ZERO BRINE

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D2.6 Report on the operation and optimization process of the pilot plants at Botlek

February 2022

FINAL

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[1] **R**=Document, report; **DEM**=Demonstrator, pilot, prototype; **DEC**=website, patent fillings, videos, etc.; **OTHER**=other

[2] **PU**=Public, **CO**=Confidential, only for members of the consortium (including the Commission Services), **CI**=Classified

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Executive Summary

In this report the main research findings of the pilot activities in the Netherlands that were part of work package two of ZERO BRINE project are presented and discussed. The pilot activities and thereafter the results described are separated to cover two pilot demonstration plants; Site 01 and Site 02.

Site 01 pilot treated the regeneration effluent (spent regenerant) of the softening ion exchange unit of the Evides Demin Water Plant located in Botlek industrial area. The experiments were separated in three categories based on the spent regenerant quality; upper limit, nominal conditions and lower limit. The spent regenerant was firstly treated by a nanofiltration unit where separation of multivalent and monovalent cations was successful: rejections of multivalent above 90% were achieved, while NaCl permeated by 54-68%. The nanofiltration concentrate, which was highly concentrated in Mg^{2+} and Ca^{2+} ions was treated by a crystallizer unit (the MF-PRF). Both cations were effectively removed (100% Mg^{2+} removal and > 90% Ca^{2+} removal) and moreover they were recovered as hydroxide crystals with purities that reached 89% for $Mg(OH)_2$ and above 90% for $Ca(OH)_2$. The target purity for $Mg(OH)_2$ crystals based on the grant agreement 730390 was achieved in some experiments, but not in all due to the co-precipitation of $CaCO_3$. The NF permeate and the MF-PRF crystallizer effluent were treated by the MED evaporator unit, where high-purity water was recovered by 80.3% under nominal conditions, which was also the overall recovery of Site 01 pilot. Moreover, a highly concentrated NaCl solution (3.9%-7.5% NaCl) with a purity above 93% was recovered as well with the MED evaporator. Finally, it was found that nominal and low limit conditions were more favorable for Site 01 pilot operation because of better separation of multivalent and monovalent ions in the NF unit.

Site 02 pilot treated the reverse osmosis concentrate stream of the Evides Demin Water Plant located in Botlek industrial area. The experiments were separated in two modes of operation; Mode I and Mode II. The configuration of the units was different in the two modes. In Mode I, the reverse osmosis concentrate was firstly treated with the Nyex unit, where TOC was removed by 82.3%. Then, the effluent of the Nyex unit was treated by a nanofiltration unit achieving 93% rejection of SO_4^{2-}, 18% rejection of Cl^- and 89% recovery of water. The nanofiltration permeate was treated by a reverse osmosis unit resulting in a water recovery of 90%. The nanofiltration concentrate was planned to be treated by a crystallizer unit (the EFC). However, it was found that further concentration of Na^+ and SO_4^{2-} in the NF concentrate was required for the operation of the EFC unit (unable to reach the eutectic concentration of Na_2SO_4). The RO unit was used to further concentrate the NF concentrate before it was fed to the EFC unit. Thereafter, the EFC unit successfully recovered ice (clean water) by 81% and Na_2SO_4 salt with a purity of 99.97%. The RO concentrate was treated by the MED evaporator recovering water by 67% and a solution rich in NaCl with a purity of 70%. In Mode II, the reverse osmosis concentrate was first treated with the nanofiltration unit recovering 90% of water and rejecting SO_4^{2-} and Cl^- by 94% and 52%, respectively. Thereafter, the nanofiltration concentrate was treated by the Nyex unit removing 89.7% TOC. The Nyex effluent was planned to be treated by the EFC

crystallizer unit. However, similar to Mode I it was found that further concentration of Na^+ and SO_4^{2-} was required in order to reach the eutectic concentration of Na_2SO_4. No EFC experiments were performed in Mode II because results were expected to be similar to those from Mode I. The nanofiltration permeate was treated by a reverse osmosis unit resulting in a water recovery of 90%. The MED evaporator treated the reverse osmosis concentrate resulting in a water recovery of 80% and a NaCl recovery with a purity of 95%. The recovery of Site 02 pilot in Mode I was 94%, whereas in Mode II was 88% without operation of the EFC unit. The expected recovery of Site 02 pilot in Mode II in case the EFC unit was in operation was estimated at 96%.

Abbreviations

AAS: Atomic Absorption Spectroscopy

BST: Bench Scale Tests

CIP: Cleaning in Place

DWP: Demin Water Plant

EC: Electrical Conductivity

EFC: Eutectic Freeze Crystallization

EIW: Evides Industry Water

En. C: Energy Consumption

IC: Ion Chromatography

ICP-MS: Inductively Coupled Plasma - Mass Spectrometry

IEX: Ion Exchange

MED: Multiple Effect Distillation

MF-PFR: Multi-Feed Plug Flow Reactor

NF: Nanofiltration

NR: Non Return

RO: Reverse Osmosis

SS: Suspended Solids

TDS: Total Dissolved solids

TMP: Trans Membrane Pressure

TOC: Total Organic Carbon

VSD: Variable Speed Drive

WP2: Work Package two

XRD: X Ray Diffractometric

ΔP: Pressure difference

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1 Overview of the Project

The ZERO BRINE project aimed at facilitating the implementation of the Circular Economy package and the Sustainable Process Industry through Resource and Energy Efficiency (SPIRE) roadmap in various process industries by developing necessary concepts, technological solutions, and business models to redesign the value and supply chains of minerals and water while dealing with present organic compounds in a way that allows their subsequent recovery. These resources were to be recovered from saline impaired effluents (brines) generated by the process industry while eliminating wastewater discharges and minimizing the environmental impacts of industrial operations through brines (ZERO BRINE). ZERO BRINE attempted to bring together and integrate several existing and innovative technologies to recover products of high quality and sufficient purity to represent good market value.

ZERO BRINE project consisted of four large-scale pilot plants, each one developed for different process industries. These industries were a demin water plant, a coal mining, a silica factory and a textile factory, which are located in the Netherlands, Spain, Poland and Turkey, respectively. This report is dedicated to the pilot activities in the Netherlands that were part of work package two (WP2) of ZERO BRINE project. The Dutch pilot was a large-scale demonstration plant consisting of two sites that were tested at Plant One premises in Botlek area of Rotterdam Port. Plant One, which is located nearby Evides Demin Water Plant (DWP), is a test facility focused on sustainable technology and innovation research in the Energy Port and Petrochemical cluster of Rotterdam Port (Botlek). The influent of the demonstration pilot plant were the saline wastewater streams (brines) of DWP of Evides Industry Water (EIW) located in Botlek industrial area. Site 01 pilot treated the regeneration effluent (spent regenerant) of the softening ion exchange (IEX) unit of the Evides DWP while recovering minerals, salts and water. Site 02 pilot treated the reverse osmosis (RO) concentrate stream of the Evides DWP while recovering salts and water. The aim for the quality of the recovered products was to meet local market specifications.

2 Objective

The main objective of ZERO BRINE project is to demonstrate a circular economy approach to treat industrial wastewater while redesigning the current water treatment process from linear to circular by combining commercial and innovative technologies. The best current practices applied in water treatment are related to linear processes that result in high brine stream discharges. ZERO BRINE targets a circular process that recovers and internally and/or externally reuses valuable mineral, salts and water, while residual heat is used to partly cover the energy requirements. The treatment of brine, recovery of resources and trade of products and residual heat will introduce a new supply chain of water and minerals and lead to a series of benefits for the process industries that are listed below:

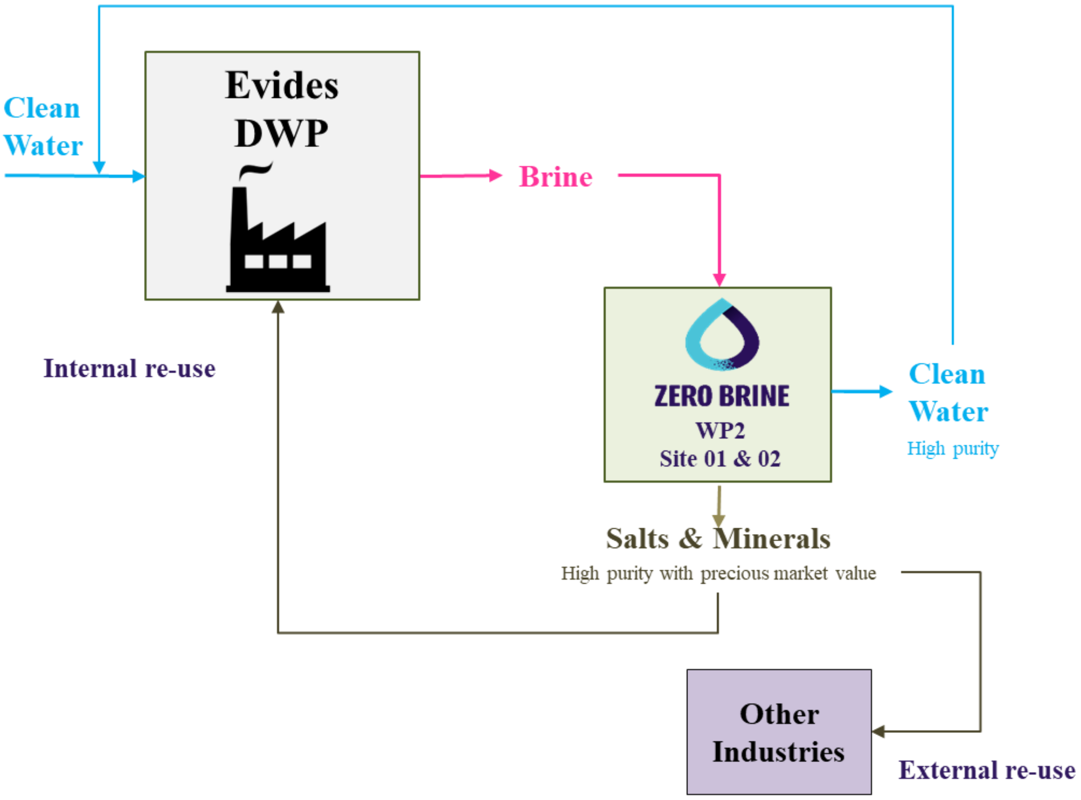
1. Lower water withdrawal with the same water demand by reusing recovered water
2. No brine discharges; No extra water demand for dilution of the brine and no environmental levies
3. Lower mineral and salt consumption from external sources by internal reuse of recovered minerals and salts (internal valorization)
4. Possible profits from external supply of products
5. Offsetting the operational costs of brine treatment by using residual heat from neighboring industries
6. Reducing the environmental impact of production by eliminating brine discharge and using residual heat

For the Dutch pilot plant, in order to demonstrate the ZERO BRINE WP2 concept (**Figure** ***1***), two individual pilots (sites) were designed, constructed and operated to treat the reject brine of Evides DWP and to recover valuable resources. These two pilots are introduced below:

- Site 01 for the treatment of the spent regenerant of IEX softener
- Site 02 for the treatment of RO concentrate

The main objective of this deliverable is to describe the start-up, the operation, the main results and the optimization of the two pilot plants (Site 01 and 02) of WP2.

Figure 1: ZERO BRINE WP2 CONCEPT; SITE 01 & 02 BRINE TREATMENT TECHNOLOGIES FOR WATER, SALT AND MINERALS RECOVERY.

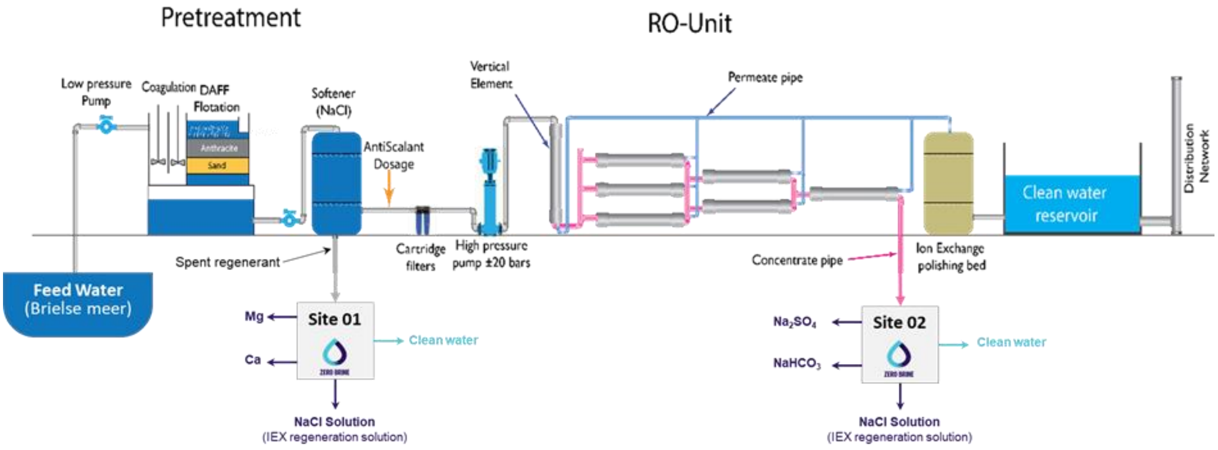


3 Introduction

3.1 Background Information

The DWP of EIW produces demineralized water (industrial process water) from raw surface water withdrawn from the Brielse meer (branch of river Maas) with a maximum production capacity of 1400 m^3/h. The process flow diagram of the DWP is given in **Figure *2***. At first, the surface water (feed water) passes through a pretreatment phase (DAFF unit) that consists of coagulation, media filtration and DAFF flotation in order to remove suspended solids (SS). Thereafter, the water enters into the IEX softening columns (cationic IEX), where divalent ions such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) from feed water are substituted by sodium (Na^+) ions. The softened water then enters into the RO units (cartridge filters are placed prior the RO unit). The RO membranes separate the softened water into permeate and concentrate. After polishing via a mixed bed IEX, the permeate is supplied to the process industries. In the RO concentrate both multivalent and monovalent anions of the feed water can be found. The cations that can be found in the RO concentrate are mostly monovalent Na^+ ions, since the main multivalent cations are removed during IEX softening. Also, the RO concentrate contains some organic matter.

Figure 2: PROCESS FLOW DIAGRAM OF THE CURRENT PROCESSES AT THE EVIDES DWP AT BOTLEK (ROTTERDAM, THE NETHERLANDS) AND THE RELEVANT LOCATIONS OF THE SITE 01 AND SITE 02.



The operation of the cationic IEX columns (softening) is a batched process that consists of a production (loading phase) and regeneration phase. When IEX resins reach the exhaustion point, they need to be regenerated. To regenerate the IEX resins, first the SS are washed out with demineralized water, then concentrated sodium chloride solution (9% NaCl) passes through the resins bed in order to replace the removed multivalent cations with Na^+ ions, finally the resin bed is rinsed to remove the excess chemicals. The stream produced during regeneration (approximately 150 m^3/day/column), also known as IEX spent regenerant, contains Ca^{2+} and Mg^{2+} among other ions. In deliverable D2.2 a detailed water quality analyses of the IEX spent regenerant is reported. The ions with the highest concentrations are chloride (Cl^-), Na^+, Ca^{2+} and Mg^{2+}. The concentration range of these ions is given in **Table *1***. Also, total dissolved solids (TDS), electrical conductivity (EC) and pH ranges can be seen in the same table. The IEX spent regenerant is considered as a wastewater stream and in the Evides DWP it is currently disposed after dilution into brackish surface water (Brittanniëhaven canal).

Table 1: CONCENTRATION RANGE OF MAIN IONS IN SPENT REGENERANT OF CATIONIC IEX COLUMNS OF DWP (ROUNDED VALUES) - SOURCED FROM DELIVERABLE D2.2.

Parameter	Unit	Range
Cl^-	g/L	1.8 – 3.1
Ca^{2+}	g/L	6.5 – 8.5
Na^+	g/L	1.7 – 8.1
Mg^{2+}	g/L	1.0 – 1.4
TDS	g/L	28.0 – 50.0
EC	mS/cm	40 - 80
pH	-	6.5 - 7.5

The RO unit of the DWP of EIW consists of 8 lines that results in RO concentrate production of 200 to 250 m^3/h, which is discharged directly into Brittanniëhaven canal (Brackish water). A detailed water quality analyses of the RO concentrate is reported in deliverable D2.2. The ions with the highest concentration are Cl^-, Na^+, bicarbonate (HCO_3^-) and sulfate (SO_4^{2-}) (**Table *2***). This brine stream might be less concentrated compared to the IEX spent regenerant, but it is considered extreme due to its high volume.

Table 2: CONCENTRATION RANGE OF MAIN IONS IN RO CONCENTRATE OF DWP (ROUNDED VALUES) - SOURCED FROM DELIVERABLE D2.2.

Parameter	Unit	Range
Cl^-	g/L	0.50 – 1.1
Na^+	g/L	0.85 – 1.2
HCO_3^-	g/L	0.85 – 0.95
SO_4^{2-}	g/L	0.25 – 0.35
TDS	g/L	2.5 – 3.5
EC	mS/cm	3 – 4
pH	-	8.8 - 9.8

It is clear that both IEX and RO treatment processes result in the production of brine streams that need to be managed. The disposal of brines is costly, requires external resources (dilution water, energy for transport) and it is associated with environmental concerns. Moreover, in most European countries a ban on the disposal of brine streams is gradually implemented. In the same time, the demineralized water demand is increasing due to global rapid industrialization, but the available water resources are limited due to climate change. Therefore, greater water reuse and reduced discharges is important to keep demineralized water production sustainable. Further research on innovative brine management methods is advised in order to reduce the negative impact of brine disposal and to advance the circular economy business models.

3.1.1 Evides Prospect on ZERO BRINE Concept

EIW in an effort to contribute in the circular economy is searching for solutions that can increase the sustainability of existing processes such as that of the DWP in Botlek. The main goal of EIW is to achieve production of water without producing waste streams and in parallel to reduce the consumption of raw materials (minerals and salts) that are required for cleaning and regeneration purposes. ZERO BRINE project offers a solution to the brine disposal challenge while recovering valuable salts and minerals. The main brine streams produced during the process of the DWP of EIW are the IEX spent regenerant and the RO concentrate. As it can been seen in **Figure *2***, these two brine streams of DWP were the influent water of Site 01 and Site 02 of ZERO BRINE pilots, respectively. The recovered products needed to be evaluated on whether or not they meet required purity specifications for reuse. Specifically, for a possible reuse of the recovered products in the regeneration process of the IEX softening columns, an assessment to determine if the product meets the required specifications for regeneration and under which operational conditions can be reused was considered crucial. Moreover, an investigation on the possibilities for external valorization of the recovered products that cannot find an internal application can benefit the business case by increasing the financial feasibility of the implementation of ZERO BRINE project in full-scale. It must be pointed out that guaranteeing operational reliability is a compelling criteria for EIW before implementing any new process. The challenge for EIW is to guarantee operational reliability when integrating complex components to an existing system. This involves the automation of the system, which results in maintaining or decreasing the required operational actions. Therefore, the system robustness needs to be evaluated.

3.1.2 Site 01 Pilot Objective

To be able to treat and recover resources from the generated brine (spent regenerant) within the IEX softening process, ZERO BRINE offered a treatment process. The proposed solution was implemented in an industrial scale demonstration pilot called Site 01. The main objective of Site 01 was the treatment of the IEX spent regenerant while recovering (i) a NaCl solution that meets required specifications for use as regeneration solution for the IEX softening columns of DWP, (ii) $Mg(OH)_2$ and $Ca(OH)_2$ minerals and (iii) clean water.

The process flow diagram (PFD) of Site 01 is given in **Figure *3***. The treatment line consisted of a nanofiltration (NF) unit provided by Lenntech B.V, a crystallization unit provided by the Università degli Studi di Palermo (UNIPA) and an evaporator unit provided by the National Technical University of Athens (NTUA). A detailed description of Site 01 pilot's operation is given in sub-chapter 4.3.1.

3.1.3 Site 02 Pilot Objective

ZERO BRINE offers a process to treat and recover resources from the RO concentrate stream of Evides DWP. The proposed process was tested in an industrial scale demonstration pilot that was named Site 02 of ZERO BRINE project. The main objective of Site 02 was the treatment of the RO concentrate while recovering (i) a NaCl solution that meets required specifications in order to be used as regeneration solution for the IEX softening columns of DWP, (ii) sodium sulfate (Na_2SO_4), sodium bicarbonate ($NaHCO_3$) salts and (iii) clean water.

The PFD of Site 02 is given in **Figure *4***. The treatment line consisted of Nyex unit, which was a TOC removal unit provided by Arvia technology Ltd, a NF unit and a RO unit both provided by Lenntech B.V, an Eutectic Freeze Crystallization (EFC) unit provided by Delft University of Technology (TU Delft) and an evaporator provided by NTUA. The operation of the pilot in Site 02 was tested in two configurations (Mode I and Mode II), where the position of the NF and the Nyex units was different. More information about the Site 02 pilot's operation and the two tested modes is given in sub-chapter 4.4.1.

Figure 3: PROCESS FLOW DIAGRAM OF SITE 01 - ZERO BRINE PROJECT

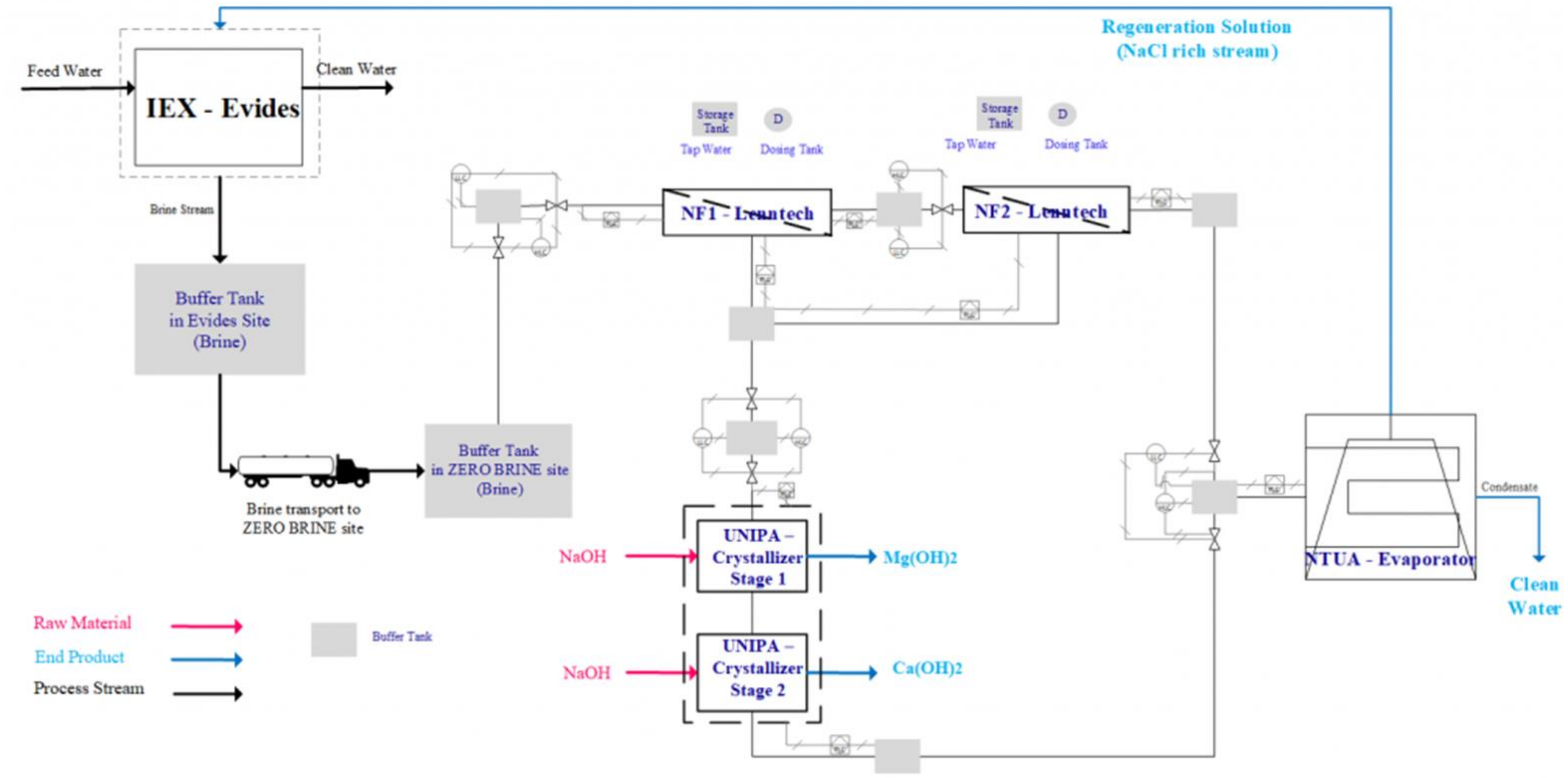
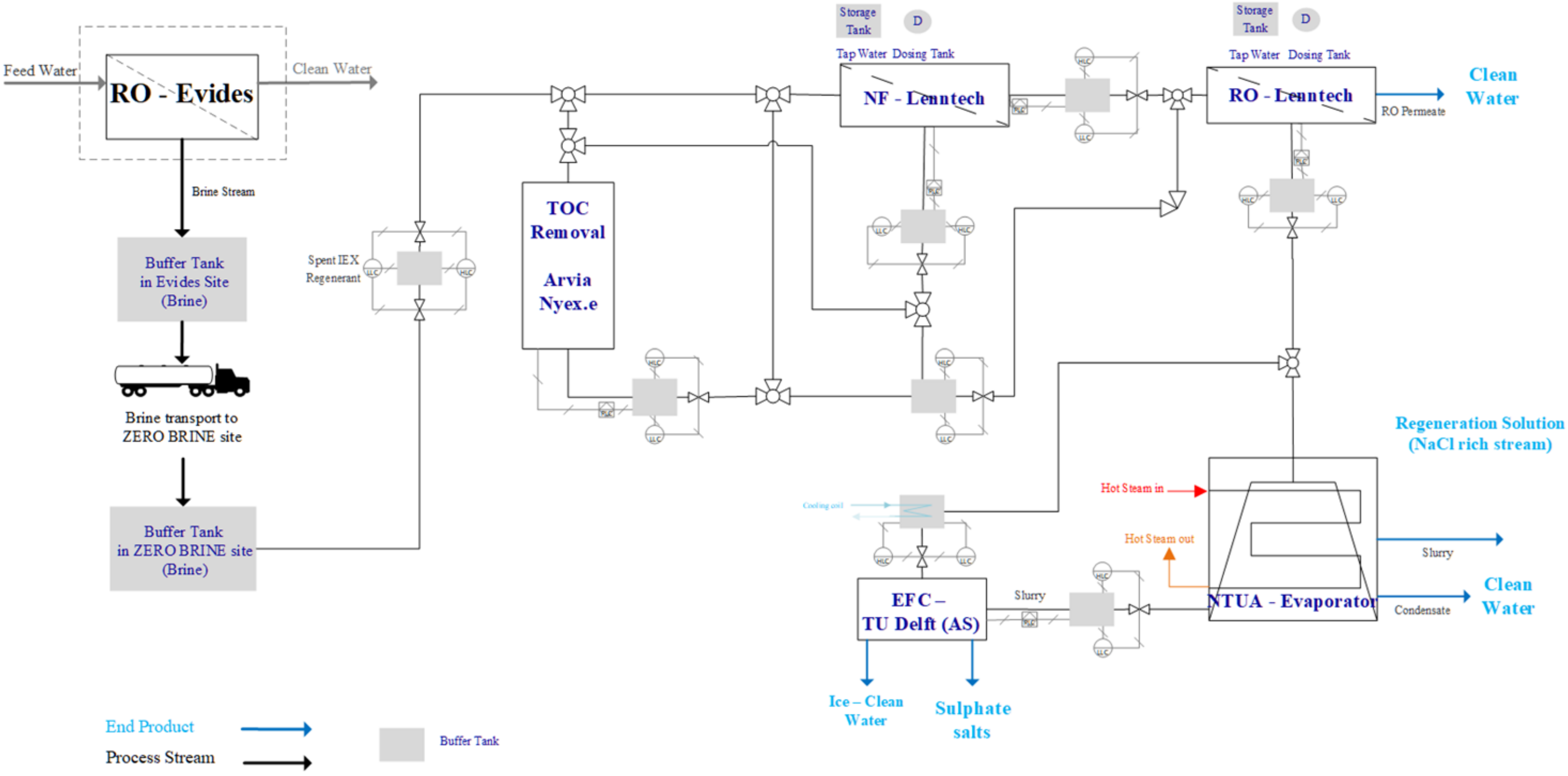


Figure 4: PROCESS FLOW DIAGRAM OF SITE 02 - ZERO BRINE PROJECT



3.2 From Concept to Pilot

The concept of the ZERO BRINE project was described in the grant agreement 730390. In order to proceed from a concept to a full-scale design, a pilot scale research is usually required. The units for both Site 01 and Site 02 were designed based on a series of requirements that were defined and explained in previous deliverables. Specifically, the first two steps for the design of all units were the wastewater characterization (physiochemical analyses) of the influent water for both sites (deliverable D2.2) and the simulation with PHREEQC of the chemical processes that can occur in the influent water as well as in the streams produced from all process units (deliverable D2.1). The third step were bench scale tests (BST) that took place for all units aiming to address preliminary design questions. Then, the design of each component consisting of complete piping and instrumentation diagrams (P&IDs) and a detailed description of the control philosophy was carried out and is presented in deliverable D2.4. In the following sub-chapters the design fundamentals and control philosophy followed for each unit component of Site 01 and Site 02 pilots are summarized.

3.2.1 Site 01 Design Fundamentals

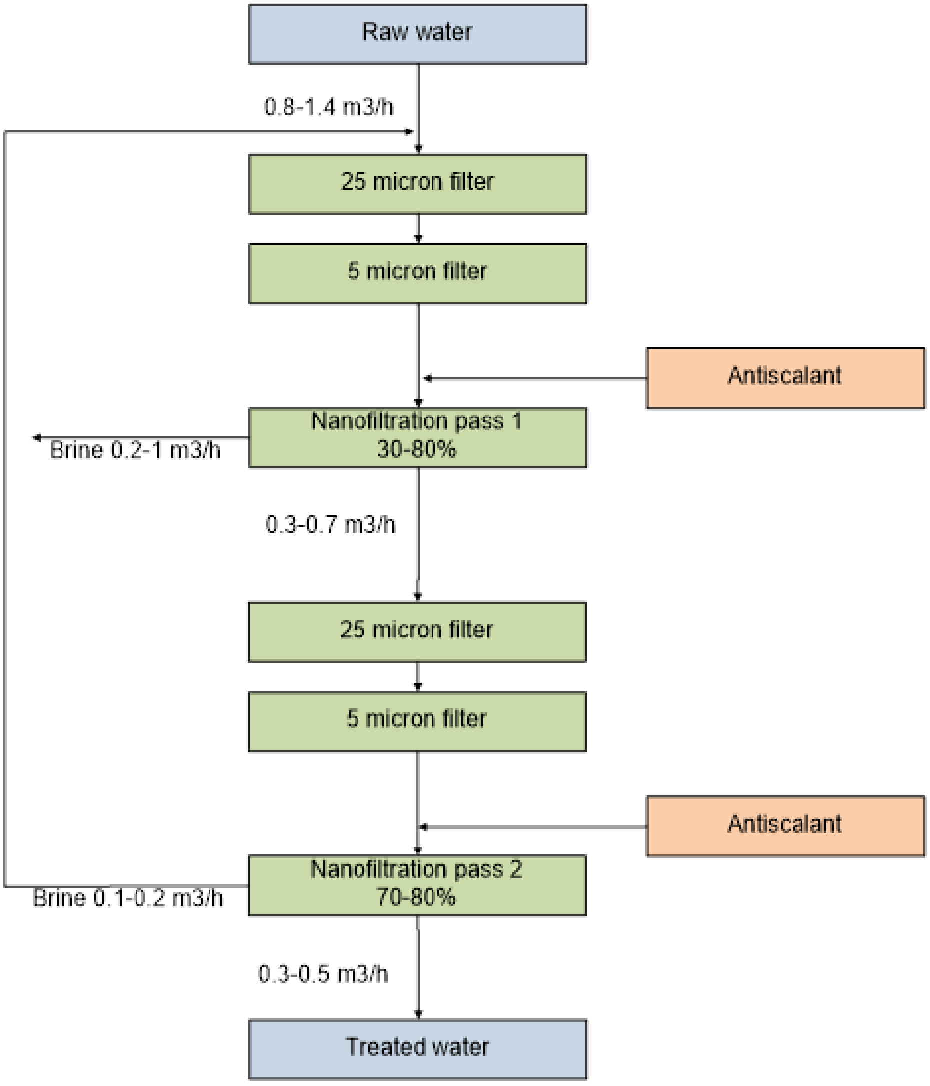
Nanofiltration unit provided by Lenntech B.V.

The design of the NF unit for Site 01 was based on a predefined feed, permeate and concentrate flow rates, as well as a predefined feed water analysis (deliverable D2.2). In the BST for the NF unit, several commercial NF membranes were tested and the quality of permeate and concentrate of these membranes was determined. Thus, the most suitable NF membrane that separated the monovalent ions from multivalent ions was found and selected to be used in the unit (deliverable D2.3). Based on the ion rejections as determined during the BST, a two pass NF configuration was required; the permeate of the first pass should be treated by the second pass of NF.

The software Avista Advisor (Avista Technologies) was used to calculate the maximum attainable recovery of the unit based on the feed water composition for several options of chemical antiscalant dosing, dosing rate, and pH values. The recovery, the feed water flow rate and composition, and the specific membrane characteristics were used to design a single array of the first NF pass. To allow flexibility in the pilot plant operation and to ensure that the permeate quality is adequate, the unit was designed taking into account the possibility to use a single pass or a two-pass unit as well as the recirculation of concentrate from the second pass to the feed of the first pass. The array of the second pass was calculated in the same way as the first pass, using the permeate of the first pass as feed water.

The design was verified using calculation tools. The unit parameters such as the produced water composition, membrane element flux, operating pressure, pH of the resulting permeate stream were estimated to make sure that all values were within acceptable operational ranges. Thereafter, the concentrate and permeate flow rates and the feed pressure requirements for both passes were set. The selection of equipment, instrumentation and control system was made in such a way that automated system operation was possible. The P&ID diagram and 3D design of the NF unit including all required equipment and instruments were drawn to facilitate the construction and assembly of the unit. Pass one and Pass two of the NF system were built with ample flexibility, allowing to test different combinations of pressure vessels (up to 6), different recoveries and different pressures. This enabled operation with a varying feed water salinity and allowed the constructed units to be used for both Site 01 and 02. The resulting PFD of the NF unit is given in **Figure 5**. For flexibility during testing, the recirculation of the second pass concentrate back to the feed of the first pass, as well as the complete isolation of the second pass were kept as options.

Figure 5: PFD OF NF UNIT

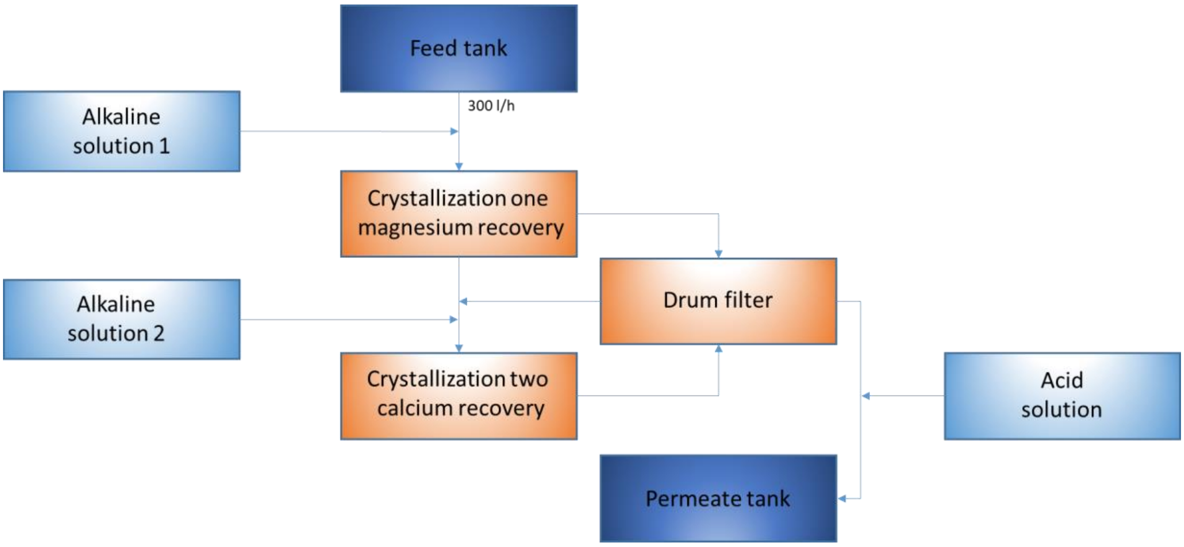


Crystallizer unit provided by UNIPA

The crystallization unit was a multi-feed plug low reactor (MF-PFR). The design of the MF-PFR was developed to process the concentrated flow coming from the NF unit. This stream contains the divalent ions Mg^{2+} and Ca^{2+} that can be removed by reactive crystallization. The feed was mixed with a suitable alkaline reagent to produce a slurry where Mg^{2+} and Ca^{2+} ions were precipitated as hydroxides.

The first design step was the choice of the alkaline reagent, that is sodium hydroxide (NaOH) because it guarantees a purer product and a better separation than other reactants. The crystallization process took place in two stages. First, Mg^{2+} was removed as magnesium hydroxide ($Mg(OH)_2$). Second, Ca^{2+} was removed as calcium hydroxide ($Ca(OH)_2$). Both hydroxides are insoluble inorganic compounds. The separation is possible because the solubility product constant is different enough, more precisely six orders of magnitude. The next design step was to use the information described in the previous paragraph and that obtained during the BST of the crystallization unit (deliverable D2.3). The NF concentrate stream (crystallizer influent) and alkaline solution were mixed until a desired reaction pH level was reached. For the crystallization of Mg^{2+} the targeted pH was between 10.4 and 10.8 . Then, the solid formed from the liquid part was separated and independently treated with a drum filter. The permeate at this point underwent a second reactive crystallization, this time a different reaction pH was reached, that was above 13 for the crystallization of Ca^{2+}. Again, the solid product was independently treated with a drum filter. The resulted PFD of the MF-PFR unit is shown in **Figure *6***.

Figure 6: PFD OF THE MF-PFR UNIT



To allow greater flexibility of operating conditions, while also maximizing the separation of divalent ions, the design of the unit took into consideration the construction of a crystallization reactor that would allow the best possible mixing. The choice fell on a drill coaxial tube positioned inside the main tube. In this way, only one inlet was needed for the brine solution after which it was mixed with the alkaline reactant in the main tube. Regarding the protection from chemicals, materials with high chemical resistance were chosen such as polypropylene or Plexiglas. Furthermore, the unit was equipped with sensors, such as pressure transducers, EC meters, flow meters, pH meters and control systems actuated by motorized regulating valves. The unit was able to operate in a wide range of concentrations without compromising the effectiveness of the separation of the two divalent ions.

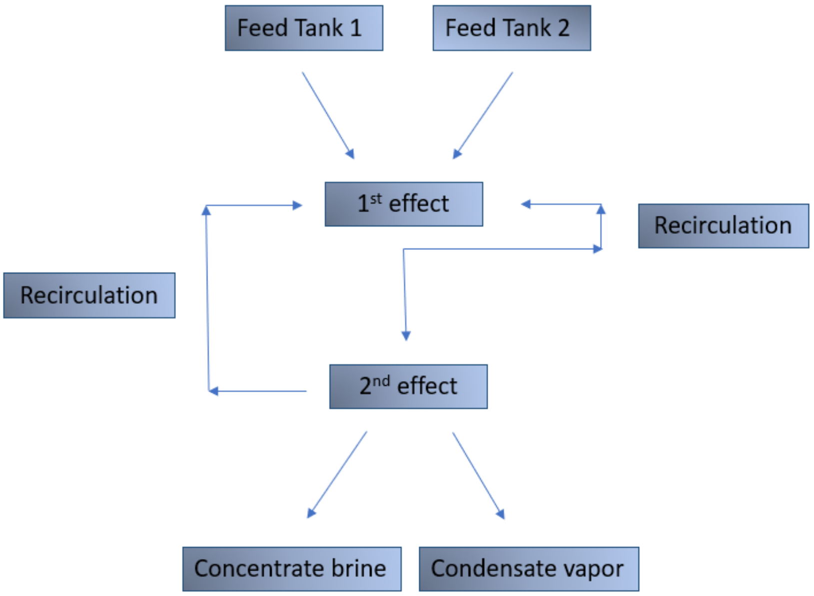
MED Evaporator unit provided by NTUA

The Multiple Effect Distillation (MED) evaporator unit was designed within the framework of the SOL-BRINE project. The main goal of SOL-BRINE project was to design, develop, test, demonstrate, optimize and evaluate an innovative energy autonomous brine treatment system for water recovery and production of dry salt with potential market value. The unit is able to eliminate brine, produced by desalination units, in line with the Zero Liquid Discharge concept and Water Framework Directive (2000/60/EC).

For each component of the MED evaporator unit a mathematical model was developed, based on mass and energy balances and on the equations used for sizing and designing purposes. These models were used for the development of a simulator that was built in Visual Basic Environment.

Thus, the MED evaporator was made up of two consecutive effects and it operated below atmospheric pressure, limiting the boiling temperatures below 100^{o}C. In each of the MED effects, brine was evaporated resulting in the production of two subsequent streams: (i) a water vapor stream that is then condensed and recovered as fresh water and (ii) a more concentrated brine stream. The vapor stream of the first effect was used to heat the concentrated brine produced in the second effect that was sprayed on top of the bundle, running down from tube to tube by gravity. Therefore, the necessary latent heat for brine vaporization in the second effect was provided by internal heat gain (heating steam from the first effect) and thus energy recovery was achieved. The vapor stream produced by the second effect was used for pre-heating purposes. Specifically, the vapor was passed through a plate heat exchanger where it was condensed, transferring its thermal energy to the brine stream of inlet feed. The PFD of the MED evaporator unit is depicted in **Figure *7***.

Figure 7: PFD OF MED EVAPORATOR UNIT

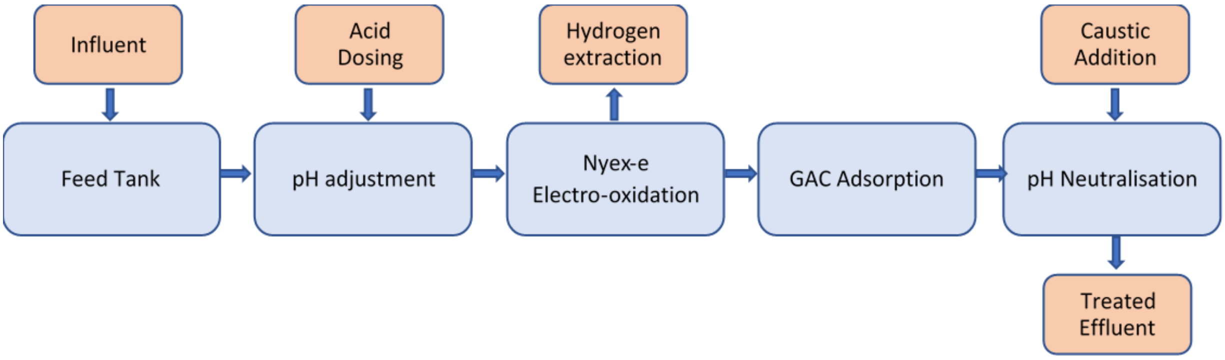


3.2.2 Site 02 Design Fundamentals

Nyex unit provided by Arvia technology Ltd

A series of BSTs took place to determine the effectiveness of removing TOC from the RO concentrate with Nyex technology. It was found that a combined pH correction, Nyex electro-oxidation and adsorption into Granular Activated Carbon (GAC) was required, followed by pH neutralization. Therefore, a pilot scale unit of the Nyex 16-50E was designed that was also combined with pH dosing and a GAC treatment step and it was integrated into a 12 m container. The PFD of Arvia's unit is given in **Figure *8***.

Figure 8: PFD OF Arvia's Nyex ELECTROCHEMICAL OXIDATION UNIT

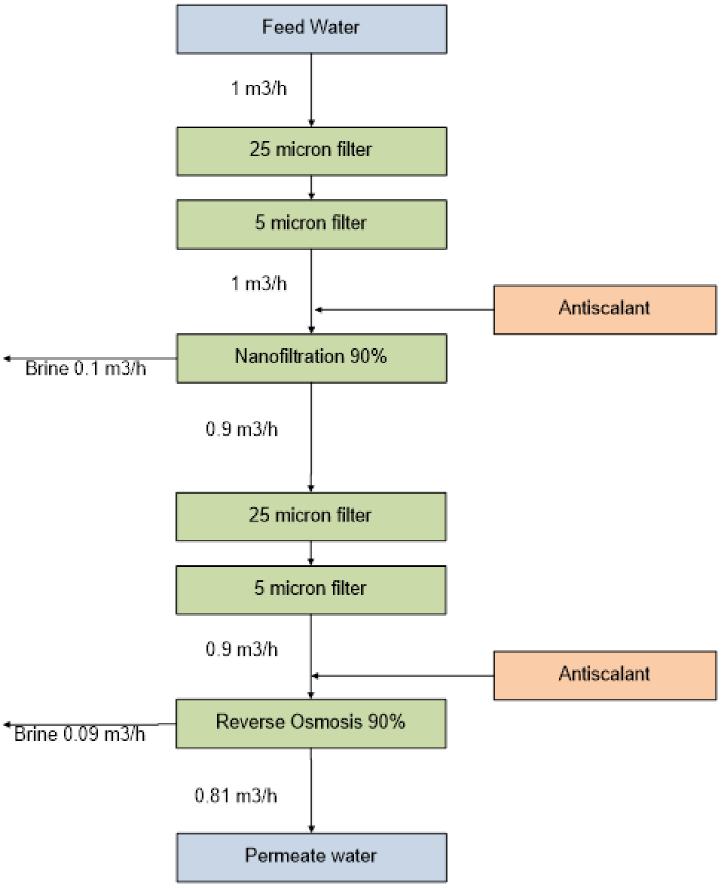


Nanofiltration and Reverse Osmosis units provided by Lenntech B.V.

BSTs were performed to treat the RO concentrate from the DWP of EIW. Based on the respective BST results, a one pass NF would suffice for the treatment of the RO concentrate. For the NF membrane selection, BSTs were conducted using two NF membranes to treat the RO concentrate from the DWP of EIW before and after treatment with Nyex. An NF membrane that highly rejects SO_4^{2-} and permeates Cl^- ions was found and selected to be used in the pilot experiments (deliverable D2.3). For the RO membrane permeate/concentrate water quality expectations no BST took place. RO is a conventional treatment process and it can be easily predicted by commercial software. In this case, ROSA software (developed by Dow) was used (deliverable D2.3).

The two NF units used in Site 01 were designed with the flexibility to operate with various flow rates, pressures and recoveries and with either NF or RO membranes. Subsequently, the same units were used in Site 02; the first pass NF unit of Site 01 was used for the NF unit in Site 02 and the second pass NF unit of Site 01 was used for the RO unit of Site 02. For the design fundamentals of both units please refer to sub-chapter 3.2.1. The PFD of the NF unit and the RO unit are given in **Figure *9***.

Figure 9: PFD OF THE NF AND THE RO UNITS



EFC unit provided by TU Delft

A few BSTs with a 2 L EFC setup were performed using a synthetic solution resembling the NF concentrate in order to test the EFC equipment and observe the eutectic conditions of the system (investigate scaling issues and identify the eutectic temperature). The effectiveness of EFC for the selective separation of a salt from hypersaline complex brine is not fully explored in the literature. The EFC unit was designed based on the BSTs to selectively recover Na_2SO_4, assuming that the main compounds on the NF concentrate stream will be NaCl, Na_2SO_4 and $NaHCO_3$. Thus, the aim of EFC unit in Site 02 was to demonstrate the applicability of EFC to recover Na_2SO_4 in a particular hypersaline brine (the NF concentrate). The unit is split into three different blocks of equipment that function simultaneously; (i) the crystallizer module, (ii) the salt or ice filtration unit and, (iii) the cooling unit. The PFD of the EFC unit is given in **Figure *10***.

In **Figure *11***, the EFC unit used during Site 02 study is given. The crystallizer module was designed in modular and flexible manner. It consisted of three crystallizers which can be operated in parallel or series mode to provide flexibility for different salt concentrations in the feed stream. Three 20 L scraped cooled triple wall glass crystallizers were used in this study for conducting the eutectic crystallization experiments. The working volume of each crystallizer was 20 L with an inner dimeter of 20 cm. The scarper consisted of three blades mounted to three equally spaced plates/discs along the height of the crystallizer, the scraper speed was set to 80 rpm, which was sufficient for good scrapping and mixing. The three crystallizer were operated in sequencing bath mode. The time of each batch was between 90 to 120 min depending on the feed concentration. So considering a maximum of 4 batches per 8 working hour, the total capacity of the crystallizer unit was 240 L per 8 hours. Cooling was performed using a Lauda Integral XT 1590 W with cooling capacity of 9.2kW.

