



ZERO BRINE

D2.3 Bench scale test using equipment from Brine Excellence Center (BEC)

October 2020

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Author(s)	Amir Haidari (CITG-TU Delft) Eduardo Bologna, Dionysia Diamantidou (Lenntech) Maria Avramidi, Despina Bakogianni (NTUA) Andrea Cipollina (UNIPA) Daniyaal Zulfiqar, Faris Elasha (ARVIA) Panos Alexopoulos (AS-TU Delft) Hamed Rastegarian (TU Delft)
Reviewer	Bas Heijman (TU Delft)
Contact(s)	h.rastegarianjahromi@tudelft.nl
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Website	www.zerobrine.eu
Name of researcher(s) with roles	See Authors

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

WP2 aims at demonstrating two pilots at the industrial demi water plant of Evides Industry Water. One pilot (Site 01) will treat the spent regenerate of Evides' Cationic Ion Exchange (IEX) units, with the purpose to recover calcium hydroxide, magnesium hydroxide, sodium chloride and clean water. This pilot will be composed of three technologies: nano-filtration unit (supplied by Lenntech), multiple feed plug flow crystalliser (supplied by UNIPA) and evaporator (supplied by NTUA). The other pilot (Site 02) will treat the concentrate of Evides' reverse osmosis units, with the purpose to recover sodium sulphate, sodium bicarbonate, salt and clean water. This pilot will be composed of four technologies: anionic exchange unit (by Lenntech), organic matter removal unit (by ARVIA), nano-filtration unit (by Lenntech), eutectic freeze crystalliser (by TU Delft), reverse osmosis unit (by Lenntech) and residual heat-driven evaporator (by NTUA). Despite the advanced technology readiness levels it was considered imperative that the selected technologies be tested individually to assess their suitability to meet the WP's objectives, that is: integrating the individual technologies in two pilots and extracting the abovementioned components from the two specific brines. The tests were performed with the bench scale equipment from the Brine Excellence Centres. This delivery D2.3 reports on the setup, execution, and results of the bench scale test executed by each technology provider.

The setup of the bench scale tests was designed by using the results of the PHREEQC simulations (deliverable D2.1 Report on the results from the simulations using PHREEQC) and the physiochemical analyses on the wastewater composition (deliverable D2.2). Each individual supplier carried out the tests with their technology. Generally, the tests consisted of running the bench scale unit under controlled experimental conditions to find the optimal configuration and settings for integrated operation in the pilots. An important requisite was that the bench scale units were tested with realistic input streams, that is: the original brines from Evides or the output of other units. Due to the specific features of the individual technologies the experimental approach and results are diverse. This deliverable D2.3 reports for each technology its characteristics, the tests carried out, the test results and the conclusions. The conclusions served to justify the modifications, configurations and settings to be used in the final design of the two pilots, as further detailed in the subsequent deliverables D2.4 (Report explaining the design procedure) and D2.5 (Detailed engineering drawings). The bench scale tests resulted in two major deviations from the original design of the Site 02 pilot:

1. The originally envisaged ion exchange membrane crystallizer for Site 01 was replaced with a multiple feed plug flow reactor, because the latter one showed better performance under the conditions of Site 01.
2. The originally envisaged anion exchange unit for Site 02 was dropped from the pilot configuration, because competition between sulphate ions and organic matter would result in short operation cycles, frequent regeneration, lower regeneration efficiency and poor removal of both organics and sulphates. Instead, an alternative arrangement of the nano-filtration unit and organic matter removal unit was proposed, which will allow an alternate mode of operation of these units.

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1 Overview of the project

The ZERO BRINE project aims to facilitate the implementation of the Circular Economy package and the 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 will 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 brings together and integrates several existing and innovative technologies to recover products of high quality and sufficient purity to represent good market value.

A large-scale demonstration plant will be tested in the Energy Port and Petrochemical cluster of Rotterdam Port by using the waste heat from one of the factories in the port. The quality of the recovered products will be aimed to meet local market specifications. Additionally, three large-scale pilot plants will be developed in other process industries in Poland, Spain, and Turkey, providing the potential for immediate replication and uptake of the project results after its successful completion.

2 Objectives

This deliverable presents the obtained results from the performed bench scale activities from each technology provider. The results of bench scale tests are based on the PHREEQC simulations (Deliverable D2.1) and the physiochemical analyses on the wastewater composition (Deliverable D2.2).

The obtained results during the bench scale tests will be used to determine the relevant process parameters and optimize experimental conditions for the final engineering design (Deliverables D2.4 and D2.5). For instance, the results related to the presence of silica in design of Site 02 will be used to fine-tune the suggested process flow diagram presented in the grant agreement, and to finalize the selection of components for the demo plant.

This deliverable starts with giving a short introduction about the designs according to the grant agreement. Then it discusses the results obtained from the bench scale test performed by the technology providers. Finally, the obtained results will be discussed, and possible adjustments in the grant designs will be proposed.

3 Introduction

The activities in the Netherlands are a part of work package two (WP2) of the ZERO BRINE project. WP2 aims to demonstrate the circular economy in the Demi Water Plant (DWP) of Evides Industry Water in the Botlek industrial area (Rotterdam, The Netherlands) through redesigning the current situation (Figure 3-1). To this aim, two pilot designs will be demonstrated during the WP2 activities: one design (Site 01) for the treatment of the spent regenerant of cationic ion exchange columns and another design (Site 02) for the treatment of concentrate from reverse osmosis unit.

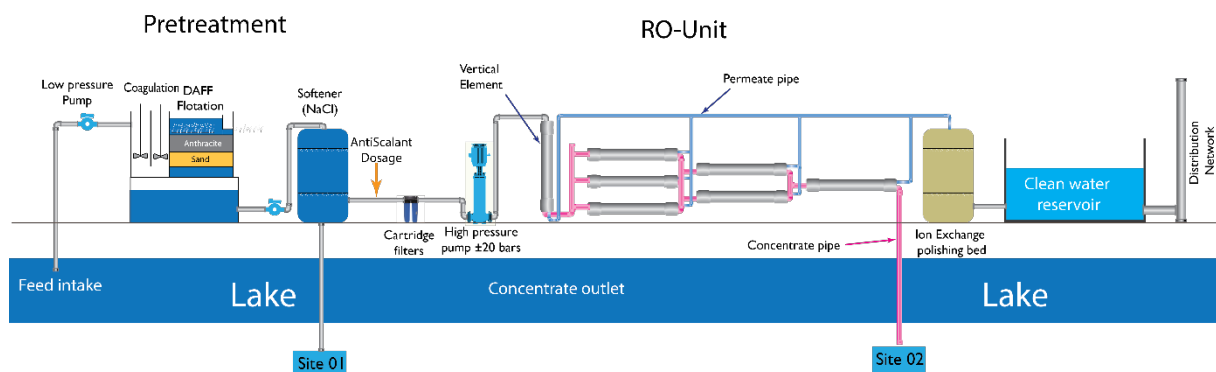


Figure 3-1: Schematic view of the current processes at the demineralized water plant of Evides Industry Water at Botlek (Rotterdam, The Netherlands). The aim of WP2 is to treat the regenerant from the ion exchange softener (Site 01) and to treat the concentrate of reverse osmosis (Site 2) and recover and reuse of salts from the wastewater (source: proofed course TU Delft)

The DWP at Evides (Figure 3-1) is fed with water from Lake Den Briel (Brielse Meer), which is one of the branches of the river Meuse (Maas). The DWP produces high-quality water by using several purification techniques. This high-quality water is supplied to a large number of companies in the Botlek area.

The DWP includes dissolved air flotation filtration (DAFF) to remove suspended matters from the intake water, cationic ion exchange (IEX) columns for removing divalent cations and soften the water, reverse osmosis (RO) to remove monovalent salts, and mixed bed ion exchange columns for polishing the RO permeate, that is: to remove traces of salts and charged organics, and make the permeate ready to be used by the companies.

3.1 Site 01

The operation of IEX columns is typically a discontinuous process and exists of a service run (loading phase) and regeneration. The produced water during the regeneration cycle is called spent regenerant, which is typically considered as wastewater and is disposed to water bodies in most cases. Spent regenerant disposal is often problematic with regard to costs and environment and is subject to regenerant quality, the site of the treatment plant and local laws and regulations. Disposal of the spent regenerant is not environment friendly mostly due to a high salt concentration of the solution.

ZERO BRINE offers a design to face the spent regenerant disposal challenge in the DWP of Evides. Before application, the suggested design will be tested on a pilot scale called Site 01 at location Plant One Rotterdam

(POR). POR is an experimental hall in the port of Rotterdam and very close to DWP of Evides. The distance from Evides to Plant One is about 500m.

In the design of Site 01, the spent regenerant from the IEX columns will pass through a nanofiltration (NF) membrane. NF separates the spent regenerant into permeate and concentrate. Theoretically, NF permeate should contain mainly water and monovalent ions such as Na^+ and Cl^- (Haidari et al. 2018). While the NF permeate flows directly toward an evaporator, the NF concentrate passes through a crystallisation unit wherein the calcium and magnesium will be recovered. The objective of the Bench Scale Tests (BST) done by Lenntech was to test several commercial NF membranes and to determine the quality of permeate and concentrate of these membranes to find the most suitable NF membrane that separates the monovalent ions from multivalent ions.

The evaporation unit is the last step of Site 01. It receives the monovalent rich NF permeate and the NaCl rich effluent from crystallisation unit. The effluent of the evaporator consists of purified water and a stream with a high NaCl concentration. The objective of the BST using the evaporator was to determine the efficiency of the evaporator and quality of the water and brine produced by evaporator.

During the crystallisation, the pH in the Multiple-Feed Plug Flow Reaction (MF-PFR) is changed to recover Mg and Ca minerals in the form of hydroxide. The main objective of the BST using the crystallisation unit was to determine the quality of the produced minerals and enhance the design of MF-PFR.

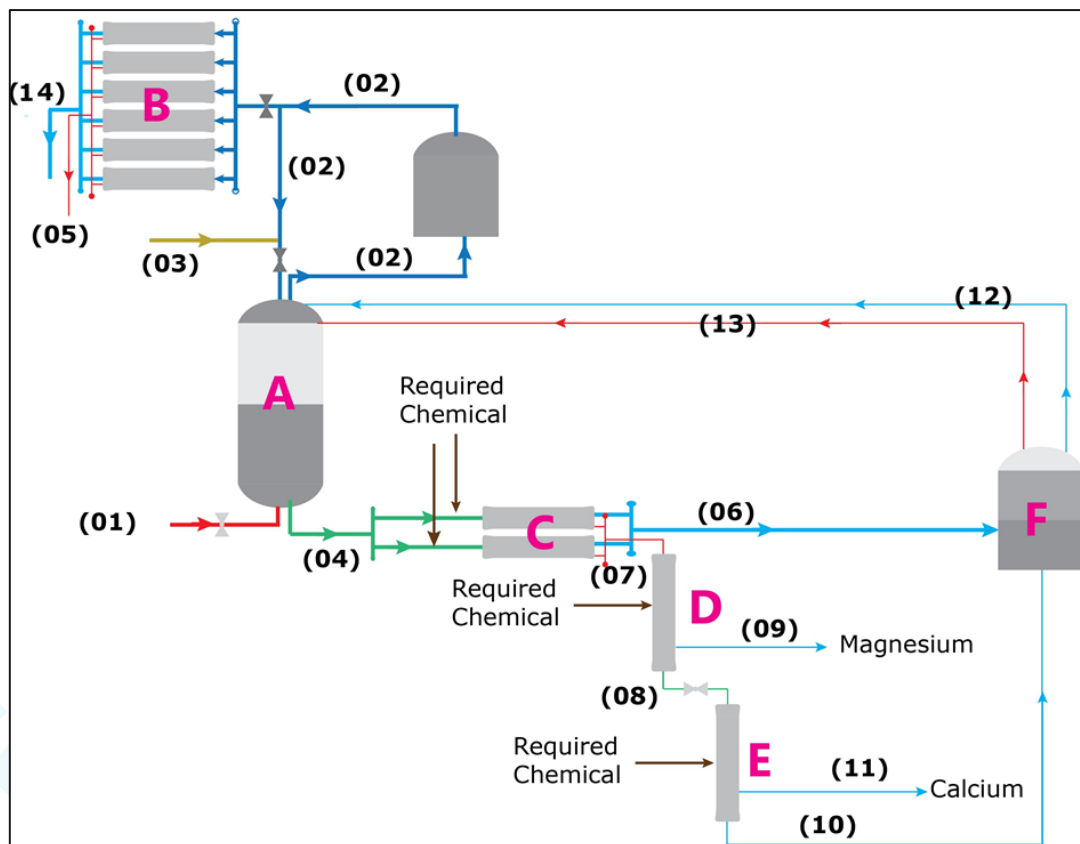


Figure 3-2: Initial design of Site 01 according to grant agreement: identification of process units and description of flows are mentioned in Table 3-1.

Table 3-1: identification of process units and description of units for Site 01 (Figure 3-2) based on the primarily calculation done in the grant agreement

process units			
A	IX: ion exchanger (existing)	existing unit at Evides	
B	RO: reverse osmosis unit (existing)	existing unit at Evides	
C	NF: nanofiltration unit	provided by Lenntech for ZERO BRINE	
D, E	crystallisation units for recovery of Mg and Ca	provided by UNIPA for ZERO BRINE	
F	evaporator unit	provided by NTUA for ZERO BRINE	
flows			
Id	Flow description	Amount	Quality
01	surface water IEX influent: pretreated	NA	NA
02	IEX effluent (softened water), used as feed for RO and for regenerating IEX (current situation)	NA	NA
03	NaCl brine for IEX regeneration	1000 L/h	See Table 3-3
04	spent regenerant (NaCl brine with exchanged cations)	1000 L/h	36 g/L TDS with 75% NaCl purity
05	RO concentrate (existing); waste	NA	NA
06	NF permeate, intended to be evaporator feed	700 L/h	11 g/L TDS with 96% NaCl purity
07	NF concentrate, intended to be metal recovery feed	300 L/h	94 g/L TDS with 69% NaCl purity
08	Mg crystallisation supernatant	300 L/h	98 g/L TDS with 75% NaCl purity
09	Mg salt suspension	0.92 kg/h	Mg Purity should be determined
10	Ca crystallisation supernatant	300 L/h	99 g/L TDS with 99% NaCl purity
11	Ca salt suspension	6.95 kg/h	Ca Purity should be determined
12	evaporator condensate (distilled water)	418 L/h	0 g/L TDS
13	NaCl brine (concentrated), for IEX regeneration	582 L/h	65 g/L TDS with 98% NaCl purity
14	RO permeate	NA	NA

3.2 Site 02

At Evides, the IEX effluent (softened water) during the service run is used as the feed water to the RO unit. The concentrate stream produced in the last stage of RO contains salts and organic matters and is discharged into the sea in the current DWP. Although, the concentration of salts and organics in the RO concentrate stream is lower than that of seawater, it could have negative environmental effects on the sea ecosystem due to use of chemicals added in the RO pretreatment. These added chemicals are rejected by the membrane and therefore will be present at an increased concentration in the concentrate stream.

Site 02 of ZERO BRINE is a proposed design that aims to treat the RO concentrate of DWP. To this aim, an anionic IEX is envisaged to be used to remove the anions and charged organic matters from the RO concentrate. The spent regenerant of anionic IEX will be fed to an organic matter (expressed as Total Organic Carbon – TOC) removal unit to remove the organics. The virtually organic-free stream will then be fed to an NF unit. The NF concentrate contains a high concentration of multivalent anions such as sulphate and monovalent ions. The NF concentrate is sent to a Eutectic Freeze Crystallisation (EFC) unit, wherein the concentrate will be separated into ice and salts.

The effluent of the anionic IEX column will pass to an RO unit that will be operated with a recovery of around 85%. The permeate of the RO unit can be used as process water and the concentrate will be sent to the evaporator, wherein it will be separated into pure water (condensate) and salts.

Monovalent-rich (mostly NaCl) permeate of NF can be mixed with the concentrate of the evaporator and be used for regeneration of the anionic IEX column.

The main objectives of the BST for this pilot are as follow:

- Determining the efficiency of the anionic IEX for removing of anions and organic matters (by Lenntech)
- Determining the Efficiency of Nyex for removing the organics (by Arvia)
- Determining the efficiency of NF for separating monovalent ions from multivalent ions in presence of organics (by Lenntech)
- Determining the highest recovery of RO (by Lenntech)
- Determining the efficiency of EFC for recovery of sulphate in saline water (AS-TU Delft)
- Determining the efficiency of evaporator for recovery of water and sodium bicarbonate salt (NTUA)

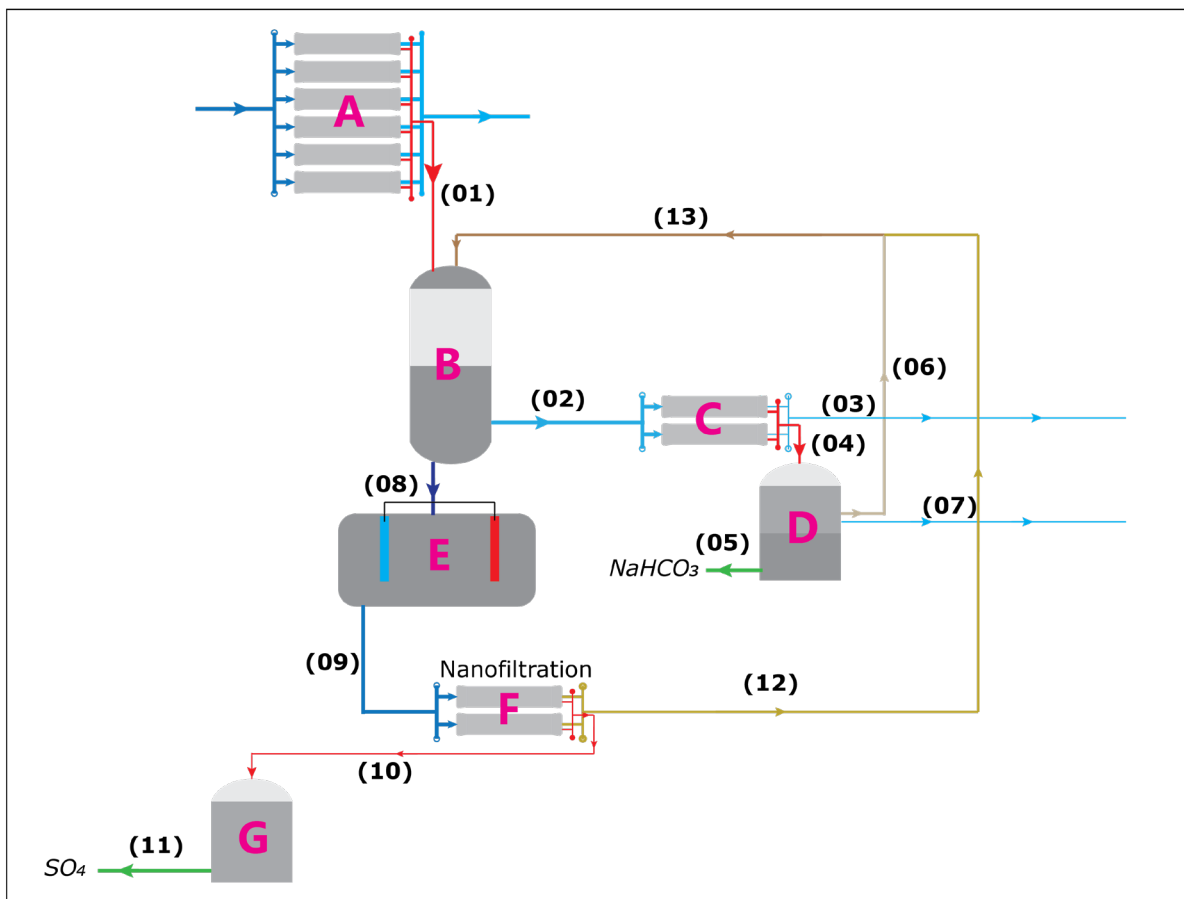


Figure 3-3: Block view of Site 02 of ZERO BRINE project

Table 3-2: identification of process units and description of units for Site 02 (Figure 3-3) based on the grant agreement

process units			
A	RO: reverse osmosis unit (existing)	existing unit at Evides	
B	IEX: Anionic Ion Exchange Column	provided by Lenntech for Zero Brine	
C	RO: Reverse Osmosis	provided by UNIPA for Zero Brine	
D	evaporator unit	provided by NTUA for Zero Brine	
E	Nyex: TOC removal unit	Provided by ARVIA	
F	NF: Nanofiltration unit	Provided by Lenntech	
G	EFC: Eutectic Freeze Crystallization unit	Provided by Applied Science of TU Delft	
flows			
Id	Flow description	Amount	Quality
01	Concentrate of existing RO at DWP of Evides	12000 L/h	NA
02	Effluent of anionic ion exchange column (removing of anions and organics)	11400 L/h	3 g/L TDS with 63% NaCl purity
03	Permeate of installed RO	10260 L/h	0.03 g/L TDS
04	Concentrate of RO intended to be the evaporator feed	1140 L/h	30 g/L TDS with 63% NaCl purity
05	Evaporator precipitations	NA	NA
06	Evaporator supernatant	646 L/h	118.5 g/L TDS with 98% NaCl purity
07	Evaporator condensate (distilled water)	974 L/h	0 g/L TDS
08	Spent regenerant of anionic ion exchange column	600 L/h	99 g/L with 0.91 NaCl Purity
09	Effluent of Nyex (organic removal unit)	600 L/h	99 g/L TDS with 91% NaCl purity
10	NF concentrate, intended to be EFC feed	120 L/h	137 g/L TDS with 71% NaCl purity
11	SO4 salt suspension	240 g/h	SO4 purity should be determined
12	NF permeate, intended to be mixed with evaporator	480 L/h	89 g/L TDS with 99% NaCl purity
13	NaCl brine (concentrated), for IEX regeneration	L/h	204 g/L TDS with 97% NaCl purity

3.3 Summary of PHREEQC calculations

PHREEQC was used to simulate precipitation of salts at Site 01 (Deliverable D2.1). The obtained results from PHREEQC calculations indicated that magnesium and Calcium may be separated with great efficiency from spent IEX regenerant. However, a recovery of 99% or greater of these materials will not be possible. Especially in the case of calcium, a small part of the material might end up as scaling before reaching the crystallisation step.

Even though selective precipitation of $Mg(OH)_2$ and $Ca(OH)_2$ is possible theoretically, under the actual conditions, the simulations indicated that it is almost impossible to produce the hydroxides in pure form. That is because together with the hydroxides, also carbonates, sulphates and other minerals may co-precipitate, depending on the anions present. The presence of these impurities varies as different concentration of anions were found in the different samples. Still, the salts contained Mg and Ca with at least 97% purity in all cases studied.

The amount of hydroxides recovered is directly dependent of the amount of hydroxide dosed, as metal hydroxides are the main minerals precipitated, and the amount of material precipitated is limited by the amount of hydroxide ion present. Thus, dosing of hydroxide should be well controlled as, especially in the first crystallization reactor, excess NaOH dosed might cause $Ca(OH)_2$ to precipitate prematurely. Thus, hydroxide dosing for Mg^{2+} and Ca^{2+} precipitation should be well controlled, probably based on supernatant pH.

No scaling problem will occur at the evaporator unit if only NF permeate is fed. While the quality with respect to the abundance of sodium and chlorine ions is higher compared to the situation that a mixture of the NF permeate

and the crystallizer effluent is fed to the evaporator. However, one drawback of a mixture feed is a possible calcium dominated scaling in the evaporator unit. Another drawback of using a mixture feed is that the produced salts by the evaporator cannot be used for regeneration of IEX columns anymore because the impurities of the produced salts will cause a faster exhausting of the IEX columns. This will result in a more frequent regeneration of the IEX columns, more frequent replacement of resin and consequently higher operational costs. To the authors view and based on the calculations done in this document, it is essential to study the effluent of crystallizer carefully and consider other possible options before deciding on mixing it with permeate of NF as feed for the evaporator.

In spite of the great detail of the modelling results, the exact effect of closing the water cycle in the process cannot yet be calculated. In the first place because a large variation between samples (process cycle input) was observed, and in the second place because the exact process conditions and process regulation is not yet defined. However, even with the actual, limited, results it can be foreseen that adjustments may be necessary, because in the scheme as suggested no bleed is present. This means that all ions present in the feed but not removed as product, like for instance Ni^{2+} , Zn^{2+} , Sr^{2+} and nitrate, to name a few, will over time accumulate in the regeneration cycle, causing deterioration of the process and product specifications in the long run. Bleeding, however, may be as simple as releasing part of the mother liquor of Ca-precipitation; or releasing part of the NF permeate. This can be calculated once process conditions are better defined, and once additional measurements of the process feed give a better indication of what will enter the process cycle.

3.4 Summary of physiochemical wastewater characteristics

Table 3-3, Table 3-4, and Table 3-5 show the inorganics in the feed stream of Site 01, inorganics in the feed steam of Site 02, and organic matters present in the feed stream of Site 02. The results shown in each column (IEX_EXP) are the average measurements for a specific period representing seasonal variation of feed water. Each average value is obtained by analysing at least four samples. Each sample is analysed at least three times using different dilution factors. Cations were measured with ICP-MS, anions with test kits and organic matters with LC-OCD.

It is difficult to give a clarification for the seasonal variation of ion concentrations obtained for the spent regenerant of IEX because taking samples at the same moment was difficult. The highest concentration ions as well as organic matter in the concentrate of RO was in March and May when ambient temperature started to increase.

