



**ZERO BRINE**

# Bench scale test using equipment from BEC

**Deliverable 2.3**



<b>Deliverable 2.3</b>	<b>Bench scale test using equipment from BEC</b>
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Deliverable lead	TU Delft
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<sup>2</sup> **PU**=Public, **CO**=Confidential, only for members of the consortium (including the Commission Services), **CI**=Classified



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# 1 Overview of the project

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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

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This deliverable presents the obtained results from the performing bench scale activities from each technology provider. The results of bench scale tests are based on the PHREEQC simulations (Deliverables 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 of grant agreement and 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 technology providers. Finally, the obtained results will be discussed and possible adjustments in the grant designs will be proposed.



### 3 Introduction

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.

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A large-scale demonstration plant will be tested in the Plant One located at the Energy Port and Petrochemical cluster of Rotterdam Port by using the waste heat. 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.

The activities in the Netherlands is 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 in the Botlek industrial area (Rotterdam, The Netherlands) through redesigning the current situation (Figure 2). To this aim, two designs will be demonstrated during the WP2 activities: one design (Site 01) for the treatment of the spent regenerant of the cationic ion exchange columns of the DWP and another design (Site 02) for concentrate treatment of reverse osmosis unit of the DWP.

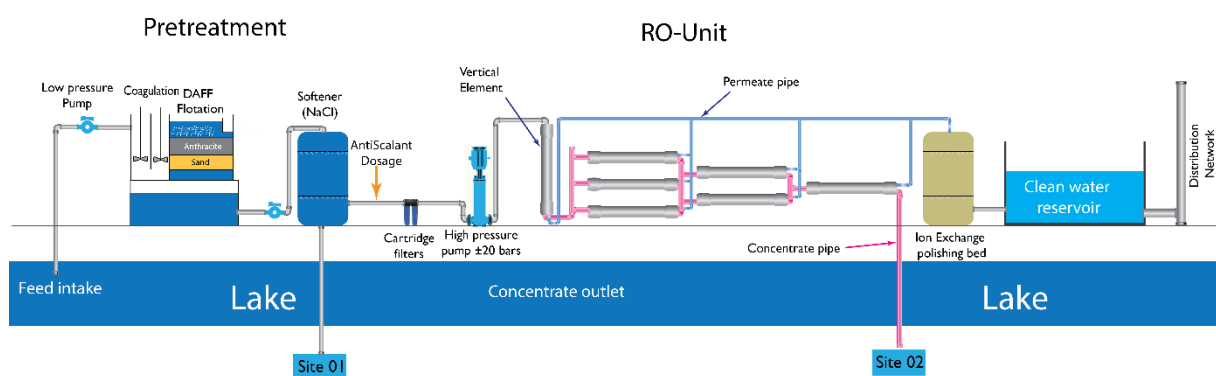


Figure 3.1: Schematic view of the current processes at the demineralized water plant of Evides at Botlek (Rotterdam, The Netherlands). The aim of WP2 is to treat the regenerant from the ion exchange softener (Pilot 01) and to treat the concentrate of reverse osmosis (site 2) and recover and reuse of salts from the wastewater.

#### 3.1 Site 01

The DWP at Evides Botlek area is fed with the water from Brielse Meer, which is one of the branches of the river Maas. The DWP produces a 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.

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 called spent regenerant, which is typically considered as the 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 the Plant One. Plant One 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). NF separates the spent regenerant into a permeate and a concentrate. NF permeate contains mainly water and monovalent ions such as  $\text{Na}^+$  and  $\text{Cl}^-$ . While the NF permeate streams directly toward an evaporator, the NF concentrate passes through a crystallisation unit wherein the calcium and magnesium will be removed from the concentrate. The evaporation unit is the last step of Site 01, which receives the monovalent rich NF permeate and the effluent of the crystallisation unit. The effluent of the evaporator consists of purified water and a flow with a high NaCl concentration. The products of Site 01 (magnesium, calcium, purified water and NaCl rich flow) can be reused in the DWP or other industries.

The design feed flow for Site 01 is 1000 L/h. The water will be transported by means of containers from Evides over a distance of about 500m to Plant One. The produced products during the pilot study will be transported .....

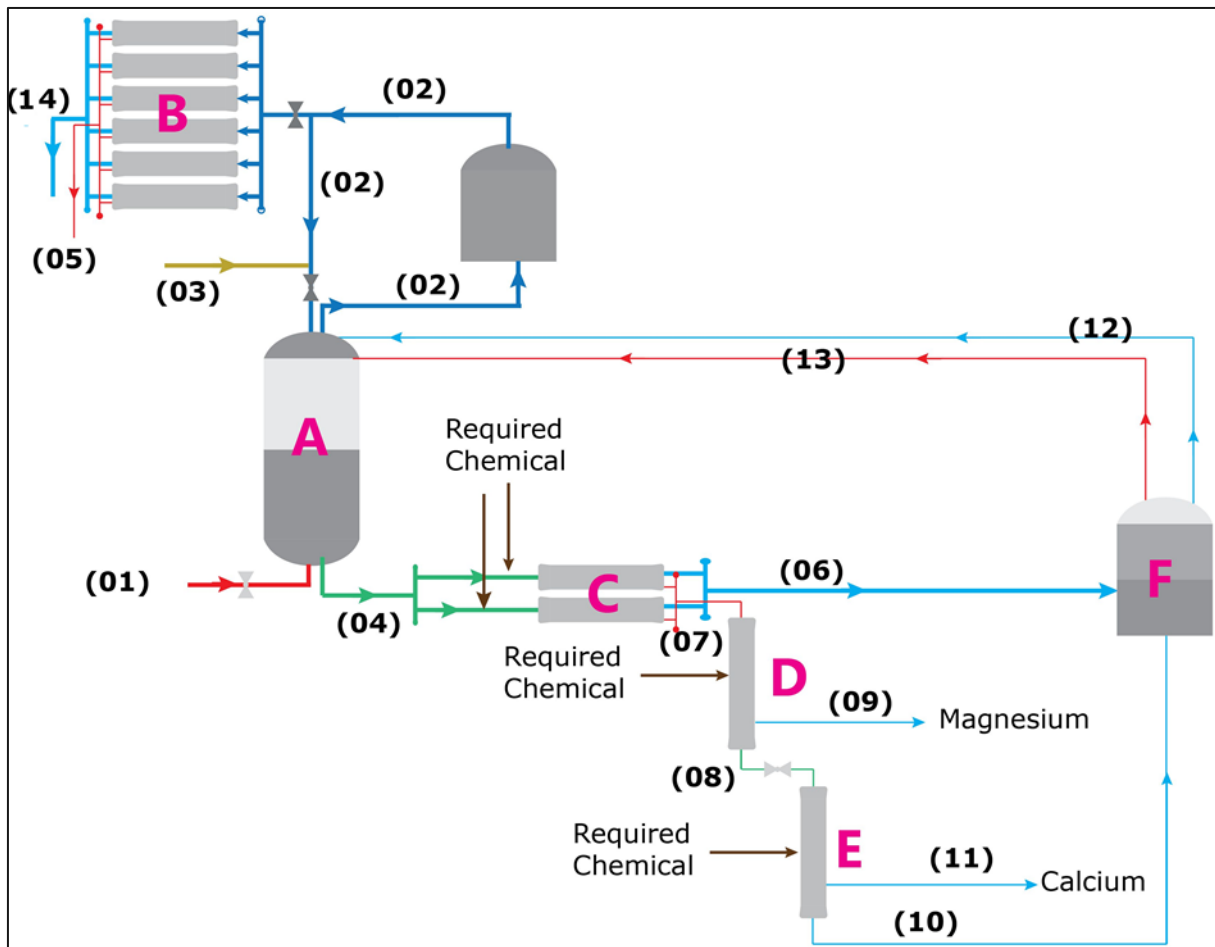


Figure 3.2: Initial design of Site O1 according to grant agreement: identification of process units and description of flows are mentioned in Table 2.