Figure 10: PFD OF THE EFC UNIT

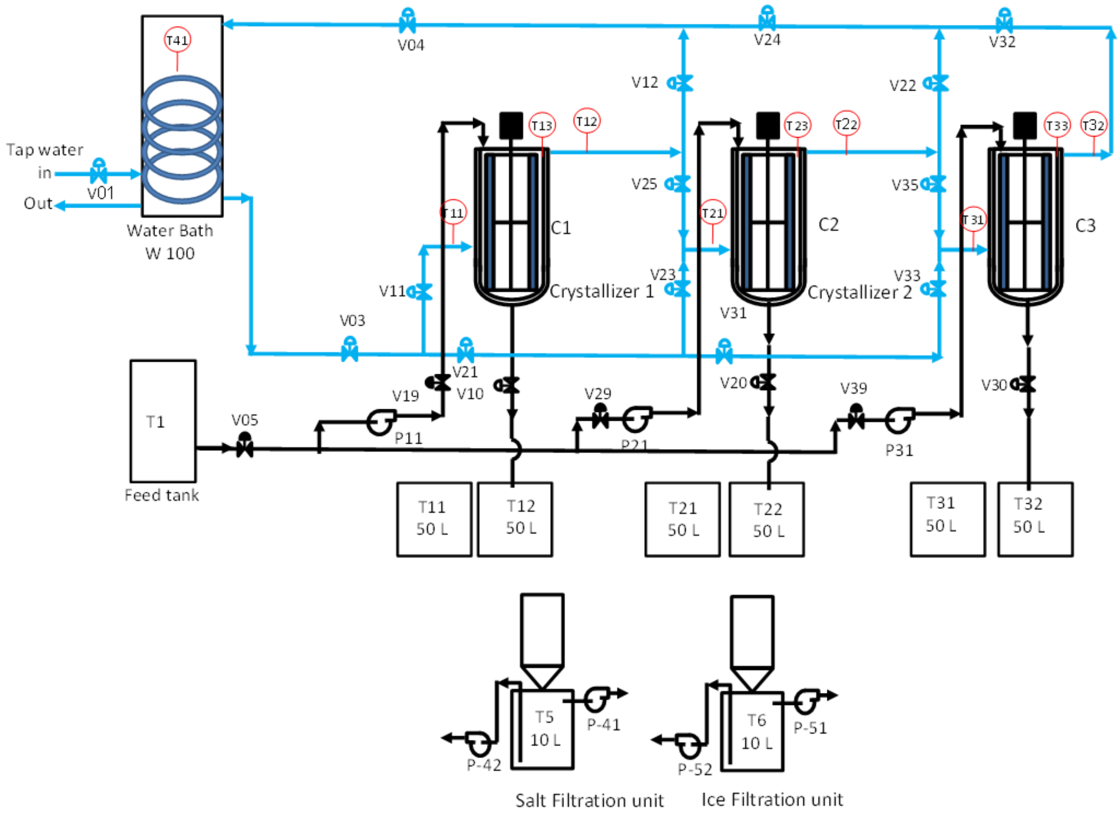


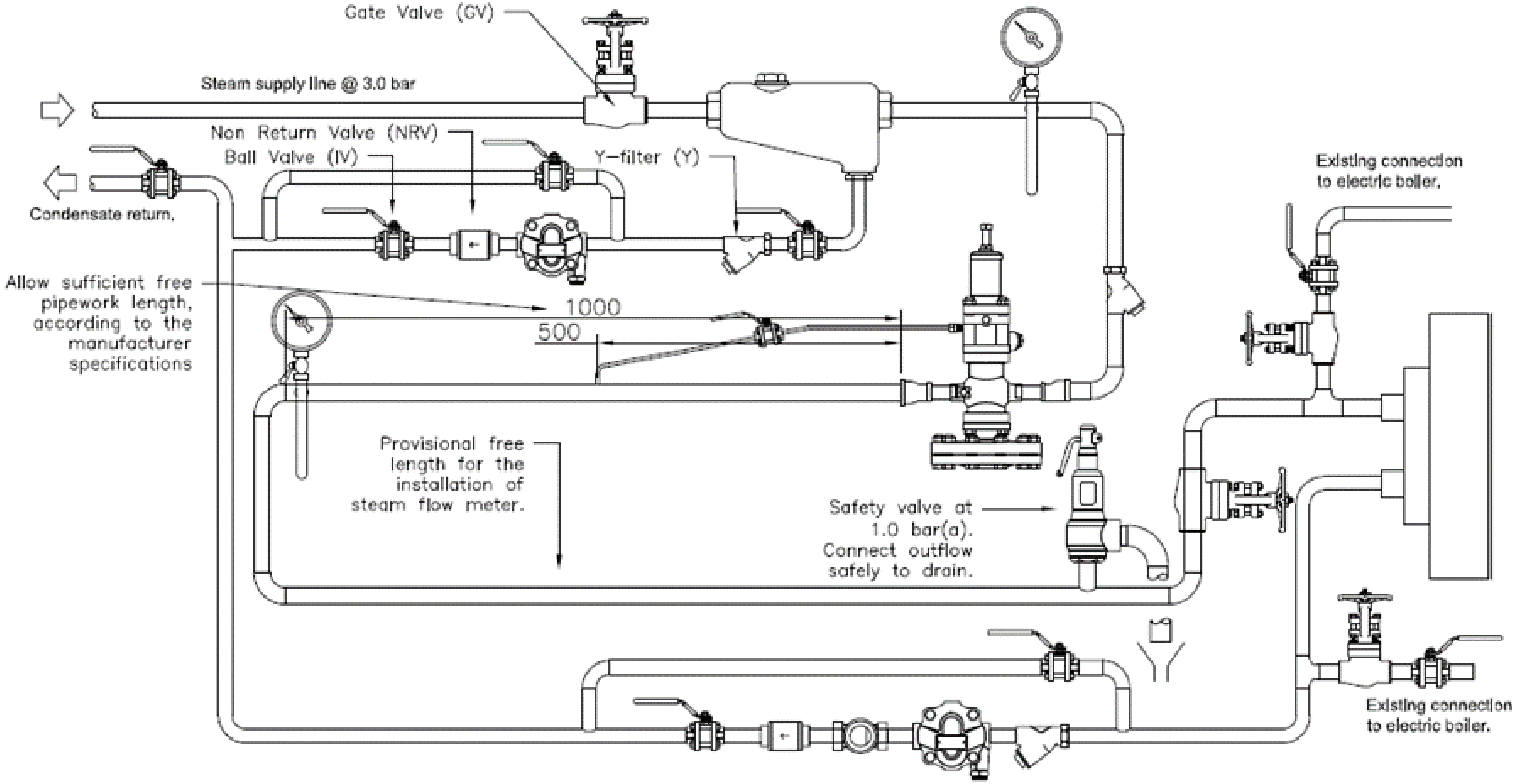
Figure 11: DEMONSTRATION OF THE EFC PLACED AT PLANT ONE ROTTERDAM

MED Evaporator unit provided by NTUA

The MED evaporator unit used in Site 01 pilot was also used in the pilot research of Site 02. Thus, for the design fundamentals please refer to sub-chapter 3.2.1. An important alteration in the operation of the MED evaporator in Site 02 compared to Site 01 was that the unit was upgraded in order to work with residual heat. The unit in Site 01 used the hot water from a boiler as a heat supply but for Site 02 the hot boiler water was taken out of operation, since steam was the main heat supply. The steam flew into the first effect (heat exchanger) transferring heat to the brine. A steam trap was installed in order to drain any remaining water or condensate in the unit. A steam regulating valve (upstream pressure) and a pressure reading valve (downstream pressure) were installed in the residual heat part to ensure that their pressures were below 3.3 bar and 1.1 bar, respectively. The residual heat connections and the P&ID of the installed equipment are depicted in **Figure *12*** and **Figure *13***.

Figure 12: INSTALLED EQUIPMENT FOR RESIDUAL HEAT USE IN MED EVAPORATOR.

Figure 13: P&ID OF INSTALLED EQUIPMENT FOR RESIDUAL HEAT USE IN MED EVAPORATOR.



3.2.3 Site 01 Control Philosophy

The following paragraph describes the main control features of the unit components. A detailed description is issued in deliverable D2.5 with specific equipment code relating to all reference documents and detailed engineering work.

Nanofiltration unit provided by Lenntech B.V.

The unit was controlled by an advanced control system and operated in semi-automatic mode. All operation sequences were automatically controlled except start-up and maintenance. Start-up was controlled in a semi-automatic manner. Maintenance took place manually. Adjustments for operation based on on-site conditions was performed by the operator by means of regulating throttle valves and potential frequency drives. Permeate production was adjusted based on recovery using concentrate regulation valves and variable speed drive (VSD) / throttle regulation pump valves. Closing the concentrate control valves resulted in a concentrate flow restriction, thus an increase in permeate production and recovery. High pressure pumps discharge pressures were adjusted by means of throttle valves or local VSD and control. Main safety functions were controlled by alarms and warnings within the control system limits. Instrumentation was mainly composed of switch-type equipment. The operator was responsible for operation within the equipment specifications when no safety was engaged.

Crystallizer unit provided by UNIPA

The control system of the crystallization unit was based on the regulation of pH and feed flow rates , which were read from analog sensors connected with a data acquisition (DAQ) system. A virtual "ring" was then created where the control system closed the loop with an electrical connection between the physical process and the internal processing logic, thus allowing for the actuation of a regulation action operating on the control valves in the alkaline and feed lines.

The pH value was a key parameter to achieve efficient separation between the two cations (Ca^{2+} and Mg^{2+}) by fractional reactive crystallization. A partially automatized pH control loop was implemented to control the pH value measured at the outlet of the crystallizer. This loop adjusted the alkaline reactant flow rate using an electro-motor valve. An effective flow rate of alkaline solution dispensed within the crystallizer consequently allowed the operator to obtain desired pH values.

MED Evaporator unit provided by NTUA

The control of the unit was accomplished via a PC-based supervisory control and data acquisition (SCADA) interface. Multiple temperature, pressure and flow transmitters were connected in many positions within the system, receiving all the important data for process control. The overall control and monitoring were achieved using SCADA. All data was collected and controlled using a programmable logic controller (PLC). The aim of the automation system was to display and record information related to the processes, the operation of the equipment etc.

3.2.4 Site 02 Control Philosophy

Nyex unit provided by Arvia technology Ltd

Arvia's containerized Nyex electrochemical oxidation unit was controlled by a PLC to maintain continuous operation of the unit. The unit, shown in Figure 8, comprised of a feed tank into which the brine to be treated was transferred to allow the Nyex unit to operate continuously. As the brine was pumped from the feed tank, it passed through a mesh filter to remove any solids in the brine and sulfuric acid (H_2SO_4, 40% solution) was dosed. An in-line mixer ensured that the acid/brine solution was fully mixed before passing into the Nyex reactor tank.

In the Nyex reactor tank, the brine passed through a number of electrochemical cells where the organics within the brine were oxidized. At the anode the organics were oxidized to carbon dioxide and water, with the possible production of chlorine (Cl_2) from Cl^- ions in the water. Reduction of water occurred at the cathode, producing hydroxide (OH^-) ions and hydrogen gas (H_2). The H_2 was vented via an extractor system, sized to ensure that the H_2 concentration remained below 10% of the lower explosive level. A H_2 sensor provided a final safety check that there were no build up in H_2 concentration.

After treatment in the Nyex unit, the brine passed through a GAC adsorption column to ensure that any breakdown products were removed from the brine and that any Cl_2 that may have remained in solution was removed.

Prior to discharge from the Arvia container, the pH of the brine was corrected back to neutral using a 25% NaOH solution.

Nanofiltration and Reverse Osmosis units provided by Lenntech B.V.

Please refer to sub-chapter 3.2.3.

EFC unit provided by TU Delft

The EFC unit consisted of three crystallization reactors operated in sequencing batch mode. These crystallization reactors could be operated in series or parallel to provide flexibility for different salt concentrations in the feed stream and subsequent concentration to the eutectic point. The feed was added to the reactors and the ice and the concentrate solutions including the salt product were removed from the reactor. The concentrate solution including the salt product was sent to the vacuum filtration unit. The salt was separated from the concentrated brine solution and the solution was recycled to the unit.

The key control parameters for the EFC unit was the temperature gradient between the coolant temperature and the reactor bulk temperature. In this study, the logarithmic mean temperature difference between coolant and crystallizer bulk solution was set to be between 7 ^{o}C to 10 ^{o}C when the ice formation occurred. Since the temperature of the crystallizer bulk solution remained almost constant when ice and salt formation occurred, the only control parameter was the coolant temperature. The mixing rate was kept constant at 80 rpm in all reactors throughout the tests.

PT-100 temperature sensors were placed inside the crystallizers to record the change in temperature of the solution with an accuracy of ±0.01 ◦C. The temperature of the reactors and inlet and outlet coolant were monitored using Applikon ADI controller. The LabVIEW software was used for the recording and capturing of temperature readings every 10 s to allow monitoring online the key parameters of the process.

MED Evaporator unit provided by NTUA

The control of the unit was accomplished via a PC-based supervisory control and data acquisition (SCADA) interface. Multiple temperature, pressure and flow transmitters were connected in many positions within the system, receiving all the important data for process control. The overall control and monitoring was achieved using SCADA. All data were collected and controlled using a programmable logic controller (PLC). The aim of the automation system was to display and record information related to the processes, the operation of the equipment etc.

4 Pilot Operation and Maintenance

In this chapter, the installation, the start-up, the operational methodology and the sampling methodology of Sites 01 and 02 Pilot will be discussed. Specifically, for each site the following sub-chapters are presented:

- Integration: installation, commissioning and start-up on site
- Operational methodology: operational process, maintenance and operational challenges
- Pilot data collection

4.1 Site 01 Pilot Integration

Lenntech B.V. was responsible for the integrated plant assembly of Site 01. The installation of the pilot took place from April to August 2019. The start-up and the trial runs took place in September and October 2019. The operation of the pilot started in November 2019 and it officially ended in March 2020. Lenntech B.V. provided the required inlet and outlet hydraulic connections between all the units and installed in/out electrical connections from the local control cabinet of each unit to the main control cabinet. 1 m^3 buffer tanks equipped with level switches were placed at the feed, concentrate and permeate side of the pilot.

All technology suppliers were responsible for the start-up operation of their respective technologies. Two 7-day trips (2 persons) were made by UNIPA (from Italy to the Netherlands) and by NTUA (from Greece to the Netherlands) to assist in the start-up operation of Site 01. Information about the commissioning and the start-up on site of each unit is given below.

Nanofiltration unit provided by Lenntech B.V.

The NF unit was assembled in Lenntech's facilities. The unit was mounted in the skid and transferred to Botlek area in the beginning of April 2019. The commissioning and the start-up of the unit was finished by the end of August 2019. The plant commissioning was carried out by qualified personnel. The latter was responsible for performing site acceptance tests (SATs), instructing the operators who were responsible for plant supervision and providing safety instructions to avoid accidents. The following activities were carried out:

- SAT after installation: several visual inspections in order to determine if all equipment, valves and instruments were installed according to the P&ID and part list.
- Flushing was carried out to clean all pipes from welding material before proceeding with the interconnecting piping pressure test and loading the skids with NF membranes.
- Ensuring that the various chemical dosing systems were primed with chemicals, tested for leaks and connected to the related injection points.

The following steps were carried out to initiate the start-up process:

- The plant was in manual operation.
- The plant was flushed on low pressure for 30 minutes at a flush gauge pressure of 2-4 bar.
- The plant ran normally for one hour to allow the system to stabilize.
- System parameters were calculated and compared with design values: water recovery and permeate EC.
- Plant was shut down and restarted in auto-mode.

With the plant in auto-mode, a final test was performed by simulating set points that determine start/ stop and rinse sequences. A final function test was carried out on the plant, checking:

- Operating sequences;
- PID regulations;
- Alarms: simulation of alarms to verify the consequences of the alarms and the correct shutdown of the plant;
- Start-up and shut-down in automatic mode.

Crystallizer unit provided by UNIPA

The shipment and the commissioning were carried out in spring 2019, with the MF-PFR unit installation and the hydraulic connections. The operational tests as standalone unit were started in summer 2019 and ended in the first week of November 2019. Then, all other units were connected and all tests for assessment of the long-term operability of the plant, monitoring and control systems followed. In the first two months, two PhD students of UNIPA with support of lead operator, worked on the installation of the unit. The following commissioning steps were taken:

- Checking the unit condition after transport
- Assessing the physical integrity and operation of all the components
- Performing necessary repairs after potential damage created during transportation/storage

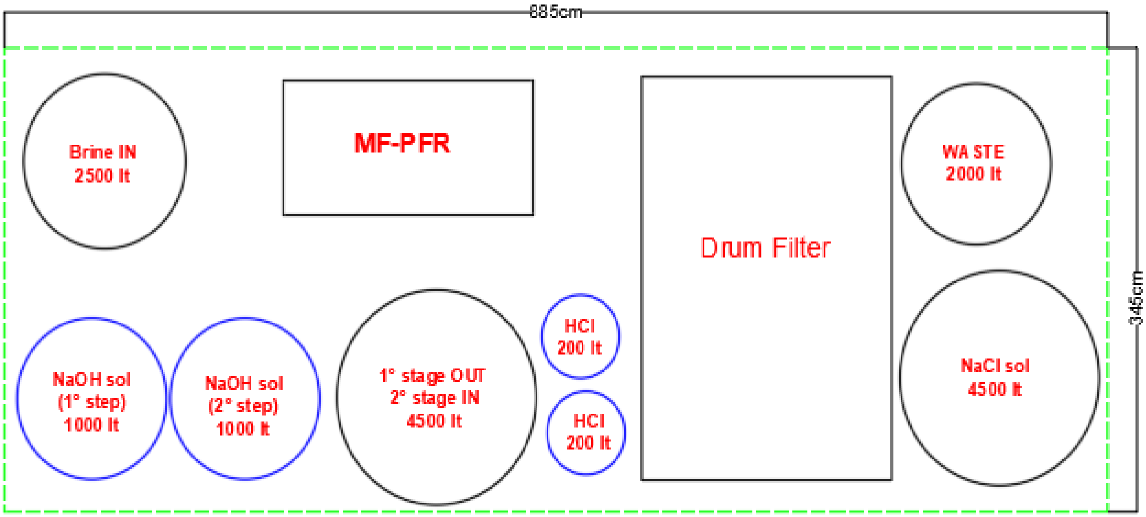
Connections between each unit followed this pre-commissioning step by UNIPA. The MF-PFR was connected both to the NF unit, from which it received the feed, and to the MED evaporator, where it supplied the concentrated brine. The integration of the MF-PFR with the other units (i.e. NF and MED) was carried out through two buffer tanks with a volume of 1 m^3. These buffer tanks were placed in order to avoid the direct connection between the various units, which also eased process control: more control on solutions passing between units. The crystallizer was also connected to a drainage tank with a volume of 3 m^3 in order to dispose/store the effluent for further use. The final PFD of the crystallizer unit is given in *Figure 6* (previous chapter).

A simplified P&ID of the crystallization unit is given in Figure *64* of Annex A: P & ID of Units. The unit was divided in three main sections. These were:

1. Precipitation section, consisting of the MF-PFR and relevant auxiliary devices (e.g. pumps, tanks and sensors);
2. Filtration section, consisting of the drum filter and auxiliary devices;
3. Neutralization section, consisting of a pH control loop with associated pumps, sensors and tanks.

The general layout is shown in Figure *14*. This lay-out was designed according to the P&ID in order to facilitate the connections between various valves and piping with the unit. This lay-out design included eight tanks of various sizes which were chosen to ensure functionality for a day's work according to project conditions. The full-scale installation was completed with a final drum filter.

Figure 14: GENERAL LAYOUT OF THE MF-PFR. BRINE IN D=130CM H=205CM; NA(OH) (1°STEP) D=110CM H=140CM(STIRRED); NA(OH) (2°STEP) D=110CM H=140CM(STIRRED); 1° STAGE OUT 2°STAGE IN D=160CM H=245CM; HCL D=62CM H=90CM; WASTE D=120CM H=195CM; NACL SOL IN D=160CM H=245CM;



MED Evaporator unit provided by NTUA

For a safe and easy transport of the MED evaporator from Greece to the Netherlands, the MED evaporator was refurbished and containerized as it can be seen in Figure *15*. NTUA was responsible for the MED evaporator start-up and training of lead operator on the unit. A representative of NTUA visited Site 01 and carried out the start-up process and operator training. The training included a complete familiarization with the unit and the different values that were measured in the SCADA system. Furthermore, several trial experiments were performed under NTUA supervision, in order to monitor the process and to provide feedback during the operation. This activity ensured that the operation on Site 01 was according to the NTUA experimental process.

The unit was placed at a defined position within the plant at 15 cm above floor level for safety reasons. The unit was then connected with the NF and crystallizer units. A 1” flexible hose with camlock fittings was installed on the tanks for the connection with other units. Electrical connections and tap water connections were the final installation activities. After the installation, testing of the unit and trial operations followed.

Figure 15: MED EVAPORATOR REFURBISHED AND CONTAINERIZED

4.2 Site 02 Pilot Integration

As it is already mentioned above, three out of five units of Site 02 pilot (NF unit, RO unit and MED evaporator unit) were used again in the Site 01 pilot. Thus, they were already in place. The adjustment of the existing and the new units (connections, membrane changes from NF to RO etc.) based on the needs of Site 02 took place from April until June 2020. The delivery of Nyex unit was in April 2020 and its assembly lasted until June 2020. Then, in July and August the start-up, commissioning and trial runs took place. All units were operational by the end of August 2020, except the EFC unit. The upgrade of the MED evaporator for the use of residual heat took place later during the experimental period of Site 02 in September 2020. The delivery of the EFC unit was in December 2020 and its assembly lasted till January 2021.

All technology suppliers were responsible for the start-up operation of their respective technologies. However, due to Covid-19 restrictions no visits of the technology suppliers to Site 02 took place during the assembly and start-up (expect of Lenntech and TU Delft). ZERO BRINE key researcher and the lead operator were responsible to perform all required actions for the assembly of the new units and the upgrade of the existing units with the remote assistance of the technology suppliers. Information about the commissioning and the start-up on site of each unit is given below.

Nyex unit provided by Arvia technology *Ltd*

The Nyex unit was designed and assembled by Arvia and Arvia's contractors. Unit's operation was tested before shipment, and once again after delivery and installation. Upon arrival on Site 02, the unit was electrically and hydraulically connected to the process stream.

An important tool for Nyex unit's operation was the "User manual", which is a collaborative user manual detailing M+E as well as process elements of plant operation. The inspection of the unit's operation based on the "User manual" ensured conformation to applicable European Union legislation. The unit's operation was tested before and after shipment as follows:

Prior to commencing trials once the unit was on site, the voltage across each power supply unit (PSU) at a range of applied currents was recorded to bench mark the operating conditions of the unit (**Table *3***). This was achieved by passing water through the unit. This showed that the unit was operating as expected. As prior laboratory testing had been undertaken to enable the design of the containerized unit to be undertaken, a flow rate of 1.0 m^3/h at an applied current of 400 A for each bank of 8 cells (current density 20 mA/cm^2) were used as the baseline operating parameters.

Table 3: CURRENT/VOLTAGE CALIBRATION Nyex

Current (A)	Current Density (mA/cm^2)	PSU1 Voltage (V)	PSU2 Voltage (V)
10	0.5	2.8	3.0
20	1	3.5	3.8
40	2	4.9	5.5
60	3	6.4	7.1
80	4	7.9	8.7
100	5	9.4	9.0

Nanofiltration and Reverse Osmosis units provided by Lenntech B.V.

Both NF and RO units were already in Plant One after Site 01. For the operation of Site 02, it was required to replace the NF membranes of the NF unit (former first pass NF unit of Site 01) with new NF membranes and change the former NF membranes to RO membranes of the RO unit (former second pass NF unit of Site 01). One pressure vessel that was used at Site 01 was isolated for the operation of Site 02. Moreover, the connections between the different units were adjusted based on the needs of Site 02 operation. In addition, some flow transmitters were replaced to adjust to the new measuring ranges of the flows. All required changes were performed by Lenntech within 2-3 days and the unit was ready for operation by May 2020. After the adjustment of the units, Lenntech operated both units to ensure that everything was well adjusted.

EFC unit provided by TU Delft

The EFC unit was built by DEMO at TU Delft and it was delivered at Plant One on October 16th, 2020. The installation and start up lasted two weeks. The EFC unit was skid mounted using three trolleys for quick installation and easy operation. The start-up and first tests were carried out under supervision of a researcher from TU Delft. The operation started in November 2020 and ended in April 2021. An operator was assigned for running only the EFC unit in a frequency of three to four batches per day from December 2020 to February 2021. Extra runs in March and April 2021 were performed by the researcher from AS department of TU Delft. The latter was also responsible to control and monitor the operational parameters including the batch time and the cooling rate.

MED Evaporator unit provided by NTUA

The unit was already in place. The required changes for the steam took place with equipment that NTUA sent to the Netherlands during August 2020 and the overall installation took one month. After that, NTUA sent a manual to the operator and the first experiments were performed under close supervision of NTUA's representative. The operation with residual heat was challenging during October 2020 due to technical issues with the part for the residual heat use. More specifically, the steam was not flowing through the unit so the non-return (NR) valve had to be removed and replaced by a new piece of pipe. As soon as the necessary connections for the re-use of the residual heat was functional, some tests were performed and the unit was set in operation.

4.3 Site 01 Operation Methodology

This sub-chapter provides an overview of the operational processes during Site 01 research. The influent water of Site 01 was the IEX spent regenerant from the softening units of DWP of EIW. This brine stream was transported in batched amounts with transportation carts from the brine tanks of EIW to the ZERO BRINE site, where it was stored in the main feed tank (30 m^3). An experienced process engineer from the DWP of EIW was given the role of brine facilitator within the project. When a brine delivery was planned, the brine facilitator was responsible for ensuring that the delivered brine had the expected water quality.

The pilot was maintained and operated by a lead operator under daily supervision of the ZERO BRINE key researcher. In addition, the operation of individual process units was monitored and supervised by the respective responsible of the unit suppliers (Lenntech, UNIPA and NTUA). Below the allocated tasks for the lead operator are listed:

- Filling up the brine tank after each brine transport and taking samples
- Preparing pilot for daily experiments (making sure all units are in good condition and ready to be operated)
- Operating the pilot and performing experiments based on the provided instruction by the key researcher
- Taking samples during the daily operation and recording the operational parameters in daily datasheet
- Performing some measurements such as quality control factors (EC and pH)

- Optimizing process conditions by close communication with the technology suppliers.
- Pilot troubleshooting together with the key researcher and technology suppliers
- Performing daily and weekly cleaning and maintenance based on the provided instruction by the key researcher and technology suppliers
- Reporting process observation and recording all the challenges that were faced
- Communicating with the key researcher and technology suppliers about any issue during the operation

4.3.1 Overall Operation of the Pilot

The general operational procedure of Site 01 pilot is described as follows. The IEX spent regenerant (brine stream) was passed through the NF units, followed by the MF-PFR and lastly the MED evaporator. When operation started, water from the main feed tank flowed to the feed tank for the first NF unit using hydrostatic pressure. The NF membranes separated the spent regenerant into permeate and concentrate. NF permeate should contain mainly water and monovalent ions such as Na^+ and Cl^-, while the NF concentrate should contain mostly divalent ions such as Mg^{2+} and Ca^{2+}. The NF performed filtration in 2 passes. The permeate formed by the first NF unit was used as the feed for the second NF unit. The concentrate produced by both NF units was stored in a tank. The permeate from the second NF unit was stored in a separate tank. The mixed concentrate was the feed for the first stage of MF-PFR while the permeate was the feed for the MED evaporator unit. The concentrate was rich in divalent ions such as Ca^{2+} and Mg^{2+}, while the permeate was rich in monovalent ions such as Na^+ and Cl^-.

The mixed concentrate was processed by the first stage of the MF-PFR in which sodium hydroxide (NaOH) dosing and pH adjustment enabled the recover $Mg(OH)_2$. After being processed by the first stage, the brine was transferred to a settling tank to allow the settling of the formed $Mg(OH)_2$ crystals. After settling, the dense slurry was separated and processed in the vacuum drum filter for dewatering and crystal recovery, while the clarified brine was used as feed for the second stage of the MF-PFR. Similar to the first stage, after the feed passed though the unit and crystallization of $Ca(OH)_2$ occurred, the brine was directed to a settling tank for the separation of $Ca(OH)_2$ dense slurry from the remaining brine (virtually Mg^{2+}- and Ca^{2+}-free). The formed ($Ca(OH)_2$ crystals was separated from the liquid phase using a vacuum drum filter. The final clarified brine was neutralized to a pH of 7 and was fed as the second feed stream to the MED evaporator unit.

The MED evaporator operated on two different feed streams. Also, two product streams were formed in the MED evaporator: (i) a highly concentrated NaCl solution (concentrate) and (ii) pure water (condensate). For this demonstration pilot plant, all the products were discharged at the end. An overflow tank was added to prevent leakages from the MED evaporator products. The overall lay-out of Site 01 pilot hall is presented in Annex B: Pilot Floor Plans (**Figure 65**).

4.3.2 Operation, Maintenance and Challenges per Technology

Nanofiltration unit provided by Lenntech B.V.

The NF process was composed of two passes NF and it was treating 0.8 to 1.4 m^3/h of brine. During the NF process, water and monovalent ions permeated through the membranes while divalent ions were rejected and concentrated in the so-called concentrate stream. The so-called permeate stream of the first pass NF (NF1) that was still rich in monovalent ions was treated by the second pass NF (NF2) so that the concentration of divalent ions was further decreased.

The operation started in November 2019 and ended in February 2020. An operator was running the NF unit in a frequency of three times per week. Lenntech B.V. was responsible to set and monitor the operating parameters (flow rates of the permeate, concentrate and recirculation stream and antiscalant dosing) in order to ensure the smooth operation of the unit. The EC of the feed stream was measured, and the brine quality and the ionic composition were assessed. Based on the brine quality and the unit's performance (feed pressure, water recovery), the operation was step by step optimized. By not exceeding the maximum pressure (40 bars) to be applied in the membranes and by meeting the hydraulic requirements of the membranes, the water recovery was adjusted. After one month of operation, the NF configuration was changed by recycling back the NF2 concentrate to the NF1 feed stream. The NF2 concentrate stream contained lower concentrations of divalent ions compared to the NF1 concentrate stream. The dilution of the second stream was prevented by not mixing the two streams.

After the end of each operation, the unit was manually rinsed to remove the salts present in the membranes that could cause scaling. In case of an alarm that was shutting down the unit, an automatic rinse was performed. The unit was also equipped with tanks and chemicals for chemical cleaning in case of scaling, but there was no need for this during the experimental campaign. At least once per month the cartridge filters were replaced by new filters as there were contaminated by rust or particulate fouling. The EC transmitters were calibrated once.

Difficulties were encountered sometimes during operation such as unstable operation or missing data logging. There were also several issues that hindered the unit's stability:

- For a few days, the unit's recovery was not kept stable as the concentrate flow rate changed by manually adjusting the concentrate needle valve
- During some days, data recording was hindered due to a poor connection between the unit and the laptop
- When the operating parameters were reported using daily pictures, the stability of the unit was not ensured

In addition, the planning was challenging as several tests were performed with different ranges of ionic composition without knowing the exact brine composition at the start of each experiment. Knowing the exact brine composition facilitates the performance assessment and the definition of optimum operating parameters.

Crystallizer unit provided by UNIPA

First, the concentrate brine was processed in order to recover Mg^{2+} as $Mg(OH)_2$ by adding an alkaline solution i.e. NaOH-solution. The recovery of Mg^{2+} was carried out by mixing the brine with the 0.5 mol/L NaOH solution until the pH reached the value of 10.5. After precipitation, the produced slurry was sent to tank one of the settling tanks to enable the settling of the crystals. The sedimentation process ranged between 12-16 hours. After crystal sedimentation, the clarified brine was sent back to the reactor for the recovery of Ca^{2+} as $Ca(OH)_2$ while the concentrate slurry of $Mg(OH)_2$ was sent to a storage tank for filtration. The $Ca(OH)_2$ precipitation followed the same procedures explained, but using a higher concentration NaOH solution for the Mg^{2+} precipitation. However, a higher pH value was required. In this case, a pH value equal to 13 or higher was maintained for the process. The produced slurry was collected in another settling tank. The clarified solution was sent to a buffer tank for neutralization while the concentrate slurry was sent to a storage tank for filtration.

At the end of each test, the MF-PFR was cleaned using 10 M hydrochloric acid (HCl) in order to remove the scaling of $Mg(OH)_2$ or $Ca(OH)_2$. The crystallizer was then flushed using tap water. During the majority of the testing period, the responsibility of operation and maintenance was under UNIPA staff consisting of 1 or 2 PhD students. Only a few weeks of operation (8 January – 9 February 2020) were attended by the lead operator.

The main operational challenges encountered during the testing were related to the variability of brine composition. This was caused mainly by two causes acting together: (i) the natural variability of the feed brine to the NF unit (as large volumes of brines were sampled from EIW plant in different times and stored for testing); (ii) stratification of brines stored in tanks for days, which generated a difference in composition from the top to the bottom of the tank. In both cases, the variable concentration of Mg^{2+} and Ca^{2+} ions in the brine led to the necessity to modify the actual flow rates of feed and alkaline solution in the MF-PFR in order to maintain the optimal condition for precipitation, i.e. optimal stoichiometric ratio between the reactants. This caused some issues in the control system that were fixed by the intervention of operators. This highlighted the necessity of developing a more robust control system, able to act also in the presence of large variations in the composition of feed brine. Another operational issue was encountered with the co-precipitation of $CaCO_3$ with $Mg(OH)_2$, which compromised the purity of precipitated product in some tests.

MED Evaporator unit provided by NTUA

The MED evaporator was a 2-stage forward-feed evaporator with a capacity of 2 m^3/day. The unit was designed to work 20 h/d but during Site 01 research the average operational hours ranged from 3 to 5 h/d due to the brine characteristics and energy consumption. The trial week showed that 3 operational hours with different inlet volumes provided the necessary results for achieving the Grand Agreement goals.

The brine effluent was pumped from the two brine vessel units using a dosing metering pump. The inlet flow from the dosing pumps related to the brine temperature. The MED evaporator unit operated under vacuum. The first stage required a pressure of approximately 0.30 bar and the second stage 0.15 bar. A vacuum pump was used to maintain constant pressure. The pressure was regulated in each stage using the SCADA control system and electric valves.

The maintenance included running the unit with clean water after four experimental circles. The operator performed general checks prior to experimentation such as turning the Low Temperature Hot Water (LTHW) electric boiler on for 90 minutes, checking that all pumps were operational and that the unit was ready for operation.

An operational challenge faced during the given operational circumstances was the cooling water temperature. The available water did not have a constant temperature which led to the adjustment of the inlet brine flow according to the cooling water temperature. In Table *4* the required inlet brine flow in relevance to the brine temperature is given. Before each experiment the operator had to check the temperature of the cooling water and according to the table he had to operate with the corresponding inlet flow. In most experiments, the brine flow ranged between 33 L/h and 50 L/h. Another technical issue that was faced and resolved was the abnormal behavior of the vacuum pump and recirculation pump during start-ups. Moreover, some optimizations of the operation were performed, which were:

- Installing flow meters in order to monitor the outlet flow. The operator was able to monitor the flow of the two effluents.
- Installing an air-pump for cleaning purposes

Table 4: RELATING BRINE TEMPERATURE AND INLET FLOW

Brine temperature (°C)	Inlet flow (L/h)
-1 to 4	40
4 to 10	50
10 to 15	60
15 to 20	70
20 to 25	90+

4.4 Site 02 Operation Methodology

This sub-chapter provides an overview of the operational processes during Site 02 research. The influent water of Site 02 was the RO concentrate from the RO units of the DWP of EIW. This brine stream was transported in batched amounts with transportation carts in a weekly basis from the RO brine tanks of EIW to the ZERO BRINE site, where it was stored in the main feed tank (30 m^3). An experienced process engineer from the DWP of EIW was given the role of brine facilitator within the project and was responsible to enable the brine delivery.

The pilot was maintained and operated by a lead operator under daily supervision of the ZERO BRINE key researcher in WP2. In addition, the operation of individual process units was monitored and supervised by the responsible for its unit partners (Arvia, Lenntech, TU Delft and NTUA). The responsibilities of the lead operator have already been mentioned in sub-chapter 4.3.

4.4.1 Overall Operation of the Pilot

The general operation procedure of Site 02 pilot is described as follows. Two different modes of operation were tested for Site 02; (i) Mode I – Nyex prior to NF unit and (ii) Mode II – Nyex in the NF concentrate stream prior to the EFC. In **Figure *16*** and **Figure *17*** simplified PFDs of the two modes are given.

In case of Mode I, the RO concentrate of DWP stored in the main feed tank was fed directly to the Nyex unit. The effluent of the Nyex unit (stored in "NF feed" tank) passed through the NF unit where it was separated in the permeate and the concentrate. The permeate of the NF, which was rich in Na^+ and Cl^-, unit was used as the feed for the RO unit. The SO_4^{2-} rich concentrate produced by the NF units was stored in a tank, from where it was sent to the EFC unit. The products of the EFC unit were the clean water in ice form and the Na_2SO_4 salt, while there was also an effluent stream produced (slurry from crystals dewatering). The permeate from the RO unit was clean water. The RO concentrate rich in Na^+ and Cl^- and the slurry of the EFC that were both stored in buffer tanks were fed to the MED evaporator unit[3] from where two product streams were generated; (i) a highly concentrated NaCl solution (concentrate) and (ii) pure water (condensate). For this demonstration pilot plant, all the products were discharged at the end.

In case of Mode II, the RO concentrate from the DWP (stored in the main feed tank) was fed to the NF unit. The concentrate of the NF unit, which had high concentration of SO_4^{2-} and TOC was sent to the Nyex unit in order to remove TOC before the concentrate was fed to the EFC for the Na_2SO_4 salt recovery. The rest of the process was the same as in Mode I. The overall lay-out of Site 01 pilot is given in Annex B: Pilot Floor Plans (**Figure *66***).

It must be pointed out that the initial plan was to fed the NF concentrate in case of Mode I and the Nyex effluent in case of Mode II directly to the EFC unit, however, this was not feasible. As explained in detail in sub-chapter 4.4.2 (EFC part) further concentration of EFC feed (NF concentrate or Nyex effluent) via the RO unit was needed.

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[3] It must be pointed out that the initial plan was to operate the MED evaporator with EFC slurry, but this was not possible as it is explained in sub-chapter 4.4.2 (MED evaporator part).

Figure 16: PFD MODE I – SITE 02

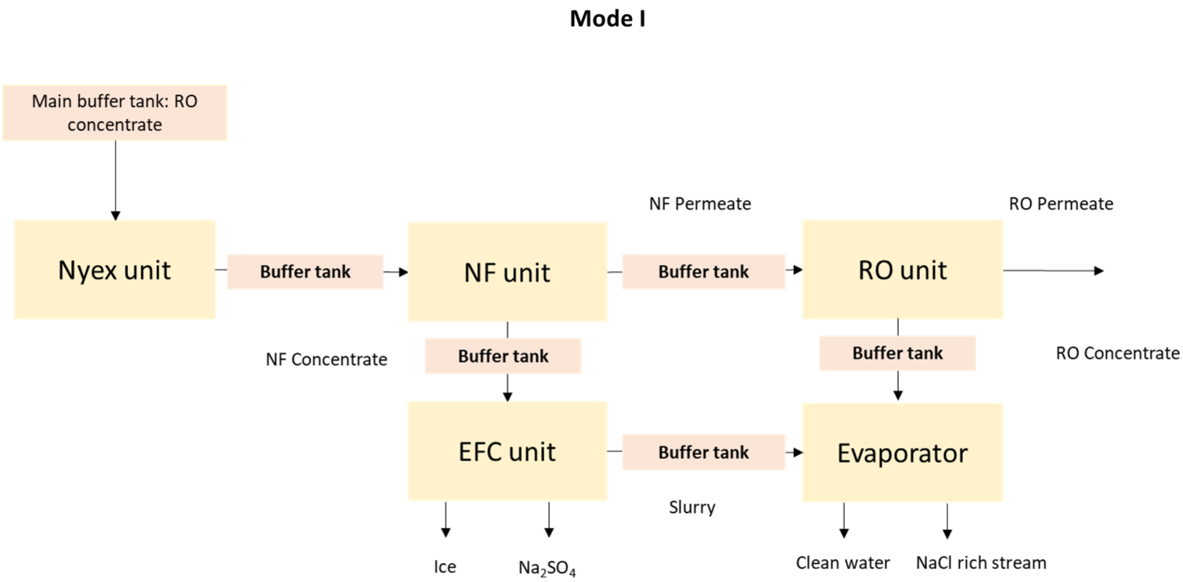
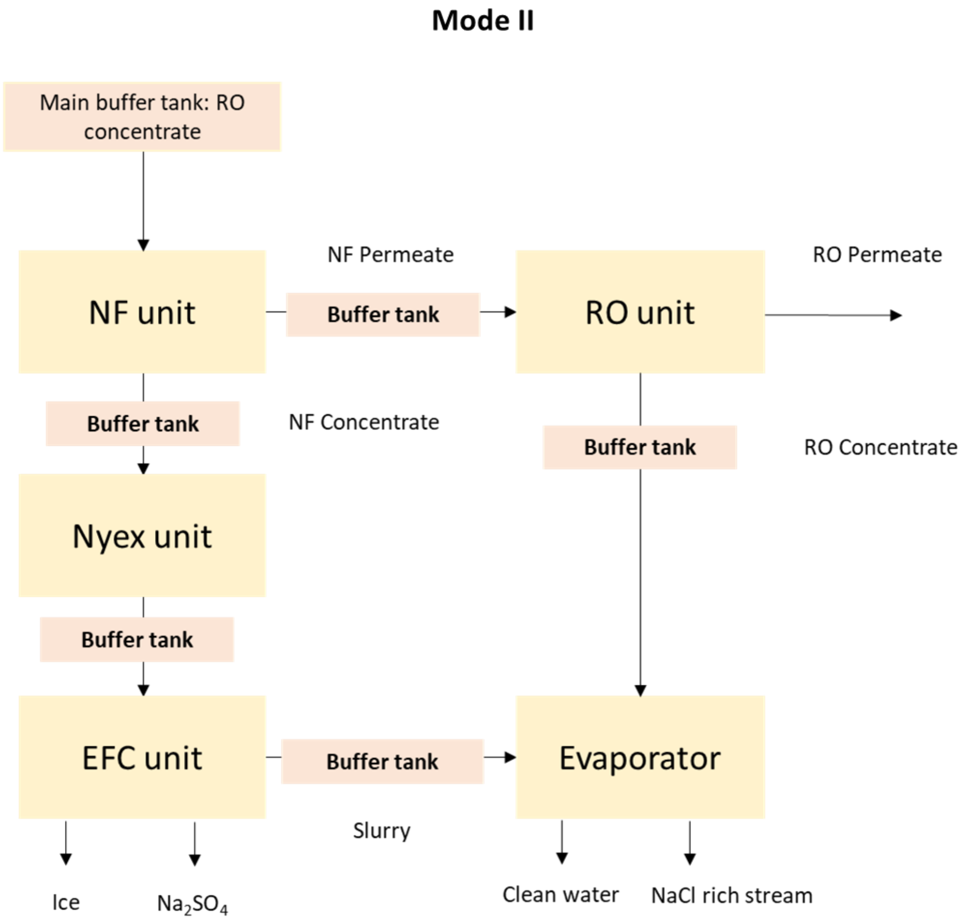


Figure 17: PFD MODE II – SITE 02



4.4.2 Operation, Maintenance and Challenges per Technology

Nyex unit provided by Arvia technology Ltd

The Nyex unit provided by Arvia Technology Ltd removed organics in the brine using a process of electrochemical oxidation of the organics via the production of hydroxyl radicals at the anode. This can sometimes be achieved more effectively in acidic conditions so the brine was acidified prior to treatments. Operation of the unit was undertaken by the lead operator under the supervision of ZERO BRINE key researcher as the covid-19 pandemic made it very difficult for Arvia personnel to visit the site. Hence commissioning and operation of the Nyex unit was undertaken remotely by Arvia working closely with the lead operator.

The Nyex unit was supplied by a batch of brine stored in a brine feed tank alongside the Nyex unit. This provided the feed to allow the Nyex unit to operate at a rate of 1 m^3/h for short periods. All the brine entering the Nyex unit passed through the process with minimal losses (possibly some evaporation of water as the brine passed through the Nyex unit).

The operation lasted from October 2020 until the end of March 2021, operating a few days per week. This operation occurred without Arvia personnel on site, although regular meetings were held between site personnel and Arvia. This close collaboration between Arvia and the site personnel was beneficial in addressing a number of technical issues that arose during the trials.

- High pressure within the GAC – the in-line mixer downstream of the GAC column and the NaOH addition resulted in a high pressure within the GAC column, which shut down the unit. This was addressed by installing a break tank with a submersible pump after the GAC column.
- Black colored water from GAC tank – after a period of shut down, black water was observed exiting the GAC column. This was believed to have been caused by the acidic nature of the brine being treated that over a period of time and in the presence of oxidizing chemicals produced within the Nyex unit causing a breakdown of the GAC particles. Analysis of these samples proved complex due to the high TDS within the sample, but it was concluded that the black color was due to very fine carbon particles (< 0.2 µm) caused by acid damage to the GAC particles. A fresh GAC column was supplied to replace the damaged GAC in the initial column, which addressed the problem.
- Extraction – to prevent the build-up of H_2 and Cl_2 within the Nyex unit, a high capacity extraction system was installed. However when this was operational, there were insufficient vents within the container to allow sufficient air to flow resulting in the shutdown of the unit due to low air flow within the extractor. This was solved by operating the container with the door open. An alternative would be to fit additional vents into the container.
- Smell of Cl_2 – On a still, calm day, the smell of Cl_2 was reported from offices close to the container. This was caused by the Cl_2 being produced within the unit not being sufficiently dispersed. This was believed to result from the presence of a mushroom cap on the extractor

pipe designed to prevent the risk of birds nesting. Removal of this cap allowed the air to be expelled upwards at faster velocities to encourage dispersion of the gases.

- Sedimentation within the pipelines/pumps – some of the brines had higher than expected suspended and dissolved solids resulting in their sedimentation and crystallization within the pumps and pipework. This was addressed by removing and cleaning the pipes. Prevention in the future can be achieved by maintaining the brine to the design parameters.
- Pipes freezing – operation of the Nyex unit was stopped as a cold period at the beginning of 2021 resulted in the freezing of pipes upstream of Arvia's container. As the weather warmed up, this problem disappeared. Although the Arvia container was insulated, operation in cold climes would necessitate either providing heating within the container or some trace heating/lagging.
- Data logging – some historical data was difficult to recover from the PLC. Hence for 2020 the data was based on the information recorded on site rather than the information stored on the data logger.

Nanofiltration unit provided by Lenntech B.V.

The NF process was treating 1 m^3/h of brine with a recovery of 90%. During the NF process, water and monovalent ions permeated through the membranes while divalent ions were rejected and concentrated in the concentrate stream.

The operation started in July 2020 and ended in March 2021. During the period of 9 months, the NF unit was operated continuously only for 4 months due to some problems that were encountered. In July and August 2020, all the other upstream/downstream technologies were not operational and for this reason the integrated pilot operation and the sampling had not started.

During normal operation, the NF unit was running in a frequency of a few times per week for a few hours depending on operator's availability. Lenntech B.V. was responsible to set and monitor the operating parameters (flow rates of the permeate, concentrate and recirculation stream and antiscalant dosing) in order to ensure the smooth operation of the unit. The EC of the feed and the permeate stream were measured, and the ionic composition was assessed. After the end of each operation, the unit was rinsed to remove the salts present in the membranes that could cause scaling. In case of an alarm that was shutting down the unit, an automatic rinse was performed. The unit was equipped with tanks and chemicals for chemical cleaning in case of fouling.

During the Site 02 operation, three different operators followed one another, resulting in less effective operation of the unit in each start until the operator became familiarized with the unit. Very often contaminated water was being filtered through the membranes and caused a change in the color of the cartridge filters. For this reason, the NF unit needed cleanings in place (CIP) or membrane replacement quite often, as indicated in **Table *5***. The cartridge filters were replaced at least once per week.

Overall, the unit's performance was difficult to be assessed and optimized throughout the operational period because of the frequent cleanings that caused unstable operation. In addition to this, the samples were analyzed several months after the operation. For this reason, the ionic separation by the NF was also evaluated several months later.

Table 5: CIPS AND MEMBRANES REPLACEMENT DURING SITE 92 OPERATION

Month	Activity
August	CIP
September	CIP
November	Membrane replacement
January	Membrane replacement
February	CIP

Reverse Osmosis unit provided by Lenntech B.V.

The RO process was treating 0.9 m^3/h of brine with a recovery of 90%. During the RO process, water permeated through the membranes, while NaCl was rejected and concentrated in the concentrate stream.

Similarly to the NF unit, the operation started in July 2020 and ended in March 2021, but it was operational only for 4 months. During normal operation, the unit was running with a frequency of few times per week for a few hours depending on operator's availability. Lenntech B.V. was responsible to set and monitor the operating parameters (flow rates of the permeate, concentrate and recirculation stream and antiscalant dosing) in order to ensure the smooth operation of the unit. The EC of the feed and the permeate stream were measured, and the ionic composition was assessed.

After the end of each operation, the unit was rinsed to remove the salts present in the membranes that could cause scaling. In case of an alarm that was shutting down the unit, an automatic rinse was performed. The unit was equipped with tanks and chemicals for chemical cleaning in case of fouling, but there was no need for this during the experimental campaign because NF, that was the upstream technology, was removing all the contaminants. The cartridge filters were replaced by new filters only a few times.

EFC unit provided by TU Delft

The design of the EFC was based on the separation of Na_2SO_4 from the concentrated stream coming from the NF unit or Nyex unit. The main chemical compounds in the feed stream were assumed to be NaCl, Na_2SO_4, and $NaHCO_3$. Although EFC has been proven to be effective in separating a single salt and water, its potential for selective separation of a salt from the complex hypersaline brines has not been explored. Thus, the aim of this pilot plant was to demonstrate the applicability of EFC to a particular hypersaline brine containing high levels of Na^+, Cl^-, HCO_3^- and SO_4^{2-}.

The crystallizer consisted of three crystallizers that were operated in parallel. The working volume of each crystallizer was 20 L. The three crystallizers were operated in a sequencing batch mode. The time of each batch was between 90 and 120 min depending on the feed concentration. Considering three or a maximum of four batches per 8 working hours, the total capacity of the crystallizer unit was between 180 to 240 L per 8 hours. The operation of the EFC unit started in November 2020 and ended in April 2021.

The initial plan for the feed of the EFC unit was in two configuration modes as follows:

- In Mode I, the concentrate of NF unit was the influent of the EFC unit.
- In Mode II, the effluent of the Nyex unit was influent of the EFC unit.

After 3 months of operation, it was found that the concentration of the feed used was too low to achieve the eutectic point and salt formation. Because samples were analyzed months later and the exact concentration of the feed used was not known, at first the opportunity to reach the eutectic point and salt formation was lost.