Table 3-3: Ions present in the spent regenerant of cationic Ion exchange

Element	Symbol	MW	Unit	IEX_EXP_Dec	IEX_EXP_Mar	IEX_EXP_Apr	IEX_EXP_Jul
Sodium	Na	23	mg/L	1703	7974	8145	6307
Magnesium	Mg	24	mg/L	1248	1337	1069	1414
Potassium	K	39	mg/L	236	228	321	257
Calcium	Ca	40	mg/L	6523	8538	7211	7038
Silica	SiO ₂	60	mg/L	1.97	0	0	0
Iron	Fe	56	mg/L	0	4.13	0.49	0.25
Strontium	Sr	88	mg/L	25	42	35	40
Titanium	Ti	48	µg/L	0.00	17.04	31.99	41.60
Vanadium	V	51	µg/L	84.57	274	0.58	0.00
Chromium	Cr	52	µg/L	13.77	154	40.0	6.14
Arsenic	As	75	µg/L	15.31	0	1.76	2.38
Selenium	Se	79	µg/L	3.63	0.66	43.7	28.23
Lithium	Li	7	µg/L	119	363	64.3	114
Boron	B	11	µg/L	20	67	1807	2223
Aluminium	Al	27	µg/L	0.14	1020	4.32	2447
Manganese	Mn	55	µg/L	10.21	226.81	0	0
Cobalt	Co	59	µg/L	0	88.98	4.86	2.35
Nickel	Ni	59	µg/L	205	2858	82.4	3.63
Copper	Cu	64	µg/L	34.16	59.52	0	60.45
Zinc	Zn	66	µg/L	103	156	173	44.6
Molybdenum	Mo	95	µg/L	1.27	13.81	7.61	0.37
Silver	Ag	107	µg/L	0.04	11.12	17.98	18.21
Cadmium	Cd	112	µg/L	0.35	0	14.19	12.22
Antimony	Sb	122	µg/L	0.59	22.8	0	0
Barium	Ba	137	µg/L	3554	4919	4436	5279
Thallium	Tl	205	µg/L	0.52	0	0	0
Lead	Pb	207	µg/L	0.03	220	502	424
Chloride	Cl	35	mg/L	17821	31305	28569	26440
Nitrate	NO ₃	62	mg/L	43.7	22.9	51.9	30.2
Phosphate	PO ₄	95	mg/L	1.78	0.29	0.02	0.72
Bicarbonate	HCO ₃	61	mg/L	143	140	115	109
Sulphate	SO ₄	96	mg/L	149	212	124	77
Total dissolved solids	TDS	-	mg/L	27874	49772	45614	41683
Electric. conductivity	EC	-	mS/cm	43.4	80.25	76.4	69.6
Averaged pH	pH	-	-	7.26	7.08	6.86	6.66

Table 3-4: Inorganic ions present in concentrate of existing RO at DWP of Evides

Element	Symbol	MW	Unit	RO_EXP_Dec	RO_EXP_Mar	RO_EXP_Apr	RO_EXP_Jul
Sodium	Na	23	mg/L	845	1202	959	1056
Magnesium	Mg	24	mg/L	0.17	2.17	0.07	0.06
Potassium	K	39	mg/L	13.4	14.3	0	18.3
Calcium	Ca	40	mg/L	0.52	3.34	2.16	2.30
Silica	SiO ₂	60	mg/L	42	38	28	16
Iron	Fe	56	mg/L	0	0.30	0.02	0.02
Strontium	Sr	88	mg/L	2.85	0	8.15	8.18
Titanium	Ti	48	µg/L	1.19	0	0	0
Vanadium	V	51	µg/L	5.38	4.72	0.05	0.16
Chromium	Cr	52	µg/L	1.81	4.09	11.3	5.10
Arsenic	As	75	µg/L	1.01	0	0.99	2.01
Selenium	Se	79	µg/L	0.69	1.75	8.27	7.35
Lithium	Li	7	µg/L	45.8	83.3	49.9	93.5
Boron	B	11	µg/L	122	123	183	98
Aluminium	Al	27	µg/L	0.70	2.70	0.06	0.06
Manganese	Mn	55	µg/L	0	0	0	0.45
Cobalt	Co	59	µg/L	0	2.92	1.61	1.81
Nickel	Ni	60	µg/L	9.02	13.6	20.1	22.1
Copper	Cu	65	µg/L	12.9	0	51.2	7.54
Zinc	Zn	66	µg/L	18.0	0	71.6	36.3
Molybdenum	Mo	95	µg/L	9.31	10.7	7.63	12.7
Silver	Ag	107	µg/L	0.15	0	0.83	0.99
Cadmium	Cd	112	µg/L	0.01	0	0.04	0.03
Antimony	Sb	122	µg/L	1.56	1.77	1.26	1.87
Barium	Ba	137	µg/L	0.60	0	4.62	3.10
Lead	Pb	207	µg/L	0.16	7.10	3.63	4.25
Chloride	Cl	35	mg/L	514	1122	704	846
Nitrate	NO ₃	62	mg/L	39.4	7.32	53.4	22.4
Phosphate	PO ₄	95	mg/L	0	2.93	0.03	0.05
Bicarbonate	HCO ₃	61	mg/L	871	863	947	955
Sulphate	SO ₄	96	mg/L	371	335	271	320
Total dissolved solids	TDS	-	mg/L	2696	3591	2966	3237
Electrical conductivity	EC	-	mS/cm	3.22	4.03	3.30	4.09
Averaged pH	pH	-	-	9.8	8.81	8.87	8.79

Table 3-5: Organic matters present in concentrate of existing RO at DWP

Sample name	biopolymers	Humic Substances	Building Blocks	LMW Neutrals	LMW Acids	HOC	POC	CDOC	DOC	TOC
	(µg/L C)	(µg/L C)	(µg/L C)	(µg/L C)	(µg/L C)	(µg/L C)	(µg/L C)	(µg/L C)	(µg/L C)	(µg/L C)
EXP_Dec	239	5215	1975	1708	<200	325	38	9133	9460	9498
EXP_Mar	630	6911	2432	2841	<200	957	18	12800	13750	13800
EXP_Apr	492	6583	2068	2413	<200	722	60	11550	12275	12325
EXP_Jul	262	5528	2073	8935	<200	901	-82	10600	11500	11425

4 Site 01

4.1 Lenntech: Nanofiltration

4.1.1 Description of technology

Nano filtration (NF) is a membrane filtration process, similar to the industrially applied reverse osmosis, however with a 'coarser' pore size. That is, the pores of the membranes are wider than RO, allowing hydrated monovalent ions to pass through it. NF is often applied to remove multivalent ions such as calcium and magnesium, to soften water, or for the removal of heavy metals. Therefore, NF membranes can be used to separate calcium (Ca^{2+}), magnesium (Mg^{2+}) and sulphate (SO_4^{2-}) ions stream from a sodium chloride rich and purified stream.

NF, like RO, requires a flow tangential to the membrane, known as cross-flow, in order to minimize fouling by concentration polarization effects. Therefore, a feed stream will be separated into a permeate stream with predominantly monovalent ions and a concentrate stream with predominantly multivalent ions. NF membranes typically achieve a multivalent ion rejection between 75-99% and monovalent ion rejection between 30-50%, depending on the chemistry of the membrane active layer. As the separation is not perfect, the permeate stream may contain multivalent ions and concentrate stream monovalent ions. Therefore, it is important to consider the design of the NF on a system level, as well as the process parameters such as pH, temperature and solution chemistry, which can influence the passage of mono- and multivalent ions through the membranes. Furthermore, the interaction of different ions in the feed will have an effect on the passage of specific ions. NF membrane performances, in fact, are characterized by means of three adjustable parameters: average pore radius, volumetric charge density and effective membrane thickness. These mechanisms are described through the steric effect, the Donnan equilibrium and the dielectric exclusion (see *Figure 4-1*).

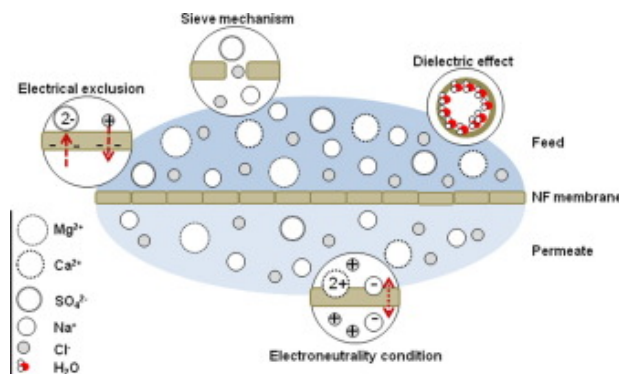


Figure 4-1: Rejection mechanisms of NF membranes

Steric partitioning concerns the sieve effect due to porosity of the membrane. Ions are rejected based on size exclusion, when their molecular weight (MW) is larger than the cut-off characteristics of the membrane or due to their hydrophobicity. Donnan equilibrium plays a relevant role in case of charged membranes by giving favourable partitioning for counter-ions and unfavourable partitioning for co-ions. Dielectric exclusion is promoted by a different dielectric constant between the bulk solution and the membrane pores. It presents a barrier to ion solvation into the pores which leads to a higher ion rejection ratio.

4.1.2 Scheme and photo of equipment

All membrane experiments were performed at the laboratory scale with cross flow module using a flow cell called “Sepa cell”. The unit was used to perform the tests with different flat sheet membranes and is basically composed of a cell body holder where the membranes are placed, a pump, a feed tank reservoir, a flow indicator on the concentrate stream, a pressure indicator on the feed pump and on the concentrate valve. Figure 4-2. represents the main components of the system used for the nanofiltration experiments.

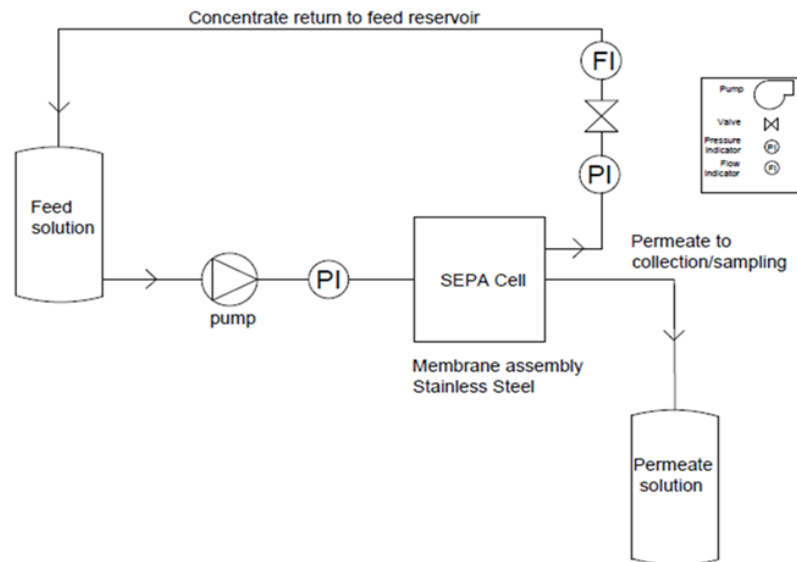


Figure 4-2: P&ID Sepa Cell testing unit for nanofiltration experiments

To conduct the experimental tests, the feed solution was separated by the nanofiltration membrane into permeate and concentrate stream. below, shows a photo of the Sepa Cell unit and the main components (left) as well the cell holder, upper cell body and bottom cell body (right side).

4.1.3 Description of tests done

To simulate as close as possible the regeneration brine stream of the ion exchange unit of EVIDES, a feed solution representing the concentration of different ionic species was prepared in the laboratory. This artificial chemical solution was prepared by a mixture of several chemicals that were precisely weighed and continuously stirred before operation in order to obtain a homogenous final solution. This chemical solution consisted of calcium chloride CaCl_2 , magnesium chloride MgCl_2 , sodium chloride NaCl , potassium chloride KCl , barium chloride BaCl_2 and strontium chloride SrCl_2 to attain the desired ionic concentrations described in Table 4-1. For each single experiment, to test each membrane a new chemical solution was prepared where the same laboratory methods was used.

Table 4-1: Chemical composition of artificial feed solution

Name	Concentration (mg/L)
Sodium (Na)	3266
Magnesium (Mg)	1769
Potassium (K)	336
Calcium (Ca)	7500
Strontium (Sr)	25
Barium (Ba)	12
Chloride (Cl)	24000

In the beginning of each experiment, three different fluxes of 15, 30 and 45 L/m²h (LMH) were tested for 90 minutes each with the recirculation of concentrate and permeate back to the feed tank. During this period, samples of permeate and concentrate were collected. The operating conditions, presented Table 4-2, were maintained throughout all the experiments. Additionally, before every experiment the membrane remained immersed in demi water during a period of approximately 24h before use. During the experiments the concentrate stream was continuously recirculated back to the feed, and the permeate was collected in a glass cylinder. To generate permeate flow through the membrane, feed pressure was applied by means of a positive displacement pump and by adjusting the concentrate valve. The flux of permeate through the membrane was monitored at regular intervals by a mass flow meter placed on the permeate stream, while the concentrate was recorded by a flow meter, both data were converted and recorded on the computer. Based on the available active area of the membrane (0.014 m²), the membrane flux was determined. Correction of pH and control of temperature during operation were done along all the experiment. The temperature was maintained constant along all the experiments by introducing a spiral heat exchanger inside of the feed tank. In addition, the conductivity was measured in the feed tank and concentrate stream. To characterize the process, samples from the permeate and concentrate streams were collected at different recoveries along the process.

Table 4-2: Experimental operating conditions

Operating conditions	
Feed flow (L/h)	430
Permeate flux (LMH)	30
Operating temperature (°C)	20
Initial volume (L)	8
pH	8

The system was operated with a flux of 30 LMH. The feed temperature maintained at 20 °C through the whole experiment. In order to select the best nanofiltration membrane, different membranes with different molecular weight cut off were tested from different suppliers. Six candidate membranes were tested to select the membrane that could give the best rejection performance of divalent ions such as Ca²⁺ and Mg²⁺. Table 4-3 shows the names and specifications of the six evaluated membranes.

Table 4-3: Nanofiltration flat sheet membranes used on the experiments.

Model	Vendor	Polymer
NFG	Synder	PA
NFW	Synder	PA
NF270	Dow	PA
SR3D	Koch	PA
TS80	Trisep	PA
NF90	Dow	PA
RO98pt	Alfa Laval	PA
LFC3-LD	Hydranautics	PA

4.1.4 Summary and discussion of tests done

Among the six membranes, TS80 with a molecular weight cut off of 150 Da showed the best separation performance of divalent from monovalent ions. The TS80 performance was evaluated in terms of rejection and it was used as single and double pass. Considering that no membrane performs a perfect separation, it was important to consider the design of the membrane system using double pass NF. The double pass was introduced in this study since some of the divalent ions such as magnesium and calcium passed through the membrane into the permeate side and could consequently lead to a lower quality of the regeneration solution the Evides IEX columns. Therefore, the divalent ions that were not rejected during the first pass may be rejected on the second, promoting a permeate stream richer in monovalent species. The test results for this membrane for single and double pass are presented and discussed along this section.

Figure 4-3 shows the rejection of the presented species tested for one pass using three different fluxes of 15, 30 and 45 LMH where the feed concentration was kept constant once both concentrate and permeate streams were recirculated back to the feed. It can be seen in Figure 4-3 that for high values of membrane flux the rejection of the diluted species increased. For a selected membrane flux of 30 LMH the rejection of the four divalent species presented on the feed such as Mg^{2+} , Sr^{2+} , Ba^{2+} and Ca^{2+} attained rejections of 91.11%, 90.77 %, 92.39% and 89.37%, respectively. However, for the same flux of 30 LMH, chloride, as monovalent ion, also showed a high rejection of 77%.

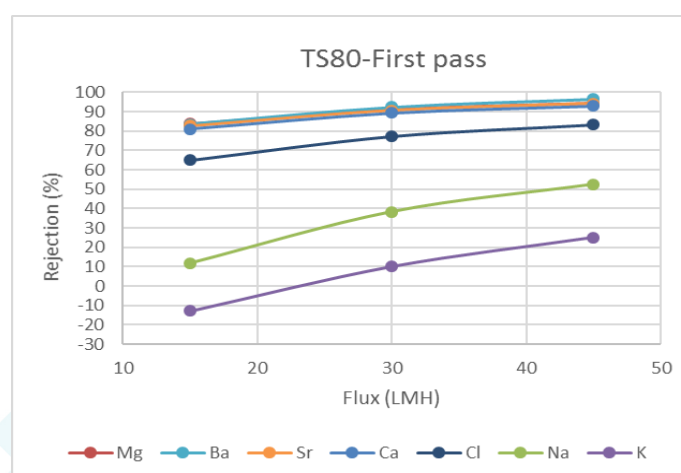


Figure 4-3: Membrane TS80 - Ionic rejection at different membrane fluxes of 15, 30, 45 LMH.

From 3 different fluxes, a constant membrane flux of 30 LMH represented a typical flux of larger scale operation and it was selected for discussion. At this flux, the membrane was then tested for its rejection of divalent ions such as Mg^{2+} , Sr^{2+} , Ba^{2+} and Ca^{2+} for 3 different concentration factors of 1, 2 and 2.5 corresponding to a certain system recovery of 0%, 50% and 60%, respectively. During the operation the membrane was able to reject Ca^{2+} and Mg^{2+} at around 89% and 91%, respectively, keeping this value constant for higher system recoveries, see *Figure 4-4*. The remaining ionic species pass through the membrane towards the permeate stream. Strontium and barium showed approximately high and constant rejections during operation of around 91% and 93%, as occurred in the case of calcium and magnesium. However, chloride as monovalent ion showed a high rejection of around 78%, thus with 22% passage to the permeate. This can be explained by the fact that chloride as the only anion remains in the feed side to maintain the electro-neutrality condition as Ca^{2+} and Mg^{2+} are highly rejected. On the other hand, sodium and potassium both showed a high passage through the membrane (*Figure 4-4*).

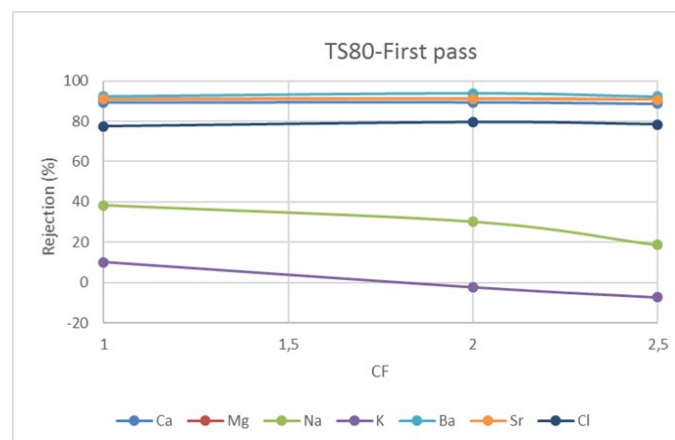


Figure 4-4: Membrane TS80 - Ionic rejection vs. concentration factor for a flux of 30LMH.

Figure 4-5a and *Figure 4-5b* show the results for the test with varying concentration factor in terms of concentration of all species in study for the permeate and concentrate streams. As expected, chloride showed the highest concentrations among all the other salts in solution. Even though the concentration of chloride in the permeate increases along with the concentration factor, this increase is desired to be higher for a monovalent ion. For instance, for a recovery of 60%, or concentration factor of 2.5, the concentration of chloride on the permeate stream was almost 7 times lower compared with the concentration of chloride that was rejected to the concentrate. The concentration of chloride in the permeate stream increased from 5500 mg/L to 7300 mg/L whereas in the concentrate stream the initial chloride was almost the same as the concentration of chloride presented in the initial feed, which was around 24000 mg/L increasing to a concentration of 49700 mg/L at a concentration factor of 2.5.

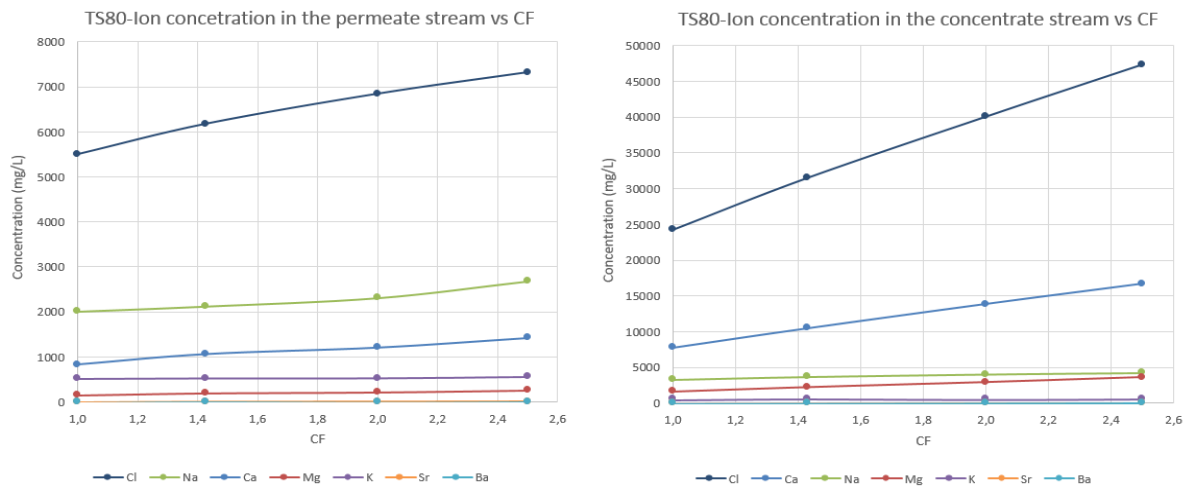


Figure 4-5: Membrane TS80 - Ionic concentration species vs. concentration factors on the permeate stream (a) and concentrate stream (b).

Highlighting the importance of the rejection of calcium and magnesium as divalent ions of added commercial value, the concentrate stream should be as rich as possible in these species whereas the permeate should contain the majority of monovalent ions. To improve this separation, additional lab tests were conducted using the membrane TS80 as a second pass. The double pass NF was conducted maintaining the same conditions of operating flux, temperature and pH as the first pass (Table 4-2). Figure 4.7 shows a schematic representation of double pass NF used during the laboratory tests where the concentrations of each ion in solution for feed, permeate and concentrate are depicted. Using the same membrane for the second pass NF, the permeate was used as the feed of the second pass.

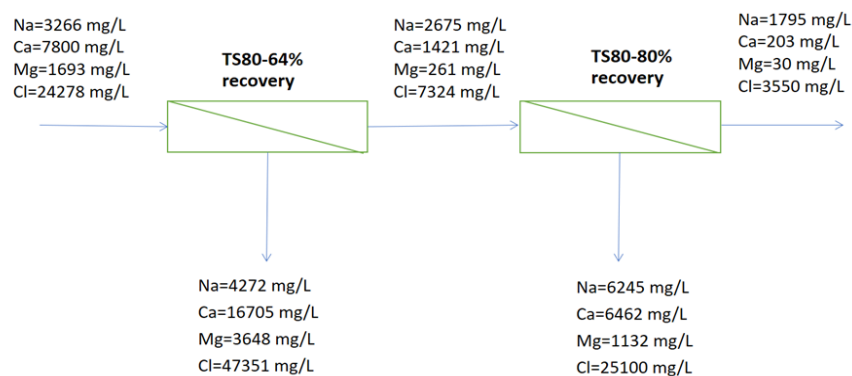


Figure 4-6: Double pass NF using TS80 membrane

The Table 4.4 and the following graphs show the achieved ionic concentrations for the different concentration factors after testing TS80 in a second pass configuration. The rejections of the divalent cations using a double pass NF with TS80 membranes gave similar results when compared with only single pass. However, the rejections of monovalent ions increased and for sodium this rejection presented an increase of 27%. The molar ratio of this solution was 60% lower than the molar ratio of the initial solution.

Table 4-4: Concentration of permeate and concentrate streams for different CF using double pass NF with TS80 membranes

Ions	Streams concentration (mg/L)					
	Feed water	Permeate				Concentrate
		CF=1	CF=2	CF=3.33	CF=5	CF=5
Ca ²⁺	1421	143	160	185	203	6462
Mg ²⁺	261	23	25	28	30	1132
Na ⁺	2675	1375	1514	1725	1795	6245
Cl ⁻	7324	2700	3000	3400	3550	25100

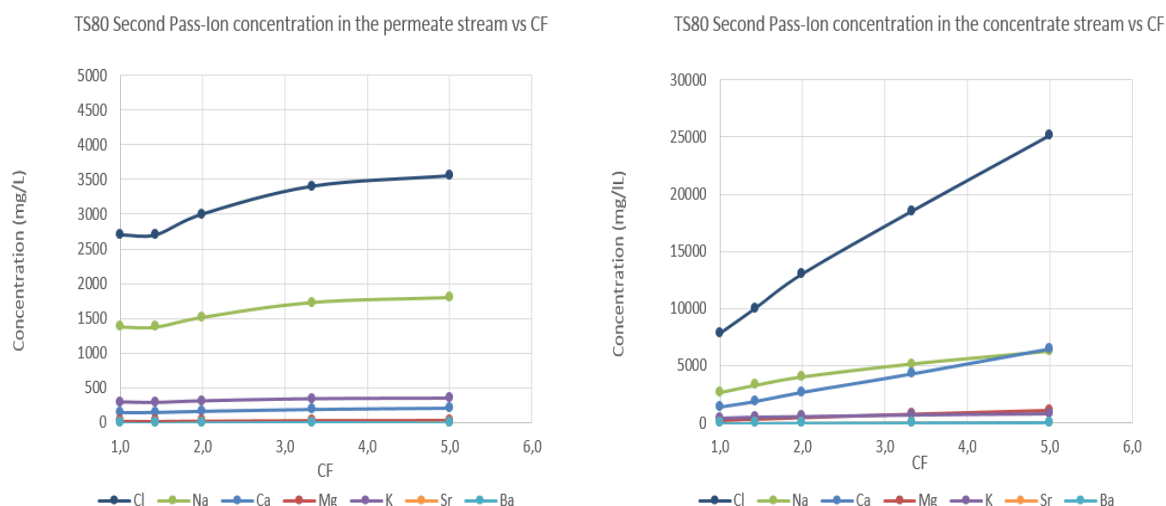


Figure 4-7: Concentration of permeate and concentrate streams for different CF using double pass NF with TS80 membranes.

A last test with the addition of 300 mg/L of sulphate ions was performed to verify its influence on rejections of other ions. This test was performed for three different fluxes of 15, 30 and 45 LMH using TS80 membrane. Results shown in Figure 5.9 indicate a slight increase of Ca²⁺ and Mg²⁺ rejection when SO₄²⁻ was added. For instance, for a single pass NF, Ca²⁺ and Mg²⁺ rejections were respectively 89% and 91%, whereas an increase of their rejections was observed of 94% for Ca²⁺ and 95% for Mg²⁺ when sulphates were added. This performance can be explained by three distinctive factors, being that the first compromising factor is related with the usage of another flat sheet coupon that might have a different MWCO and consequently a different ionic rejection performance. However, assuming that the MWCO of both membranes were the same, if SO₄²⁻ was present besides Cl⁻ in the feed phase, both ions were competing as counterions in the transport of the cations. Since SO₄²⁻ is larger than Cl⁻, this resulted in a lower transport of certain ions to the permeate side and consequently a higher rejection. Another explanation can be found in the ionic pairing of Ca²⁺ and SO₄²⁻ that might occur and lead to higher rejection according to the steric effect. The steric effect is a size-based mechanism, meaning that the rejection is based on the pore size of the membrane and the ionic size.

