ZERO BRINE

D8.4 Report on replication studies/ Roadmap for replicability

November 2021

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▪ Brines ▪ Coal Mine ▪ Precipitated Silica ▪ Seawater Desalination ▪ Bench-scale experiments ▪ Techno-economic analysis ▪ Model Simulation ▪ RCE ▪Replication studies ▪ Roadmap for replicability

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Abbreviations and Acronyms

BEC	Brine Excellence Center
BTSP	Brine Treatment Specific Cost
CAPEX	Capital Expenses
ED	Electrodialysis
LBC	Levelized Brine Cost
LCO	Levelized Cost
LCOC	Levelized Cost Of $Ca(OH)_2$
LCOM	Levelized Cost Of $Mg(OH)_2$
LCOs	Levelized Cost Of NaCl
LCOW	Levelized Cost Of Water
MED	Multi-Effect Distillation
MLD	Minimal Liquid Discharge
MRC	Mg Reactive Crystallizer
NF	Nanofiltration
NTC	NaCl Thermal Crystallizer
OPEX	Operational Expenses
RCE	Remote Component Environment
RO	Reverse Osmosis
SCADA	Supervisory Control And Data Acquisition
SWRO	Seawater Reverse Osmosis
TBT	Top Brine Temperature
TDS	Total Dissolved Solids
ZLD	Zero Liquid Discharge

Executive Summary

In this report, the main research findings of six replication case studies that were part of the WP8 of the ZERO BRINE project are presented and discussed. The replication case studies examined the brines originated from the following industries: one seawater desalination plant in Nisyros island, Greece (Section 2), one seawater desalination plant in Pantelleria island, Italy (Section 3), one coal mine (Dębieńsko) in Poland (Section 4), one plant that produces drinking water in Spain (Section 5) and finally two precipitated silica industries, SOLVAY in France and GRACE in Germany (Section 6).

All the replication case studies are structured as follows. Firstly, a short presentation for each case study is given. In these sections, details about the location and the selection of the case studies are presented together with the proposed process treatment chains and the technologies employed. Next, the advanced simulation platform (implemented in RCE software) that was used to perform a techno-economic analysis for each case study is presented and analyzed the respective process treatment chains. This RCE software has been developed by DLR in the context of the ZERO BRINE project (WP5).

Following, the bench-scale experiments required for the model validation assumptions are provided for the different technologies. Regarding the Greek case study, tests were conducted for the following processes: Nanofiltration, Reverse Osmosis and Multiple Effect Distillation (Section 2.2). For the Italian case study, the following technology was validated: Magnesium/Calcium Hydroxide Crystallization (Section 3.3). The Polish case study performed experiments for the electrodialysis process (Section 4.2). The Spanish case study tested the chemical precipitation of Calcium Carbonate, Nanofiltration and Chemical precipitation of Magnesium Hydroxide (Section 5.3). Lastly, in the Dutch case studies, the Eutectic Freeze Crystallization process was tested (Section 6.2). For the technologies that no bench scales tests were done either due to the availability of reliable information at an industrial scale or due to the complexity of performing bench-scale tests, the model equations were validated with literature information or the RCE platform.

After the bench-scale experiments, the simulation campaign is presented for all the studies. In these sections, all the units were simulated in the RCE platform and the modelled treatment chains were given along with the technical results obtained from the RCE mode, meaning the mass balances for all the processes. After that, the economic results of the RCE modes are given, including the CAPEX and the OPEX for each unit and the revenues from the products recovered (salts and water). Finally, a sensitivity analysis for the proposed process trains is performed and more specifically a sensitivity analysis for the recovered products since, in simulation models like the RCE modelling platform, the uncertainty may be relatively significant. The Levelized Cost of the recovered products is calculated to compare it with the cost of the products that already exist in the market.

Finally, in Section 7, the conclusions for all the replication studies are drawn. Furthermore, the roadmap for replicability is given (Section 8). Based on the 5 Brine Excellence Centers that developed throughout the project implementation, the replication of the project results to other process industry sectors was feasible and presented in detail in this deliverable.

1. Background and scope of this deliverable

The ZERO BRINE project aims to facilitate the implementation of the Circular Economy package and the SPIRE Roadmap in various process industries by developing the necessary concepts, technological solutions and business models to redesign the value and supply chains of minerals (including magnesium) and water, while dealing with present organic compounds in a way that allows their subsequent recovery.

Within the framework of ZERO BRINE project, Work Package 8 is focusing on the business plan, market exploitation and intellectual property management (IPR) activities. WP8 is structured on the following three Tasks:

- **Task 8.1**: Circular business model, economic mechanisms and governance related to the large-scale demonstration activity of the project;
- **Task 8.2**: Replicability of case studies across EU – Business Plan by sector; and
- **Task 8.3**: Intellectual Property Rights Management.

The results from the implementation of this work package is presented through six (6) deliverables:

- **Deliverable 8.1**: Framework agreement between technology providers/suppliers – ZERO BRINE TASK FORCE (connected to Task 8.2);
- **Deliverable 8.2:** Report on the circular business model suggested for the large scale demonstration in Rotterdam Port (connected to Task 8.1);
- **Deliverable 8.3**: Memorandum of Understanding between relevant stakeholders in Botlek area (connected to Task 8.1);
- **Deliverable 8.4**: Report on replication studies / Roadmap for replicability (connected to Task 8.2);
- **Deliverable 8.5**: Business plans for three industrial sectors (connected to Task 8.2); and
- **Deliverable 8.6**: Business plans for participating SMEs (connected to Task 8.2).

The current deliverable comprises the fourth deliverable of WP8. It was carried out within Task 8.2. In particular, Subtask 8.2.3 is about the replication of the project results in six industries. The Online Brine Platform that was developed in WP6 played a key role in replicating the paradigms generated in the framework of the ZERO BRINE project. Two process industries were selected in the Netherlands, one in Poland, one in Spain, one in Italy and one industry in Greece. The replication case studies aim to serve a key role for making bench-scale tests and suggest a technically and economically feasible solution for different end-users while the simulation tools that were developed in Task 5.3, were also used here for determining key parameters such as CAPEX, OPEX and thus produce an outline business case.

2. Greek Replication Case Study

2.1. Presentation of the case study

Water availability in some of the Aegean Sea islands is extremely low. During the summer and dry seasons, the water demand is higher than the water availability for household use and irrigation. The main reason for the increase in water consumption is the increase in the water consumed by the hospitality industry. Currently, the main way to meet deficient water balance on the “semi-arid” islands is water transportation and desalination. On Greek islands, Reverse Osmosis desalination is mostly used with a total capacity of 22,860 m^3/d.

The desalination plants were always a feasible solution for the production of clean water in Greece. There are more than 200 desalination pants (mostly RO) in Greece, so the management of the resalted brine is a crucial issue. The brine disposal depends on the volume of the brine, the quality, the location of the plant and the National Policy, but in general, the submerge disposal, through pipes that transport the brine far into the sea is mostly used. So, the Zero Liquid Discharge is a crucial strategy that should be used for the protection of the environment.

Nisyros is a volcanic Greek island located in the Aegean Sea. The island has 3 desalination plants with a capacity of 1,000 m^3/day of freshwater produced. For the Greek replication study, one of the desalination plants of Nysiros will be used as a part of a Zero Liquid Discharge (ZLD) proposed system.

The proposed treatment chain is illustrated in Figure 2-1.

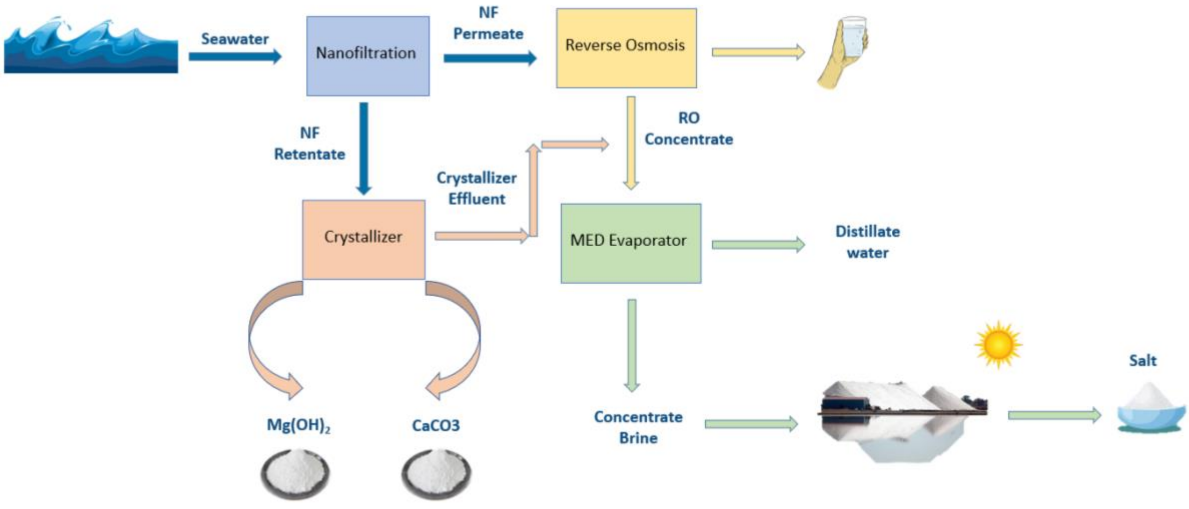

Seawater
Nanofiltration
NF Permeate
Reverse Osmosis
NF Retentate
RO Concentrate
Crystallizer Effluent
Crystallizer
MED Evaporator
Distillate water
Salt
Mg(OH)$_2$
CaCO3
Concentrate Brine

Figure 2-1. *Proposed ZLD process chain*

The treatment chain consists of 4 technologies:

(i) Nanofiltration (NF);
(ii) Reactive membrane crystallizers;
(iii) Reverse Osmotis Unit (RO from Nysiros);
(iv) Multi-Effect Distillation (MED);

The proposed seawater process treatment train is based on the Zero Liquid Discharge (ZLD) concept. The first part of the process train consists of a nanofiltration unit. The NF unit produces two streams (permeate and retentate) and separates the monovalent from the divalent ions. The CO_3^-, Mg^{2+}, Ca^{2+} ions pass to the retentate stream and are sent to a crystallizer in which $Mg(OH)_2$, $CaCO_3$ minerals are selectively recovered using NaOH and Na_2CO_3 respectively. The NF permeate stream which is rich in Na^+ and Cl^- is fed into the RO unit where a concentrate brine stream and a clean water stream are produced. The brine from RO is mixed with the membrane crystallizer effluent which then flows in the MED unit. In the MED unit, this brine is concentrated near the saturation point of NaCl (26%), producing a very concentrated stream and a distillate water stream. The MED outlet brine is sent into salt ponds where the recovery of high purity salt can be achieved. With the proposed treatment system the recovery of $Mg(OH)_2$, $CaCO_3$ and NaCl is achieved. The $Mg(OH)_2$ is one of the critical raw materials for Europe and the cost of magnesium hydroxide is estimated to be $ 1000/ton while the $CaCO_3$ and NaCl with high purity can be easily placed on the market.

At subtask 8.2.3 the technical and economic analysis of the proposed process train is performed. With the bench-scale experiments, technologies were evaluated and with the use of the RCE platform created by DLR, the simulation and the economic analysis allow to verify the feasibility of the proposed process train.

2.2. Bench test experiments required for model validation assumptions

2.2.1. Nano-Filtration (NF)

During the first months of the sub-task implementation, bench scale tests were conducted by the NTUA team using NF unit (single module) with a capacity of about 0,5 m^3/h and synthetic solutions. The objectives of the bench scale tests, conducted by NTUA in the Labs of Environmental Science and Technology Unit of NTUA, were to find:

- the highest possible divalent ions rejection,
- the lowest monovalent rejection

The membrane used in the NF unit is a FILMTEC NF270-4040 membrane which is a Polypiperazine Thin-Film Composite membrane. The system that was used for the NF bench scale test is shown in Figure 2-2.

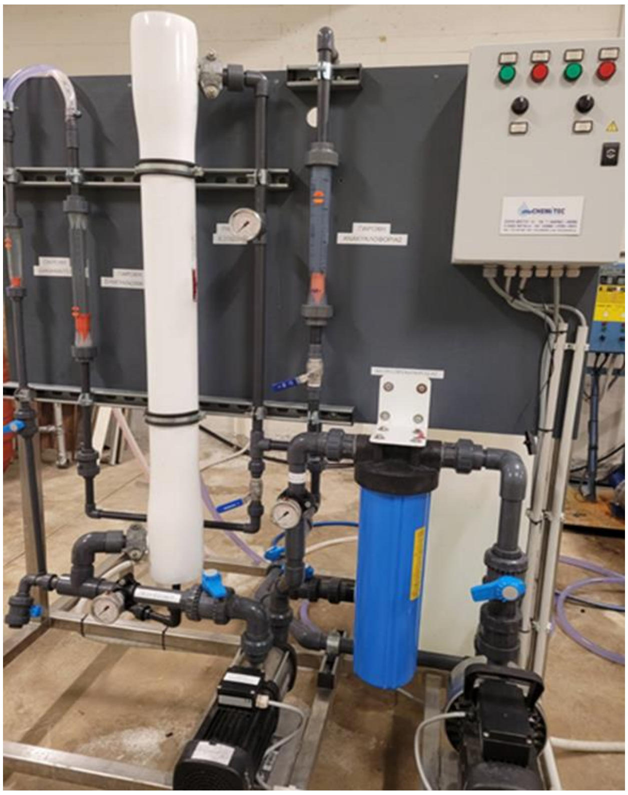


Figure 2-2. *NF unit for bench scale tests*

A synthetic solution was prepared in the laboratory of NTUA to simulate the seawater that is the inlet of the NF unit. The concentrations of major ions in this solution are:

Table 2-1. *Seawater ion concentration*

Ions	Concentration, mg/L
Na^+	13,551
Cl^-	24,561
Mg^{+2}	1,520
Ca^{+2}	575
SO_4^{-2}	2,770
TDS	42,907

At the beginning of each experiment, the system has been run for 10 -15 min in order to achieve stable operating conditions. During the experiments, samples of permeate and concentrate were collected. The pH value was corrected between 6 and 6.5, by the addition of hydrochloric acid solution, to avoid the use of antiscalant during experiments.

The samples from the inlet and outlet streams were examined with atomic absorption (for cations concentrations) and spectrophotometry (for anions concentrations). The result of the best experiment with 22% recovery is summarized in the following charts (Figure 2-3 and Figure 2-4).

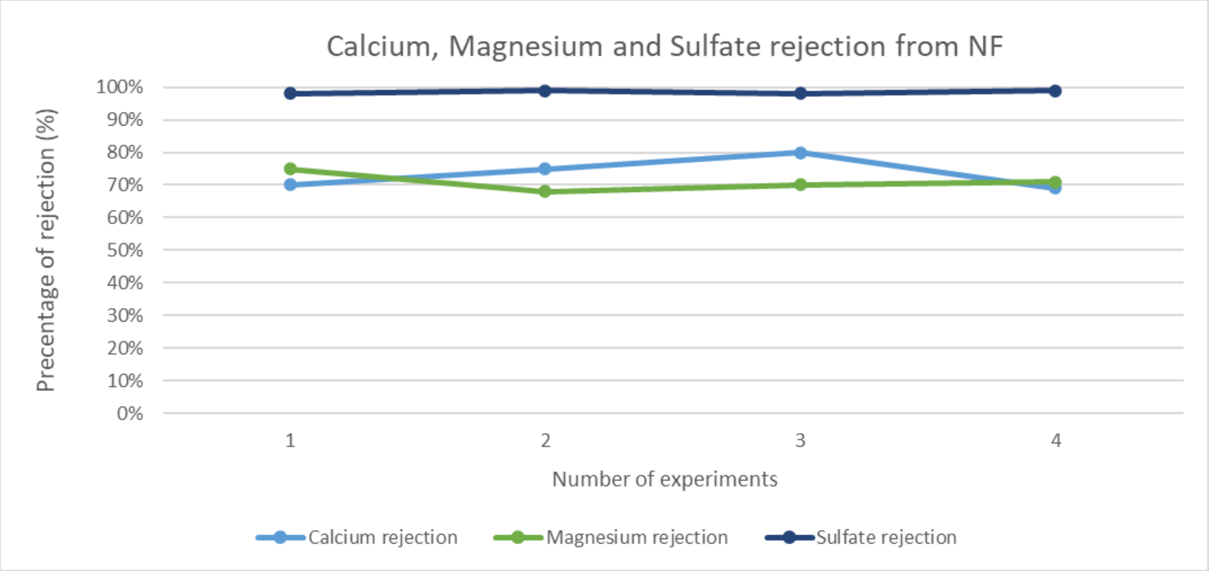


***Figure 2-3**. Divalent ions rejection with NF unit*

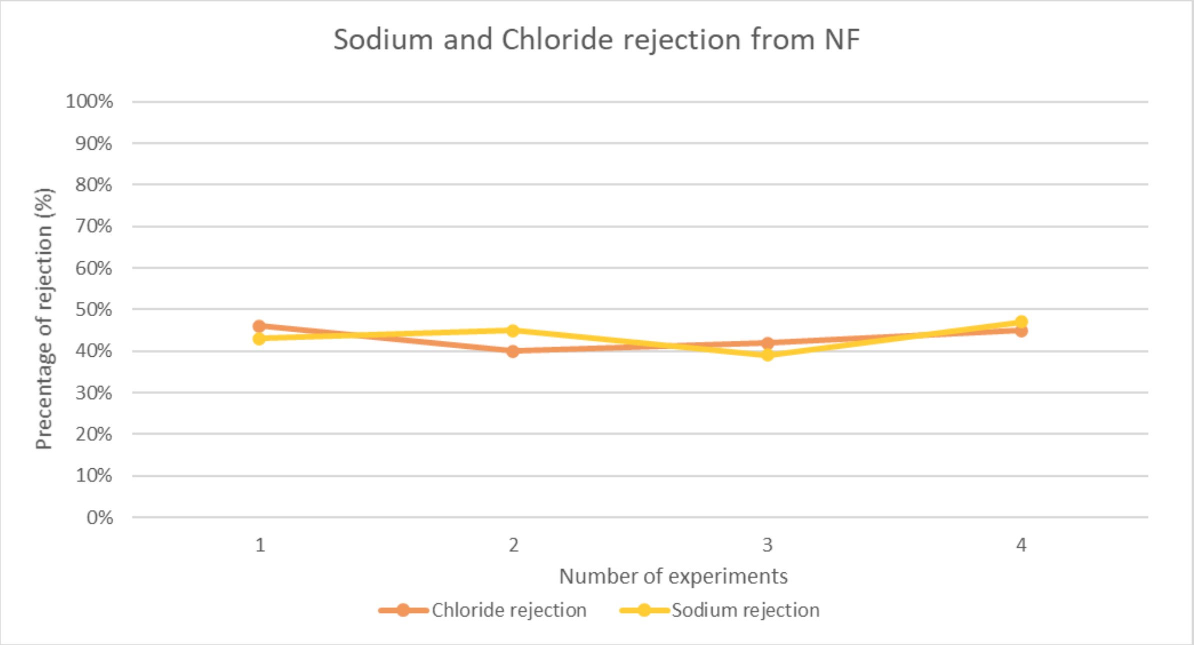


***Figure 2-4.** Monovalent ions rejection from NF*

It could be observed that NF 270 4040 membrane reached high divalent ion rejection around 80% both for the Calcium and Magnesium and on the other hand low rejection of monovalent ions were observed.