The typical feed concentrations for the EFC unit are given in **Table *39*** and **Table *40*** of sub-chapter 6.2.1. Because in the EFC unit in each batch the solution should be concentrated from 10 to 15% to achieve the eutectic concentration of Na_2SO_4, which is about 38 g/L, it was necessary to run about 10 subsequent batches, which was practically impossible. Therefore, the RO unit was used after the output of the TOC/ NF units to concentrate the feed to the EFC unit in February 2021. The concentrate of the RO unit was stored in a 5 m^3 tank, and the EFC tests were performed with this concentrated feed afterwards.

It should be noted that the problem of low salt concentration was related to the glass unit used in which the ice formed cannot be continuously removed from the unit. On an industrial scale, low salt concentrations would not pose a particular problem when the EFC unit would be operated in continuous mode and ice removal would be continuous. However, at very low salt concentrations the use of the EFC unit may not be economically justified due to its high energy consumption for cooling. In January 2021, due to the cold weather and some technical issues, there was an interruption in supplying brine from Evides DWP to Site 02 units, making it impossible to supply feed to EFC unit as well. Therefore, after solving the problem, the RO-concentrated feed was stored in two 5 m^3 tanks, and the operation of the EFC unit continued until the end of April 2021, even after the dismantling of the other units.

A typical operational process for the EFC unit goes as follows:

The feed was added to the reactors and the ice and the concentrated solution were removed from the crystallizer at the end of each batch. After the end of each batch, the unit was manually rinsed with tap water to remove the ice crystals. The concentrate solution was drained and collected for further concentration in subsequent batches. When the concentration of salt reached the eutectic point, further cooling resulted into the simultaneous formation of ice and salt crystals. Then, the concentrated solution including solid was drained from the reactor and was sent to the filtration unit for salt separation. As the slurry was fed to the filter unit the product cake was recovered and the mother liquor[4] was collected and then it was pumped to the buffer vessel for further salt recovery.

MED Evaporator unit provided by NTUA

The MED evaporator was a 2-stage forward-feed evaporator with a capacity of 2 m^3/day. The unit was designed to work 20 h/d . During Site 02 research the average operational hours ranged from 3 to 5 h/d for each experiment depending on the availability of the operator and the required concentration that had to be achieved. Each day 1 or 2 experiments were performed. NTUA was responsible for monitoring the operating parameters (flow rates of the inlet brine, concentrate, condensate and cooling water). Also, the flow of the steam was monitored via SCADA every day. The EC of the feed stream as well as the concentrate and condensate streams were measured after each experiment. Furthermore, the pressures and the temperatures for the two effects were recorded regularly and based on each day's measurements the operation was optimized. Once a week cleaning runs with tap water were performed for removing any remaining salt.

During the operation some challenges with the residual heat part occurred due to the blockage of the NR valve as was already mentioned in sub-chapter 4.2. Furthermore, a greenish color of some concentrate sample was observed (**Figure *18***). An analysis was carried out at the Department of Environmental Science and Technology of NTUA and the green color was explained by the presence of nickel salts. After a few cleaning runs with tap water the greenish color had faded, so the operation continued as usual. Another challenge was the presence of some SS (**Figure *19***). The SS, after drying at 105 ^{o}C, were characterized by X ray diffractometric (XRD) analyses. The diffractogram in ***Figure 20*** exhibits two major peaks at 20 and 23 degrees. These peaks were attributed to gypsum (blue line) and $CaSO_4$ anhydrate (red line). The presence of $CaCO_3$ in the SS could not be excluded also.

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[4] The mother liquor is the solution remaining after a component has been removed by the crystallization.

Figure 18: GREENISH COLOR OF SOME CONCENTRATE SAMPLES.

Figure 19: SS IN SOME CONCENTRATE SAMPLES

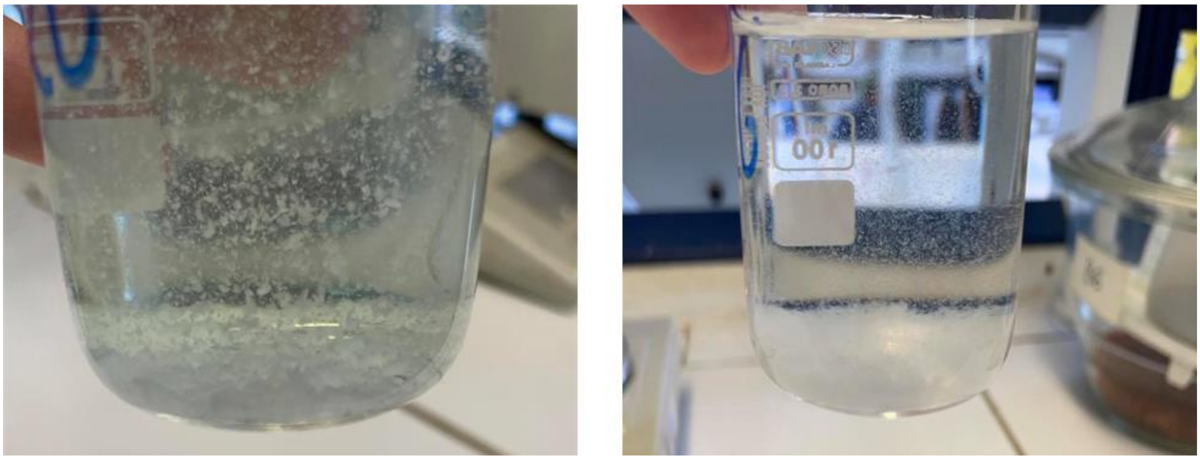
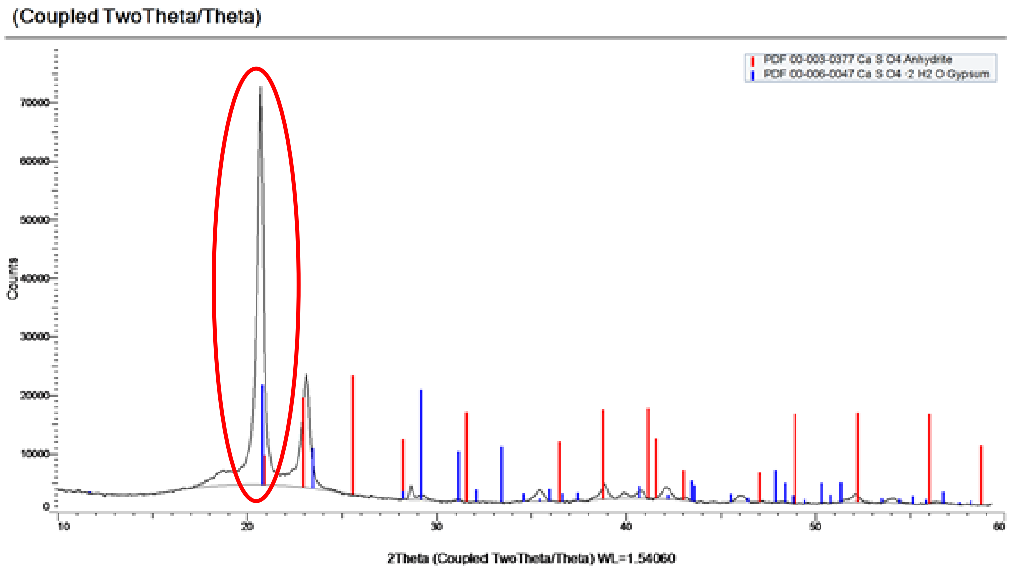


Figure 20: XRD RESULTS REPORT FOR THE SAMPLES WITH SS



Moreover, one of the project objectives was to recover $NaHCO_3$ as one more end-product. Thus, NTUA provided a crystallizer for Site 01 and Site 02 that was located in the same container with the MED evaporator. However, the concentration of Na^+ and HCO_3^- at the inlet brine was found to be not sufficient for crystallization, because during TOC removal and pH adjustment inorganic carbon was removed from the solution.

Finally, the MED evaporator did not operate with the EFC unit because the EFC unit was not operational during most of the experimental period of the MED evaporator. The EFC unit was operated only for a short period in the end of the research, but the effluent volume of EFC was not sufficient to be used continuously in the MED evaporator unit and after a prolonged storage (in order to obtain sufficient amounts) the quality of the effluent was negatively affected.

4.5 Site 01 Pilot Data Collection

4.5.1 Pilot Operation and Observation Data

The lead operator was responsible to fill in a “data sheet”, given in Annex C: Daily Data Sheet - Site 01, on a daily basis. The data that had to be recorded for each unit based on the data sheet are given below:

1. NF units - both for NF1 and NF2:
    a. Feed flow (L/h), EC (mS/cm) and pressure (bar)
    b. Recovery rate
    c. Permeate flow (L/h) and EC (mS/cm)
    d. Concentrate flow (L/h) and EC (mS/cm)
2. MF-PFR unit – both for stage 1 ($Mg(OH)_2$ and stage 2 ($Ca(OH)_2$):
    a. Feed flow (L/h) and pH
    b. NaOH concentration (M) and flow (L/h)
    c. Volume ratio slurry/supernatant
    d. Settling time (min)
    e. Operation duration (h)
3. Drum filter:
    a. Feed flow (L/h)
    b. Flow mother liquor (L/h)
4. MED Evaporator unit:
    a. Feed flow (L/h) and EC (mS/cm)
    b. Effect 1 pressure (bar) and temperature (°C)
    c. Effect 2 pressure (bar) and temperature (°C)
    d. Condensate 1 flow (L/h) and EC (mS/cm)
    e. Condensate 2 flow (L/h) and EC (mS/cm)

Moreover, the morning and evening values of the water counter, the electricity counter and the 2nd electricity counter had to be logged. Finally, the volumes of the samples taken on that day from all units was recorded in the in the data sheet.

4.5.2 Sampling and Lab Analysis

In **Figure 21** the overall sampling scheme for Site 01 pilot is given. The description and the sampling frequency for 12 sampling points of Site 01 are given in **Table 6**.

Figure 21: OVERALL SAMPLING SCHEME FOR SITE 01

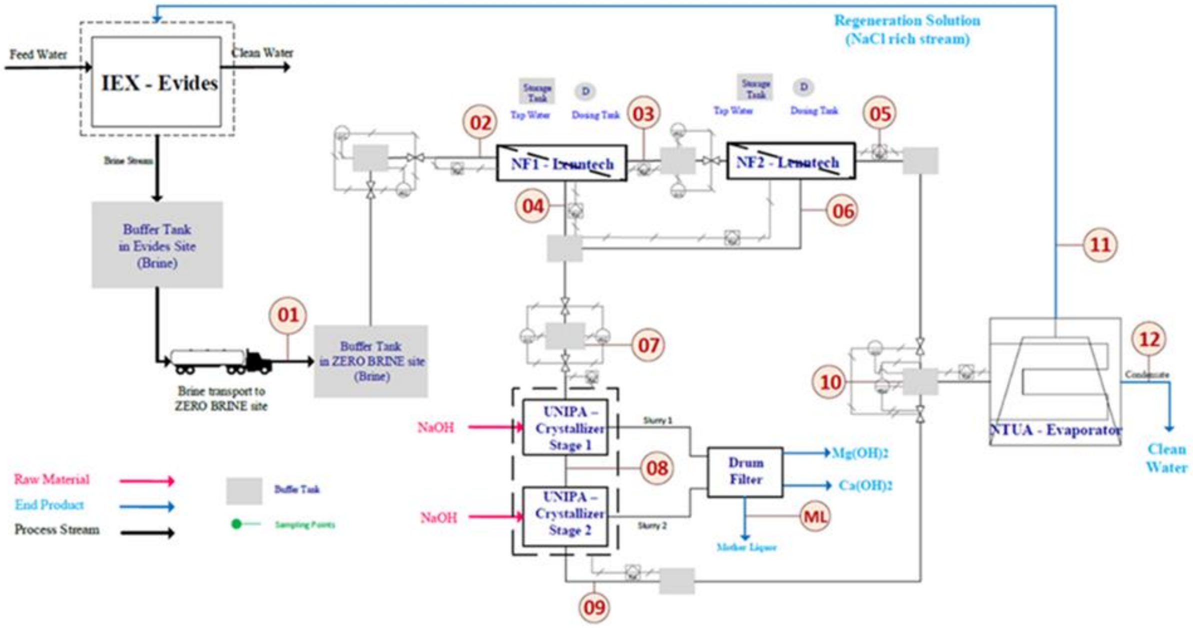


Table 6: SITE 01 SAMPLING POINTS AND FREQUENCIES

Label	Description	Frequency
01a	Brine (feed water) before transport	2 times/ week
01b	Brine (feed water) from next batch	2 times/ week
02	Feed NF1	3 times/ week
03	Permeate NF1/ Feed NF2	3 times/ week
04	Concentrate NF1	3 times/ week
05	Permeate NF2	3 times/ week
06	Concentrate NF2	3 times/ week
07	Feed MF-PRF	1-2 times/ week
08-Mg	Effluent stream stage 1 MF-PFR	1-2 times/ week
08-Ca	Effluent stream stage 1 MF-PFR	1-2 times/ week
09	Effluent stream stage 2 MF-PFR	1-2 times/ week
10	Feed MED Evaporator	3 times/ week
11	NaCl rich stream MED Evaporator	3 times/ week
12	Condensate MED Evaporator	3 times/ week

In order to characterize the physio-chemical properties of each stream and to monitor mass transport within the process units, the following analyses, performed at TU Delft laboratories, were done for every sample collected during the operation:

- Basic analysis; pH and EC
- HCO_3^- and SiO_2 concentrations using measuring kits and a spectrophotometer
- Anion concentration using Ion Chromatography (IC)
- Cations and trace elements concentration using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)
- TOC using TOC analyzer

Moreover, XRD analyses were used in order to derive the type of precipitate that were formed during the production of crystals in the crystallizer unit. These analyses were performed by the UNIPA laboratory.

4.6 Site 02 Pilot Data Collection

4.6.1 Pilot Operation and Observation Data

The operation of all units from Site 02 was monitored by the lead operator by following a step by step check list document provided by TU Delft, which assured the smooth operation of all units. Moreover, a “data sheet”, given in Annex D: Daily Data Sheet - Site 02, was filled on a daily basis. A series of data were noted, the outline for each unit of the gathered data is given below:

1. Nyex:
    a. Feed, acid, product and NaOH flows (L/h)
    b. pH transmitters values
    c. Current (A) and the voltage (V)
    d. pH and EC (mS/cm) of grab samples on location measurements
2. NF and RO units:
    a. Feed flow (L/h), EC (mS/cm), pressure (bar) and temperature (°C)
    b. Permeate flow (L/h), EC (mS/cm) and pressure (bar)
    c. Recirculation flow (L/h)
    d. Concentrate flow (L/h) and EC (mS/cm)
    e. pH and EC (mS/cm) of grab samples on location measurements
3. MED Evaporator unit:
    a. Feed flow (L/h), temperature (°C) and EC (mS/cm)
    b. Cooling flow (L/h) and temperature (°C)
    c. Effect 1 pressure (bar) and temperature (°C)
    d. Effect 2 pressure (bar) and temperature (°C)
    e. Condensate 1 flow (L/h) and EC (mS/cm)

   f. Condensate 2 flow (L/h) and EC (mS/cm)
   g. Ratio of condensate recovery (%v)
4. EFC:
   a. Batch volume at 20 L
   b. Crystallizer temperature (°C)
   c. Inlet and outlet coolant temperature (°C)
   d. Ice volume (L)
   e. Slurry Volume (L)
   f. Ice formation time (h)
   g. Batch duration (h)

The total operational time and the time of sampling was recorded for all units. Also, it must be noted that the EFC unit was not included in the daily datasheet. Since its operation was delayed it was not included in the daily routine of the pilot operation. The datasheet for EFC was separate because it was operated by specialized personnel, and it was integrated into the pilot data in a later phase (EFC datasheet can also be found in Annex D: Daily Data Sheet - Site 02.

4.6.2 Sampling and Lab Analysis

In **Figure 22** the overall sampling scheme for Site 02 pilot is given. The description and the sampling frequency for the 14 sampling points are given in ***Table 7***.

Figure 22: OVERALL SAMPLING SCHEME FOR SITE 02

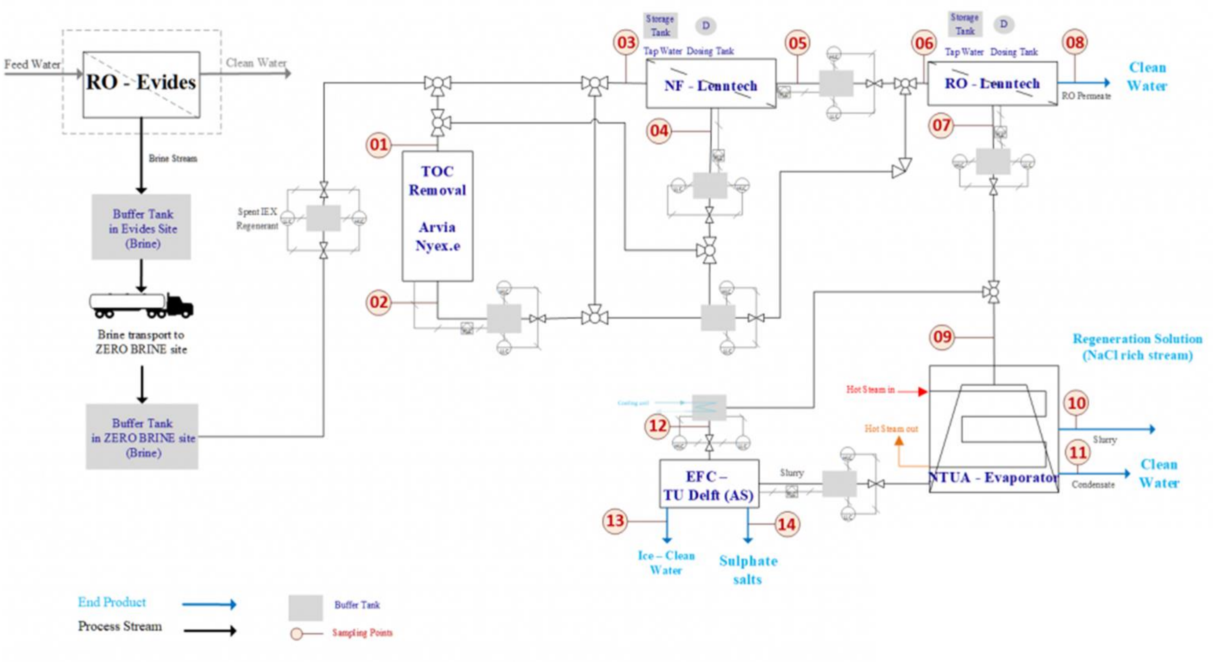


Table 7: SITE 02 SAMPLING POINTS AND FREQUENCIES

Label	Description	Frequency
01	Feed Nyex	1-2 times/ operational day
02	Effluent Nyex	1-2 times/ operational day
03	Feed NF	1-2 times/ operational day
04	Concentrate NF	1-2 times/ operational day
05	Permeate NF	1-2 times/ operational day
06	Feed RO	1-2 times/ operational day
07	Concentrate RO	1-2 times/ operational day
08	Permeate RO	1-2 times/ operational day
09	Feed MED Evaporator	1-2 times/ operational day
10	NaCl rich stream MED Evaporator	1-2 times/ operational day
11	Condensate MED Evaporator	1-2 times/ operational day
12	Feed EFC	1-2 times/ operational day
13	Clean water – Ice product EFC	1-2 times/ operational day
14	Na_2SO_4 salt product EFC	1-2 times/ operational day

In order to characterize the physio-chemical properties of each process stream and to monitor mass transport within the process unit, the following analyses, performed at TU Delft laboratories, were done for every sample collected during the operation:

- Basic analysis; pH and EC
- HCO_3^- and SiO_2 concentrations using measuring kits and a spectrophotometer
- Anion concentration using IC
- Cations and trance elements concentration using ICP-MS
- TOC using TOC analyzer

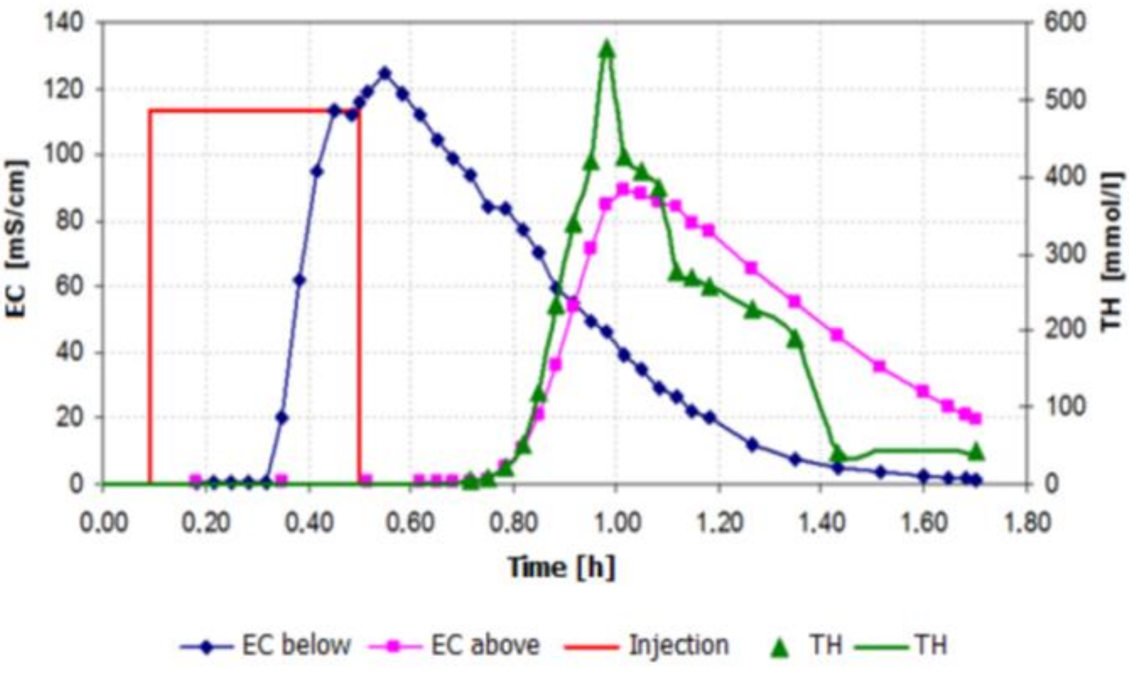
Moreover, some extra nickel analyses with Atomic Absorption Spectroscopy (AAS) and XRD analyses in the dried SS of certain problematic samples were carried out at the Department of Environmental Science and Technology of NTUA.

5 Pilot experiments

5.1 Site 01 Experimental Design

In order to design the experiments of Site 01, it was importance to take into account the spent regenerant patterns during the regeneration process. The regeneration process of IEX resins in DWP of EIW lasts 3.5 to 4.5 hours. To regenerate resins, first the regeneration solution passes the IEX column and afterwards the excess chemical is rinsed from the column with clean water. As it is shown in Figure *23*, during the injection of the regeneration solution, the spent regenerant reaches the highest TDS concentration (average EC=110 mS/cm). During the rinsing, the spent regenerant has the lowest TDS concentration (average EC=0.5 mS/cm).

Figure 23: SPENT REGENERANT PATTERNS DURING A REGENERATION PROCESS OF THE IEX COLUMNS IN THE DWP OF EIW



The experiments of Site 01 were design in order to evaluate the performance of each technology and integrated pilot in response to the fluctuations of brine concentration (nominal, low and upper). For this reason, the experiments planning of Table *8* was created for Site 01 pilot research, in which the targeted ranges of EC and TDS for the nominal conditions, the low limit and upper limit can be seen. It must be mentioned that for the NF unit results processing the lower limit was divided in low and lowest limit. Also note that in case of the MED evaporator unit, an extra distinction between experiments took place based on the source of the feed treated water. The two streams used as feed of the MED evaporator unit were (i) the NF permeate and (ii) the MF–PFR effluent. It was important to evaluate the performance of the MED evaporator receiving feed independently or mixed stream from these sources, in order to investigate what option would be the best for full-scale implementation. Therefore, experiments were performed with different contribution of each one of the two streams. Specifically, the different streams tested were:

(i) 100% NF permeate,
(ii) 100% MF-PFR effluent,
(iii) 50% NF permeate – 50% MF-PFR effluent,
(iv) 75% NF permeate – 25% MF-PFR effluent and
(v) 25% NF permeate – 75% MF-PFR effluent.

After the termination of each experiment and before proceeding with the next experiment all units were cleaned, all hydraulic connections were checked for leakages and the pumps were checked for malfunctions. Moreover, the operating conditions of each unit were adjusted based on preliminary projections resulting from the expected water quality.

Table 8: EXECUTED EXPERIMENTS SITE 01

Description	Brine EC [mS/cm]	Brine TDS [g/L]
Upper Limit	50-100	35-70
Nominal condition	30-50	20-35
Lower limit	10-30	5-20

5.2 Site 02 Experimental design

The main purpose of the experimental design in case of Site 02 was to test different possible configurations of the units, since the feed water (RO concentrate) does not demonstrate significant differences in water quality (unlike Site 01). Therefore, as it was already explained in the previous chapter, two modes of operation were tested for Site 02. The goal of the two modes was to investigate the optimal point for TOC removal, the subsequent effect in the associated units (Nyex, NF and EFC) and the end products qualities.

Several experiments were carried out in both modes as it can be seen in Table *9*. It must be mentioned that due to the delay caused by difficulties with the EFC operation a lot of experiments took place without the EFC unit.

Table 9: EXECUTED EXPERIMENTS SITE 02

Experiments	Description	Brine EC [mS/cm]	Brine TDS [g/L]

1	Trial Run	3-6	2-4
2	Trial Run	3-6	2-4
3	Trial Run Mode I (NYEX->NF) – without EFC	3-6	2-4
4	Trial Run Mode II (NF>NYEX) – without EFC	3-6	2-4
5	Mode I (NYEX->NF) – without EFC	3-6	2-4
6	Mode I (NYEX->NF) – without EFC	3-6	2-4
7	Mode I (NYEX->NF) – without EFC	3-6	2-4
8	Mode I (NYEX->NF) – without EFC	3-6	2-4
9	Mode I (NYEX->NF) – without EFC	3-6	2-4
10	Mode I (NYEX->NF) – without EFC	3-6	2-4
11	Mode II (NF>NYEX) – without EFC	3-6	2-4
12	Mode II (NF>NYEX) + Troubleshooting	3-6	2-4
13	Mode II (NF>NYEX) –> only NF & RO	3-6	2-4
14	Mode II (NF>NYEX) –> only NYEX & NF & RO	3-6	2-4
15	Mode II (NF>NYEX) –> only NYEX & NF & RO	3-6	2-4
16	Mode II (NF>NYEX) –> only NYEX & NF & RO	3-6	2-4
17	Mode II (NF>NYEX) –> only NYEX & NF & RO	3-6	2-4
18	Mode II (NF>NYEX) – without EFC	3-6	2-4
19	Mode II (NF>NYEX) – without EFC	3-6	2-4
20	Mode II (NF>NYEX) – without EFC	3-6	2-4
21	Mode I (NYEX->NF)	3-6	2-4
22	Mode I (NYEX->NF)	3-6	2-4
23	Mode I (NYEX->NF)	3-6	2-4
24	Mode II (NF>NYEX)	3-6	2-4
25	Mode II (NF>NYEX)	3-6	2-4
26	Mode II (NF>NYEX)	3-6	2-4
27	Mode I (NYEX->NF)	3-6	2-4
28	Mode I (NYEX->NF)	3-6	2-4
29	Mode I (NYEX->NF) – without MED Evaporator	3-6	2-4
30	Mode I (NYEX->NF) – without MED Evaporator	3-6	2-4
31	Only EFC experiments	-	-
32	Only EFC experiments	-	-

6 Evaluation of results

This chapter describes the evaluation of the experimental results and it contains information about the performance of each technology separately, the quality and quantity of end-products and the process robustness. Finally, the overall pilot's performance is evaluated.

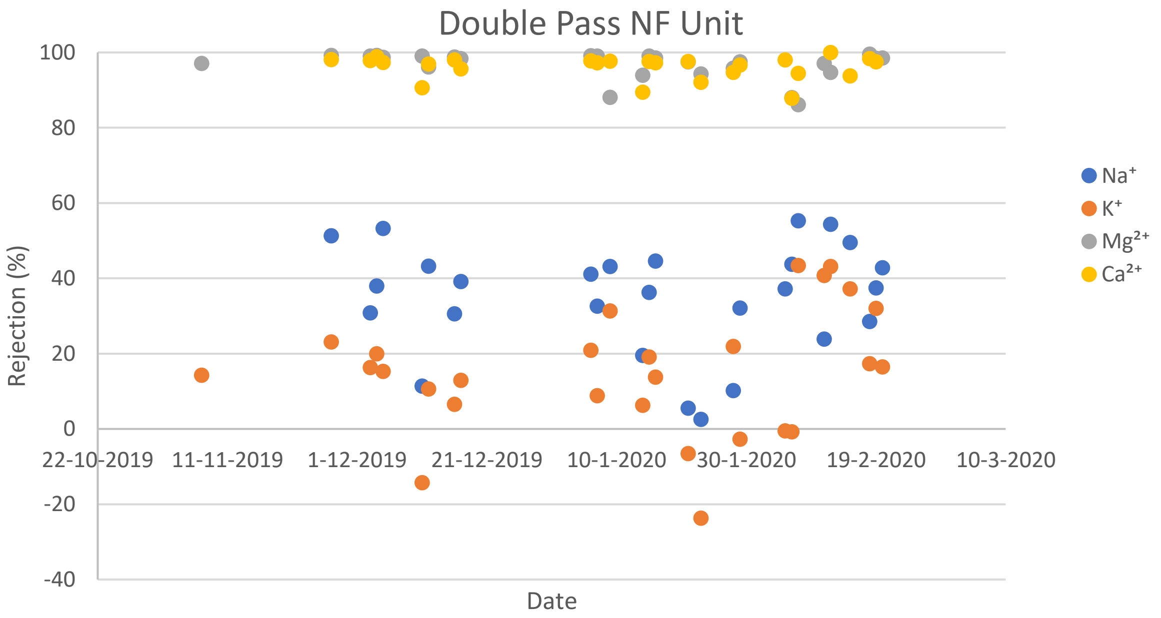
6.1 Site 01 Performance Evaluation

6.1.1 Site 01 Performance Evaluation per Technology

Nanofiltration unit provided by Lenntech B.V.

As it can be seen in **Figure *24***, Ca^{2+} and Mg^{2+} were highly rejected by the double pass NF, while Na^{+} and K^{+} showed much lower rejections. More specifically, divalent ions were rejected by 96% on average and Na^{+} and K^{+} were rejected by 32% and 15% on average, respectively. This proves that NF was suitable for the separation of multivalent and monovalent cations of the IEX-brine. The rejection of the divalent ions was stable by showing a standard deviation of less than 3.7%. On the other hand, the rejection of the monovalent ions showed higher fluctuations with a standard deviation of 14-16%, showing that the monovalent ion rejection was more sensitive to the feed water quality and the operating conditions.

Figure 24: IONIC SEPARATION BY THE DOUBLE PASS NF UNIT



Depending on the TDS of the feed water, the recovery, the Trans Membrane Pressure (TMP) and the flux of each NF pass are reported in Table *10*. In addition, the recovery, and the energy consumption[5] are also presented in the table. Limited by the maximum applied pressure (40 bar) that the NF membranes was able to handle, the NF1 recovery in high TDS concentrations had an average of 32%, whereas for nominal TDS concentrations the NF1 recovery was 68%. For low TDS concentrations, the NF1 recovery was 72-74%. The flux of both passes ranged between 8 and 18 L/m^2/h. The energy consumption of the double pass NF per m^3 of permeate was equal to 25 kWh/m^3, on average, in high TDS concentrations, 14.5-16.5 kWh/m^3 under nominal and low TDS concentrations and 10 kWh/m^3 in the lowest limit. The pressure losses over the membranes from the feed to the concentrate stream were always 1-1.5 bar. There was no need for chemical cleaning of the membranes throughout the experimental campaign.

Table 10: RECOVERIES, FLUXES, TMP AND ENERGY CONSUMPTION OF THE NF UNITS IN DIFFERENT TDS CONCENTRATIONS OF THE FEED WATER

	EC	**NF-First Pass**			**NF-Second Pass**			**Overall**	
-	(mS/cm)	Recovery (%)	Flux (L/m^2/h)	TMP (bar)	Recovery (%)	Flux (L/m^2/h)	TMP (bar)	Recovery (%)	En. C (kWh/m^3)
Upper Limit	68-82	32%	10	38	71%	8	14	23%	25
Nominal Condition	33-45	68%	14	37	75%	10	12	54%	16
Low Limit	27-30	72%	18	34	80%	13	13	57%	14
Lowest Limit	17-20	74%	18	21	79%	13	10	58%	10

The average water quality of the NF feed, permeate and concentrate during upper limit, nominal condition, low and lowest limit experiments are given in **Table *11***, **Table *12***, **Table 13** and **Table 14**, respectively. For all conditions, the divalent cation rejection was more than 94%, except for Mg^{2+} rejection that was 90% in the low limit condition. The monovalent cation rejection was less than 46% in all conditions. For nominal TDS concentrations, the divalent cations were concentrated by the first pass NF approx. 3 times, allowing for more effective recovery of $Ca(OH)_2$ and $Mg(OH)_2$ by the subsequent crystallizer. For high TDS concentrations, it was possible to concentrate the divalent cations only by 1.4 times, whereas they were concentrated by 3-4.2 times in the low limit conditions. Higher concentration factors of Ca^{2+} and Mg^{2+} under nominal condition, in low and lower limits, were reached due to the higher water recoveries that were achieved compared to the high limit.

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[5] The “energy consumption” is referred as “En. C” in the tables of this report.

Table 11: NF FEED, PERMEATE AND CONCENTRATE WATER QUALITY – UPPER LIMIT

Upper Limit						
	NF-First Pass			NF-Second Pass		Rejection (%)
Parameter	Feed	Permeate	Concentrate	Permeate	Concentrate	
Na^+ (g/L)	11.6	9.7	11.6	7.9	12.8	32
K^+ (g/L)	0.3	0.3	0.2	0.2	0.3	13
Mg^{2+} (g/L)	1.8	0.1	2.4	0.0	0.4	98
Ca^{2+} (g/L)	13.8	1.5	18.8	0.5	4.0	97
Cl^- (g/L)	38.4	20.0	53.3	23.6	23.6	39

Table 12: NF FEED, PERMEATE AND CONCENTRATE WATER QUALITY – NOMINAL CONDITION

Nominal Conditions						
	NF-First Pass			NF-Second Pass		Rejection (%)
Parameter	Feed	Permeate	Concentrate	Permeate	Concentrate	
Na^+ (g/L)	6.2	5.2	7.3	3.9	7.8	37
K^+ (g/L)	0.2	0.2	0.2	0.1	0.2	22
Mg^{2+} (g/L)	0.7	0.0	1.9	0.0	0.1	99
Ca^{2+} (g/L)	4.9	0.5	13.4	0.1	1.5	99
Cl^- (g/L)	17.1	9.6	36.7	6.5	13.5	62

Table 13: NF FEED, PERMEATE AND CONCENTRATE WATER QUALITY – LOW LIMIT

Low Limit						
	NF-First Pass			NF-Second Pass		Rejection (%)
Parameter	Feed	Permeate	Concentrate	Permeate	Concentrate	
Na^+ (g/L)	5.4	4.1	7.9	2.9	7.4	46
K^+ (g/L)	0.2	0.2	0.2	0.1	0.2	17
Mg^{2+} (g/L)	0.3	0.1	1.2	0.0	0.2	90
Ca^{2+} (g/L)	2.5	0.4	9.3	0.2	1.7	94
Cl^- (g/L)	11.9	5.2	16.2	5.2	13.6	57

Table 14: FEED, PERMEATE AND CONCENTRATE WATER QUALITY – LOWEST LIMIT

Lowest Limit						
	NF-First Pass			NF-Second Pass		Rejection (%)
Parameter	Feed	Permeate	Concentrate	Permeate	Concentrate	
Na^+ (g/L)	3.7	3.7	5.6	2.2	4.7	41
K^+ (g/L)	0.1	0.1	0.1	0.1	0.2	40
Mg^{2+} (g/L)	0.3	0.0	0.8	0.0	0.1	95
Ca^{2+} (g/L)	1.6	0.2	5.6	0.1	0.7	97
Cl^- (g/L)	6.1	7.0	12.7	4.4	10.9	27

The fully automated NF unit provided a stable operation by only regulating the permeate, the concentrate, the recirculation flow rates and the antiscalant dosing in the beginning of each experimental campaign. Without changing the operating conditions, the unit could continuously be functional and operational without much supervision.

The ionic separation by NF proved that the process was always efficient, independently of the feed water composition. Limitations in the unit's recovery were observed in the higher feed TDS concentrations (upper limit experiments), where the osmotic pressure of the water in high recoveries overcame the maximum applied pressure of 40 bar that the NF could handle.

Crystallizer unit provided by UNIPA

Long run experimental tests were performed. The duration of these tests were on average 8 hours. The energy consumption per m^3 of treated water was equal to 8.1 kWh/m^3. The mean ion-concentrations of the feed brines exiting from the NF unit are shown in **Table *15***. These long run tests allowed the analysis of MF-PFR stability in terms of flow-rate and outlet pH. These tests also demonstrated the stability of the MF-PFR in terms of the quality of the produced Mg^{2+} and Ca^{2+}. **Figure *25*** and **Figure *26*** display the concentration of Mg^{2+}, Ca^{2+} and Na^+ for the three tested brines. These figures also display the maximum and minimum value of each concentration.

Table 15: CATION AND ANION ANALYSIS OF THE CRYSTALLIZER FEED (NF CONCENTRATE)

Brine coming from NF	Na^+ [g/L]	K^+ [g/L]	Ca^{2+} [g/L]	Mg^{2+} [g/L]	CO_3^{2-} [g/L]	Cl^- [g/L]	SO_4^{2-} [g/L]
Low and Lowest Limit	9.2	0.20	12.5	1.5	0.33	30.5	0.11
Normal Condition	9.1	0.24	13.4	1.8	0.12	66.5	0.40
Upper Limit	11.7	0.24	17.4	2.2	0.17	45.3	0.65

Figure 25: Ca^{2+} CONCENTRATION VS. Mg^{2+} CONCENTRATION VS. FEED

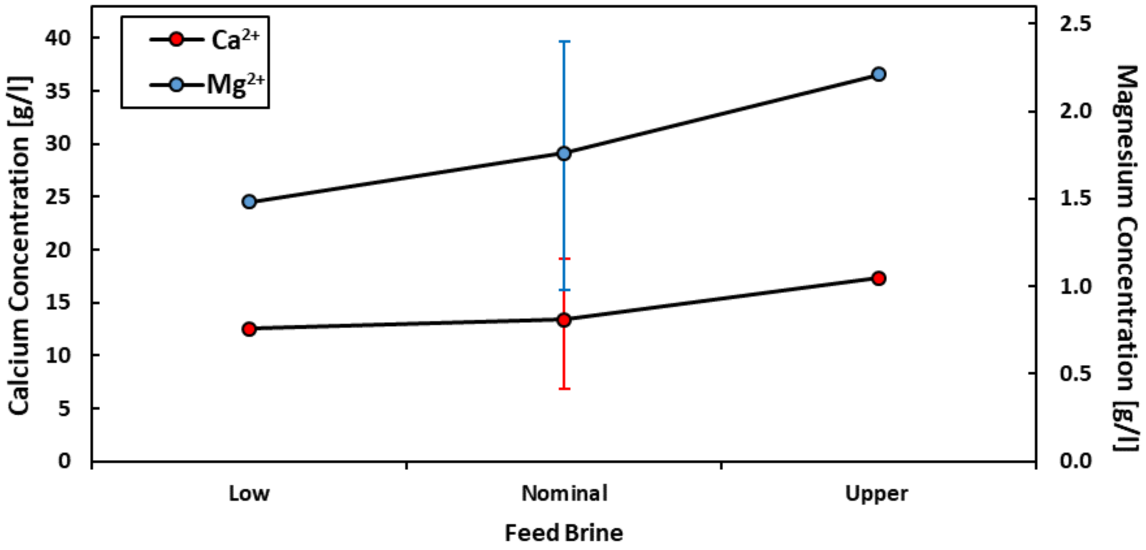
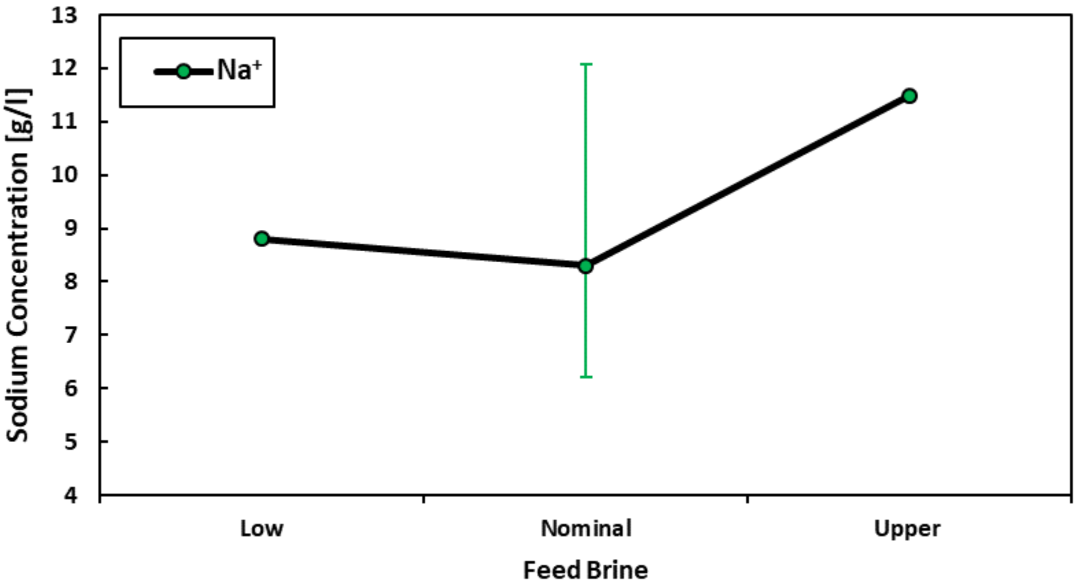
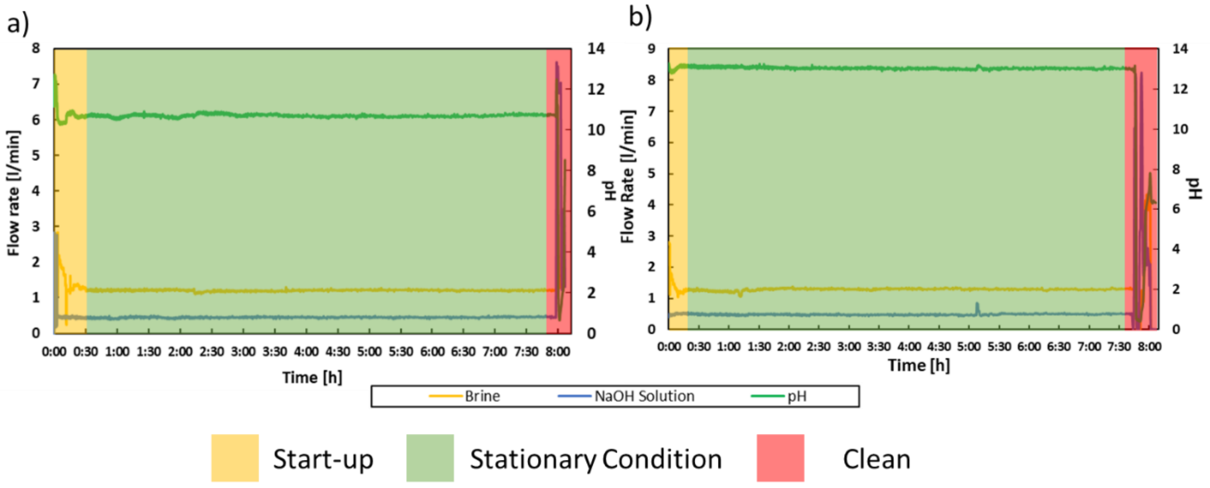


Figure 26: Na^+ CONCENTRATION VS. FEED



Firstly, the stability and robustness of the MF-PFR was analyzed over time. During experiments, relevant operation parameters such as outlet pH and flow rate of the brine and alkaline solutions, were recorded in order to assess the behavior of the unit. The assessment was performed by plotting the outlet pH and brine flowrate over time for both precipitations (*Figure 27*). The operative parameters set to test a normal feed brine are displayed in *Figure 27*a for Mg^{2+} precipitation and *Figure 27*b for Ca^{2+} precipitation.

Figure 27: VARIATION OF THE pH, BRINE AND ALKALINE FLOW RATE OVER TIME; a) Mg^{2+} PRECIPITATION STEP, b) Ca^{2+} PRECIPITATION STEP



As displayed in **Figure 27**, the experiment consisted of three main parts: (i) start-up, (ii) steady-state condition and (iii) cleaning. This procedure was followed for the precipitation of the Mg^{2+} and Ca^{2+} hydroxides. During the start-up, the flow rates of the brine and the alkaline solution were adjusted until reaching the required outlet pH values. Once the two flow rates were set, the MF-PFR reached the stationary condition and remained operational for 7-8 hours. At the end of the experiment, the MF-PFR was cleaned using a solution of HCl in order to dissolve the Mg^{2+} or Ca^{2+} hydroxide scaling. The cleaning process required 10-15 minutes for Mg^{2+} precipitation and 20 minutes for Ca^{2+} precipitation. Finally, the reactor was flushed using tap water.

As shown in **Figure 27**, the outlet pH and both flow rates were stable, which highlights the stability of the MF-PFR once the stationary-condition was reached. **Figure 27** also displays that it was possible to precipitate Mg^{2+} and Ca^{2+} in a fractionated way, through a fine control of the outlet pH. Moreover, a small adjustment during the experiment was needed due to the change in brine composition as mentioned in sub-chapter 4.3.2.

In **Table 16** and **Table 17**, the operative conditions for the recovery of Mg^{2+} and Ca^{2+} hydroxide are given, respectively. The quality of the $Mg(OH)_2$ and $Ca(OH)_2$ recovered through the two precipitation steps was assessed using sample analysis following the analytical procedure reported in sub-chapter 4.5.2.

The purity and conversion of $Mg(OH)_2$ are reported in **Figure 28** and **Figure 29** for each performed test, respectively. The purity of the $Mg(OH)_2$ was determined in terms of % of Mg of the total mass of cations detected in the solid sample. Crystal analysis results showed that only Mg^{2+} and Ca^{2+} were present in the solid product and that the purity was affected by the co-precipitation of $CaCO_3$, as confirmed by the XRD analysis. As it can be seen in **Figure 30**, Mg^{2+} precipitated as $Mg(OH)_2$ (Brucite), but the Ca^{2+} precipitated as $CaCO_3$ (Aragonite and Calcite). The precipitation of $CaCO_3$ occurred when high concentration of HCO_3^- ions in the feed brine were observed.

Table 16: OPERATIVE CONDITION FOR THE $Mg(OH)_2$ RECOVERY

Brine coming from NF	**pH**	**Operative Condition**			**Volume Treated**	**Worked Hours**
		Brine Flow Rate	NaOH Flow Rate	NaOH		
		L/min	L/min	mol/L	L	h
Nominal 03/12/2019	10.5	2	0.35	0.4	600	4
Nominal 11/12/2019	10.6	1.2	0.45	0.4	1,000	8.5
Nominal 13/12/2020	10.5	1.3	0.46	0.4	1,000	8.5
Nominal 17/12/2019	10.5	1.2	0.42	0.4	1,000	8.5
Low 12/02/2020	10.5	4.6	0.17	0.5	1,000	6
Low 14/02/2020	10.5	3.8	0.12	0.5	1,000	4.5
Nominal 18/02/2020	10.5	2.7	0.38	0.5	600	4
Nominal 20/02/2020	10.8	1.6	0.4	0.5	1,000	8.5
Nominal 22/02/2020	10.3	2.5	0.3	0.5	1,000	5.5
Nominal 26/02/2020	10.3	2.8	0.3	0.5	1,000	7.5
Nominal 03/12/2019	10.5	2	0.35	0.4	600	4

Table 17: OPERATIVE CONDITION FOR THE $Ca(OH)_2$ RECOVERY

Brine coming from NF	**pH**	**Operative Condition**			**Volume Treated**	**Worked Hours**
		Brine Flow Rate	NaOH Flow Rate	NaOH		
		L/min	L/min]	mol/L	L	h
Nominal 04/12/2019	13.2	3	0.70	2	1,000	5
Nominal 12/12/2019	13.0	1.3	0.42	2	1,000	8.5
Nominal 18/12/2019	13.0	1.1	0.45	2	1,000	8.5
Low 13/02/2020	13.2	1.4	0.35	4	1,000	7.5
Low 15/02/2020	13.1	1.8	0.30	4	900	7
Nominal 19/02/2020	13.1	1.6	0.36	4	900	7
Nominal 21/02/2020	13.3	1.2	0.30	4	600	6
Upper 28/02/2020	13.1	1.5	0.32	-	500	5
Nominal 04/12/2019	13.2	3.0	0.70	2	1,000	5
Nominal 12/12/2019	13.0	1.3	0.42	2	1,000	8.5
Nominal 18/12/2019	13.0	1.1	0.45	2	1,000	8.5

Figure 28: BAR-CHART SHOWING THE PURITY OF THE $Mg(OH)_2$ PRODUCED, THE CONCENTRATION OF Mg^{2+} (BLACK LINE WITH ORANGE MARKER) AND Ca^{2+} (BLACK LINE AND MARKER) IN THE FEED BRINE AND THE RECOVERY EFFICIENCY OF Mg^{2+} IN THE FORM OF $Mg(OH)_2$.