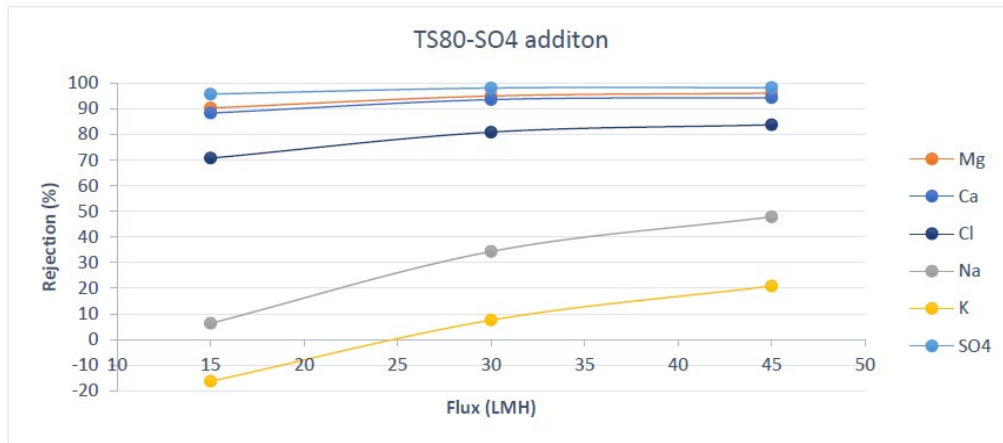


Figure 4-8: Ion rejection of TS80 with the addition of 300 mg/L of sulphates.

4.1.5 Conclusions

From the obtained results, TS80 NF membrane using a single pass showed the best separation of mono- and multivalent ions among all the other tested membranes. The single pass NF gave the best rejection performance of 89% for Ca^{2+} and 91% for Mg^{2+} for a constant membrane flux of 30 LMH.

A double pass NF using TS80 was used to increase the separation of mono- and multivalent ions considering that no membrane performs a perfect separation. In conclusion, the rejections obtained by using a double pass configuration were close to the rejections when a single pass was tested. Additionally, the rejection of monovalent ions was increased, of which sodium showed an increase of 27% in comparison with the test done with only one pass.

4.2 UNIPA

4.2.1 Description of technology

The Crystallisation physical phenomenon includes the formation of particles in vapours, the solidification of melted mixtures or the species precipitation in aqueous solutions. In particular, reactive crystallisation can be used to produce an insoluble salt by reaction of two ions when the species are dissolved in an electrolyte solution. This is the case of magnesium hydroxide precipitation from electrolytic solution by means of a reaction with an alkaline specie such as sodium hydroxide. Different reactors can be consider for this purpose. In particular, at UNIPA BEC laboratory the following equipment was built and tested:

- Batch and semi-batch system;
- CSTR (Continuous Stirred Tank Reactor);
- MF-PFR (Multiple Feed – Plug Flow Reactor)
- CrIEM (Ion Exchange Membrane Crystallizer), patented by UNIPA team within a previous project.

The batch system is a conventional and not continuous reactor in which a certain volume of both solutions are filled together in a tank at the beginning of the test, after that the reaction takes place. This configuration was used for the proof of the concept to recovery magnesium hydroxide and remove calcium hydroxide from the waste industrial brine. This Configuration can be slightly modified if the brine is one of the solutions that is fed at the beginning in the reactor and the other one is continuously fed until the reaction achieved the complete conversion. This is the case of a semi-batch reactor.

A CSTR, is constituted by a tank with a stirrer in which two solutions are continuously fed with the possibility to have a recycle of solution if this is required by the plant configuration.

A Plug Flow Reactor (PFR) is a process in which, ideally, the solution containing the reactants moves with a piston flow, i.e. with a speed without radial gradients; the reaction occurs along the entire length of the reactor and at steady state, and is not a function of time but only of space. Passing from ideality to reality, the piston flow hypothesis becomes only an approximation. This traditional reactor was slightly modified introducing more than one feed for the alkaline solution, in order to have a better supersaturation distribution along the reactor. This configuration is called “Multiple Feed – Plug Flow Reactor” (MF-PFR).

The CrIEM is a membrane reactor in which the brine is separated from the alkaline solution by means of an ionic exchange membrane. The OH^- ions move from the alkaline solution to the brine to allow the precipitation of magnesium hydroxide while the chlorides present in the brine move in the opposite direction to re-balance the electric charge. This reactor is patented and has already aroused interest in many research sectors.

4.2.2 Scheme and photo of equipment

A batch and semi-batch system was widely used in the past to perform preliminary tests and to confirm the possibility to produce magnesium hydroxide and calcium hydroxide by reactive precipitation process. The batch system operated in a semi-continuous system by adding the alkaline solution drop by drop with a syringe pump, and was used to simulate time-dependent operation of a continuous system. The process scheme is depicted in Figure 4-9.

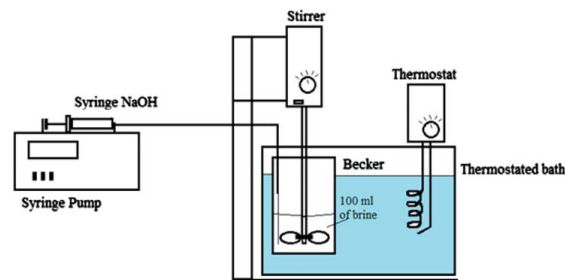


Figure 4-9: Scheme of semi-batch system for the precipitation of magnesium hydroxide and calcium hydroxide from waste brine.

A beaker is positioned in a thermostatic bath in order to control the temperature. The solution is continuously stirred to have a homogenous suspension.

A CSTR is used to test the performance of a continuous system in which both solutions, alkaline solution and electrolyte solution, are continuously fed. In this configuration, there is a recycle in order to reduce a local supersaturation and improve the crystal size distribution.

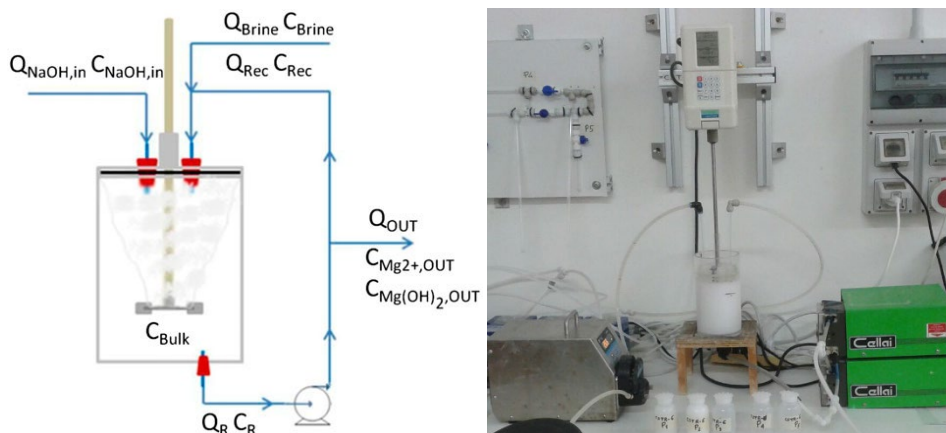


Figure 4-10: Scheme process of CSTR for the precipitation of magnesium hydroxide and calcium hydroxide from waste brine.

The plug flow reactor (PFR) is a cylindrical reactor, in which the “reagent” solution moves with a plug flow, with negligible radial gradient of velocity, concentration and temperature. At steady state, the reaction is only a function of space. As said before, in real conditions, the plug flow is only an approximation because in reality the no slip condition near the wall tube necessarily produces a velocity profile. The MF-PFR used in the first experimental campaign had one inlet for the feed brine and four inlets for the alkaline reactant. Since reaction is practically instantaneous, magnesium ions precipitate after each injection having enough space to react along the reactor segment.

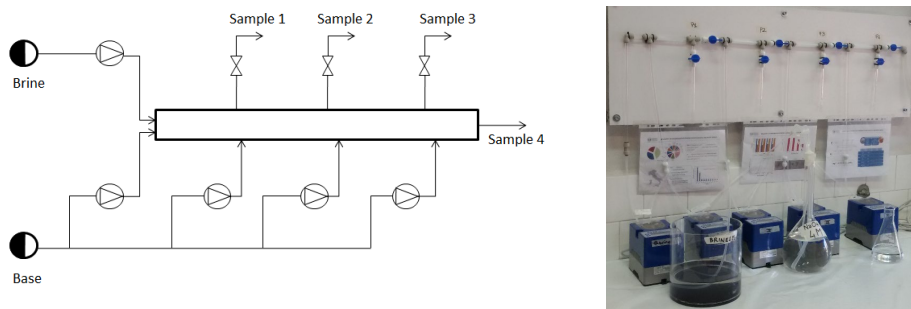


Figure 4-11: Simplified scheme of MF-PFR adopted for the experimental campaign.

The reactor layout is essentially formed by a main tube and the injection system for reagents consisting of T-junctions, each of them connected with a pump for the fluid movement. The reactor was built in polymeric material, chosen because of the high aggressiveness of salt solutions on metallic materials. Silicon tubes were used for the alkaline solution, from feed tank to the reactor. Several sampling points are foreseen before each input. The flow rate can be controlled changing the revolutions per minute (rpm) and the tubes section. The delivery pipe of each pump is normally positioned upward to facilitate the air expulsion from the reactor.

The CrIEM is an innovative technology that allows the controlled mixing of ionic solutes from two different solutions, aiming at a reactive crystallization process, finely controlling the presence of useful reactive species and the absence of dangerous ones through the use of an ion exchange membrane. A CrIEM reactor consists of two channels separated by an ionic exchange membrane, one for the feed stream from which a product has to be crystallized, and the other for the stream containing the ionic reagent.

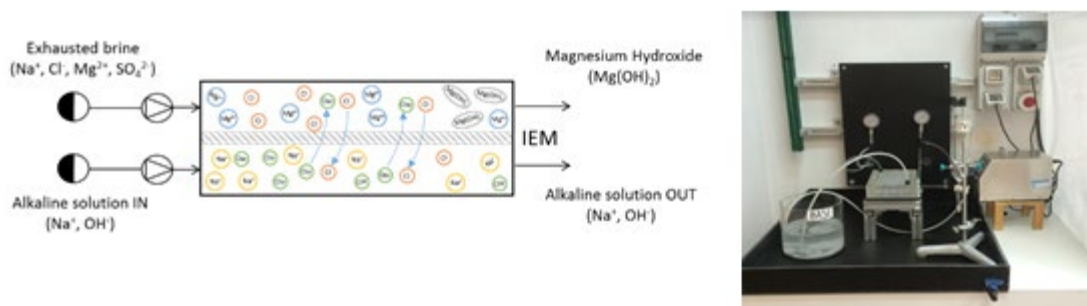


Figure 4-12: Simplified scheme of CrIEM adopted for the experimental campaign

The OH^- ions pass from the alkaline solution channel to the brine channel driven by concentration difference between the two solutions. In order to restore the electroneutrality, chloride ions pass through the membrane in an opposite direction. When the OH^- meet the magnesium ions, magnesium hydroxide precipitates due to its low solubility in the aqueous solution.

4.2.3 Description of tests done

The semi-batch system was widely used for the preliminary tests. A number of screening tests were performed in the first months of the project in order to identify constraints and goals of the operation within the project scenarios conditions. Following such extended phase (whose results are not reported for the sake of brevity), a systematic experimental campaign was implemented and results are here summarized.

An artificial solution was prepared using chloride salts of magnesium and calcium in order to mimic the typical conditions of the brine to be treated in the Botlek case study. In particular, the concentration were the following:

- Magnesium: 3 g/L
- Calcium: 24 g/L

This solution was filled in a beaker and the alkaline solution was added slowly with a syringe pump. The pH was monitored in order to follow the reaction trend in time.

The same set-up was used to perform different tests in order to select the best operative conditions for the pilot system. In particular, the reaction was made mixing the brine with a certain amount of magnesium hydroxide seed, in order to find the best configuration to minimize the time required for the filtration of the product suspension. Alkaline and seed-suspension were prepared before starting the experiments. The concentration of the solutions were as follows:

Four different brine solutions:

1. 0.164 M Mg^{2+}
2. 0.164 M Mg^{2+} + 0.596 M Ca^{2+}
3. 0.164 M Mg^{2+} + 0.00625 M SO_4^{2-}
4. 0.164 M Mg^{2+} + 0.596 M Ca^{2+} + 0.00625 M SO_4^{2-}

Four different seed-suspensions:

1. 6.3 g/L seeds
2. 6.3 g/L seeds + 0.596 M Ca^{2+}
3. 6.3 g/L seeds + 0.00625 M SO_4^{2-}
4. 6.3 g/L seeds + 0.596 M Ca^{2+} + 0.00625 M SO_4^{2-}

Alkaline:

1.0 M OH^-

The solutions were selected in order to better understand the effect of different ions on the precipitation, to check a possible co-precipitation of other salts instead of pure magnesium hydroxide and calcium hydroxide. Six different tests with different initial ratios between brine and seed-suspension were carried out, which were: [1:1], [1:2], [1:3], [1:4], [1:5] and [1:10]. The experiment was started at $t = 0$ with incipient dripping the alkaline on the surface and ends at $t = 34$ min. The results showed that a higher amount of seed-suspension led to a lower filtration time. From the results of these preliminary tests, the ratio [1:10] was selected for further experiments.

The MF-PFR at bench scale was tested in the ZERO BRINE condition, before design and assembling of the pilot system, in order to confirm the possibility to recover magnesium and remove calcium, obtaining high performance in terms of purity and conversion. The conditions and the solution concentration are reported below:

- Magnesium: 4 g/L; Calcium: 22.9 g/L; Sodium: 25.6 g/L
- NaOH concentration: 1M
- N_{Base}/N_{stoich} : 1 (note: this condition implies that the moles of OH^- are equivalent to the amount needed to have a stoichiometric reaction (2 moles of OH^- for each mole of Mg^{2+} or Ca^{2+}).

The test was performed in two steps in order to precipitate separately the two hydroxide compounds. In the first step, the reaction was controlled for the complete precipitation of magnesium as magnesium hydroxide. Then the suspension was filtered. The solid was collected and dried, whereas the filtrate was used in a second step to remove all the calcium present in the solution as calcium hydroxide. The remaining solution consisted of water and sodium chloride as required by the ZERO BRINE project in the specific condition of Evides Site 01.

The CSTR bench scale was also tested in order to compare the performance of this traditional reactor with the MF-PFR. The conditions adopted are reported as follows:

- Magnesium: 4 g/L; Calcium: 22.9 g/L; Sodium: 25.6 g/L
- NaOH concentration: 1M
- N_Base/N_stoich: 1
- Stirrer rpm: 400

Also in this case, the test was performed in two steps in order to recover magnesium and remove calcium.

Finally, although it was decided that the CrIEM will be used solely in WP3 for the production of magnesium hydroxide from waste brine produced in a coal mine in Poland, this innovative reactor was also tested in the condition of Evides Site 01. Commercial anionic exchange membranes were used for this purpose. A small amount of brine was recirculated until all magnesium was recovered while monitoring the co-precipitation of calcium. In this case, calcium hydroxide was chosen as alkaline solution for the precipitation of magnesium due to its low price compared to sodium hydroxide. The operation conditions were as listed below:

- Magnesium: 3 g/L; Calcium: 23.7 g/L; Sodium: 25.9 g/L
- $\text{Ca}(\text{OH})_2$ concentration: 1.5 g/L (higher than the solubility in water)

4.2.4 Summary and discussion of tests done

Proof of concept: fractionated crystallisation

The semi-batch tests were performed in order to have a confirmation of the proof of concept of the idea presented in the ZERO BRINE proposal. Magnesium and calcium can be recovered in two different steps by controlling the reaction path. The preliminary results are reported in Figure 4-13:

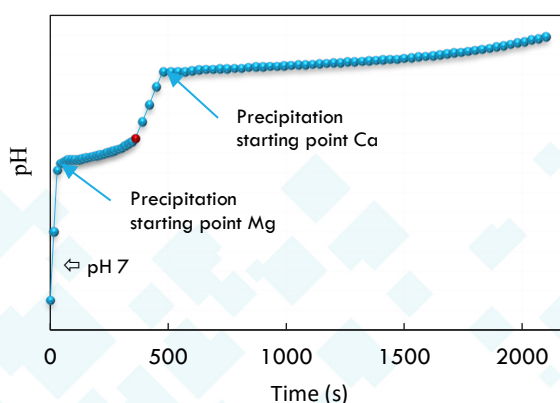


Figure 4-13: Precipitation path for the recovery of magnesium and the removal of calcium

The pH increased quickly until a plateau was reached in which the precipitation of magnesium hydroxide started. During the plateau phase the pH increased slowly until the red point where all the magnesium was precipitated as magnesium hydroxide. The suspension was filtered and the magnesium hydroxide was recovered. The obtained solution was used to remove calcium with a precipitation step similar to that of magnesium hydroxide. This easy test was essential to confirm the possibility to produce a good magnesium hydroxide and remove calcium to obtain a solution of sodium chloride with the specification required by the project.

Table 4-5: Proof of concept test: purity and conversion of magnesium and calcium hydroxide

	Ca ²⁺ [g/L]	Mg ²⁺ [g/L]
Initial Concentration	24.12	3.08
1° step (filtrate)	22.53*	0.02
2° step (filtrate)	0	0
Mg(OH) ₂	Purity	>98%
	Conversion	>99%
Ca(OH) ₂	Purity	>98%
	Conversion	>99%

* Note that the concentration reduction of Ca²⁺ ions in the 1st step filtrate is only due to the dilution of the brine due to the addition of 4M NaOH solution. On the contrary, concentration reduction for Mg²⁺ is predominantly generated by the precipitation reaction, though a small dilution effect is also present with the same dilution factor as for Ca²⁺.

Proof of concept: reaction seeding for filtration performance enhancement

As already mentioned, the semi-batch system was exploited to investigate the time required for the filtration of the magnesium hydroxide solid from the mother liquor. Different conditions were tested as reported above and the main results are represented in Figure 4-14:

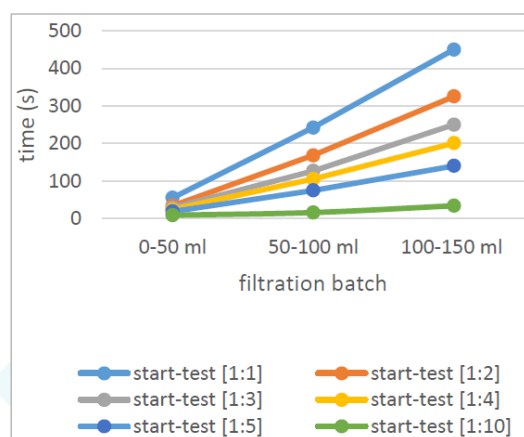


Figure 4-14: Filtration time of the suspensions with different start conditions, $t = 34 \text{ min}$ [1:1], [1:2], [1:3], [1:4], [1:5] [1:10].

As can be observed in Figure 4-14, the best result (i.e. a high filtration volume per unit of time) was obtained with a ratio [1:10] between brine and seed of magnesium hydroxide suspension added. In order to understand

the effect of the seed, the same test was repeated several times by recirculating the suspension for a maximum 10 tests. As an example the results with different solutions are reported below:

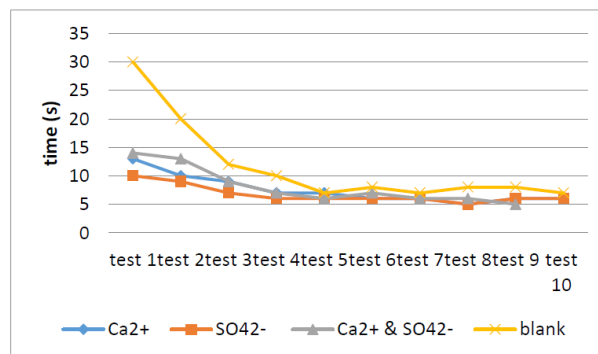


Figure 4-15: Filtration time (0 – 50 mL) of ten step test of Ca²⁺, SO₄²⁻, Ca²⁺ & SO₄²⁻, blank, t = 68s [1:10]

The influence of the presence of calcium and sulphate was first tested separately and then it was tested together. In Figure 4-15, the filtration time of the first 50 mL of the ten-step test with calcium, sulphate and calcium with sulphate are given. To compare, the filtration time without the presence of calcium or sulphate is shown in Figure 4-15 as 'blank'. The filtration time of the start-test with the presence of calcium or sulphate were lower than the blank, but they eventually all reached more or less the same filtration time after 6 tests. In all cases, the filtration time became fast after test 4 that means 4 times a recirculation of the suspension. Interestingly, solids purity was not affected by the presence of sulphates.

The preliminary results with the MF-PFR and the CSTR reactors have shown a good performance for the precipitation of magnesium and the removal of calcium. In both cases, the purity of the magnesium hydroxide is close to 100% with total conversion. After the second step, all the calcium was removed producing a sodium chloride solution ready for the evaporation step.

The CrIEM was tested under the condition of Evides Site 01 showing a good performance, with good ions flux and conversion. Nevertheless, the final product of magnesium hydroxide was contaminated by a small amount of calcium because locally the supersaturation was uncontrolled causing a co-precipitation of calcium and magnesium.

4.2.5 Conclusions

The semi-batch tests have confirmed the feasibility of the process. Magnesium and calcium hydroxide can be recovered from an industrial waste brine through a reactive crystallization process. The reaction path must be controlled by pH measurement. As shown, if seeds were added into the brine, the filtration time was improved a lot compared to the tests without seeding. The preliminary tests made with bench scale MF-PFR have shown good performance in terms of purity and conversion.

Thanks to these preliminary results, a MF-PFR pilot plant was designed and assembled in the BEC UNIPA lab. A wide experimental campaign will be carried out in the next months in order to confirm the first preliminary results on a large scale. A drum filter will be coupled and tested at the pilot system, for the continuous production of magnesium hydroxide. In Figure 4-16 a picture of the new pilot system is presented:



Figure 4-16: MF-PFR pilot system for the production of magnesium hydroxide and calcium hydroxide from brine

4.3 NTUA

4.3.1 Description of technology

The Multiple Effect Distillation evaporator (MED-NTUA) was developed in the framework of the BEST LIFE project SOL-BRINE (LIFE09 ENV/GR/000299). The MED-NTUA evaporator is a 2-stage forward-feed evaporator with a capacity of 2 m³/day.

Multiple Effect Distillation/evaporation (MED) is a low-temperature thermal desalination process and the first desalination technology used to produce fresh water in an industrial scale. The feed saline water is distributed in evaporators of different chambers (called stages or effects). The evaporator tubes in the first effect are heated by steam and the resulting steam is condensed inside the evaporator tubes of the subsequent effect, where again vapor is produced. (Xevgenos et al., 2018). Each of effect is maintained at a lower temperature than its preceding one. The feed water is sprayed or distributed over the surface of the evaporator tubes in a thin film to promote rapid boiling and evaporation (Figure 4-17). Pressure reduction decreases the boiling point of the water. Hence, the boiled-off vapor in one vessel can be used to heat the next one. Only the first vessel (at the highest pressure) requires an external heat source. The steam produced in the last effect is condensed in a separate heat exchanger, which is cooled by the incoming saline water.

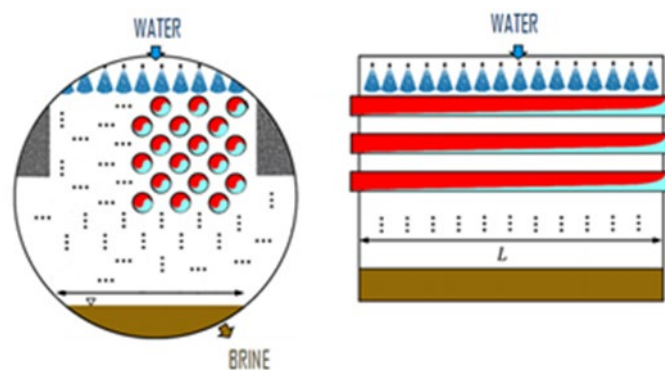


Figure 4-17: Schematic of horizontal tube-bundle, left: cross section, right: Longitudinal section. (Azimibavil & Jafarian Dehkordi, 2016)

The MED-NTUA evaporator is made up of two consecutive effects. In each of the MED effects, brine is evaporated resulting in the production of two subsequent streams: (1) a water vapor stream that is then condensed and recovered as fresh water and (2) a more concentrated brine stream. The vapor stream of the first effect is used to heat the concentrated brine produced in the second effect that is 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 is provided by internal heat gain (heating steam from the first effect) and thus energy recovery is achieved.

The vapor stream produced by the second effect is used for pre-heating purposes. Specifically, the vapor is passed through a plate heat exchanger where it is condensed, transferring its thermal energy to the brine stream of inlet feed. The unit is built from Super Duplex, EN 1.4410, with a thickness of 5.0 mm. The heating element is designed according to the specifications of TEMA (Tubular Exchanger Manufacturers Association). The heating element is mounted eccentrically in the head by means of a flanged neck. The element consists of U-shaped

tubes in a hexagonal arrangement. Inflow and outflow are separated by a custom-made stationary-head bonnet with pass partition. In order to achieve the maximum density of the tube bundle in the direction of the showered brine flow, a small pitch of 1.25 is selected for the tube bundle arrangement.

4.3.2 Scheme and photo of equipment

As mentioned before, the MED-NTUA evaporator consists of two sequential effects. Figure 4-18 illustrates the main components of the system used for the evaporation experiments.