Table 3.1: identification of process units and description of units for Site O1 (Figure 3.2)

process units			
A	IEX: 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	??	?? g/L 98% NaCl Purity
04	spent regenerant (NaCl brine with exchanged cations)	1000 L/h	36 g/L NaCl
05	RO concentrate (existing); waste	NA	NA
06	NF permeate, intended to be evaporator feed	700 L/h	???g/L % NaCl Purity
07	NF concentrate, intended to be metal recovery feed	300 L/h	???g/L NaCl Purity
08	Mg crystallisation supernatant	300 L/h	???g/L NaCl Purity
09	Mg salt suspension	???Kg/h	??? Mg Purity

10	Ca crystallisation supernatant	300 L/h	???? Ca Purity
11	Ca salt suspension	???Kg/h	???? Ca Purity
12	evaporator condensate (distilled water)	L/h	???/ NaCl Purity
13	NaCl brine (concentrated), for IEX regeneration	L/h	???? NaCl Purity
14	RO permeate	NA	NA

## 3.2 Site 02

In WP, the IEX effluent (softened water) during the service run is used as the feed water for the RO unit. The concentrate stream produced in the last stage of RO contains salts and organic matters and is discharged to 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 a higher concentration, than concentration they are added, in the concentrate stream.

Site 02 of ZERO BRINE is an innovative design that aims to treat the RO concentrate of DWP. To this aim, an anionic IEX will be used to remove the anions and charged organic matters from the RO concentrate. The spent regenerant of anionic IEX will be fed to 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 an RO unit, which will be operated with a recovery of around 85%. The permeate of the RO unit can be used as the 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 could be mixed with the condensate of the evaporator and be used for regeneration of the anionic IEX column.

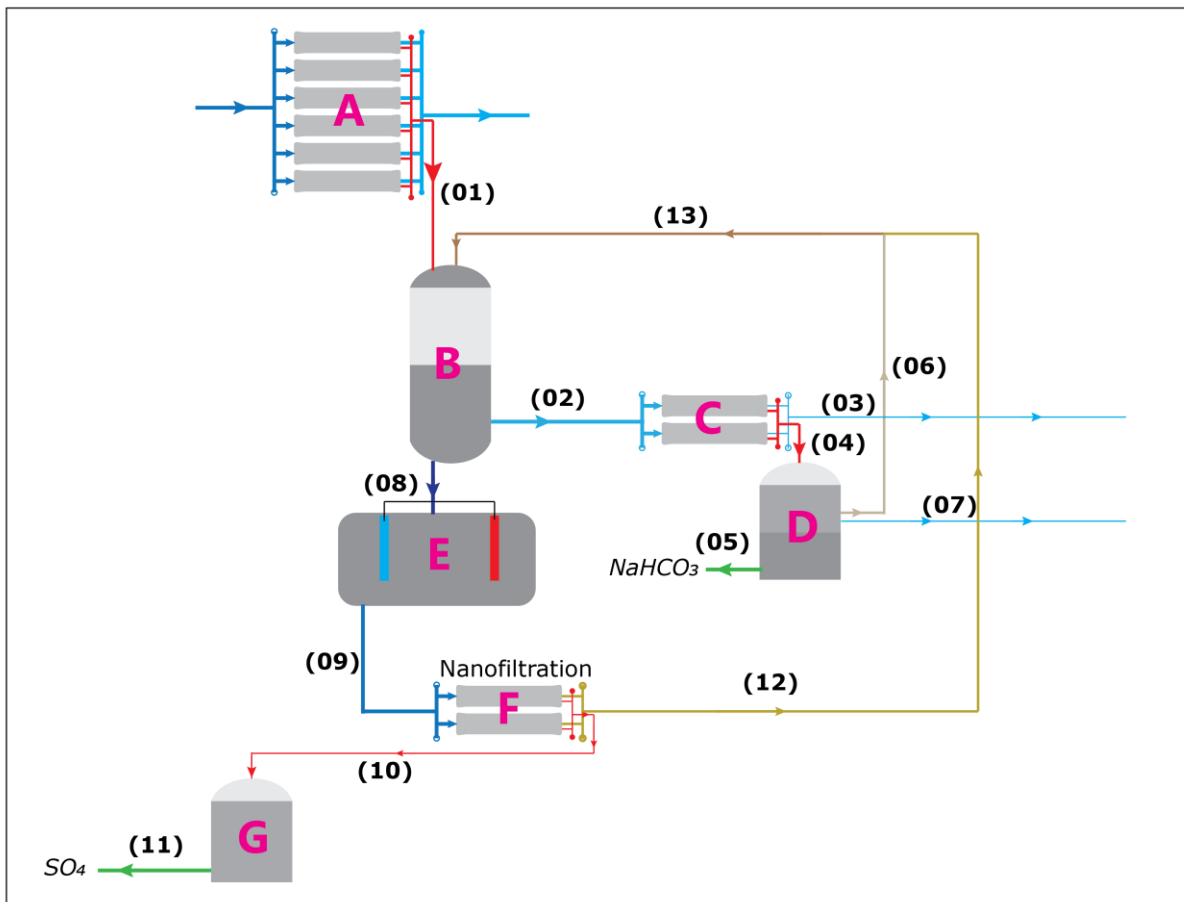


Figure 3.3: Block view of Site 02 of ZERO BRINE project

Table 3.2: identification of process units and description of units for Site 02 (Figure 3.3)

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	1000 L/h	NA
02	Effluent of an anionic ion exchange column (removing of anions and organics)	1000 L/h	NA
03	Permeate of installed RO	??	0 g/L NaCl
04	Concentrate of RO intended to be the evaporator feed	1000 L/h	36 g/L NaCl
05	Evaporator precipitations	NA	NA
06	Evaporator supernatant	700 L/h	???g/L % NaCl Purity
07	Evaporator condensate (distilled water)	300 L/h	???g/L NaCl Purity
08	Spent regenerant of anionic ion exchange column	300 L/h	???g/L NaCl Purity

09	Effluent of Nyex (organic removal unit)	??Kg/h	??? Mg Purity
10	NF concentrate, intended to be EFC feed	300 L/h	??? Ca Purity
11	SO <sub>4</sub> salt suspension	??Kg/h	??? Ca Purity
12	NF permeate, intended to be mixed with evaporator	L/h	??/ NaCl Purity
13	NaCl brine (concentrated), for IEX regeneration	L/h	??? NaCl Purity

### 3.3 Summary of PHREEQC calculations

PHREEQC is used for simulation of precipitating salts at Site 01 ((Deliverable D2.1). The obtained results from PHREEQC calculations indicate that magnesium and Calcium may be separated with great efficiency from spent IEX regenerant. However, a recovery of 99% or greater of these materials is not 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)<sub>2</sub> and Ca(OH)<sub>2</sub> is possible theoretically, under the actual conditions, 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 contain 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)<sub>2</sub> to precipitate prematurely. Thus, hydroxide dosing for Mg<sup>2+</sup> and Ca<sup>2+</sup> 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 at the evaporator unit. Another drawback of the using the mixture feed is that the produced salts by the evaporator cannot be used for regeneration of IEX columns anymore because the impurity of produced salts cause a faster exhausting of the IEX column. This will be resulted in a more frequent regeneration of the IEX column, 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 the feed for evaporator.

In spite of the great detail of the modelling results, the exact effect of closing the water cycle in the process can't 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, as 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<sup>2+</sup>, Zn<sup>2+</sup>, Sr<sup>2+</sup> 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 at feed stream Site 01, inorganics at feed steam Site 02, and organic matters presents at Site 02 respectively. The results showed in each column (IEX\_EXP...) are the average measurements for a specific period representing seasonal version of feed water. Each average value is obtained by analysing at least four samples. Each sample is analysed at least three time using different dilution factor. Cations were measured with ICPMS, anions with test kits and organic matters with LC-OCD method.