2.2.2. Reverse Osmosis (RO)

The permeate of the NF unit, which is the flow reach in Sodium Chloride (NaCl), then passed through the RO unit. The RO unit that was used for the bench-scale tests is a 0,5 m^3/h capacity unit and the objectives of the bench scale tests were to:

- Achieve as high water recovery as possible.
- Achieve permeate/concentrate ratio: 90/10

The RO unit that was used for the bench-scale experiments is shown in Figure 2-5. Low-pressure RO membranes FILMTEC LP-2540 were used to deliver high-quality water.

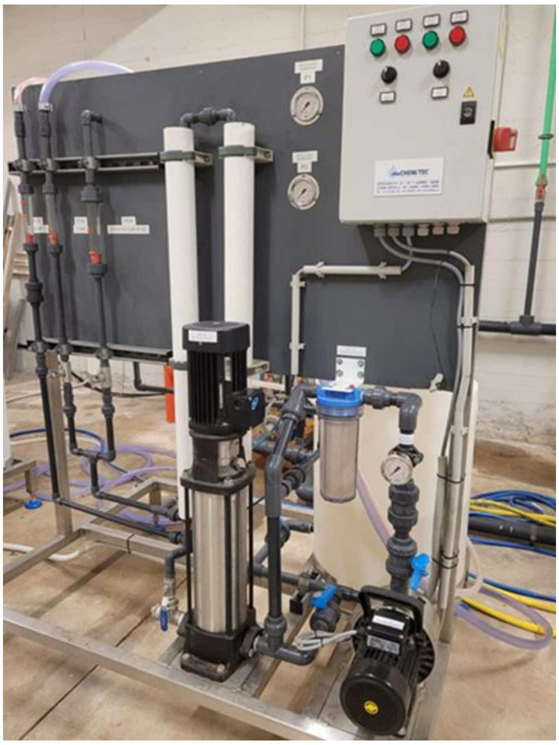


Figure 2-5. RO unit for bench scale tests

At the beginning of each experiment, the system ran for 10 -15 min in order to achieve stable operating conditions. During the experiments, samples of permeate and concentrate were collected.

The samples from the inlet and outlet streams were examined with atomic absorption (for cations concentrations) and spectrophotometry (for anions concentrations). The results of the above experiments are summarized in the following charts (Figure 2-6 and Figure 2-7).

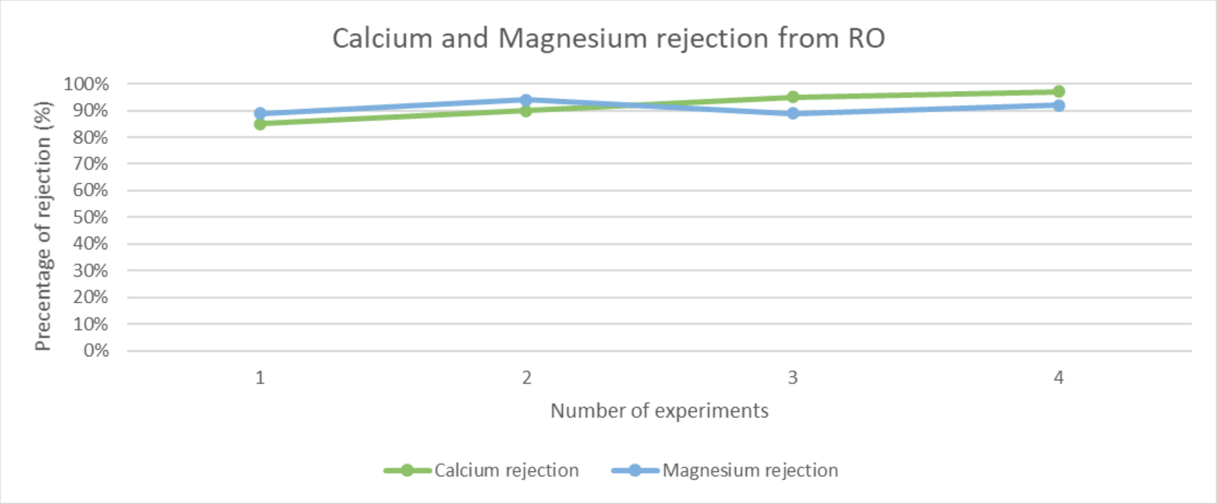


Figure 2-6. *Calcium and Magnesium rejection from the RO unit*

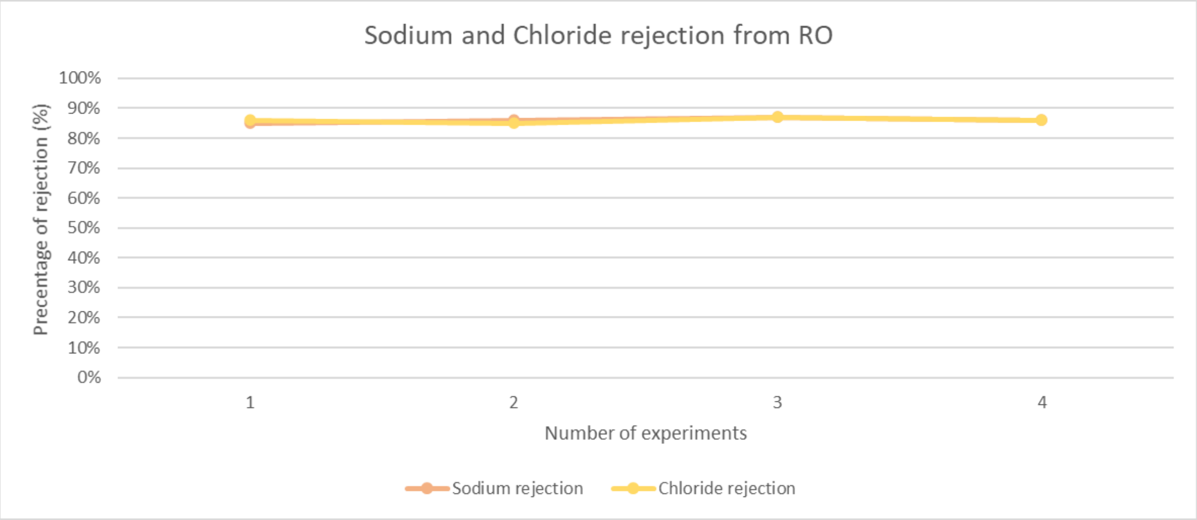


Figure 2-7*. Sodium and Chloride rejection from the RO unit*

The RO has shown a stable rejection of divalent ions (>80% rejection) and sodium chloride (>85%). Experiments were also performed changing recirculation but it was observed that these changes did not strongly affect the ions rejection.

2.2.3. Magnesium and calcium precipitation with crystallizer

For the Magnesium hydroxide and Calcium Carbonate precipitation, no bench scale experiments were performed. Instead, the quantity of the recovered minerals was simulated via the RCE platform.

2.2.4. Multiple Effect Distillation (MED)

The MED evaporator is made up of two consecutive effects and it operates below atmospheric pressure, limiting the boiling temperatures below 100°C. In each of the MED effects, brine is evaporated resulting in the production of two subsequent streams: (i) a water vapor stream that is then condensed and recovered as fresh water and (ii) a more concentrated brine stream. The vapor stream of the first effect 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. More 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.

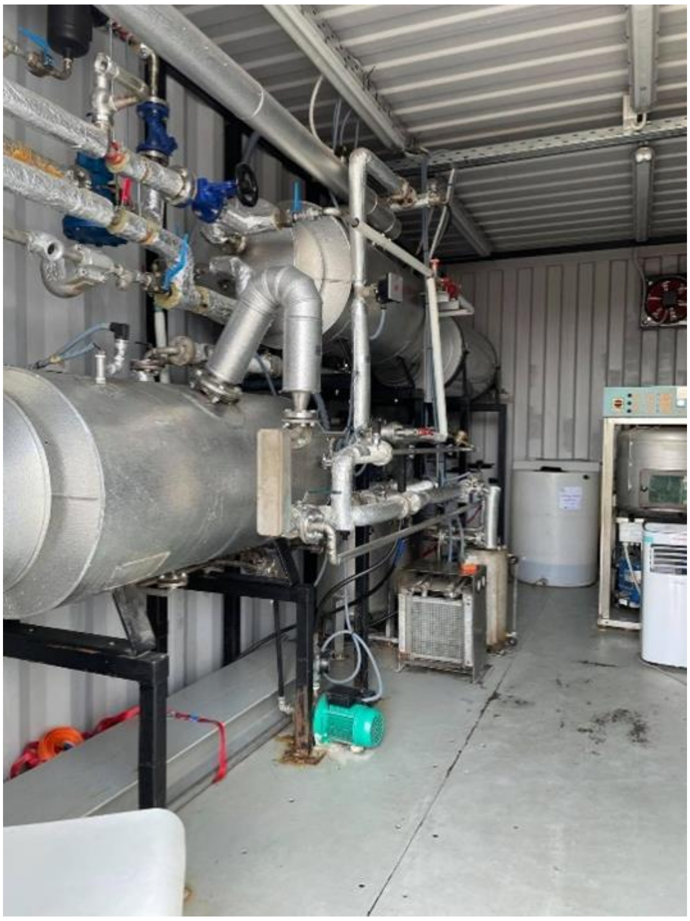


Figure 2-8. *Photo of the MED containerized system*

Some experiments with synthetic brine and major ions were performed with the system and analyzed at the lab. The results of these experiments are presented in Table 2-2 and Table 2-3. For synthetic brine production, sodium chloride was mixed with tap water. The mean value of inlet brine TDS was 5.4% and the value of concentrated brine TDS was 20.6%.

Table 2-2. *Quality and quantity of the inlet brine solution*

Inlet Brine Volume (L)	Sodium (mg/L)	Chloride (mg/L)	Magnesium (mg/L)	Calcium (mg/L)	Inlet brine TDS (mg/L)
100	19,987	30,860	12	25	50,884
100	21,700	35,468	11.6	22.3	57,201

Table 2-3. *Quality and quantity of the concentrated brine solution*

Concentrated Brine Volume (L)	Sodium (mg/L)	Chloride (mg/L)	Magnesium (mg/L)	Calcium (mg/L)	Concentrated brine TDS (mg/L)
30	67,987	123,900	43.1	84.3	192,014
25	86,800	133,872	56.4	90.4	220,818

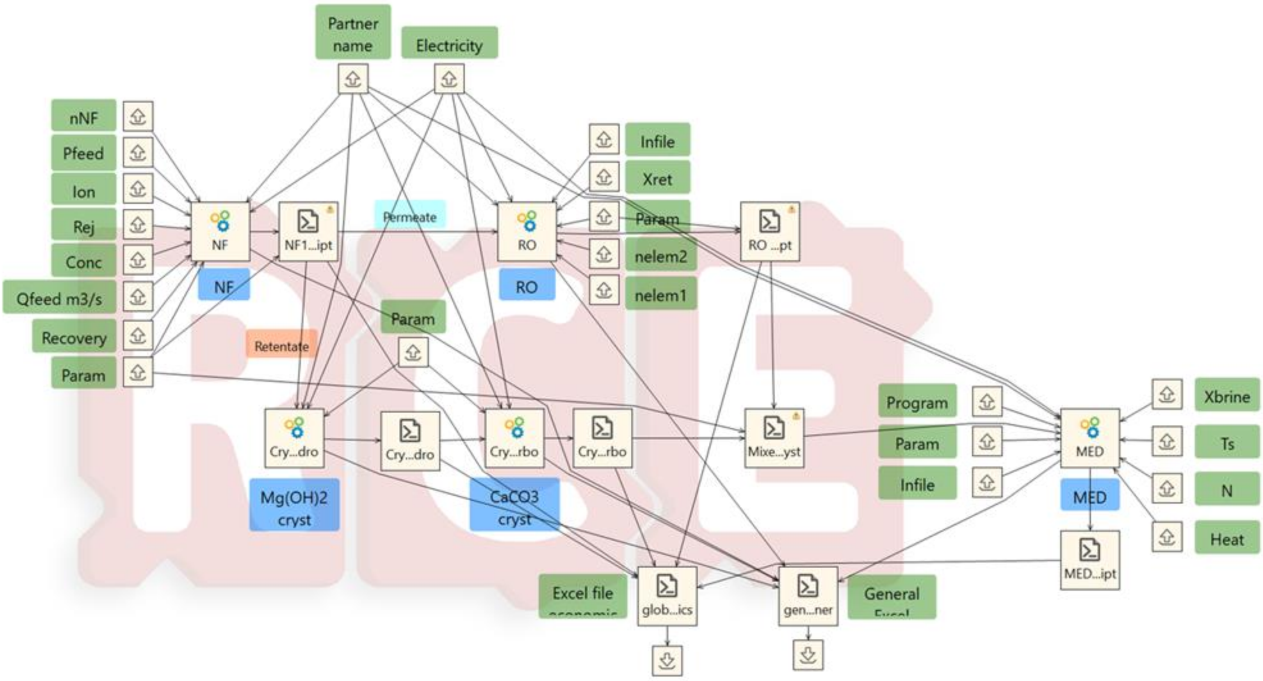
The control of the system is accomplished via a PC-based supervisory control and data acquisition (SCADA) interface. Multiple temperature, pressure and flow transmitters are connected in many positions within the system, receiving all the important data for process control. The energy consumption can be measured from SCADA and for the above experiments, the mean energy consumption was 450 kWh/m^3 of condensate.

2.3. Simulation campaign

2.3.1. Description of the case study case and results

For the simulation of the proposed treatment chain, the DLR's RCE platform was used and all the units were simulated. For more details regarding the platform and the technical data please refer to Deliverable 5.2 of DLR.

The proposed treatment chain is presented in Figure 2-9. It consists of an NF unit, 2 crystallizers/precipitators (for $Mg(OH)_2$ and $CaCO_3$), an RO unit and MED. The NF retentate is sent to the crystallizer for crystallization of Mg^{+2} and Ca^{+2} ions using NaOH and Na_2CO_3 solution to obtain crystals of $Mg(OH)_2$ and $CaCO_3$ respectively. The NF permeate rich in Na^+ and Cl^- is sent to RO. The RO retentate is mixed with the crystallizer effluent and sent to the MED. The products for the chain are $Mg(OH)_2$, $CaCO_3$ crystals, pure water (both RO and MED) and NaCl brine (which is finally crystallized in salt ponds). The only part that has not been modelled at the RCE platform is the salt ponds part. Thus, the economic calculation from RCE does not reflect the revenue from the NaCl recovery.


Partner name
Electricity
nNF
Pfeed
Ion
Rej
Conc
Qfeed m3/s
Recovery
Param
NF
NF1...ipt
NF
Permeate
RO
RO
Infile
Xret
Param
nelem2
nelem1
RO ...pt
Retentate
Param
Cry...dro
Cry...dro
Cry...rbo
Cry...rbo
Mixe...yst
Program
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MED
MED
Xbrine
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N
Heat
MED...ipt
Mg(OH)2 cryst
CaCO3 cryst
Excel file economic
glob...ics
gen...ner
General Excel

Figure 2-9. *Modelled treatment chain on RCE*

With the RCE model, the recovery of sodium chloride after drying could not be modelled so the Total CAPEX, Total OPEX and the revenue will be calculated in Section 2.3.4.

2.3.2. Technical results of the RCE mode

For all units at the following Table 2-4 to Table 2-8, all the results from the RCE platform are presented.

Table 2-4. *Results from the RCE platform for NF*

	Feed brine (mg/L)	Retentate (mg/L)	Permeate (mg/L)
CFeedNa	13,557	14,149	14,072
CFeedCl	24,562	29,013	22,665
CFeedMg	1.51	3,247	0.43
CFeedCa	0.57	1,233	0.15
CFeedS0$_4$	2.76	5,978	0.73

Table 2-5. *Results from the RCE platform for NaOH-MgHydro crystallizer*

	NF retentate (mg/L) – Crystallizer inlet	MgHydro Crystallizer out
CFeedNa	14,149	16,109
CFeedCl	29,013	22,414
CFeedMg	3,247	0
CFeedCa	1,233	0.95
CFeedS0$_4$	5,978	4.60

	NF retentate (mg/L) – Crystallizer inlet	MgHydro Crystallizer out
$CFeedCO_3$	0.00004	0.016

***Table 2-6**. Results from the RCE platform for NaCarbo-CaCarbo crystallizer.*

	MgHydro Crystallizer out -Crystallizer inlet	CaCarbo Crystallizer out
CFeedNa	16,109	16,790
CFeedCl	22,414	21,878
CFeedMg	0	0
CFeedCa	0.95	0
$CFeedS0_4$	4.60	4.49
$CFeedCO_3$	0.016	0

***Table 2-7**. Results from the RCE platform for RO unit.*

NF Permeate (mg/L) – RO inlet	RO Retentete mg/L	RO Permeate mg/L
31,802	68,853	230

***Table 2-8.** Results from the RCE platform for MED unit.*

RO retentate + Crystallizer out – MED inlet	MED concentrate mg/L	RO Permeate mg/L
51,840	182,557	0

The RCE platform for the modelling of each unit uses various programming environments, namely Python and Matlab, and simulates the proposed completed treatment chain via technical models.