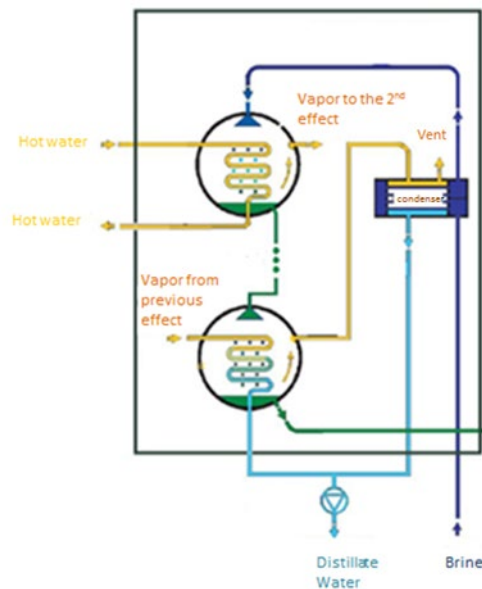


Figure 4-18: Schematic diagram of the innovative vacuum evaporator unit, (SOL-BRINE project, solbrine.uest.gr)

The MED-NTUA evaporator was refurbished and containerized in order to be easily transported. The experiments were carried out with the new arrangement of the evaporator that is presented in the following pictures.



Figure 4-19: The equipment of the Greek Brine Excellence Center (BEC)

The control of the system is accomplished via a PC-based SCADA interface. Multiple temperature, pressure and flow transmitters are connected in many positions within the system, receiving all the important data for the

control of the process. Data is collected in a PLC controller, with the necessary programming for the control of the unit. Through the use of SCADA, overall control and monitoring can be achieved.

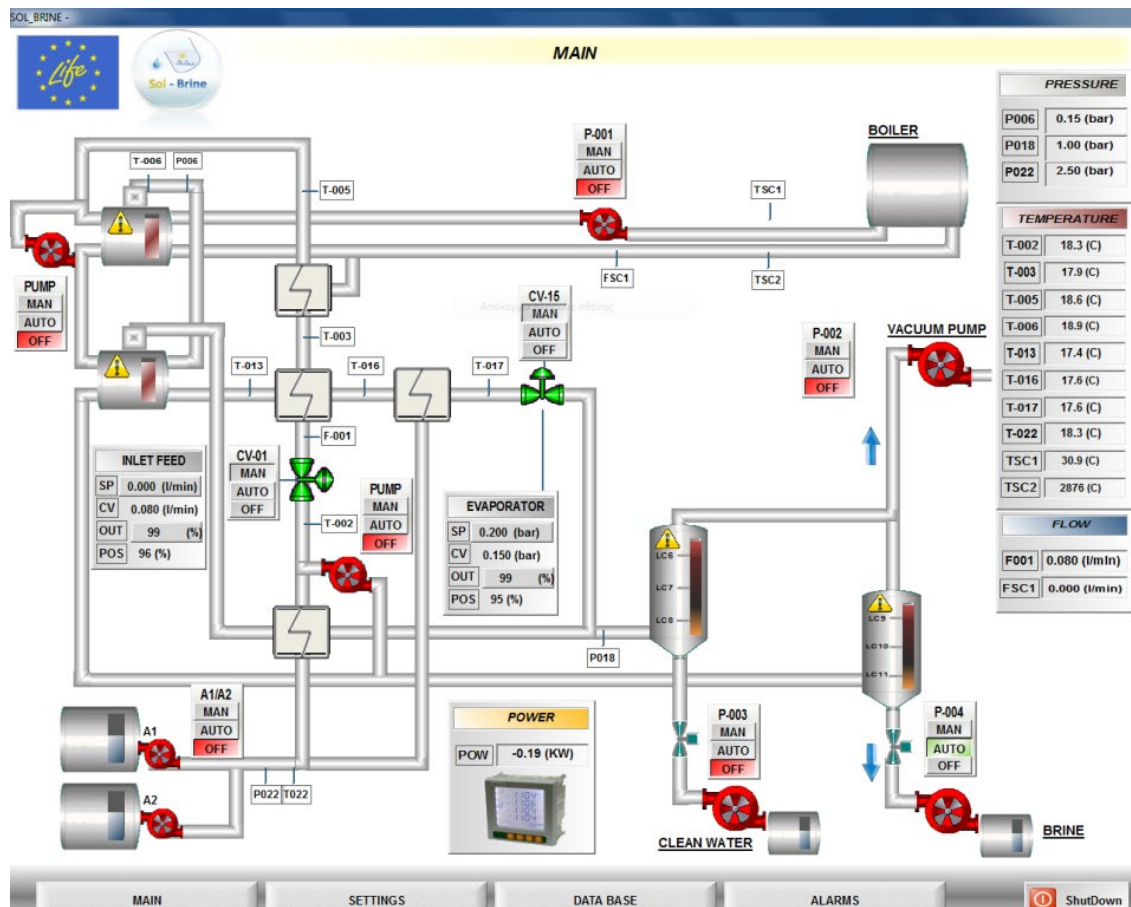


Figure 4-20: View of the operation software tool

4.3.3 Description of tests done

The experiments were carried out with the use of synthetic solutions. The synthetic solutions were prepared in order to have similar concentration of the streams that will be the input of the evaporator at Evides Site 01. Data for the preparation of the synthetic solutions was received from Lenntech (for the nanofiltration effluent, NF permeate) and from UNIPA (for the crystallizer effluent, MC II effluent). It was assumed that the addition only of NaCl is sufficient, because the concentration of other ions (except Na^+ and Cl^-) in the inlet effluents of the evaporator is very low and considered not important.

The characteristics of the prepared and used synthetic solutions are presented in the below table.

Table 4-6: The characteristics of the synthetic solutions

	Description	TDS (g/L)
Synthetic Solution 1 (SS1)	NF permeate	4.73
Synthetic Solution 1 (SS2)	effluent	43.69

The above solutions were individually fed into the MED evaporator.

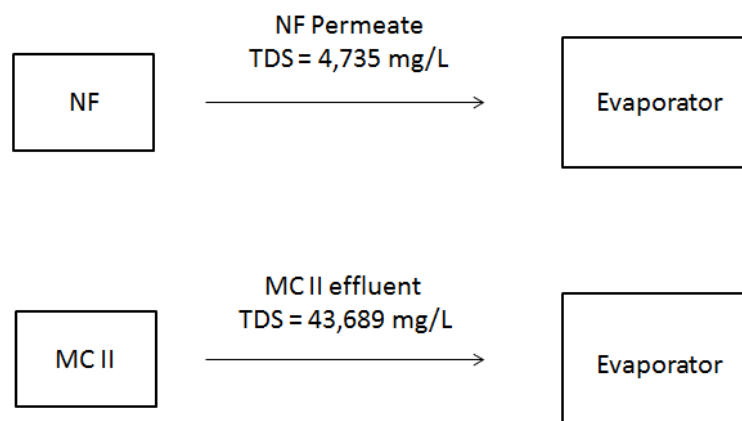


Figure 4-21: Flow diagram for the evaporator at Site 01

In total, ten (10) batch experimental series took place at the Greek Brine Excellence Center. Specifically, five (5) experiments with 'SS1' as feed brine stream to the evaporator and five (5) experiments with 'SS2' as feed brine stream to the evaporator.

Each experiment lasted about 12 hours. Additionally, the temperature (T) and Total Dissolved Solids (TDS) of each feed brine stream were measured before the start of each experimental series.

The water which was fed into the evaporator was heated using a boiler in order to raise its temperature to 70°C. The Boiler has the ability to reach 90 °C, the higher the temperature, the greater the efficiency. The monitoring of the experimental series and in particular of the components of the evaporator was performed using the SCADA / PLC. The recorded measurements are presented in Table 4-8.

Table 4-7: Operating Parameters of MED Evaporator

1 st Effect MED	2 nd Effect MED
T = 55 °C	T = 45 °C
P = (0.13 – 0.15) bar	P = (0.06 – 0.10) bar

The collected evaporator effluent of each experiment was analyzed in the Unit of Environmental Science and Technology (UEST) of the School of chemical engineering of NTUA. The laboratory is accredited by ISO17025.

The method used in order to measure the TDS value of the samples is APHA-AWWA-WEF Standard Methods for the Examination of water and wastewater, 20th Edition, 1998: part 2540C.

The results of the experimental series are presents in the following table

Table 4-8: Results of the 10 experimental series (brine effluent)

Experimental Series	Stream	Temperature (T, °C)	Total Dissolved Solids (TDS, mg/L)
1	SS1 (Synthetic Solution 1)	25	4,756
2		25	4,892
3		25	4,560
4		25	3,999
5		25	4,975
6	SS2 (Synthetic Solution 2)	25	43,625
7		25	43,527
8		25	42,728
9		25	42,732
10		25	43,746

In order to verify the chemical quality of the production, several samples of the feed brine stream and the evaporator effluent were taken regularly for measuring their ion composition. The ion concentrations of the feed brine and evaporator effluent were measured using inductively coupled plasma optical emission spectrometry (ICP-MS) and Ion Chromatography (IC). At the end of each experiment, the thermal supply was cut off and the system was terminated

Finally, to ensure that the conditions in each experiment are replicable, the effects were rinsed after each completed experiment using the condensate vapor as cleansing water. The cleaning procedure lasted 30 minutes.

4.3.4 Summary and discussion of tests done

At the end of the 10 experimental series, all data collected was processed in order to reach a final conclusion on the performance of the evaporator and the quality characteristics of the evaporator effluent. The following Table 4-9 shows the total volume of the condensate vapor and evaporator effluent which was recorded in the collector tanks.

Table 4-9: Volumes of Condensate vapor and evaporator effluent from the 10 experimental series

Experimental Series	Feed Stream	Feed Brine Streams flow (L/h)	Condensate vapor effluent (L)	Evaporator effluent (L)
1	SS1	2,000	1,211	789
2			1,205	795
3			1,205	795
4			1,204	796
5			1,202	798
Average SS1		2,000	1,206	794
6	SS2	2,000	1,247	753
7			1,264	736
8			1,264	736
9			1,265	735
10			1,265	735
Average SS2			1,261	739
Total Average		2,000	1,231	769

SS1 (NF Permeate)

The mass of Feed Brine Steam was 1,988 kg Deionized water + 12 kg Salts = 2,000 kg Feed Brine Stream. Consequently, the daily mass balance was 2,000 kg Feed Brine Stream = 1,206 kg Condensate vapor + 794 kg Evaporator effluent.

SS2 (MC II effluent)

The mass of Feed Brine Steam was 1917 kg Deionized water + 83 kg Salts= 2,000 kg Feed Brine Stream. Consequently, the daily mass balance was 2,000 kg Feed Brine Stream = 1,261 kg Condensate vapor + 739 kg Evaporator effluent.

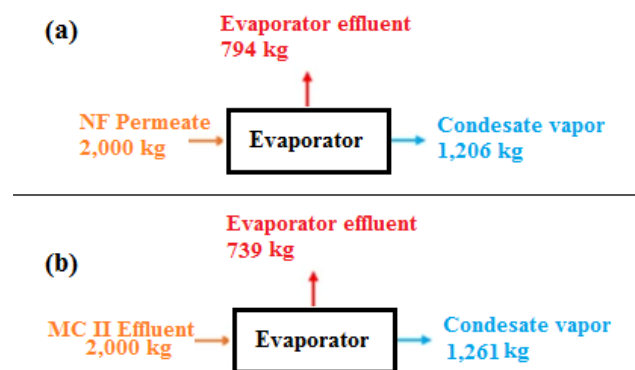


Figure 4-22: Flow diagram of daily mass balance for the two individual feed brines

Therefore, the evaporator's recovery rate was the following:

Stream I (NF Permeate): $R = \frac{1,206 \text{ L}}{2,000 \text{ L}} * 100 = 60\%$

For Stream II (MC II effluent): $R = \frac{1,261 L}{2,000 L} * 100 = 63\%$

The following Table 4-10 shows the TDS measurements of the Feed Brine Stream plus Evaporator effluent and the evaporator's water recovery rate.

Table 4-10: TDS measurements and the evaporator's water recovery rate

Experimental Series	Stream	Feed Brine Stream TDS (mg/L)	Evaporator effluent TDS (mg/L)	Concentration Factor	Water Recovery (R) %
1	SS1	5,990	15,187	2.54	61
2		5,987	15,067	2.52	60
3		5,990	15,075	2.52	60
4		5,991	15,055	2.51	60
5		5,996	15,034	2.51	60
				Average	60
6	SS2	41,736	110,861	2.66	62
7		41,730	113,324	2.72	63
8		41,739	113,439	2.72	63
9		41,732	113,602	2.72	63
10		41,746	113,549	2.72	63
				Average	63
				Total Average	62

Results from the 10 experimental series are presented in Figure 4-23 and Figure 4-24.

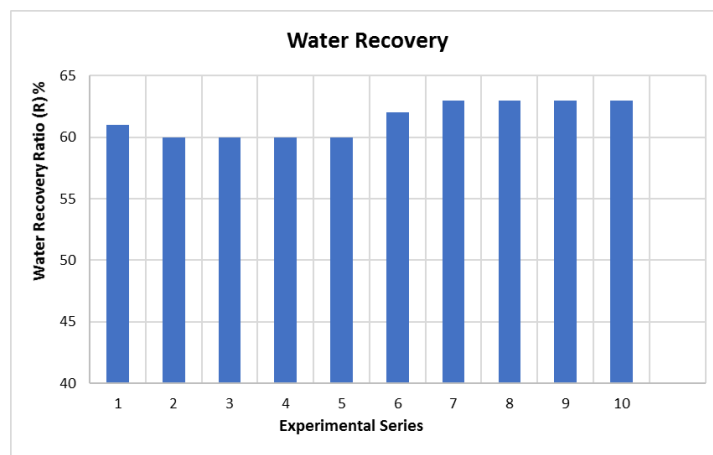


Figure 4-23: Water recovery on the 10 Experimental Series

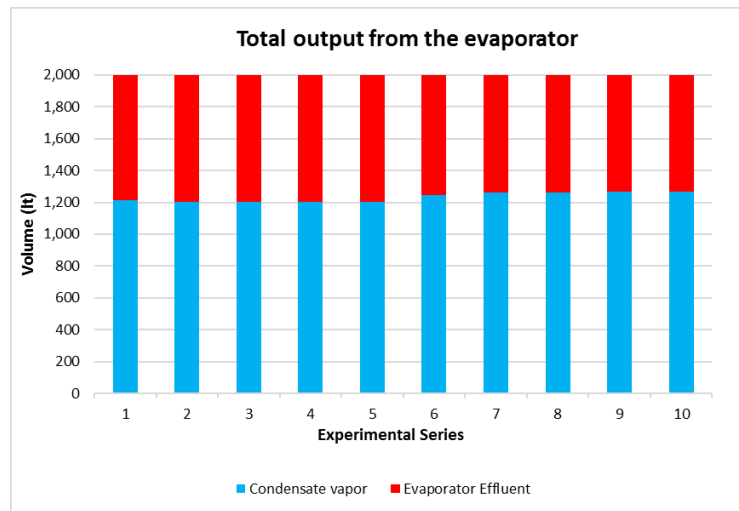


Figure 4-24: Total output from the evaporator on the 10 Experimental Series

4.3.5 Conclusions

The performance of the MED-NTUA was evaluated for the treatment of brine. From the experiments, the following conclusions were made:

- The multiple effect distillation system demonstrated a steady performance.
- The overall water recovery achieved was about 62%. For the Stream I (NF Permeate) the water recovery was 60% whereas for the Stream II (MC II effluent) the water recovery was 63%.
- The concentration factor range was 2.51 - 2.72.

Based on the experience obtained from the operation of the BEC system, it is seen that the system performance could be enhanced. This improvement requires some modifications in the design, such as tanks arrangement and piping system, as well as pumps.

5 Site 02

5.1 Lenntech: Anionic Ion Exchange

5.1.1 Description of technology

Anionic Ion Exchange is a purification process by which soluble negatively charged (anionic) ions, or contaminants, are separated from a solution by being exchanged with another negatively charged ion. Such negatively charged ions or contaminants may be sulphates (SO_4^{2-}) or naturally occurring organic matter expressed as total organic carbon - TOC), which is typically negatively charged, as in the case of the RO brine treated at ZERO BRINE Site 02.

The exchange media, or ion exchanger, is usually a porous resin bead with functional groups. Resin beads are typically 5 mm in diameter, depending on the ionic loading. These beads are porous and contain invisible water inside, measured as “humidity” or “moisture content”. The structure of the resin is a polymer (like all plastics) on which a fixed charged ion has been permanently attached. This ion cannot be removed or displaced; it is part of the structure. To preserve the electrical neutrality of the resin, each fixed ion must be neutralised with a counterion. This counterion is mobile and can get into and out of the resin bead. *Figure 5-1* shows a schematic anion exchange resin bead. The dark lines represent the polymeric skeleton of the resin bead: it is porous and contains water. The fixed functional group ions of this anion exchange resin are quaternary ammonium cations shown in the picture as N^+R_3 ; a more accurate formula would be $\text{CH}_2\text{N}^+(\text{CH}_3)_3$. The mobile ions in the anion resin bead are chloride anions (Cl^-). This is also the standard delivery form for many anion resins. Each ion going into the bead has to be replaced by an ion getting out of the bead, again to preserve electrical neutrality. This is what is called ion exchange. Only ions of the same electric sign are exchanged.

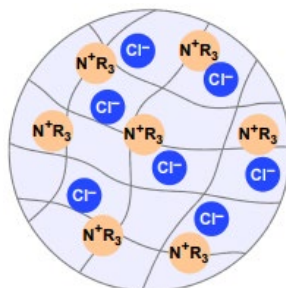


Figure 5-1: Schematic anion exchange resin bead

Due to differences of affinity for different ions, common ion exchange resins can be used to remove selectively ions from water. Fairly selectively ions can be removed from water, such as nitrate or sulphate, using an anion exchange resin in the chloride form.

In the laboratory as well as in industrial plants, ion exchange resins are used in columns. The water or solution to be treated flows through the resin. In *Figure 5-2*, the fresh resin is shown and how the resin gets progressively loaded with the ions from the feed solution. Ions from the resin not shown in the picture are released into the treated solution. At the end some of the “blue” ions escape into the pure solution, and operation is stopped.

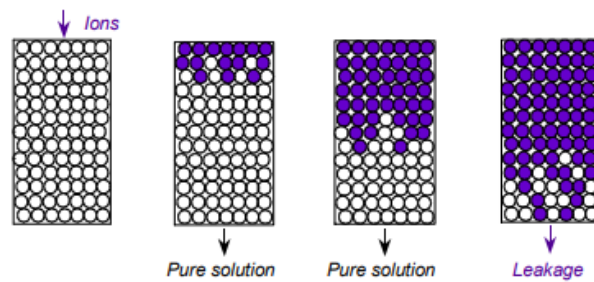


Figure 5-2: Column operation.

When the resins are exhausted, they can be brought back to the initial state and be used again. Regeneration of ion exchange resins is a reversal of the exchange reactions. For instance, the softening resin is regenerated with chloride (Cl^-) ions supplied by a salt (common salt: NaCl) solution. Regeneration can only be performed when the concentration of the regenerant is high, typically 1000 times higher than the concentration in normal water. For instance, salt is used as a brine with 10 % (about 100 g/L) concentration. The regeneration step produces saline waste, or brine, which is the principal disadvantage of ion exchange.

5.1.2 Scheme and photo of equipment

To design and size an ion exchange column certain parameters should be determined. Some of these parameters can be highlighted such as: feed flow to be treated; volume occupied by the resin; filtration velocity; adequate time to promote the exchange between ions which is known as EBCT (empty bed contact time); type of resin to be applied according with the application/process (food grade e.g), among others. In a simplified manner, Figure 5.3 on the left represents the main components that are part of an ion exchange column and on the right a typical ion exchange column used for bench scale tests. The ion exchange tests were performed using the bench scale unit Figure 5.3b.

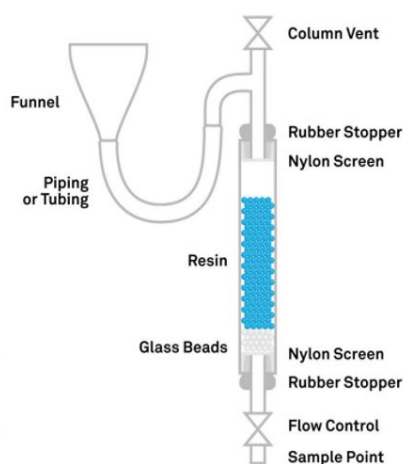


Figure 5-3: Scheme of ion exchange components (left a), bench scale ion exchange column (right b)

5.1.3 Description of tests done

Water Source

Samples of the reverse osmosis concentrate from the Evides DWP in the Botlek area, Rotterdam, the Netherlands, were provided twice during May (RW1) and July (RW2). The samples were stored in room temperature and tested within two months. Prior to experiments samples were analysed in terms of Dissolved Organic Carbon (DOC), UV₂₅₄, pH, conductivity, sulphate concentration and chloride concentration.

Resins

In the experiments, the effectiveness of both conventional and magnetic anionic ion exchange resins was tested, respectively, in packed bed and fluidized conditions. The main properties of the resins are displayed in Table 5.1.

Table 5-1: Properties of anionic resins

Resin	Manufacturer	Structure	Matrix	Capacity (eq/L)	Water Content (%)	Particle Size (µm)
SCAV4	Dupont	Polyacrylic	MP**	0.80	66.0 – 72.0	630 - 850
A860	Purolite	Polyacrylic	MP**	0.80	66-72	300 - 1200

Experimental Set-up

Experiments were conducted in chromatographic glass columns with 25 cm diameter and 600 cm length, filled with 125 mL of wet resin. The RO-brine was fed downwards into the column with a B&S DIGI 40 peristaltic pump (SEM) and the effluent was collected at the bottom. The column configuration is depicted in Figure 5.4. Two columns were run in parallel and different parameters were analysed. The settings for the column tests are specified in Table 5.2.

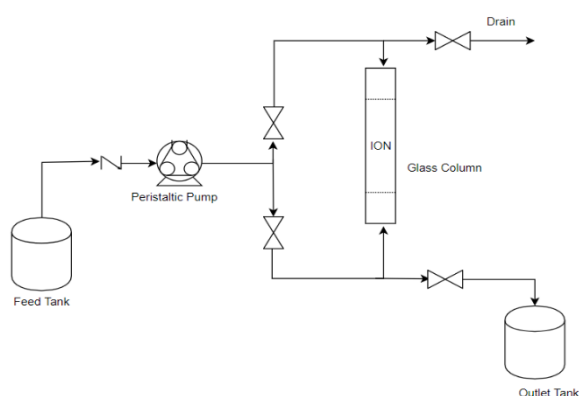


Figure 5-4: Laboratory set-up of the ion exchange column

Table 5-2: Experimental settings for the column tests during service. Source waters: RO-concentrate collected in May (RW1) and July (RW2). BV = bed volume.

	Resin	Source water	Specific Velocity
Column 1	A860	RW 1	5 BV/h
Column 2	SCAV 4	RW 1	5 BV/h
Column 1	SCAV 4	RW 2	5 BV/h
Column 2	SCAV 4	RW 2	20 BV/h

Because the resins were delivered in the desired ionic form (R-Cl), conditioning consisted only on backwash with demineralized water, in order to remove impurities from the manufacturing process, eliminate air bubbles trapped during loading and to classify the bed. Backwashing was performed for 30 min, after which the flow was slowly decreased, allowing the resin to settle in the bottom of the column. The water was drained until the level fell just above the resin bed. Co-flow regeneration was performed with 3 to 6 BV of 10% NaCl regenerant solution at 2-3 BV/h. The regeneration effluent was collected at the bottom of the column. After regeneration, slow rinse was performed with 2 BV of demineralized water at regeneration flow rate, and for rapid rinse 6 BV of demineralized water were fed at service flow rate.

Analytatics

Electrical conductivity and pH were measured with Hach Lange HQ40D – Multi/2 Channels Portable Meter and an Intellical CDC401 Laboratory Conductivity Cell and an Intellical PHC101 Laboratory pH electrode. UV light absorbance measurements were taken in a Real Tech UV254 Field Meter using 0.45µm pre-filtered samples. The samples were measured in quartz cuvette rinsed twice with demineralized water and once with filtered sample.

The DOC content of the samples was measured by oxidative combustion-infrared analysis with a Shimadzu TOC-V Series Analyser. The samples were pre-filtered in 0.45µm CHROMAFIL PET-45/25 syringe filter and acidified with a 2M HCl. Sulphate, chloride and nitrate concentrations were measured by ion chromatography with a Metrohm 881-IC compact pro. SUVA was calculated as the UVA_{254} normalized in terms of DOC.

5.1.4 Summary and discussion of tests done

Raw Water Characterization

The waters collected in different times of the year exhibited different DOC content and concentration of the major competing anion in solution, sulphate, as specified in Table 5.3. Both waters are considered hydrophilic in character, based on SUVA-values, with RW2 exhibiting a slightly higher hydrophobic character than RW1. Regardless of variations of the species in solution, sulphate-DOC ratio was approximately the same for both waters.

Table 5-3: Properties of RO-concentrate samples collected in May (RW1) and July (RW2).

Parameter	RW1	RW2
pH	9.1	9
UV_{254} (cm ⁻¹)	0.248	0.172
DOC (mg C·L ⁻¹)	14.1	8.1
SUVA (L·m ⁻¹ ·mg ⁻¹ C)	1.76	2.12
Sulphate (mg·L ⁻¹)	415	239
EC (mS·cm ⁻¹)	3.54	2.90

Column Tests

The choice of the particle size of the resins is a compromise between kinetics and flow through the column. The comparison of resins with different size distribution shows no advantage of one over the other in terms of uptake of organics. DOC removal decreased fast in the first 200 BV of treated water, after which more stable removals, around 50%, were observed, Figure 5.5. UV-absorbing compounds were only slightly favoured by the anionic resins in comparison to DOC, with SUVA removal of circa 20 % up to 550 BV and decreasing to 4% after 1600 BV

of treated water. DOC and UV₂₅₄ concentration in the SCAV 4 IX-effluent after 1600 BV of treated RO-brine were 7.97 mg C·L⁻¹ and 0.130 cm⁻¹, respectively, Up to 30 BV sulphate was completely removed from the RO-brine. The breakthrough of sulphate occurred before 80 BV, but the exact point was not detected.