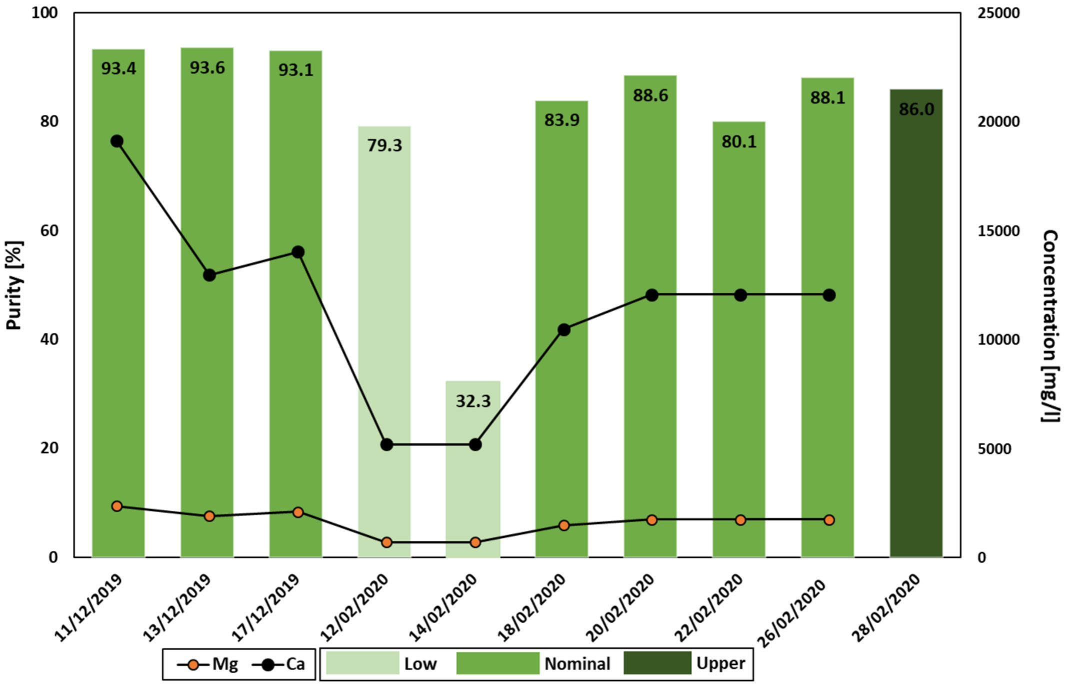


Figure 29: BAR-CHART SHOWING THE RECOVERY OF THE Mg^{2+} DURING THE FIRST STEP.

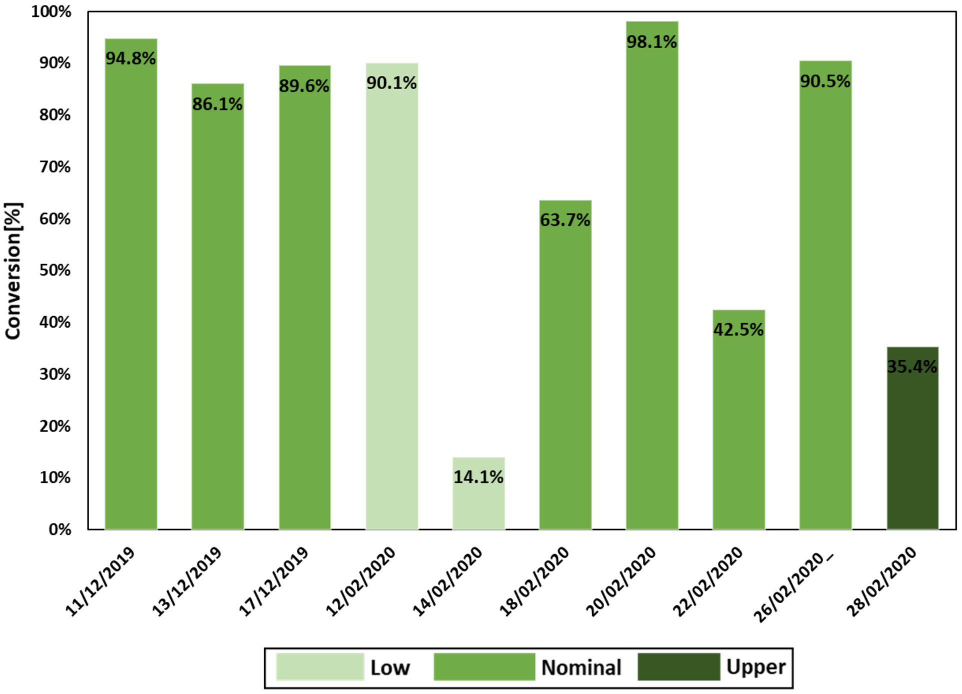
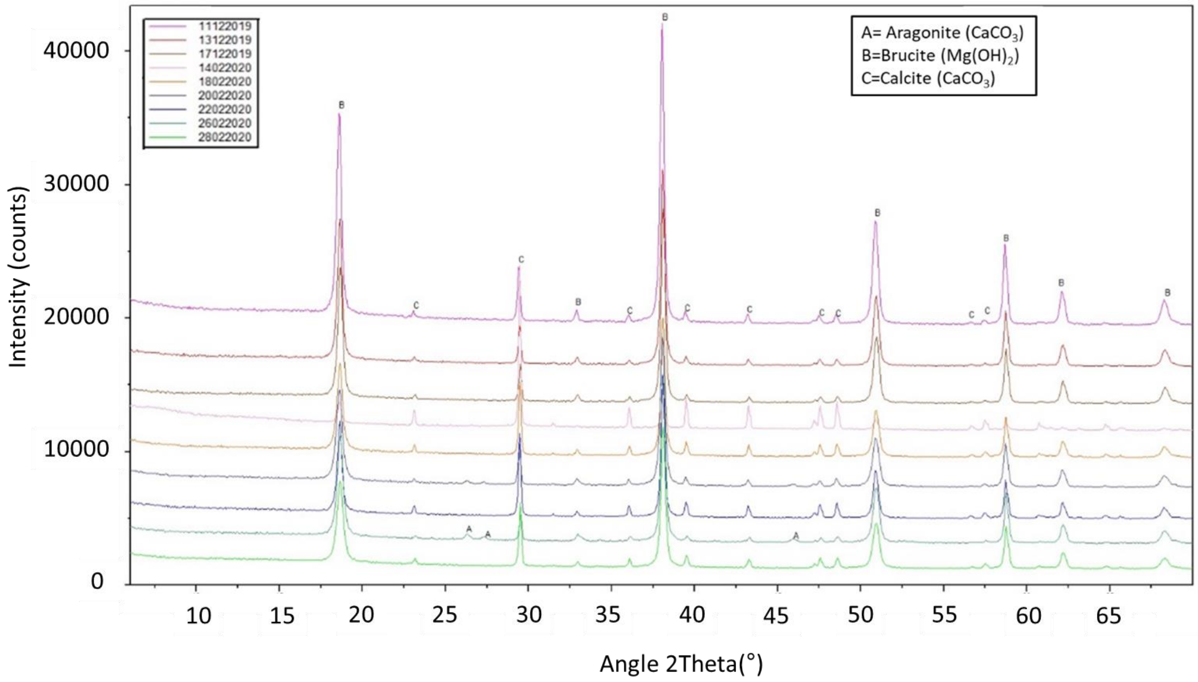


Figure 30: CUMULATIVE XRD RESULTS OF ALL $Mg(OH)_2$ SAMPLES; THE Y-AXIS IS THE INTENSITY (COUNTS), WHICH REPRESENTS THE INTENSITY OF X-RAY AFTER THE DIFFRACTION WITH THE CRYSTAL LATTICE. THE X-AXIS IS THE ANGLE WITH

WHICH THE X-RAY IS DIVERTED BY THE CRYSTAL LATTICE, WHICH CHANGES BASED ON THE TYPE OF STRUCTURE AND COMPOSITION OF THE CRYSTAL LATTICE.



The purity and conversion of $Ca(OH)_2$ are reported in **Figure *31*** and **Figure *32*** for each performed test, respectively. The purity of the $Ca(OH)_2$ was determined using the same method as for $Mg(OH)_2$. The results of IC showed that only Mg^{2+} and Ca^{2+} were present in $Ca(OH)_2$ which indicates that the purity was only affected by the co-precipitation of Mg^{2+} as $Mg(OH)_2$. This was due to the incomplete recovery of Mg^{2+} in the first step of precipitation.

Interestingly, the overall recovery of Mg^{2+} considering the first and the second step was of 100% in all tests performed, whereas for Ca^{2+} values were always above 90% and often approaching 100% were achieved, thus indicating a very high efficiency of removal of divalent ions preparing the feed to the evaporation/concentration step.

Moreover, it should be pointed out that during all experiments with MF-PFR no scaling was observed. During operation there was a formation of hydroxide scaling on the surface of the reactor, which was $Mg(OH)_2$ (first precipitation step) and $Ca(OH)_2$ (second precipitation step). Nevertheless, it did not cause any instability or malfunction on the reactor's operation. However, a cleaning step was carried out after every experiment in order to dissolve any formed scaling as explained in sub-chapter 4.3.2.

Figure 31: BAR-CHART SHOWING THE PURITY OF THE $Ca(OH)_2$ PRODUCED, THE CONCENTRATION OF Mg^{2+} (BLACK LINE WITH ORANGE MARKER) AND Ca^{2+} (BLACK LINE AND MARKER) IN THE FEED BRINE AND THE RECOVERY EFFICIENCY OF Ca^{2+} IN THE FORM OF $Ca(OH)_2$.

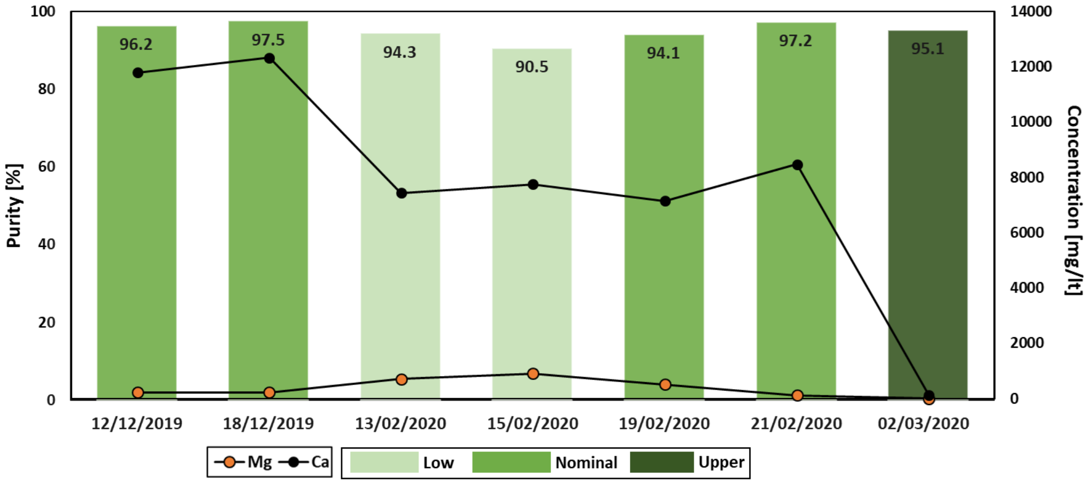
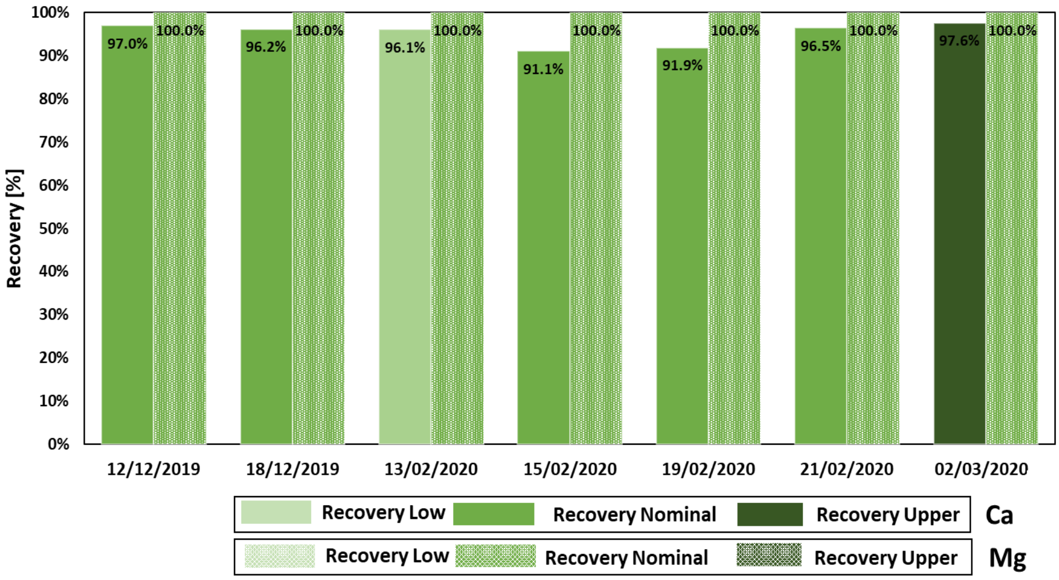


Figure 32: BAR-CHART SHOWING THE RECOVERY OF THE Ca^{2+} and Mg^{2+} DURING THE SECOND STEP



Overall, satisfying results were found both in terms of removal efficiency (between 95 and 100%) for the divalent cations (Mg^{2+} and Ca^{2+}), which allows for effective processing of the remaining brine in the MED evaporator.

However, the target purity of $Mg(OH)_2$ crystals (above 90% based on grant agreement 730390) produced in the reactor was achieved in many, but not all experiments. As commented above, the undesired presence of $CaCO_3$ co-precipitated with $Mg(OH)_2$ was likely due to the very high concentration of Ca^{2+} and HCO_3^- ions in the feed brine. The high concentration of these ions in combination with the high pH values in the MF-PFR reactor, led to the co-precipitation of these undesired products.

A strategy to solve this problem was identified, that consists of a simple and fast de-gassing step of the feed brine (for CO_2 and HCO_3^- removal), before the MF-PFR. This strategy was tested in a new experimental campaign carried out at UNIPA Brine Excellent Center (BEC) satellite laboratory using artificial/real brines with a similar composition to the brines provided by DWP of EIW. The outcome of this research can be found in Annex E: Further Testing for Improved Performance and Reliability – Site 01.

The experimental campaign highlighted the intrinsic robustness of the unit when operated in long-run tests. However, the lack of a fully automated control, required significant care from the operator, when unexpected variation in the feed brine composition occurred, which made this controlling system not suitable for an industrial scale-up. On this basis, UNIPA along with collaborating partners, highlighted the need of improving the control system in order to allow a more robust management of the brine and alkaline solution flow-rates minimizing any human erroneous evaluation. The outcome of this research can be found in Annex E: Further Testing for Improved Performance and Reliability – Site 01.

MED Evaporator unit provided by NTUA

The MED evaporator was the last part of the pilot for brine treatment. As it was already mentioned, it concentrated the inlet brine, producing two subsequent streams. The unit received brines from two streams; (i) the NF permeate and (ii) a mixed stream of MF –PFR effluent and NF permeate. The average concentrations of major ions in inlet brine in the different conditions are presented in Table *18* and Table *19* for the two brine streams. The NF permeate as expected contained low concentrations of Ca^{2+} (0.04g/L to 0.07g/L) and the average TDS for the different conditions (low limit, nominal conditions, upper limit) that ranged from 6.4 g/L to 23 g/L. The MF-PFR effluent and the NF permeate mix stream had also low concentrations of Ca^{2+} and the TDS for the different mixed inputs ranged from 22.4 g/L to 35.8 g/L. The conditions under which the unit was tested with the mixed brine were the low limit and nominal conditions.

Table 18: INLET BRINE WATER QUALITY - NF PERMEATE CASE

Parameter	Low Limit	Nominal Conditions	Upper Limit
Na^+ (g/L)	2.7	6.4	9.7
Ca^{2+} (g/L)	0.07	0.04	0.04
Mg^{2+} (g/L)	0.0	0.0	0.0
Cl^- (g/L)	3.6	12.1	12.7
TDS (g/L)	6.4	19.0	23.0
NaCl (%)	0.64	1.9	2.3

Table 19: INLET BRINE WATER QUALITY FROM MF-PFR EFFLUENT MIXED WITH NF PERMATE.

Parameter	100% MF-PFR	50% Permeate – 50% Effluent	75% Effluent – 25% Permeate	75% Permeate– 25% Effluent
Na^+ (g/L)	17.7	14.8	16.9	10.5

Ca^{2+} (g/L)	0.03	0.04	0.03	0.01
Mg^{2+} (g/L)	0.0	0.0	0.0	0.0
Cl^{-} (g/L)	14.5	10.1	18.9	12.0
TDS (g/L)	32.2	24.9	35.8	22.4
NaCl (%)	3.2	2.4	3.5	2.2

Experimental results from NF permeate brine

The average concentrations of major ions of the product water (condensate) and produced concentrate solution from the NF inlet brine are presented in **Table *20*** and **Table *21*** for all examined conditions (low, nominal and upper limit). The following tables present the average values of each condition. The water quality results show that the condensate vapor was a high-quality water that can be used in several industrial sectors.

Table 20: PRODUCT WATER QUALITY (CONDENSATE) IN CASE OF NF PERMEATE AS INLET BRINE

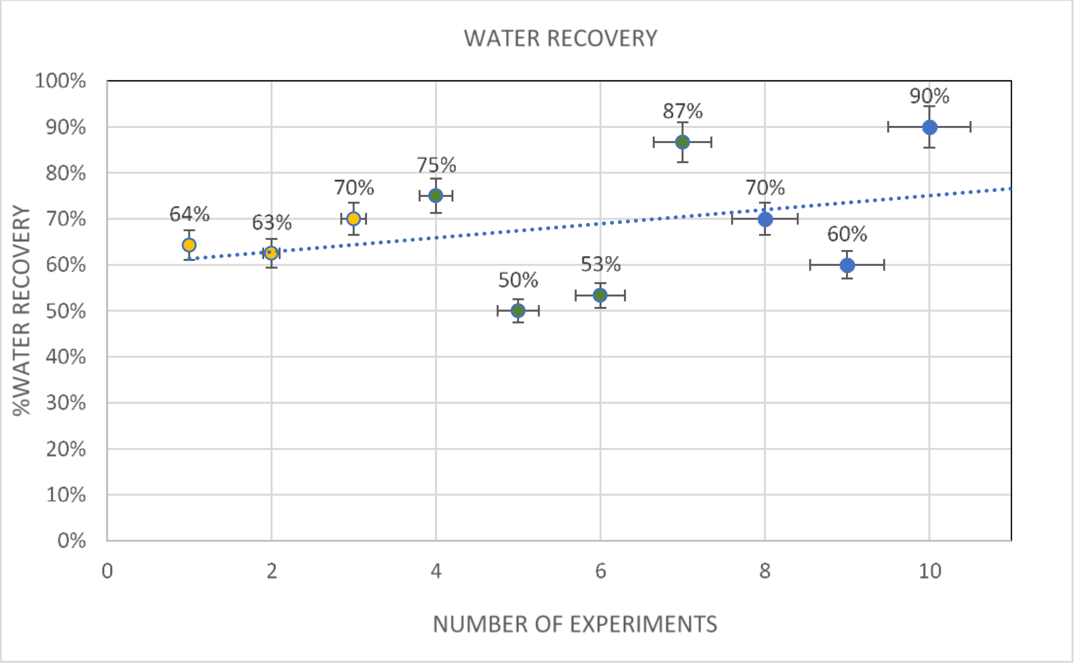
Parameter	Low Limit	Nominal Conditions	Upper Limit
Na^{+} (g/L)	0.16	0.14	0.13
Ca^{2+} (g/L)	0.02	0.01	0.03
Mg^{2+} (g/L)	0.0	0.0	0.0
Cl^{-} (g/L)	0.18	0.14	0.13
TDS (g/L)	0.40	0.29	0.29

Table 21: BRINE QUALITY OF PRODUCED REGENERATION SOLUTION (NaCl RICH) IN CASE OF NF PERMEATE AS INLET BRINE

Parameter	Low Limit	Nominal Conditions	Upper Limit
Na^{+} (g/L)	15.6	23.9	35.0
Ca^{2+} (g/L)	0.63	0.93	1.1
Mg^{2+} (g/L)	0.0	0.0	0.0
Cl^{-} (g/L)	23.5	44.2	38.2
TDS (g/L)	39.7	69.0	74.2
NaCl (%)	3.9	6.8	7.5

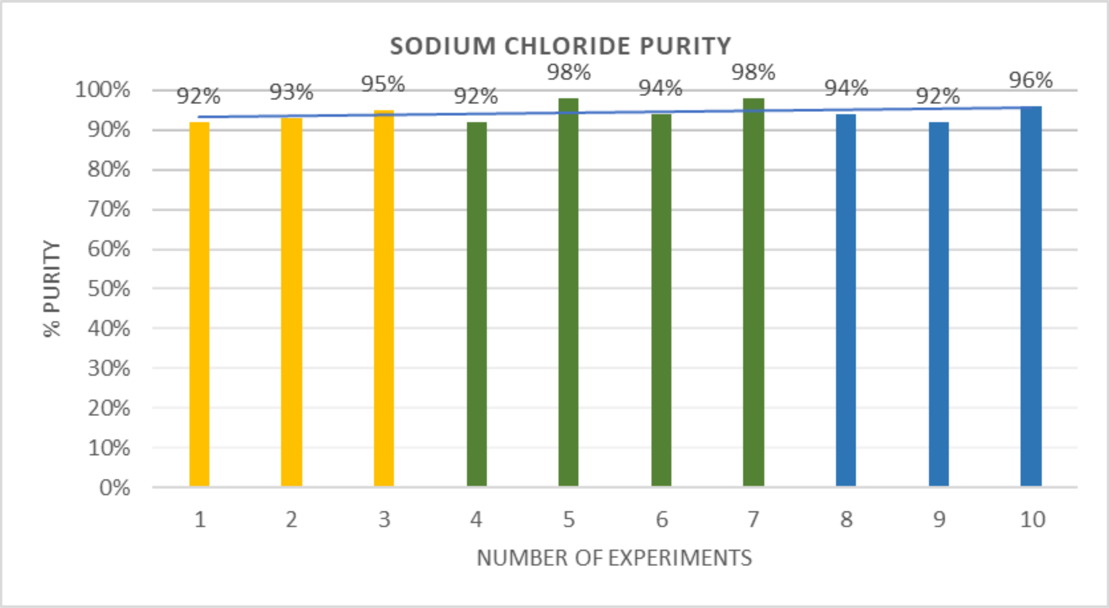
In **Figure *33*** and **Figure *34***, the water recovery of the unit and the NaCl purity are presented. The most representative experiments have been selected. The water recovery ranged from 63 to 90%, with an average value for (i) nominal conditions 65.6%, (ii) the upper limit 66.3% and (iii) the lower limit 73.3%. The NaCl purity ranged from 92 to 98% with an average value for (i) nominal conditions 93.3%, (ii) the upper limit 95.5% and (iii) the lower limit 94%. The produced regeneration solution with a NaCl content from 3.9% to 7.5% seemed to have a sufficient quality to be reused by the same factory for IEX resins regeneration (**Table *21***).

Figure 33: WATER RECOVERY OF THE UNIT IN CASE OF NF PERMEATE AS INLET BRINE



Nominal Condition **Upper Limit** **Lower Limit**

Figure 34: NaCl PURITY OF THE BRINE IN CASE OF NF PERMEATE AS INLET BRINE



Nominal Condition **Upper Limit** **Lower Limit**

Experimental results from mixed stream of MF-PFR Effluent with the NF Permeate

The average concentrations of major ions of the product water (condensate) and produced concentrate solution from the NF permeate mixed with MF-PFR Effluent brine are presented in Table *22* and Table *23*. The following tables present the average values. The water quality results show that the condensate vapor produced from the mixed stream was also a high-quality water that can be used in several industrial sectors.

Table 22: PRODUCT WATER QUALITY (CONDENSATE) IN CASE OF MIXED STREAM AS INLET BRINE

Parameter	100%MF-PFR Effluent	50% NF Permeate – 50% MF-PFR Effluent	75% MF-PFR Effluent – 25% NF Permeate	75% NF Permeate– 25% MF-PFR Effluent
Na^+ (g/L)	0.12	0.14	0.13	0.12
Ca^{2+} (g/L)	0.01	0.01	0.01	0.01
Mg^{2+} (g/L)	0	0	0	0
Cl^- (g/L)	0.12	0.13	0.13	0.14
TDS (g/L)	0.24	0.41	0.27	0.24

Table 23: BRINE QUALITY OF PRODUCED REGENERATION SOLUTION (NaCl REACH) IN CASE OF MIXED STREAM AS INLET BRINE

Parameter	100%MF-PFR Effluent	50% NF Permeate – 50% MF-PFR Effluent	75% MF-PFR Effluent – 25% NF Permeate	75% NF Permeate– 25% MF-PFR Effluent
Na^+ (g/L)	26.2	28.8	32.9	22.35
Ca^{2+} (g/L)	0.03	0.03	0.02	0.02
Mg^{2+} (g/L)	0	0	0	0
Cl^- (g/L)	28.4	17.1	20.2	16.3
TDS (g/L)	54.6	45.8	52.8	38.6
NaCl (%)	5.4	4.6	5.3	3.8

In **Figure *35*** and **Figure *36*** the water recovery of the unit and the NaCl purity are presented. The most representative experiments were selected. The water recovery ranged from 70 to 90%, with an average value for (i) nominal conditions 80.6%, and (ii) the lower limit 87.2%. The NaCl purity ranged from 70 to 99% with an average value for (i) nominal conditions 98.4%, (ii) the upper limit 95.5% and (iii) the lower limit 91.2%. The obtained product (regeneration solution) with a NaCl content ranging between 3.8% and 5.4% seemed to have a sufficient quality to be reused by the same factory for IEX resins regeneration (**Table *23***).

Figure 35: WATER RECOVERY OF THE UNIT IN CASE OF MIXED STREAM AS INLET BRINE

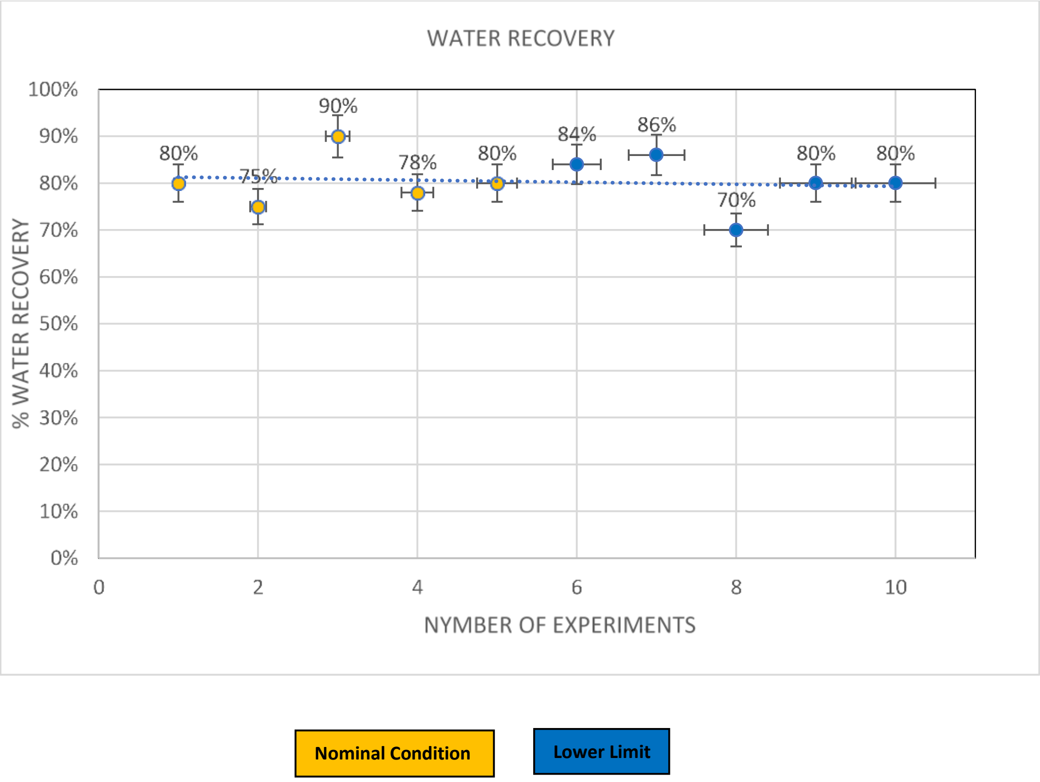
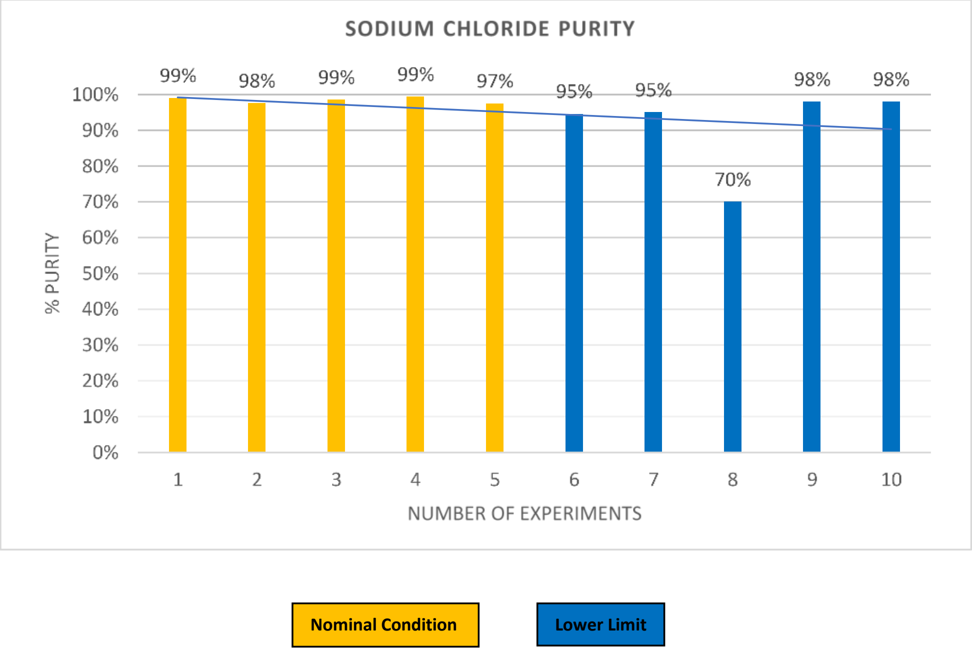


Figure 36: NaCl PURITY OF THE BRINE IN CASE OF MIXED STREAM AS INLET BRINE



Regarding the energy consumption, during Site 01 pilot operation the unit worked with electricity. The energy consumption of the unit ranged from 300 kWh/m^3 of condensate to 500 kWh/m^3 of condensate. The monitoring was carried out by the SCADA control system. In **Table *24*** a heat balance is presented from a representative experiment. The volume of the inlet brine at this experiment was 100 L, the condensate 70 L and the concentrate 30 L. The temperature of the inlet brine was 12 °C, while the temperatures of the condensate and the concentrate were 65 °C and 55 °C, respectively.

Table 24: INLET AND OUTLET HEAT TO THE MED EVAPORATOR UNIT (example on 14/01/2020)

Process Part	Energy (kWh/100 L inlet brine)
1st effect	26.7
2nd effect	21.7
in Preheater	1.6
out Preheater	21.7
Losses	3.5

The total heat input to the unit was the sum of the heat inlet at the 1st effect, the heat inlet at the preheater and the losses, which equaled to 32 kWh or 457 kWh/m^3 of condensate (water produced). The heat input required for the 2nd effect was obtained from the vapors of the 1st effect.

As an overall evaluation, the MED evaporator unit helped the pilot to reach the initial objectives of the project. The required concentration for the IEX regeneration, as well as high quality and purity water recovery were achieved.

When the unit worked with NF permeate, the TDS concentration of the brine at the end of the process ranged between 39 g/L and 74 g/L and when the mixture of the MF-PFR and NF permeate was tested the TDS concentration ranged between 38 g/L and 48 g/L. The NaCl purity ranged between 92% and 99% and the water recovery between 70% and 90%.

6.1.2 Site 01 Overall Pilot Performance Evaluation

In **Figure *37*** an overview of Site 01 pilot performance is given. An important achievement of Site 01 operation was the proof of principle. The application of the NF unit for the separation of multivalent and monovalent cations from the IEX-brine was successful, since rejections of multivalent cations was above 90% whereas NaCl permeated by 54-68%. In this way a concentrate stream with high Mg^{2+} and Ca^{2+} concentration was produced for the operation of the MF-PFR. The latter was found to highly remove Mg^{2+} and Ca^{2+}, while recovering them as hydroxides. Specifically, the removal of Mg^{2+} after both stages reached 100% (<90% after 1 stage), while Ca^{2+} was above 90%. The purity of recovered $Mg(OH)_2$ crystals was on average 88.69% under nominal conditions. The target purity of 90% was achieved in some experiments, but not all due to the co-precipitation of $CaCO_3$. The purity of recovered $Ca(OH)_2$ particles was above 90%. It can be concluded that MF-PFR performance was satisfactory in terms of Mg^{2+} and Ca^{2+} removal efficiency, which resulted in an effluent stream with minimal concentration of divalent ions that could effectively be processed by the subsequent MED evaporator unit. Since the MED evaporator was the final component of the whole process at Site 01, the results of this unit reflect the effectiveness of the entire process. The recovered water by the MED evaporator obtained with either one of the MED evaporator's feed streams (NF permeate and MF-PFR effluent) as well as the tested mix streams was a high-purity water (TDS < 0.4 g/L) that may be used in several industrial sectors. The overall water recovery of Site 01 pilot in case of the mixed stream treatment by the MED evaporator reached a value of 80.3% (under nominal conditions). Simultaneously, a highly concentrated NaCl solution (3.9%-7.5% NaCl) was recovered that may be suitable to be used for the regeneration of IEX units. Finally, it can be noted that nominal and low limit conditions were more favorable for Site 01 pilot operation whereas upper limit conditions was more challenging due to lower separation of multivalent and monovalent ions in the NF unit.

From a research perspective, Site 01 pilot results demonstrated ZERO BRINE as an effective concept for the treatment of the regeneration effluent of the softening IEX unit while recovering minerals, salts and water. Implementation of ZERO BRINE concept and technologies can potentially eliminate the discharge of IEX brine into the harbor, furthermore, it can reduce the overall water consumption and NaCl salt requirements for regeneration of IEX resins of the Evides DWP. However, from an industrial application perspective, the energy and raw material consumption required for the process need to be further investigated in order to assess the economic feasibility of the full-scale implementation. It is necessary to assess the environmental and economic impacts of brine treatment and recovery of salts and minerals at the industrial area of Botlek. This entails the investigation of the life cycle costing for Site 01 treatment process and the exploration of a market for the recovered products and energy sources in order to demonstrate an economic circularity and to minimize the environmental impacts and maximize the economic benefits of production (these investigations were performed in WP8 and WP9 of the ZERO BRINE project).

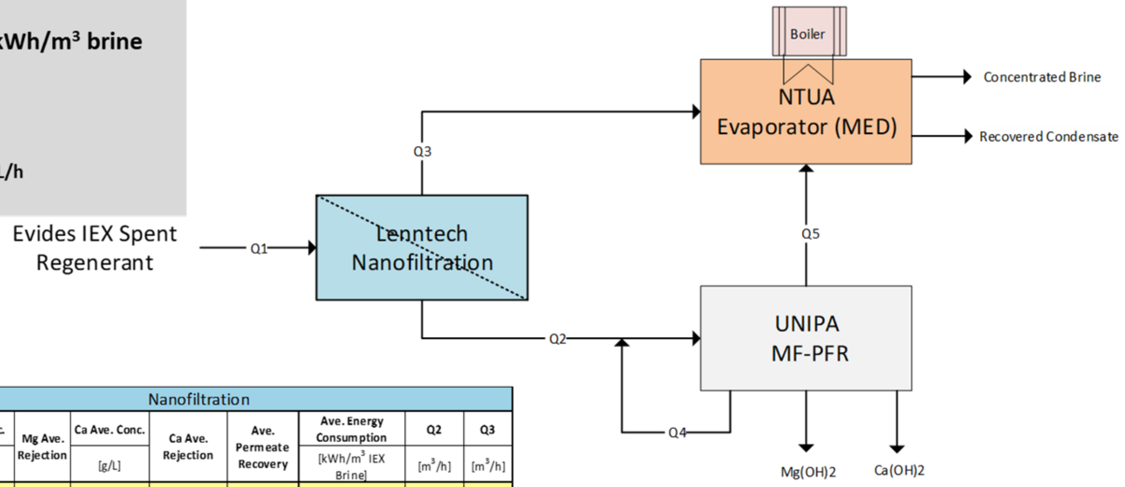
Figure 37: OVERVIEW PILOT PERFORMANCE – SITE 01

Pilot 1
DWP IEX Brine

- Pilot capacity: **1 m³/h**
- Pilot recovery: **80%**
- Total energy consumption ≈ **140 -320 kWh/m³ brine**
- Raw material use
  - Anti-Scalant (NF) ≈ **2 mL/h**
  - NaOH (MF-PFR) ≈ **3 kg/h**
  - HCl (MF-PFR) ≈ **7.5 L/h (10M)**
  - Clean water (clearing and other uses) ≈ **150 L/h**
  - Cooling water for MED (<17°C) ≈ **250 L/h**

Element	Concentration Range [mg/L]
Magnesium	150 – 2250
Calcium	1300 – 16800
Sodium	3000 - 14500
Chloride	3400 - 45000

Experiments		Brine Salinity [gTDS/L]
1	Low limit	10 – 30
2	Nominal	30 – 50
3	Upper limit	50 – 70



MED Evaporator						
Feed to MED	Ave. Water Recovery	NaCl Conc. [Wt%]	NaCl Purity	Ave. Energy Consumption [kWh/m³ IEX Brine]	Conc. Brine [m³/h]	Cond. [m³/h]
Q3	73.3%	3.9%	94.0%	160	0.15	0.43
Q3	65.7%	6.8%	93.4%	140	0.19	0.35
Q3	66.3%	7.5%	95.5%	130	0.08	0.15
Mix Q3 & Q5 in nominal condition	80.3%	5.1%	97.6%	300	0.22	0.88

Nanofiltration								
Q1 [m³/h]	Mg Ave. Conc. [g/L]	Mg Ave. Rejection	Ca Ave. Conc. [g/L]	Ca Ave. Rejection	Ave. Permeate Recovery	Ave. Energy Consumption [kWh/m³ IEX Brine]	Q2 [m³/h]	Q3 [m³/h]
1	0.3	93%	2.5	96%	58%	5.8	0.42	0.58
1	0.7	99%	4.9	99%	54%	8.1	0.46	0.54
1	1.8	98%	13.8	97%	23%	5.8	0.77	0.23

MF-PFR Crystallizer								
Mg Recovery	Mg Purity	Ave. $Mg(OH)_2$ Production [kg/m³ IEX Brine]	Ca Recovery	Ca Purity	Ave. $Ca(OH)_2$ Production [kg/m³ IEX Brine]	Ave. Energy Consumption [kWh/m³ IEX Brine]	Q4 [m³/h]	Q5 [m³/h]
52.1%	55.8%	0.3	96.1%	92.4%	4.5	3.4	0.46	0.51
80.8%	88.7%	1.3	94.5%	96.3%	8.9	3.7	0.51	0.56
35.4%	86.0%	1.5	97.6%	95.1%	25.5	6.2	0.85	0.93

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

6.2 Site 02 Performance Evaluation

6.2.1 Site 02 Performance Evaluation per Technology

Nyex unit provided by Arvia technology Ltd

During the trial period, the Nyex unit was operated both upstream (Mode I) and downstream (Mode II) of the NF unit. In both positions the aim of the Nyex unit was to remove the organic contaminants present in brine. The aim of the NF unit was to concentrate both the ions and the organic content, prior to organic treatment in the Nyex unit. **Table *25*** below summarizes the main parameters that could have an impact on the performance of the Nyex unit.

Table 25: Nyex AVERAGE WATER QUALITY RESULTS – MODE I AND II

Symbol	**Unit**	**Mode I**		**Mode II**	
		Feed	Effluent	Feed	Effluent
Cl^-	g/L	0.78	0.71	2.9	2.6
Na^+	g/L	1.1	1.3	6.8	5.6
HCO_3^-	g/L	0.46	0.11	0.81	0.39
SO_4^{2-}	g/L	0.36	1.4	3.8	7.9
TOC	mg C/L	13.0	2.3	314	32
EC	mS/cm	5.0	5.7	20.9	19.8
pH	-	8.7	6.2	8.9	6.9

From the data of the overall performance operating in the two modes, a number of observations were immediately apparent. These were:

- The concentrations of ions and organic contaminants in the brine after NF were significantly higher than before concentration. Hence, the EC and organic concentration in the feed to the Nyex unit operating in Mode II was much higher than when operating in Mode I. There was a 10 fold increase in TOC content (and SO_4^{2-} ions) with lower increase in the ionic content of smaller ions (for example there was a 6.2 and 3.7 fold increase in Na^+ and Cl^- ions, respectively), due to the size selection of the NF process (more details in the NF discussion part).

- There was a small drop in the Cl^- concentration when the unit was both operated in Mode I and Mode II (9.0% and 8.6% respectively). This was likely due to the electrochemical oxidation of Cl^- ions to Cl_2. This is supported by the observation that Cl_2 was produced during the process as the smell was noticeable, particularly on days where the unit was out of operation. Cl_2 production was expected due to the high Cl^- concentration and a Cl_2 sensor was installed to ensure that health and safety risks were minimized.
- The treatment of the brine occurred under acidic conditions (based on results from the earlier research phase) which was achieved by adding H_2SO_4 to the brine. As expected, there was a reduction in HCO_3^- ions as the acidic conditions would result in the loss of HCO_3^- through its

conversion to carbon dioxide. The use of H_2SO_4 to achieve acidification also explains the increase in SO_4^{2-} ions in both Mode I & II operation.

- After treatment, the brine effluent was neutralized, using, in this case, NaOH. Hence an increase in Na^+ concentration when the brine was in more dilute form (Mode I) was expected. However, there was a reduction in Na^+ concentration when the brine TDS concentration was higher (Mode II). This was not expected, but the result was based on only 2 samples.
  TOC reductions of 82.3% and 89.8% for Mode I & II, respectively, was achieved.

Figure *38* shows that the organics removal in Mode I, which was typically 70 – 90%, visually appeared to show small increases in the outlet TOC when there was an increase in the inlet TOC concentration. *Figure 39* below confirms that there was a weak correlation ($R^2 = 0.55$) between the inlet and outlet TOCs, with the treated effluent having a higher TOC when there was a higher inlet TOC. However, there was a stronger correlation between the mass ($R^2 = 0.98$) and concentration ($R^2 = 0.98$) of TOC removed and the inlet TOC concentration (***Figure 40***). These similar correlations between mass and concentration removal with the inlet TOC can be attributed to the fact that the flow rate was reasonably consistent (average flow rate 934 L/h, range 907 – 990 L/h). This result is to be expected as electrochemical oxidation at the lower organics level is usually mass transport controlled with the limiting factor being the transport of organics to the electrode surface (Scialdone, 2009). This suggests that increasing the turbulence between the electrodes may enhance the removal rates as it will increase the mass transport. Increasing the inlet organic concentration will achieve a similar increase in organic removal rates.

Figure 38: INLET AND OUTLET TOC SHOWING THE VARIATION IN ORGANICS REMOVAL IN MODE I

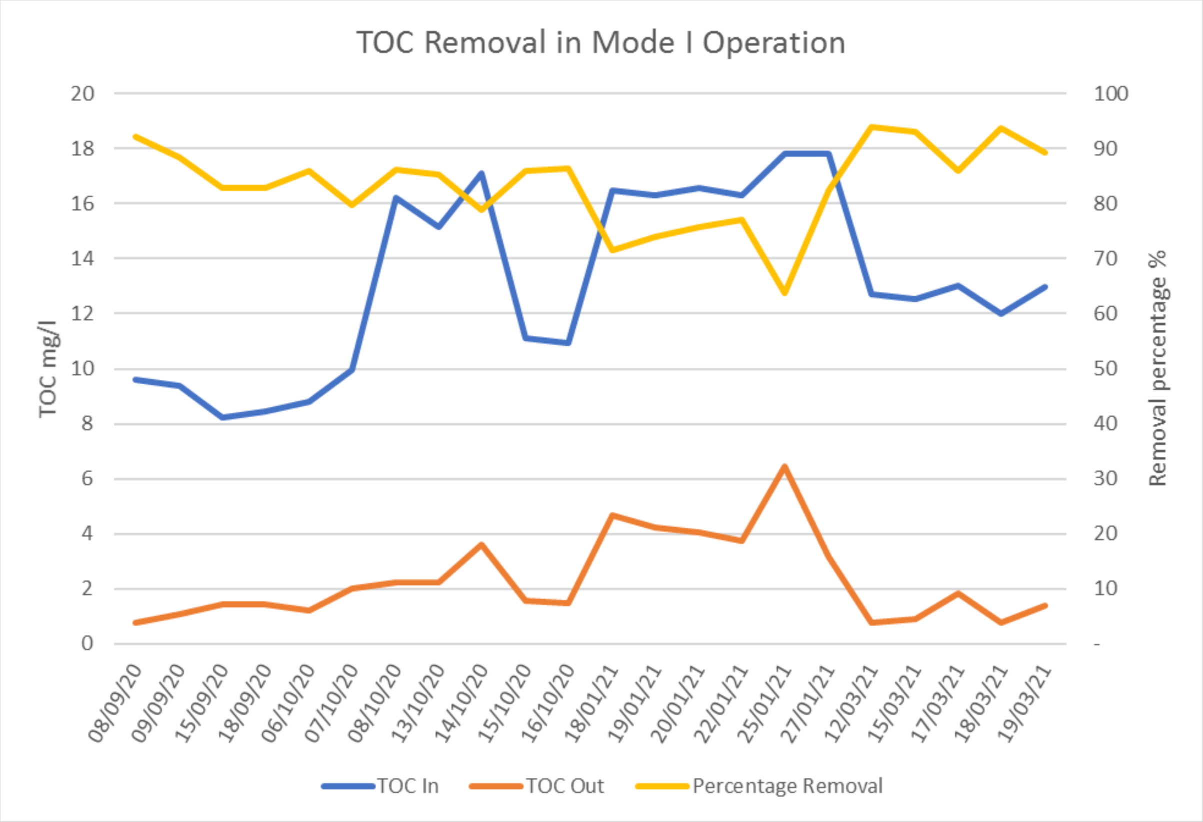


Figure 39: IMPACT OF INLET CONCENTRATION ON OUTLET TOC CONCENTRATION AND PERCENTAGE REMOVAL IN MODE I

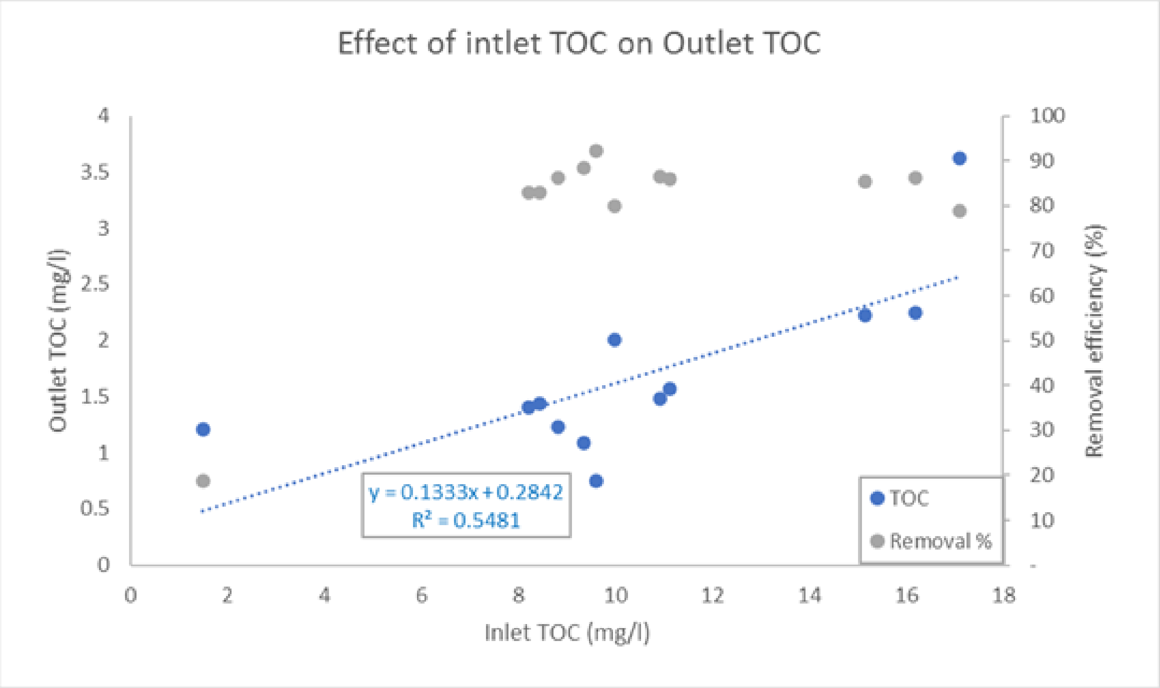
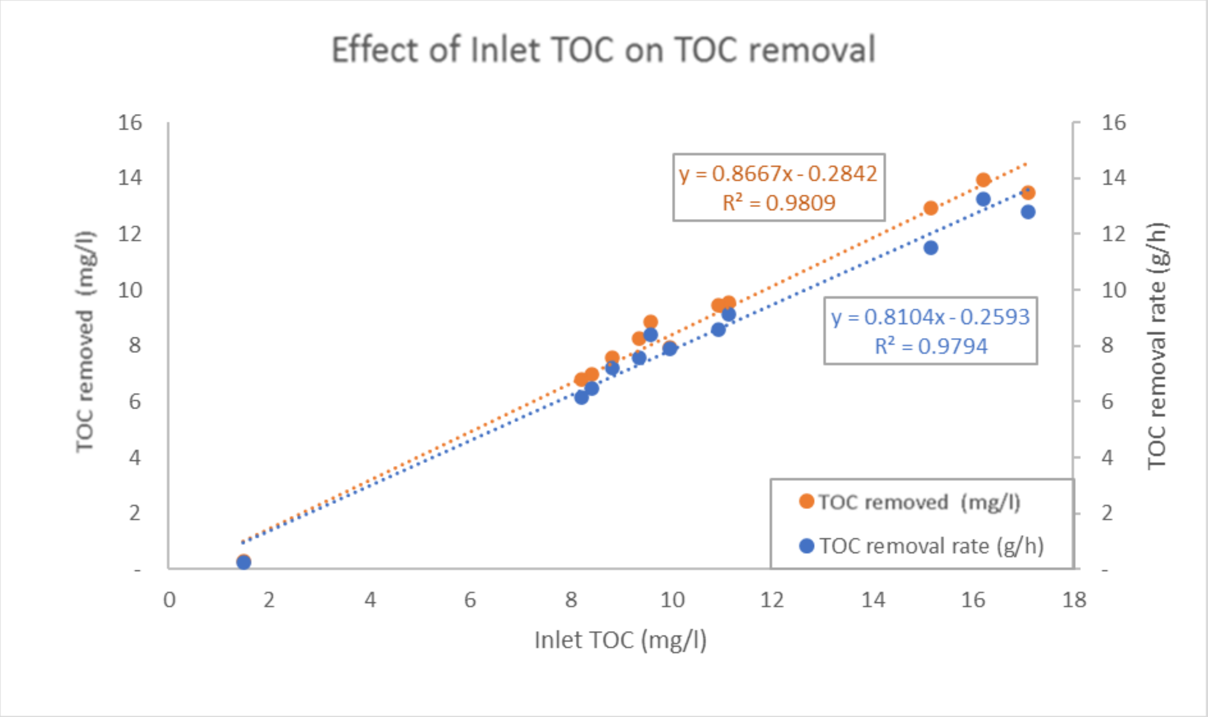


Figure 40: IMPACT OF INLET TOC CONCENTRATION ON TOC REMOVAL AND REMOVAL RATE IN MODE I



Interestingly this pilot trial demonstrated that with the exception of the sample with a very low inlet TOC concentration (< 1.5 mg/L), the removal efficiency was not affected by the inlet concentration. There was only one sample with an inlet TOC < 1.5 mg/L, which makes it difficult to make comments on the significance of this sample. Since the treated brine TOC concentration of this sample was very much in line with the outlet TOCs of the other treated brines, it may be that the result from the inlet brine sample was either a sampling mistake or analytical anomaly. Alternatively it may be that there is a limit to the final concentration that can be achieved. As there was only one sample, it was not possible to speculate as to whether it was an anomaly or a function of the design. Further investigation will be needed to validate this hypothesis.