For the NF unit the main technical parameters that were considered are:

- The Feed Flow – 18 m^3/h
- The pore size of nanofiltration membrane -0.45 nm
- The feed pressure – 34 bar
- Recovery of the system – 60%

For the two crystallization steps the main technical parameters that were considered are:

a) For the NaOH-MgHydro crystallizer
    - The Feed Flow –8.2 m^3/h
    - The concentration of the NaOH solution – 1 mol

b) For the NaCarbo_CaCarbo crystallizer
    - The Feed Flow –10.7 m^3/h
    - The concentration of the Na_2CO_3 solution – 1 mol

For the RO unit the main technical parameters that were considered are:

- The Feed flow – 12.2 m^3/h
- Elemets number (vessels) – 16
- Number of stages – 2

For the MED evaporator unit the main technical parameters that were considered are:

- The Feed flow – 16,73 m^3/h
- Number of effects – 6
- Steam temperature – 100^oC

2.3.3. Economical results of the RCE modes

Regarding the economic analysis, the total annualized capital costs (CAPEX [$/y]) and the total operating costs (OPEX [$/y]) are the most significant parameters for each unit. At the Table 2-9, the CAPEX and OPEX of each unit and the revenues from the products $Mg(OH)_2$, $CaCO_3$, clean water from RO and MED are presented.

Table 2-9. *CAPEX and OPEX results from the replication case study*

Model input/output	Units	Global (USD)	Global (EUR)
CAPEX NF	$/y	272,425.08	231,561.31
OPEX NF	$/y	182,714.48	155,307.30
CAPEX NaOH-MgHydro crystallizer	$/y	30,651.54	26,053.80
OPEX NaOH-MgHydro crystallizer	$/y	302,585.81	257,197.93
Revenue $Mg(OH)_2$		837,887.44	542,204.32
CAPEX NaOH-MgHydro crystallizer	$/y	23,998.85	20,399.02
OPEX NaOH-MgHydro crystallizer	$/y	63,919.10	54,331.24
Revenue $CaCO_3$	$/y	73,160.33	53,686.29
CAPEX RO	$/y	256,321.64	217,873.39
OPEX RO	$/y	133,368.51	113,363.23
Water Revenue (RO)	$/y	64,638.75	46,442.94
CAPEX MED	$/y	198,596.84	168,807.31
OPEX MED	$/y	398,046.23	338,339.29
Water Revenue (MED)	$/y	105,681.73	89,829.47

The total CAPEX, OPEX and Revenue are presented in the following Table 2-10 and the following formula was used :

$$Total\_CAPEX = \sum(CAPEX_{NF1} + CAPEX_{cryst\_NaOH\_MgHydro} + CAPEX_{cryst\_NaCarbo\_CaCarbo} + CAPEX_{RO} + CAPEX_{MED})\ [\$/yr]\ (2.1)$$

$$Total\_OPEX = \sum(OPEX_{NF1} + OPEX_{cryst\_NaOH\_MgHydro} + OPEX_{cryst\_NaCarbo\_CaCarbo} + OPEX_{RO} + OPEX_{MED})\ [\$/yr]\ (2.2)$$

$$Total\_Revenue = \sum(R_{MgOH2} + R_{CaCO3} + R_{waterRO} + R_{waterMED})\ [\$/yr]\ (2.3)$$

Table 2-10. *Total CAPEX, OPEX and revenue results*

	Units	Global (USD)	Global (EUR)
Total CAPEX	$/y	781,993.96	664,694.87
Total OPEX	$/y	1,080,634	994,793.03
Total Revenue	$/y	975,687.27	732,163.03

As it can be seen from Table 2-10, the higher CAPEX and OPEX of the process train is this of MED evaporator. The total OPEX of the MED evaporator is calculated by the following formula:

Total_OPEX = ∑(Annual personnel cost + Annual manteinance cost + Annual electric cost + Annual heat cost + Annual chemical cost)

The higher operational cost is the annual personnel cost (141,125 $/y).

2.3.4. Sodium Chloride recovery

Except for the $Mg(OH)_2$ and $CaCO_3$ recovery, also sodium chloride is a salt that can be recovered. The concentrated brine from the MED evaporator can be sent into salt ponds where the water can be evaporated. Greece, as it can be seen in the following Figure 2-10, has yearly more than 2,500 h sunshine. For this reason, salt ponds are an attractive solution for the recovery of sodium chloride. The salt ponds need large land areas, but in Nysiros island, there are many available areas (with very low cost) that can be used for this purpose.

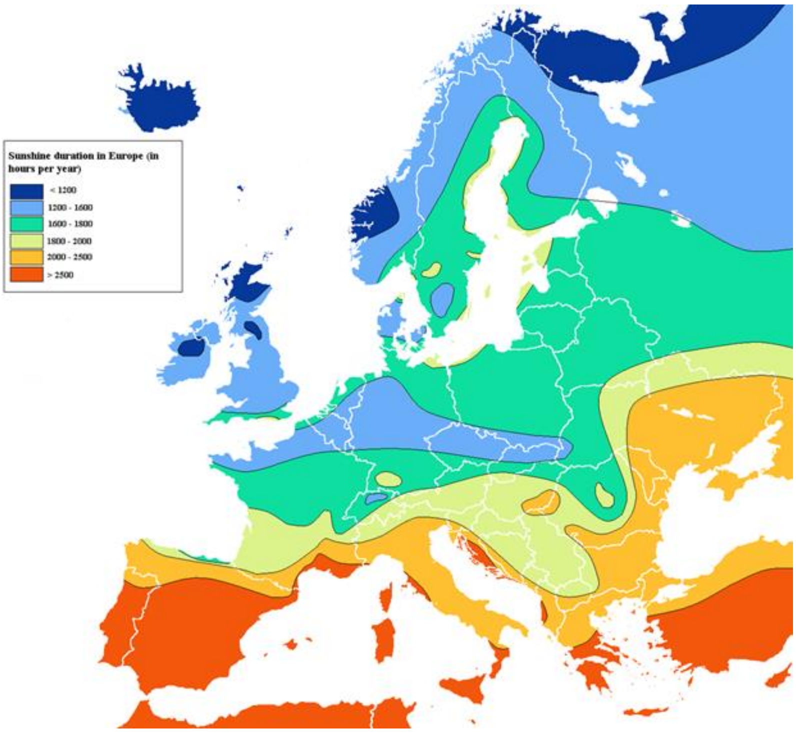


Figure 2-10. *Europe sunshine hour map (Wikipedia, 2010)*

32m^3/hr brine are produced from the proposed system yearly. So, in total 6,000 tons of sodium chloride per year can be recovered. The sodium chloride costs about 68 €/ton (Table 2-12) so the Table 2-10 can change as follow.

Table 2-11*. The total revenue with the NaCl profit*

	Units	Global (USD)	Global (EUR)
Total CAPEX	$/y	781,993.96	664,694.87
Total OPEX	$/y	1,080,634	994,793.03
Total Revenue	$/y	1,387,687.27	1,189,971.05

2.3.5. Sensitivity analysis of process profitability performances

In simulation models like the RCE modelling platform, the uncertainty may be relatively significant. For this reason, a sensitivity analysis for the proposed process train is performed and more specifically a sensitivity analysis for the recovered products. The current market of the recovered product is presented in the following Table 2-12.

Table 2-12. *The specific cost of the recovered products from the market*

Specific Cost*		
$Mg(OH)_2$	996	€/ton
$CaCO_3$	100	€/ton

Specific Cost*		
NaCl	68	€/ton
Water	0.83	$€/m^3$

In order to compare the cost of the recovered products with the ones that already exist in the market, the Levelized Cost must be evaluated.

In general, the Levelized Cost is the selling price of a product (i.e. water, salt, etc.) that reaches the break-even point after a certain plant lifetime. Assuming that the produced flow rate of a specific product and the operating costs are the same every year in the plant lifetime, the Levelized Cost of the ith product can be calculated as follows:

Levelized cost of (LBC):

LC0_capex = capex / Q annual product (2.4)

LBC_opex = (opex - total_revenue) / Qannual product (2.5)

LBC_tot = LBC_capex + LBC_opex (2.6)

Figure 2-11 shows that the NF and the RO units have the higher CAPEX followed by the CAPEX of the MED evaporator. The high capital cost of NF and RO systems is due to the high depreciation (depreciation period 15 years) and membranes cost. For the MED evaporator, the main cost is this of the multiple effects (heat exchanger). Furthermore, regarding the OPEX, as it is shown in the following Figure 2-12, the MED evaporator has the higher operating cost but by combining the system with waste heat the operating cost will be decreased.

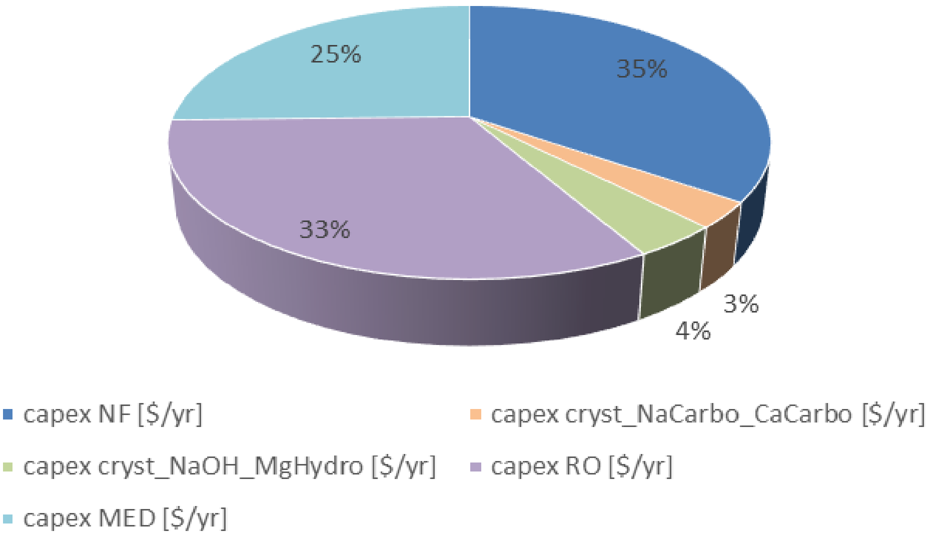


Figure 2-11. *Percentage of the total CAPEX for each unit*

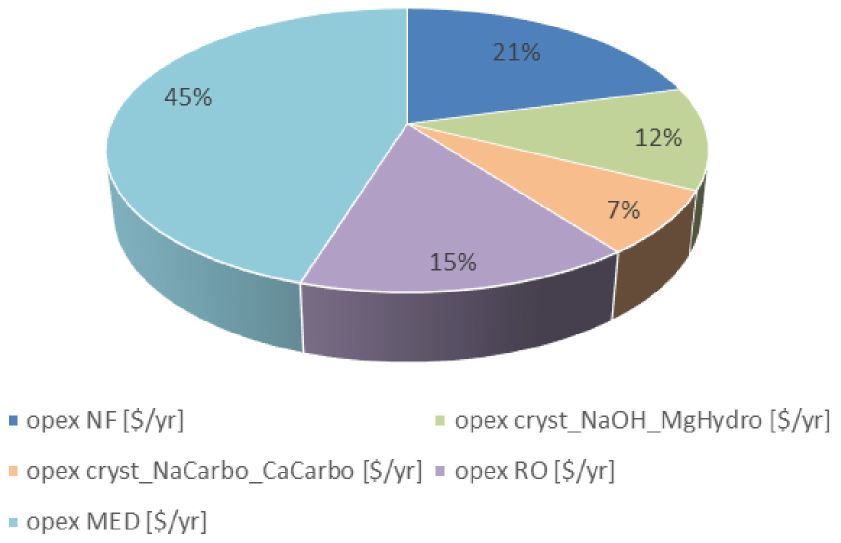


Figure 2-12. *Percentage of the total CAPEX for each unit*

However, regardless of the high overall costs, the total revenue achieved is very close to the CAPEX and OPEX, which makes the proposed process feasible. On the other hand, the Levelized costs were calculated and as it is shown in Table 2-13 the recovered salts and water have approximately similar prices in comparison with those already exist in the market.

Table 2-13. *Cost of salts and water in comparison with the market*

	Specific cost on the market	Levelized cost of the ZLD system
$Mg(OH)_2$	996	940
$CaCO_3$	100	95
NaCl	68	65
Water	0.83	0.75

2.3.6. Estimated economic potentials

The economic analysis showed that the proposed system has a revenue approximately equal to the CAPEX and OPEX of the proposed system. The main profit from the proposed system is coming from the $Mg(OH)_2$ and the NaCl recovery. The economic feasibility of the proposed system combined with the ZLD principle invests such systems interesting. In Nysiros especially, renewable energy can be used for the electric demand of the proposed train. Geothermal energy, solar and wind energy can be used for the operation leading to the minimization of the system operating cost.

3. Italian Replication Case Study

3.1. Presentation of the case study

The Italian case study focuses on the valorisation of brine produced by the seawater desalination plant of the Sicilian island, Pantelleria (Figure 3-1).

Figure 3-1. *Seawater Reverse Osmosis Plant in the "Satarua" District, Pantelleria (IT)*

The Seawater Reverse Osmosis (SWRO) desalination plant in question, located in the "Sataria" district of Pantelleria (Figure 3-1), is made up of 4 reverse osmosis units, each one with a capacity of 1250 m^3/d of freshwater produced. Nevertheless, only three of the four modules (with an average water recovery = 45%) operate contemporarily resulting in an average total capacity of about 3750 m^3/d. The produced brine presents an average TDS equal to 70 g/L and more specifically, the average ionic concentration values of the brine are reported in Table 3-1.

Table 3-1. *Average ionic concentration of the brine produces by the desalination plant*

Ionic species	Na^+	Ca^{2+}	Mg^{2+}	K^+	Cl^-	SO_4^{2-}	HCO_3^-
Concentration [g/L]	21.4	0.88	2.70	0.78	39.0	5.50	0.18

For the present case study, an innovative Minimal Liquid Discharge (MLD) system was proposed and analysed to valorise around 50% of the total brine produced by the three operating RO modules of the "Sataria" SWRO plant.

The proposed treatment chain is illustrated in Figure 3-2.

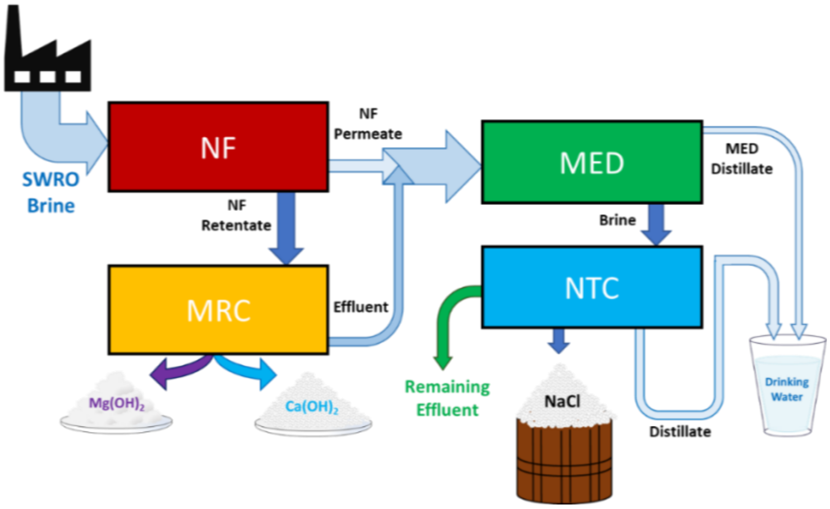


Figure 3-2. *Conceptual scheme of the proposed MLD system*

The chain consists of 4 technologies:

- **(i) Nanofiltration (NF);**
- **(ii) Mg Reactive Crystallizer (MRC);**
- **(iii) Multi-Effect Distillation (MED);**
- **(iv) NaCl Thermal Crystallizer (NTC).**

The SWRO brine is fed to a nanofiltration unit producing two streams, namely retentate and permeate. The NF retentate is rich in bivalent ions such as SO_4^{2-}, Ca^{2+} and Mg^{2+} meanwhile the NF permeate is characterised by a high concentration of monovalent ions such as Na^+ and Cl^-. The retentate, containing the majority of Mg^{2+} and Ca^{2+}, is therefore sent to an MRC in which both minerals are selectively recovered under the form of hydroxides via direct mixing with an alkaline reactant (NaOH solution). The effluent exiting the reactive crystallizer is mixed with the NF permeate and sent to an MED unit. The MED unit concentrates the brine via evaporation within its multiple effects producing a distillate (high-quality freshwater). Contemporarily, the MED reduces the brine volume that exits the unit at a salt concentration near that of saturation. The MED outlet brine is sent to a final NTC in which Na is recovered in the form of NaCl crystals along with a distillate and a remaining effluent. Other than reducing the final volume of brine discharged into the environment, what is an attractive aspect of the chain is that it produces many valuable goods ($Mg(OH)_2$, $Ca(OH)_2$, drinking water and NaCl), implementing in this way the concept of the circular economy.

The main target of Subtask 8.2.3 consists in evaluating the feasibility of the proposed MLD treatment chain of such a case study from a technical and economic point of view. A techno-economic analysis will allow us to verify whether the system is economically sustainable and whether there is potential to be implemented at an industrial scale.

3.2. Presentation of the modelling platform

The techno-economic analysis of the proposed MLD treatment chain was performed via an advanced simulation platform implemented in RCE software (Figure 3-3). The accessibility of such software was made possible thanks to the Zero Brine partner, DLR (the inventor of RCE).