It is difficult to give a clarification for the seasonal variation of ion concentration 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 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	26	mg/L	1248	1337	1069	1414
Potassium	K	39	mg/L	236	228	321	257
Calcium	Ca	44	mg/L	6523	8538	7211	7038
Silica	SiO <sub>2</sub>	28	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	47	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	78	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
Aluminum	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	60	µg/L	205	2858	82.4	3.63
Copper	Cu	65	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	114	µg/L	0.35	0	14.19	12.22
Antimony	Sb	121	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 <sub>3</sub>	62	mg/L	43.7	22.9	51.9	30.2
Phosphate	PO <sub>4</sub>	94	mg/L	1.78	0.29	0.02	0.72
Bicarbonate	HCO <sub>3</sub>	61	mg/L	143	140	115	109

Sulphate	SO4	96	mg/L	149	212	124	77
Total dissolved solids	TDS	-	mg/L	<b>27874</b>	<b>49772</b>	<b>45614</b>	<b>41683</b>
Electrical conductivity	EC	-	mS/cm	<b>43.4</b>	<b>80.25</b>	<b>76.4</b>	<b>69.6</b>
Averaged pH	pH	-	-	<b>7.26</b>	<b>7.08</b>	<b>6.86</b>	<b>6.66</b>

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	26	mg/L	0.17	2.17	0.07	0.06
Potassium	K	39	mg/L	13.4	14.3	0	18.3
Calcium	Ca	44	mg/L	0.52	3.34	2.16	2.30
Silica	SiO2	28	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	47	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	78	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
Aluminum	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	114	µg/L	0.01	0	0.04	0.03
Antimony	Sb	121	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	NO3	62	mg/L	39.4	7.32	53.4	22.4
Phosphate	PO4	94	mg/L	0	2.93	0.03	0.05
Bicarbonate	HCO3	61	mg/L	871	863	947	955
Sulphate	SO4	96	mg/L	371	335	271	320
Total dissolved solids	TDS	-	mg/L	<b>2696</b>	<b>3591</b>	<b>2966</b>	<b>3237</b>
Electrical conductivity	EC	-	mS/cm	<b>3.22</b>	<b>4.03</b>	<b>3.30</b>	<b>4.09</b>
Averaged pH	pH	-	-	<b>9.8</b>	<b>8.81</b>	<b>8.87</b>	<b>8.79</b>



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

Nanofiltration (NF) is a membrane filtration process, similar to the industrially applied reverse osmosis, however with a 'coarser' membrane. 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 ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ) and sulphate ( $\text{SO}_4^{2-}$ ) ions 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 the 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, both permeate stream will contain multivalent ions and concentrate stream will contain 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 and temperature and solution chemistry, which can influence the passage of mono- and multivalent ions through the membranes. Furthermore, the interaction of different concentrations of 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).

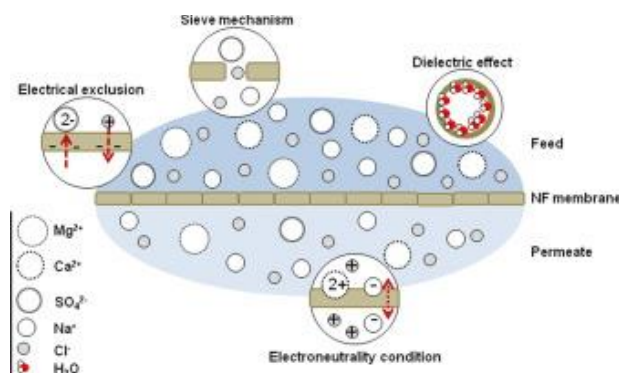


Figure 4.1: Rejection mechanisms of NF membranes *Invalid source specified.*

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 favorable partitioning for counter-ions and unfavorable 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 Experimental setup

Figure 4.2 is represented the main components of the system used for the nanofiltration experiments. Mainly, the system is composed by a Sepa Cell lab test unit to test different flat sheet membranes, 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.

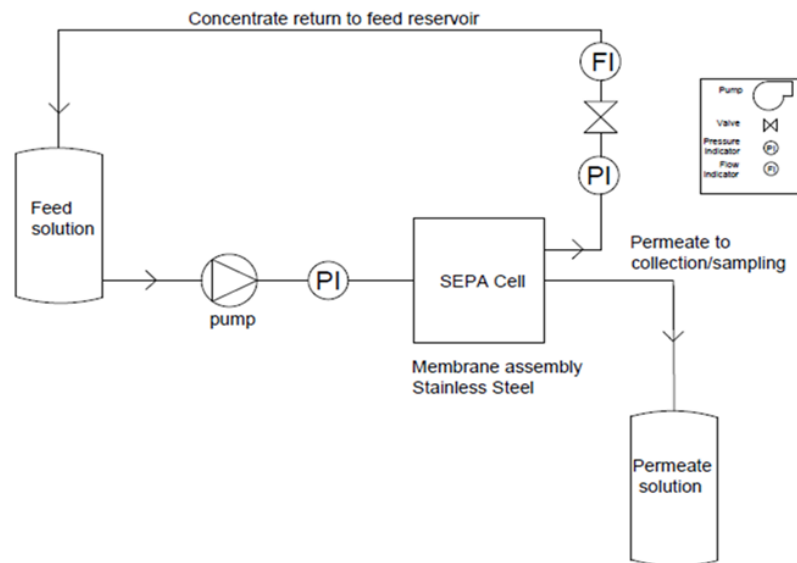


Figure 4.2: Sepa Cell P&ID.

To conduct the experimental tests the feed solution was separated over a nanofiltration membrane into a permeate and concentrate stream, using the Sepa Cell unit. Before every experiment the membrane remained immersed in demi water during a period approximately of 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 was converted and recorded on the computer. Based on the available active area of the membrane (0.014 m<sup>2</sup>), the membrane flux could be calculated.

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 on 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.

Figure 4.3 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).

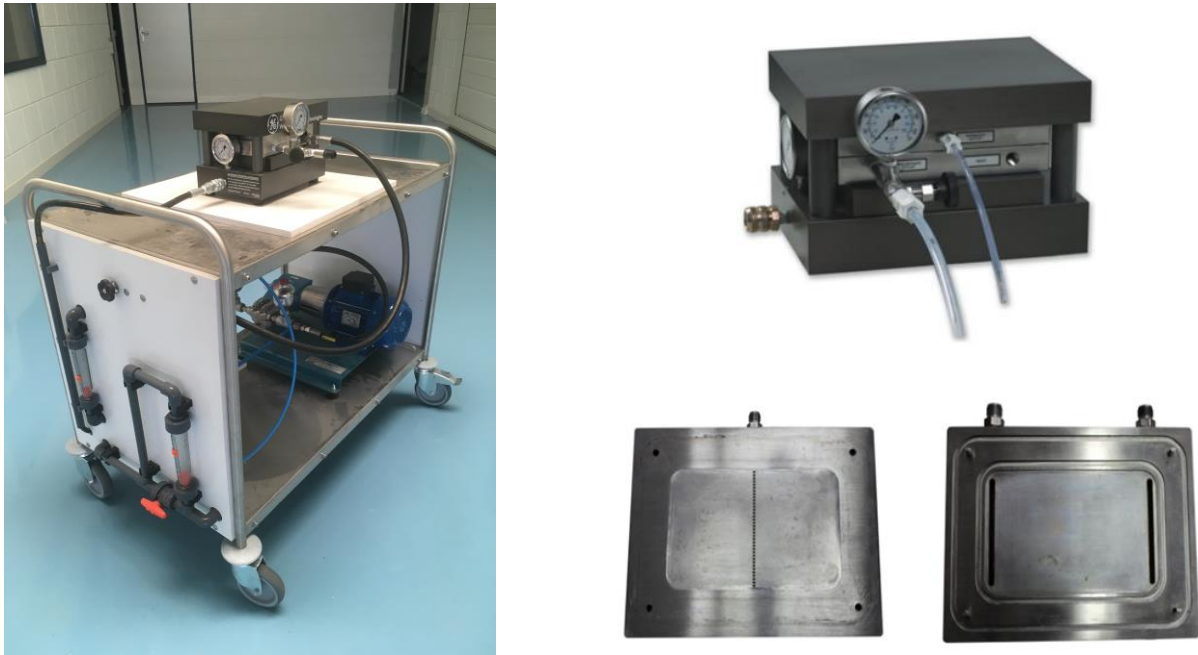


Figure 4.3: Sepa cell lab unit (left) pressure holder (top), bottom and top cell.

### 4.1.3 Methodology

A feed solution was prepared artificially in the laboratory with the addition of different salts to attain the same concentration of salts from the regeneration brine stream of the ion exchange of EVIDES. In Table 4.1 are represented the salt concentrations used during the experiments.

Table 4.1: Chemical composition of artificial water.

Name	Concentration (mg/L)
Sodium (Na)	3266.03
Magnesium (Mg)	1769.44
Potassium (K)	336.33
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/m<sup>2</sup>h (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 on Table 4.2, were maintained throughout all the experiments.

Table 4.2: Experimental operating conditions.