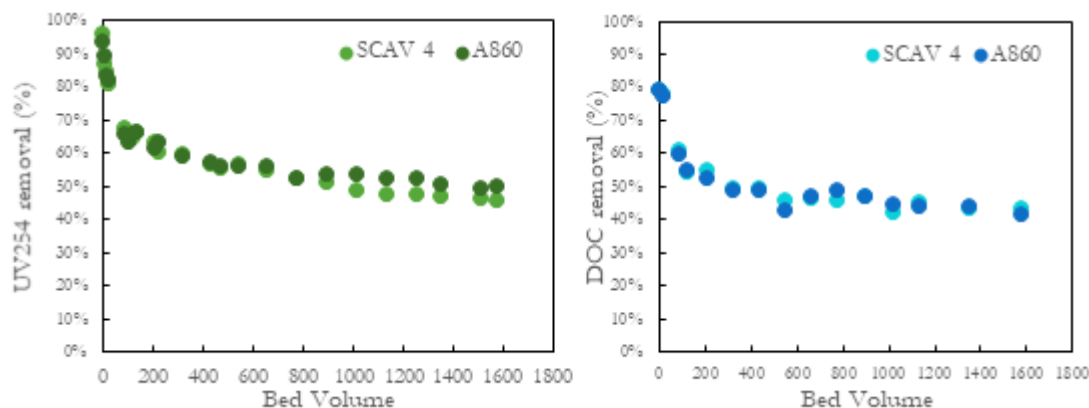


Figure 5-5: DOC and UV₂₅₄ removals by anionic resins SCAV4 and A860 operating in a fixed bed configuration at 5 BV·h⁻¹

The impact of different waters in the resin performance is shown in Figure 5-6. Despite the higher sulphate concentration of RW1, the percentage removal of DOC decreased with 10% for the RW2 in comparison to RW1, with DOC effluent concentration of 5.5 mg C·L⁻¹ (28% removal) after 1500 BV of treated water. At the point of maximum DOC removal, residual organic content was approximately the same for both feed waters, around 3 mg C·L⁻¹. This result indicates a higher proportion of natural organic matter that is refractory to ion exchange treatment, reflected in lower DOC removals. For RW2, UV-absorbing compounds were preferentially removed and after 1500 BV SUVA removal of circa 30% was observed, against 6% from RW1. For the column fed with RW2, sulphate breakthrough was estimated to happen close to 70 BV, based on pH variations of the collected samples. For columns operating with empty bed contact of 3 and 15 min, similar uptake behaviour was observed.

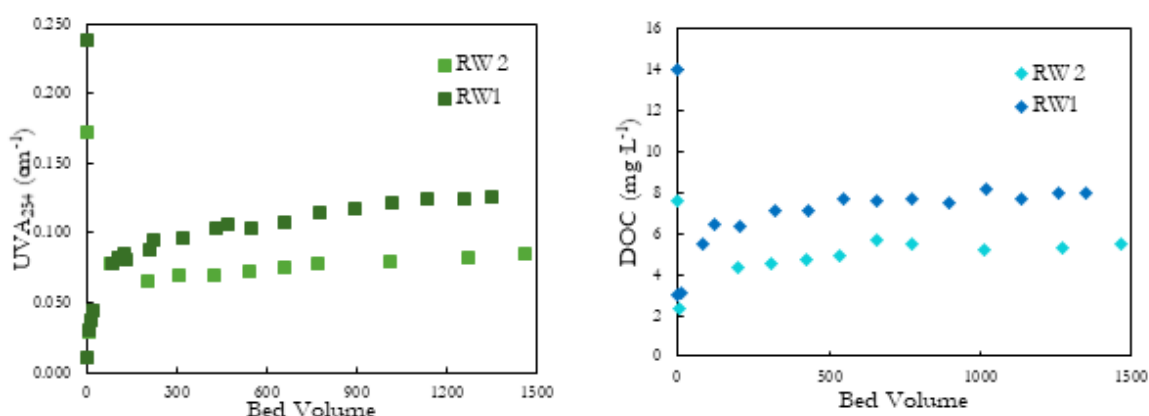


Figure 5-6: DOC and UV₂₅₄ profiles for SCAV4 resins operated in a fixed bed column at 5 BV·h⁻¹

Regeneration Efficiency

Regeneration efficiency of the resins was calculated as the mass of the carbon desorbed from the resins during the regeneration process divided by the estimated mass of carbon adsorbed by the resins during service. SCAV4 resins were more efficiently regenerated in comparison to A860 resins, see Table 5.4. Regeneration with approximately 3 BV of regenerant was enough for optimal regenerant use.

Table 5-4: Organic content of the spent regenerant

	Resin	Loading rate (BV·h ⁻¹)	Brine (BV)	DOC Adsorbed (mg C)	DOC Desorbed (mg C)	Regeneration Efficiency
R1	A860	5	2.4	1381.4	1019.6	74%
R1	SCAV 4	5	2.4	1333.21	1111.22	83%
R2	SCAV 4	5	–	624.56	560.44	90%
R2	SCAV 4	20	6	581.04	450.53	78%

5.1.5 Conclusions

The effectiveness of anionic resins for removal of organic matter is highly dependent on the properties of the feed water and may vary along the year. For simultaneous removal of sulfate and DOC operation cycles of 30 – 60 BVs, approximately, should be considered. In scenarios where sulfate removal is not critical, 30 – 45% DOC removal could be achieved over 2000 BV, and possibly longer. An empty bed contact time of 3 min was enough to drive organic removal by the resins. In terms of regeneration efficiency, SCAV4 resins performed better than A860 resin. Nevertheless, the total capacity of the resins could not be completely restored and the effect on long-term column operation should be investigated.

However, as it is important to remove both organics and sulfates with the IEX, it is decided to find a better alternative to treat the organics of this brine stream. The high salinity of the water results in competition between the organics and the sulfate ions and lower removal of both. The operating times would be determined based on the sulfate leakage. Since the resins were only partially regenerated, lower efficiency is expected after multiple operating cycles, resulting in shorter service cycles and more frequent regeneration.

5.3 Arvia (Nyex™)

5.3.1 Description of technology

Arvia's Nyex™ treatment technologies are water and wastewater treatment systems designed to reduce recalcitrant, hydrophobic organics and remove problem pollutants as well as colour from contaminated water.

Arvia's Nyex™-e oxidation technology uses in-situ electrochemical regeneration within a single continuous treatment solution. The influent flows through the electrochemically active treatment zone, and a low voltage electric current proportional to the organic concentration is passed through it, producing OH^\cdot radicals which effect electrochemical oxidation.

Arvia's Nyex™-a combined adsorption and oxidation technology utilises a proprietary adsorbent to first concentrate adsorbable organics onto the adsorbent surface, then electrochemically regenerate (by producing OH^\cdot radicals which oxidise adsorbed organics) the adsorbent in-situ, concomitantly and continuously - without requiring replacement or disposal of the adsorbent media.

The treated water flows into and out of the cell, at a flow rate appropriate to the demands of the application as well as the desired Hydraulic Residence Time (HRT), where it can either be re-used in-process or the treated water can better meet current and future water quality standards.

The technology is modular, and can be scaled up to suit requirements. It is easily integrated into existing and new installations alike, and in containerised form, it is 'plug and play', from both a hydraulic and electrical perspective. When necessary, the Nyex™ Technology can be placed in-line before or after ancillary technologies, for example Ion Exchange or Granular Activated Carbon, in order to gain the most benefit from all technologies, and reduce TOTEX accordingly. This is particularly useful in cases where there is a mix of hydrophilic and hydrophobic organics present in the (waste)water, as Nyex™ more efficiently destroys more hydrophobic organics.

A schematic of the combined adsorption and electrochemical regeneration Nyex™-a process is shown below in Figure 5-8

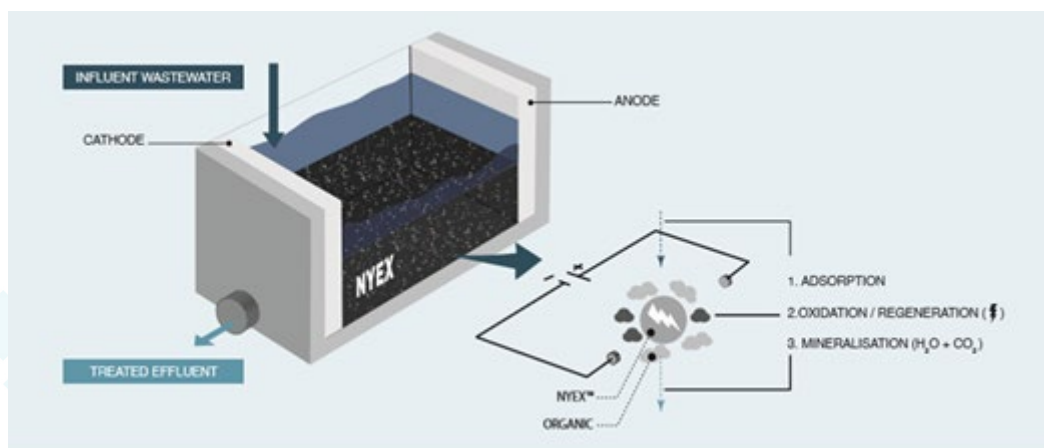


Figure 5-8: Schematic of Nyex™-a technology

5.3.2 Experimental: Scheme and photo of equipment

Figure 5-9 shows a scheme of the bench scale treatment system. Figure 5-10 and Figure 5-11 show photographs of the bench scale system used for the tests and a full scale system, respectively.

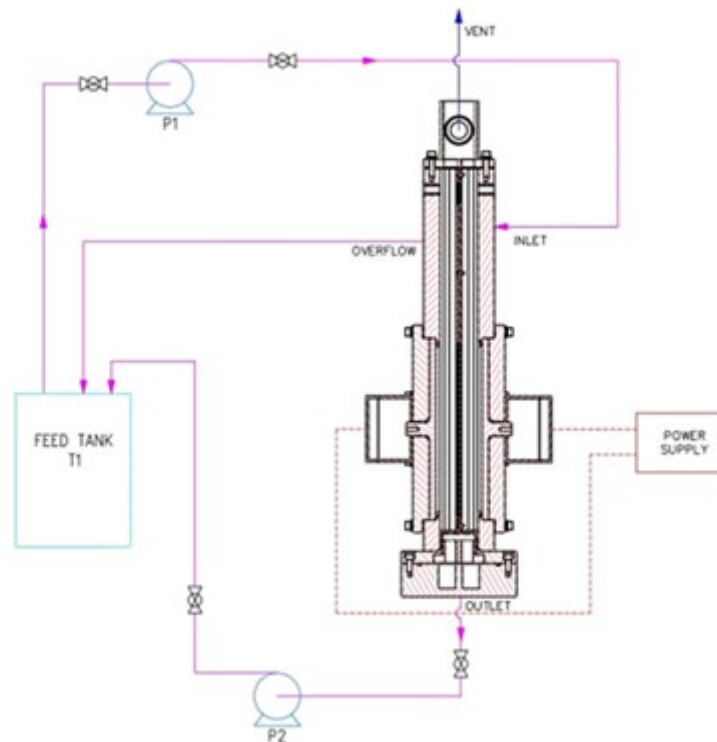


Figure 5-9: Process Flow Diagram (PFD) of Nyex™ 1-20a/e bench-scale treatment system set up in recirculation mode



Figure 5-10: Photograph of Nyex™ 1-20e bench-scale treatment system



Figure 5-11: Photograph of Nyex™ 16-50e full-scale treatment system

5.3.3 Description of tests done

The Nyex systems were initially operated in recirculation mode. The wastewater was top fed into either the Nyex 1-20a or the Nyex 1-20e reactor units from a wastewater container. The effluent was then pumped out of the bottom of the unit, into the same container via the outlet valve of the unit. The outlet point also served as the sampling point for treatment. The flow rate and current density applied were varied to optimise the treatment process dependent on the treatment achieved. Figure 5-9 shows a schematic diagram of the treatment setup in a recirculation operation.

Any overflow was directed back into the feed tank. Monitoring of ventilation (by directing an extraction hose around the top of unit for the Nyex-a system and running trials in a fume cupboard for the Nyex-e system) were maintained throughout the trials due to the risks caused by chlorine gas released due to the NaCl content of the wastewater. Following the optimisation of the recirculation trials the optimum treatment achieved could then be translated into a single-pass configuration.

For the Granular Activated Carbon trial, the sample was passed through a fixed bed of Nyex in a once-through configuration, in order to assess the adsorption characteristics and loading capacity of the GAC, specifically the mg/g loading rate. This was conducted at a hydraulic residence time of ca. 3 minutes.

Table 5-5 indicates the tests done, where tests are denoted according to the technology followed by an experiment number i.e. A1 is the first experiment conducted on the Nyex-a system, E1 the first conducted on the Nyex-e system, and GAC1 the first conducted on GAC.

Table 5-5: Description of tests done

Test ID	Type of waste	Volume (L)	Flow rate (L/h)	Current density (mA/cm ²)	Duration (h)	Configuration
A1	Brine	10	10	-	24	Recirculation
A2	Brine pH 3	10	10	-	24	Recirculation
A3	Brine pH 2	10	10	-	24	Recirculation
A4	Brine	10	10	2.5	24	Recirculation
A5	Brine pH 3	10	10	2.5	24	Recirculation
A6	Brine pH 2	10	10	2.5	24	Recirculation
A7	Brine pH 2	-	2	2.5	65	Single-Pass
E1	Brine	2	20	12.5	4	Recirculation
E2	Brine pH 3	2	20	12.5	4	Recirculation
E3	Brine pH 2	2	20	12.5	4	Recirculation
E4	Brine-H ₂ O ₂	2	20	12.5	4	Recirculation
E5	Brine re- adjusted pH	2	20	12.5	4	Recirculation
E6	Brine pH 2	2	20	25	4	Recirculation
GAC1	Brine pH 2	50	20	N/A	93.5	Once-through

5.3.4 Summary and discussion of tests done

Trials A1, A2 and A3 were carried out on the Nyex 1-20a system in recirculation-mode to determine the adsorption capability. The pH of the wastewater was adjusted in order to determine the effect of pH on the adsorption kinetics for the Nyex. As displayed in Figure 5-12 for the neat sample the adsorption capacity was lower than when pH adjusted down to 2 or 3. There was no overall change in the concentration for the adsorption on the raw sample, for the pH 3 adjusted samples the TOC reduced from circa 16mg/L to 4 mg/L TOC.

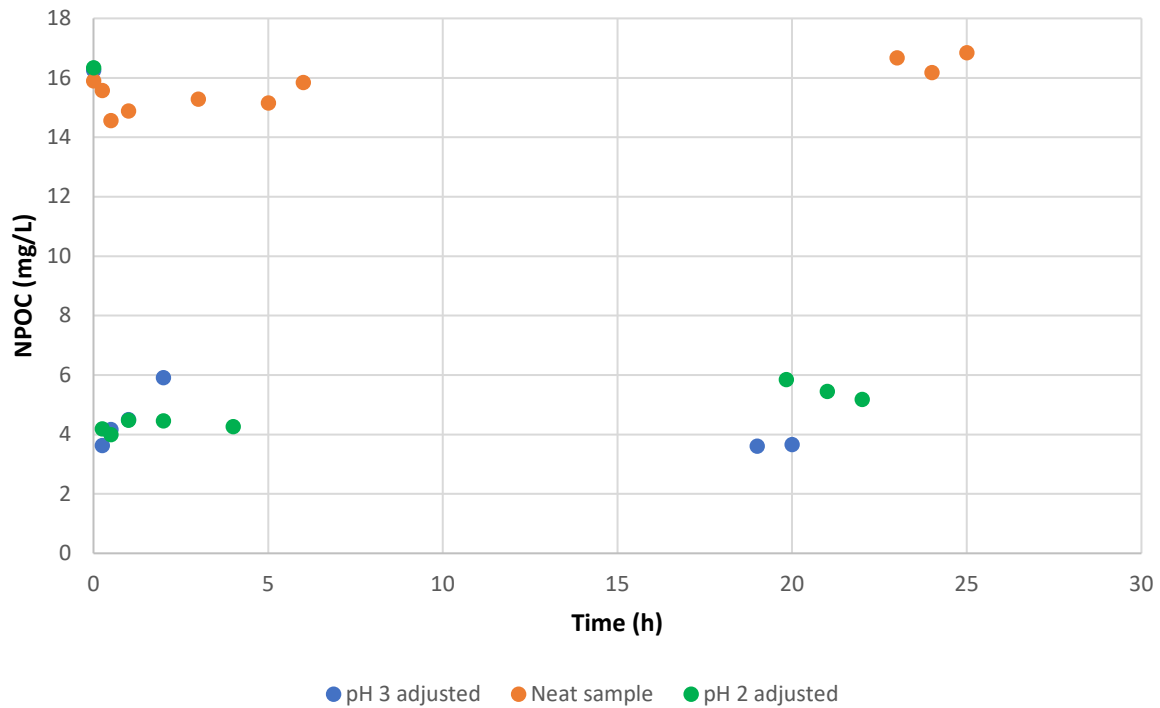


Figure 5-12: Trials A1, A2 and A3 – Adsorption

Trials A4, A5 and A6 were carried out on the Nyex 1-20a system in recirculation mode, these trials are the equivalent of trials A1, A2 and A3 but with both adsorption and oxidation. The purpose of the trial was to determine the contribution of adsorption and oxidation to treatment of the ZB wastewater. As can be seen, the pH adjusted samples achieved better treatment of the TOC, this further suggests that there is benefit in operating at a lower pH due to adsorption. However, in order to prove oxidation of the organics in this system it was expected that the concentration would fall below approximately 4 mg/L TOC based on the adsorption trials. This does not prove that the organics were being oxidised but adsorbed on the surface of the Nyex to a certain extent. The results of this experiment were then used to formulate the basis for trial A7.

Trial A7 was carried out on the Nyex 1-20a system in single-pass mode with the wastewater at pH 2. The main aim of this experiment was to try and ensure the Nyex adsorbent was saturated before applying a current across the bed to carry out the oxidation of the organics. It involved passing through a large volume of wastewater through the system to allow enough time for adsorption.

On initial observation the concentration of TOC did not fall significantly as in the case of trial A3. This may be attributed to adsorbed organics on the previous trial which were not oxidised but still occupying an adsorption site. The level of TOC increased at 8 hours and 35 hours owing to desorption after the unit was left static over the weekend - following the commencement of the trial adsorption can be observed.

Current was applied at approximately 40 hours after which an increase in TOC was observed. On the basis of this trial, it is not clear if the oxidation of the organics has taken place or if the Nyex has been oxidised forming fines that are registered as TOC.

Trials E1, E2 and E3 were run on the Nyex 1-20e system in recirculation mode. This system relies purely on power and water to generate the OH^- radicals that carry out oxidation. Trial E1 was carried out on the raw wastewater whereas trials E2 and E3 were carried out with pH adjusted samples. As can be seen in Figure 5-13 for trial E1 the TOC looks to be rising sharply whereas the pH adjusted samples did not observe this trend. It is not possible for the organic concentration to rise, therefore this indicates the interference of a species within the wastewater matrix. It is expected that the contribution arises from the carbonate in solution. After pH adjusting the inorganic carbon would be converted to carbon dioxide and leave the sample.

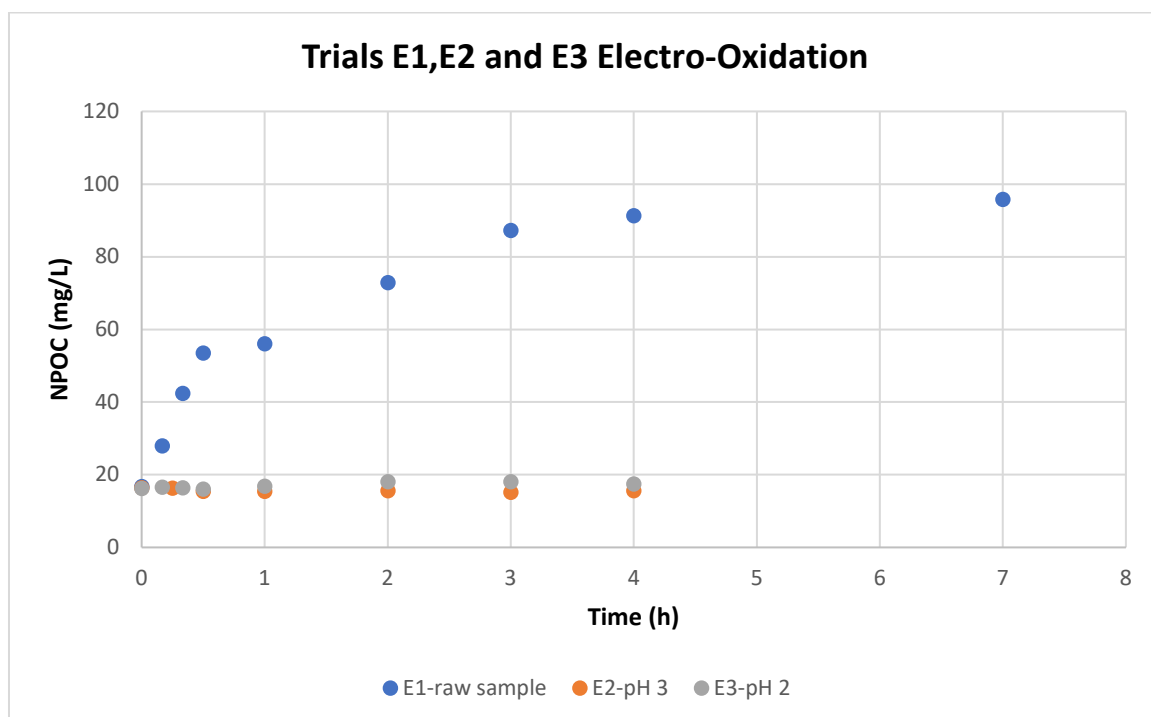


Figure 5-13: Trials E1, E2 and E3 Electro-Oxidation

For the pH adjusted samples the TOC concentration did not change significantly indicating that this interfering species was eliminated and that the actual organics are recalcitrant and resist oxidation, even after an application of $12.5\text{mA}/\text{cm}^2$.

Trial E4 was carried out on the Nyex 1-20e system in recirculation mode. The aim of this trial was to build on trial E1 to see if it was possible to boost the oxidation potential by stoichiometrically introducing hydrogen peroxide to the wastewater. This would increase the number of OH^- radicals available in the wastewater to carry out oxidation of the organics. As can be seen in the Figure 5-14, the addition of the hydrogen peroxide did not reduce the TOC of the wastewater although there was not a large increase as in the case of trial E1.

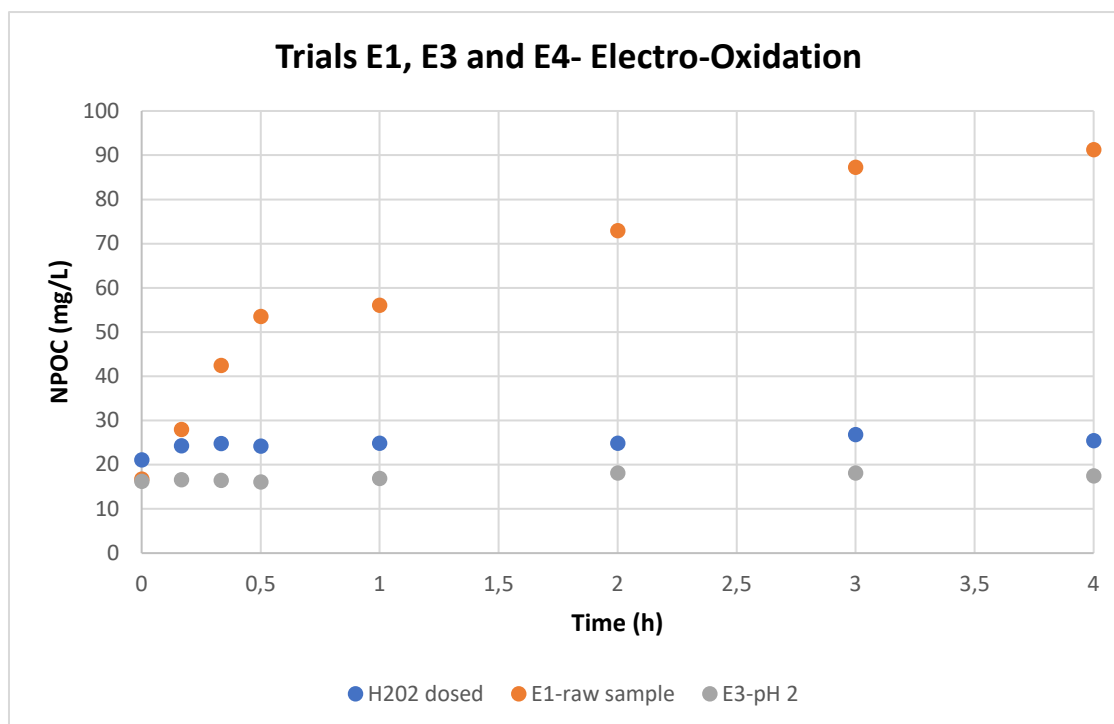


Figure 5-14: Effect of Hydrogen Peroxide Addition on TOC Removal

Trial E5 was carried out on the Nyex 1-20e system in recirculation mode. The aim of this experiment was to carry out a trial with E1 as the reference trial. Trial E5 involved pH adjusting the wastewater down to pH 2 and then re-adjustment of the pH was carried out to the initial pH of approximately 8.5. As can be seen there is a significant difference between E1 and E5, which indicates the removal of an interfering species. This however does not prove oxidation of the organics.

Trial E6 was carried out on the Nyex 1-20e system in recirculation mode. The aim of the experiment was to see if increasing the current density applied to the system would yield a benefit in treatment of organics. The principle of increasing the current means that more OH^\cdot radicals are formed to carry out the oxidation. Owing to the differences in start samples there was no significant benefit in the removal of organics, however upon repetition of this trial, ca. 8% treatment was achieved.

Trial GAC1 was conducted in order to assess the adsorption profile, specifically the mg/g loading rate, which was determined at 40.8 mg/g. This was conducted at a hydraulic residence time of ca. 3 minutes, so this loading rate is deemed conservative and with room for improvement.

5.3.5 Conclusions

The nature of the brine wastewater indicates that the organics are mainly highly hydrophilic. This is evident on trials carried out on the Nyex 1-20a system. There is a hydrophobic contribution which is observed when the pH was adjusted to acidic conditions and the adsorption kinetics were favourable. Subsequent trials showed that the adsorption capacity of the Nyex was reduced which meant that the organics that were loaded on the Nyex were occupying adsorption sites and resistant to oxidation.

The recalcitrant nature of the organics was further observed in trials on the Nyex 1-20e system which showed little removal of TOC.