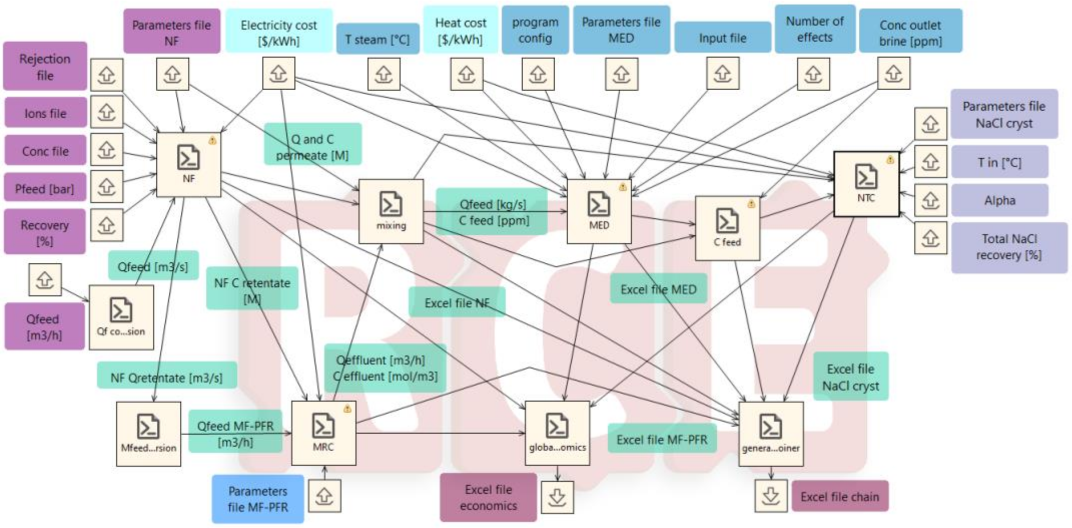

Parameters file NF
Electricity cost [$/kWh]
T steam [°C]
Heat cost [$/kWh]
program config
Parameters file MED
Input file
Number of effects
Conc outlet brine [ppm]
Rejection file
Ions file
Conc file
Pfeed [bar]
Recovery [%]
Qfeed [m3/h]
NF
Q and C permeate [M]
mixing
Qfeed [kg/s]
C feed [ppm]
MED
C feed
NTC
Parameters file NaCl cryst
T in [°C]
Alpha
Total NaCl recovery [%]
Qfeed [m3/s]
Qf co...sion
NF C retentate [M]
Excel file NF
Excel file MED
NF Qretentate [m3/s]
Qeffluent [m3/h]
C effluent [mol/m3]
Excel file NaCl cryst
Mfeed...rsion
Qfeed MF-PFR [m3/h]
MRC
globa...omics
Excel file MF-PFR
genera...oiner
Parameters file MF-PFR
Excel file economics
Excel file chain

Figure 3-3. Workflow of the NF-MCR-MED-NTC chain implemented in RCE

Within a single workflow sheet, techno-economic models of all technologies present in the treatment chain were interconnected. Technical and Economic models developed by (Micari, Cipollina, et al., 2019) for Work Package 5 (WP5) of the Zero Brine Project were employed. More specifically, Micari et al. developed a multi-scale process model capable of simulating a Nanofiltration unit. Since the model was validated for similar brine compositions and operating conditions to those of the Italian replicability case study, it was employed to evaluate the performance of the NF in the newly proposed MLD treatment chain. Details of the NF model are described in (Micari, Cipollina, et al., 2019). A similar approach was adopted for the MED unit whose model is presented in (Micari, Moser, et al., 2019). As for the MRC, no existing model had been yet developed. To the best of the authors' knowledge, kinetics concerning the chemical precipitation of magnesium hydroxide are still unknown and not available in the literature. Therefore a process model was developed, based on mass balance equations considering an instantaneous reaction between magnesium and hydroxyl ions. Such assumption was possible since it reflects what has been observed experimentally by UNIPA. To such model, an economic one was coupled applying the Bare Module Technique (Turton et al., 1998) for capital costs estimation and taking into account NaOH costs, HCl costs and energy consumption for the calculation of the MRC operating costs. Finally, a process model for the NTC was developed. The model was implemented in Python employing mass and enthalpy balance equations. Moreover, PHREEQC software was also employed to identify the compounds that typically precipitate at specific operating conditions. This allowed the introduction of logical conditions within the process model to take into account the precipitation of by-products that could compromise the final purity of NaCl produced. As for the economic model, operating costs of the NTC took into account electricity for pumping and the thermal energy required for the precipitation of NaCl crystals. Capitals costs, on the other hand, were estimated via the Bare Module Cost Technique (as was done in the case of the MRC).

The economic feasibility of the entire chain was evaluated by 5 main global parameters, four of which are: (i) Levelized cost of water (LCOW), (ii) Levelized cost of $Mg(OH)_2$ (LCOM), (iii) Levelized cost of $Ca(OH)_2$ (LCOC), (iv) Levelized cost of NaCl (LCOS). In general, the Levelized Cost is the selling price of a certain product (i.e. water, salt, etc.) that reaches the break-even point after a certain plant lifetime. Assuming that the produced flow rate of a specific product and the operating costs are the same for every year in the plant lifetime, the Levelized Cost of the i^{th} product can be calculated as follows:

$$LCOi^{th} = \frac{\sum_{units} capEX + \sum_{units} opEX - (\sum_{units} REV - (REV_{i^{th}}))}{Q_{i^{th}}} \tag{3.1}$$

Where the $LOCi^{th}$ is the Levelized Cost of the i^{th} product of interest [€/kg or €/m^3 (according to the units in which the product quantity is expressed)], $capEX$ are the depreciated capital costs of each unit/technology within the treatment chain [€/year], $opEX$ are the operating costs of each unit [€/year], REV is the revenue of each technology [€/year] and $Q_{i^{th}}$ is the annual quantity of the product of interest produced [kg/year or m^3/year]. The last main parameter is the Brine Treatment Specific Cost defined as:

$$BTSC = \frac{\sum_{units} capEX + \sum_{units} opEX}{Q_{Brine\ feed}} \tag{3.2}$$

Where the $BTSC$ is the Brine Treatment Specific Cost [€/m^3 of brine fed] and $Q_{Brine\ feed}$ is the annual brine fed to the treatment chain [m^3/year].

3.3. Bench test experiment required for model validation assumptions

3.3.1. Nano-Filtration (NF)

Due to the availability of reliable information concerning Nanofiltration at an industrial scale on one side and the complexity of performing bench-scale tests on the other side, model equations were validated with literature information.

3.3.2. Magnesium/calcium hydroxide crystallizer (MF-PFR)

Three different experiments were performed using three different concentrations of the inlet brine. Artificial brines were prepared in order to mimic the retentate produced by NF, which was fed by three different spent brines in terms of total dissolved solids (TDS). Brine solutions were prepared by dissolving the following salts: $NaHCO_3$ (Natural products, purity 99%), $CaCl_2 2(H_2O)$ (Ciech, purity 99%), Na_2SO_4 (Fluka, purity 99%), $MgCl_2 6(H2O)$ (purity 99%) and KCl (Honeywell Fluka, purity 99%), while the alkaline solution was made dissolving micro-pellet of NaOH (Inovyn, high-grade purity 99%) into the deionized water.

Mean compositions of the three brines and alkaline solution are reported in Table 3-2.

***Table 3-2**. Main composition of inlet brine and alkaline solution*

<table>
<tr><th colspan="9">Inlet Brine</th><th colspan="4">Alkaline solution</th></tr>
<tr><th rowspan="3">Test</th><th colspan="7" rowspan="2">Composition
[g/l]</th><th rowspan="3">Volume
[l]</th><th colspan="2">Composition
[mol/l]</th><th colspan="2">Volume
[l]</th></tr>
<tr><th>Mg Step</th><th>Ca Step</th><th rowspan="2">Mg Step</th><th rowspan="2">Ca Step</th></tr>
<tr><th>Na^+</th><th>K^+</th><th>Mg^{2+}</th><th>Ca^{2+}</th><th>Cl^-</th><th>SO_4^{2-}</th><th>HCO_3^-</th><th>NaOH</th><th>NaOH</th></tr>
<tr><td>A</td><td>9.67</td><td>0.55</td><td>1.87</td><td>14.77</td><td>46.75</td><td>0.16</td><td>0.43</td><td rowspan="3">200</td><td rowspan="3">0.5</td><td rowspan="3">2</td><td colspan="2" rowspan="3">200</td></tr>
<tr><td>B</td><td>8.96</td><td>0.54</td><td>1.74</td><td>13.39</td><td>42.71</td><td>0.43</td><td>0.11</td></tr>
<tr><td>C</td><td>10.74</td><td>0.73</td><td>2.44</td><td>16.84</td><td>53.70</td><td>0.65</td><td>0.17</td></tr>
</table>

Analysis of system stability in terms of reaction pH and flow rates

Firstly, the stability of MF-PFR was tested. For the sake of brevity, the trend of the operative conditions for test B is reported in Figure 3-4a for the precipitation of magnesium hydroxide and in Figure 3-4b for the precipitation of calcium hydroxide.

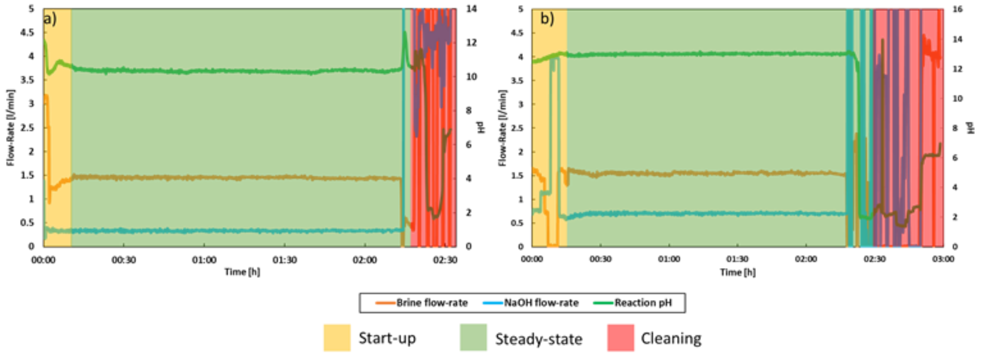


Figure 3-4. *Variation of the outlet pH and both inlet flow rates over the experimental time a) Precipitation of the magnesium hydroxide, and b) precipitation of the calcium hydroxide*

As shown in Figure 3-4, the reaction pH and both flow rates are stable when the MF-PFR reached the steady-state condition. The stability of both flow rates and pH throughout the experiment may be subjected to change as a result of the variation of some operating parameters. One of these is the pressure drop. A variation of pressure drop could lead to the reduction/increase of the flow rate. As an example, the variation of the NaOH solution flow rate may lead to an increase of the reaction pH, causing the precipitation of calcium as calcium hydroxide affecting the purity of the recovered magnesium hydroxide. Overall, the fine control of the reaction pH allowed to recover magnesium and calcium as hydroxides by means of fractionated precipitation.

Operative conditions of each experiment for the recovery of $Mg(OH)_{2(s)}$ and $Ca(OH)_{2(s)}$ are reported in Table 3-3 and Table 3-4, respectively.

Table 3-3. *Operative conditions for the recovery of* $Mg(OH)_{2(s)}$

Tests	pH	Operative Condition of system		Worked Hours [h]
		Brine Flow Rate [l/min]	NaOH Flow Rate [l/min]	
A	10.3	1.71	0.44	2.0
B	10.35	1.46	0.33	2.5
C	10.4	1.0	0.38	3.5

Table 3-4. *Operative conditions for the recovery of* $Ca(OH)_{2(s)}$

Tests	pH	Operative Condition of system		Worked Hours [h]
		Brine Flow Rate [l/min]	NaOH Flow Rate [l/min]	
A	13.0	1.62	0.78	2
B	13.0	1.57	0.7	3
C	13.0	1.05	0.6	3.5

Performance of the reactive precipitation processes

To evaluate the quality of the recovered crystals, i.e. $Mg(OH)_{2(s)}$ and $Ca(OH)_{2(s)}$, the samples were analysed to evaluate the reaction performance parameters.

Magnesium hydroxide precipitation step

In Figure 3-5, the purity and conversion are reported and supported by magma density and magnesium/calcium concentration in the inlet brines.

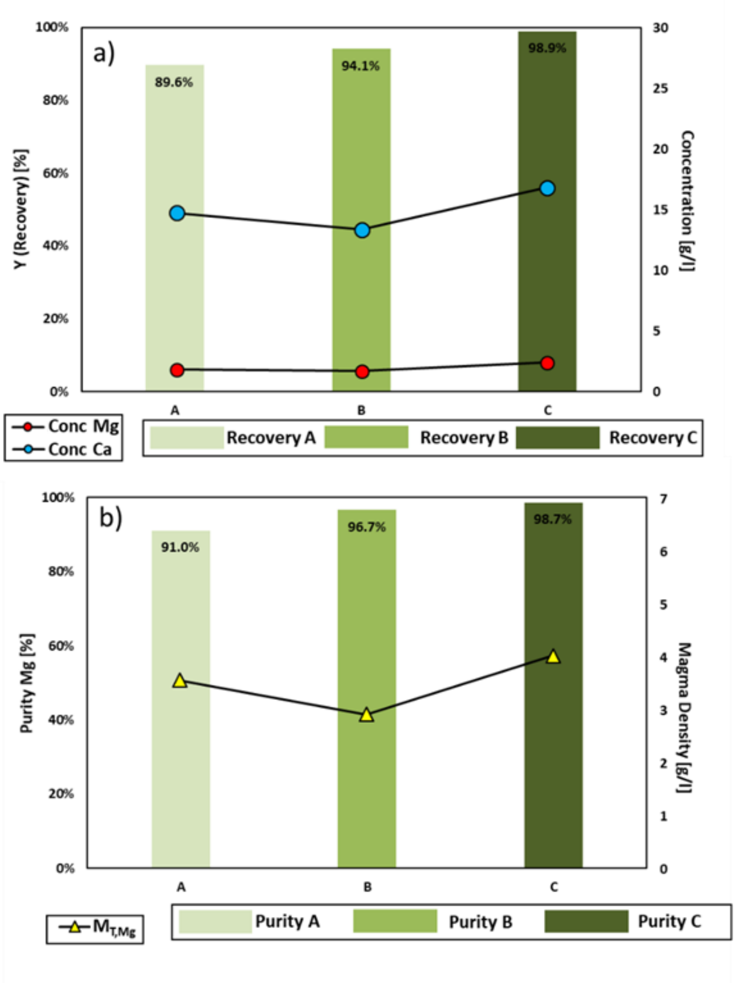


Figure 3-5*. a) Ca and Mg recovery efficiency, b) Purity of $Ca(OH)_{2(s)}$ solids, accompanied by magnesium and calcium concentration in the feed brine; and magma density*

Regarding the purity of the produced magnesium hydroxide (see Figure 3-5), the IC analyses highlighted that only Mg and Ca are present in the $Mg(OH)_{2(s)}$ precipitate, although the pH was kept below 10.5 to avoid the precipitation of calcium as calcium hydroxide. Nevertheless, calcium affected the purity of the produced crystals. The purity increases from 91% (test A) up to 98.7% (test B). The precipitation of calcium in form of calcium carbonate during the reactive precipitation step of magnesium hydroxide was due to the presence of bicarbonate (HCO_3^-) in the feed brines. With reference to the bicarbonate ions, they are involved in chemical equilibrium reactions (Coto et al., 2012), as in Eq. 2.3 - 2.6:

$$CO_{2(g)} \Leftrightarrow CO_{2(l)} \qquad (2.3)$$

$$CO_{2(l)} + H_2O \Leftrightarrow H_2CO_3 \quad (2.4)$$

$$H_2CO_3 \Leftrightarrow HCO_3^- + H^+ \quad (2.5)$$

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+ \quad (2.6)$$

When the pH increased up to about 10.4, all chemical equilibriums were shifted in order to convert CO_2 dissolved and bicarbonate ions into carbonates, which were the most stable form in the brine.

In order to better understand the presence of the $CaCO_3$ in the precipitated $Mg(OH)_{2(s)}$ and taking into account all chemical equilibriums involved during the precipitation, a numerical simulation was carried out via the MEDUSA software (Jansson, 2016), along with the hydro-chemical equilibrium-constant database (HYDRA). The main inputs required by the software are: (i) concentration of the cations and anions in the brine and (ii) temperature at which the magnesium precipitation occurs.

Figure 3-6 shows the results of the simulation carried out with the Medusa software for case B.

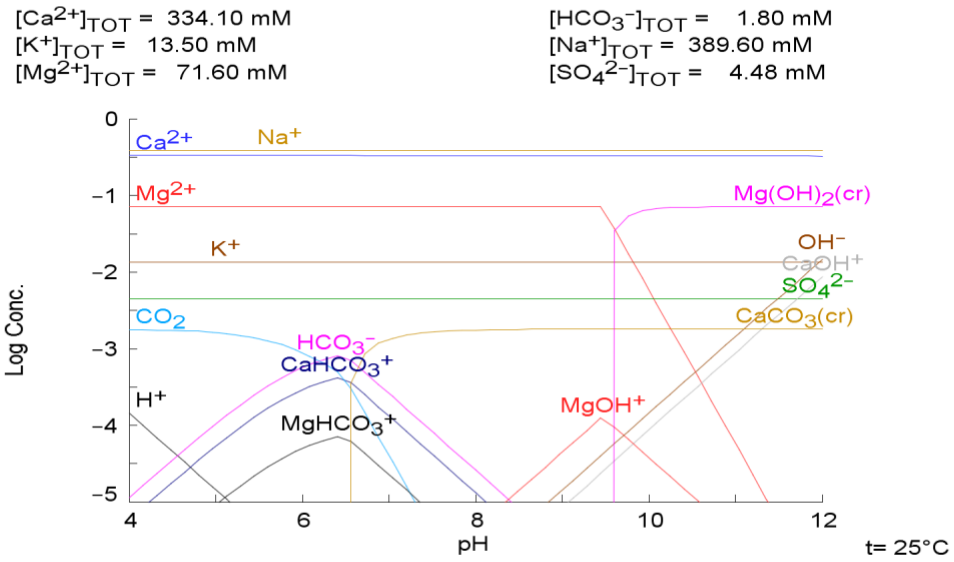


***Figure 3-6**. pH versus log concentration plot for the case A at 25°C, fixing the [Na+]=0.389M (8.96 g/l),[k+]=0.0135M (0.54 g/l) [Mg2+]=0.072M (1.74 g/l), [Ca2+]=0.334M (13.39g/l), [HCO_3^-]= 0.0018M (0.110 g/l) and [SO_4^{2-}]=0.00448 (0.43g/l).*

As seen in Figure 3-6, the Medusa software predicts the precipitation of the magnesium, which starts at pH 9.5 and ends around pH 11. This latter value is higher than the one measured during the laboratory precipitation test (final pH of total magnesium recovery equal to 10.4 Figure 3-6), due to the complexity of the brine composition that could affect the solubility of magnesium hydroxide. Moreover, the software predicts the co-precipitation of the calcium in the form of calcium carbonate.

As shown in Figure 3-6, the pH value of the tested brines, case B, was equal to 10.35. It is worth noting that the Medusa software predicted the variation of the amount of precipitated magnesium as a function of the pH. In fact, the recovery predicted by the software was 97.7% with a purity equal to 96.0%, while the experimental ones were 94.1% and 96.7%, respectively.