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

A flux of 30 LMH was considered to operate the system and the feed temperature was maintained at 20 °C along all the experiment with the help of a spiral heat exchanger that was placed inside of the feed tank.

In order to select the best nanofiltration membrane performance, different membranes were tested from four different suppliers. Five candidate membranes were tested to select the membrane that could give the best rejection performance of divalent ions such as Ca<sup>2+</sup> and Mg<sup>2+</sup>. Table 4.3 shows the specifications of the 5 evaluated membranes.

Table 4.3: Flat sheet membranes used on the experiments.

Model	Vendor	Approx. MW (Da)	Operating Flux (LMH)	Max P (bar)	Avg. MgSO <sub>4</sub> Rejection (%)	Avg. NaCl Rejection (%)
<b>NFW</b>	Synder	300-500	76-85	41	97 <sup>(1)</sup>	20 <sup>(2)</sup>
<b>NFG</b>	Synder	600-800	94-102	41	50 <sup>(1)</sup>	10 <sup>(2)</sup>
<b>NF270</b>	Dow	200-400	52	41	97 <sup>(1)</sup>	-
<b>SR3D</b>	Koch	200	-	44.8	99 <sup>(3)</sup>	-
<b>HL</b>	GE	150-300	15-35	41	98 <sup>(1)</sup>	-

#### 4.1.4 Summary and discussion

Among the five candidate membranes tested, so far, the SR3D Koch membrane showed the best separation performance of divalent ions on the concentrate stream and monovalent ions on the permeate. Therefore, the results for this membrane will be presented below.

Figure 4.4 shows the rejection of the presented species tested at 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 4.4 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 69%, 64%, 60% and 59%, respectively, however, for the same flux of 30 LMH, chloride, as monovalent ion, also showed a high rejection of 46%.

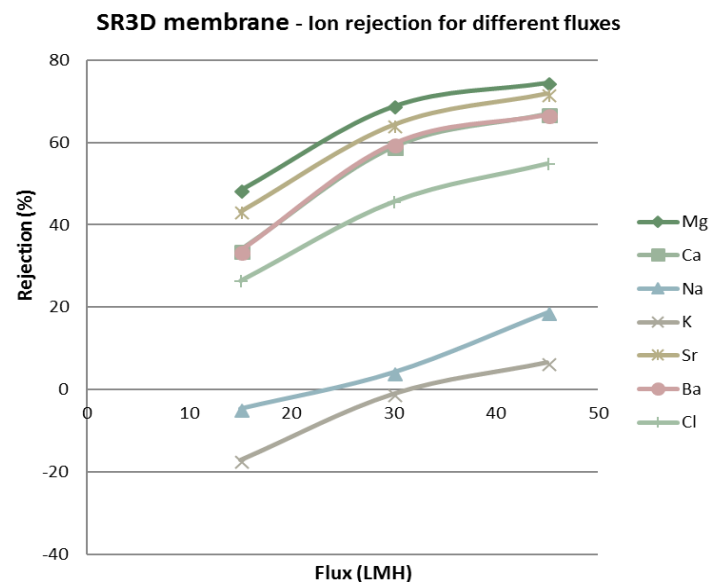


Figure 4.4: Ionic rejection at different membrane fluxes of 15,30,45 LMH

From the 3 different membrane fluxes, a constant membrane flux of 30 LMH represents a typical flux of larger scale operation. 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 3 corresponding to a certain system recovery of 0%, 50% and 70%. During the operation system the membrane was able to reject  $Ca^{2+}$  and  $Mg^{2+}$  at around 58% and 68%, respectively, keeping this value constant for higher system recoveries, see Figure 4.5. Consequently, the rest passes through the membrane remaining on the permeate stream.

Strontium and barium showed approximately the same rejections as  $Ca^{2+}$  and  $Mg^{2+}$  of around 65% and 60%, respectively.

However, chloride as monovalent ion should pass towards the permeate stream at a high extent but in this case presented a rejection of around 55% in the concentrate, thus with 45% passage to the permeate. This high

rejection might be due to the repulsive forces between the  $\text{Cl}^-$  charge and the negative charge of the membrane surface. Another reason for this result might be related with the high concentration of this specie in solution of 24000 mg/L (see Table 4.1). On the other hand, sodium and potassium both showed a high passage through the membrane (Figure 4.5).

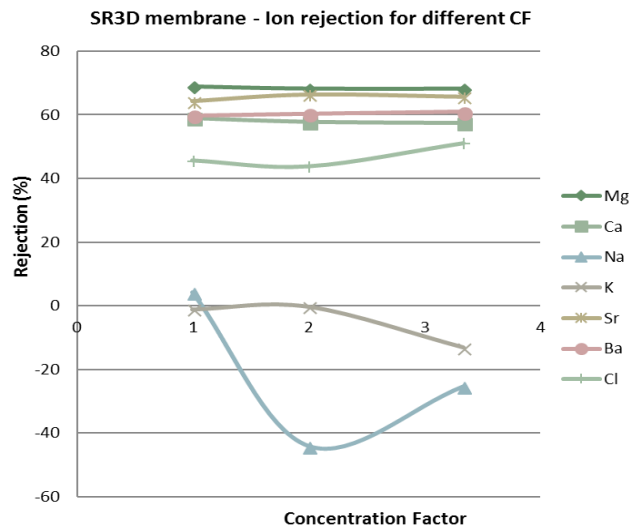


Figure 4.5: Ionic rejection vs. concentration factor of SR3D membrane for a flux of 30LMH.

Figure 4.6a and Figure 4.6b show the results for the test of varying concentration factor in terms of concentration of all species in study for the permeate and concentrate streams. As expected, chloride showed the high 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 be higher for a monovalent ion. For instance, for a recovery of 80%, or concentration factor of 5, the concentration of chloride on the permeate stream is almost 3 times lower compared with the concentration of chloride that is rejected to the concentrate. The concentration of chloride in the permeate stream increases from 13400 mg/L to 18400 mg/L while in the concentrate stream the initial chloride is almost the same the concentration of chloride presented on the initial feed, which is around 24000 mg/L increasing to a concentration of 49700 mg/L at a concentration factor of 5.

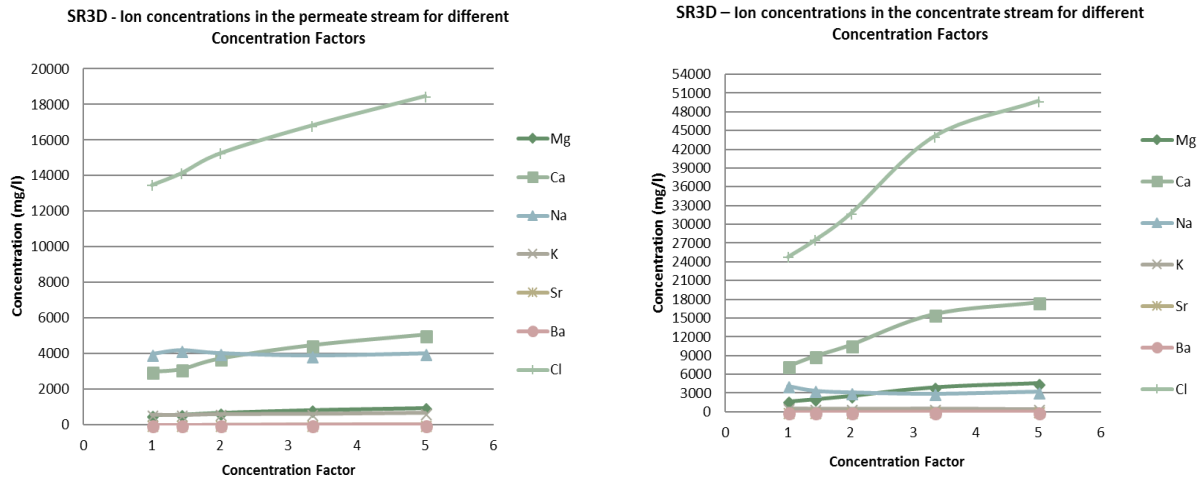


Figure 4.6: Ionic concentration species vs. concentration factors on the permeate stream (a) and concentrate stream (b)

### 4.1.5 Conclusions

With the tests performed so far, SR3D membrane showed best separation of mono- and multivalent ions once it gave the best rejection performance of 58% for  $Ca^{2+}$  and 68% for  $Mg^{2+}$  for a constant membrane flux of 30 LMH.