Addition of hydrogen peroxide to boost the oxidation potential by generating more OH^\bullet radicals was also unsuccessful in removing the organics.

A COD measurement of the raw wastewater was carried out to be between 16-20 mg/L. This deviates significantly from the standard correlations observed for 1 : 2.5 for TOC to COD ratio and further suggests that the organics are resistant to oxidation.

Adsorption onto GAC was shown to be favourable, which combined with the previous trials run, indicates that a combined pH correction, Nyex-e electro-oxidation, and adsorption onto GAC would be the most favourable pathway to achieving removal of organics. Therefore, the combination of Nyex-e electro-oxidation and GAC adsorption processes was chosen for this project as it is most suited for the brine solution. Furthermore, this was shown to achieve a TOC removal rate of approximately 50% (Figure 5-15).

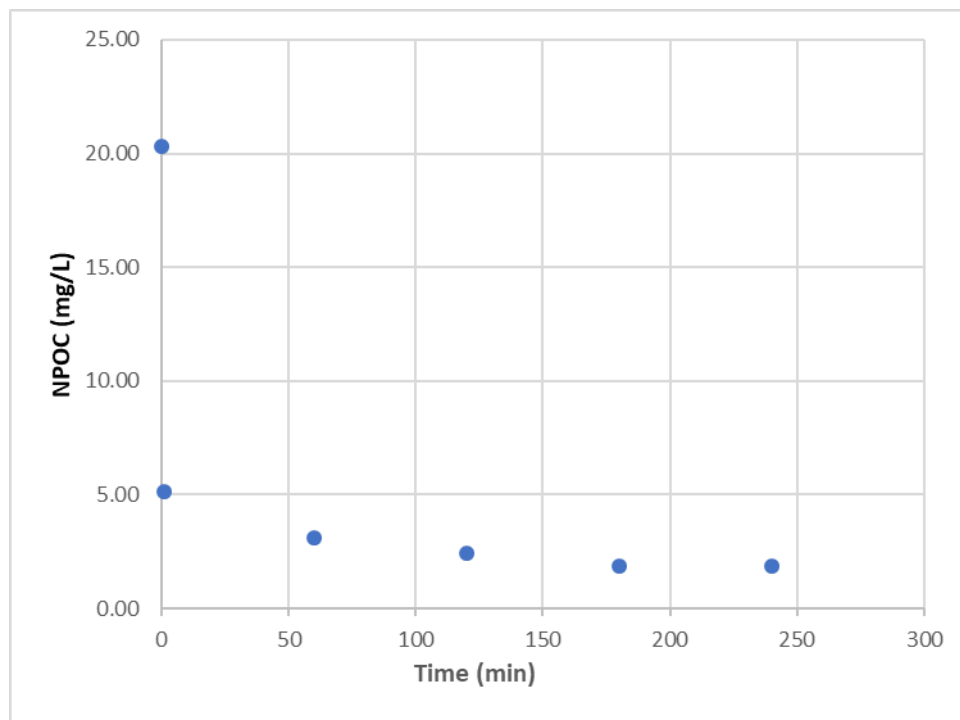


Figure 5-15: Effect of Combining Arvia 1-20e and GAC on TOC Removal.

5.4 Lenntech: Nanofiltration

5.4.1 Description of technology

Please refer to section 4.1.

5.4.2 Scheme and photo of equipment

Please refer to section 4.1.

5.4.3 Description of tests done

Two different feed water were tested with a water quality described in Table 5-6. The first solution (Influent 1) was sampled from the concentrate stream produced by the Reverse Osmosis unit of Evides. The second solution (Influent 2) was an 8 L sample produced by the effluent of Arvia's technology.

Table 5-6: Nanofiltration: experimental operating conditions

Name	Influent 1	Influent 2
EC (mS/cm)	2.9	4.8
pH	8.8	3
Sodium (Na)	651	964
Potassium (K)	16	16
Calcium (Ca)	<4	4.4
Magnesium (Mg)	<2.5	<2.5
Nitrate (NO ₃)	17	109
Chloride (Cl)	427	76
Sulphate (SO ₄)	256	2041
Bicarbonate (HCO ₃)	607	<6
Phosphate (PO ₄)	<5	<5

The same experimental approach was followed as in section 4.1 except for the pH correction. A looser (NF270) and a tighter membrane (TS80) were tested whose specification can be found in Table 4-3 . NF270 was selected to treat the Influent 1 due to its good performance for organic removal recommended by its manufacturer (Dow).

5.4.4 Summary and discussion of tests done

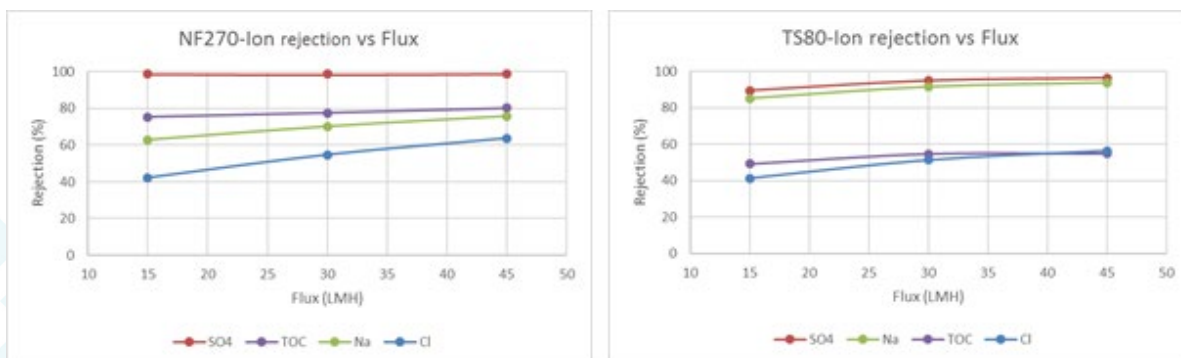


Figure 5-16: : Ionic rejection at different membranes fluxes of 15, 30, 45 LMH

Figure 5-16 shows the rejection of the presented species by NF270 and TS80 using three different fluxes 15, 30 and 45 LMH. A high SO_4 -rejection of 98% and 95% was attained by NF270 and TS80, respectively. NF270 is a semi aromatic membrane and is has a more negative zeta potential than the fully aromatic membrane, TS80. This can explain the higher rejection of the negatively charged ion, SO_4^{2-} , that is better repulsed by the NF270 membrane. In addition, NF270 membrane rejected higher percentage of organics compared to TS80. This can be explained by two reasons. A presence of negatively charged organics (humid acids) resulted in a higher repulsion by the NF270 membrane, as it is explained before for the SO_4^{2-} rejection. However, the second explanation could be that Arvia already removed the bigger or the more negatively charged organics from the RO concentrate and the remaining organics could pass easier through the TS80 membrane. The monovalent ions were rejected less by the two membranes. Both membranes rejected the same percentage of chloride. Na is rejected more by TS80. This can be attributed to the higher concentration of SO_4^{2-} in this feed water that has a big influence on Na rejection. SO_4^{2-} is highly rejected by TS80 and Na is also highly rejected in order to keep the electroneutrality in the feed side.

Table 5-7 and Table 5-8 and the following graphs show the achieved ionic concentration for the different concentration factors (CF) by NF270 and TS80 membranes. By increasing the CF, the ion concentrations in the concentrate were also increased. The goal of these bench scale experiments is to produce a concentrate stream as rich as possible in Na_2SO_4 . The second case experiment better serves this purpose as the Na concentration is equal to 5304 mg/L and the SO_4 concentration is equal to 11651 mg/L.

Table 5-7: Concentration of permeate and concentrate streams for different Concentration Factors (CF) with NF270

Streams concentration (mg/L)					
Ions	Feed Water	Concentrate			Permeate
	CF=1	CF=1.5	CF=2	CF=5.9	CF=5.9
Na	651	843.6	1053.8	2300	377
Cl	437.0	488.9	541.6	1329.0	400.0
SO4	256.0	332.6	482.6	1773	7.9
TOC	9.18	12.5	16.1	45.32	2.03

Table 5-8: Concentration of permeate and concentrate streams for different CF with TS80

Streams concentration (mg/L)					
Ions	Feed Water	Concentrate			Permeate
	CF=1	CF=1.5	CF=2	CF=5.9	CF=5.9
Na	964	1553.1	2122.7	5304	144
Cl	76	67.7	77.7	132	62
SO4	2041.0	2482.1	3653.5	11651	165
TOC	4.2	5.2	5.2	16.2	2.13

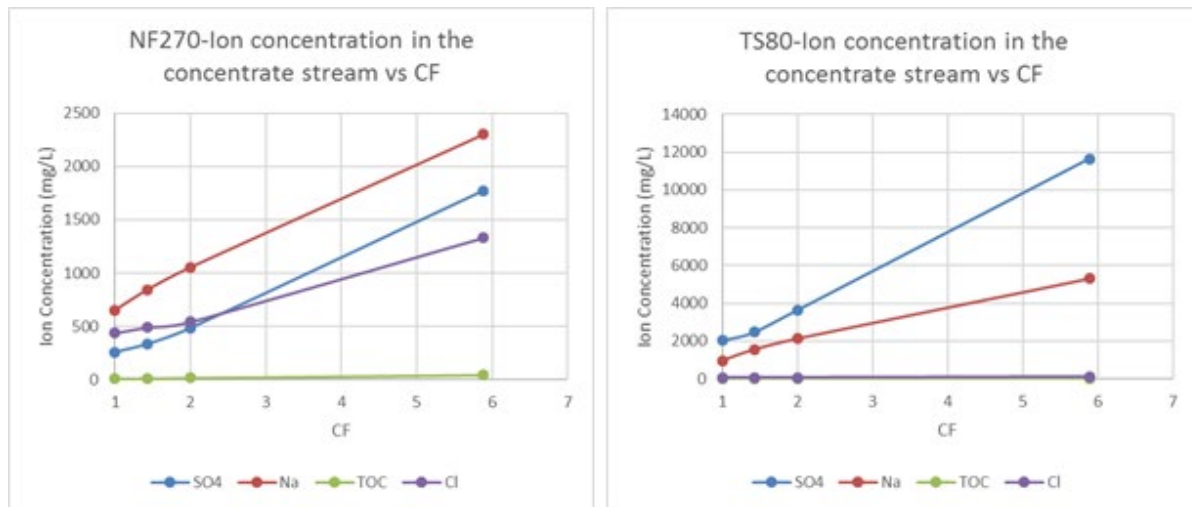


Figure 5-17: Ionic concentration species vs. concentration factors on the concentrate stream for NF270 and TS80 membrane

5.4.5 Conclusions

Two bench scale experiments were conducted using nanofiltration membranes to treat the concentrate stream produced by reverse osmosis from Evides. In the first experiment, the influent 1 with the corresponding ionic concentration presented in Table 6.5 was filtered using the NF270 membrane while the influent 2 was treated using the TS80 membrane. Comparing the two bench scale experiments, higher Na_2SO_4 concentrations were produced when influent 2 was treated and TS80 membrane was used. NF270 membrane rejected higher percentage of organics, which was probably due to the different feed water composition. Both membranes can concentrate Na_2SO_4 as they can reject more than 95% of the SO_4 .

5.5 Lenntech: Reverse Osmosis

5.5.1 Description of technology

Reverse osmosis, as the name suggests, it is the opposite of osmosis. In osmosis, a solvent spontaneously moves, thanks to the naturally occurring osmotic pressure, through a semi-permeable membrane in the direction of the higher solute ion concentration, tending to equalize the chemical potential, or ion concentration, on either side of the membrane. As shown in Figure 5-18, this process would continue until the pressure on the high solute ion concentration side equals the osmotic pressure. Therefore, RO is the process by which a solvent is de-mineralized or de-ionized as it is forced through a semi-permeable membrane by applying a pressure to it to overcome the osmotic pressure [2].

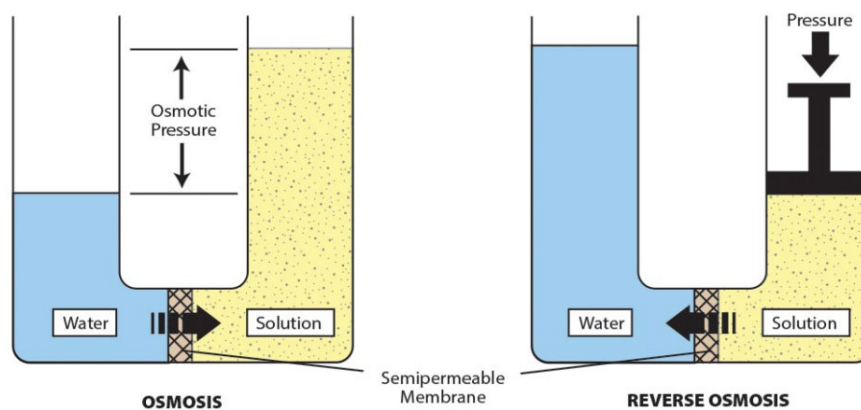


Figure 5-18: Principle of operation of osmosis and reverse osmosis.

The semi permeable RO membrane is typically made of ion chain polymer molecules with functional groups that interact with water allowing water molecules to diffuse through it, however most contaminants in the water do not have the same ability and are therefore left behind. A cross flow configuration is therefore applied for RO membrane separation. As shown in Figure 5-19, the feed water stream flows tangentially to the membrane surface. A fraction of the water in this feed stream passes through the membrane, whereas most of the feed flow travels along the surface. Thus, two streams are collected: the permeate, almost pure water containing low concentration of ions, and the concentrate, having high concentration of small particles and dissolved ions.

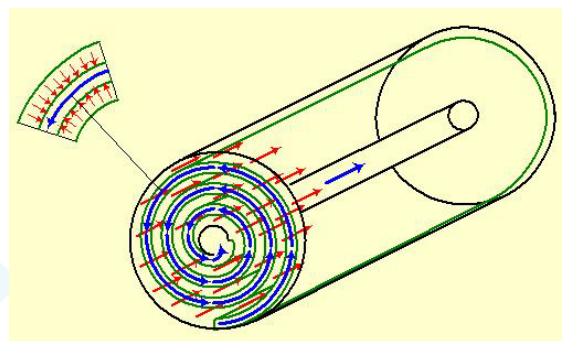


Figure 5-19: Typical cross flow configuration of a spiral wound RO membrane.

In operation, the RO membrane system is continuously supplied with feed water which produces a constant water movement from feed to concentrate. When in cross-flow operation, there is little accumulation of the rejected solutes and fouling or scaling can be minimized.

The recovery of permeate from feed water is desirably kept as high as possible, however this would increase the concentration of ions in the concentrate side of the membrane and this would require increasingly higher pressures, and thus energy, to drive the process, as well as making the membranes more subject to fouling and scaling, and shortening their lifetime.

5.5.2 Scheme and photo of equipment

As referred in the section 4.1, different nanofiltration membranes were tested in order to select the most promising that would attain the best divalent rejection. In order to test the feasibility and rejection of reverse osmosis membranes for Site 02, Sepa cell lab unit was also used to perform screening tests. During these tests two reverse osmosis membranes were used as it will be reported along the section.

As explained in the previous section, Figure 5-20 represents the main components of the system used for the reverse osmosis experiments. Mainly, the system is composed by a stainless steel unit where the different flat sheets can be placed, a pump, and a feed tank reservoir. To conduct the experimental tests the feed solution was separated over a reverse osmosis membrane into a permeate and concentrate stream. Before every experiment the membrane remained immersed in demineralized water during a period of approximately 24h before use. During the experiments the concentrate stream was continuously recirculated back to the feed and the permeate was collected in a glass cylinder.

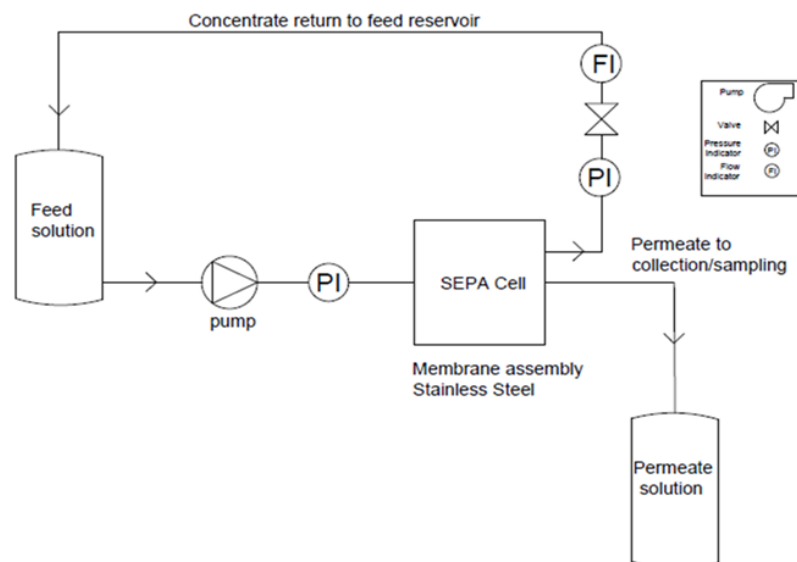


Figure 5-20: Sepa Cell P&ID

To generate permeate flow through the membrane, feed pressure was applied by means of a positive displacement pump and by adjusting the concentrate valve. The flux of permeate through the membrane was monitored at regular intervals by a mass flow meter placed on the permeate stream, while the concentrate was recorded by a flow meter; both data were converted and recorded on the computer. Based on the available active area of the membrane (0.014 m^2), the membrane flux could be calculated. The temperature was maintained constant during all the experiments by introducing a spiral heat exchanger inside of the feed tank. In

addition, the conductivity was measured in the feed tank and concentrate stream. Along time, to characterize the process, samples from the permeate and concentrate streams were collected at different recoveries.

Figure 5-21 shows the Sepa cell unit where different membranes were tested (left side). The main components are the cell holder, upper cell body and bottom cell body (right side).

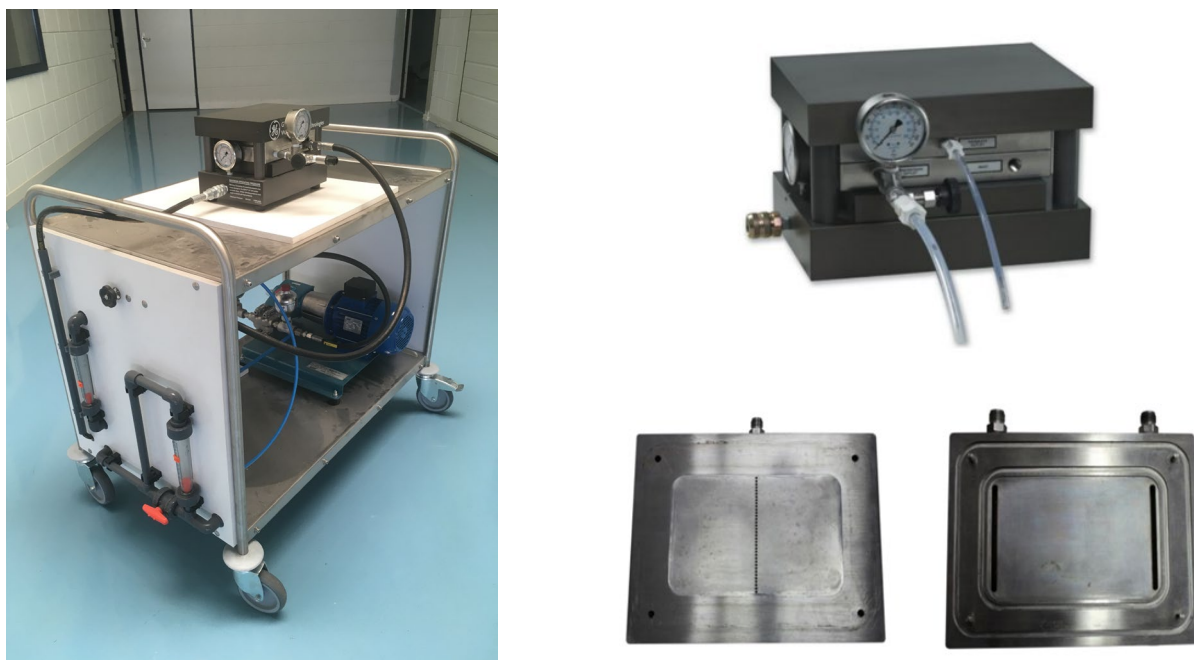


Figure 5-21: Sepa cell lab unit (left) pressure holder (top), bottom and top cell

5.5.3 Description of projections

Reverse osmosis is a conventional treatment process and it can be easily predicted by commercial software. In this case, ROSA software (developed by Dow) was used to predict the ionic rejection of the feed stream by a reverse osmosis membrane. The reverse osmosis membrane that was used is presented in Table 5-9.

Table 5-9: Commercial RO membrane

Model	Vendor	Polymer	Max pressure (bar)	Max temperature (°C)	Avg. NaCl rejection (%)
SW30	Dow	PA	69	45	99.4

Test conditions: 32000 ppm NaCl solution at 800 psi (550kPa) operating pressure, 25°C

Following the bench scale experiments presented in 5.4, the permeate and the concentrate water quality produced by the two membrane NF filtration experiments was entered as feed water in ROSA software.

5.5.4 Summary and discussion of the projections

Reverse osmosis – NF permeate concentration

The first projection refers to the first scenario when the nanofiltration was treating directly the water produced by the RO concentrate from Evides. The second projection refers to the second scenario when nanofiltration followed Arvia (TOC removal). Same conditions of pH, flow rates and temperature were used with the bench scale experiments. Figure 5-22 and Figure 5-23 describe the reverse osmosis projections of the two scenarios. 90% recovery was reached in both cases. In the first case, 96% reduction of the TDS was observed whereas 95% TDS reduction was achieved in the second scenario. In the case that the water temperature was lower, the membrane pore became tighter resulting in higher pressures and higher ionic rejections.

As it is expected, the monovalent ions, Na and Cl, showed lower rejection than divalent ions as SO₄. Hydrated SO₄ ions are larger compared to monovalent ions and they are better retained by the membrane due to size exclusion. In addition, they are better repulsed by the negatively charged polyamide membrane due to Donnan exclusion mechanism. Finally, Na and Cl ions are more mobile and have higher diffusion rates and can easier pass through the membrane.

Reverse osmosis – NF brine concentration

Reverse osmosis is used to concentrate further the brine produced by the nanofiltration treatment step before it ends to EFC technology. Same pH and temperature were used in ROSA as the bench scale experiments. In Figure 5-24 and in Figure 5-25, the RO projections for NF brine concentration are presented when both scenarios are implemented. The system recoveries were 88% and 80% for scenario 1 and 2, respectively. Sulfates increased from 1773 mg/L to 14554 mg/L in the first scenario and from 11651 mg/L to 57758 mg/L in the second scenario.

It should be noted that silica scaling was not considered as limiting factor for the system recovery in ROSA projections. It should be investigated whether the scales will be colloidal or dissolved to assess if they can be removed by flushing of the membrane.