It is worth noting that the purity of the precipitate $Mg(OH)_{2(s)}$ depends on the amount of the recovered magnesium, as well as the bicarbonate concentration in the inlet brine. Indeed, looking at tests A and

B, which have similar magnesium concentration. The purity of the produced $Mg(OH)_{2(s)}$ increases from 91% (test A), up to 97% (test B), due to the reduction of the bicarbonate concentration along with the increase of magnesium recovery.

As regards the recovery of magnesium, it ranged from about 90% (test A) up to almost 99% (test C) implying partial recovery.

As said previously, the recovery of the magnesium is affected by the value of the pH. Indeed, the lower recovery is obtained due to the outlet pH equal to 10.3, while the higher value of the recovery is obtained at pH equal to 10.4.

Calcium hydroxide precipitation step

After the first precipitation step, the produced slurry was stored in a settling tank T4 in order to settle the precipitated crystals. After that, the crystals were ready for filtration, while the clarified brine was collected in an intermediate storage tank, and then re-sent into the MF-PFR for the calcium recovery.

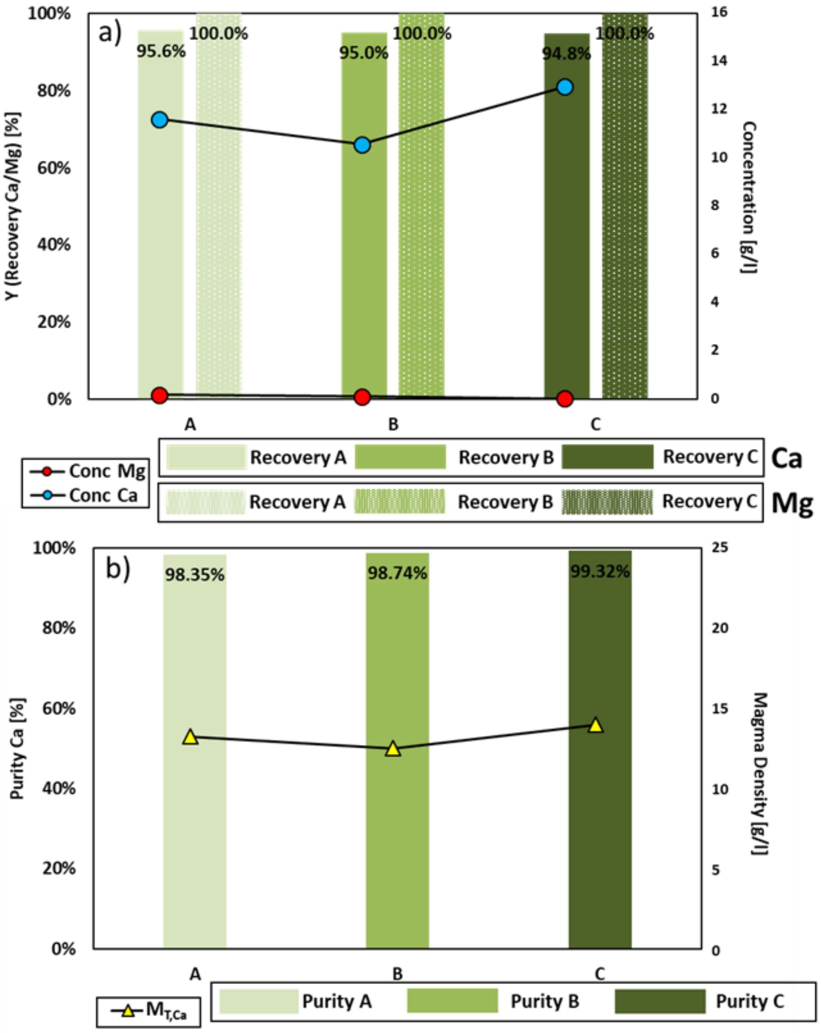


Figure 3-7. *a) Ca and Mg recovery efficiency, b) Purity of $Ca(OH)_{2(s)}$ solids, accompanied by magnesium and calcium concentration in the feed brine; and magma density*

In Figure 3-7, purity, conversion of magnesium and calcium are reported, supported by magnesium and calcium concentration in the feed brine and magma density of the calcium hydroxide for the second precipitation step.

The purity of the produced $Ca(OH)_2(s)$ was determined by the same procedure described above. The IC analyses highlighted that only Mg and Ca are present in the $Ca(OH)_2(s)$ precipitate. As reported, the purity of the $Ca(OH)_2(s)$ increases from about 98%, (test A), up to almost 99% (test C) because the magnesium concentration in the interstage brine decreases from 155 mg/l (test A) down to about 2 mg/l (test C).

As regards the recovery of calcium, it ranged from about 96% (test A) down to 95% (test C). Nevertheless, the outlet pH was kept equal to 13, which allows the complete precipitation of calcium. However, tested brines required a reaction pH higher than 13 due to the high calcium concentration in the inlet brine. Moreover, the recovery of magnesium was equal to 100% in all tests.

3.3.3. Multiple Effect Distillation (MED)

Please refer to Section 2.2.4.

3.3.4. Sodium Chloride (NaCl) crystallizer

Due to the availability of reliable information concerning Nanofiltration at an industrial scale on one side and the complexity of performing bench-scale tests on the other side, model equations were validated with literature information.

3.4. Simulation campaign

3.4.1. Description of case study analysis

The techno-economic analysis of the Italian case study was essentially split into two parts:

(i) a **technical sensitivity analysis** to investigate the influence of specific parameters (i.e. NF membrane rejections) on the characteristics of a final valuable selling product;

(ii) a **parametric economic analysis** seeking to identify the main contributors to the global economic feasibility of the chain.

3.4.2. Sensitivity analysis of the technical operating parameters

For the technical analysis (and also for the economic analysis) the brine composition reported in Table 3-1 was considered and an inlet brine flow rate equal to 95 m^3/h was fixed (50% of the total brine produced by 3 of the 4 operating RO units of the SWRO plant). As for the NF plant, a number of pressure vessels were positioned in series to reach a certain ions concentration target and in parallel to reach a certain permeate recovery. Each pressure vessel contained 6 spiral-wound elements. Operating conditions of the NF plant were (i) permeate recovery equal to 60% and (ii) operating pressure of 20 bar. As far as the membrane ion rejections were concerned, a detailed analysis of existing works in the literature concerning NF rejections was carried out. It was discovered that mainly the commercial membrane NF270 (Filmtec) has been employed till now to treat desalination brines. Taking into account the several set of rejections reported in the literature at similar operating conditions and similar brine compositions (i.e. (Ali, 2021; Mitko et al., 2020b; Pérez-González et al., 2015), an average value for each ion was considered for this particular case study. The set of rejections is reported in Table 3-5:

Table 3-5. *Set of ion rejections of the NF membrane (operating conditions: Permeate recovery = 60%; Pressure = 20 bar)*

Ionic Species	Na^+	Ca^{2+}	Mg^{2+}	K^+	Cl^-	SO_4^{2-}	HCO_3^-
Membrane rejection [%]	6	50	71	5	12	91	45

However, as can be observed in Table 3-5, the membrane does not present high membrane rejections for calcium and magnesium. Only 50% of calcium would be rejected, causing a severe negative impact on the remaining chain for two reasons: (i) only 50% of calcium is recovered as calcium hydroxide (less total revenue) and (ii) 50% of calcium that enriches the permeate is more likely to incite scaling formation within the MED unit and reduce the purity of the final NaCl product. The same considerations are applicable to magnesium too. In order to produce NaCl at food grade, it is essential to reach a final purity of at least 97% (according to (Codex Alimentarius Commission, 2006). Therefore, a technical analysis of the influence of NF ions rejections on the NaCl purity was carried out, consisting firstly in the introduction of two correction factors: α and β. Rejections of Mg^{2+}, Ca^{2+} and SO_4^{2-} (which present a similar dimension and behaviour) were corrected by α. As for HCO_3^- and Cl^-, β was employed. Meanwhile, the rejections of Na^+ and K^+ (which usually vary little at different operating conditions) were considered to be constant. Equations (2.7) and (2.8) describe how the bivalent and monovalent ions vary with α and β, respectively:

$$R_{ith}^{NEW} = R_{ith}^{\circ} + \alpha * (1 - R_{ith}^{\circ}) \tag{2.7}$$

$$R_{jth}^{NEW} = R_{jth}^{\circ} + \beta * (1 - R_{jth}^{\circ}) \tag{2.8}$$

Where ith and jth refer to the generic bivalent ion (Mg^{2+}, Ca^{2+} and SO_4^{2-}) and monovalent ion (Cl^- and HCO_3^-), respectively. R° and R^{NEW} are the initial rejection value (reported in Table 3-5) and the updated rejection value. α and β are the correction factors for the bivalent and monovalent ions, respectively.

The technical analysis consisted in varying the value α within a range of 0 to 1 at fixed intervals of 0.1. When α is equal to 0, R^{NEW}=R°, meanwhile for α equal to 1, R^{NEW} = 100%. On the other hand, for each fixed value of α, β was calculated in order to ensure electroneutrality of the solution (NF permeate and NF retentate). Results of the analysis are reported in Figure 3-8.

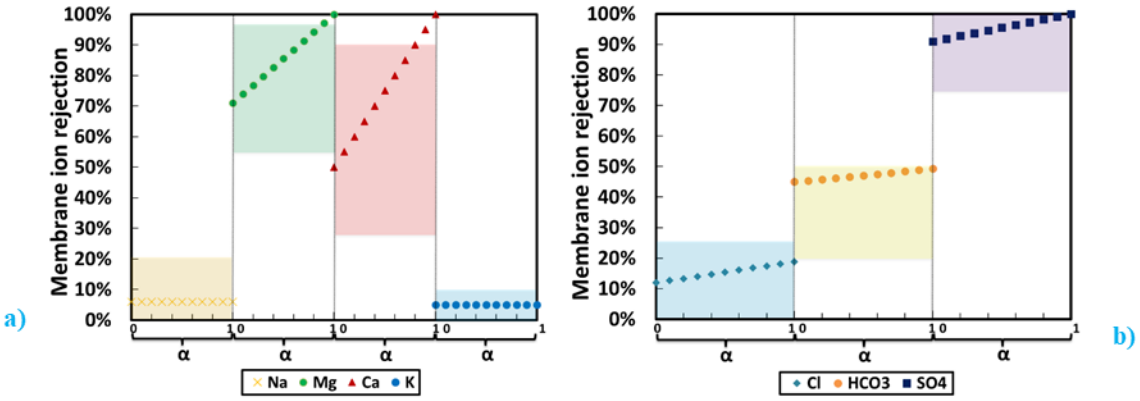


Figure 3-8. *a) Trend of membrane rejection of cations with α (ranging from 0 to 1); b) Trend of membrane rejection of anions with α (ranging from 0 to 1)*

Furthermore, Figure 3-8 depict the ranges within which each ion rejection can vary based on real NF membranes that have been tested and employed in the past for seawater brines (i.e (Pérez-González et al., 2015), Mitko et al., 2020a and Ali, 2021). As can be observed, values of α higher than 0.8 produce unrealistic sets of rejection with single ion rejections that are out of the so-called realistic range. α= 0.8 is considered to be a critical scenario whereas 0.7 is an optimal value.

However, the main aim of the analysis was to identify the minimum value of the correction factor α that guarantees a minimum NaCl purity of 97% to be sold as a food-grade product. Therefore, PHREEQC software was used to assess the purity of NaCl produced at different NaCl recoveries. Reasons for using PHREEQC lie within its reliability demonstrated for such purposes in literature (Macedonio et al., 2013). For the simulations, considering the MED and NTC as a single unit, MED inlet concentrations were required as inputs. Since the latter are given by mixing of the NF permeate and MRC, all parameters of the MRC (geometrical and operating conditions) were fixed in order to not influence whatsoever the analyses based on different values of α. In particular, typical experimental values were fixed for the concentration of NaOH (1 mol/L) and for the conversion factors of Mg^{2+} (95%) and Ca^{2+} (97%) for the first and second stage, respectively. These conditions are not varied for the economic analysis. Along with the concentrations given as inputs in PHREEQC, the quantity of water (to evaporate) was fixed. It was fixed accordingly to ensure a certain recovery of NaCl. Subsequently, based on the products precipitated, the purity of NaCl produced was calculated.

As previously mentioned, for each value of α, the purity was evaluated at three different values of NaCl recovery: 30%, 50% and 75%. Results are depicted in Figure 3-9.

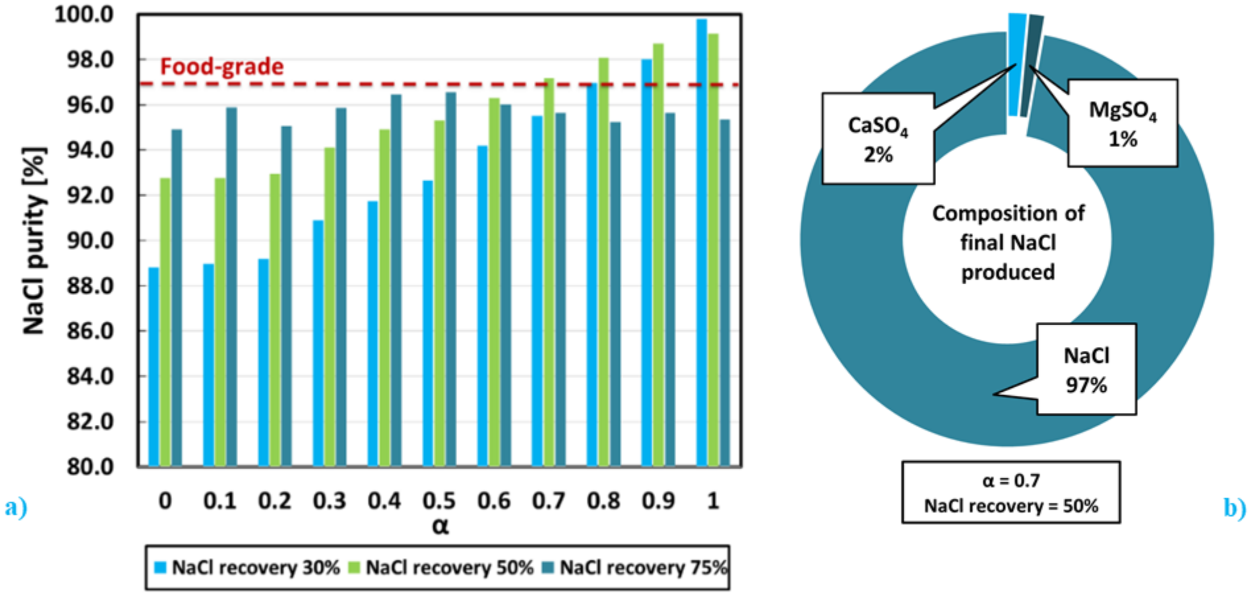


***Figure 3-9**. a) Trend of purity of NaCl produced at different values of α and NaCl recovery; b) Composition of the final NaCl produced at food-grade obtained with α=0.7 and NaCl recovery = 50%*

Results illustrated in Figure 3-9 show how purity increased with α at low recoveries (30%) of NaCl. This was mainly due to the fact that greater quantities of magnesium and calcium were rejected by the NF membrane and subsequently recovered as hydroxides in the MRC. This, therefore, led to minor quantities that could precipitate and compromise the purity of the final selling product. A similar trend could be observed for a NaCl recovery of 50%. However, the increase of purity in this specific case presented a reduced slope. The reason for this is that when attempting to recover more NaCl (evaporating more water), more impurities tend to precipitate. As a matter of fact, very high NaCl recoveries (75%) did not rather lead to a net increase of purity with α but tended to fluctuate around an average value. It is also interesting to see that this value was always lower than 97%, therefore unsuitable for the food-grade target. The target, on the other hand, was possible to reach a NaCl recovery of 50% and α equal to 0.7. As mentioned earlier, 0.7 is still an acceptable value that allows operating within a realistic range of NF membrane ion rejections. Finally, taking into account these suitable conditions, Figure 3-9 represents the percentage of the impurities of the final NaCl product. Precisely, the main compounds that precipitate with NaCl are $CaSO_4$ and $MgSO_4$ that represent 2% and 1% of the total solid product, respectively.

3.4.3. Sensitivity analysis of process profitability performances

To evaluate the economic feasibility of the proposed MLD system an economic analysis was performed. For such analysis, the specific costs of chemicals and energetic sources reported in Table 3-6 were employed.

Table 3-6. *Specific costs of chemicals and energetic sources employed in the economic analysis*

Specific Cost*		
$Mg(OH)_2$	996	€/ton (Micari et al., 2020)
$Ca(OH)_2$	125	€/ton (Intratec, 2021a)
Water	0.83	€/m3 (Micari et al., 2020)
NaOH	332	€/ton (Intratec, 2021b)
HCl	125	€/ton (Culcasi et al., 2019)
NaCl	66	€/ton (Panagopoulos, 2020)
Electricity	0.2	€/kWh **
Waste Heat	0.0083	€/kWh (Micari, Moser, et al., 2019)

**All specific costs were converted in € considering a currency conversion factor April 2021 equal to 0.83€/$*
***The specific cost of electricity is the typical value of Pantelleria, Italy*

In particular, typical electricity and waste heat costs of Pantelleria were employed. Furthermore, waste heat was used for the analysis since at the moment renewable energy still suffers from high capital costs.

For the economic analysis of the entire chain, it was necessary to fix also the operating conditions of the technologies that were not taken into account in detail in the technical analysis. As far as the MED is considered, 10 effects were considered operating at a TBT (Top Brine Temperature) of 110°C. This temperature was chosen to prevent potential scaling phenomena that could occur. The NTC, on the other hand, presented 5 effects at a maximum operating temperature of 100°C. Both the MED and NTC employed waste heat (supplied from flue gases produced in a nearby power plant). This allowed to reduce operating costs for the energy-intensive technologies of the chain such as MED and NTC. As can be observed in Figure 3-10, MED consumes more than double the amount of heat when compared to the NTC. Moreover, it is worth noting how the specific electric consumption of the MRC is the highest. This is due to the Drum filter employed for the recovery of hydroxide solids from the produced slurry.