Further tests will be conducted with other membranes including loose tight NF and RO membranes. In this range there is minimal difference between NF and RO

To increase the separation of mono- and multivalent ions, considering that no membrane performs a perfect separation, it will be important to consider the design of the membrane system. This could be, for example, by using two passes of NF; the first with a loose membrane that allows almost all monovalent to pass through, as well as many bivalent, and the second with a tighter membrane that only monovalent to pass while the rest is recirculated back to the feed of the first pass (Figure 4.7). This may mean increasing the size of the NF system, however the separation should improve.

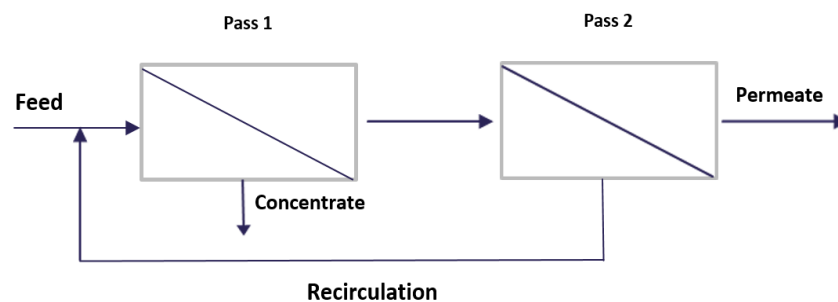


Figure 4.7: 2-pass NF system with recirculation



## 4.2 UNIPA - Crystallization

### 4.2.1 Description of technologies

The Crystallization physical phenomenon includes the formation of particles in vapours, the solidification of melted mixtures or the species precipitation in aqueous solutions. In particular, reactive crystallization 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 species as sodium hydroxide. Different reactors can be considered 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 recover 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 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 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 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 the steady state, 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  $\text{OH}^-$  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 Experimental setup

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 adding the alkaline solution drop by drop with a syringe pump was used to simulate time-dependent operation of a continuous system. The process scheme is reported below:

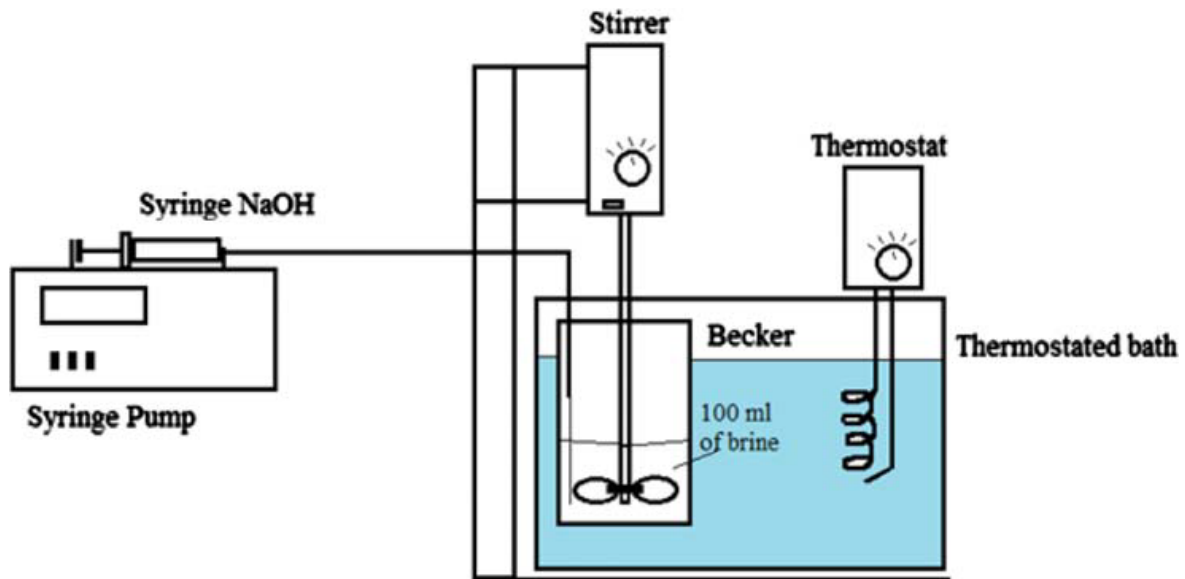


Figure 4.8: Scheme of semi-batch system for the precipitation of magnesium hydroxide and calcium hydroxide from waste brine.

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

A CSTR (Continuous Stirred Tank Reactor) 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.

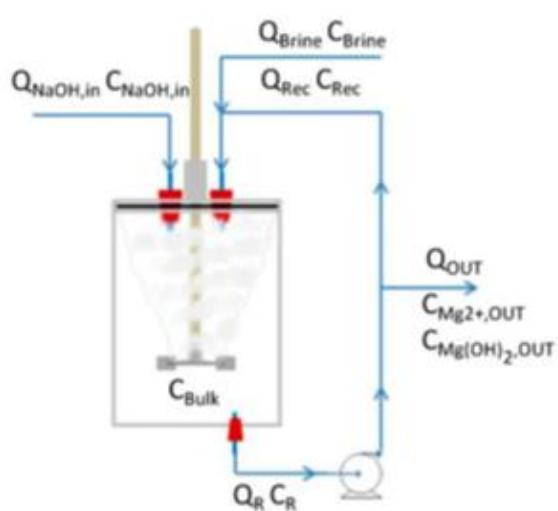


Figure 4.9: Scheme process of CSTR for the precipitation of magnesium hydroxide and calcium hydroxide from waste brine

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 already said before, in real conditions, the plug flow is only an approximation because 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.

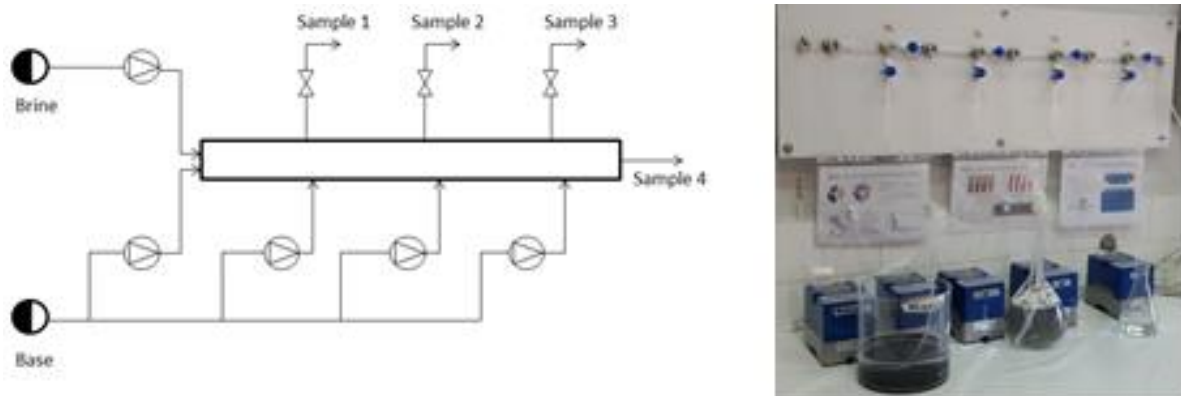


Figure 4.10: Simplified scheme of MF-PFR adopted for the experimental campaign.

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.

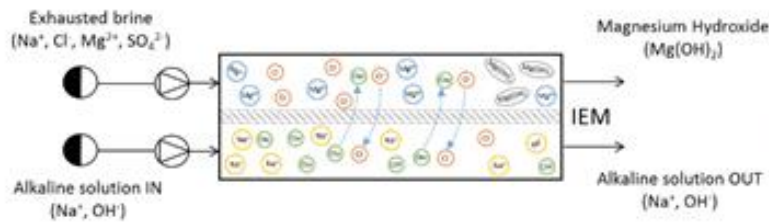


Figure 4.11: Simplified scheme of CrIEM adopted for the experimental campaign

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

### 4.2.3 Methodology

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 reproduce the typical conditions of the brine to be treated in the Bottlek case study. In particular, the concentration are the following:

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

This solution was filled in a becker 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 found 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  $\text{Mg}^{2+}$
2. 0.164 M  $\text{Mg}^{2+}$  + 0.596 M  $\text{Ca}^{2+}$
3. 0.164 M  $\text{Mg}^{2+}$  + 0.00625 M  $\text{SO}_4^{2-}$
4. 0.164 M  $\text{Mg}^{2+}$  + 0.596 M  $\text{Ca}^{2+}$  + 0.00625 M  $\text{SO}_4^{2-}$

Four different seed-suspensions:

1. 6.3 g/L seeds
2. 6.3 g/L seeds + 0.596 M  $\text{Ca}^{2+}$
3. 6.3 g/L seeds + 0.00625 M  $\text{SO}_4^{2-}$
4. 6.3 g/L seeds + 0.596 M  $\text{Ca}^{2+}$  + 0.00625 M  $\text{SO}_4^{2-}$

Alkaline:  
1.0 M  $\text{OH}^-$

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 have shown that a higher amount of seed-suspension leads to a lower filtration time. From the results of these preliminary tests, it was selected the ratio [1:10] for further experiments.