Case-specific

System Details

Feed Flow to Stage 1	2.30 m ³ /h	Pass 1 Permeate Flow	0.72 m ³ /h	Osmotic Pressure:
Raw Water Flow to System	0.80 m ³ /h	Pass 1 Recovery	90.00 %	
Feed Pressure	20.19 bar	Feed Temperature	20.0 C	
Flow Factor	1.00	Feed TDS	1080.39 mg/l	
Chem. Dose	None	Number of Elements	4	Average NDP
Total Active Area	29.36 M ²	Average Pass 1 Flux	24.53 lmh	Power
Water Classification: Surface supply SDI < 3				Specific Energy

Stage	Element	#PV	#Ele	Feed Flow (m ³ /h)	Feed Press (bar)	Rejection (m ² /h)	Conc. Flow (m ² /h)	Conc. Press (bar)	Perm Flow (m ³ /h)	Avg Flux (lmh)	Perm Press (bar)	Boost Press (bar)	Perm TDS (mg/l)
1	SW30-4040	1	1	2.30	19.84	1.50	2.10	19.64	0.20	27.81	0.00	0.00	37.23
2	SW30-4040	1	1	2.10	19.30	0.00	1.91	19.12	0.19	25.66	0.00	0.00	43.89
3	SW30-4040	1	1	1.91	18.78	0.00	1.74	18.63	0.17	23.45	0.00	0.00	59.20
4	SW30-4040	1	1	1.74	18.29	0.00	1.58	18.16	0.16	21.19	0.00	0.00	62.65

Name	Feed	Adjusted Feed		Pass Streams (mg/l as ion)				Permeate				Total	
		Initial	After Recycles	Stage 1	Stage 2	Stage 3	Stage 4	Stage 1	Stage 2	Stage 3	Stage 4	Total	
NH4+ + NH3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	377.00	377.60	2514.27	2758.00	3068.89	3327.55	3653.03	11.85	13.99	16.66	20.02	15.32	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Str	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO3	8.83	8.83	97.33	107.69	119.32	132.30	146.61	0.00	0.00	0.01	0.01	0.00	0.00
HCO3	267.00	267.00	1665.72	1855.95	2002.58	2196.91	2408.20	14.06	16.52	19.59	23.44	18.05	0.00
NO3	19.00	19.00	113.35	124.14	136.10	149.24	163.51	2.55	3.01	3.57	4.29	3.29	0.00
Cl	400.00	400.00	2688.74	2950.86	3241.13	3561.28	3910.27	8.74	10.33	12.32	14.84	11.33	0.00
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO4	7.90	7.90	54.04	59.30	65.15	71.61	78.65	0.03	0.04	0.05	0.06	0.04	0.00
SiO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Brom	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO2	0.88	0.88	5.31	5.68	6.27	7.66	8.69	4.63	5.22	5.88	6.63	5.51	0.00
TDS	1079.79	1080.39	7135.31	7855.99	8593.24	9438.93	10360.31	37.23	43.89	52.20	62.65	48.04	0.00
pH	8.60	8.60	8.48	8.46	8.43	8.41	8.38	6.71	6.72	6.74	6.76	6.74	0.00

Figure 5-22: Projection of the RO for NF permeate concentration, scenario 1

System Details

Feed Flow to Stage 1	2.30 m ³ /h	Pass 1 Permeate Flow	0.72 m ³ /h	Osmotic Pressure:	
Raw Water Flow to System	0.80 m ³ /h	Pass 1 Recovery	90.01 %	Feed	0.28 bar
Feed Pressure	15.23 bar	Feed Temperature	20.0 C	Concentrate	2.50 bar
Flow Factor	1.00	Feed TDS	479.20 mg/l	Average	1.39 bar
Chem. Dose	None	Number of Elements	4	Average NDP	11.94 bar
Total Active Area	29.35 M ²	Average Pass 1 Flux	24.53 l/mh	Power	1.22 kW
				Specific Energy	1.69 kWh/m ³

Stage	Element	#PV	#Ele	Feed Flow (m ³ /h)	Feed Press (bar)	Reconc Flow (m ³ /h)	Conc Flow (m ³ /h)	Conc Press (bar)	Perm Flow (m ³ /h)	Avg Flux (l/mh)	Perm Press (bar)	Boost Press (bar)	Perm TDS (mg/l)
1	SW30-4040	1	1	2.30	14.88	1.50	2.10	14.69	0.20	26.74	0.00	0.00	17.91
2	SW30-4040	1	1	2.10	14.34	0.00	1.92	14.17	0.19	25.28	0.00	0.00	20.66
3	SW30-4040	1	1	1.92	13.82	0.00	1.74	13.67	0.17	23.80	0.00	0.00	24.00
4	SW30-4040	1	1	1.74	13.33	0.00	1.58	13.20	0.16	22.30	0.00	0.00	28.08

Name	Feed	Adjusted Feed		Pass Streams (mg/l as ion)								Permeate				Total
		Initial	After Recycles	Stage 1	Stage 2	Stage 3	Stage 4	Stage 1	Stage 2	Stage 3	Stage 4	Stage 1	Stage 2	Stage 3	Stage 4	
NH4+ + NH3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	144.00	155.20	1033.28	1129.19	1237.85	1361.16	1501.33	5.12	5.90	6.86	8.03	6.40	6.40	6.40	6.40	6.40
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Str	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HCO3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO3	97.00	97.00	595.14	649.62	711.22	786.98	860.68	11.09	12.80	14.86	17.38	13.88	13.88	13.88	13.88	13.88
Cl	62.00	62.00	418.76	457.72	501.87	551.99	608.99	1.13	1.30	1.52	1.78	1.41	1.41	1.41	1.41	1.41
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO4	165.00	165.00	1129.67	1235.00	1354.41	1490.00	1644.25	0.57	0.66	0.76	0.90	0.71	0.71	0.71	0.71	0.71
SiO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Brom	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO2	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
TDS	468.00	479.20	3176.05	3471.54	3805.36	4184.12	4614.64	17.91	20.66	24.00	28.08	22.41	22.41	22.41	22.41	22.41
pH	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00

Figure 5-23: Projection of the RO for NF permeate concentration, scenario 2

Feed Flow to Stage 1	1.70 m³/h	Pass 1 Permeate Flow	0.18 m³/h	Osmotic Pressure:	
Raw Water Flow to System	0.20 m³/h	Pass 1 Recovery	88.00 %	Feed	4.79 bar
Feed Pressure	40.76 bar	Feed Temperature	20.0 C	Concentrate	35.96 bar
Flow Factor	0.85	Feed TDS	8608.64 mg/l	Average	20.37 bar
Chem Dose	None	Number of Elements	4	Average NDP	6.05 bar
Total Active Area	29.36 M²	Average Pass 1 Flux	6.00 lmh	Power	2.39 kW
Water Classification: Surface Supply < 3				Specific Energy	13.58 kWh/m³

Stage	Element	#PT	#Ele	Feed Flow (m³/h)	Feed Press (bar)	Concentrate				Permeate				Avg Flux (lmh)	Perim Press (bar)	Boost Press (bar)	Perim TDS (mg/l)
						Stage 1	Stage 2	Stage 3	Stage 4	Stage 1	Stage 2	Stage 3	Stage 4				
1	SW30-4040	1	1	1.70	40.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	715.91
2	SW30-4040	1	1	1.63	39.93	0.00	0.00	0.00	1.63	40.28	38.81	0.05	6.51	0.00	0.00	0.00	896.28
3	SW30-4040	1	1	1.58	39.46	0.00	0.00	0.00	1.54	39.34	5.17	0.04	5.17	0.00	0.00	0.00	1129.74
4	SW30-4040	1	1	1.54	39.00	0.00	0.00	0.00	1.51	38.88		0.03	4.19	0.00	0.00	0.00	1393.06

Name	Feed	Adjusted Feed		Pass Streams (mg/l as Ion)								Total					
		Initial	After Recycles	Stage 1	Stage 2	Stage 3	Stage 4	Stage 1	Stage 2	Stage 3	Stage 4						
NH4 + NH3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	58.00	58.00	351.20	363.66	374.31	383.14	390.54	9.56	12.08	15.34	18.99	13.14					
Na	2833.02	2839.85	19240.22	19935.53	20299.70	21023.67	21444.50	219.90	277.79	353.03	438.11	300.44					
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Si	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO3	610.29	610.29	4088.20	4236.52	4363.06	4468.43	4537.16	45.99	65.53	91.81	121.98	74.39					
HCO3	2015.51	2015.51	12321.10	12738.16	13130.56	13490.32	13700.91	333.74	405.40	496.56	598.32	434.60					
NO3	10.92	10.92	48.39	50.02	51.39	52.50	53.42	3.85	4.85	6.12	7.54	5.25					
Cl	1209.85	1209.85	8341.49	8643.49	8901.66	9117.27	9299.44	80.23	101.98	130.41	162.72	111.36					
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO4	1773.00	1773.00	13940.62	13516.52	13994.21	14265.60	14534.90	22.34	28.30	36.11	45.03	30.89					
SiO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Boron	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO2	1.42	1.42	26.75	28.15	29.35	30.36	31.22	0.25	0.27	0.30	0.34	0.27					
TDS	8490.80	8508.64	57431.27	59593.97	61274.93	62752.96	64000.91	715.91	866.28	1129.74	1393.06	972.43					
PH	9.10	9.10	8.41	8.41	8.41	8.41	8.41	9.26	9.31	9.33	9.34	9.33					

Figure 5-24: Projection of the RO for NF brine concentration, scenario 1

Feed Flow to Stage 1														1.70 m³/h	Pass 1 Permeate Flow		0.16 m³/h	Osmotic Pressure:	
Raw Water Flow to System														0.20 m³/h	Pass 1 Recovery		80.00 %		
Feed Pressure														42.36 bar	Feed Temperature		20.0 C	Feed	
Flow Factor														0.85	Feed TDS		17945.83 mg/l	Concentrate	
Chem. Dose														None	Number of Elements		4	Average	
Total Active Area														29.36 M²	Average Pass 1 Flux		5.45 lmh	Power	
Water Classification: Surface Supply SDI < 3																		Specific Energy	

Figure 5-25: Projection of the RO for NF brine concentration, scenario 2

5.5.5 Conclusion

Four simulation campaigns were conducted to predict the SW30 reverse osmosis membrane behavior, using the ROSA projection software. Initially, two projections of the RO membrane filtration were performed to treat the permeate water produced by the two nanofiltration bench scale experiments. The permeate water produced by the reverse osmosis membrane for both scenarios had a TDS concentration lower than 50 mg/L and an applied pressure lower than 20 bar. The projections were made for the worst case scenario when the water temperature was 20°C. Lower water temperatures will result in higher permeate water quality as the membrane pore size will become tighter, resulting in higher ionic rejections.

The last two RO projections aimed to simulate the membrane behavior when the membrane treats the brine stream produced by the two nanofiltration bench scale experiments. Sulfate concentration significantly increased after the RO concentrating step when both scenarios were implemented.

5.6 NTUA: Evaporator

5.6.1 Description of technology

The innovative Multiple Effect Distillation evaporator (MED-NTUA) was developed in the framework of the BEST LIFE project SOL-BRINE (LIFE09 ENV/GR/000299). The MED-NTUA evaporator is a 2-stage forward-feed evaporator with a capacity of 2 m³/day.

Multiple Effect Distillation/evaporation (MED) is a low-temperature thermal desalination process and the first desalination technology used to produce fresh water in an industrial scale. The feed saline water is distributed in evaporators of different chambers (called stages or effects). The evaporator tubes in the first effect are heated by water and the resulting steam is condensed inside the evaporator tubes of the subsequent effect, where again vapor is produced. (Xevgenos et al., 2018). Each of effect is maintained at a lower temperature than its preceding one. The feed water is sprayed or distributed over the surface of the evaporator tubes in a thin film to promote rapid boiling and evaporation. Pressure reduction decreases the boiling point of the water. Hence, the boiled-off vapor in one vessel can be used to heat the next one. Only the first vessel (at the highest pressure) requires an external heat source. The steam produced in the last effect is condensed in a separate heat exchanger, which is cooled by the incoming saline water.

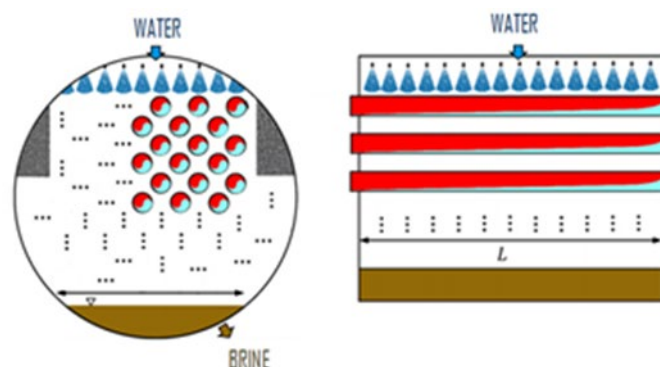


Figure 5-26: Schematic of horizontal tube-bundle, left: cross section, right: Longitudinal section.(Azimibavil& Jafarian Dehkordi.,2016)

The MED - NTUA evaporator is made up of two consecutive effects. In each of the MED effects, brine is evaporated resulting in the production of two subsequent streams: (1) a water vapor stream that is then condensed and recovered as fresh water and (2) a more concentrated brine stream. The vapor stream of the first effect is used to heat the concentrated brine produced in the second effect that is 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 is provided by internal heat gain (heating steam from the first effect) and thus energy recovery is achieved.

The vapor stream produced by the second effect is used for pre-heating purposes. Specifically, the vapor is passed through a plate heat exchanger where it is condensed, transferring its thermal energy to the brine stream

of inlet feed. The unit is built from Super Duplex, EN 1.4410, with a thickness of 5.0 mm. The heating element is designed according to the specifications of TEMA (Tubular Exchanger Manufacturers Association). The heating element is mounted eccentrically in the head by means of a flanged neck. The element consists of U - shaped tubes in a hexagonal arrangement. Inflow and outflow are separated by a custom - made stationary - head bonnet with pass partition. In order to achieve the maximum density of the tube bundle in the direction of the showered brine flow, a small pitch of 1.25 is selected for the tube bundle arrangement.

5.6.2 Experimental: Scheme and photo of equipment

As mentioned before, the MED-NTUA evaporator consists of two sequential effects. Figure 5-27 shows the main components of the system used for the evaporation experiments.

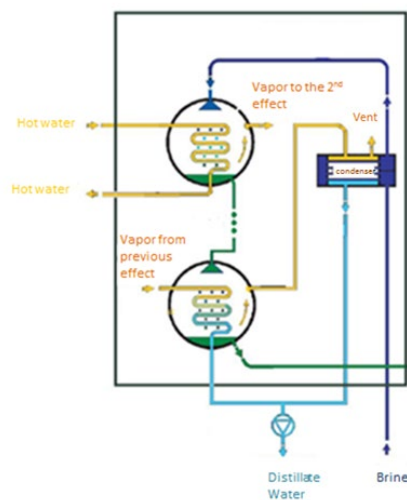


Figure 5-27: Schematic diagram of the innovative vacuum evaporator unit, (SOL-BRINE project, solbrine.uest.gr)

The MED-NTUA evaporator was refurbished and containerized in order to be easily transported. The experiments were carried out with the new arrangement of the evaporator that is presented in the following pictures.



Figure 5-28: The equipment of the Greek Brine Excellence Center (BEC)..

The control of the system is accomplished via a PC-based SCADA interface. Multiple temperature, pressure and flow transmitters are connected in many positions within the system, receiving all the important data for the control of the process. Data is collected in a PLC controller, with the necessary programming for the control of the unit. Though the use of SCADA, overall control and monitoring can be achieved.

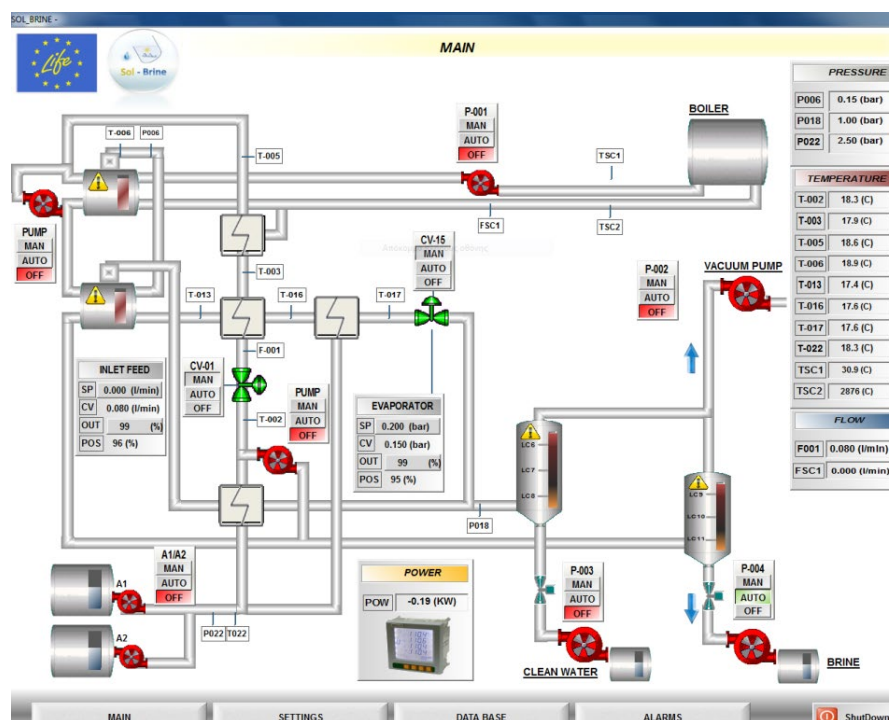


Figure 5-29: View of the operation software tool.

5.6.3 Methodology: Description of tests done

The experiments were carried out with the use of synthetic solutions. The synthetic solutions were prepared in order to have similar composition as the streams that will be the input of the evaporator at Evides Site 02. Data for the preparation of the synthetic solutions were received from Lenntech (for the nanofiltration concentrate , NF concentrate) and also from Lenntech (for the Reverse Osmosis concentrate , RO concentrate). It was assumed that the addition of just NaCl is sufficient, because the concentration of other ions (except Na⁺ and Cl⁻) in the inlet effluents of the evaporator is very low and considered not important.

The characteristics of the prepared and used synthetic solutions are presented in Table 5-10.

Table 5-10 :The characteristics of the feed synthetic solutions.

	Description	TDS (mg/L)
Synthetic Solution 3 (SS3)	NF concentrate	23,229
Synthetic Solution 4 (SS4)	RO concentrate	10,958

These solutions were individually fed into the MED evaporator.

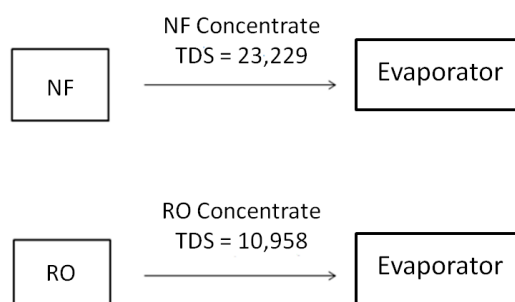


Figure 5-30: Flow diagram for the evaporator at Site 02.

In total, ten (10) batch experimental series took place at the Greek Brine Excellence Center. Specifically, five (5) experiments with 'SS3' as feed brine stream to the evaporator and five (5) experiments with 'SS4' as feed brine stream to the evaporator. Each experimental series lasted about 2 hour.

Additionally, the temperature (T) and Total Dissolved Solids (TDS) of each feed brine stream were measured before the start of each experimental series.

The water that was fed into the evaporator was heated using a boiler in order to raise its temperature to 80°C. The Boiler has the ability to reach 107 °C, the higher the temperature, the greater the efficiency. The monitoring of the experimental series and in particular of the components of the evaporator was performed using the SCADA / PLC. The recorded measurements are presented in Table 5-11.

Table 5-11: Operating Parameters of MED Evaporator.

1 st Effect MED	2 nd Effect MED
T = 55 °C	T = 45 °C
P = (0.13 – 0.15) bar	P = (0.06 – 0.10) bar

The collected evaporator effluent of each experiment was analyzed in the Unit of Environmental Science and Technology (UEST) of the School of chemical engineering of NTUA. The lab oratory is accredited by ISO17025.

The method used in order to measure the TDS value of the samples is APHA-AWWA-WEF Standard Methods for the Examination of water and wastewater, 20th Edition, 1998: part 2540C.

The results of the experimental series are presents in Table 5-12.

Table 5-12: The TDS concentration of the Brine

Experimental Series	Stream	Temperature (T, °C)	Total Dissolved Solids (Feed Brine) (TDS, mg/L)
1	SS3 (Synthetic Solution 3)	25.3	23,638
2		25	22,875
3		24.6	22,994
4		24.8	23,527
5		26.5	23,114
Average			23,229
6	SS4 (Synthetic Solution 4)	27.2	11,234
7		26.9	10,962
8		27.4	10,971
9		26.8	11,357
10		27.2	10,958
Average	-	-	11,096

In order to verify the chemical quality of the production, several samples of the feed brine stream and the evaporator effluent were taken regularly for measuring their ion composition. The ion concentrations of the feed brine and evaporator effluent were measured using inductively coupled plasma optical emission spectrometry (ICP-MS) and Ion Chromatography (IC). At the end of each experiment, the thermal supply was cut off and the system was terminated.

Finally, to ensure that the conditions in each experiment are replicable, the effects were rinsed after each completed experiment using the condensate vapor as cleansing water. The cleaning procedure lasted 30 minutes.

5.6.4 Summary and discussion of tests done

At the end of the 10 experimental series, all data collected was processed in order to reach a final conclusion on the performance of the evaporator and the quality characteristics of the evaporator effluent. Table 5-13 shows the total volume of the condensate vapor and evaporator effluent which was recorded in the collector tanks.

Table 5-13: The condensate vapor and evaporator effluent from the 10 experimental series.

Experimental Series	Feed Stream	Feed Brine Streams flow (kg)	Condensate vapor effluent (kg)	Evaporator effluent (kg)
1	SS3	100	58	42
2			62	38
3			61	39
4			59	41
5			59	41
Average SS3		100	59.8	40.2
Standard Deviation			1.5	
6	SS4	100	59	41
7			61	39
8			60	40
9			58	42
10			59	41
Average SS4			59.4	40.6
Standard Deviation			1.0	
Total Average		100	59.6	40.4

SS3 (NF Concentrate)

The mass of Feed Brine Stream was: 97.9 kg Deionized water + 2.3 kg Salts= 100 kg Feed Brine Stream. Consequently, the daily mass balance was: 100 kg Feed Brine Stream = 59.8 kg Condensate vapor + 40.2 kg Evaporator effluent

SS4 (RO Concentrate)

The mass of Feed Brine Stream was: 98.9 kg Deionized water + 1.1 kg Salts= 100 kg Feed Brine Stream. Consequently, the daily mass balance was: 100 kg Feed Brine Stream = 59.4 kg Condensate vapor + 40.6 kg Evaporator effluent

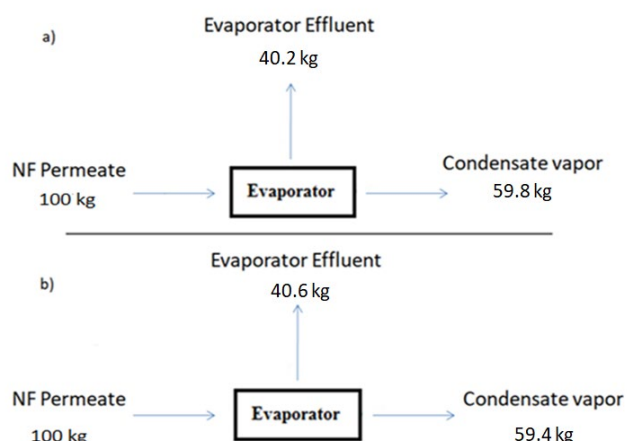


Figure 5-31: Flow diagram of daily mass balance for the two individual feed brines.

Therefore, the evaporator's average recovery rate is the following:

Stream I (NF Permeate): $R = \frac{59.8 \text{ L}}{100 \text{ L}} * 100 = 59.8\%$

For Stream II (MC II effluent): $R = \frac{59.4 \text{ L}}{100 \text{ L}} * 100 = 59.4\%$

Table 5-14 shows the TDS measurements of the Feed Brine Stream and Evaporator effluent and the evaporator's salt recovery percentage.

Table 5-14: TDS measurements and the evaporator's salt recovery percentage.

Experimental Series	Stream	Feed Brine Stream	Evaporator effluent	Concentration Factor	Salts Recovery (R)
		TDS (mg/L)	TDS (mg/L)		%
1	SS3	23,638	56,281	2.38	55
2		22,875	55,793	2.43	57
3		22,994	53,474	2.32	59
4		23,527	56,016	2.38	57
5		23,114	53,753	2.32	59
6	SS4	11,234	27,400	2.43	59
7		10,962	26,100	2.38	57
8		10,971	27,428	2.5	58
9		11,357	29,121	2.56	60
10		10,958	27,395	2.5	57

Results from the 10 experimental series are presented in Figure 5-31, Figure 5-32 and Figure 5-33.

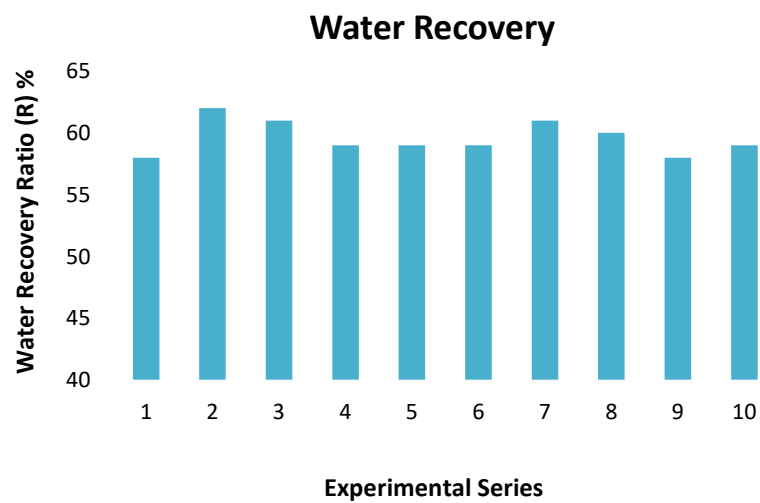


Figure 5-32: Water recovery on the 10 Experimental Series.

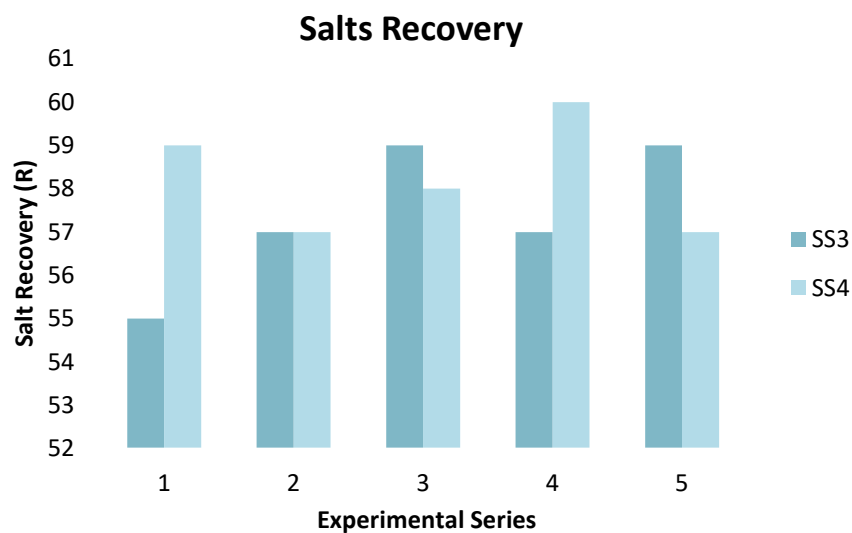


Figure 5-33: Water recovery on the 10 Experimental Series.

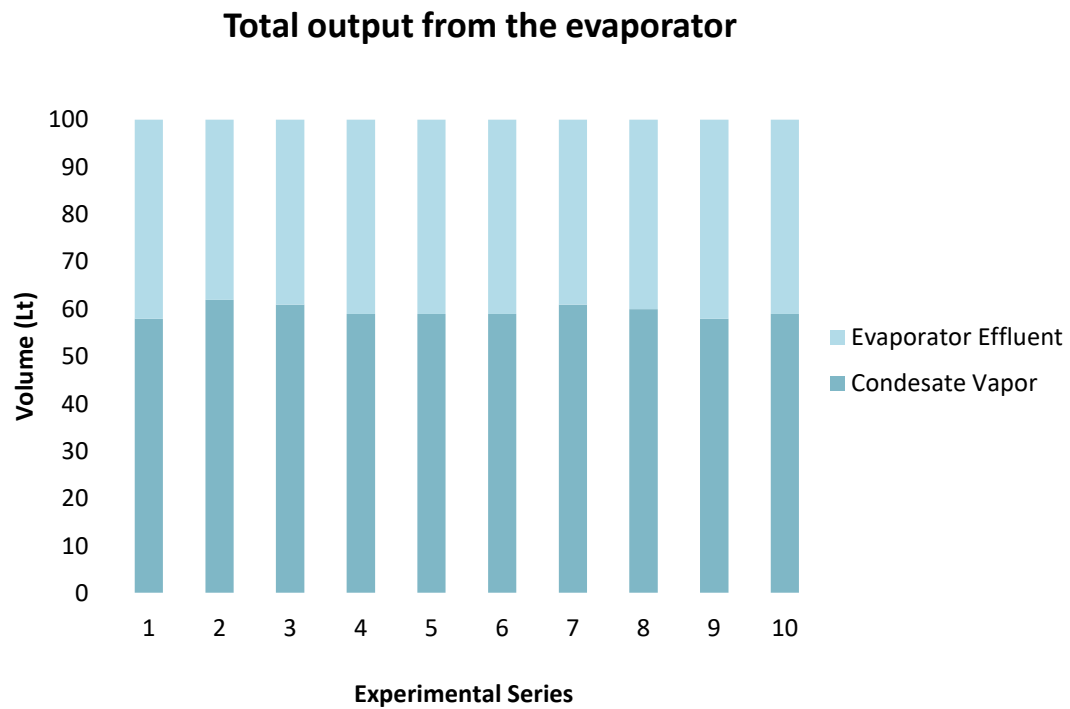


Figure 5-34: Total output from the evaporator on the 10 Experimental Series.