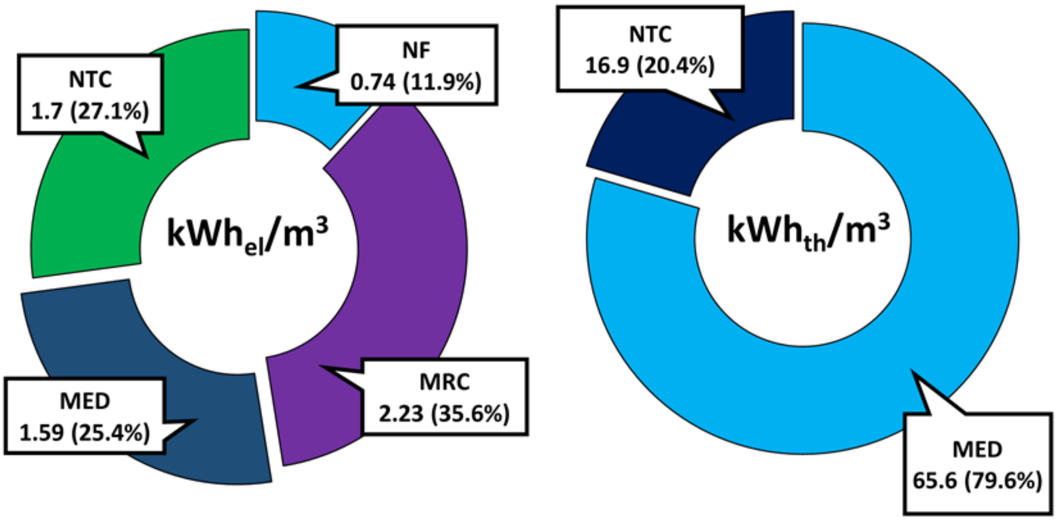


Figure 3-10. Distribution of the electrical and thermal energy consumption per m³ of intake brine in the MLD system

Energy consumption is just one of the several factors that contribute to the treatment chain's total cost. Results of the global economics of the entire MLD system can be observed in Figure 3-11.

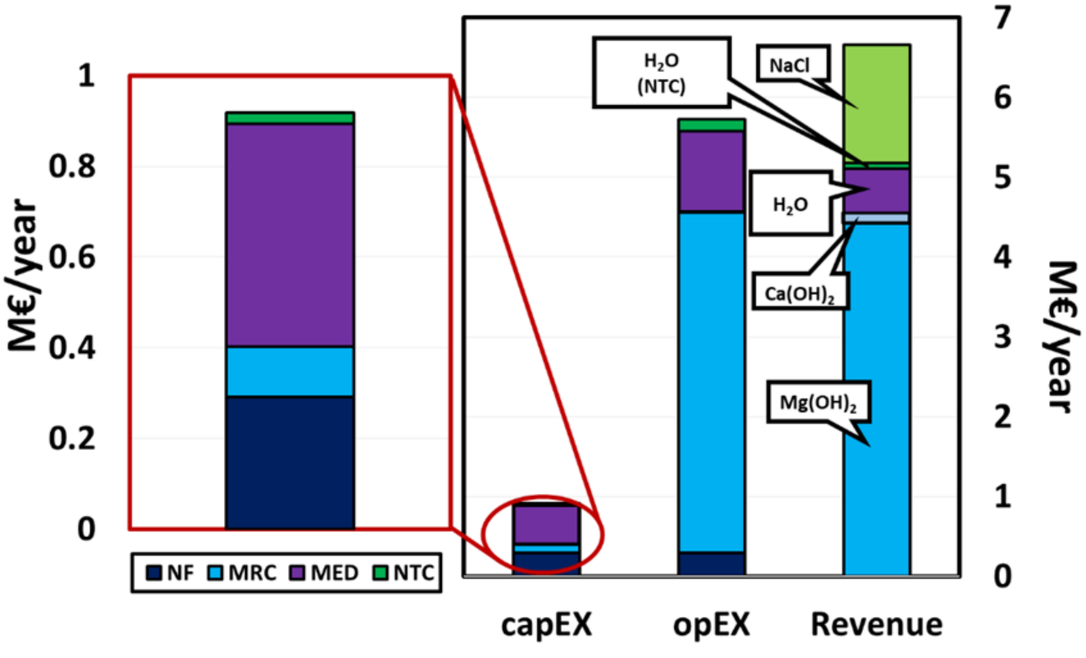


Figure 3-11. Global economics of the proposed MLD system expressed in million (M) euros per year

In Figure 3-11 it is possible to see how capital costs are much less than the operating costs. NF and MED contribute to the majority of the capital costs: NF for its membranes and MED for its multiple effects with its several heat exchangers. As for the operating costs, it is the MRC that leads to overall high operating costs. This is mainly due to the use of large amounts of expensive alkaline reactants (i.e. NaOH) followed by the use of chemicals (HCl water solution) for the final neutralization step. As can be expected, another major contributor was the MED. However, regardless of the high overall costs, the total revenue achieved is higher than the capEXs and opEXs of the MLD system. Revenues are so high thanks to the high selling price of $Mg(OH)_2$ followed by the large amounts of NaCl produced. The matter of having revenues higher than the sum of capital and operating costs led to lower Levelized Costs of the valuable products obtained from the chain. Figure 3-12 illustrates all Levelized costs. From Figure 3-12 it is possible to observe that the Levelized cost of salt (LCOS) is equal to the typical market price (i.e. 66 €/ton) making the treatment chain still a competitive integrated technology for the production of salt. All other Levelized Costs are slightly lower than their respective market price.

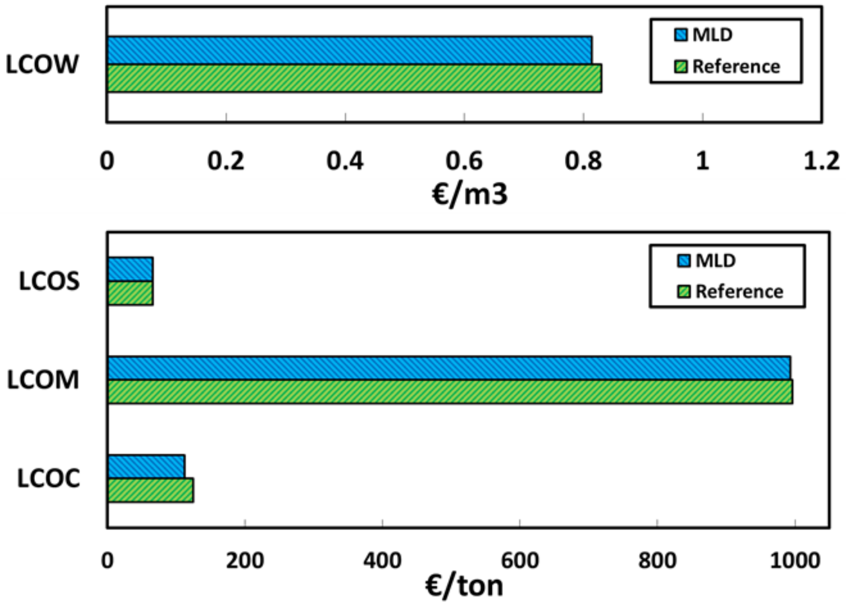


Figure 3-12. *Levelized costs of valuable products (LCOW = Levelized Cost of Water; LCOS = Levelized Cost of Salt; LCOM = Levelized Cost of $Mg(OH)_2$; LCOC = Levelized Cost of $Ca(OH)_2$) compared to their actual market prices*

Furthermore, the economic feasibility of the entire chain was evaluated by means of the BTSC factor (defined in Section 2.4). Figure 3-13 compares the proposed MLD system with the conventional brine disposal methods. When taking into account only capital and operating costs (Figure 3-13a)), the chain is much less convenient than the already existing brine treatment methods. More precisely, the BTSC factor is equal to 8.49 €/m^3 (much higher than the 4.65 €/m^3 required with evaporation ponds). However, when the sale of all the valuable goods produced by the integrated chain is taken into consideration, the brine treatment specific cost BTSC is much lower than the one of all other methods (Figure 3-13b)). In particular, the BTSC (= -0.01 €/m^3) assumes a negative value. This is due to the fact that the sum of capEXs and opEXs of the treatment chain is to some extent lower than the overall revenue achieved. Having a BTSC factor generally lower than the conventional brine disposal costs can be translated into dealing with an admirable market-competitive technology.

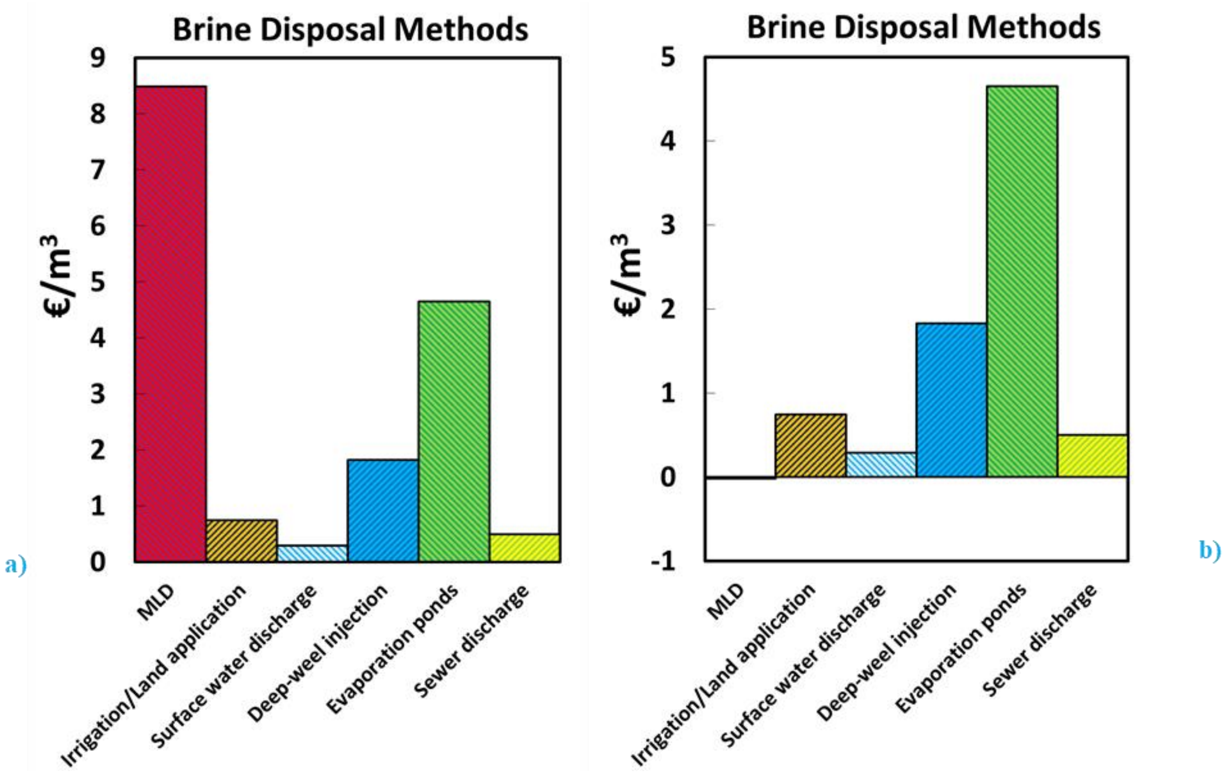


Figure 3-13. *a) Comparison between conventional methods costs and BTSC of proposed MLD without revenue; b) Comparison between conventional methods costs and BTSC of proposed MLD with revenue*

The overall techno-economic analysis has shown and demonstrated the economic feasibility of the MLD system, applied as a hybrid technology to promote brine volume minimization, mineral recovery and water production.

3.5. Final discussion and overview of implementation potentials

3.5.1. Global data on brine availability

Sicily is one of the main Italian regions in which fresh water scarcity is a severe issue, especially in the minor islands. It is in such islands (Lampedusa, Linosa, Pantelleria, Ustica, Lipari and Vulcano) that the only solution to overcome water scarcity is by means of seawater desalination. Nowadays, most minor Sicilian islands produce fresh water from Reverse Osmosis plants. On the main island of Sicily, however, there are a few MED industrial plants that provide water within the major industrial areas of the island (Milazzo and Priolo Gargallo). The distribution of the seawater RO and MED plants in the Sicilian region is shown in Figure 3-14.

If the volumes of brine produced by all SWRO and MED plants present in Sicily were to be considered, a total of 65,277 m^3 of brine would be produced every day. This means that the proposed MLD system could be potentially employed due to the large availability of brine.

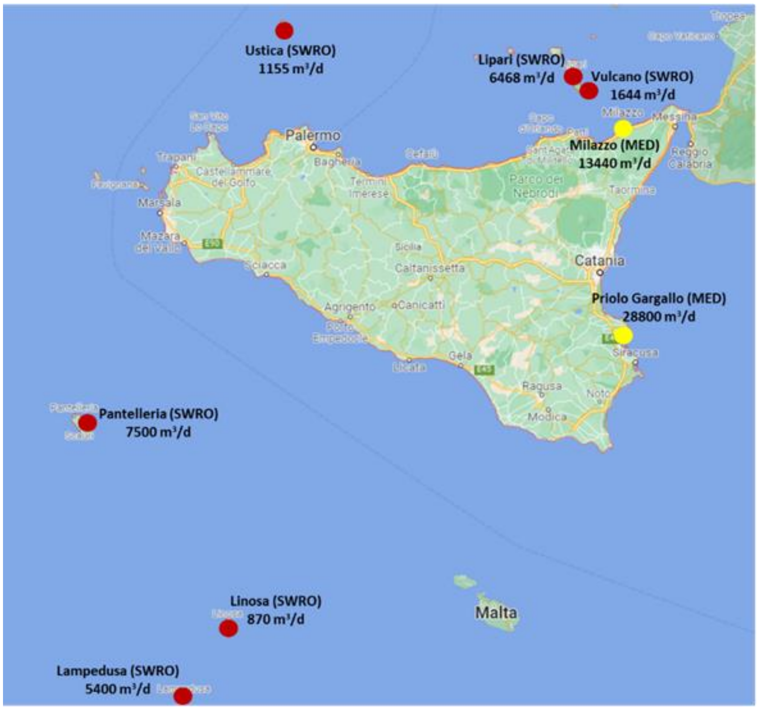

Ustica (SWRO)
1155 m³/d
Lipari (SWRO)
6468 m³/d
Vulcano (SWRO)
1644 m³/d
Milazzo (MED)
13440 m³/d
Palermo
Catania
Priolo Gargallo (MED)
28800 m³/d
Pantelleria (SWRO)
7500 m³/d
Linosa (SWRO)
870 m³/d
Malta
Lampedusa (SWRO)
5400 m³/d

***Figure 3-14**. Distribution of SWRO (red point) and MED (yellow point) plants in Sicily with their respective daily volume of brine discharged (Regione Siciliana, 2019)(ISAB Energy, n.d.)*

3.5.2. Estimated economic potentials

Results of the techno-economic analysis of the Italian Case Study have widely demonstrated the economic feasibility of the proposed MLD chain. Such feasibility is exclusively possible thanks to the sale of valuable goods such as $Mg(OH)_2$ and NaCl (products that mainly contribute to the total revenue of the chain). In particular, taking into account the magnesium present in the total amount of brine produced in Sicily, it is possible to produce around 90,000 tons/yr of $Mg(OH)_2$. As for NaCl, the amount produced from the total amount of brine is around 712,000 tons/yr. Considering the specific costs of $Mg(OH)_2$ and NaCl reported in Table 3-4. Operative conditions for the recovery of $Ca(OH)_{2(s)}$, it is possible to achieve revenues as high as 90 million €/yr and 47 million €/yr, respectively. Results of the techno-economic analysis have demonstrated that the MLD system in question can be a useful alternative integrated technology contemporarily for the production of valuable goods and for brine disposal. As a matter of fact, it was shown that the Brine Treatment Specific Cost (BTSC) was much lower than the cost concerning conventional brine disposal methods, making the MLD system an extremely better alternative for brine treatment.

4. Polish Replication Case Study

4.1. Presentation of the case study

One of the industries that may benefit from the implementation of membrane-based technologies is coal mining. Despite the fact that coal mining is being phased out in favor of alternative, cleaner sources of energy, it is still very important for the metallurgical industry. Coking coal is considered to be a critical raw material by the European Union. Deep mining of hard coal generates the problem of saline waste water, as the mines need constant dewatering. Mine water discharges have an important influence on surface water quality and quantity.

The utilization of coal mine waters bears the promise of recovering valuable raw materials: demineralized water, sodium chloride, magnesium hydroxide, calcium sulphate, boron, and other chemicals present in the discharge. The recovery of raw materials does not only mitigate the environmental problems caused by the coal mine water discharge, but it can also generate new sources of profit for the coal mining industry. So far in Poland, there is one salt production plant in operation, which produces salt evaporated from saline mine waters, “Dębieńsko”, located in Czerwionka-Leszczyny. In July 2015, this installation, previously owned by Zakład Odsalania Dębieńsko Sp. z o.o., was taken over by Przedsiębiorstwo Gospodarki Wodnej I Rekultywacji S.A. (PGWiR), which is a part of the Jastrzębska Spółka Węglowa (JSW) Group. The feed water for the plant comes from the “Budryk” mine, which is still in operation. Chemical treatment is not used. Two kinds of “Budryk” waters are used: brackish one (TDS of 30.8 kg/m^3) and saline one (TDS of 72.7 kg/m^3). The brackish Budryk water is pre-concentrated by reverse osmosis (RO); the RO retentate is mixed with the saline Budryk water and fed to a vapor compression (VC) evaporator, where it’s concentrated to approximately 290 g/dm^3 as NaCl. In order to improve the salt economy, low-quality rock salt is added to the RO retentate. The energy consumption of VC is 44 kWh/m^3 of condensate. The brine is directed to the VC evaporative crystallization, which has an energy consumption of 66 kWh/m^3 of condensate. See Figure 4-1 for the overall scheme of treatment technology (pretreatment not included).

The chief concern of PGWiR is the energy consumption. The current technology consumes 713 kWh of electric energy per 1 t of salt produced. According to the PGWiR executives, at the current energy prices, they are still managing to break even, but a substantial increase in energy price will kill their business model. That is why the company needs new, less energy-intensive salt recovery technologies, which makes ZERO BRINE a compelling solution.

The proposed ZERO BRINE technology consists of two-pass nanofiltration (NF) with intermediate recovery of gypsum and magnesium hydroxide, followed by concentration of NF permeate in a hybrid reverse osmosis (RO)-electrodialysis (ED) system. The ED concentrate can then be further concentrated with thermal methods, with the eventual recovery of evaporated salt. In this report, the focus has been put on testing if the application of ZERO BRINE technology will indeed improve the performance of the Dębieńsko plant in terms of energy consumption in kWh/t of produced salt. Two cases have been modelled: the application of the full ZERO BRINE technology (NF-RO-ED) or the application of NF part only as pre-treatment. PGWiR has confirmed its interest in ZERO BRINE replication by providing a Letter of Intent (see Annex B).