The MF-PFR at bench scale was tested in the Zero Brine condition, before design and assemble the pilot system, in order to confirm the possibility to recovery magnesium and remove calcium, obtaining high performance in terms of purity and conversion. The operative 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
- $N_{\text{Base}}/N_{\text{stoich}}$ : 1

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 while the filtrate was used in a second step to remove all the calcium present in the solution as calcium hydroxide. The remaining solution is constituted by water and sodium chloride as required by the Zero Brine project in the specific condition of Evides site 1.

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
- $N_{\text{Base}}/N_{\text{stoich}}$ : 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 the 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 1. Commercial anionic exchange membranes were used for this purpose. A small amount of brine was recirculated until all magnesium was recovered 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 with sodium hydroxide. The operative conditions are listed below:

- Magnesium: 3 g/l; Calcium: 23.7 g/l; Sodium: 25.9 g/l
- Ca(OH)<sub>2</sub> concentration: 1.5 g/l (higher than the solubility in water)

#### 4.2.4 Summary and discussion

##### *Proof of concept: fractionated crystallisation*

The semi-batch tests have been performed in order to have a confirmation on the proof of concept of the idea reported in the Zero Brine proposal. Magnesium and calcium can be recovered in two different steps, controlling the reaction path. The preliminary results are reported in figure x:

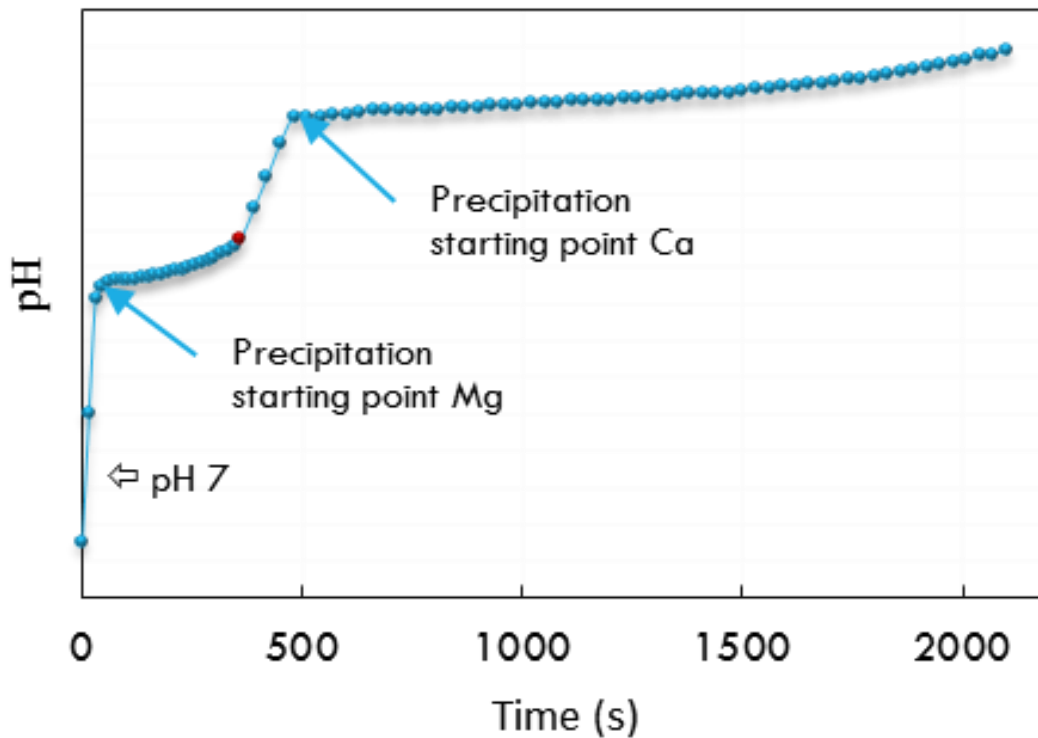


Figure 4.12: Precipitation path for the recovery of magnesium and the removal of calcium

The pH increases quickly until a plateau in which starts the precipitation of magnesium hydroxide. The pH increase slowly until the red point in which all the magnesium is precipitated as magnesium hydroxide. The suspension was filtered and the magnesium hydroxide was recovered. The solution so obtained was used to remove calcium with a trend of precipitation similar to the 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 4.4: Proof of concept test: purity and conversion of magnesium and calcium hydroxide

	Ca <sup>2+</sup> [g/L]	Mg <sup>2+</sup> [g/L]
Initial Concentration	24.12	3.08
1° step (filtrate)	22.53	0.02
2° step (filtrate)	0	0

Mg(OH) <sub>2</sub>	Purity	>98%
	Conversion	>99%
Ca(OH) <sub>2</sub>	Purity	>98%
	Conversion	>99%

**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 already reported above and the main results are represented below:

