Distillate produced	m3/h	4,5								€ 19.710	
Maintenance		2,5%			€ 75.000						
Crystalliser											
Feed Capacity	m3/h	0,5	€ 2.000.000	€ 350.489		0,5	€ 2.000.000	€ 350.489			
Energy Cons./costs	kWh/m3	50			€ 21.900	50			€ 21.900		
Fresh water produced	m3/h	0,4				0,4				€ 1.752	
Maintenance		2,5%			€ 50.000	2,5%			€ 50.000		
Salt disposal	kg/hr	405			€ 531.676	247			€ 324.762		
Total Equipment			€ 5.116.667				€ 5.616.667				
Total Capex			€ 7.675.000				€ 8.425.000				
Total Opex				€ 898.003	€ 851.565	€ -43.362		€ 985.625	€ 679.051	€ -76.174	

TABLE VII.2 DETAILS OF UNIT COSTS AND REVENUES OF OPEX

Unit Costs				
Fresh Water costs		€/m3	0,25	
Fresh Water revenues		€/m3	0,25	
RO water revenues		€/m3	0,50	
Fresh water treatment/disposal		€/m3	0,15	
Brine treatment/disposal		€/m3	0,50	
NaCl salt revenues		€/ton	50,00	
Mixed salt disposal		€/ton	150,00	
Energy costs		€/kWh	0,10	
H2SO4 costs	98%	€/ tonne	70	
HCl costs	30%	€/ tonne	200	
NaOH costs	50%	€/ tonne	125	
Anti scalant costs		€/ kg	5	
Investment				
Cost factor			1,5	
			Equipment	Membranes
Depreciation of equipment	year		15	5
Interest rate	%		8,0%	
Depreciation rate	%/year		11,68%	25,05%
Labour/Maintenance % of equipment cost				
Civil			0,5%	
Mechanical			2,0%	
Electrical			4,0%	
Average value			2,5%	