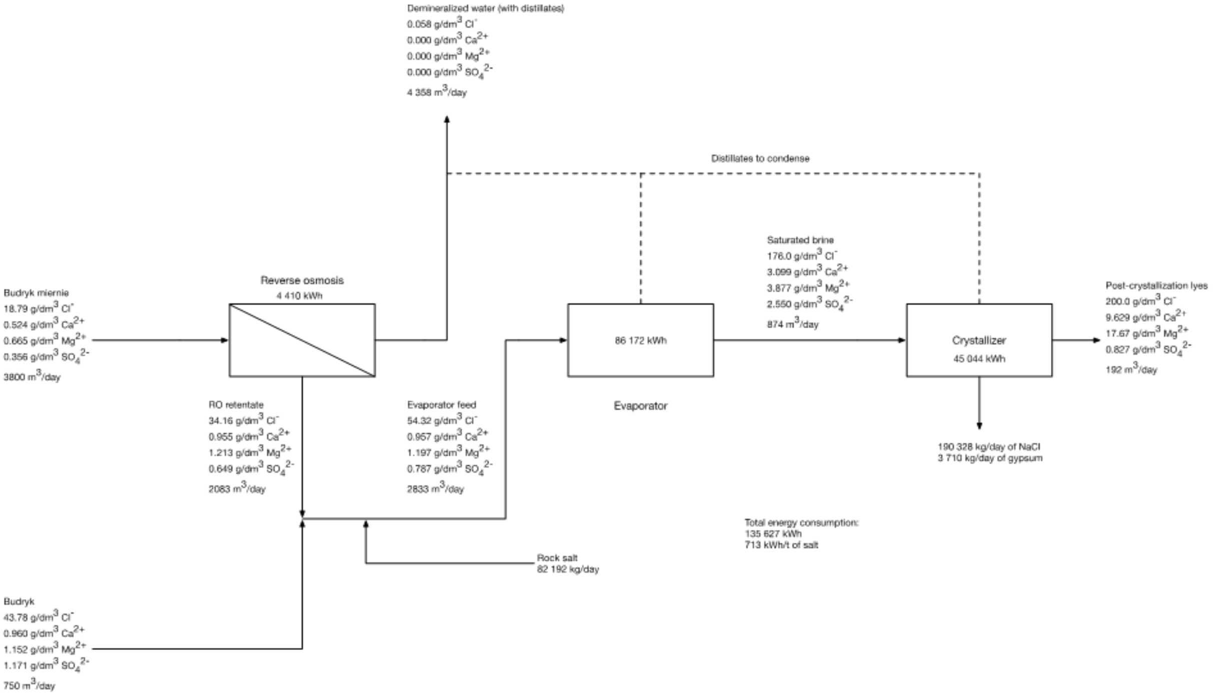

Demineralized water (with distillates)
0.058 g/dm^3 Cl$^-$
0.000 g/dm^3 Ca^{2+}
0.000 g/dm^3 Mg^{2+}
0.000 g/dm^3 SO$_4^{2-}$
4 358 m^3/day
Distillates to condense
Saturated brine
176.0 g/dm^3 Cl$^-$
3.099 g/dm^3 Ca^{2+}
3.877 g/dm^3 Mg^{2+}
2.550 g/dm^3 SO$_4^{2-}$
874 m^3/day
Budryk miernie
18.79 g/dm^3 Cl$^-$
0.524 g/dm^3 Ca^{2+}
0.665 g/dm^3 Mg^{2+}
0.356 g/dm^3 SO$_4^{2-}$
3800 m^3/day
Reverse osmosis
4 410 kWh
86 172 kWh
Evaporator
Crystallizer
45 044 kWh
Post-crystallization lyes
200.0 g/dm^3 Cl$^-$
9.629 g/dm^3 Ca^{2+}
17.67 g/dm^3 Mg^{2+}
0.827 g/dm^3 SO$_4^{2-}$
192 m^3/day
RO retentate
34.16 g/dm^3 Cl$^-$
0.955 g/dm^3 Ca^{2+}
1.213 g/dm^3 Mg^{2+}
0.649 g/dm^3 SO$_4^{2-}$
2083 m^3/day
Evaporator feed
54.32 g/dm^3 Cl$^-$
0.957 g/dm^3 Ca^{2+}
1.197 g/dm^3 Mg^{2+}
0.787 g/dm^3 SO$_4^{2-}$
2833 m^3/day
190 328 kg/day of NaCl
3 710 kg/day of gypsum
Total energy consumption:
135 627 kWh
713 kWh/t of salt
Rock salt
82 192 kg/day
Budryk
43.78 g/dm^3 Cl$^-$
0.960 g/dm^3 Ca^{2+}
1.152 g/dm^3 Mg^{2+}
1.171 g/dm^3 SO$_4^{2-}$
750 m^3/day

***Figure 4-1**. Current treatment train at Dębieńsko salt production plant*

4.2. Bench-scale tests

The nanofiltration of the Budryk water has already been tested in the literature (Turek, Laskowska, Mitko, Chorążewska, et al., 2018; Turek, Laskowska, Mitko, & Jakóbik-Kolon, 2018). Reverse osmosis of coal mine water is a well-established technology, already used by the PGWiR at the Dębieńsko site. Electrodialysis, however, required additional testing, so it became the main focus of experimental research in Task 8.2.3.

4.2.1. Electrodialytic concentration of model RO retentate

The electrodialytic concentration of model RO retentate was investigated in batch mode in a plate-and-frame MEGA EDR-Z module of effective membrane area of 64 cm^2, equipped with 10 pairs of Ralex CMH/AMH membranes and 0.8 mm thick spacers. The initial volume of diluate was 1000 cm^3, whereas the initial volume of concentrate was 100 cm^3. Both compartments were filled with a model solution of RO retentate, assuming the mixture of Budryk miernie was pretreated with NF as a RO feed. The linear flow velocity of both diluate and concentrate was 1 cm/s. Two experiments were conducted as follows: initially, the electrodialysis was performed in a constant-current mode (4.1 A = 640 A/m^2), until the maximum voltage of 20 V or 15 V was reached; after that, the experiment was continued in constant-voltage mode until the total charge passed through the electrodialyzer reached 3 Ah. During both experiments, the samples of diluate and concentrate were analyzed each 0.3 Ah of charge passed through the electrodialyzer. The collected samples were analyzed using Dionex ICS-5000 ion chromatograph. See Table 4-1 and Table 4-2 for the ionic compositions of diluate and concentrate during both experiments. The final volume of diluate/concentrate was 220 cm^3 and 880 cm^3, respectively, in both experiments. The results allowed to establish the ratios of molar fluxes of sodium, magnesium, sulfate ions to the molar flux of chlorides, which were then used in modelling the ED performance during the techno-economic assessment of the proposed ZERO BRINE replication.

Table 4-1. *Ionic composition of diluate and concentrate during the 20 V ED experiment on the model solution of RO retentate*

U [V]	I [A]	Q [Ah]	Diluate [mg/dm^3]					Concentrate [mg/dm^3]				
			Na^+	Cl^-	Mg^{2+}	Ca^{2+}	SO_4^{2-}	Na^+	Cl^-	Mg^{2+}	Ca^{2+}	SO_4^{2-}
0	0	0	20200	31300	44.2	82.4	14.6	19000	29000	50.2	63.6	< 10
20.0	4.1	0.3	18200	28200	39.7	74.4	15.3	34100	52300	70.7	149	13.6
17.0	4.1	0.6	16200	25100	36.1	64.0	16.9	46000	70800	70.3	199	13.2
16.1	4.1	0.9	14300	22200	31.6	54.1	17.1	53200	81100	62.3	229	12.7
15.7	4.1	1.2	12300	19000	26.8	45.4	17.1	61200	94100	70.7	258	13.6
16.6	4.1	1.5	10500	16300	22.5	37.4	17.3	65900	10100	74.8	229	15.0
18.1	4.1	1.8	8560	13200	18.7	30.5	15.7	70900	10900	76.6	236	16.7
20.0	3.9	2.1	6130	9440	13.4	21.8	13.3	71300	11000	75.0	232	18.7
20.0	3.2	2.4	4480	6850	< 10	15.9	11.5	77100	11900	73.7	237	20.6
20.0	2.2	2.7	2480	3750	< 10	< 10	< 10	77300	11900	70.0	233	22.9
20.0	1.2	3.0	910	1320	< 10	< 10	< 10	77200	11800	59.4	231	27.3

Table 4-2. *Ionic composition of diluate and concentrate during the 15 V ED experiment on the model solution of RO retentate*

U [V]	I [A]	Q [Ah]	Diluate [mg/dm^3]					Concentrate [mg/dm^3]				
			Na^+	Cl^-	Mg^{2+}	Ca^{2+}	SO_4^{2-}	Na^+	Cl^-	Mg^{2+}	Ca^{2+}	SO_4^{2-}
0.0	0.0	0.0	20400	31900	49.5	90.0	20.5	22500	34900	72.7	94.5	52.3
13.8	4.1	0.3	18300	28600	44.3	75.8	21.3	40400	62800	124	175	32.0
14.5	4.1	0.6	16100	25100	38.5	64.0	21.7	51000	79300	109	216	27.4
15.0	3.9	0.9	14200	22000	33.7	55.3	21.9	58500	90900	110	240	26.0
15.0	3.5	1.2	12100	18700	28.6	47.5	21.3	64600	100000	107	222	23.9
15.0	3.4	1.5	10200	15900	23.8	40.2	20.1	71300	111000	117	236	27.0
15.0	2.9	1.8	8340	12900	19.2	29.4	19.2	72600	112000	109	230	27.6
15.0	2.7	2.1	6660	10300	15.1	24.9	17.6	76600	119000	110	239	30.6
15.0	2.2	2.4	4000	6110	< 10	14.2	13.6	76600	119000	103	239	36.3
15.0	1.3	2.7	1860	2800	< 10	< 10	9.20	77700	121000	87.8	228	40.7
15.0	0.5	3.0	407	569	< 10	< 10	6.70	72000	112000	53.6	216	46.0

4.2.2. Water transport across the ion-exchange membranes

The amount of water that passes across the ion-exchange membranes during the electrodialysis limits the maximum salinity of ED concentrate. As such, the ratio of the number of moles of hydration water per number of moles is an important parameter for modelling the electrodialytic concentration of saline solutions. The water transport was investigated using plate-and-frame CS-0 electrodialyzer of effective membrane area of 172 cm^2, equipped with 4 pairs of Neosepta CMX/AMX and 0.75 mm intermembrane spacers. The diluate was pumped through the module in a single-pass mode, whereas the concentrate (initial volume of 200 cm^3) was recycled. The results are presented in Table 4-3. The average hydration number of sodium chloride was estimated as 13 for a current density of 300 A/m^2 and 11.2 for a current density of 500 A/m^2. Based on the estimated hydration numbers of sodium chloride, the maximum ED concentrate salinity was established as 241 g/dm^3 as NaCl (146 g/dm^3 as Cl^-) – see Figure 4-2- which is high enough for the implementation of ZERO BRINE technology at Dębieńsko site, especially with the rock salt being added. Additionally, the addition of rock salt significantly decreases the energy consumption, as less salt has to be transported across the ion-exchange membranes in the electrodialysis step.

***Table 4-3**. Results of hydration number determination. i - current density, u - linear flow velocity, Q - charge passed through the electrodialyzer, V - volume, C – concentration*

			Concentrate				Diluate		
i [A/m^2]	u [cm/s]	Q [Ah]	V [cm^3]		C [g/dm^3]		C [g/dm^3]		Hydration number [mol/mol]
			initial	final	initial	final	initial	final	
300	0.6	10.32	200	276	274	254	62.3	57.8	15.2
300	0.6	10.32	200	280	265	254	62.3	57.8	13.1
300	3.2	18.92	200	336	259	244	62.3	59.3	13.4
300	3.1	13.76	200	300	239	235	60.8	59.3	13.1
300	3.2	20.64	200	352	219	225	63.7	59.3	12.7
300	3.8	10.32	200	277	231	229	59.3	56.3	13.2
300	3.8	20.64	200	352	222	226	60.8	58.5	12.8
300	3.5	20.64	200	362	223	222	41.5	38.5	13.5
500	4.6	17.2	200	314	243	250	61.1	57.8	11.1
500	4.3	17.2	200	319	268	264	63.9	59.3	11.4
500	3.7	25.8	200	380	261	262	63.1	57.8	11.1
500	3.6	25.8	200	385	261	262	42.4	37	11.1

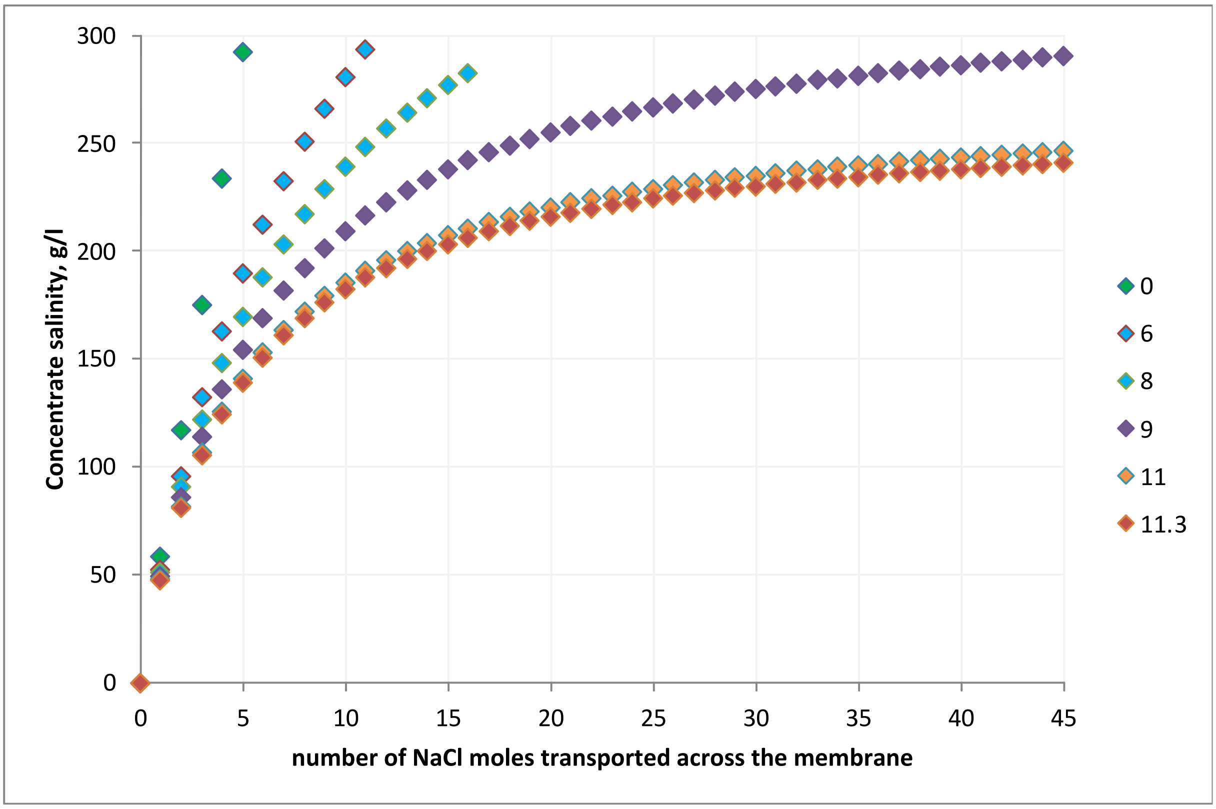


Figure 4-2. *Influence of sodium chloride hydration number on maximum ED concentrate salinity*

4.3. Modelling platform and assumptions

To model the ionic composition of the streams, a modification of an Excel sheet (file ZEROBRINE_D3.2_SIM_WARIANT3_v0.1.xlsx in Deliverable D3.2) developed in WP3 for coal mine case was used – see file in the WP3 database. The sheet uses the empirical parameters (e.g. ion rejection coefficients, water flux across the membrane, applied pressure) observed either during the pilot plant run in Bolesław Śmiały coal mine (see Deliverable 3.5), which were updated with the data obtained during the bench-scale tests of the electrodialysis described above. The techno-economic modelling was performed on a common simulation platform called RCE (Remote Component environment - https://rcenvironment.de), which uses Python to implement and integrate the relevant models for each unit operation. The assumptions of the RCE model are presented in Table 4-5.

A mixture of two kinds of feed water (Budryk and Budryk miernie – see Table 4-1) was assumed as a feed for the replication study. The pre-treatment was excluded from the techno-economical modelling, as PGWiR already has the required pre-treatment in place, so there would be no need to set up a new one in the case of full-scale implementation of ZERO BRINE technology. While the existing technology at Dębieńsko uses rock salt addition to increase the salinity of RO retentate (see Figure 4-1), it is not a requirement for the ZERO BRINE technology; however, according to the PGWiR executives, the company is more interested in increasing the amount of produced high-quality edible salt than in decreasing the consumption of low-quality rock salt. For that reason, it was assumed that ZERO BRINE uses the same amount of rock salt the current technology uses to remove the need for an evaporator working on the ED concentrate.

Table 4-4. *Composition of feed waters*

		Budryk	**Budryk miernie**
C_{Cl-}	kg/m^3	43.783	18.790
C_{Ca2+}	kg/m^3	0.960	0.524
C_{Mg2+}	kg/m^3	1.152	0.665
C_{SO42-}	kg/m^3	1.171	0.356
C_{Na+}	kg/m^3	25.616	10.467
TDS	kg/m^3	72.682	30.802
V	m^3/day	750	3800

Table 4-5. *RCE model assumptions*

Nanofiltration	
r_{pore} [nm]	0.45
Skin layer thickness [µm]	3
ε_{pore}	56.5
Charge [mol/m^3]	40
Reverse osmosis	
Number of elements	8
Single membrane area [m^2]	40.9
Electrodialysis	
Diluate/concentrate ratio	6.15
Current density [A/m^2]	400
Voltage drop per membrane pair	2.1
Electricity cost [$/kWh]	0.1035
$CaSO_4$/$Mg(OH)_2$ recovery	
Dolime solution concentration [mol/dm^3]	2.173522
NaCl crystallizer	
Inlet temperature [°C]	38
Operating temperature [°C]	100
Number of effects	10
NaCl saturation concentration [ppm]	400000

4.4. Results

4.4.1. Comparison of current technology with ZERO BRINE solution

Three cases have been considered:

- ZOD: the technology currently used at the Dębieńsko site, without any modifications – see Figure 4-1,
- NF-ZOD: application of two-pass nanofiltration with intermediate gypsum crystallization, followed by unchanged Dębieńsko technology – nanofiltration only works as a pretreatment, meaning PGWiR would not need to invest in the brine concentration step of the ZERO BRINE technology – see Figure 4-3
- ZERO BRINE: implementation of a full ZERO BRINE technology – see Figure 4-4.