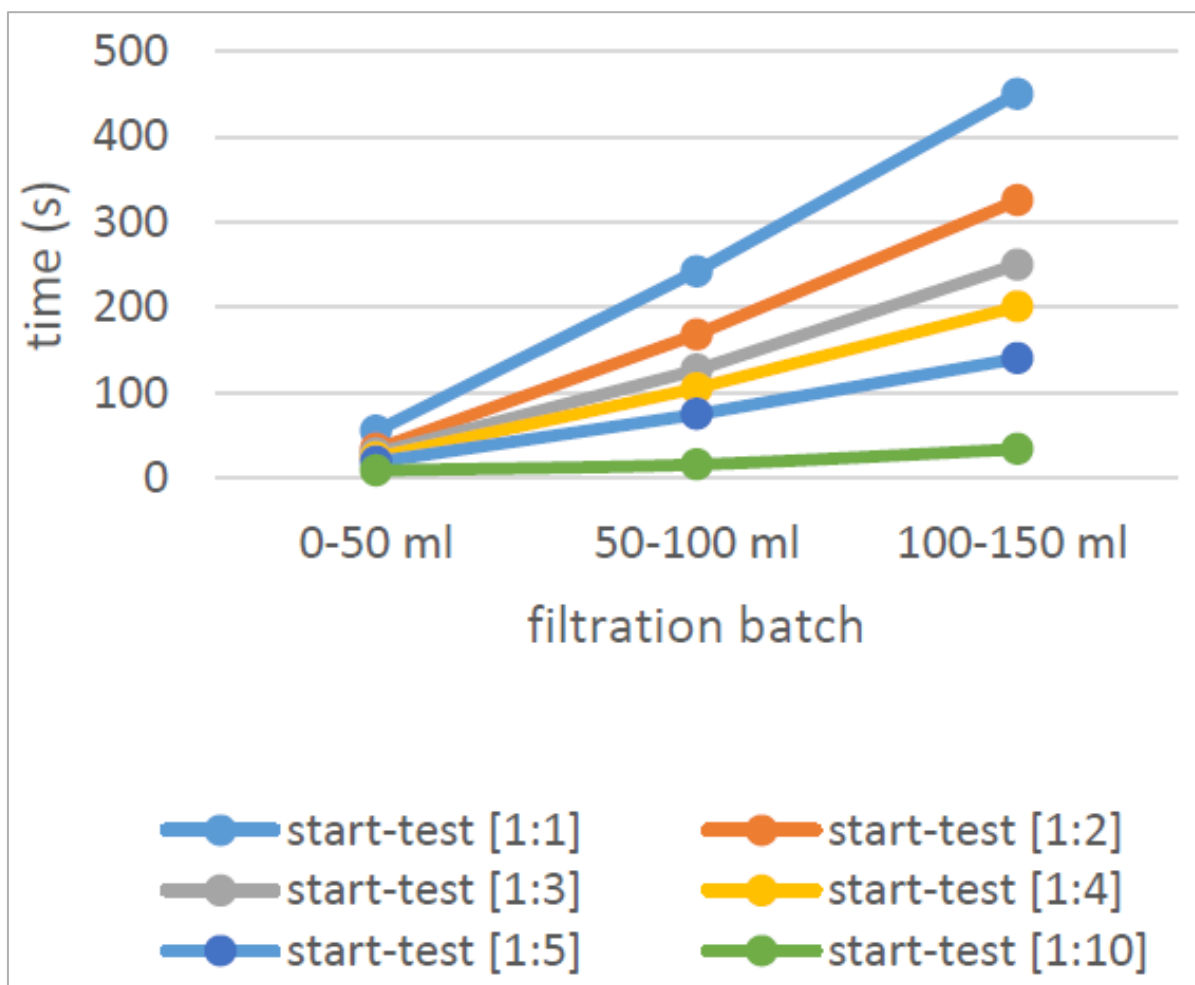


Figure 4.13: Filtration time of the suspensions with different start conditions,  $t = 34$  min [1:1], [1:2], [1:3], [1:4], [1:5] [1:10].

As can be observed in figure x, the best result was obtained with a ratio [1:10] between magnesium hydroxide produced and seed of magnesium hydroxide added. In order to understand the effect of the seed, the same test was repeated several times recirculating the suspension for a maximum of 10 tests. As an example, the results with different solutions are reported below:

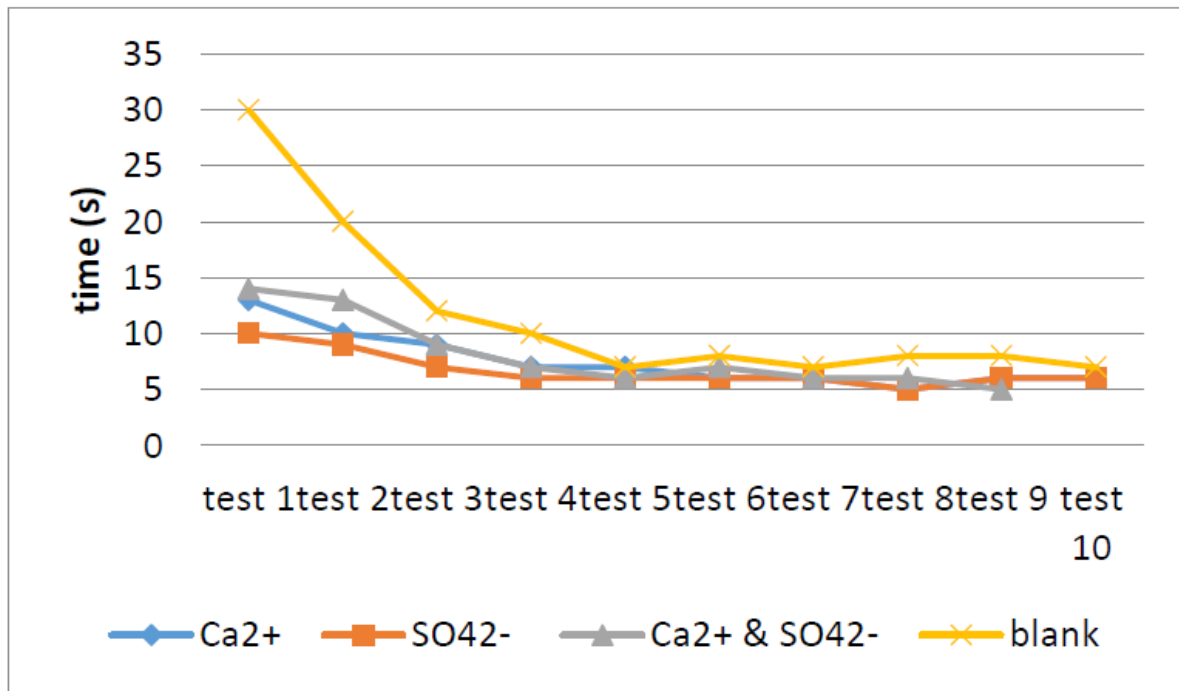


Figure 4.14: Filtration time (0–50 mL) ten step test of Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup> & SO<sub>4</sub><sup>2-</sup>, blank, t = 68s [1:10]

The influence of the presence of calcium and sulphate was first tested separately and after it was tested together. In figure X, 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 x as 'blank'. The filtration time of the start-test with the presence of calcium or sulphate are lower than the blank, but they eventually all reach more or less the same filtration time after 6 tests. In all the case, 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 steps, all the calcium is removed producing a sodium chloride solution ready for the evaporation step.

The CrIEM was tested in the condition of Evides site 1 showing a good performance, with good ions flux and conversion. Nevertheless, the final product of magnesium hydroxide was contaminated by small amount of calcium because locally the supersaturation is uncontrolled causing a co-precipitation of calcium and magnesium.

## 4.2.5 Conclusions

The semi-batch tests have been 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 are added into the brine, the filtration time is improved a lot compared to the tests without it. The preliminary tests made with bench scale MF-PFR have been shown good performance in terms of purity and conversion.



Thanks to these preliminary results, a MF-PFR pilot plant has been 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 in a large scale. A drum filter will be coupled and tested at the pilot system, for the continuous production of magnesium hydroxide. In figure x a picture of the new pilot system is reported:



*Figure 4.15: MF-PFR pilot system for the production of magnesium hydroxide and calcium hydroxide from waste industrial plant*

## **4.3 NTUA**

**4.3.1 Description of technology (1 page)**

**4.3.2 Experimental: Scheme + photo of equipment (2 page)**

**4.3.3 Methodology: Description of tests done (2 page)**

**4.3.4 Summary and discussion of tests done (2 pages)**

**4.3.5 Conclusions (0.5 page)**

## 4.4 Conclusion site 01

## 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 ( $\text{SO}_4^{2-}$ ) or total organic carbon (TOC) or naturally occurring organic matter, which is typically negatively charged, as in the case of the RO brine treated at Site II of WP2, ZERO BRINE.

The exchange media, or ion exchanger, is usually a porous resin bead with functional groups. Resin beads are approximately 5 mm in diameter, which vary depending on the ionic loading. These beads are porous and contain invisible water inside the beads, 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  $\text{N}^+\text{R}_3$ ; 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 ( $\text{Cl}^-$ ). 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.

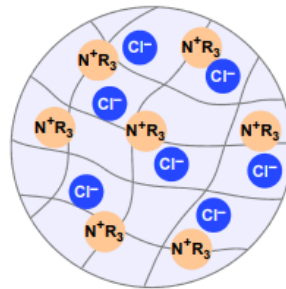


Figure 5.1: Schematic anion exchange resin bead

Thanks 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, you see the fresh resin, then you see how the resin gets progressively loaded with the ions from the feed solution. Ions from the resin not shown on 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.

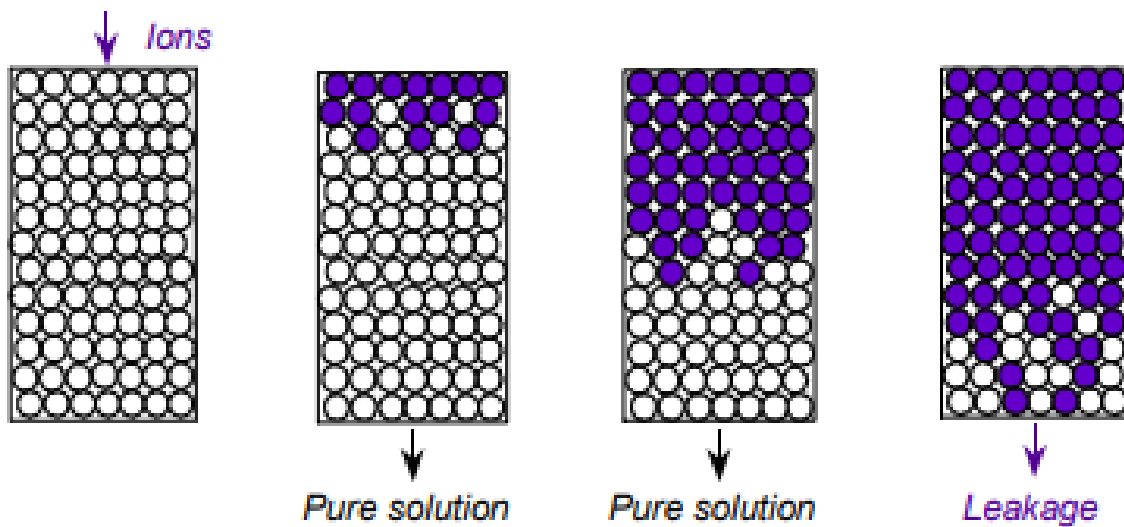


Figure 5.2: Column operation

When the resins are exhausted, they can be brought back to the fresh state and start over again. Regeneration of ion exchange resins is a reversal of the exchange reactions. For instance, the softening resin is regenerated with chloride ( $\text{Cl}^-$ ) ions supplied by a salt (common salt:  $\text{NaCl}$ ) 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 Experimental: Scheme + photo of equipment (2 page)