In Mode II operation, the concentration of inorganics in the liquid phase was over 10 times higher due to the concentration achieved by NF. This increased the removal efficiency of the unit operating in Mode II at 89.9% (***Figure 41***) compared to Mode I (82.3%), but the concentration in the treated brine effluent was higher in Mode II (32 mg/L) compared to Mode I (2.3 mg/L).

In Mode II operation there was also a good correlation between the inlet TOC and the outlet TOC, providing a good correlation of the inlet TOC with the TOC removal (mg/L), while with the removal efficiency again not showing any correlation with the inlet TOC (***Figure 42*** and ***Figure 43***). However, as it can be seen in ***Figure 43***, the TOC removal rate (g/h) at the higher organic concentration showed much greater scatter than TOC removal rate (g/h) achieved at the lower inlet TOC concentration in Mode I. This is because the flow rate used during these trials varied from 387 – 950 L/h. As shown in ***Figure 44*** there was a high correlation between the flow rate and the TOC removal rate (g/h). This strong correlation between flow and TOC removal was expected because the electrochemical process is mass transfer controlled at these comparatively low organic concentrations (typically below 1,000 mg/L electrochemical oxidation processes will be mass transfer controlled (Scialdone, 2009)). Enhancing the turbulence within the unit is likely to result in improved removal efficiencies as the mass transfer coefficient will be improved. As anticipated, the organic (as measured by TOC) removal rate (g/h) was much greater at the higher inlet organic concentrations.

Figure 41: INLET AND OUTLET TOC SHOWING THE VARIATION IN ORGANICS REMOVAL IN MODE II

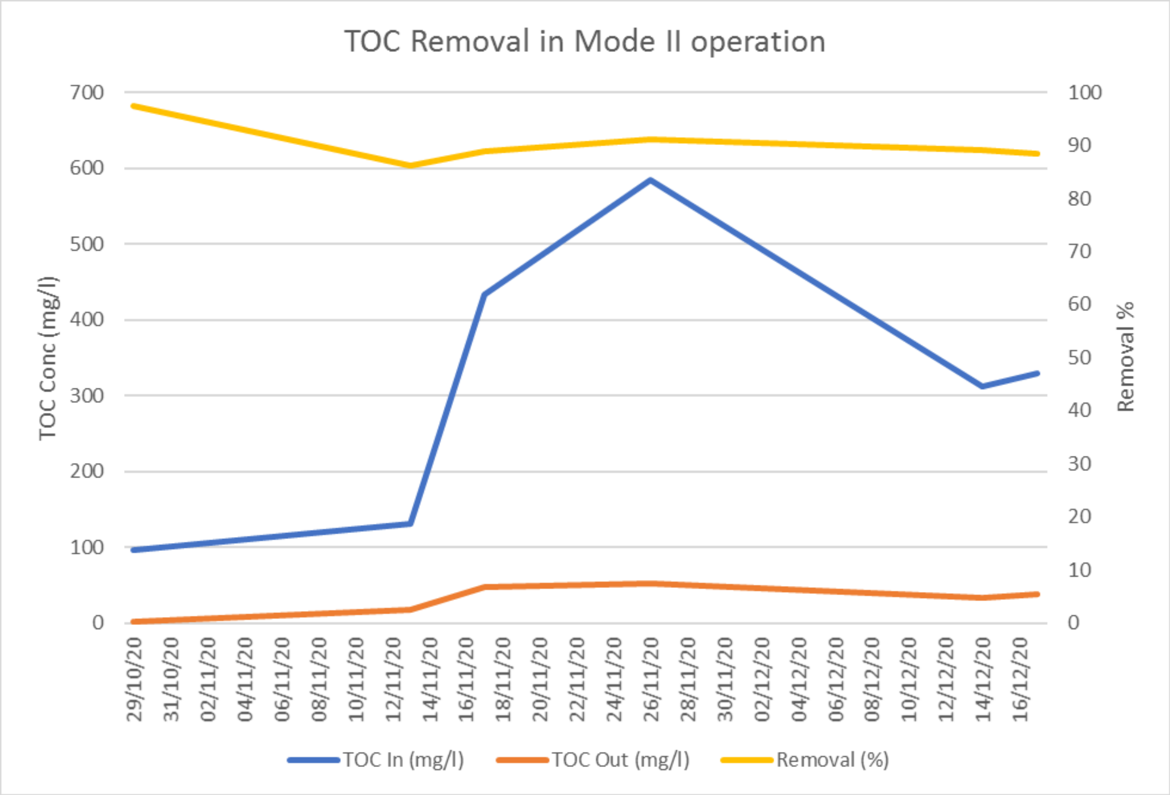


Figure 42: IMPACT OF INLET TOC CONCENTRATION ON OUTLET TOC CONCENTRATION AND REMOVAL EFFICIENCY IN MODE II

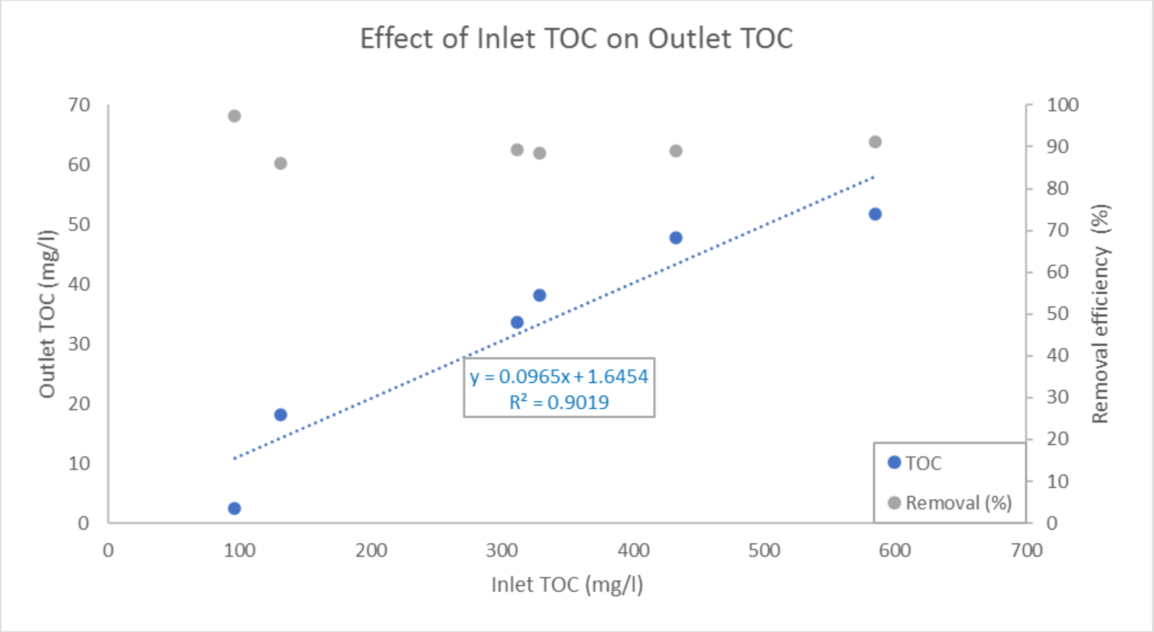


Figure 43: IMPACT OF INLET TOC CONCENTRATION ON TOC REMOVAL AND REMOVAL RATE IN MODE II

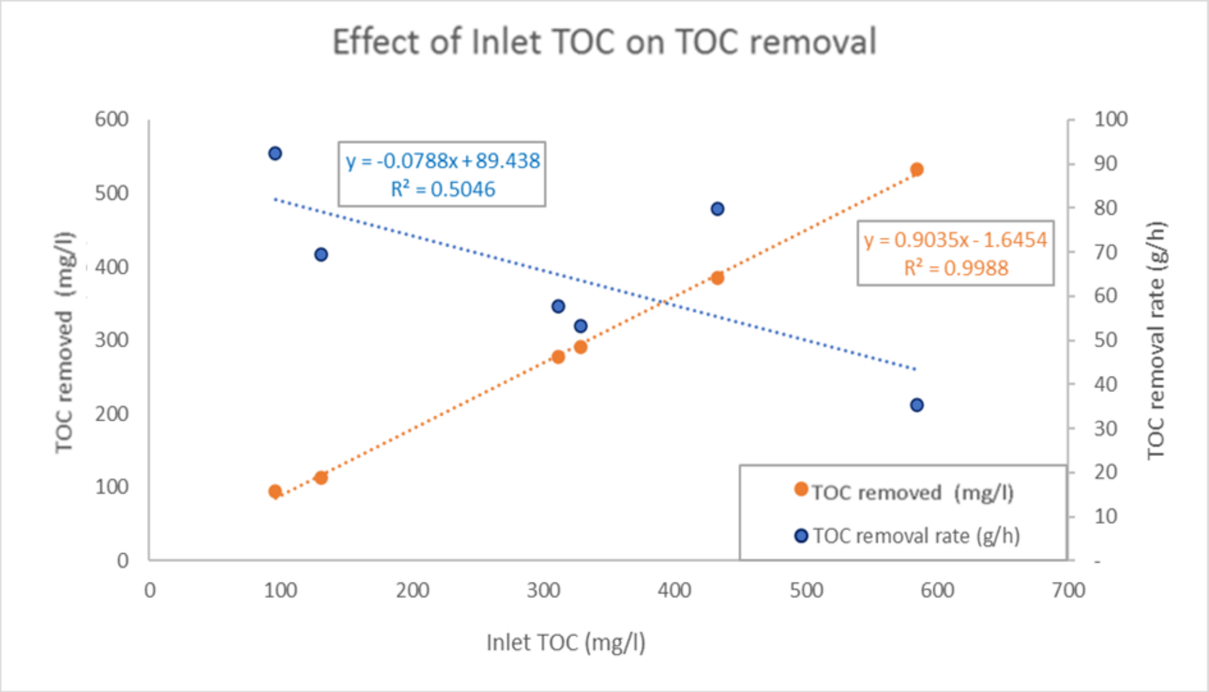
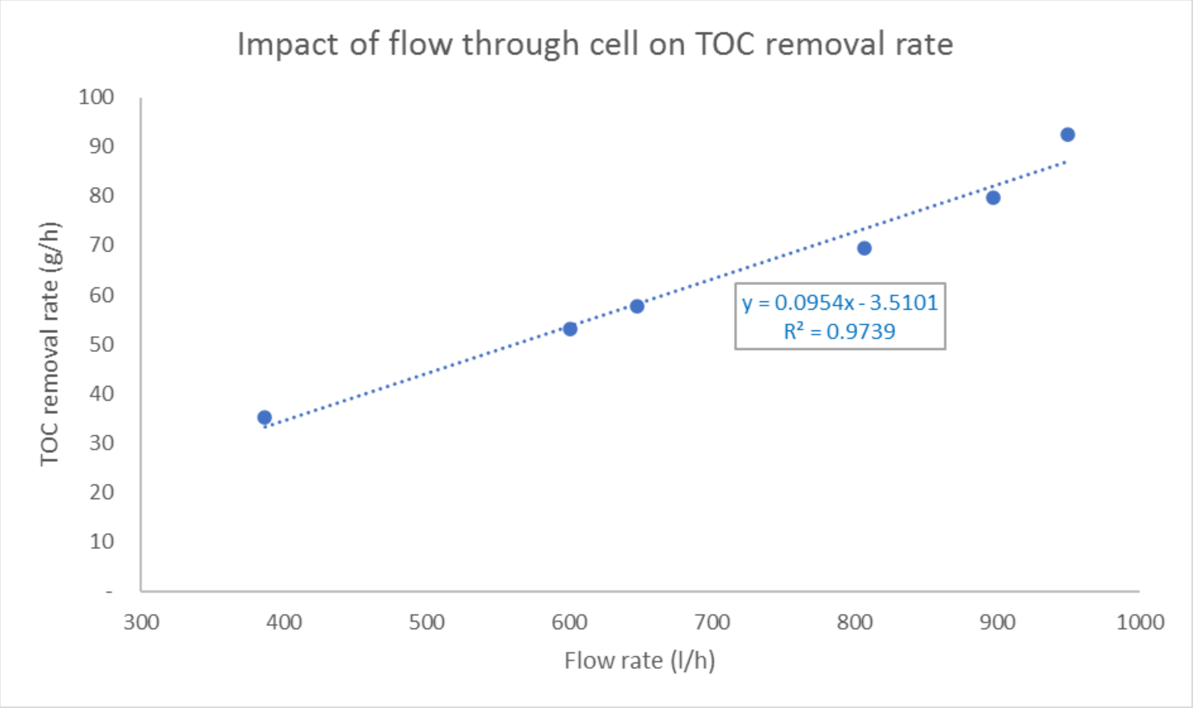


Figure 44: IMPACT OF FLOW RATE ON TOC REMOVAL IN MODE II

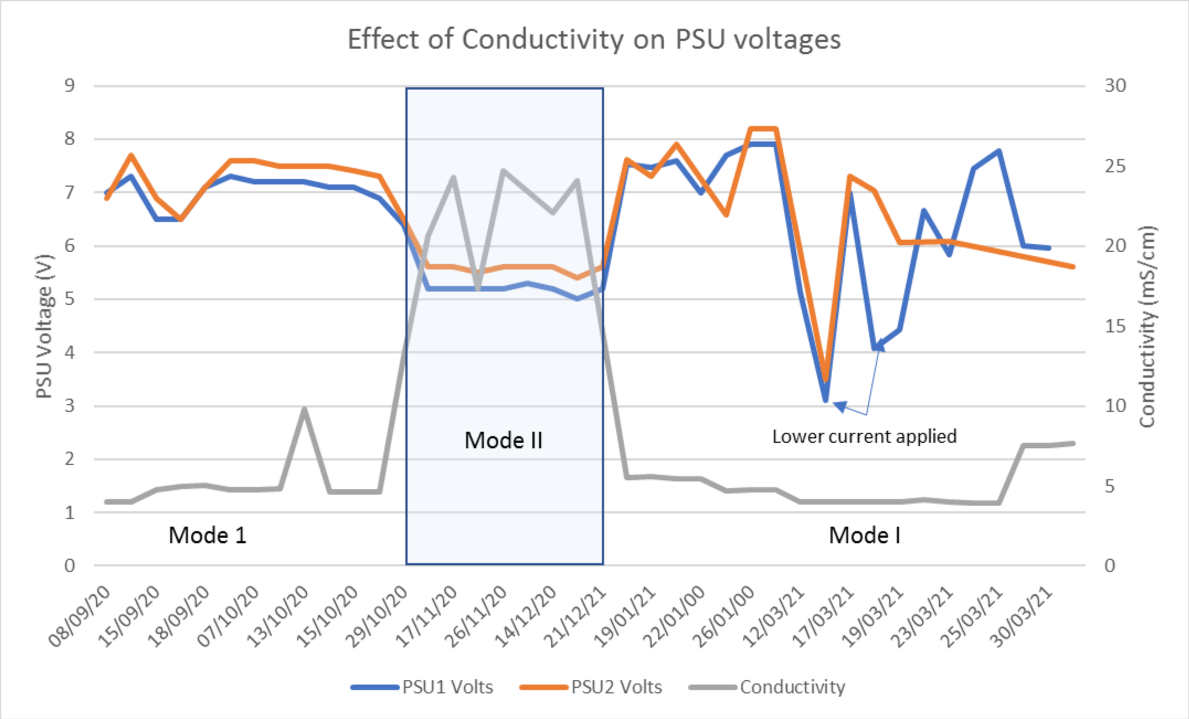


The major energy required by the Nyex unit was for the electrochemical treatment of the water. Hence, the energy use was based on this parameter. The average energy required to treat 1 m^3 of brine in Modes I and II was calculated to be 5.7 and 6.0 kWh/m^3 brine respectively. The key electrochemical parameters are summarized in ***Table 26.***

Table 26: VOLTAGE AND CURRENT USAGE IN MODE I AND II

	EC (mS/cm)	**Voltage (V)**		**Current (A)**	
	-	PSU1	PSU2	PSU1	PSU2
Mode I	5.0	6.7	7.0	373	379
Mode II	20.9	5.3	5.7	400.4	399.8

Figure 45: VARIATION OF EC AND POWER SUPPLY VOLTAGES OVER TIME



Whilst *Figure 45* clearly shows a reduction in voltage when there was a large increase in EC as the trial converted from Mode I operation to Mode II operation and then back again, it is clear that there appears to be no link between the smaller changes in EC within a mode of operation. The lack of correlation between applied voltage and EC when operating in one mode or another indicates that the voltage fluctuations from internal processes were masking any small change in voltage due to EC changes in the brine. The most likely cause of these internal variations is likely to be the bubbles generated at both the cathode and anode. Within the electrochemical cell, when a current is passing, a number of electrochemical reactions take place. These include the generation of H_2 at the cathode through the electrochemical reduction of water and carbon dioxide (from the oxidation of the organics), Cl_2 (from the oxidation of Cl^- ions) and oxygen (O_2, from the oxidation of water) (Shestakova & Sillanpää, 2017). All these form bubbles on the electrodes and these bubbles create a non-conducting area on the surface of the electrodes until they are large enough to coalesce and escape, providing a varying surface area available for the current to pass through, which gives a fluctuating current density at the electrodes resulting in voltage variations. These voltage variations were sufficient to mask the relatively small changes observed when there were small changes in EC.

However, the EC in Mode II operation was a factor of four larger than during Mode I operation and this was sufficiently large that a noticeable difference in voltage was observed between the two modes of operation (typical reduction in voltage was about 1.4 V).

The Nyex unit operated with two banks of cells within the treatment tank, treating the same water, operating at the same nominal current of 400 A. Hence the voltage across both power supplies should be very similar. During this trial the differences in the applied voltage on PSU1 and PSU2 when operating in Mode I and Mode II were 0.33 V and 0.31 V, respectively, a significant difference to suggest that the unit operated slightly differently. The fact that the difference was similar suggests that there was an additional resistance within the electrical system from PSU2 to the cell as it is not impacted by the change in EC (hence the change is a result of factors outside the electrochemical reaction zone).

Overall, it was observed that the energy required was 5.7 and 6.0 kWh/m^3 brine when operating in Mode I and Mode II, respectively. The slightly higher value observed whilst operation in Mode II was a result of the flow through the unit being lower during these trials (average flow 766 L/h in Mode II against 915 L/h in Mode I). If a similar flow rate had been used during Mode II then a lower energy per m^3 brine would have been expected, as the voltage in Mode II operation was lower.

However, the mass of organic material removed per m^3 of the brine treated was significantly greater in Mode II (observed removal rates were 9.9 and 190 g/h in Modes I and II, respectively). Calculating the energy required to remove a kg of TOC in Mode I and II, gives 535 and 31.6 kWh/kg TOC respectively.

Lab research by Arvia has shown that pH adjustment at a value of 2 gives better results, but this requires additional chemical usage. Table *27* below summarizes the changes in pH through the unit and the chemical additions required.

Table 27: SUMMARY OF pH CHANGES THROUGH THE NYEX UNIT AND THE ASSOCIATED CHEMICAL ADDITIONS

Parameter	Mode I	Mode II
Inlet pH	8.9	9.1
Acid added (L/h)	3.6	5.7
Acid added (L/m^3)	4.0	8.5
pH pre Nyex	2.7	3.6
pH post Nyex	3.1	5.9
Base added(L/h)	3.8	1.3
Base added (L/m^3)	4.1	1.9
Outlet pH	6.6	8.2

In order to obtain suitable treatment, it was found necessary to acidify the brine before treatment through the Nyex unit. Treating the concentrated brine solution (Mode II) required over 50% more acid and even with this addition the pH achieved was not as low as when acidifying the dilute solution (acidified pH was 2.7 in Mode I and 3.6 in Mode II). This is likely to be due to the buffering effect from the higher ionic content within the concentrated brine.

However to neutralize the brine before discharge required only a third of the NaOH operating in Mode II (and it achieved a higher discharge pH = 8.2 compared to 6.6 in Mode I). It can be seen from the table that less NaOH was required because after electrochemical treatment, the pH was much higher when a concentrated brine was treated (5.9 in Mode II compared with 3.1 during Mode I). As OH^- ions were produced at a rate that dependents on the current and the current was similar in both trials, it is evident that the increase in pH during electrochemical treatment in Mode II was not a result of increased OH^- production at the cathode. It should be noted that this is an assumption based on previous Arvia experience that the only significant reaction at the cathode was the reduction of water. Hence it is likely that the change happened due to reactions at the anode.

When treating the concentrated organic brine in Mode II, significantly more of the electric charge went into the oxidation of the organics, shown by the much higher organic removal rate. Similarly operating in Mode II means that there was a higher Cl^- concentration in the water. Thus, some of the charge also went towards the oxidation of the Cl^- ions to Cl_2. However, a similar charge was passed when treating the dilute brine solution in Mode I, but much less charge went towards the oxidation of organics or Cl^-. Hence more of the charge resulted in a different electrochemical oxidation reaction that might have taken place at the anode. This was the oxidation of water to form O_2. During this reaction, hydrogen (H^+) ions were also produced. These H^+ ions then reacted with the OH^- ions produced at the cathode. As more H^+ ions were produced in Mode I to react with the OH^- ions produced at the cathode, there were fewer OH^- ions in the brine to cause an increase in pH. As fewer H^+ ions were produced when operating in Mode II, the rise in pH was much greater as less of the OH^- ions produced reacted with the H^+ ions. Hence in Mode II there were two oxidation reactions reducing the water oxidation reaction, so the pH was able to rise more in Mode II, reducing the quantity of NaOH needed for neutralization.

Table *28* summarizes the effect of the two different modes to the Nyex unit. As it can be seen, operating in Mode II gave a number of operational benefits compared with Mode I operation, particularly the OPEX saving. This was due to the pre-concentration stage where NF increases the ionic strength and organic concentration within the brine. This obviously involved additional upstream processing and the additional costs of this need to be considered. The higher organic content and EC leads to considerable OPEX saving and higher organic removal rates as the process was mass transport limited. However, the final organic concentration achieved was not as low as when operating in Mode I. This may be a deciding factor depending on the expected use of the brine downstream of the Nyex unit. Each brine will need assessment to determine whether there is benefit in the upstream processing. Two Nyex units operating in series with NF unit upstream may provide an optimal operational arrangement for the treatment of brine solutions, but the additional CAPEX and operational complexity would need to be considered.

Table 28: BENEFITS AND PROBLEMS WITH OPERATING IN MODE I AND II

Conductivity	Mode I	Mode II
Voltage	-	+
Removal rate	-	+
Removal efficiency	-	+

OPEX	-	+
CAPEX (Nyex unit only)	-	+
Additional pre-treatment	+	-
Final organic concentration	+	-

Nanofiltration unit provided by Lenntech B.V.

Not all acquired data from the NF unit was considered for the evaluation of its performance. Many cleaning in place (CIP) and membranes replacements occurred during the pilot operation. The reasons that led to CIP and membrane replacement can be justified by the graphs in *Figure 46*, *Figure 47* and *Figure 48*. Membrane fouling occurred in the end of July, resulting in high TMP (pressure difference between two sides of the membrane), (*Figure 47*). A sample of the concentrate stream was collected, showing a white color and having a pH > 12 (Figure *49*). Moreover, when the sample was stored for some minutes, a layer of white precipitate appeared at the bottom of the sample bottle. As this sample was obtained from the NF concentrate, the white water was in contact with the NF membranes, potentially causing inorganic fouling. The membranes were cleaned in the beginning of August. Alkaline cleaning did not result in an improved performance of the NF unit, based on the TMP and the delta pressure (ΔP, the hydraulic pressure loss between the feed water and the concentrate). However, acid cleaning using citric acid resulted in a decrease of the ΔP and the required TMP to permeate water. Hence, the fact that the acid cleaning proved to be effective, supports the suggestion that the white pH>12 water depicted in Figure *49* fouled the membrane. It is unclear how this water was used as feed to the NF unit, since the RO concentrate from the RO units of Evides DWP has typically a brown color and a close-to neutral pH. Furthermore, spacer fouling resulting in high ΔPs led to a second CIP of the membranes in mid-September. Interestingly, this time the alkaline cleaning, using NaOH, proved to be effective, suggesting that the spacer fouling was caused by organic matter. Later in October, the membranes were fouled, witnessed by the high TMP (up to 40 bars). The cartridge filters were black, as it can be seen in Figure *50* (left). At that point, the NF membranes were replaced with new ones. By the end of December, the TMP pressure was increased again, indicating membrane fouling. A photo of the cartridges was taken in mid-November 2020, and presented in Figure *50* (middle). The greenish color might be algal growth. In the end of January, the NF membranes were replaced once again. Finally, in the end of February, the ΔP increased again, resulting in a final CIP. After the last CIP, the TMP started to increase again until the end of March 2021. The cartridge filters in Figure *50* (right) showed a brown color, indicating organic pollution. As it can be seen in Figure 48, the unit's performance became stable in the beginning of November 2020, after the replacement of the membranes for the first time. For this reason, the evaluation of the NF unit's performance was based on the operational period after the beginning of November 2020 until the end of March 2021. The period that was excluded from the data analysis is indicated in *Figure 46*, *Figure 47* and *Figure 48* with a pink color. The cause of fouling was assessed by further analyses that can be found in Annex F: Further Analyses for Identifying the Fouling of the NF Membranes.

Figure 46: DELTA PRESSURE (ΔP) OF THE NF UNIT

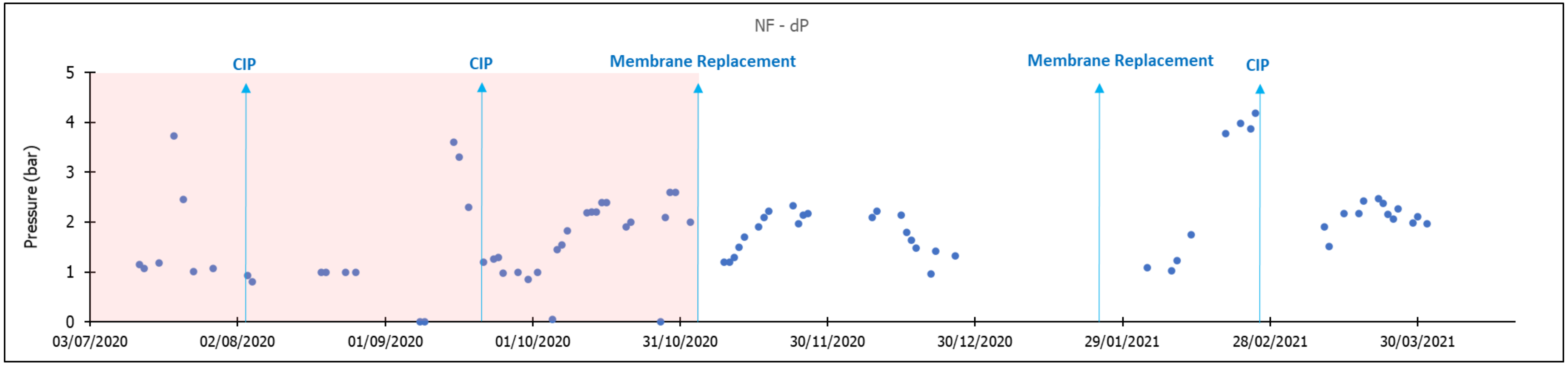


Figure 47: TRANSMEMBRANE PRESSURE OF THE NF UNIT

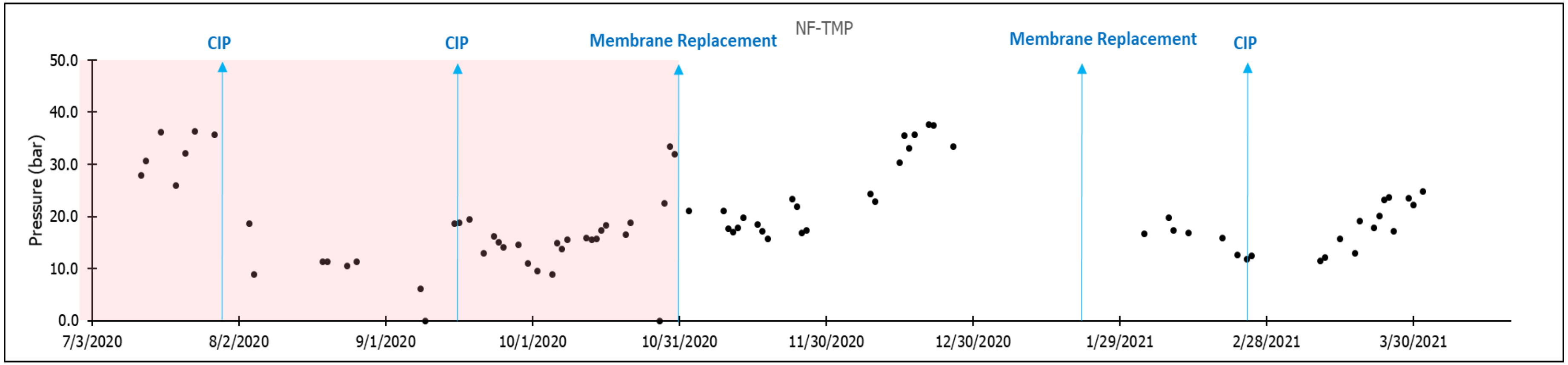


Figure 48: ION REJECTION BY THE NF UNIT

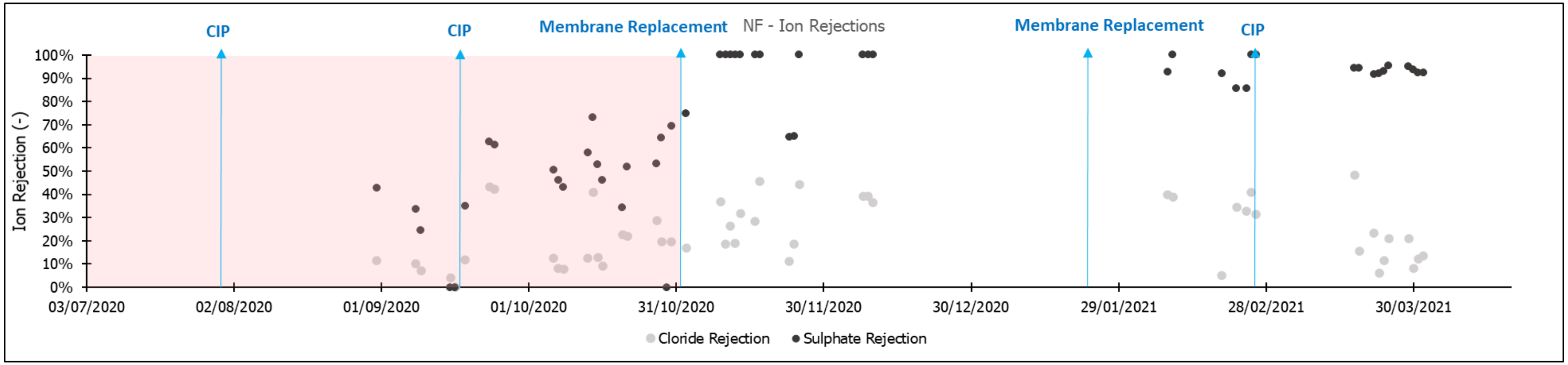


Figure 49: SAMPLE OF THE NF CONCENTRATE ON 14 JULY 2020

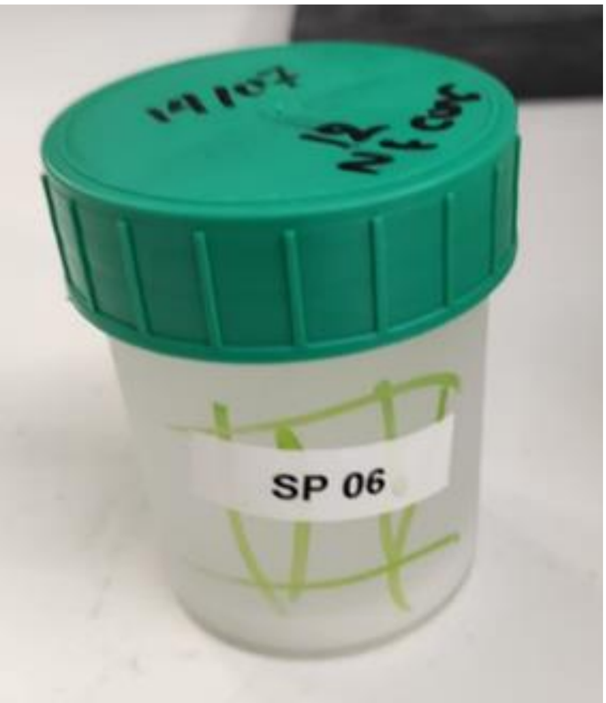


Figure 50: CARTRIDGE FILTERS OF THE NF UNIT ON 12 OCTOBER 2020 (LEFT), 18 NOVEMBER 2020 (MIDDLE) and 19 MARCH 2021 (RIGHT)

The recoveries, fluxes, TMP and energy consumption per m^3 of permeate of the NF unit for both modes are presented in Table 29 and Table 30. It should be noted that minimum fluxes and recoveries, and high TMP occurred when the membranes were fouled. More specifically, the recovery and the flux decreased (Figure 51 and Figure 52) in December because of the high TMP (Figure 47). Overall, an average recovery of 90%, a flux of 22 L/m^2/h and TMP of approximately 20 bars were maintained. The average energy consumption was 4.5-5.5 kWh/m^3 permeate. Antiscalant VITEC 4000 was used, and the dose was 2.1 mL/m^3 permeate.

Table 29: RECOVERIES, FLUXES, TMP AND ENERGY CONSUMPTION OF THE NF UNIT - MODE I

	En. C (kWh/m^3)	Recovery (%)	Flux (L/m^2/h)	TMP (bar)
Minimum	3.2	87%	23	11.5
Average	4.5	89%	23	18.8
Maximum	5.6	89%	23	24.8

Table 30: RECOVERIES, FLUXES, TMP AND ENERGY CONSUMPTION OF THE NF UNIT - MODE II

	En. C (kWh/m^3)	Recovery (%)	Flux (L/m^2/h)	TMP (bar)
Minimum	3.6	69	15	11.8
Average	5.5	90	22	22.0
Maximum	9.5	90	23	37.6

Figure 51: RECOVERY OF THE NF UNIT

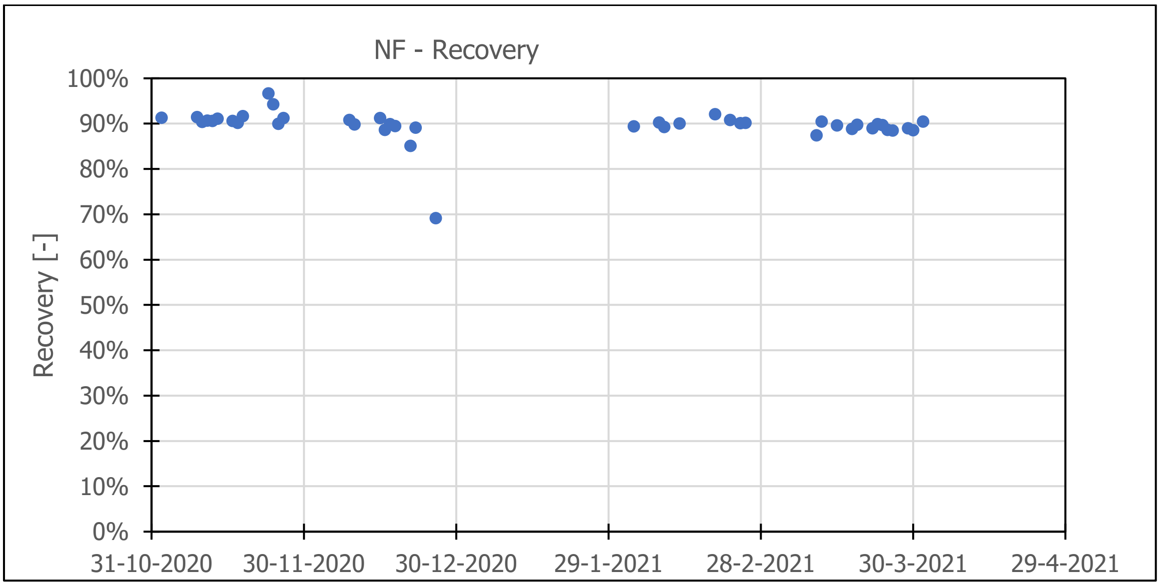
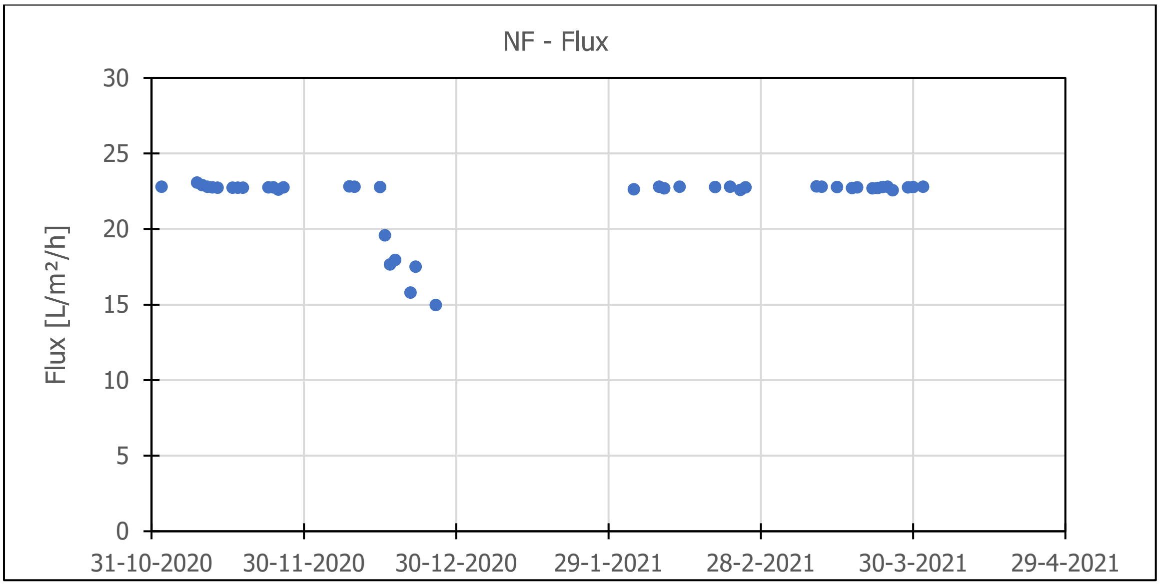


Figure 52: FLUX OF THE NF UNIT



Monovalent ions were less rejected by the NF membranes compared to divalent ions. In Mode I, the average Cl^- rejection was 18% , while the average SO_4^{2-} rejection was 93% (Table 31). The Cl^- rejection was always below 23%, except for one experiment where it was 48%. The SO_4^{2-} rejection was stable varying from 92-95%. TOC rejection fluctuated between 43 and 68%. The concentration of the interesting for the NF unit components in the feed, permeate and concentrate streams in Mode I are presented in Table 32. SO_4^{2-} was concentrated by 8-9 fold.

In Mode II, Cl^- was rejected by 31% in average, while SO_4^{2-} was rejected by 93% (Table *33*). Cl^- rejection fluctuated from 5 to 46%. SO_4^{2-} rejection reached a minimum of 65%. This occurred only in two experiments whereas in the rest of the experiments SO_4^{2-} rejection was above 86%. TOC was rejected by 83% on average with a standard deviation of 12%. TOC rejection in Mode I was lower compared to Mode II because the bigger particles were already removed by Nyex. The concentrations of the ions in the feed, permeate and concentrate streams of the NF unit in Mode II are presented in Table 34. SO_4^{2-} was concentrated by 12 fold approximately.

Table 31: NF COMPOUND REJECTIONS – MODE I

Parameter	Unit	Minimum	Average	Maximum	SD
Na^+	%	27.0	32.0	37.0	6.0
Cl^-	%	6.0	18.0	48.0	12.0
SO_4^{2-}	%	92.0	93.0	95.0	1.0
TOC	%	43.0	52.0	68.0	14.0

Table 32: NF FEED, PERMEATE AND CONCENTRATE WATER QUALITY – MODE I

Parameter	Unit	Feed	Permeate	Concentrate
Na^+	g/L	1.7	1.2	6.2

Cl^-	g/L	1.2	1.0	2.5
SO_4^{2-}	g/L	1.4	0.87	11.3
TOC	mg C/L	1.4	0.6	5.5

Table 33: NF COMPOUND REJECTIONS – MODE II

Parameter	Unit	Minimum	Average	Maximum	SD
Na^+	%	52.0	59.0	68.0	10.0
Cl^-	%	5.0	31.0	46.0	11.0
SO_4^{2-}	%	65.0	94.0	100	12.0
TOC	%	63.0	83.0	99.0	12.0

Table 34: NF FEED, PERMEATE AND CONCENTRATE WATER QUALITY – MODE II

Parameter	Unit	Feed	Permeate	Concentrate
Na^+	g/L	1.0	0.41	6.1
Cl^-	g/L	0.65	0.45	2.8
SO_4^{2-}	g/L	0.31	0.022	3.9
TOC	mg C/L	13.0	2.8	260

The NF unit separated Cl^- from SO_4^{2-} in both modes, based on the SO_4^{2-} and Cl^- rejections. SO_4^{2-} was rejected by 93-94 % in both modes on average. However, the rejection was more stable in Mode I, having a SD of only 1%. Furthermore, Cl^- was less rejected in Mode I (18%) compared to Mode II (31%). Therefore, on the one hand, it is concluded that the ionic separation was better in Mode I. On the other hand, TOC was more rejected in Mode II. However, this was attributed to the different organic composition in the feed stream of the NF in the two modes. The TOC concentration in the permeate stream was lower and equal to 0.6 mg/L compared to Mode II, where it was equal to 2.8 mg/L. The energy consumption was lower in Mode I (4.5 kWh/m^3) compared to Mode II (5.5 kWh/m^3). The maximum values of the energy consumptions and TMP in Mode II were much higher, indicating that more severe fouling occurred when NF was placed before Nyex. Overall, NF performed better when Nyex was upstream, thus during Mode I operation.

Reverse Osmosis unit provided by Lenntech B.V.

The energy consumption per m^3 of permeate, recovery, flux and TMP of the RO unit in Mode I and II are presented in **Table *35*** and **Table 36**. In both modes, the average energy consumption was 5.5-6.0 kWh/m^3 while the average TMP was 21-24 bar. The average recovery and flux were 90 and 24-26 $L/m^2/h$, respectively. The low values of TMP (14 bar) in Mode II can be related to the low EC values in the feed of the RO. For lower EC values (representative for the ion concentration), the RO needs to overcome a lower osmotic pressure to produce permeate, leading to a lower applied pressure, resulting in a lower energy consumption. In addition, the decrease in the flux and recovery of the RO unit in December (**Figure** *53* and ***Figure*** *54*) were caused by fouling of the NF unit. Specifically, NF membranes were fouled, resulting in lowering the capacity in order to continue the operation and not exceed 40 bar. This also caused a decrease in the capacity of the RO so that they could both run simultaneously. The ΔP over the RO membranes and the TMP remained stable during operation, implying that the membranes also remained clean throughout the experimental campaign. Antiscalant VITEC 4000 was used with a dose of 1.7 mL/m^3 permeate.

Table 35: RECOVERIES, FLUXES, TMP AND ENERGY CONSUMPTION OF THE RO UNIT - MODE I

	En. C (kWh/m^3)	Recovery (%)	Flux (L/m^2/h)	TMP (bar)
Minimum	5.9	90.0	27.2	24.0
Average	5.9	90.0	27.3	24.0
Maximum	5.9	90.0	27.4	25.0

Table 36: RECOVERIES, FLUXES, TMP AND ENERGY CONSUMPTION OF THE RO UNIT - MODE II

	En. C (kWh/m^3)	Recovery (%)	Flux (L/m^2/h)	TMP (bar)
Minimum	4.2	85.0	18.2	14.0
Average	5.5	90.0	25.9	21.0
Maximum	6.5	90.0	27.4	27.0

Figure 53: RECOVERY OF THE RO UNIT

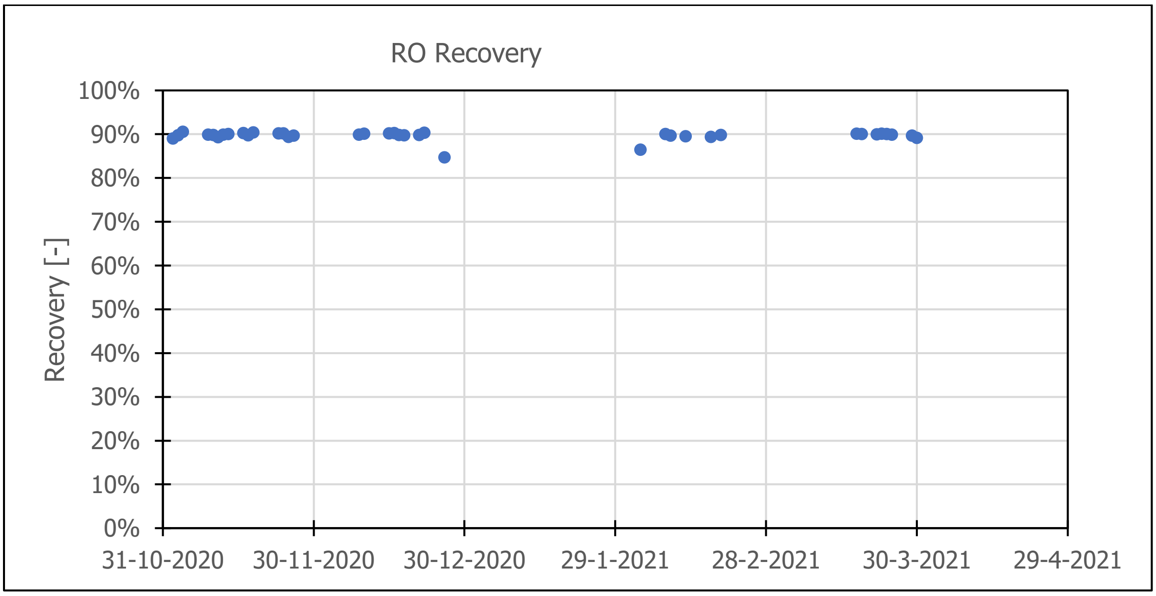
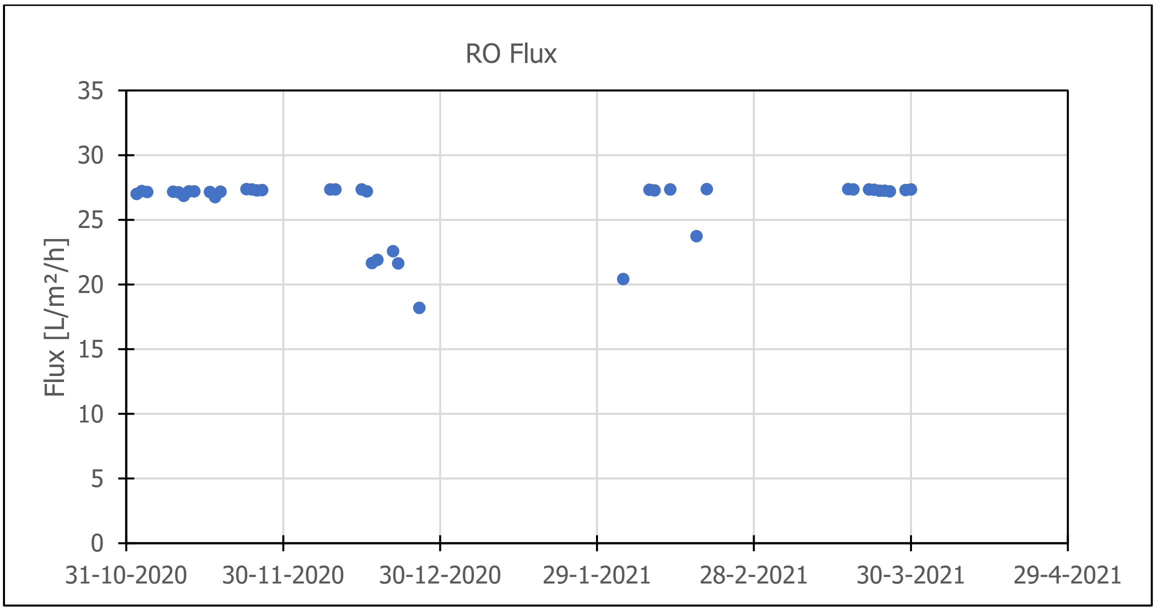


Figure 54: FLUX OF THE RO UNIT



The RO performance was evaluated by the EC rejection. As presented in Figure 55, the RO unit rejected 98% of the EC on average. The difference in Na^+ and Cl^- concentrations in the RO feed and concentrate between Mode I and II were caused by the composition fluctuations of the RO concentrate of Evides DWP, because also the NF feed and permeate had higher Na^+ and Cl^- concentrations during the last experiments in Mode II (March 2021). The EC in the permeate stream is presented in Figure 56. In Table 37 and Table 38, the feed, permeate and concentrate streams of the RO are reported. Na^+ and Cl^- were concentrated by approximately 10 fold before the MED evaporator, based on the ion rejection and the achieved water recovery.