5.6.5 Conclusions

The performance of the MED-NTUA was evaluated for the treatment of brine. From the experiments, the following conclusions were made:

- The multiple effect distillation system demonstrated a steady performance.
- For the SS3 (NF) the water recovery was 59.8%, whereas for the SS4 stream (RO) it was 59.4%.
- The concentration factor range was 2.32 - 2.50.

5.7 TU Delft (EFC)

5.7.1 Description of technology

This section introduces the concept of Eutectic Freeze Crystallization (EFC). Crystallization is a solid-liquid separation method, in which the solute crystallizes from the liquid solution and turns into a pure solid crystalline phase. EFC can be considered as a combination of cooling and freeze crystallization, that can be used to separate both organic and inorganic compounds from aqueous solutions. It is a fairly recent technology that has been studied and applied mainly for the recovery of water and salts from wastewater.

The present tests focused on the separation of sodium sulphate decahydrate (also known as mirabilite) from an aqueous brine stream, by employing EFC. The basic principle of this process can be described using a phase diagram of a binary sodium sulphate (Na_2SO_4) - water mixture, shown in Figure 5-34 (Fernández-Torres, 2012; Hougen, 1954). Starting from an under-saturated aqueous solution with a concentration of Na_2SO_4 higher than the eutectic composition (point A), the system can be cooled down slightly below the solubility line of Na_2SO_4 (point B). At this level of supersaturation, mirabilite crystals start to form. Further cooling decreases the temperature and the concentration of Na_2SO_4 with the formation of mirabilite crystals along the solubility line B to C. At point C (Eutectic point: intersection of ice and Na_2SO_4 solubility line), the freezing point of the solution is reached, and further cooling will result in the formation of ice and mirabilite crystals simultaneously. Similarly, starting with a solution of lower concentration than the eutectic composition, would result in the formation of ice crystals first and following the ice line, the eutectic point would be reached, where mirabilite crystals would also start forming. The two solid products (ice and mirabilite crystals) can be separated gravitationally based on their density difference. Mirabilite crystals would sink to the bottom of the vessel, while ice would rise to the surface.

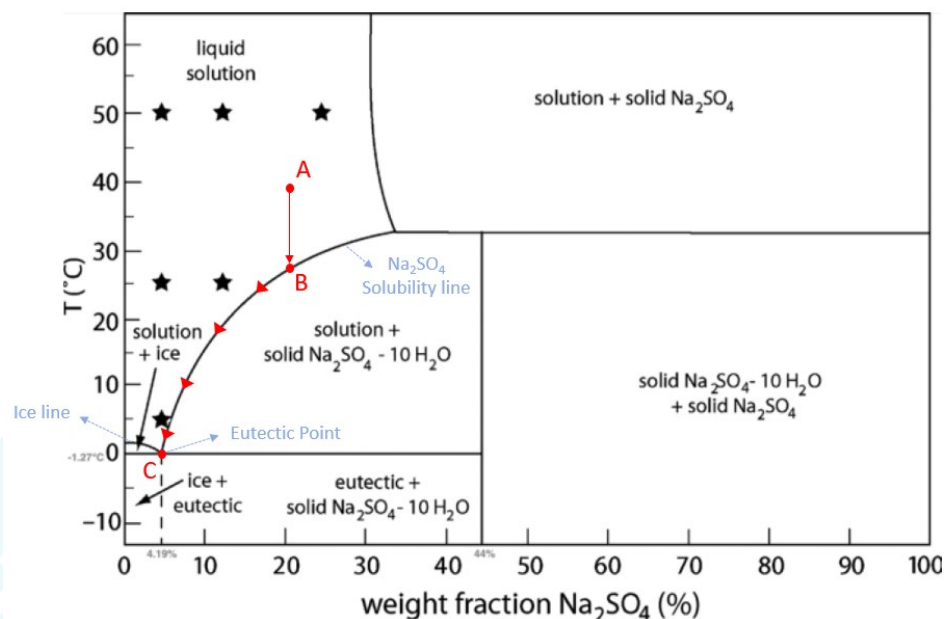


Figure 5-35: Solid – liquid phase diagram of a binary sodium sulphate – water solution

The most important design characteristics of an EFC crystallizer are the heat transfer rate, that dictates the production rate, and the separation efficiency. The working point of a continuous eutectic freeze crystallizer is slightly below the eutectic point of the system. At this point, the thermodynamic equilibrium condition prevails, keeping the temperature stable by balancing the cooling load of the coolant and the heat of the crystallization of ice and mirabilite. The composition of the solution is also constant due to the simultaneous crystallization of ice and mirabilite from the solution.

As shown in Figure 5-35, the eutectic composition and temperature of the binary Na_2SO_4 -water system were found to be 4.2 wt% Na_2SO_4 and -1.27°C , respectively. The selectivity of crystal growth leads to very pure products even when the solution contains many impurities. However, these impurities can shift the eutectic point of the pure binary system, by depressing the freezing point of ice and consequently the eutectic point of the whole system.

One of the main advantages of using EFC to recover and separate mirabilite crystals from the brine is that EFC is a physical separation method that does not involve any chemicals and thus, further contributes to the sustainability of the whole process. Moreover, EFC requires up to 70% less energy compared to evaporative crystallization, due to the fact that heat of fusion of ice (6.01 kJ/mol) is six times less than the heat of evaporation of water (40.65 kJ/mol) (Lu, 2017; van der Ham, 1999). Compared to cooling crystallization, EFC is not limited by the remaining solubility at low temperature, leading to a theoretical separation efficiency of 100%, if no purge streams are needed.

5.7.2 Scheme and photo of equipment

For the purpose of performing lab-scale EFC tests an experimental setup was designed and assembled within the ZERO BRINE project. The setup can be divided into separate sections such as the crystallizer vessel, the scraper and the auxiliary equipment.

a) Crystallizer

For the bench-scale EFC experiments, a triple-wall, cylindrical, glass vessel with a capacity of 2 L was used. This jacketed crystallizer can be thermostated via a cooling bath (LAUDA RP 4090 CW with Kryo 90 as cooling liquid). The outer layer of the wall is sealed with vacuum in order to minimize any heat transfer with the environment and prevent condensation on the walls of the reactor. The bottom of the vessel is curved and includes an outlet for slurry removal that can be manually controlled using a valve.

b) Scraper

Scrapers are essential in an EFC process in order to prevent ice scaling and enhance heat transfer. Local undercooling within the crystallizer is highest at the inner wall, due to the lowest temperature at that surface. Therefore, the probability of secondary nucleation, crystal growth or attachment of crystals or nuclei at this point is the highest. This effect can lead to an accumulation of ice crystals on the subcooled surface that aggravates the heat transfer from the coolant side to the solution through the crystallizer wall and results in an unsteady EFC operation. Hence, the main purpose of the scrapers is to wipe the cooled wall surface and remove the forming ice layer, before it creates a solid crust. Finally, scrapers are also used to promote agitation that improves the homogeneity and heat transfer in the solution.

In this system, an anchor shaped scraper is used to allow the insertion of measurement probes or sampling tubes from the top of the vessel. This main body of the scraper consists of two parts cut out of high density polyethylene (HDPE), for high resistance in low temperatures, connected with stainless steel screws. Towards the outer side and between the two parts, silicone is inserted to apply the required force on the walls and wipe the ice layer. The silicone flaps are inserted between the two parts and are stabilized by the screws connecting the two parts. These flaps extend around the HDPE part, applying the necessary force on the walls. The scraper is attached to an axis and connected to a motor stirrer. The rotating axis of the motor (made out of stainless steel) is inserted and screwed into a polyoxymethylene (POM) socket, on top of the HDPE part, in order to avoid any contact with the working solution.

c) Auxiliary Equipment

Auxiliary equipment is used in this setup for controlling the conditions of the system, washing of the crystal products and sampling or measuring of certain parameters.

A LAUDA RP 4090 CW cooling bath is used for the cooling of the crystallizer with Kryo90 as the circulating cooling liquid. The temperature inside the reactor is measured with the PT-100 probe that is connected to the bath. The temperature of the system can be monitored and controlled through the *LAUDA Wintherm Plus* thermostat control (version 3.5) software.

A Hei-TORQUE Precision 400 motor is connected to the scraper rotating axis, allowing measurement of torque up to 400 Ncm and a speed range between 10 and 2000 rpm. A metal frame is constructed to hold the motor, adjust its height and stabilize it together with the glass vessel. The stirrer is connected to a computer and can be controlled and monitored through the *Hei Control* software.

For the washing and filtering of crystal products a double-wall, glass Buchner filter is used. The filter is connected to a cooling bath (LAUDA RK20 KS) that keeps the temperature of the filter interior at low temperature. A vacuum pump is also connected to the filter for the vacuum filtration stage of the process. The filtration/washing setup is presented in Figure 5-36.

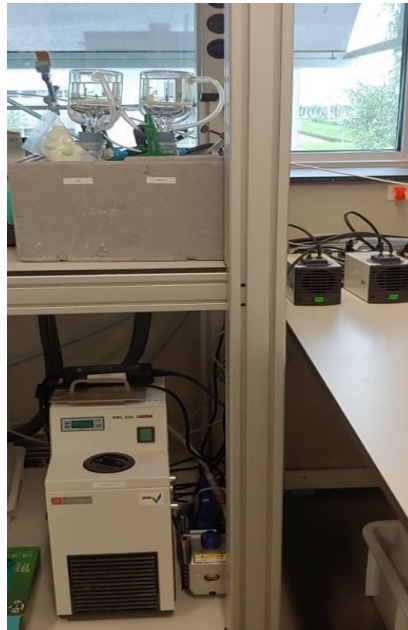


Figure 5-36: Setup used for the filtration and washing of the salt crystals.

An overview of the crystallization setup is shown in Figure 5-37.



Figure 5-37: Setup used for the EFC trials.

5.7.3 Description of tests done

a) Eutectic Freeze Crystallization

In order to confirm the eutectic point of the Nanofiltration (NF) concentrate stream, as well as to observe the performance of the system and the recovery of Na_2SO_4 crystals, an EFC experiment of the NF concentrated outlet was performed using the 2 L setup.

This trial was conducted using a synthetic solution that represents the NF concentrate stream based on the tests and analysis by Lenntech. Since the main components of the stream are sodium, sulphate and chloride ions, the solution was prepared by dissolving Na_2SO_4 and NaCl with water. For this test, the organic contents of the stream were not considered.

Based on the values of the NF concentrate, the solution would be too diluted to perform a bench-scale test. The synthetic solution would have a 0.44 wt % composition of Na_2SO_4 , while the eutectic composition is close to 4.2 wt%. This means that we would have to concentrate the solution approx. ten times in the 2 L batch reactor, which is not possible.

That is why a more concentrated solution was prepared to simulate the conditions closer to the eutectic point in a continuous system, while keeping the ratios of Na_2SO_4 and NaCl to TDS the same. The 2 L synthetic mixture that was used for the trial had a concentration of 46.9 g Na_2SO_4 /L and 23.1 g NaCl /L.

15 mL of the initial solution were taken as a sample for elemental analysis with Ion Chromatography (IC) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

2 L of the synthetic mixture were transferred to the 2 L EFC setup to observe any changes that the NaCl impurities might have on the eutectic conditions of Na_2SO_4 found in literature, observe the system and test the salt crystals for elemental impurities. The speed of the motor was set to 70 rpm and the system was cooled down gradually. At a temperature close to -2°C , approximately 1 g of ice was added to the reactor as seed crystals, to promote ice nucleation. After reaching and maintaining eutectic conditions for close to 30 minutes, the cooling was stopped. Approximately 250 mL of the slurry were removed from the bottom outlet of the reactor and transferred to the filtration setup in order to filter and wash the salt crystals.

b) Filtering & Washing of crystals

The effect of washing on the purity of crystals was also tested. In order to evaluate if there are any impurities on the surface of the sodium sulphate crystals, the unwashed reactor contents were washed with a saturated Na_2SO_4 solution at room temperature. The 250 mL removed from the reactor were filtered under vacuum, using the filtration setup that was described in the previous section. 5 g of the unwashed retentate crystals that remained on the filter and 20 mL of the permeate were stored for elemental analysis.

The remaining cake of Na_2SO_4 crystals was washed using 25 mL of saturated Na_2SO_4 solution. The saturated solution was poured in the Buchner filter and the slurry was stirred gently for a few seconds before turning on the vacuum. After the liquid was filtered out, 5 g of the washed crystals (1st washing step) were taken as a sample and 20 mL of the permeate washing solution were stored for analysis.

The washing procedure was repeated two more times by pouring 25 mL of saturated Na_2SO_4 solution for each washing step to the remaining crystals, while collecting samples of the cake and permeate as before. The concentration of Na, S and Cl ions in the samples was then measured to evaluate whether any impurities were attached to the surface of the crystals.

c) Elemental Composition

The elemental analysis of the samples was done using IC and ICP-MS. To that end, the stored samples were diluted to an ionic concentration close to 5 mg/L for each element, using Milli-Q water. The solid samples of sodium sulphate crystals were first dissolved with water and later diluted to the appropriate concentration. The samples were then filtered using filters with a pore size of 0.45 μm .

For the ICP-MS analysis, 69% concentrated nitric acid was used to acidify the samples, up to a concentration of 1% (v/v) nitric acid in the resulting solution. The samples were then analysed for the Na and S concentration with ICP-MS (Plasma Quant MS, Analytik Jena, Jena, Germany), using acidified Milli-Q water as blank.

For the IC analysis, a standard curve was prepared for the analysis of SO_4^{2-} and Cl^- anions. Milli-Q water was used as blank and the concentrations of SO_4^{2-} and Cl^- anions were measured using the Ion Chromatography setup (883 Basic IC plus, Metrohm, Switzerland).

5.7.4 Summary and discussion of tests done

A ternary synthetic mixture of sodium sulphate, sodium chloride and water was tested in the 2L EFC setup in order to evaluate the eutectic conditions of the system, observe its performance and assess the purity of salt crystals.

a) Eutectic conditions

The temperature and torque profiles of the crystallization process are presented in Figure 5-38 and Figure 5-39 respectively.

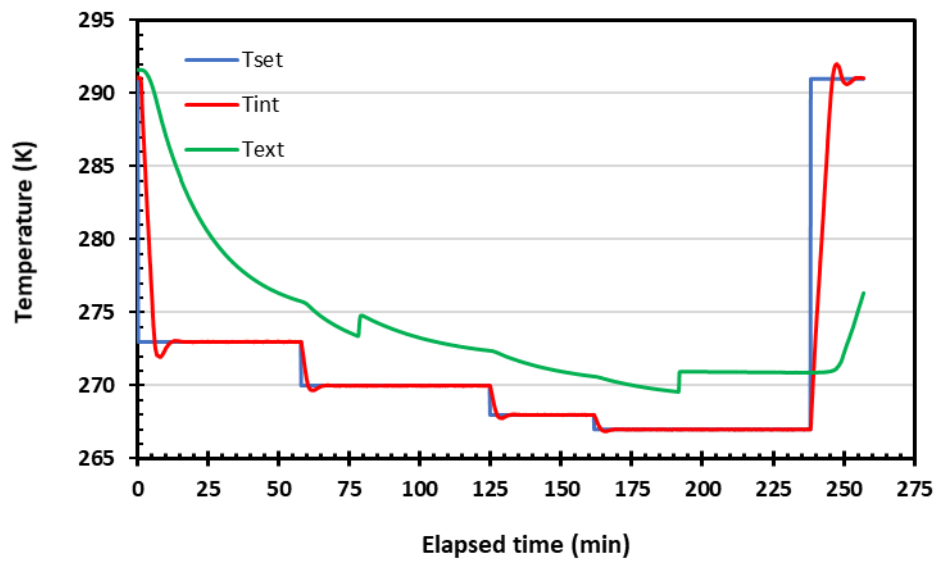


Figure 5-38: Temperature profile during the 2 L EFC test with the synthetic ternary solution.

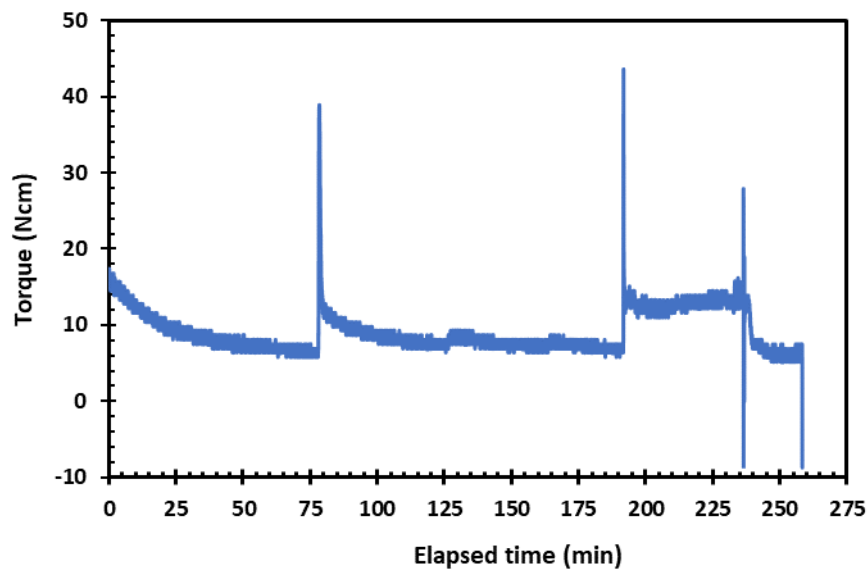


Figure 5-39: Torque profile during the 2 L EFC test with the synthetic ternary solution.

As it can be seen in Figure 5-37, the mixture was cooled down from room temperature. T_{set} indicates the set point temperature that we define, T_{int} is the temperature of the cooling liquid inside the LAUDA cooling bath and T_{ext} is the temperature measured by the probe inside the EFC reactor.

The working solution became turbid at a temperature of 0.4°C indicating the production of Na_2SO_4 crystals. At the same time, a sudden increase of torque is observed in Figure 5-38 due to the appearance of solid crystals in the bulk of the solution. The system was cooled down further to a temperature of -3.4°C at which point, another

spike in torque was observed due to ice crystallization. Because of the heat released by the production of ice crystals, the temperature was elevated and finally, stabilized at the eutectic conditions at a temperature of approx. -2.1 °C. At this point, ice crystals floating on the top of the slurry were clearly visible. The temperature in the reactor remained stable at the eutectic value, while production of ice and Na₂SO₄ crystals continued. Furthermore, no ice scaling was visually observed on the walls of the reactor, which was also suggested by the low torque values. The trial was terminated, and the temperature was increased, when the solid contents of the reactor were considerably higher, approx. 240 min after the start of the trial. At this point, the solution was very turbid due to the production of salt and ice crystals, while ice was observed to float at the top of the mixture and salt crystals were suspended in the bulk of the solution.

Eutectic conditions were achieved at a temperature of -2.1 °C. There is a slight deviation compared to the temperature of the binary sodium sulphate and water mixture found in literature (-1.27 °C). This slight depression of the eutectic point can be explained due to the freezing point depression caused by the sodium chloride impurities that are present in the working solution.

b) Quality of crystal products

In order to assess the quality of the crystal products, the samples that were taken during the EFC test were analysed with IC for the concentration of Cl and SO₄ anions and with ICP-MS for the concentration of Na, S.

The results are presented in Table 5-15 and Table 5-16.

Table 5-15: Concentrations of ions from the samples of the 2 L EFC test.

Sample	Concentration (g/L)			
	Na	S	SO ₄	Cl
Initial Solution	34.36	43.18	36.1	28.85
Permeate @ eutectic	230.65	107.05	117.86	102.26
1st washing step permeate	29.92	118.95	82.08	78.43
2nd washing step permeate	20.18	116.06	77.56	-
3rd washing step permeate	17.79	113.82	75.03	-

Table 5-16: Composition of salt crystals from the samples of the 2 L EFC test.

Sample	Composition (wt%)		
	Na	SO ₄	Cl
Unwashed crystals	28.5	71.5	-
1x washed crystals	18	44.2	37.8
2x washed crystals	19	44.3	36.6
3x washed crystals	28.4	71.6	-

Unfortunately, this first analysis (performed on 29/10/2019) was not successful because the ICP-MS equipment failed and a problem occurred with the standard curve of the IC. Therefore, the results presented above are not accurate enough and cannot be used to properly evaluate the process and the quality of the produced salt crystals.

5.7.5 Conclusions

A bench-scale test with the 2 L EFC setup using a synthetic solution was performed in order to test the EFC equipment, observe the eutectic conditions of the system and evaluate the quality of the crystal products.

A synthetic solution was prepared according to the analysis of the NF concentrate stream (after treating the RO concentrate) and tested with the 2 L EFC setup that was designed within the ZERO BRINE project.

The 2 L EFC reactor was successfully operated during this trial. Eutectic conditions were reached without observing any ice scaling issues on the walls of the reactor, suggesting that the design of the wiper is very efficient. The eutectic temperature of the ternary system was found to be approx. -2.1 °C, which is slightly lower compared to the temperature found in literature for the binary sodium sulphate-water mixture. This depression of the eutectic point was caused due to the NaCl impurities that were included in the solution.

Finally, the quality of the salt crystal products could not be assessed based on the ICP-MS and IC analysis due to inaccurate results. It is strongly recommended to repeat the analysis in order to get more reliable measurements and assess the purity of the crystals. Additional experiments in the 2 L or 5 L setup with a synthetic solution including organics or with a real NF concentrate solution would also be useful to evaluate the EFC process more accurately.

6 Conclusions

The following conclusions can be drawn from the bench scale tests using the various technologies of Site 01 and Site 02:

For Site 01:

- The nanofiltration membrane type TS80, when using a single pass, showed the best separation of mono- and multivalent ions, i.e. 89% for Ca^{2+} and 91% for Mg^{2+} for a constant membrane flux of 30 LMH.
- Rejections of multivalent ions obtained by using a double pass configuration TS80 were close to the rejections obtained with a single pass configuration. However, the rejection of monovalent ions was increased, of which sodium showed an increase of 27% compared to the test with only one pass.
- The semi-batch tests with the Multiple Feed - Plug Flow Reactor (MF-PFR) showed that magnesium and calcium hydroxide can be recovered from an industrial waste brine through a reactive crystallization process. The reaction path must be controlled by pH measurement.
- If seeds were added into the brine, the filtration time was improved substantially compared to the tests without seeding.
- The Multiple Effect Distillation evaporator achieved an overall water recovery of about 62%. For the NF permeate the water recovery was 60%, whereas for the MF-PFR effluent the water recovery was 63%. The concentration factor range was 2.51–2.72.
- Based on the experience obtained from the operation of the evaporator, it was seen that the system performance could be enhanced. This improvement requires some modifications in the design, such as tanks arrangement and piping system, as well as pumps.

For Site 02:

- For simultaneous removal of sulfate and dissolved organic carbon, using anionic resins, operation cycles of approximately 30–60 bed volumes should be considered. In scenarios where sulfate removal is not critical, 30–45% dissolved organic carbon removal could be achieved over 2000 bed volumes.
- An empty bed contact time of 3 min was enough to drive organic removal by the resins.
- In terms of regeneration efficiency, SCAV4 resins performed better than A860 resin. Nevertheless, the total capacity of the resins could not be completely restored and the effect on long-term column operation should be investigated.
- Trials carried out on the Nyex 1-20a electro-oxidation system showed that the brine organics were mainly highly hydrophilic.
- Subsequent trials showed that the adsorption capacity of the Nyex was reduced, which meant that the organics that were loaded on the Nyex were occupying adsorption sites and were resistant to oxidation. The recalcitrant nature of the organics was further observed in trials on the Nyex 1-20e system which showed little removal of TOC.
- Addition of hydrogen peroxide to boost the Nyex oxidation potential by generating more OH^\bullet radicals was unsuccessful in removing the organics.
- The TOC to COD ratio of the brine was 1 : 2.5, which further suggested that the organics were resistant to oxidation.

- Adsorption onto granular activated carbon was shown to be favourable, which indicates that a combined pH correction, Nyex-e electro-oxidation, and adsorption onto GAC would be the most favourable pathway to achieving removal of organics.
- The TS80 nanofiltration membrane produced higher concentrate Na_2SO_4 concentrations. NF270 membrane rejected higher percentage of organics but that was probably due to the different feed water composition, i.e. after treatment with Nyex. Both membranes could concentrate Na_2SO_4 as they could reject more than 95% of the SO_4^{2-} .
- Reverse osmosis permeate The permeate water produced by the reverse osmosis membrane for both scenarios was less than 50 mg/L and the applied pressure was less than 20 bar. The projections were made for the worst case scenario when the water temperature was 20°C. Lower water temperatures will result in higher permeate water quality as the membrane pore size will become tighter, resulting in higher ionic rejections.
- The multiple effect distillation evaporator showed a recovery of 59.8% for the nanofiltration permeate and a recovery of 59.4% for the reverse osmosis stream. For both streams the concentration factor was in the range of 2.32 - 2.50.
- The 2 L Eutectic Freeze Crystallization reactor was successfully operated and eutectic conditions were reached without observing any ice scaling issues on the walls of the reactor.
- The eutectic temperature of the ternary system was found to be approx. -2.1 °C, which is slightly lower compared to the temperature found in literature for the binary sodium sulphate-water mixture. This depression of the eutectic point was caused due to the NaCl impurities that were included in the solution.
- The quality of the salt crystal products could not be assessed based on the ICP-MS and IC analysis due to inaccurate results. It is strongly recommended to repeat the analysis in order to get more reliable measurements and assess the purity of the crystals. Additional experiments in the 2 L or 5 L setup with a synthetic solution including organics or with a real NF concentrate solution would also be useful to evaluate the EFC process more accurately.

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