### 5.1.3 Methodology: Description of tests done (2 page)

### 5.1.4 Summary and discussion of tests done (2 pages)

### 5.1.5 Conclusions (0.5 page)

## 5.2 Lenntech: Reverse Osmosis

### 5.2.1 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 equalise the chemical potential, or ion concentration, on either side of the membrane. As shown in Figure 5.3, 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-mineralised or de-ionised as it is forced through a semi-permeable membrane by applying a pressure to it to overcome the osmotic pressure [2].

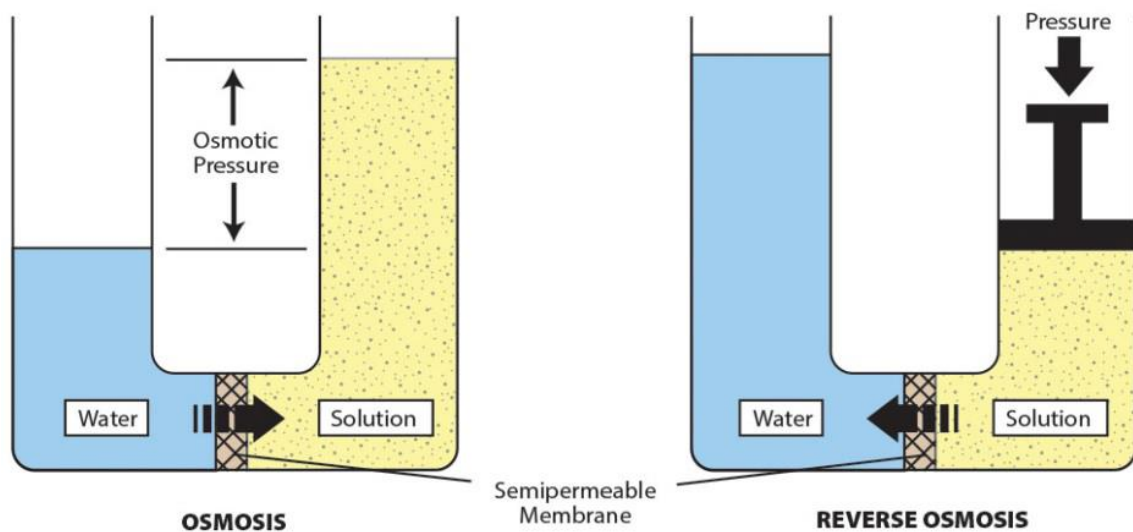
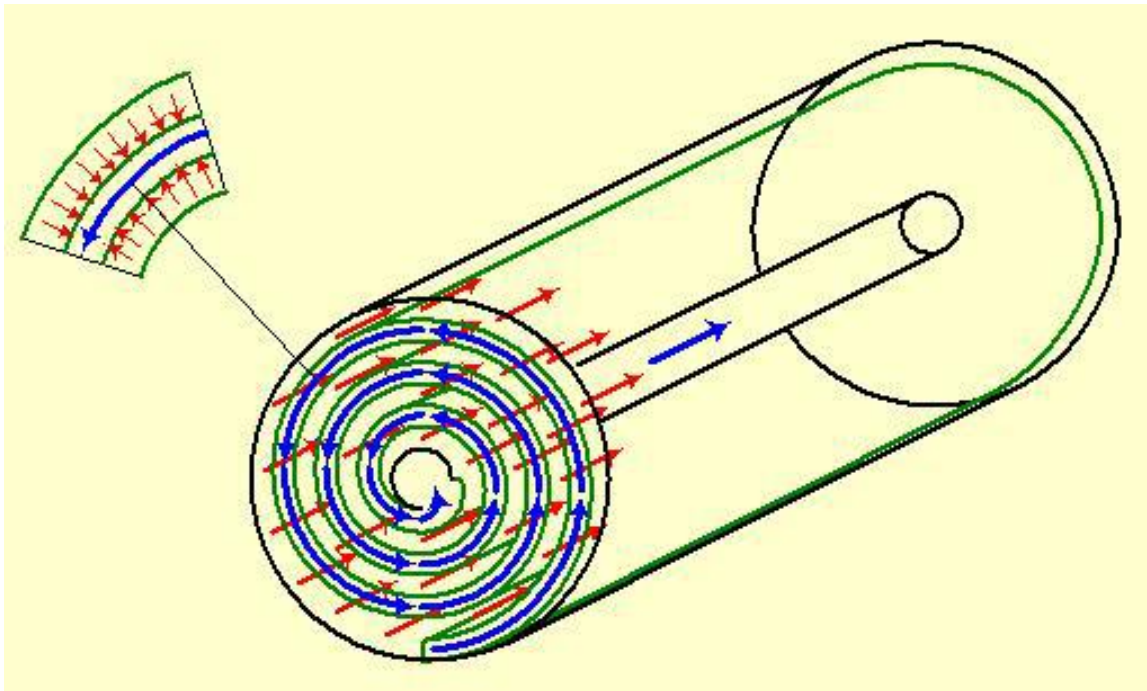


Figure 5.3: Principle of operation of osmosis and reverse osmosis

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 5.4, 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 5.4: Typical cross flow configuration of a spiral wound RO membrane*

In operation, the RO membrane system is continuously supplied with feedwater 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 increasing this would increase the concentration of ions on 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, shortening their lifetime.

### **5.2.2 Experimental: Scheme + photo of equipment (2 page)**

### **5.2.3 Methodology: Description of tests done (2 page)**

### **5.2.4 Summary and discussion of tests done (2 pages)**

### **5.2.5 Conclusions (0.5 page)**

## **5.3 Lenntech: Nanofiltration**

**5.3.1 Description of technology (1 page)**

**5.3.2 Experimental: Scheme + photo of equipment (2 page)**

**5.3.3 Methodology: Description of tests done (2 page)**

**5.3.4 Summary and discussion of tests done (2 pages)**

**5.3.5 Conclusions (0.5 page)**



## **5.4 NTUA: Evaporator**

**5.4.1 Description of technology (1 page)**

**5.4.2 Experimental: Scheme + photo of equipment (2 page)**

**5.4.3 Methodology: Description of tests done (2 page)**

**5.4.4 Summary and discussion of tests done (2 pages)**

**5.4.5 Conclusions (0.5 page)**

## **5.5 Arvia (Nyex™)**

**5.5.1 Description of technology (1 page)**

**5.5.2 Experimental: Scheme + photo of equipment (2 page)**

**5.5.3 Methodology: Description of tests done (2 page)**

**5.5.4 Summary and discussion of tests done (2 pages)**

**5.5.5 Conclusions (0.5 page)**

## **5.6 Conclusion site 02**

## **5.7 TU Delft (EFC)**

**5.7.1 Description of technology (1 page)**

**5.7.2 Experimental: Scheme + photo of equipment (2 page)**

**5.7.3 Methodology: Description of tests done (2 page)**

**5.7.4 Summary and discussion of tests done (2 pages)**

**5.7.5 Conclusions (0.5 page)**

## 6 Overall conclusions of deliverable D2.3

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## 7 Bibliography

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Nicolini, J. V., Borges, C. P., & Ferraz, H. C. (2016). Selective rejection of ions and correlation with surface properties of nanofiltration membranes. *Separation and Purification Technology* 171 , pp. 238-247.