Overall, the EC rejections were stable and always higher than 94-95% in both modes. In addition, the energy consumption showed less than 10% difference between the two modes. Therefore, there was not a significant difference in the RO performance between the two modes.

Figure 55: EC REJECTION BY THE RO UNIT

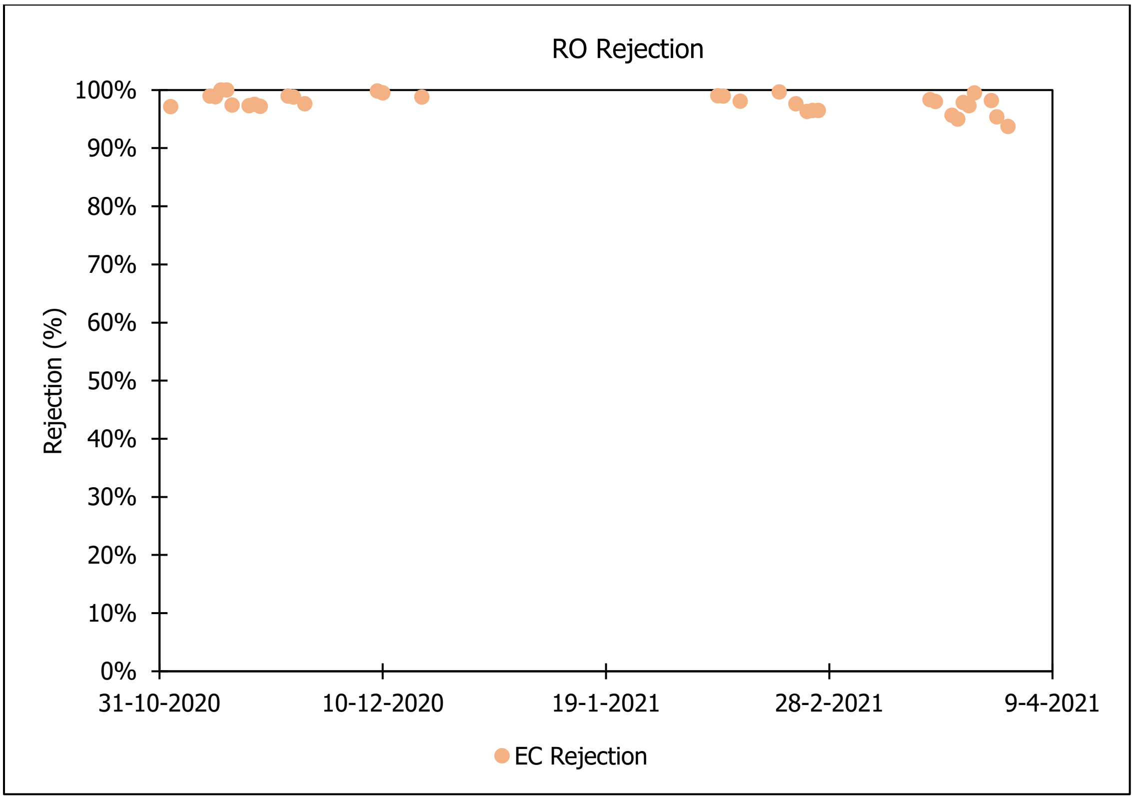


Figure 56: EC VALUES IN THE RO PERMEATE STREAM

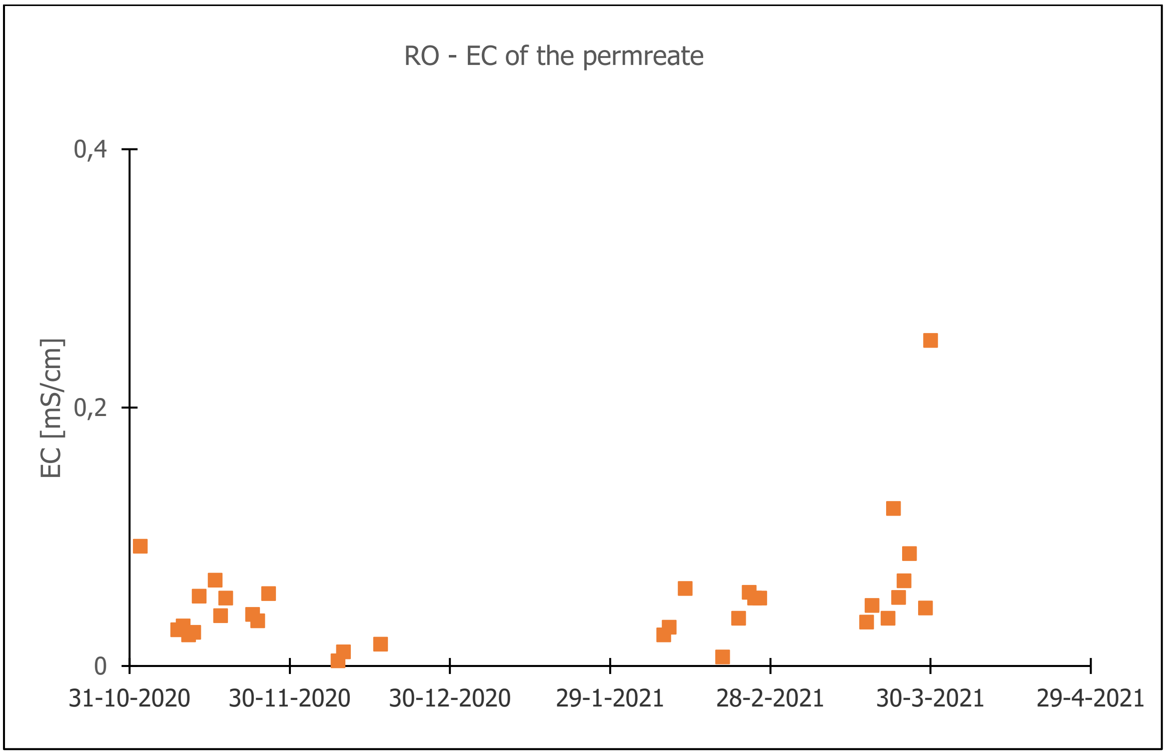


Table 37: RO FEED, PERMEATE AND CONCENTRATE WATER QUALITY – MODE I

Parameter	Unit	Feed	Permeate	Concentrate
Na^+	g/L	1.1	0.08	11.2
Cl^-	g/L	0.9	0.04	8.9
SO_4^{2-}	g/L	0.07	0.003	0.83
TOC	mg/L	0.6	0.5	2.0

Table 38: RO FEED, PERMEATE AND CONCENTRATE WATER QUALITY – MODE II

Parameter	Unit	Feed	Permeate	Concentrate
Na^+	g/L	0.48	0.02	4.5
Cl^-	g/L	0.46	0.06	4.9
SO_4^{2-}	g/L	0.03	0.03	0.09
TOC	mg/L	3.5	0.5	44.0

EFC unit provided by TU Delft

Because the concentration of the solution used for the EFC tests was far less than the eutectic concentration, it was not possible to achieve the eutectic point and therefore solid and ice production simultaneously in one batch. Therefore, the solution had to be concentrated in sequential batches by separating ice formed. The amount of ice formed determines the time of each batch. After the formation of about 10 to 15% ice in the crystallizers, the cooling and stirring were stopped to remove the ice formed. First the concentrated salt solution was drained and transferred to the buffer tank, and then the ice was removed from the crystallizer by washing using tap water. The collected concentrated salt solutions of different batches in the buffer tank were transferred to the crystallizer to repeat the concentration process. This concentration process was repeated in sequential batches. The concentration process had to be repeated in successive batches until the salt content in the solution approached the eutectic concentration. Cooling of the concentrated solution at the eutectic point would result in the simultaneous formation of ice and solid.

In practice, it was found that the feed concentration of the NF concentrate and the Nyex effluent (used as EFC feed depending of the mode of operation) was too dilute for the EFC unit. The typical feed concentrations for the EFC unit in the two modes are given in **Table *39*** and **Table *40***. Since in the EFC unit each batch solution can be concentrated up to 10 – 15%, to achieve the eutectic concentration of Na_2SO_4, which is about 38 g/L, the sequencing batches had to be repeated several hundred times. This was practically impossible due to the high volume of operational work.

Table 39: EFC FEED IN MODE I (DATES 20-01-2021 TO 30-01-2021)

Parameter	Unit	Feed
Na^+	g/L	1.7
Mg^{2+}	g/L	0.01
Cl^-	g/L	1.8
SO_4^{2-}	g/L	3.5

Table 40: EFC FEED IN MODE II (DATES 04 -02-2021 TO 19-03-2021)

Parameter	Unit	Value
Na^+	g/L	0.1
Mg^{2+}	g/L	0.001
Cl^-	g/L	3.2
SO_4^{2-}	g/L	4.0

The reasons for the need of many consecutive batches were the following:

1. For proper separation, it was not possible to form more than about 10 to 15% ice per batch. After 10 to 15% ice had formed, the reactor had to be stopped to first remove the solution and then remove the ice from the reactor.
2. During drainage, some of the solution was lost along with the wet ice.
3. The initial volume of liquid inside the reactor for the batch should be about 20 L. Therefore, taking into account the formed ice and the lost liquid along with the wet ice, about 14 to 16 L were available for the next batch. Therefore, for instance four batches had to be run to feed up to about three subsequent batches.

To solve the problem of excessive dilution of the initial solution, the RO unit was used after the output of the TOC/ NF units to concentrate the feed to the EFC unit as explained already in sub-chapter 4.4.2. Table 41 shows an average composition of the RO-concentrated feed to the EFC unit during MODE I[6].

The first ice formation point where the spontaneous ice nucleation occurred was at -1.1°C. After seven consecutive batches, in which the solution was concentrated about 10 to 15% in each batch to form ice, the solution reached the eutectic point. Thereafter, simultaneous production of solid and ice occurred. Again, after the formation of about 10 to 15% of the ice, the reactor was stopped and the salt was sent to the filter along with the concentrated solution. The resulting salt was washed with

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[6] The RO-concentrated feed for the EFC was analyzed by the external laboratory Groen Agra Control Co, since issues with TU Delft laboratory were encounter at that time.

saturated pure Na_2SO_4 solution at 20°C, with a mass ratio of 1:1 between the washing liquid and the wet crystals on the filter.

The eutectic temperature and composition for the binary pure $Na_2SO_4 \cdot 10H_2O$ system in lab experiments was found to be −1.109°C and 3.801 wt%, respectively. The eutectic temperature of the RO-concentrated solution fed to the EFC was -1.45 °C and the Na_2SO_4 concentration obtained was 3.71 wt% (starting point for salt production). The eutectic point for the RO-concentrated solution was significantly lower than the pure binary system eutectic point (-1.109°C). This shows that the presence of impurities, even in low concentrations, had a clear effect on the eutectic temperature by depressing the freezing point of ice and, subsequently, the eutectic point.

The operation of the EFC unit was successful when the NF concentrate was further concentrated by the RO unit and then used as feed of the EFC, therefore only during MODE I[7]*. The purity of the Na_2SO_4 crystals and the effect of the washing with pure salt is given in* **Table 42***. The impurities found in the salt crystals can also be seen in* **Table 42***. The ice crystal and the effect of the washing with water at 0 °C is given in*

Table *43*. In **Table *44***, the estimated composition of impurities (different salts) in the ice crystal are given as well as the effect of the washing.

Table 41: A COMPLETE ANALYSIS OF THE RO-CONCENTRATED FEED TO THE EFC in MODE I.

Parameter	RO-concentrated Feed	Unit
EC	32.0	mS/cm
pH	8.0	-
NH_4^+	<0.001	g/L
K^+	0.20	g/L
Na^+	10.4	g/L
Ca^{2+}	0.14	g/L
Mg^{2+}	0.02	g/L
Si	0.05	g/L
NO_3^-	0.11	g/L
Cl^-	1.9	g/L
SO_4^{2-}	19.4	g/L
HCO_3^-	0.82	g/L
PO_4^{3-}	<0.005	g/L

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[7] It must be noted that experiments in MODE II with further concentration of EFC feed with the RO unit were not performed due to time limitations, not because they were unsuccessful.

Fe^{3+}	502	μg/L
Mn^{2+}	151	μg/L
Zn	42.5	μg/L
B	169	μg/L
Cu	77.5	μg/L
Mo	22.1	μg/L

Table 42: EFC PRODUCT QUALITY: PURITY OF Na_2SO_4 CRYSTALS OBTAINED AND THE EFFECT OF THE WASHING -MODE I.

Parameter	Unit	Unwashed	1st Wash	2nd Wash	3rd Wash	4th Wah
Na_2SO_4	(% w/w)	94.62	99.74	99.91	99.95	99.97
KCl	(% w/w)	2.0	0.11	0.04	0.03	0.02
$CaCl_2$	(% w/w)	1.5	0.06	0.02	0.01	0.005
$MgCl_2$	(% w/w)	0.433	0.02	0.004	0.00	0.00
$Ca(HCO_3)_2$	(% w/w)	1.4	0.07	0.02	0.02	0.01

Table 43: EFC PRODUCT QUALITY: PURITY OF ICE CRYSTALS OBTAINED AND THE EFFECT OF THE WASHING OF THE ICE CRYSTALS WITH WATER AT 0 °C - MODE I.

Parameter	Unit	Ice unwashed	Ice 1st Wash
EC	mS/cm	3.4	0.8
pH	-	7.8	6.9
NH_4^+	g/l	<0.0001	<0.0001
K^+	g/l	0.06	0.02
Na^+	g/l	4.0	0.9
Ca^{2+}	g/l	0.06	0.01
Mg^{2+}	g/l	0.005	<0.0001
Si	g/l	0.02	0.003
NO_3^-	g/l	0.01	<0.0001
Cl^-	g/l	0.12	0.04
SO_4^{2-}	g/l	7.07	1.6
HCO_3^-	g/l	0.06	0.02
PO_4^{3-}	g/l	<0.0001	<0.0001
Fe^{3+}	μg/l	0.47	0.02
Mn^{2+}	μg/l	0.09	0.01
Zn	μg/l	0.03	<0.1
B	μg/l	0.09	<0.1
Cu	μg/l	0.04	0.01
Mo	μg/l	<0.1	<0.1

Table 44: EFC PRODUCT QUALITY: ESTIMATED COMPOSITIONS OF DIFFERENT SALTS IN ICE CRYSTALS OBTAINED AND THE EFFECT OF WASHING OF THE ICE CRYSTALS - MODE I.

Parameter	Unit	Unwashed	1st Wash
Na_2SO_4	g/L	10.5	2.3
KCl	g/L	0.10	0.03
$CaCl_2$	g/L	0.11	0.01
$MgCl_2$	g/L	0.08	0.03
$Ca(HCO_3)_2$	g/L	10.7	2.4

Based on the RO-concentrated feed used in MODE I, the recovery rate of Na_2SO_4, the energy consumption per 1 m^3 and the fraction of the ice and slurry as final products are given in **Table *45***.

Table 45: RECOVERY OF ICE AND NA$_2$SO$_4$ AND ENERGY CONSUMPTION -MODE I

Parameter	Unit	Value
Electricity	kWh/m^3	29.4
Na_2SO_4 production	kg/m^3	19.9
Demi water production - Ice stream	m^3/m^3	0.81
Concentrate to Brine Management – Slurry stream	m^3/m^3	0.16

MED Evaporator unit provided by NTUA

As it has already been mentioned, the units were operated in two modes. The unit in Mode I ran with electricity, whereas in Mode II residual heat was used. The overall evaluation of the MED evaporator was based on the following parameters:

- The water recovery (concentrating factor).
- The quality of end-products (purity)
- The energy (electricity or residual heat) consumption per m^3 of recovered condensate

The main ions average concentrations of the inlet brine are presented in **Table *46***. Several experiments were performed using both operating modes. As it can be seen the average TDS concentrations were 17.3 g/L and 8.6 g/L when using operating Mode I and II, respectively. The average concentration of Mg^{2+} and Ca^{2+} at the inlet brine was very low for the majority of the experiments (high rejection of divalent ions during the NF process). The average TOC concentration, during Mode I was 16.9 mg/L, whereas during Mode II was 5.6 mg/L. This indicates that better organic carbon removal was achieved in Mode II.

Table 46: MED EVAPORATOR INLET BRINE WATER QUALITY CHARACTERISTICS

Parameter	Unit	Mode I	Mode II
Na^+	g/L	6.4	3.9
Mg^{2+}	g/L	0.01	n.a.
Ca^{2+}	g/L	0.05	n.a.
Cl^-	g/L	5.7	4.3
NO_3^-	g/L	0.19	0.23
SO_4^{2-}	g/L	4.9	0.21
TDS	g/L	17.3	8.6
TOC	mg/L	23.7	5.6
EC	µS/cm	21.9	16.3
pH	-	8.0	8.5

The main ions average concentrations of the concentrated solution produced by MED are presented in Table 47. The average TDS, after operation of Site 02 pilot in Mode I, was 33.5 g/L, which was 2 times more concentrated than the inlet brine. The average TDS after operation of treatment train in Mode II was 39.2 g/L, which was approximately 5 times more concentrated than the inlet brine. The average concentrations of Mg^{2+} and Ca^{2+} were in both modes quite low. The TOC content was 9.7 mg/L after operation of the treatment train in Mode I and 9.2 mg/L after operation of treatment train in Mode II. During the operation in Mode II, TOC concentration was almost 2 times higher than that of the inlet brine. During operation in Mode I the TOC concentration decreased from 23.7 to 9.7 mg/L. This could be attributed to the presence of volatile organic compounds in the initial brine. These volatile organic compounds could have passed during evaporation of water to the vapor stream and this justifies the observed TOC concentrations in the condensate stream (*Table 49*).

The NaCl purity of the end-product in all experiments for Mode I and Mode II are given in Figure 57 and *Figure 58*, respectively. The purity of NaCl produced after operation of the unit in Mode I ranged from 32% to 98% and after operation in Mode II from 75% to 99% (Table 48). The main explanation of low purity of the end-product was the existence of sulfates in the inlet brine. The sulfates in the brine produced after the operation in Mode I ranged between 0.5 g/L and 22.4 g/L and at the second one between 0.2 g/L and 10.7 mg/L. As it can be seen in Figure 57 for Mode I, in the first months of operation the purity of the end-product (NaCl) ranged from 32% to maximum 80% due to the presence of sulfates in the inlet brine, then it was improved achieving a purity of 99%, which indicates a better removal of sulfates during the NF process.

Table 47: CHARACTERISTICS OF THE PRODUCED REGENERATION SOLUTION (RICH IN NaCl) BY THE MED EVAPORATOR - MODE I AND II

Parameter	Unit	Mode I	Mode II

		Concentration	SD	Concentration	SD
Na^+	g/L	13.5	5.4	16.4	2.4
Mg^{2+}	g/L	0.007	0.006	0.003	0.004
Ca^{2+}	g/L	0.02	0.04	0.04	0.02
Cl^-	g/L	12.9	4.3	15.2	3.2
NO_3^-	g/L	0.31	0.10	0.36	0.45
SO_4^{2-}	g/L	6.9	15.5	7.2	3.4
TDS	g/L	33.5	n/a	39.2	n/a
NaCl	(%)	2.1	0.7	2.5	0.5
TOC	mg/L	9.7	4.2	9.2	2.2
EC	µS/cm	38.7	15.9	28.5	12.4
pH		8.9	0.50	9.1	0.13

Table 48: MINIMUM, MAXIMUM AND AVERAGE NACL PURITY AFTER OPERATION OF TRAIN IN MODE I AND II

	Mode I	Mode II
Minimum	32%	75%
Maximum	98%	99%
Average	70%	95%

Figure 57: NaCl PURITY OF THE BRINE – MODE I

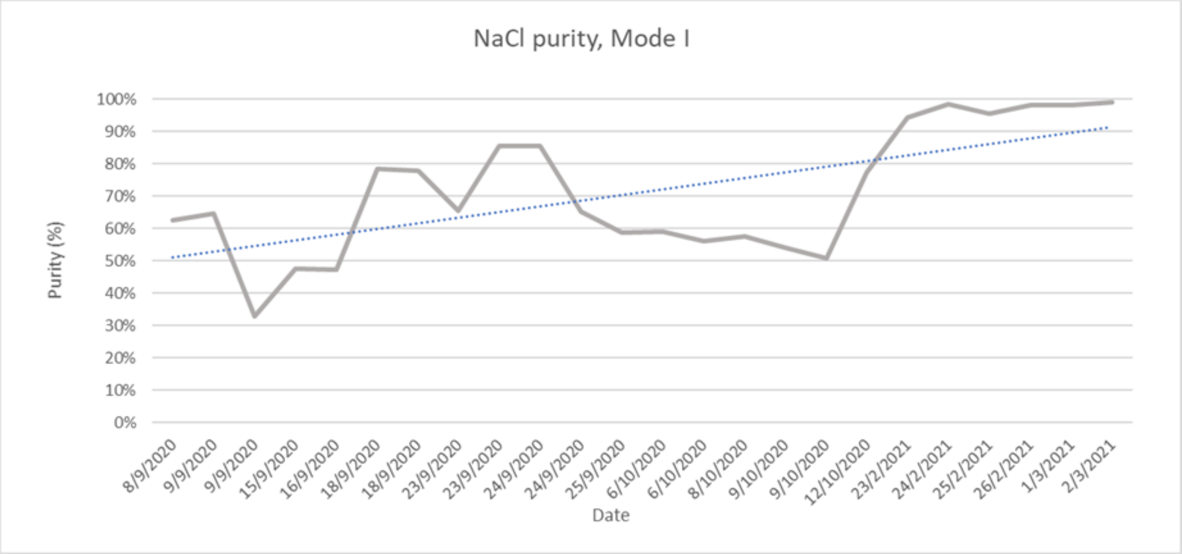
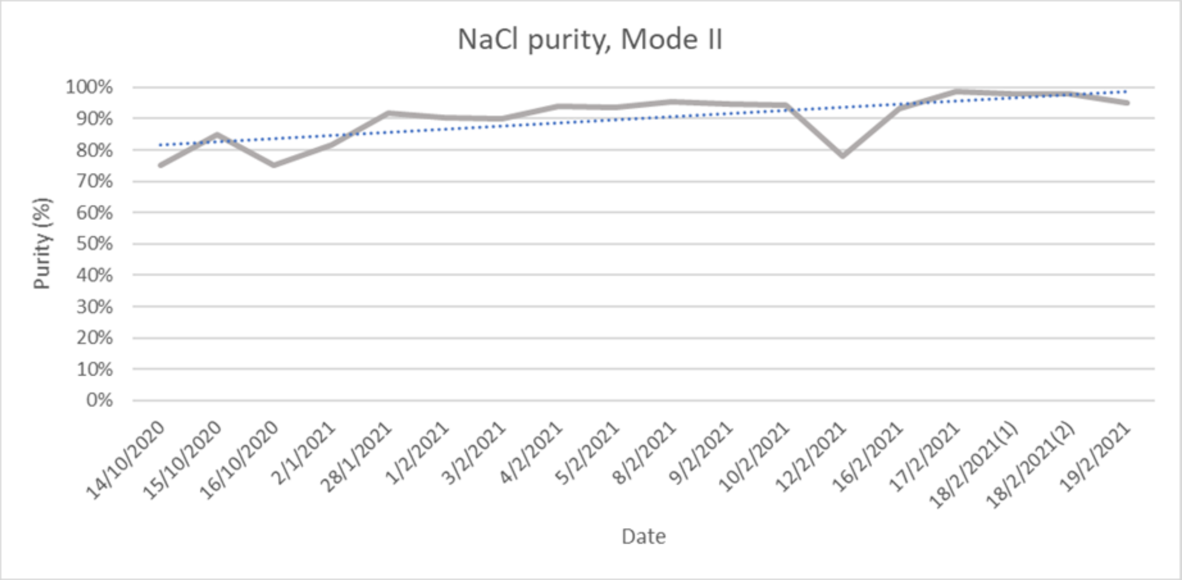


Figure 58: NaCl PURITY OF THE BRINE – MODE II



The average concentrations of main ions in the condensate after unit's operation in both Modes are given in **Table *49***. The permeate, as expected, contained low concentrations of Ca^{2+} (ranging between 0.07g/L and 0.01 g/L) and in general the water quality parameters show that the permeate was a high-quality water that reached the specifications needed in many industrial processes. Furthermore, the water recovery that the MED evaporator achieved during Site II operation in Mode I and Mode II are presented in **Figure *59*** and ***Figure 60***, respectively. The maximum water recovery was 90% for both modes and the lowest was 40% in case of Mode I and 44% in case of Mode II.

Table 49: MED EVAPORATOR PRODUCT WATER (CONDENSATE) QUALITY CHARACTERISTICS– MODE I AND II

Parameter	Unit	Mode I		Mode II	
		Concentration	SD	Concentration	SD
Na^+	g/L	0.13	0.11	0.08	0.24
Mg^{2+}	g/L	0.07	0.15	0.10	0.19
Ca^{2+}	g/L	0.01	0.21	0.03	0.27
Cl^-	g/L	0.12	0.32	0.11	0.12
NO_3^-	g/L	0.17	0.10	0.18	0.25
SO_4^{2-}	g/L	0.23	0.13	0.19	0.18
TDS	g/L	0.62	-	0.69	-
TOC	mg/L	2.6	2.4	3.8	3.9
EC	µS/cm	60.0	5.8	55.2	2.8
pH	-	7.6	1.2	8.2	1.8

Figure 59: WATER RECOVERY OF THE MED EVAPORATOR IN MODE I

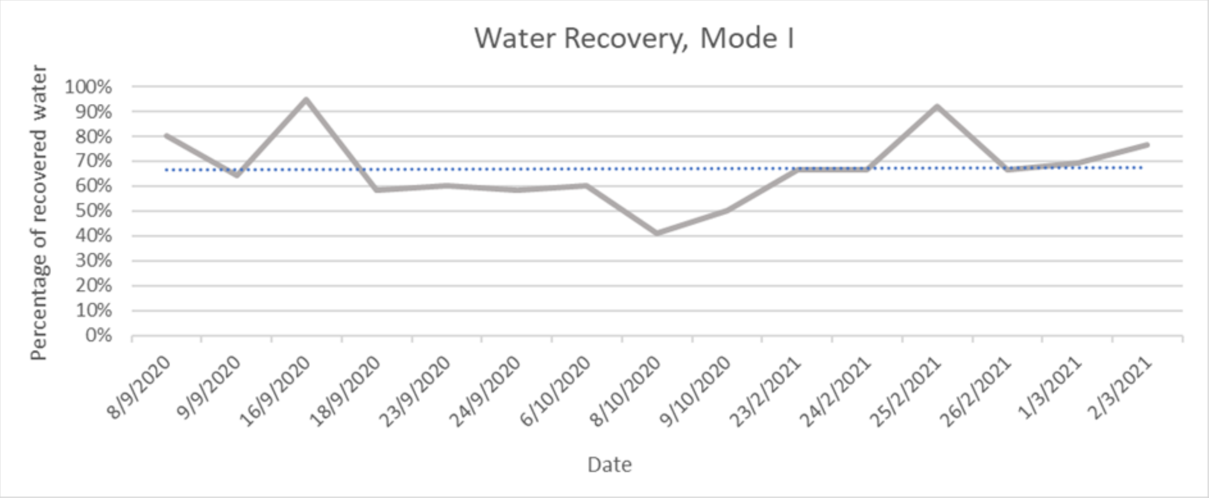
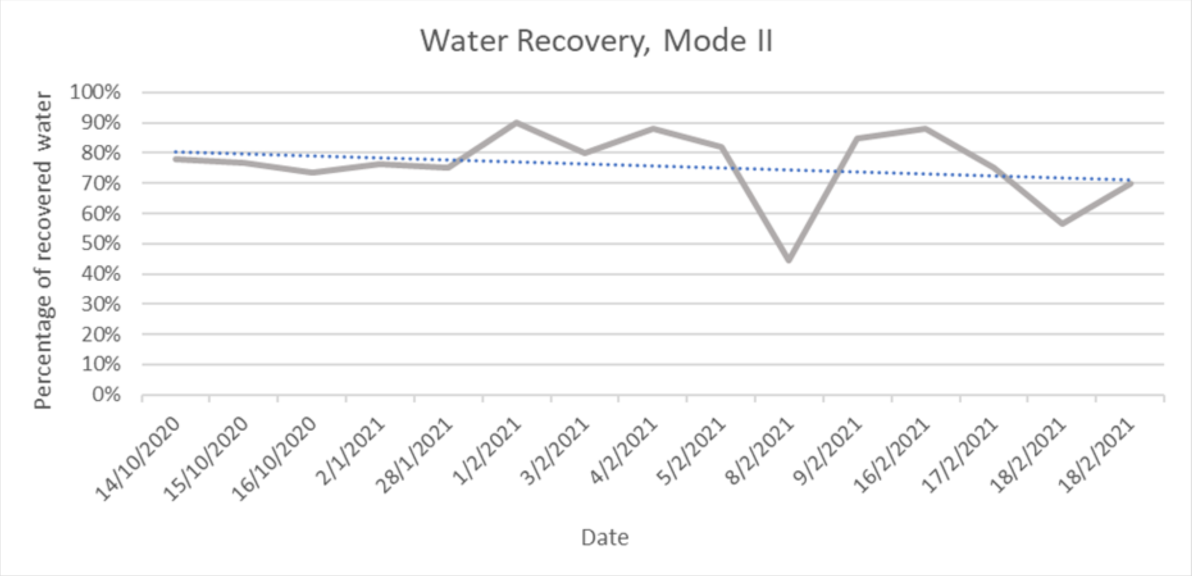


Figure 60: WATER RECOVERY OF THE MED EVAPORATOR IN MODE II



As it was already mentioned, the unit operated using electricity when operated in Mode I and residual heat when operated in Mode II. The monitoring of the unit for both energy sources was carried out by SCADA. The energy consumption of the unit when using electricity ranged between 350 and 600 kWh /m^3 of condensate. In Table *50* the heat balance from a representative experiment is given. The inlet brine at this experiment was 120 L, the condensate 70 L and the concentrate 50 L. The temperature of the inlet brine was 15 °C, while the temperatures of the condensate and the concentrate were 70 °C and 50 °C, respectively. High temperatures of condensate were due to batch operation of the unit.

Table 50: INLET AND OUTLET HEAT TO THE MED EVAPORATOR UNIT (example on 24/09/2020)

Process Part	Energy (kWh/120 L inlet brine)
1st effect	28.5

2nd effect	23.2
in Preheater	1.8
out Preheater	28.5
Losses	3.5

The total heat input to the unit was the sum of the heat inlet at the 1st effect, the heat inlet at the preheater and the losses, which was equal to 33.8 kWh or 483 kWh/m^3 of condensate (water produced). The heat input required for the 2nd effect was acquired from the vapor of the 1st effect.

The energy consumption of the unit with residual heat ranged from minimum 250 to 635 kWh/m^3 of condensate. The SCADA during each experiment measured the residual heat into kg/h (steam) and the results are reported at the column FSC1 of SCADA (data available in deliverable 2.7). **Figure *61*** and **Figure *62*** show the energy consumption for some representative experiments in Mode I and II, respectively.

Figure 61: ENERGY CONSUMPRION ON SOME REPRESENATIVE EXPERIMENTS IN MODE I

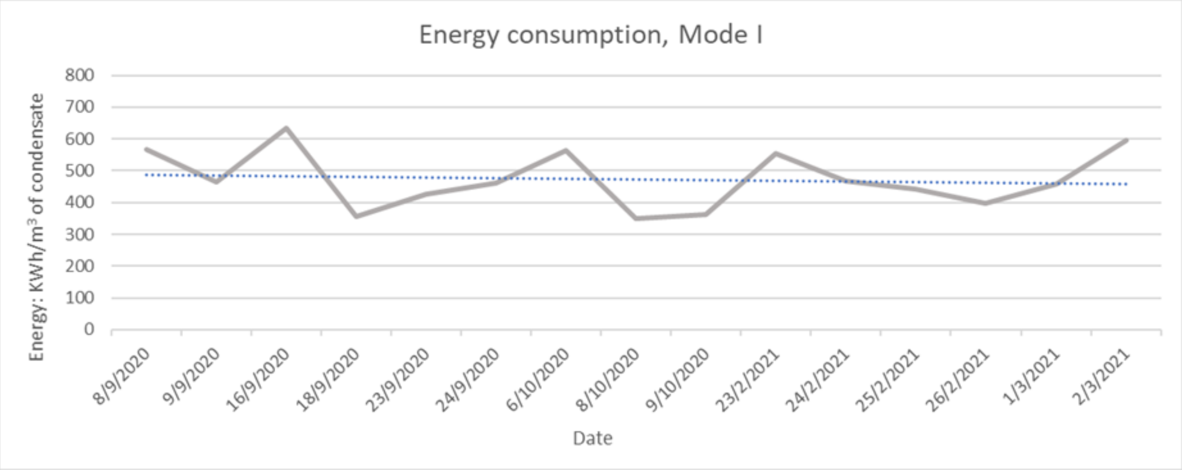
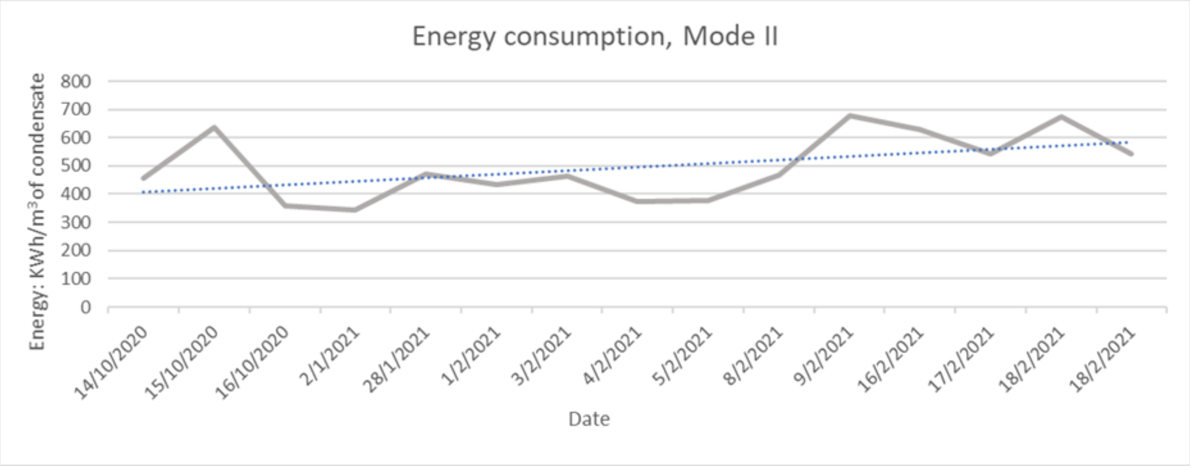


Figure 62: ENERGY CONSUMPRION ON SOME REPRESENATIVE EXPERIMENTS IN MODE II



In general, in Mode I the MED evaporator did not achieve high NaCl purity due to the presence of SO_4^{2-} in the inlet brine, so in the first months of operation the purity of the end-product (NaCl) ranged from 32% to maximum 80%. In Mode II the purity was improved and reached 99%. Regarding the water recovery in Mode I the unit was unstable because the operator was trying to familiarize himself with the unit. However, in Mode II the overall water recovery was higher and more stable. Furthermore, the energy consumption of the unit during Mode I was higher in general because the boiler had a high electric requirement. Finally, as it was expected, the use of residual heat increased the performance of the unit in Mode II. **Table *51*** summarizes the average values for each mode which indicate the best mode for each parameter. It can be concluded that Mode II resulted in better operation of the MED evaporator.

Table 51: MODE I AND II COMPARISON FOR THE MED EVAPORATOR

Parameter	Mode I		Mode II	
	Average	SD	Average	SD
NaCl Purity	70%	0.19%	95%	0.07%
Water Recovery	67%	0.14%	80%	0.17%
En. C (kWh/m^3)	473 kWh/m^3	115.3	390 kWh/m^3	90.5

As mentioned already in sub-chapter 4.4.2, one of the project objectives that was not achieved was the recovery of $NaHCO_3$ as another end-product. In the Nyex unit during the TOC removal and the pH adjustment, inorganic carbon (carbonates) was removed as well, resulting in insufficient concentration for crystallization of HCO_3^- at the inlet brine of the MED evaporator.

6.2.2 Site 02 Overall Pilot Performance Evaluation

In **Figure *63*** an overview of Site 02 pilot performance is given both for Mode I and II. During the experimental period of Site 02 pilot many technical and research related difficulties were encountered, but in the end an important achievement was met; the pilot's performance in both modes was evaluated and the proof of principle was achieved.

Taking into account each unit separately it can be seen that a different mode seems to result in a better performance. Specifically, for Nyex, positioning the Nyex unit after the NF unit (Mode II) gave a number of operational advantages (see sub-chapter 6.2.1). The TOC removal in Mode I and II was 82.3% and 89.7%, respectively. However, the organic concentration in the brine to be treated by Nyex in Mode II was higher than in Mode I and therefore the organic concentration in the Nyex effluent in Mode II was higher. As a result, the NF unit encountered more issues with its operation (less stable operation, lower ionic separation and severe fouling) during Mode II due to higher organic concentrations in the NF feed. Thus, operation in Mode I was found to be the optimal for the NF unit. In case of the RO unit operation no difference between the two modes was found.

The EFC unit operation in both modes faced an issue with the feed Na^+ and SO_4^{2-} concentrations being lower than required to achieve the eutectic concentration of Na_2SO_4. It was found that further concentration of the EFC feed (NF concentrate in Mode I and Nyex effluent in Mode II) was required. Experiments only in Mode I were performed using the RO unit to further concentrate the EFC feed. The experiments were successful and the final product recovered after four washes had a purity that reached 99.97%. Note that in the EFC experiments during Site 02 operation a pure external Na_2SO_4 solution was used for the washes, even though in practice this solution must be recovered in a closed loop (part of the product should be used for this purpose). Finally, it must be pointed out that the EFC unit operation with further concentration of the feed by the RO unit was not tested in Mode II. The EFC unit performance is expected to be similar in that case based on the Na^+ and SO_4^{2-} concentrations in Nyex effluent. However, some concerns lay in a potential negative effect of the higher TOC in Nyex effluent (EFC feed in Mode II) on the RO unit (used for further concentration).

The MED evaporator had a higher water recovery and final product purity (NaCl) during Mode II. However, during Mode I the lower purity observed in the MED evaporator was related to the lower performance of the NF unit (fouling issues mention in sub-chapter 6.2.1 NF part) during the start of the experimental period. If this period was not taken into account then the NaCl purity achieved reached a value of 99%, which is higher than that of Mode II. Moreover, if only the last period was taken into account (optimal NF operation), the water recovery of the MED evaporator increased from 67% to 74%. Therefore the difference compared to Mode II (80%) is smaller. Finally, during Mode II the unit operated more efficiently with residual heat as a heat source achieving higher performance because the heat exchangers perform better with steam than with water. However, if it the use of residual heat would have been applied in the same way in Mode I, similar results would be expected. The overall recovery of Site 02 pilot in Mode I was 94%, whereas in Mode II was 88% since the EFC unit did not operate in this mode. If the EFC unit performance in Mode II is assumed to be similar to that of Mode I (expectation that was mentioned above), the overall recovery of Site 02 pilot would be 96%.

Figure 63: OVERVIEW PILOT PERFORMANCE – SITE 02

Pilot 2
DWP RO Brine

- Pilot capacity: 1 m³/h
- Pilot recovery: **94% in Mode I and 88% in Mode II**
- Total energy consumption ≈ **40 - 50 kWh/m³ brine**
- Raw material use:
  - Anti-Scalant ≈ **3.23 mL/h**
  - NaOH (1 – 1.5 M) ≈ **3.76 L/h (mode I) – 1.26 L/h (mode II)**
  - H2SO4 [85 wt%] ≈ **3.64 L/h (mode I) – 5.71 L/h (mode II)**
  - Cooling water for MED (<17°C) ≈ **250 L/h**
  - Clean water ≈ **100 - 200 L/h**

Element	Concentration Range [mg/L]
Sulfate	190 – 450
Organic Matter	8.2 – 20.2
Sodium	550 – 1600
Chloride	370 – 1300

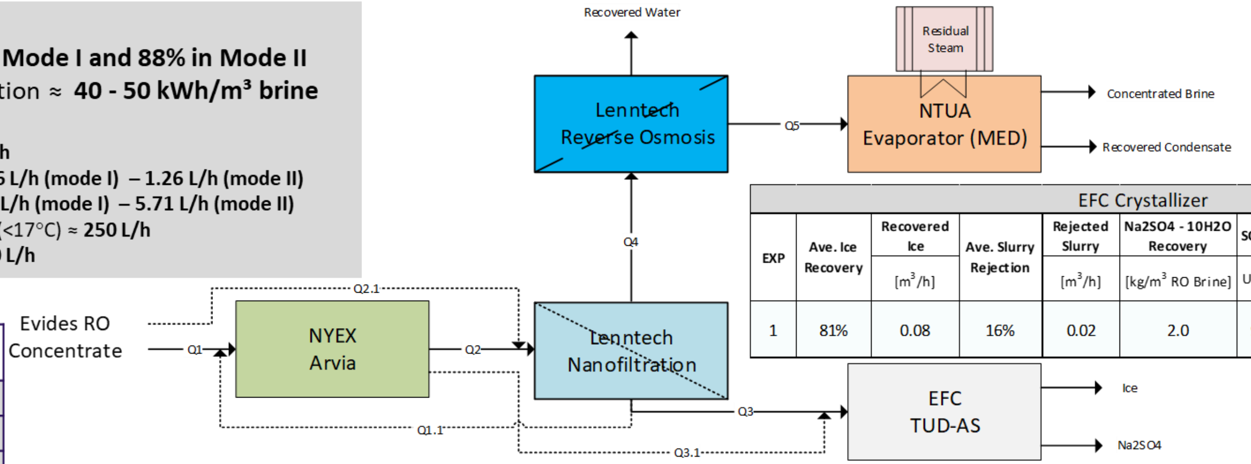
EXP	Operation Mode
1	NYEX-NF (Mode I)
2	NF-NYEX (Mode II)

Revers Osmosis

Ave. Permeate Recovery	Ave. Energy Consumption	Q5	Recovered Water
	[kWh/m3 RO Brine]	[m³/h]	[m³/h]
90%	5.3	0.09	0.80
90%	5.0	0.09	0.81

MED Evaporator

Ave. Water Recovery	NaCl Conc.	NaCl Purity	Ave. Energy Consumption	Recovered Condensate	Recovered Brine
	[Wt%]		[kWh/m³ RO Brine]	[m³/h]	[m³/h]
67%	2.1	70%	28.2	0.06	0.03
80%	2.5	95%	28.1	0.07	0.02



EFC Crystallizer

EXP	Ave. Ice Recovery	Recovered Ice	Ave. Slurry Rejection	Rejected Slurry	Na2SO4 - 10H2O Recovery	SO4 Purity	SO4 Purity	Energy Consumption
		[m³/h]		[m³/h]	[kg/m³ RO Brine]	Unwashed	Washed (4 times)	[kWh/m³ RO Brine]
1	81%	0.08	16%	0.02	2.0	94.62%	99.97%	2.9

NYEX - Organic Matter Removal

Q1	Ave. TOC Removal	Ave. Current	Ave. Voltage	Ave. Energy Consumption	Ave. Energy Consumption
[m³/h]		PSU 1 [A] – PSU 2 [A]	PSU 1 [V] – PSU 2 [V]	[kWh/m3 RO Brine]	[kWh/Kg TOC]
1	82.3%	373 – 379	6.7 – 7.03	5.7	535
0.1	89.7%	400.4 – 399.8	5.3 – 5.7	0.60	31.6

Nanofiltration

Q2	Ave. SO4 Rejection	Ave. Cl Rejection	Ave. TOC Rejection	Ave. Permeate Recovery	Ave. Energy Consumption	Q3	Q4
[m³/h]					[kWh/m3 RO Brine]	[m³/h]	[m³/h]
1	93%	18%	52%	89%	4.0	0.11	0.89
1	94%	31%	83%	90%	5.0	0.10	0.90

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

7 Recommendations

7.1 Site 01 Full-Scale Design Recommendations

This chapter describes several design recommendations from all partners for the full-scale.

Nanofiltration unit provided by Lenntech B.V.

The divalent ion rejection of the second pass NF can be increased by improving the NF2 operation. This can be achieved by increasing the permeate flux through the membrane or by testing a tighter NF membrane. However, this could result in a higher NaCl rejection and less salt permeation that is beneficial for the MED evaporator. In addition to this, as there was no scaling or fouling of the membrane, the NF unit recovery could be much higher and close to 90%.

The energy consumption calculated for the NF unit is expected to be much lower in the full-scale installation. This can be explained by the fact that the pumps in the units were designed for large ranges of flows and pressures resulting in low efficiencies of the pump and motor during operation compared with a potential full-scale operation. In addition, high recirculation flows, that were required due to the small flow rates, resulted in oversizing of the pumps.

Crystallizer unit provided by UNIPA

The recommendations for the full-scale design is to design a fully automated control system able to provide full robustness to the unit even in the presence of unexpected variation of the feed brine composition, and able to guarantee a good enough control of the outlet pH in order to always reach the target of purity of the $Mg(OH)_2$ and $Ca(OH)_2$.

As it was mentioned in sub-chapter 6.1.1 no scaling occurred during the experiments with the MF-PFR unit. However, as a part of the typical procedure after each experiment a cleaning step was performed in order to remove any possible formed scaling, which allowed the MF-PFR to work stably in all experiments and for the whole experimental period. As a result, a cleaning step is suggested to be included in the full-scale design to remove possible scaling formation of hydroxides over longer operation periods.

***MED Evaporator unit provided by NTU**A*

Based on the experiments performed during Site 01 research, it is recommended that a full-scale MED evaporator consists of more stages (effects), in order to improve the efficiency and capacity of the unit. Moreover, better automation of the full-scale MED evaporator is considered valuable to enable a smooth operation and control of it. Finally, cleaning runs would be needed in full-scale in order to prevent possible scaling and organic fouling formation.

7.2 Site 02 Full-Scale Design Recommendations

Nyex unit provided by Arvia Technology Ltd

The ZERO BRINE pilot research presented in this report demonstrated that a Nyex unit combined with granular activated carbon can be used to successfully remove organic contaminants from the brine, operating either on a low organic concentration brine solution or on a solution where the concentration of both organic and ions had been increased by NF.

Various problems that occurred during the pilot trial needed to be addressed, with the impact of the acidified brine requiring the replacement of the GAC column. The full-scale unit should be designed in a way to provide improved pH neutralization, improved extraction facilities (including additional venting if a containerized unit is supplied) and an improved data-logging capability. The generation of Cl_2 will need to be specifically addressed with a dedicated scrubber system to minimize any health and safety implications.

Nanofiltration unit provided by Lenntech B.V.

For the full-scale design it is necessary to achieve a stable operation as well as good maintenance of the NF unit. Continuous operation of the NF unit to prevent stagnant water and organic growth is considered crucial. The energy consumption calculated for the NF unit is expected to be much lower in the full-scale installation. This can be explained by the fact that the pumps in the units were designed for large ranges of flows and pressures resulting in low efficiencies of the pump and motor during operation compared with a potential full-scale operation. In addition, high recirculation flows, that were required due to the small flow rates, resulted in oversizing of the pumps.

Reverse Osmosis unit provided by Lenntech B.V.

As described above, the energy consumption of the full-scale installation is expected to be much lower compared to the RO unit in the pilot, because of the reasons already mentioned.

EFC unit provided by TU Delft

The recommendations for the full-scale is to design a continuous crystallizer made of stainless steel (necessary due to the corrosivity of the recovered salt solution) with possibility of separating ice and solid in place as well as using two filter belts for continuous washing of ice and solid crystals, respectively. If a continuous system is used, the dilute solution can be fed directly to the crystallizer. Further economic calculations are required to determine whether an RO unit is necessary or not.

MED Evaporator unit provided by NTUA

Similar to Site 01 recommendations for full-scale in case of the MED evaporator, more stages (effects) are expected to increase the efficiency and capacity of the unit and also less energy consumption to be achieved. Furthermore, more cleaning runs with clean water and also chemical cleanings during maintenance of the unit can prevent possible scaling and organic fouling. Finally, more temperature and pressure sensors should be installed in the steam part of the unit and be connected to SCADA to facilitate the monitoring of the process. A larger-scale MED evaporator was constructed by NTUA in Athens to operate with Mode II brine (pilot's RO concentrate), which was delivered to Greece. The results of these experiments are reported in Annex G: Experiments with a larger scale MED evaporator for Site 02 – Mode II.

References

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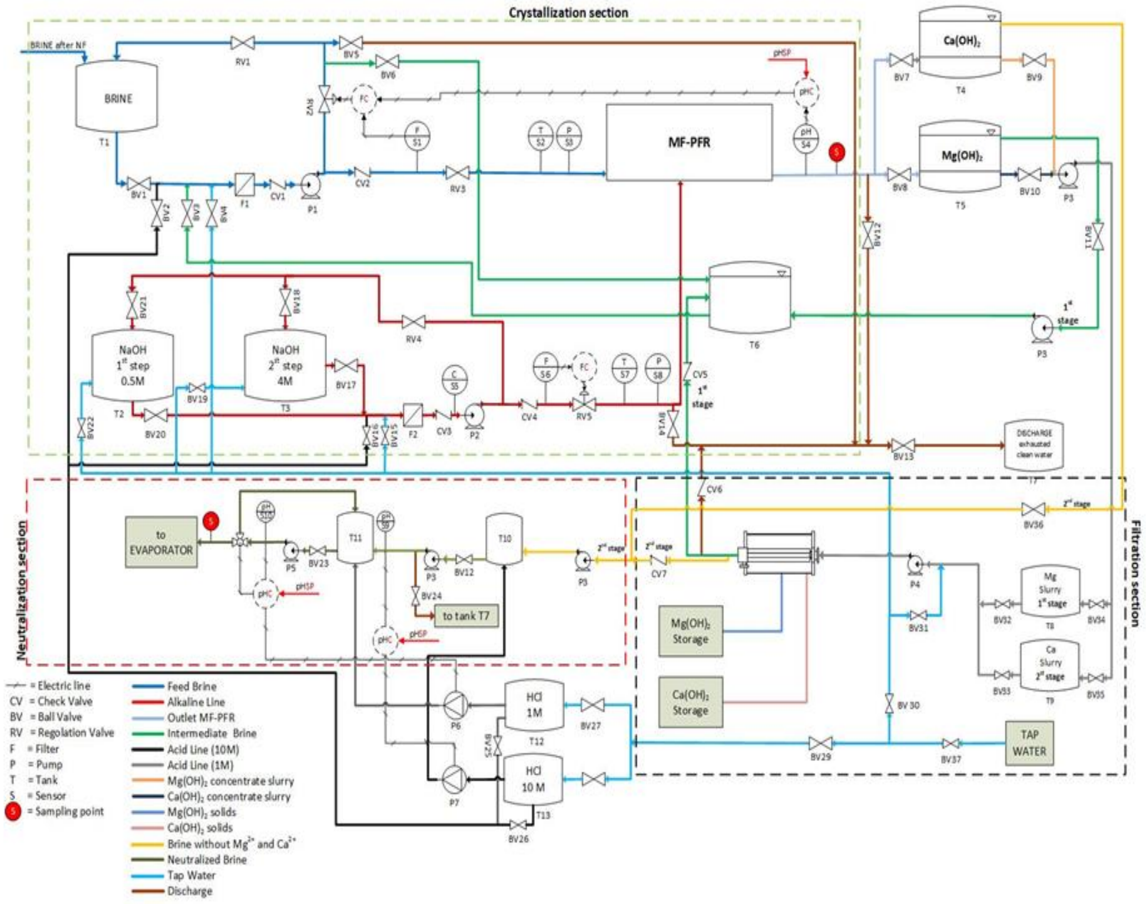
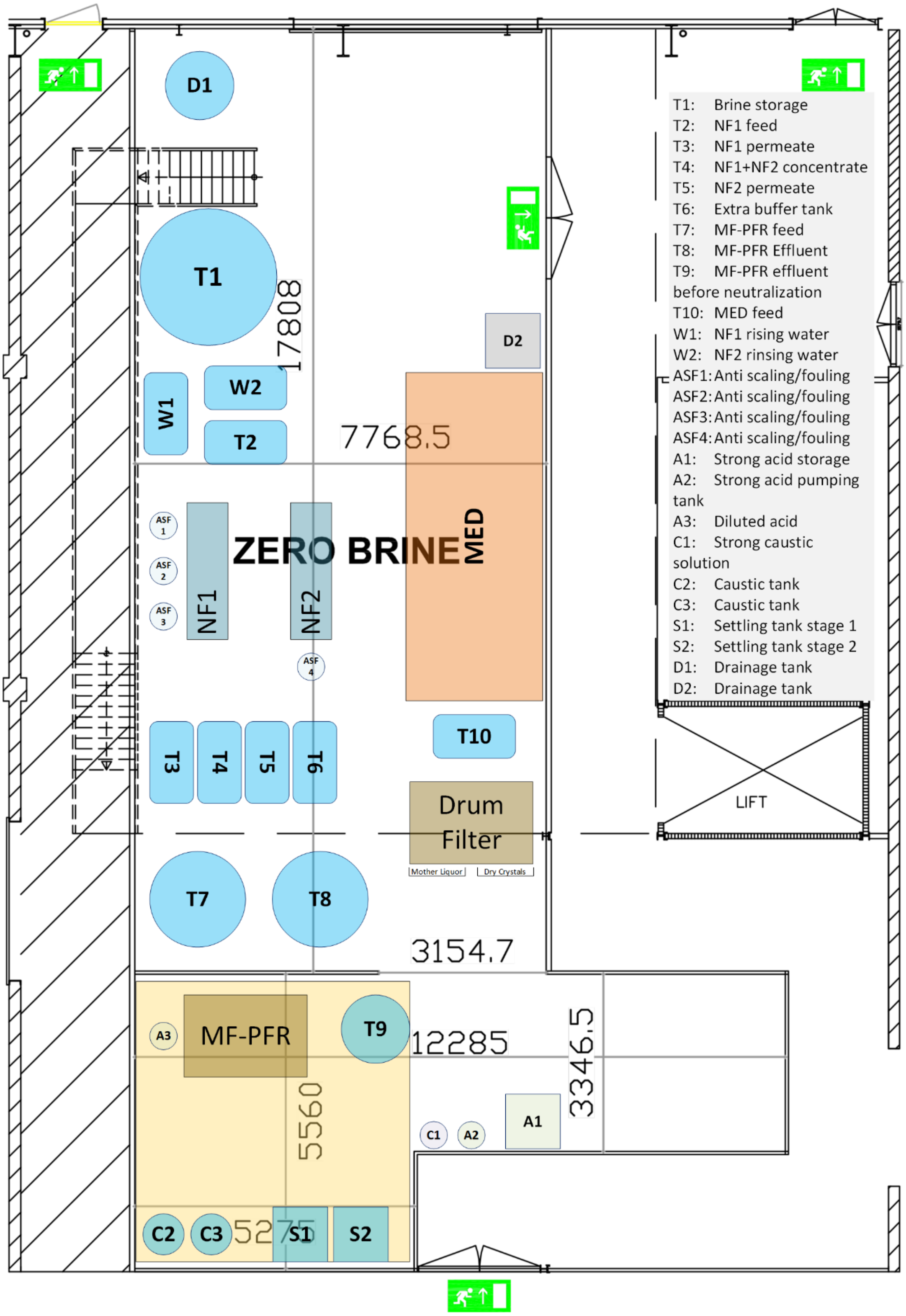
Annex A: P & ID of Units

Figure 64: SIMPLIFIED P&ID OF THE MF-PFR UNIT.



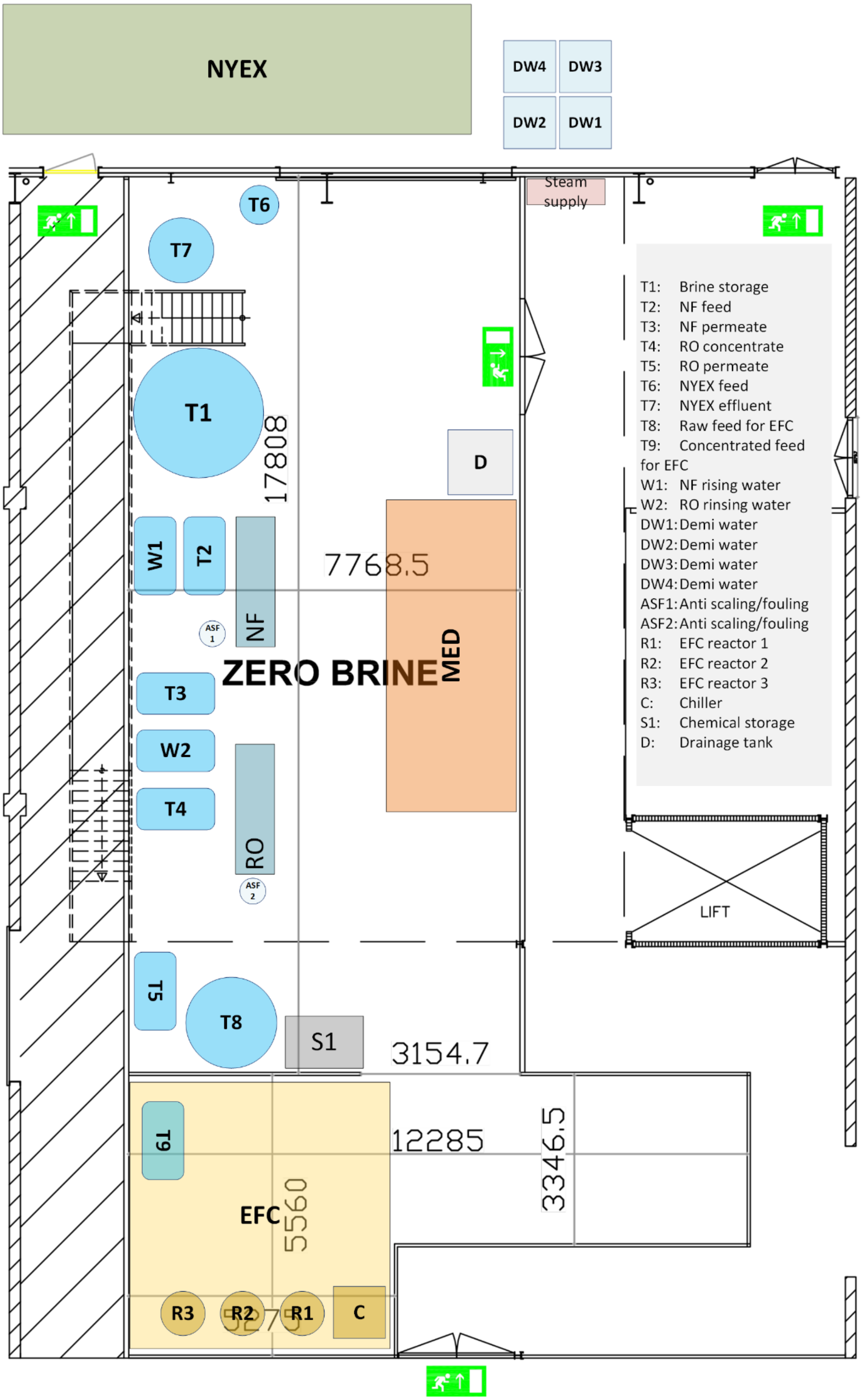
Annex B: Pilot Floor Plans

Figure 65: PILOT FLOOR PLAN – SITE 01

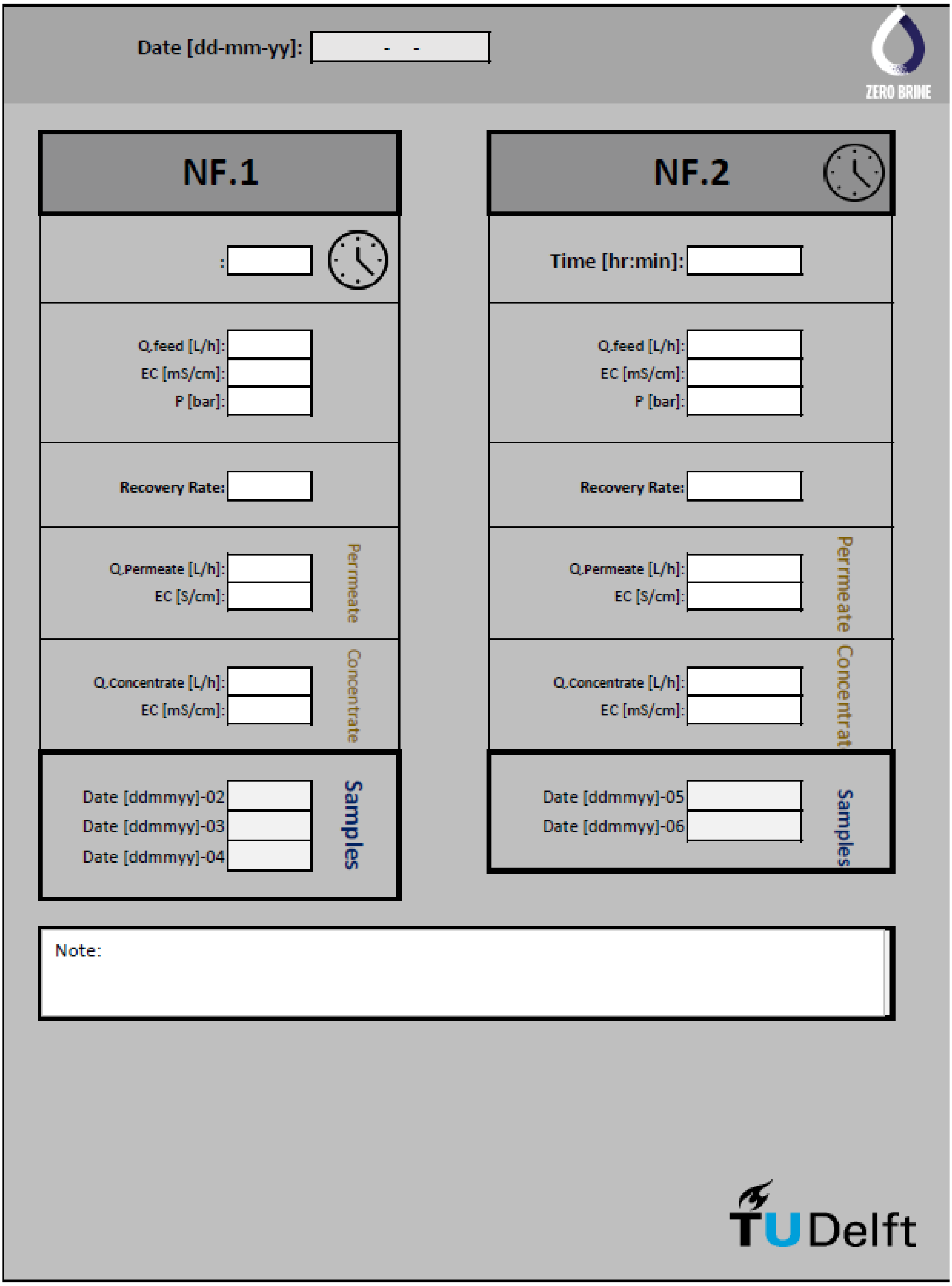


T1:	Brine storage
T2:	NF1 feed
T3:	NF1 permeate
T4:	NF1+NF2 concentrate
T5:	NF2 permeate
T6:	Extra buffer tank
T7:	MF-PFR feed
T8:	MF-PFR Effluent
T9:	MF-PFR effluent before neutralization
T10:	MED feed
W1:	NF1 rising water
W2:	NF2 rinsing water
ASF1:	Anti scaling/fouling
ASF2:	Anti scaling/fouling
ASF3:	Anti scaling/fouling
ASF4:	Anti scaling/fouling
A1:	Strong acid storage
A2:	Strong acid pumping tank
A3:	Diluted acid
C1:	Strong caustic solution
C2:	Caustic tank
C3:	Caustic tank
S1:	Settling tank stage 1
S2:	Settling tank stage 2
D1:	Drainage tank
D2:	Drainage tank

Figure 66: PILOT FLOOR PLAN – SITE 02



Annex C: Daily Data Sheet - Site 01



Date [dd-mm-yy]: - -

NF.1

:

Q.feed [L/h]:
EC [mS/cm]:
P [bar]:

Recovery Rate:

Perrmeate

Q.Permeate [L/h]:
EC [S/cm]:

Concentrate

Q.Concentrate [L/h]:
EC [mS/cm]:

Samples

Date [ddmmyy]-02
Date [ddmmyy]-03
Date [ddmmyy]-04

NF.2

Time [hr:min]:

Q.feed [L/h]:
EC [mS/cm]:
P [bar]:

Recovery Rate:

Perrmeate

Q.Permeate [L/h]:
EC [S/cm]:

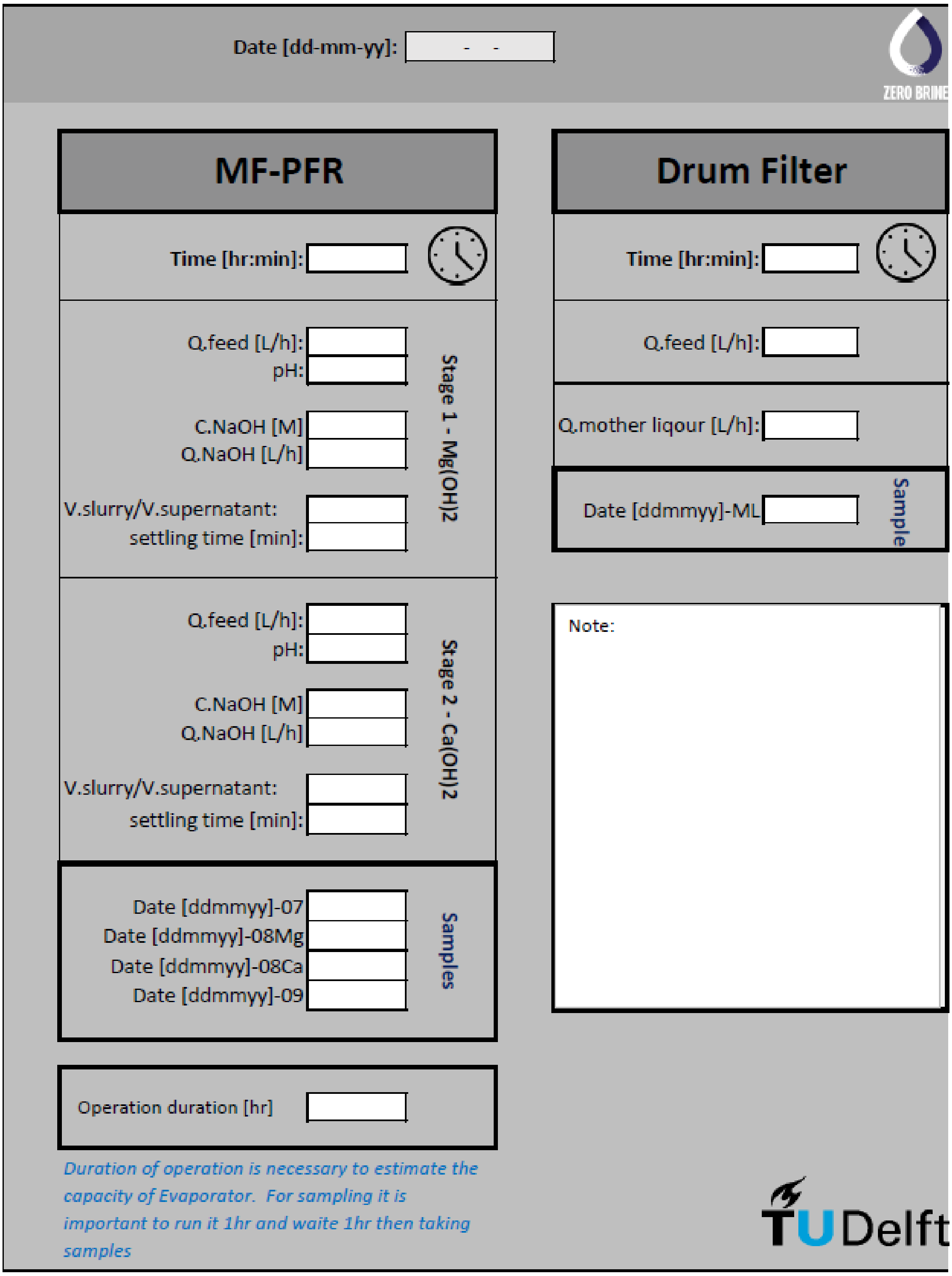
Concentrat

Q.Concentrate [L/h]:
EC [mS/cm]:

Samples

Date [ddmmyy]-05
Date [ddmmyy]-06

Note:



Date [dd-mm-yy]: - -

MF-PFR

Time [hr:min]:

Stage 1 - Mg(OH)2

Q.feed [L/h]:
pH:

C.NaOH [M]
Q.NaOH [L/h]

V.slurry/V.supernatant:
settling time [min]:

Stage 2 - Ca(OH)2

Q.feed [L/h]:
pH:

C.NaOH [M]
Q.NaOH [L/h]

V.slurry/V.supernatant:
settling time [min]:

Samples

Date [ddmmyy]-07
Date [ddmmyy]-08Mg
Date [ddmmyy]-08Ca
Date [ddmmyy]-09

Operation duration [hr]

Duration of operation is necessary to estimate the capacity of Evaporator. For sampling it is important to run it 1hr and waite 1hr then taking samples

Drum Filter

Time [hr:min]:

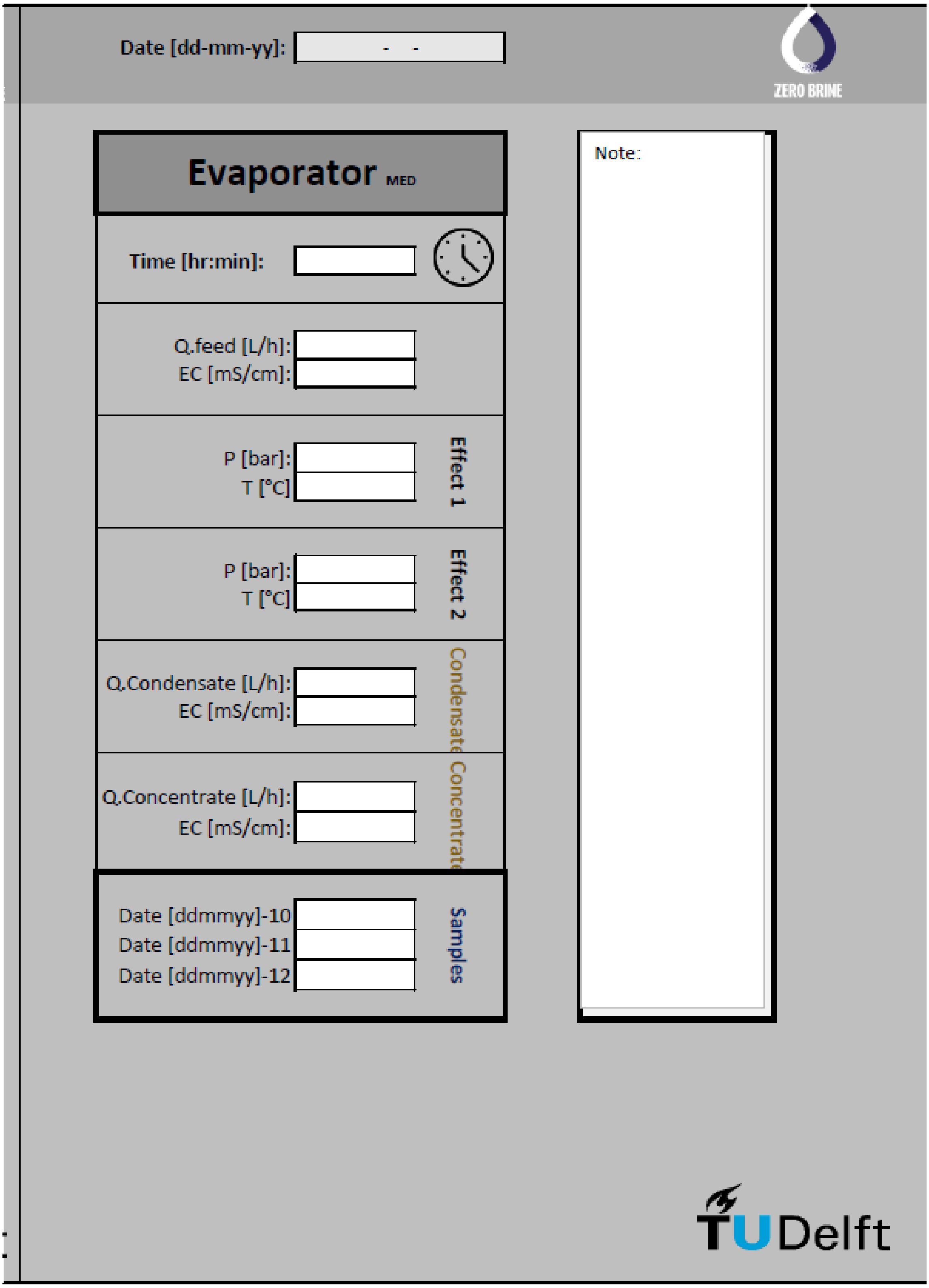
Q.feed [L/h]:

Q.mother liqour [L/h]:

Sample

Date [ddmmyy]-ML

Note:



Date [dd-mm-yy]: - -

Evaporator MED

Time [hr:min]:

Q.feed [L/h]:
EC [mS/cm]:

Effect 1
P [bar]:
T [°C]

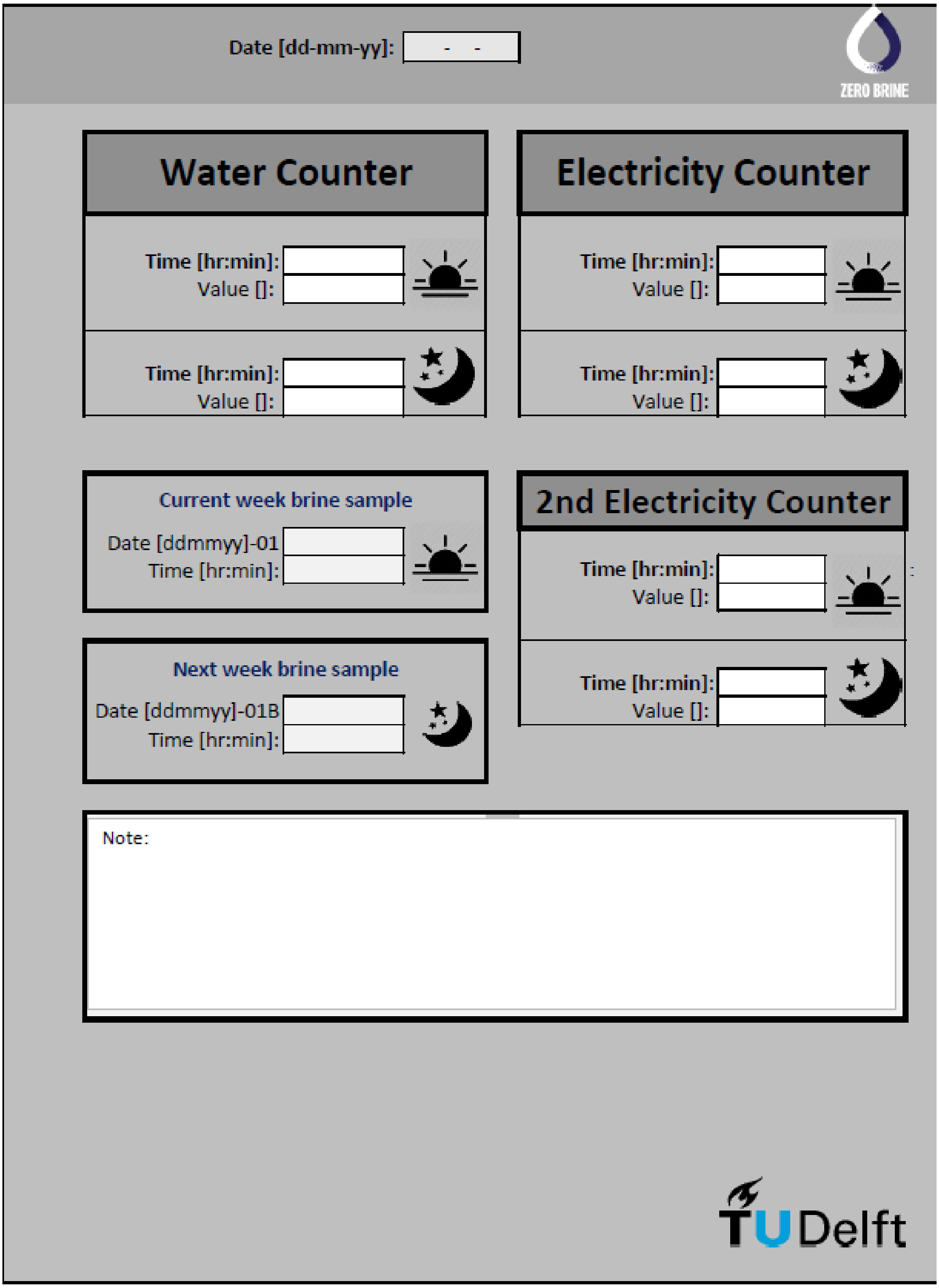
Effect 2
P [bar]:
T [°C]

Condensate
Q.Condensate [L/h]:
EC [mS/cm]:

Concentrate
Q.Concentrate [L/h]:
EC [mS/cm]:

Samples
Date [ddmmyy]-10
Date [ddmmyy]-11
Date [ddmmyy]-12

Note:



Date [dd-mm-yy]: - -

ZERO BRINE

Water Counter

☀ Time [hr:min]:
Value []:

☾ Time [hr:min]:
Value []:

Electricity Counter

☀ Time [hr:min]:
Value []:

☾ Time [hr:min]:
Value []:

Current week brine sample

☀ Date [ddmmyy]-01
Time [hr:min]:

Next week brine sample

☾ Date [ddmmyy]-01B
Time [hr:min]:

2nd Electricity Counter

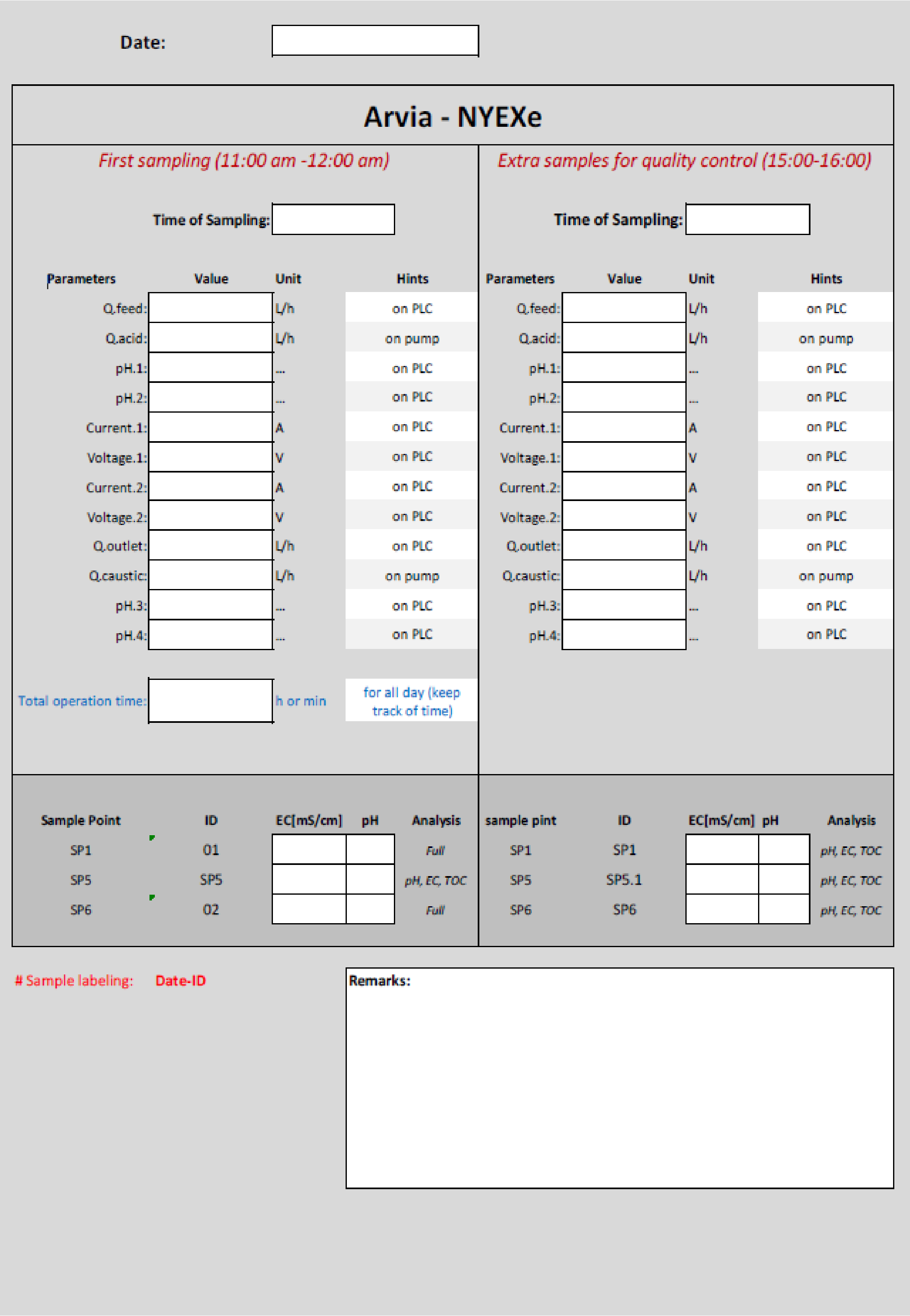
☀ Time [hr:min]:
Value []:

☾ Time [hr:min]:
Value []:

Note:

TU Delft

Annex D: Daily Data Sheet - Site 02



Date:

Arvia - NYEXe

First sampling (11:00 am -12:00 am)

Time of Sampling:

Parameters	Value	Unit	Hints
Q.feed:		L/h	on PLC
Q.acid:		L/h	on pump
pH.1:		...	on PLC
pH.2:		...	on PLC
Current.1:		A	on PLC
Voltage.1:		V	on PLC
Current.2:		A	on PLC
Voltage.2:		V	on PLC
Q.outlet:		L/h	on PLC
Q.caustic:		L/h	on pump
pH.3:		...	on PLC
pH.4:		...	on PLC
Total operation time:		h or min	for all day (keep track of time)

Extra samples for quality control (15:00-16:00)

Time of Sampling:

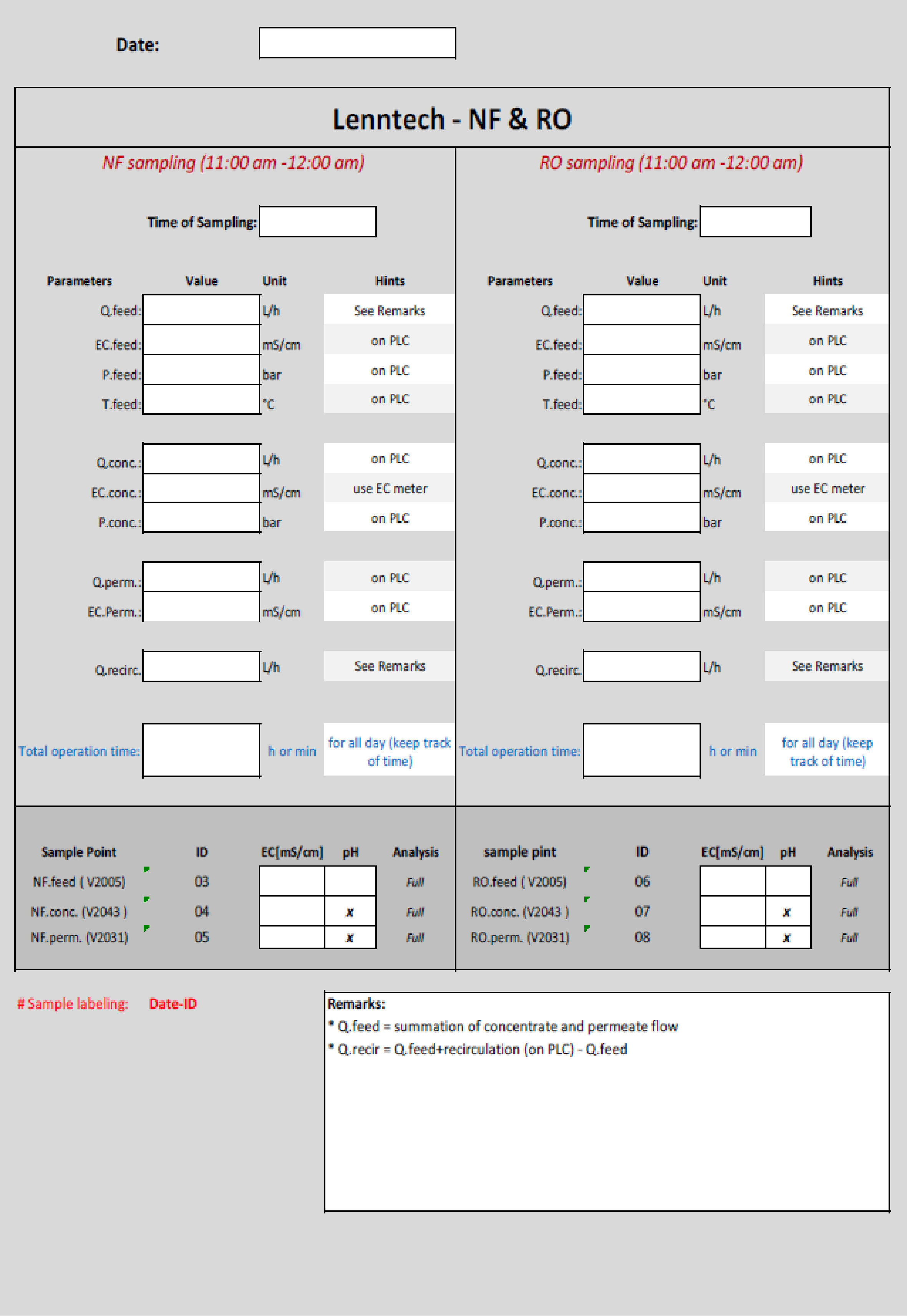
Parameters	Value	Unit	Hints
Q.feed:		L/h	on PLC
Q.acid:		L/h	on pump
pH.1:		...	on PLC
pH.2:		...	on PLC
Current.1:		A	on PLC
Voltage.1:		V	on PLC
Current.2:		A	on PLC
Voltage.2:		V	on PLC
Q.outlet:		L/h	on PLC
Q.caustic:		L/h	on pump
pH.3:		...	on PLC
pH.4:		...	on PLC

Sample Point	ID	EC[mS/cm]	pH	Analysis
SP1	01			*Full*
SP5	SP5			*pH, EC, TOC*
SP6	02			*Full*

sample pint	ID	EC[mS/cm]	pH	Analysis
SP1	SP1			*pH, EC, TOC*
SP5	SP5.1			*pH, EC, TOC*
SP6	SP6			*pH, EC, TOC*

Sample labeling: Date-ID

Remarks:



Date:

Lenntech - NF & RO

NF sampling (11:00 am -12:00 am)

Time of Sampling:

Parameters	**Value**	**Unit**	**Hints**
Q.feed:		L/h	See Remarks
EC.feed:		mS/cm	on PLC
P.feed:		bar	on PLC
T.feed:		°C	on PLC
Q.conc.:		L/h	on PLC
EC.conc.:		mS/cm	use EC meter
P.conc.:		bar	on PLC
Q.perm.:		L/h	on PLC
EC.Perm.:		mS/cm	on PLC
Q.recirc.		L/h	See Remarks
Total operation time:		h or min	for all day (keep track of time)

RO sampling (11:00 am -12:00 am)

Time of Sampling:

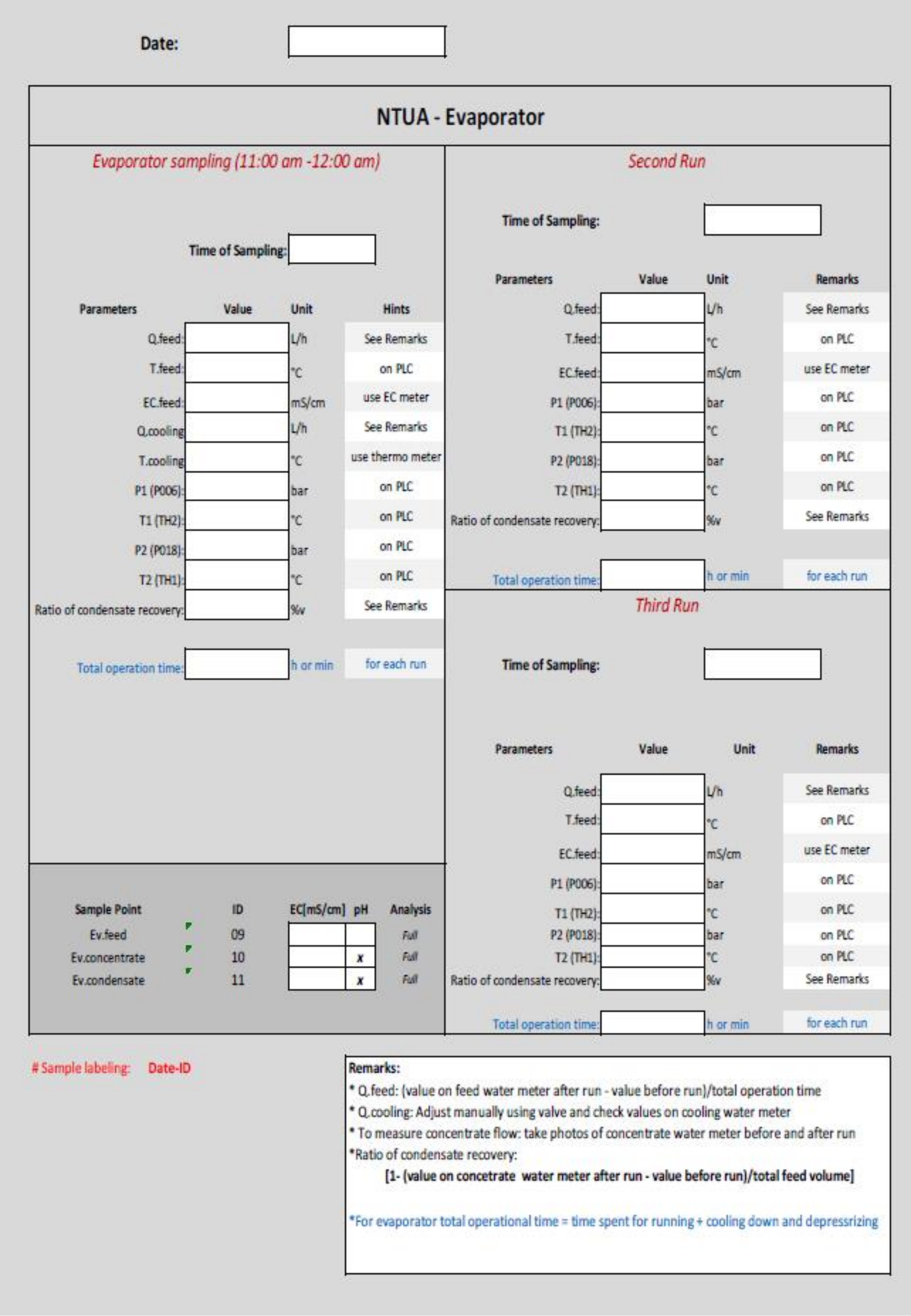
Parameters	**Value**	**Unit**	**Hints**
Q.feed:		L/h	See Remarks
EC.feed:		mS/cm	on PLC
P.feed:		bar	on PLC
T.feed:		°C	on PLC
Q.conc.:		L/h	on PLC
EC.conc.:		mS/cm	use EC meter
P.conc.:		bar	on PLC
Q.perm.:		L/h	on PLC
EC.Perm.:		mS/cm	on PLC
Q.recirc.		L/h	See Remarks
Total operation time:		h or min	for all day (keep track of time)

Sample Point	**ID**	**EC[mS/cm]**	**pH**	**Analysis**
NF.feed (V2005)	03			*Full*
NF.conc. (V2043)	04		x	*Full*
NF.perm. (V2031)	05		x	*Full*

sample pint	**ID**	**EC[mS/cm]**	**pH**	**Analysis**
RO.feed (V2005)	06			*Full*
RO.conc. (V2043)	07		x	*Full*
RO.perm. (V2031)	08		x	*Full*

Sample labeling: **Date-ID**

Remarks:
* Q.feed = summation of concentrate and permeate flow
* Q.recir = Q.feed+recirculation (on PLC) - Q.feed



Date:

NTUA - Evaporator

Evaporator sampling (11:00 am -12:00 am)

Time of Sampling:

Parameters	Value	Unit	Hints
Q.feed:		L/h	See Remarks
T.feed:		°C	on PLC
EC.feed:		mS/cm	use EC meter
Q.cooling		L/h	See Remarks
T.cooling		°C	use thermo meter
P1 (P006):		bar	on PLC
T1 (TH2):		°C	on PLC
P2 (P018):		bar	on PLC
T2 (TH1):		°C	on PLC
Ratio of condensate recovery:		%v	See Remarks
Total operation time:		h or min	for each run

Sample Point	ID	EC[mS/cm]	pH	Analysis
Ev.feed	09			*Full*
Ev.concentrate	10		x	*Full*
Ev.condensate	11		x	*Full*

Second Run

Time of Sampling:

Parameters	Value	Unit	Remarks
Q.feed:		L/h	See Remarks
T.feed:		°C	on PLC
EC.feed:		mS/cm	use EC meter
P1 (P006):		bar	on PLC
T1 (TH2):		°C	on PLC
P2 (P018):		bar	on PLC
T2 (TH1):		°C	on PLC
Ratio of condensate recovery:		%v	See Remarks
Total operation time:		h or min	for each run

Third Run

Time of Sampling:

Parameters	Value	Unit	Remarks
Q.feed:		L/h	See Remarks
T.feed:		°C	on PLC
EC.feed:		mS/cm	use EC meter
P1 (P006):		bar	on PLC
T1 (TH2):		°C	on PLC
P2 (P018):		bar	on PLC
T2 (TH1):		°C	on PLC
Ratio of condensate recovery:		%v	See Remarks
Total operation time:		h or min	for each run

Sample labeling: **Date-ID**

Remarks:
* Q.feed: (value on feed water meter after run - value before run)/total operation time
* Q.cooling: Adjust manually using valve and check values on cooling water meter
* To measure concentrate flow: take photos of concentrate water meter before and after run
*Ratio of condensate recovery:

[1- (value on concetrate water meter after run - value before run)/total feed volume]

*For evaporator total operational time = time spent for running + cooling down and depressrizing

Extra Datasheet – only EFC

EFC pilot			
Dtae:			
	Reactor 1	Reactor 2	reactor 3
Fill all three reactors	O	O	O
Take sample from the feed	Date_EFC11	Date_EFC12	Date_EFC13
Set the set point for the first hour to-15oC			
Start the stirrer	O	O	O
Start the water bath	O	O	O
Start: Write the start time			
write the ice formation time			
write the salt formation time			
Stop (after 1.5h): Write the stop time			
Stop the water bath	O	O	O
Stop the stirrers	O	O	O
Transfer the bottom solution to buffer tank 1	O	O	O
Take sample from the bottom solution	Date_EFC21	Date_EFC22	Date_EFC23
Take sample from the Ice	Dtae_EFC21A	Date_EFC22A	Date_EFC23A
Take sample from the washed Ice	Dtae_EFC21B	Date_EFC22B	Date_EFC23B
Wash the ice with tap water and drain the reactor	O	O	O

Annex E: Further Testing for Improved Performance and Reliability – Site 01

Results of Testing for Improved Performance

As mentioned in the previous paragraph, further tests were carried out in the BEC satellite laboratory at UNIPA with MF-PFR unit in order to improve the quality of obtained crystals using artificial brine mimicking the average composition of the brines tested. The average cation/anion composition of brines tested in the BEC is listed in **Table *52*.**

Table 52: MAIN COMPOSITION OF INLET BRINE AND ALKALINE SOLUTION

	Inlet Brine							**Alkaline solution**	
Test	Composition [g/l]							Composition [mol/l]	
								Mg^{2+} Step	Ca^{2+} Step
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	NaOH	NaOH
A	9.7	0.55	1.9	14.8	46.6	0.16	0.43	0.50	2.0
B	9.0	0.54	1.7	13.4	42.7	0.43	0.11		
C	10.7	0.73	2.4	16.8	53.7	0.65	0.17		

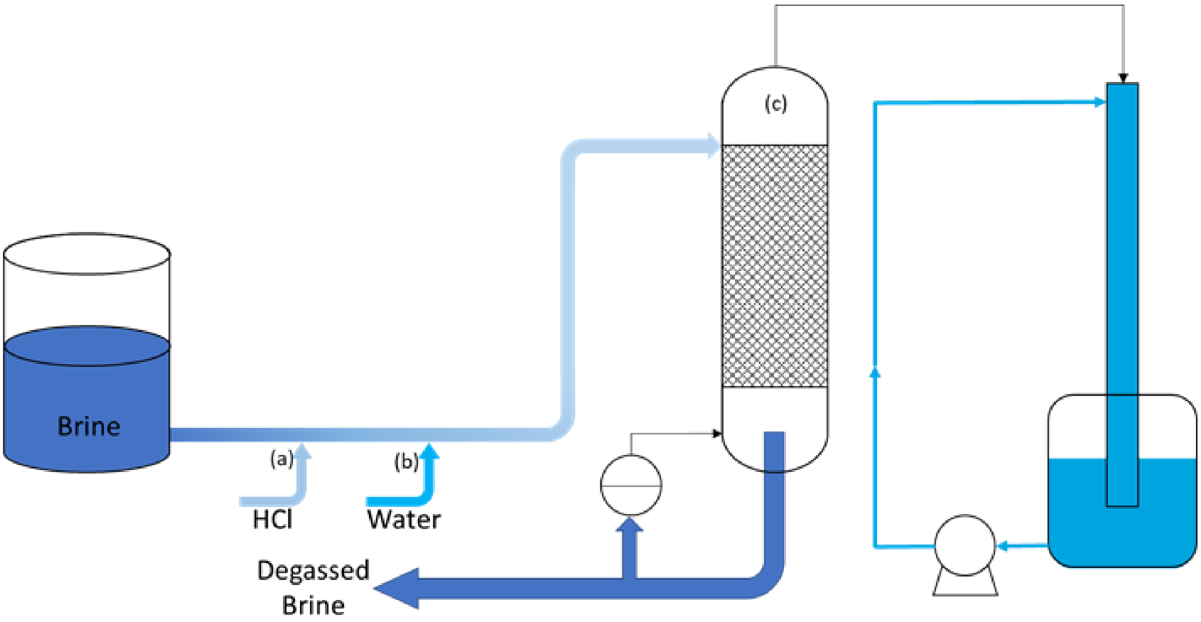
For each brine, two experimental runs were carried out. In the first run, the brine along with the alkaline solution was fed directly to the MF-PFR for the two precipitation steps. In the latter run, the brine was pre-treated by means of a degassing step in order to minimize the concentration of CO_3^{2-}/HCO_3^- ions, and, finally, fed to the MF-PFR. The pre-treatment step consisted of two main steps:

i. Acidification of the brines in order to convert the carbonate/bicarbonates ions to CO_2

ii. Removing the carbon dioxide by means of a stripping process.

Thus, the pre-treatment step of the inlet brine consisted of two main sections: (i) acidification section, where an acid solution was added in the brine in order to convert bicarbonate/carbonate ions into carbon dioxide and (ii) removal section, where the brine was de-gassed by mean of a stripping process. The process scheme of the pre-treatment step is reported in **Figure *67***.

Figure 67: PROCESS SCHEME OF THE PRE-TREATMENT SECTION.



The pre-treatment step can be described as follow:

(a) *Acidification:* The inlet brine was mixed with a 1 M of HCl solution. The amount of the acid was equal to the moles of HCO_3^-/CO_3^{2-} in the inlet brine plus a small excess in order to reach a final pH value less than 4.

(b) *Water Rebalance:* Before entering in the stripping column, a small amount of water was added in order to restore the water content in the brine due to the water losses in the stripping column.

(c) *Stripping section:* Following the water rebalancing, the brine was preheated and fed in the top of the stripping column, where it was distributed over the packing material and put in contact with the rising vapor. The stripping vapor was produced in the reboiler, which was in the bottom of the column, vaporizing of a part of the brine. The heat and mass exchange between the liquid and vapor promoted the stripping of the CO_2 and thus reduced its concentration in the brine. After the pre-treatment step, the degassed brines were analyzed. The average anion/cation concentrations of the degassed brines are listed in Table 53.

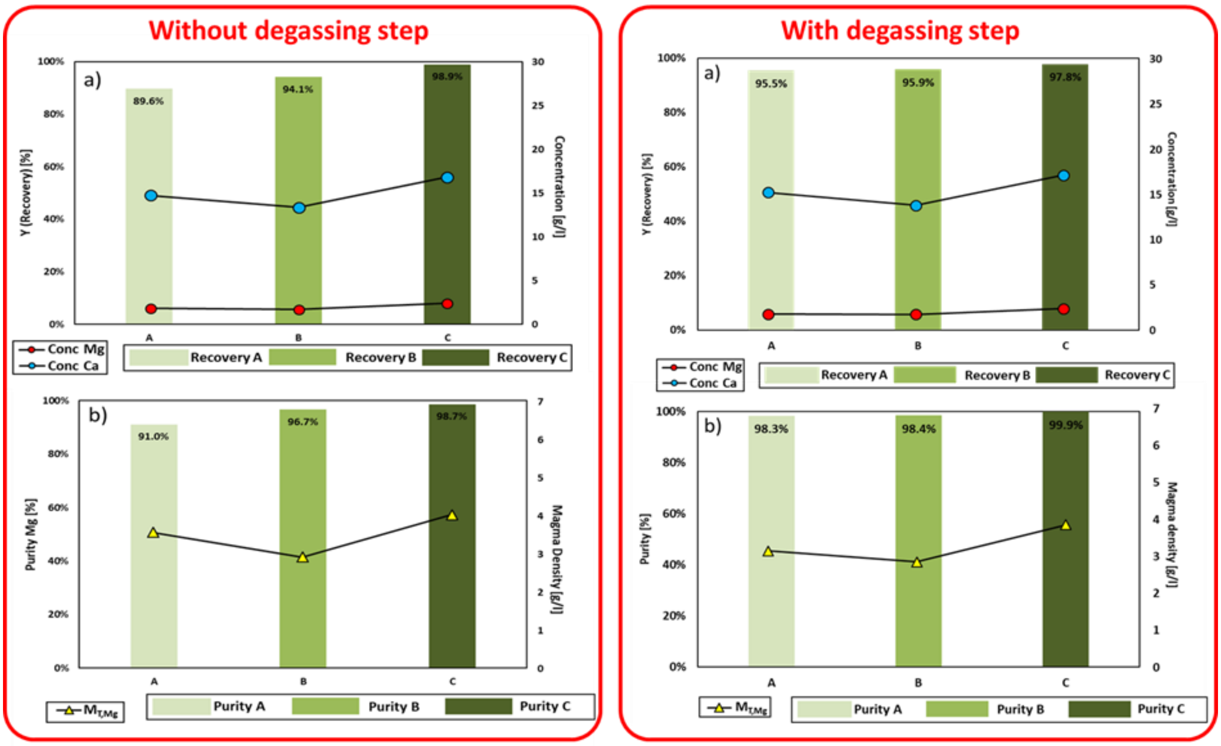
The quality of the $Mg(OH)_2$ and $Ca(OH)_2$ obtained through the two precipitation steps in the two experimental campaign was assessed following the analytical procedure described in Chapter 4. The purity and conversion of $Mg(OH)_2$ and $Ca(OH)_2$ for the two performed experimental campaigns are reported in Figure 68 and Figure 69, respectively.

Table 53: MEAN COMPOSITIONS OF DEGASSED BRINE AND REMOVAL EFFICIENCY OF HCO_3^-/CO_3^{2-} IONS

Degassed Brine								
Test	Composition [g/l]							Removal efficiency [%]
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	
A	9.6	0.93	1.8	15.3	47.9	0.16	0.05	89
B	9.4	0.75	1.8	13.8	44.6	0.11	0.05	55
C	11.2	0.92	2.4	17.2	55.1	0.65	0.05	71

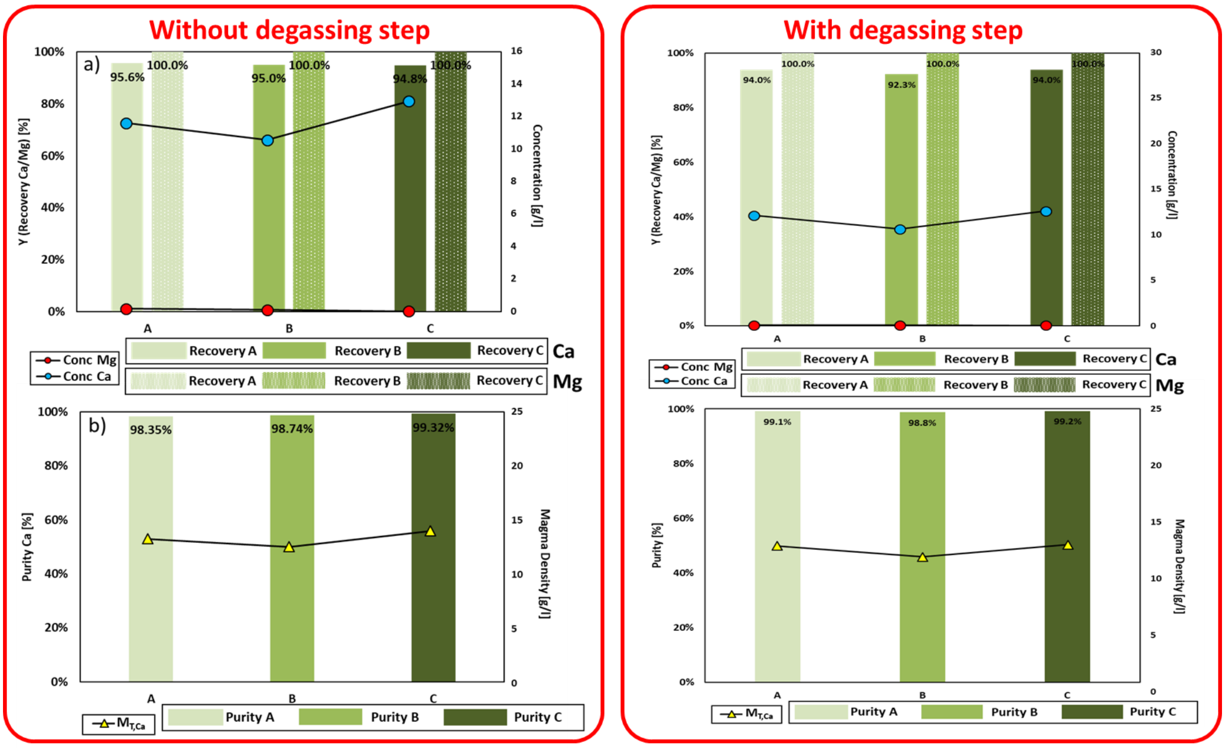
For both experimental campaigns, satisfying results have been obtained in term of removal overall efficiency (between 95 and 100%) for the Mg^{2+} and Ca^{2+}. The purity of $Mg(OH)_2$ particles produced in the reactor increase from 96% up to about 99% after the degassing step. Moreover, the recovery of Mg^{2+} increased from 94% up to about 97% increasing the production of $Mg(OH)_2$ crystals. Overall, a beneficial effect of the degassing step on the purity of $Mg(OH)_2$ was observed, obtaining a purity of Mg^{2+} higher than the target (90%).

Figure 68: a) Mg^{2+} RECOVERY EFFICIENCY, b) PURITY OF $Mg(OH)_2$ SOLIDS FOR ALL PRECIPITATION TESTS, ACCOMPANIED BY Mg^{2+} AND Ca^{2+} CONCENTRATION IN THE FEED BRINE; AND MAGMA DENSITY FOR THE TWO EXPERIMENTAL CAMPAIGNS.



Also for the precipitation of Ca^{2+}, the degassing step has a beneficial effect on the purity of $Ca(OH)_2$. In fact, the average purity of obtained $Ca(OH)_2$ was higher than 90% due to the higher Mg^{2+} recovery during the precipitation of Mg^{2+}.

Figure 69: a) Ca^{2+} RECOVERY EFFICIENCY, b) PURITY OF $Ca(OH)_2$ SOLIDS FOR ALL PRECIPITATION TESTS, ACCOMPANIED BY Mg^{2+} AND Ca^{2+} CONCENTRATION IN THE FEED BRINE; AND MAGMA DENSITY FOR THE TWO EXPERIMENTAL CAMPAIGNS.



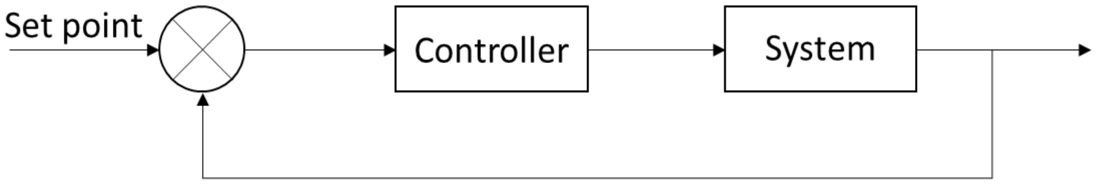
Results of Testing for Improved Reliability

The improvement of the MF-PFR consists in developing a system in order to automate the control of two main operative parameters, which are:

1. The level production consisting of the brine flowrate fed to the MF-PFR from which the amount of $Mg(OH)_2$ and $Ca(OH)_2$ production depends;
2. The pH which is linked to the conversion of $Mg(OH)_2$ in the first precipitation step and the removal of all divalent cations in the second precipitation step.

In both cases, the strategy adopted to control the level production (inlet brine flow rate) and the pH is the classical feedback control configuration (**Figure 70**).

Figure 70: CONCEPTUAL REPRESENTATION OF A FEEDBACK CONTROL CONFIGURATION



Moreover, a small modification in P&ID diagram was made, such as the control loop proposed for the pH level production, with respect to the one reported in **Figure** ***64***. The updated P&ID diagram is displayed in **Figure** ***71***.

Level of production control

The level of production control was carried out via a motorized valve (RV2, see **Figure** ***71***) placed along the recycle line. The feedback control loop configuration was performed via a Proportional and Integral (PI) controller implemented in the software used to monitor all parameters in the MF-PFR. The logic behind the level production control loop is: (i) the brine flowmeter reads the flowrate and converts the measured signal into an electrical signal 4-20 mA, (ii) the electrical signal is sent to the PI controller along with the set-point, appropriately converted into an electrical signal, then processed and finally (iii) the PI sends an electrical signal (also in this case 4-20 mA) to the motorized valve in order to regulate the percentage of opening/closing.

pH control

The pH control was performed varying the flowrate of alkaline solution by means of a variable speed pump (RV5, see **Figure** ***71***). The feedback control loop configuration was carried out via a PI controller. Also in this case, the controller was implemented in the same software (reported above). The logic behind the pH control loop is: (i) pH-meter measures the pH of outlet brine from the MF-PFR, the measurement is converted into a current signal (4-20 mA), (ii) the current signal along with the set point, appropriately converted into current signal, then sent to the PI controller, and then processed, finally (iii) the PI controller sends a voltage signal (from 0 V up to 5 V) to the motor of the pump in order to change the flow-rate.

Before proceeding with the test of both control loops, a crucial step is to identify the nominal functioning pH. For this purpose, a test with MF-PFR was carried out in order to study how the pH changes with varying the alkaline flowrate. This test was carried out with a fixed brine flow-rate of 2.5 L/min and the NaOH solution was increased from 0 up to 1.1 L/min. In **Figure 72** the variation of the pH as a function of the alkaline flow rate is reported.

Figure 71: UPDATED SIMPLIFIED P&ID OF THE MF-PFR UNIT

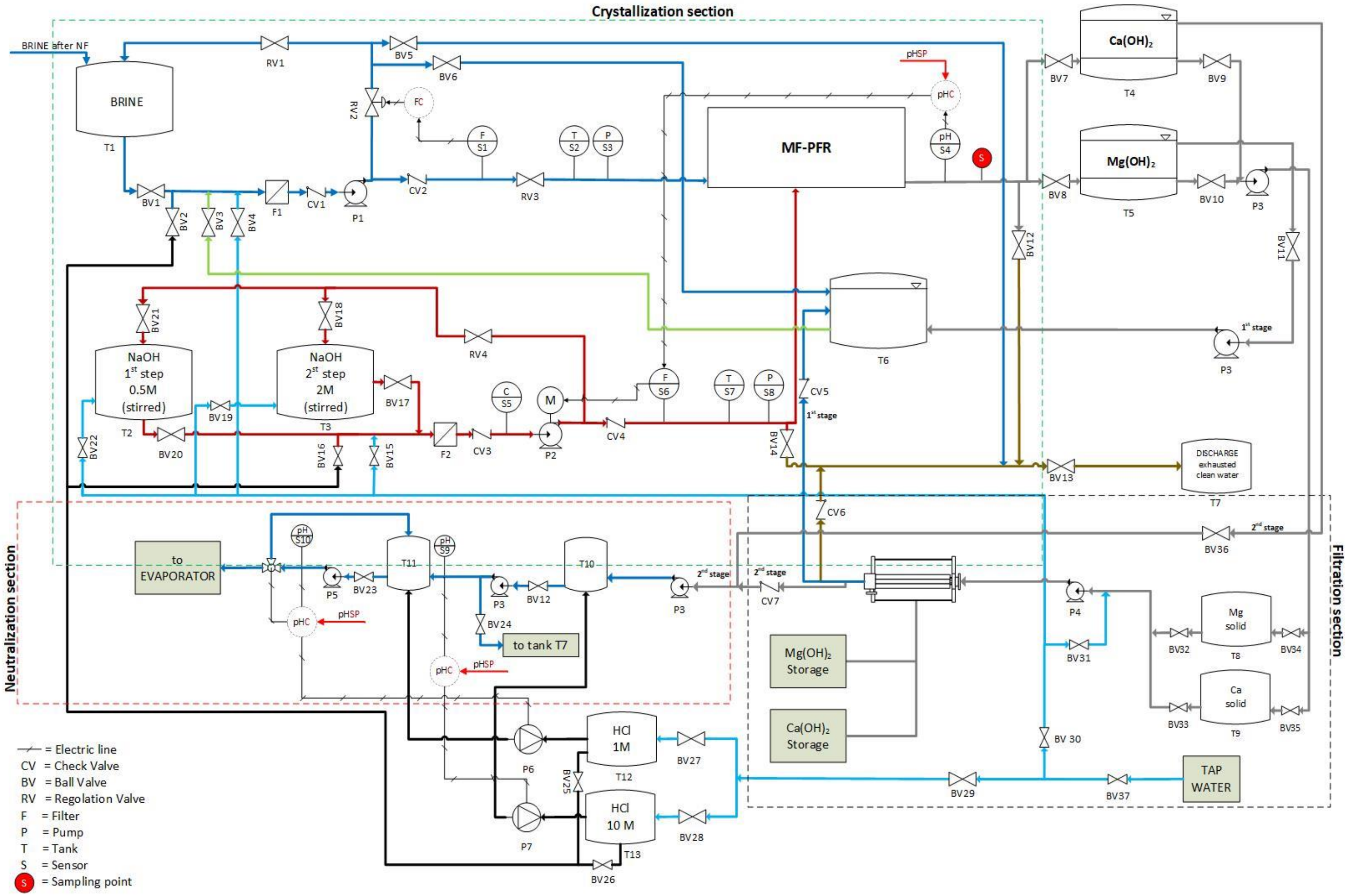
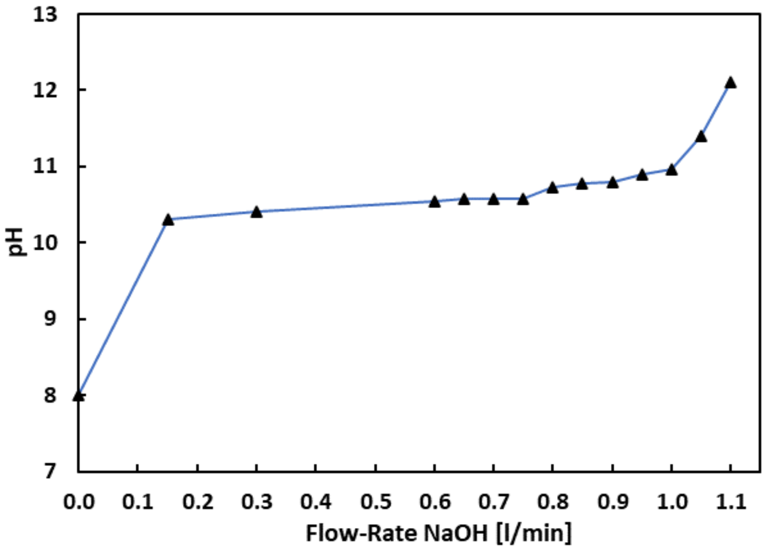


Figure 72: VARIATION OF THE PH AS FUNCTION OF ALKALINE FLOWRATE

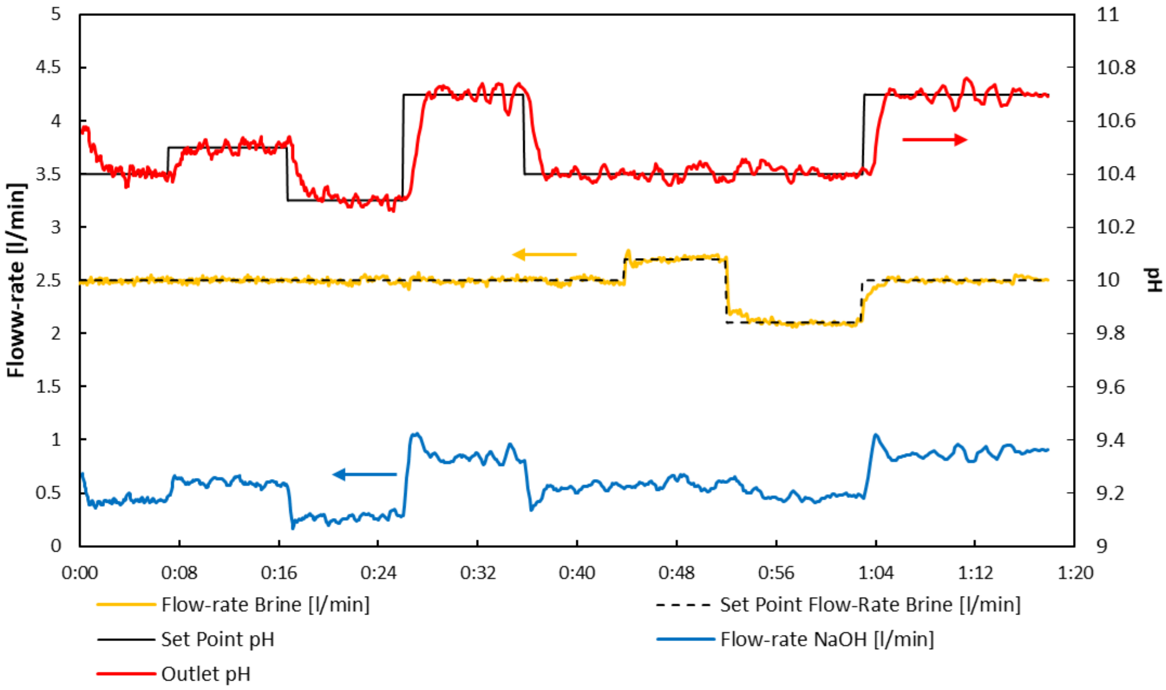


As shown in Figure 72, at the beginning the brine pH was around 8. Subsequently, the flowrate of NaOH solution was added and then the pH started increasing. The pH rapidly increased from 8 to 10.5 at an alkaline flowrate equal to 0.1 L/min. Afterwards, the pH was almost constant at a value equal to 10.5 at the increase of alkaline flowrate from 0.10 L/min up to 0.75 L/min. Then, the pH continued increasing from 10.5 (0.75 L/min) to 10.96 (1.0 L/min). Finally, a sharp increase of the pH was observed when the alkaline flowrate increased from 1.0 L/min (pH of 10.96) to 1.1 (pH of 12.1).

This experiment demonstrated how the flowrate variation of alkaline solution influenced the pH, highlighting that an accurate control of the reaction pH can be obtained by changing the alkaline flowrate from 0.1 to 0.9 L/min.

Once the operative condition were fixed, i.e. brine flowrate equal to 2.5 L/min and the reaction pH at 10.4, a controllability test was carried out to test the effectiveness of the developed MF-PFR’s control loop by changing the set point of pH and brine flowrate. Figure 73 shows the variation of alkaline solution (blue solid line) caused by the variation of pH set point (solid black line) and/or brine flowrate set point (dashed black line). Moreover, the recorded reaction pH (red line) and brine flowrate (yellow line) are also displayed to show how the control system reacted either by changing the alkaline flowrate to vary the reaction pH or by varying the percentage of the opening valve to reach the desired value of the brine flowrate.

Figure 73: VARIATION OF THE ALKALINE FLOWRATE (BLUE SOLID LINE) DUE TO THE VARIATION OF PH (SOLID BLACK LINE) AND/OR BRINE FLOWRATE (DASHED BLACK LINE) SETPOINT. VARIATION OF THE RECORDED REACTION PH (RED SOLID LINE) AND BRINE FLOWRATE (YELLOW SOLID LINE) TO REACH THE NEW SETPOINT VALUE.



The experiment started by regulating the alkaline flowrate in order to reach a reaction pH equal to 10.4. Once the reaction pH was equal to 10.4, the pH set point was increased to 10.5 at fixed brine flowrate. As reported in Figure 73, when the pH set point was increased, the control system reacted by increasing the alkaline flowrate, and then the reaction pH started to increase until the new value of set point after a couple of minutes is reached. Once the new set point was reached, the MF-PFR worked for about 10 min at the new set point. Afterwards, the pH set point dropped from 10.5 to 10.3. In this case, the control system reacted by reducing the alkaline flowrate. The MF-PFR reaction pH reached the new set point after a couple of minutes and the MF-PFR worked at this new set point for almost 10 minutes. Subsequently, a larger variation of pH set point than before occurred, in fact, the pH increased from 10.3 to 10.7. Again, the control system increased the alkaline flow rate and the MF-PFR reaction pH reached the new set point after a few minutes. Once the new stationary condition was reached, the MF-PFR operated for about 10 minutes and then the pH decreased to the initial value of 10.4. When the MF-PFR reaction pH was stable at the 10.4, a brine flowrate set point variation was carried out by increasing the brine flowrate from 2.5 to 2.7 L/min. The increase in the brine flowrate resulted in higher productivity of the unit and in lower reaction pH. Once the brine flowrate set point changed, the control system reacted by closing the automatic valve to increase the brine flowrate and at the same time increased the alkaline flowrate so as to maintain the reaction pH at 10.4. It can be observed that the dynamic of brine flowrate variation was a few seconds faster than the variation of MF-PFR reaction pH dynamic. After that, the brine flowrate set point was decreased from 2.7 to 2.1 L/min. In this case, the control system reacted by opening the valve and reducing the alkaline flow rate to maintain the reaction pH constant. However, an initial increase of the pH was observed due to the different dynamics, that was rapidly corrected by the control system. Finally, the variation of brine flowrate and pH set points were carried out increasing the brine flow rate from 2.1 up to 2.5 L/min and the pH from 10.4 up to 10.7. Also in this case, the control system reacted by increasing the alkaline flowrate and closing the automatic valve to increase the brine flowrate. Moreover, the control system was able to adjust the alkaline flowrate in order to avoid the increase of MF-PFR reaction pH.

In conclusion, the control system developed was able to guarantee a fixed level production, i.e. to guarantee a constant brine flowrate, at constant reaction pH. Moreover, the controllability experiment highlighted the robustness of the control system under variation of pH and/or brine flowrate set point.

Annex F: Further Analyses for Identifying the Fouling of the NF Membranes

Further analyses were performed to identify the cause of the fouling of the NF membranes used in Site 02. Samples from the NF feed water (**Figure 74**), the NF membranes (**Figure 75**), the NF cartridge filters (**Figure 76**), and sediments in the piping (**Figure 77**) were analyzed under a microscope. Further chemical analysis was done to assess whether the fouling was organic or inorganic. COD was measured in all samples, implying that organic substances were present. Samples from the membranes and the cartridge filters of the NF were sent for ionic analyses. There were no clear indications for presence of inorganics. The summary of the findings is presented in **Table 54**.

Figure 74: NF FEED STREAM (11-11-2020) ANALYZED BY MICROSCOPE AT 100 μm (LEFT) and 1000 μm (RIGHT)

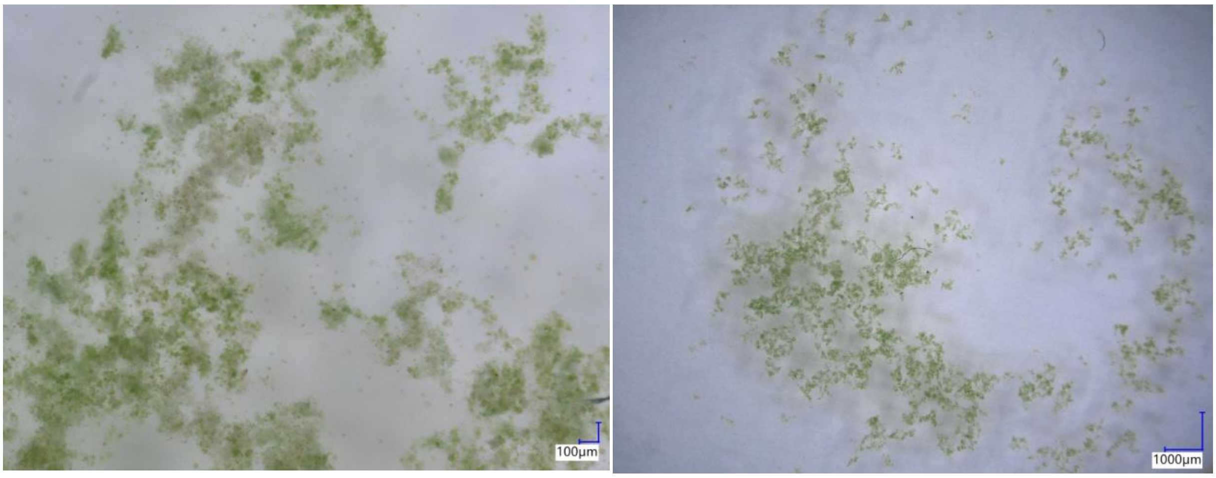


Figure 75: NF MEMBRANES FROM FIRST REPLACEMENT (LEFT AND MIDDLE) AND FROM SECOND REPLACEMENT (RIGTH) ANALYZED BY MICROSCOPE

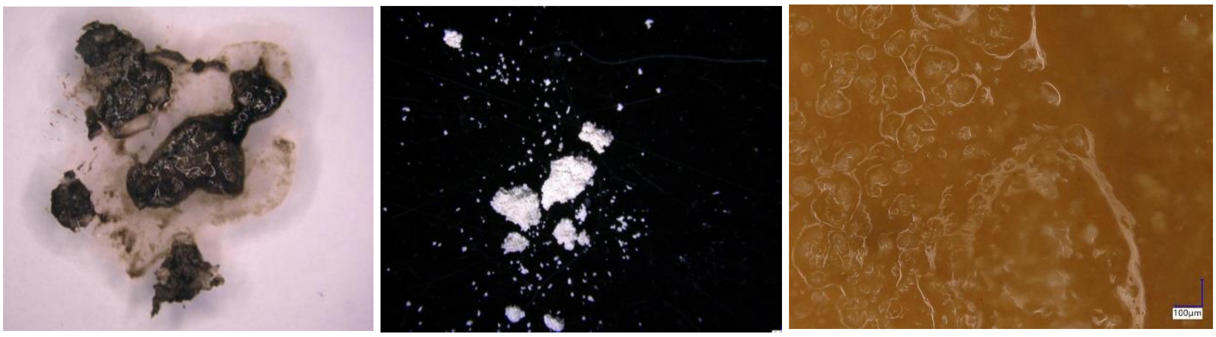
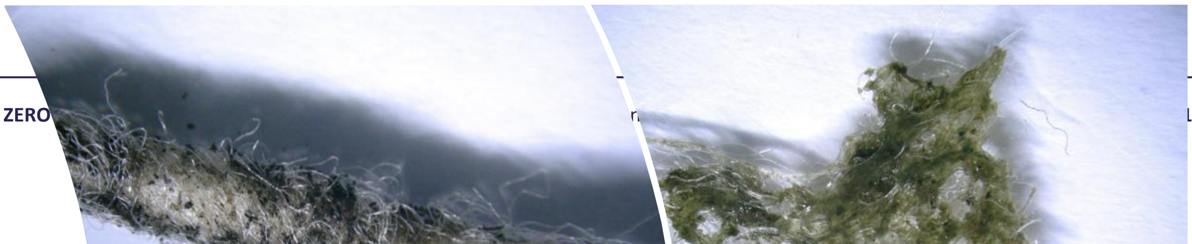


Figure 76: NF CARTRIDGE FILTERS ANALYZED BY MICROSCOPE



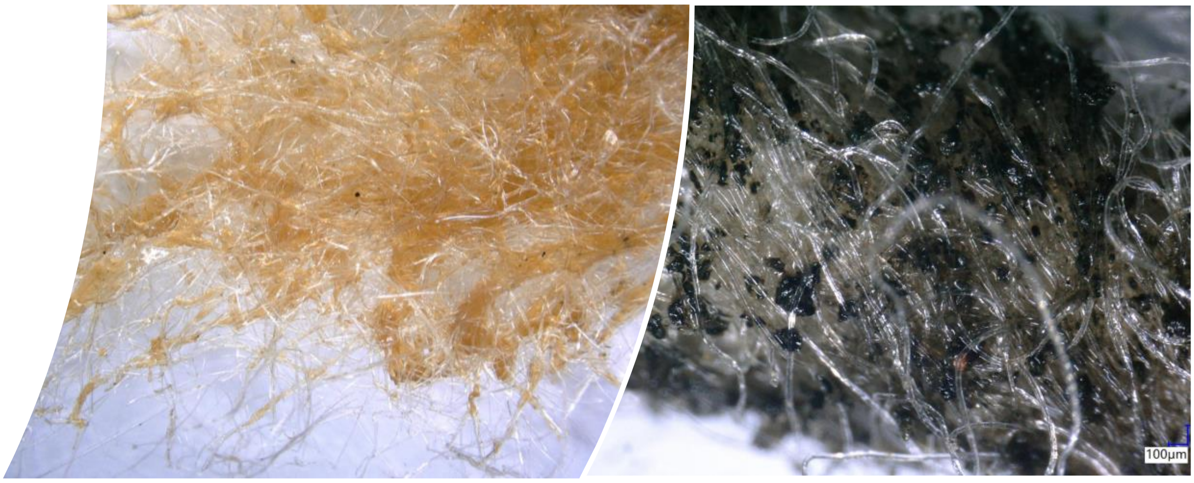


Figure 77: SEDIMENTS OF THE PIPING BEFORE THE NF FEED TANK (LEFT) AND AFTER NYEX EFFLUENT (RIGHT)

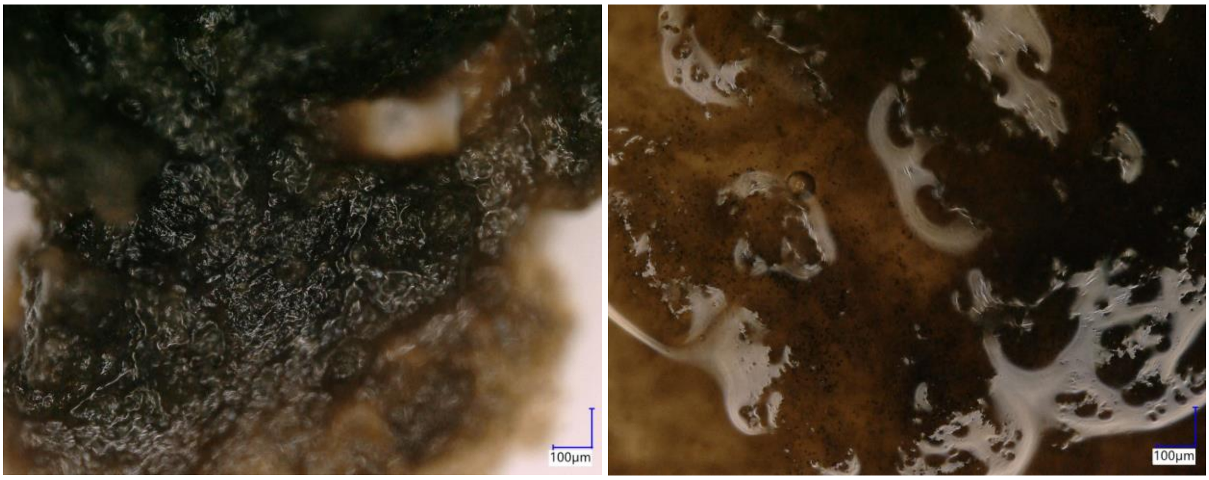


Table 54: SUMMARY OF THE PRESENCE AND CAUSE OF FOULING FOR NF

	Visual Contamination	Organics Measured	Inorganics Measured
NF Feed Stream	Yes	Yes	-
NF Cartridge Filters	Yes	Yes	No
NF Membranes	Yes	Yes	No
Piping before NF tank and after Nyex	Yes	Yes	-

Annex G: Experiments with a larger scale MED evaporator for Site 02 – Mode II

Description of the technology

The evaporator has been designed following the principles of MED process. MED systems are considered to be the most energy efficient systems among other evaporators.

The unit consists of five evaporation effects, all connected in line (*Figure 78* and *Figure 79*). The system is of forward feed type, where brine is fed from one effect to the next. In each effect, part of the water content of the brine is evaporated, increasing progressively the dissolved solid content of the brine solution.

In the first effect, brine is sprayed on the heat exchanger, which consists of horizontal tubes in rectangular arrangement. Service steam flows inside the first effect tubes and condenses as it transfers latent heat to the brine. Water content of the brine is evaporated on the external surface of the heat exchanger tubes. Then, in the form of superheated steam, it flows from the first effect to the inside of the heat exchanger tubes of the second effect, where it condenses to water, transferring heat to the brine of the second effect. Water is then subcooled further transferring heat to the brine before it is collected in the water product vessel.

Concentrated brine from the last effect is subcooled, transferring its heat content to preheat the fresh inflowing brine, before it is collected in the brine product vessel.

Heat to the first effect is provided in the form of saturated steam at low pressure. In an industrial environment, steam will be produced by any source of waste heat or secondary process steam. In this test unit, steam is produced by an electric steam generator provided with the unit. Service condensate is collected in the service tank and recycled to the steam generator.

The control of the system is accomplished via a PC-based supervisory control and data acquisition (SCADA) interface. Multiple temperature, pressure and flow transmitters are connected in multiple places, receiving all the important data for process control. The overall control and monitoring can be achieved using SCADA. Also, two types of motorized valves are being used in the system and controlled by SCADA, an electric and Pneumatic. Electric valves are used mainly for continuous flow adjustment, but also for ON/OFF control where reaction time is not critical and Pneumatic valves are used for ON/OFF control only, where fast response time is necessary.

Scheme and photo of equipment

Figure 78: 3D SCHEME OF THE MED EVAPORATOR LAYOUT.

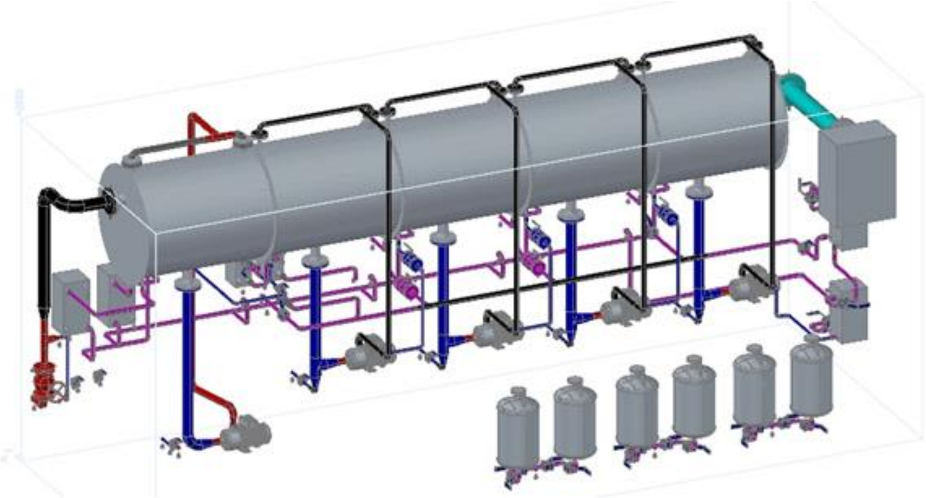


Figure 79: PHOTOS OF THE MED EVAPORATOR.

Description of tests done

During Site 02 at EVIDES case study, a 2 m^3/d evaporator operated with waste heat aiming the recovery of a NaCl solution that met required specifications in order to be used as regeneration solution for the

IEX softening columns of DWP. To achieve higher efficiency and quality of the end products (clean water and brine solution) a larger scale evaporator (5 m^3/d) was constructed by NTUA. Brine (1,000 L) from Mode II operation on site, was transferred to NTUA in order to perform additional experiments with the new evaporator.

The experimental process of each experiment was the following:

1. Samples from the inlet brine were collected and analyzed at the lab of Department of Environmental Science and Technology before the beginning of each experiment.
2. During the experiment the monitoring of the temperature and pressure of each effect and regular inspections of the vacuum were conducted.
3. After each experiment samples from the brine and the condensate vapor vessels were collected and analyzed at the lab and the volumes of the products were recorded.
4. Finally, after each experiment a cleaning run was carried out using the condensate vapor produced by the system.

In **Table *55*** the inlet brine concentration of each experiment is presented.

Table 55: INLET BRINE SOLUTION CONCENTRATION.

Ion	**First Experiment-** Concentration (g/L)	**Second Experiment-** Concentration (g/L)	**Third Experiment-** Concentration (g/L)	**Forth Experiment-** Concentration (g/L)	**Fifth experiment-** Concentration (g/L)
Na^+	9.0	8.6	9.0	9.0	9.0
K^+	0.20	0.12	0.20	0.20	0.21
Mg^{2+}	0.009	0.008	0.009	0.009	0.01
Ca^{2+}	0.06	76	70	67	64
Fe^{3+}	0.0005	0.0007	0.0008	0.0006	0.0002
Cl^-	13.7	13.1	13.6	12.8	13.8
TDS	23.1	21.9	22.8	22.2	23.1

In **Table *56***, it is shown that the concentration of the inlet brine was approximately 22 g/L. The average concentration of Mode II inlet brine of evaporator was 8.6 g/L. However, the concentration of the brine sent to NTUA for the final experiments with the new evaporator was 22 g/L.

During each experiment the pressure and the temperature of the brine on each effect were measured. The fluctuation of those parameters for each experiment are presented in the **Figure *80*** and **Figure *81***.

Figure 80: BRINE TEMPERATURE FLUCTUATION ON EACH EFFECT

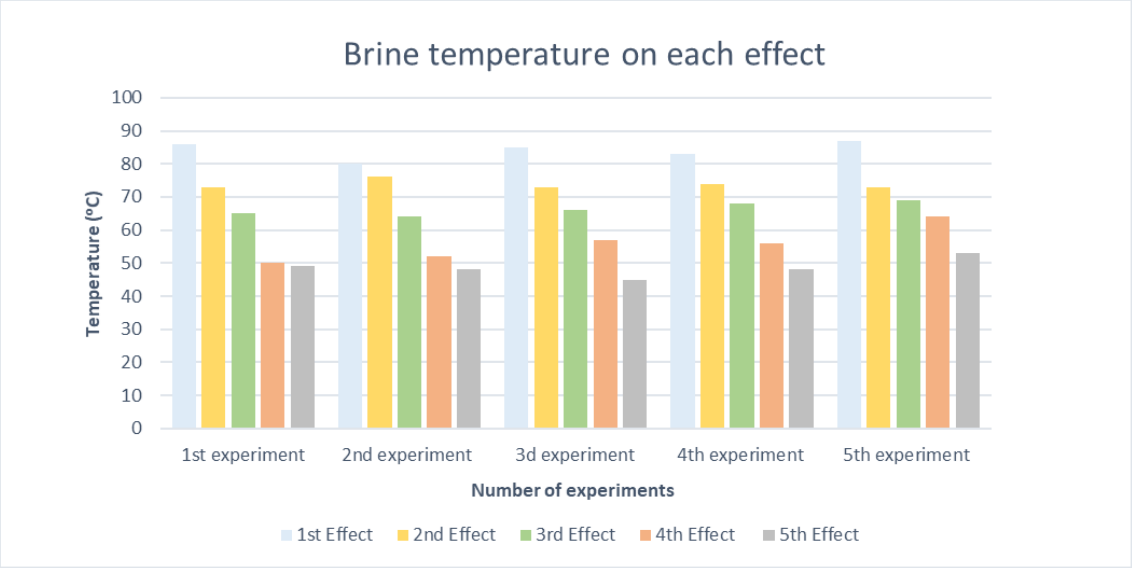
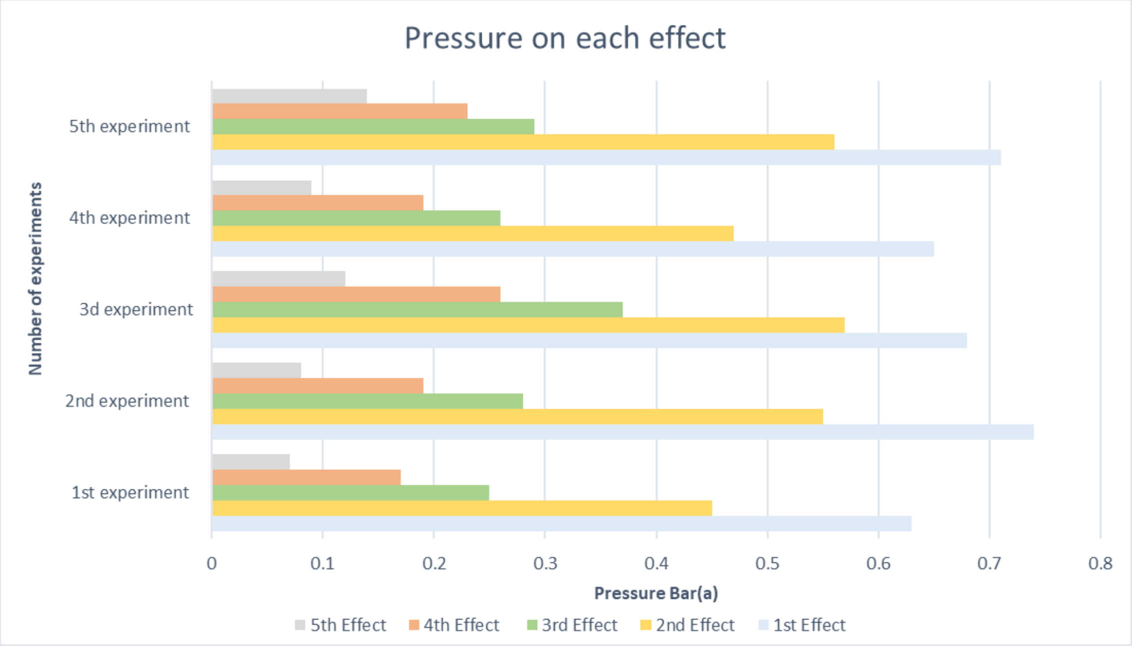


Figure 81: PRESSURE FLUCTUATION ON EACH EFFECT.



Regarding the temperature it can be concluded that on each subsequent effect the temperature dropped approximately 10 °C. At the first effect the temperature was on average 81 °C and on the final effect it was 49 °C. Concerning the pressure on each effect, as it can be seen in *Figure 81* the pressure fluctuated from 0.48 bar(a) on first effect to 0.08 bar(a) on final effect.

After each experiment samples of the concentrate brine and the condensate vapor were collected and analyzed in the lab. The results are presented in *Table 56* and *Table 57*.

Table 56: CONCENTRATED BRINE AFTER EACH EXPERIMENT

Ion	First Experiment-Concentration (g/L)	Second Experiment-Concentration (g/L)	Third Experiment-Concentration (g/L)	Forth Experiment-Concentration (g/L)	Fifth experiment-Concentration (g/L)
Na$^+$	70.7	73.6	85.5	81.0	88.2
K$^+$	1.6	1.0	1.9	1.8	2.0
Mg^{2+}	0.07	0.07	0.09	0.09	0.09
Ca^{2+}	0.51	0.65	0.66	0.61	0.63
Fe^{3+}	0.004	0.006	0.007	0.005	0.002
Cl$^-$	107.1	112.8	128.8	115.6	135.0
TDS	179.9	188.1	216.9	199.1	226.0

Table 57*:* CONDENSATE VAPOR AFTER EACH EXPERIMENT

Ion	First Experiment-Concentration (g/L)	Second Experiment-Concentration (g/L)	Third Experiment-Concentration (g/L)	Forth Experiment-Concentration (g/L)	Fifth experiment-Concentration (g/L)
Na$^+$	0.01	0.01	0.01	0.01	0.01
K$^+$	0.0002	0.0001	0.0003	0.0003	0.0002
Mg^{2+}	0.007	0.007	0.007	0.007	0.007
Ca^{2+}	0.01	0.009	0.01	0.01	0.01
Fe^{3+}	n.d	n.d	n.d	n.d	n.d.
Cl$^-$	0.02	0.02	0.02	0.02	0.02
TDS	0.051	0.05	0.05	0.05	0.05

The effluent brine at the end of each experiment reached the 216 g/L TDS concentration. That solution met the required specifications in order to be used for the regeneration of the IEX softening columns of the DWP. Regarding the product distilled water, it was a high-quality water that may be used in many industrial sectors. Additionally, the concentration factor of each experiment is presented in Figure *82*. As it can been seen in this figure, the system concentrated the inlet brine by 9 times on average.

Figure 82: CONCENTRATION FACTOR OF EACH EXPERIMENT

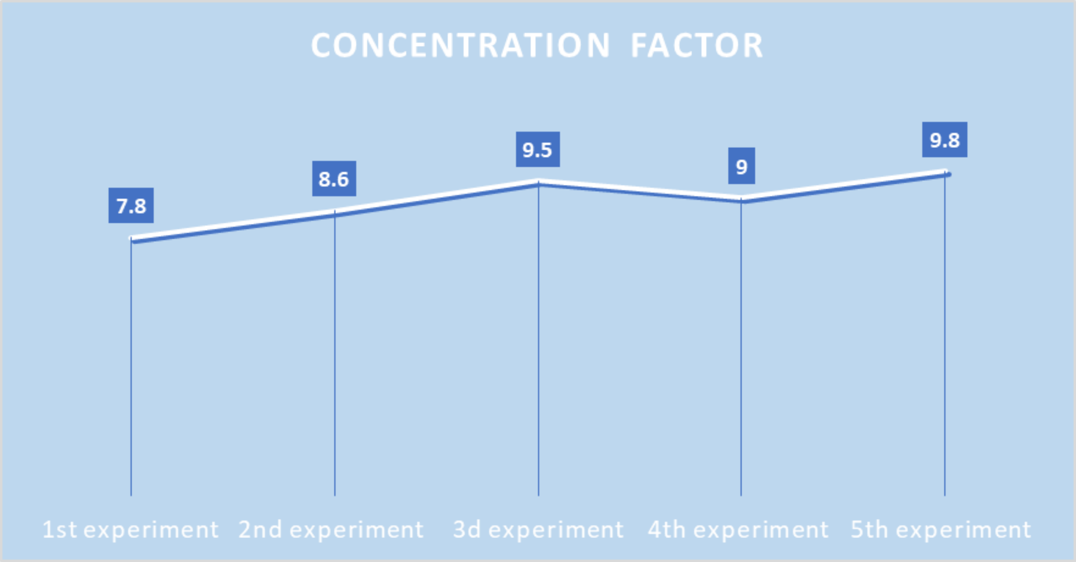


Table *58* presents the average (of the five experiments) heat exchange, mass balance, temperature and pressure on each effect. The duration of each experiment was approximately one hour.

Table 58: AVERAGE HEAT EXCHANGE, MASS BALANCE, TEMPERATURE AND PRESSURE

EFFECT	STEAM	E-01	E-02	E-03	E-04	E-05
Brine inflow (L/h)	-	160	131	101	72	44
Vapor required (kg/h)	29.9	29.5	29.2	28.9	28.6	28.3
Brine out (L/h)	-	130.5	101.3	72.4	43.8	15.5
Power (KW)	19	19	19	19	19	19
Operating pressure (bar(a))	0.63	0.48	0.36	0.24	0.18	0.08
Operating temperature (°C)	87	81	74	66	56	49

The preheat exchanger power was 23 kW and the first effect was 19 kW. The rejected energy from cooling purposes was calculated to be 7.2 kW. So, the total energy consumption for the production of 1 m^3 of condensate was 290 kWh, and for the evaporator with two effects the energy consumption was 500 kWh, hence more than 40% energy saving was achieved.