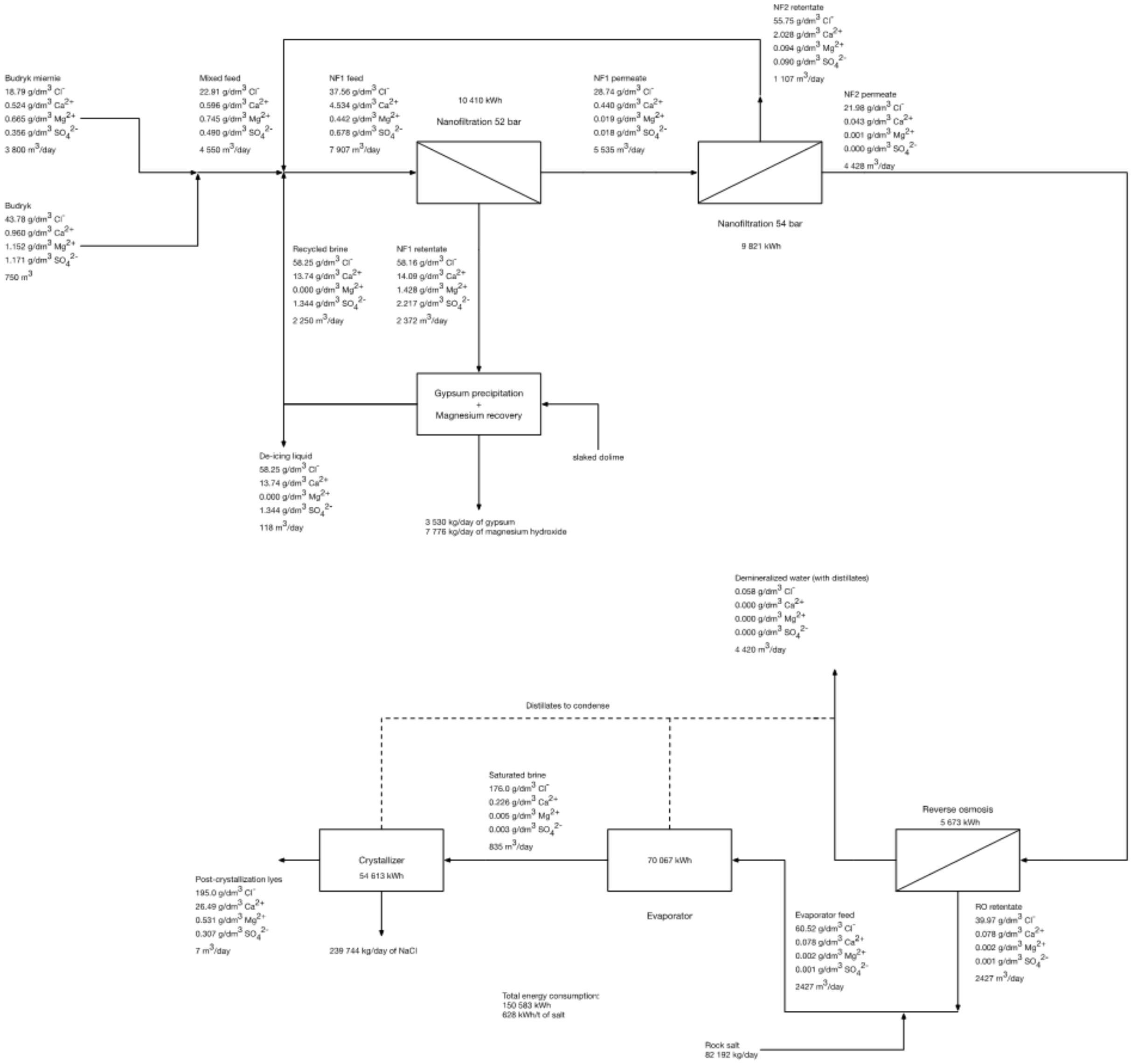

NF2 retentate
55.75 g/dm^3 Cl$^-$
2.028 g/dm^3 Ca^{2+}
0.094 g/dm^3 Mg^{2+}
0.090 g/dm^3 SO$_4^{2-}$
1 107 m^3/day
Budryk miernie
18.79 g/dm^3 Cl$^-$
0.524 g/dm^3 Ca^{2+}
0.665 g/dm^3 Mg^{2+}
0.356 g/dm^3 SO$_4^{2-}$
3 800 m^3/day
Mixed feed
22.91 g/dm^3 Cl$^-$
0.596 g/dm^3 Ca^{2+}
0.745 g/dm^3 Mg^{2+}
0.490 g/dm^3 SO$_4^{2-}$
4 550 m^3/day
NF1 feed
37.56 g/dm^3 Cl$^-$
4.534 g/dm^3 Ca^{2+}
0.442 g/dm^3 Mg^{2+}
0.678 g/dm^3 SO$_4^{2-}$
7 907 m^3/day
10 410 kWh
Nanofiltration 52 bar
NF1 permeate
28.74 g/dm^3 Cl$^-$
0.440 g/dm^3 Ca^{2+}
0.019 g/dm^3 Mg^{2+}
0.018 g/dm^3 SO$_4^{2-}$
5 535 m^3/day
NF2 permeate
21.98 g/dm^3 Cl$^-$
0.043 g/dm^3 Ca^{2+}
0.001 g/dm^3 Mg^{2+}
0.000 g/dm^3 SO$_4^{2-}$
4 428 m^3/day
Budryk
43.78 g/dm^3 Cl$^-$
0.960 g/dm^3 Ca^{2+}
1.152 g/dm^3 Mg^{2+}
1.171 g/dm^3 SO$_4^{2-}$
750 m^3
Nanofiltration 54 bar
9 821 kWh
Recycled brine
58.25 g/dm^3 Cl$^-$
13.74 g/dm^3 Ca^{2+}
0.000 g/dm^3 Mg^{2+}
1.344 g/dm^3 SO$_4^{2-}$
2 250 m^3/day
NF1 retentate
58.16 g/dm^3 Cl$^-$
14.09 g/dm^3 Ca^{2+}
1.428 g/dm^3 Mg^{2+}
2.217 g/dm^3 SO$_4^{2-}$
2 372 m^3/day
Gypsum precipitation
+
Magnesium recovery
De-icing liquid
58.25 g/dm^3 Cl$^-$
13.74 g/dm^3 Ca^{2+}
0.000 g/dm^3 Mg^{2+}
1.344 g/dm^3 SO$_4^{2-}$
118 m^3/day
slaked dolime
3 530 kg/day of gypsum
7 776 kg/day of magnesium hydroxide
Demineralized water (with distillates)
0.058 g/dm^3 Cl$^-$
0.000 g/dm^3 Ca^{2+}
0.000 g/dm^3 Mg^{2+}
0.000 g/dm^3 SO$_4^{2-}$
4 420 m^3/day
Distillates to condense
Saturated brine
176.0 g/dm^3 Cl$^-$
0.226 g/dm^3 Ca^{2+}
0.005 g/dm^3 Mg^{2+}
0.003 g/dm^3 SO$_4^{2-}$
835 m^3/day
Reverse osmosis
5 673 kWh
Crystallizer
54 613 kWh
70 067 kWh
Evaporator
Post-crystallization lyes
195.0 g/dm^3 Cl$^-$
26.49 g/dm^3 Ca^{2+}
0.531 g/dm^3 Mg^{2+}
0.307 g/dm^3 SO$_4^{2-}$
7 m^3/day
239 744 kg/day of NaCl
Evaporator feed
60.52 g/dm^3 Cl$^-$
0.078 g/dm^3 Ca^{2+}
0.002 g/dm^3 Mg^{2+}
0.001 g/dm^3 SO$_4^{2-}$
2427 m^3/day
RO retentate
39.97 g/dm^3 Cl$^-$
0.078 g/dm^3 Ca^{2+}
0.002 g/dm^3 Mg^{2+}
0.001 g/dm^3 SO$_4^{2-}$
2427 m^3/day
Total energy consumption:
150 583 kWh
628 kWh/t of salt
Rock salt
82 192 kg/day

Figure 4-3. Process scheme of Dębieńsko technology with NF-NF pretreatment

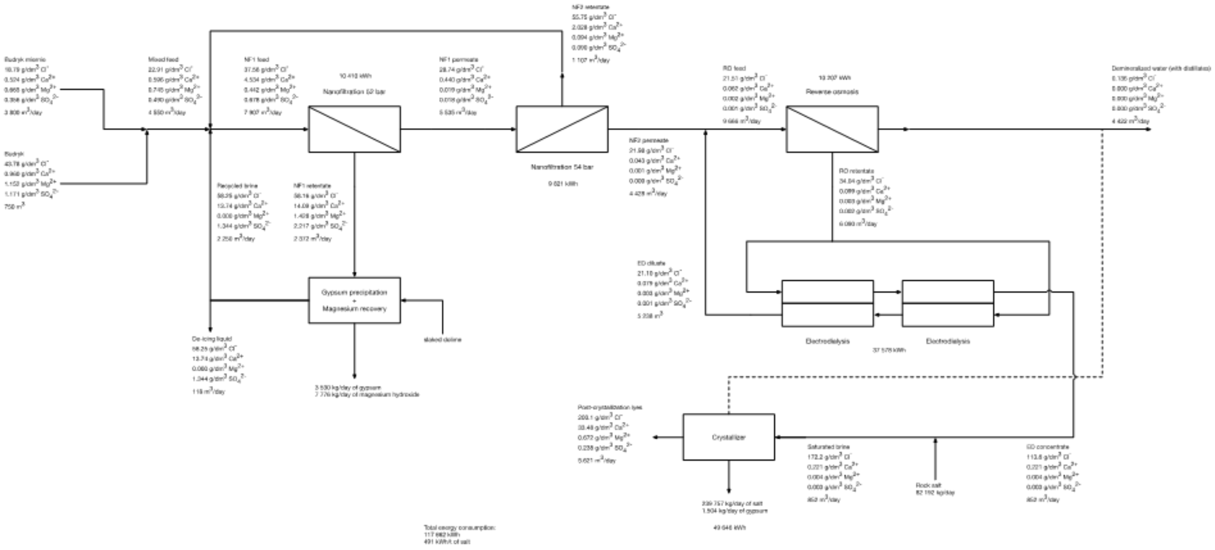

Budryk mixed
18.79 g/dm3 Cl-
0.524 g/dm3 Ca2+
0.865 g/dm3 Mg2+
0.356 g/dm3 SO42-
3 800 m3/day
Budryk
43.78 g/dm3 Cl-
0.960 g/dm3 Ca2+
1.152 g/dm3 Mg2+
1.171 g/dm3 SO42-
750 m3
Mixed feed
22.91 g/dm3 Cl-
0.596 g/dm3 Ca2+
0.745 g/dm3 Mg2+
0.490 g/dm3 SO42-
4 550 m3/day
NF1 feed
37.56 g/dm3 Cl-
4.534 g/dm3 Ca2+
0.442 g/dm3 Mg2+
0.878 g/dm3 SO42-
7 907 m3/day
10 410 kWh
Nanofiltration 52 bar
NF1 permeate
28.74 g/dm3 Cl-
0.440 g/dm3 Ca2+
0.019 g/dm3 Mg2+
0.018 g/dm3 SO42-
5 535 m3/day
NF2 retentate
55.75 g/dm3 Cl-
2.028 g/dm3 Ca2+
0.094 g/dm3 Mg2+
0.056 g/dm3 SO42-
1 107 m3/day
Nanofiltration 54 bar
9 821 kWh
NF2 permeate
21.98 g/dm3 Cl-
0.043 g/dm3 Ca2+
0.001 g/dm3 Mg2+
0.008 g/dm3 SO42-
4 428 m3/day
RO feed
21.51 g/dm3 Cl-
0.062 g/dm3 Ca2+
0.002 g/dm3 Mg2+
0.001 g/dm3 SO42-
9 666 m3/day
10 307 kWh
Reverse osmosis
RO retentate
34.84 g/dm3 Cl-
0.089 g/dm3 Ca2+
0.003 g/dm3 Mg2+
0.002 g/dm3 SO42-
6 080 m3/day
Demineralized water (with distillates)
0.135 g/dm3 Cl-
0.000 g/dm3 Ca2+
0.000 g/dm3 Mg2+
0.000 g/dm3 SO42-
4 422 m3/day
Recycled brine
58.25 g/dm3 Cl-
13.74 g/dm3 Ca2+
0.008 g/dm3 Mg2+
1.344 g/dm3 SO42-
2 258 m3/day
NF1 retentate
58.16 g/dm3 Cl-
14.09 g/dm3 Ca2+
1.408 g/dm3 Mg2+
2.217 g/dm3 SO42-
2 372 m3/day
Gypsum precipitation
+
Magnesium recovery
slaked dolime
De-icing liquid
58.25 g/dm3 Cl-
13.74 g/dm3 Ca2+
0.080 g/dm3 Mg2+
1.344 g/dm3 SO42-
118 m3/day
3 530 kg/day of gypsum
7 776 kg/day of magnesium hydroxide
ED diluate
21.10 g/dm3 Cl-
0.079 g/dm3 Ca2+
0.003 g/dm3 Mg2+
0.001 g/dm3 SO42-
5 238 m3
Electrodialysis
Electrodialysis
37 578 kWh
Post-crystallization lyes
209.1 g/dm3 Cl-
33.48 g/dm3 Ca2+
0.672 g/dm3 Mg2+
0.238 g/dm3 SO42-
5.621 m3/day
Crystallizer
239 757 kg/day of salt
1 504 kg/day of gypsum
49 646 kWh
Saturated brine
172.2 g/dm3 Cl-
0.221 g/dm3 Ca2+
0.004 g/dm3 Mg2+
0.003 g/dm3 SO42-
852 m3/day
Rock salt
82 192 kg/day
ED concentrate
113.6 g/dm3 Cl-
0.221 g/dm3 Ca2+
0.004 g/dm3 Mg2+
0.003 g/dm3 SO42-
852 m3/day
Total energy consumption:
117 662 kWh
491 kWh/t of salt

***Figure 4-4**. Process scheme of a full ZERO BRINE implementation*

Table 4-6 presents the calculated energy consumption, salt products, and investment costs for each of the investigated cases. The results indicate that the application of two-pass nanofiltration alone can improve the economics of the process; however, a substantial decrease in energy consumption (31%) can be achieved with full-scale ZERO BRINE implementation. To calculate if the ZERO BRINE is economically viable, the following assumptions were taken into account:

- Energy cost = 0.1035$/kWh,
- Dolime cost for Mg(OH)2 precipitation = 60$/t,
- $Mg(OH)_2$ price of 1200$/t,
- $CaSO_4$ price 40 $/t,
- Evaporated salt price of 140$/t,

Table 4-7 presents the breakdown of annual expenditures and revenue streams, Figure 4-5 presents the share of each unit operation in the total investment cost, and Figure 4-6 presents the share of each unit operation in the operational costs (including the energy consumption). The main part of the investment costs is the two-pass nanofiltration (46% combined) and electrodialysis (37%), whereas the main part of OPEX is the NaCl crystallizer cost (26%). This is because the simulations assume the ZERO BRINE technology can utilize the already existing NaCl crystallizer. Because the detailed OPEX calculations are PGWiR's trade secret, the maintenance, chemicals & personnel costs of ZOD technology were not taken into consideration; however, even assuming these unfavourable conditions, both NF-ZOD and ZERO BRINE technologies manage to outperform the existing technology. This is caused by two reasons: the increased revenue caused by the increase in salt production, and the creation of completely new revenue streams. The recovery of magnesium hydroxide is especially valuable here, as it's over 8 times more expensive than the evaporated salt.

Table 4-6. *Comparison of investment cost (assuming ZOD crystallizer can stay in place) and energy consumption for each of the investigated cases*

	Energy consumption [kWh/t]	Salt production [t/d]	CAPEX [$]
ZOD (current state)	713	190.3	N/A
NF-ZOD	628	239.7	12,329,357
ZEROBRINE	491	239.8	23,108,389

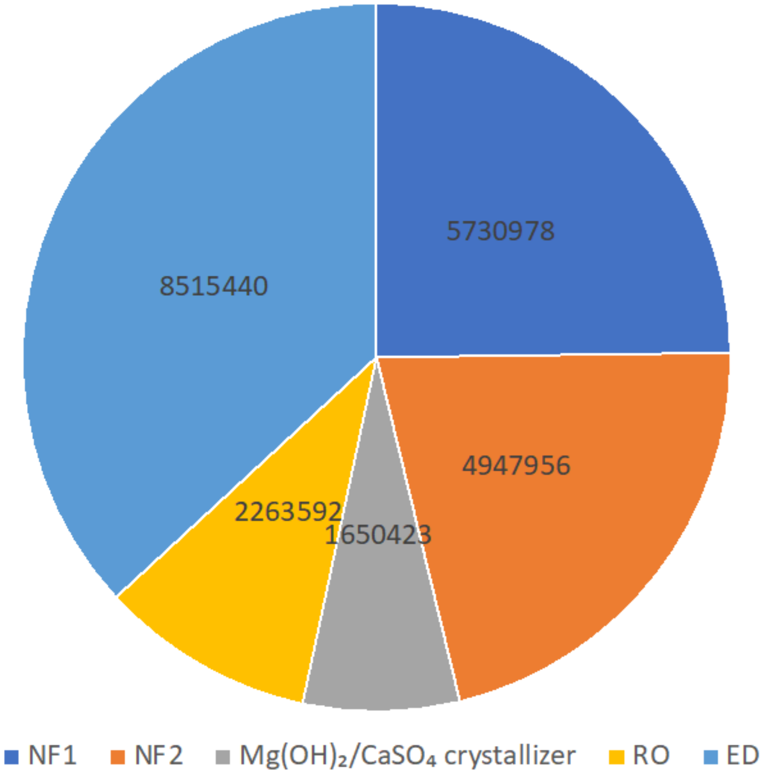


Figure 4-5. *Breakdown of CAPEX [$] for the ZEROBRINE technology*

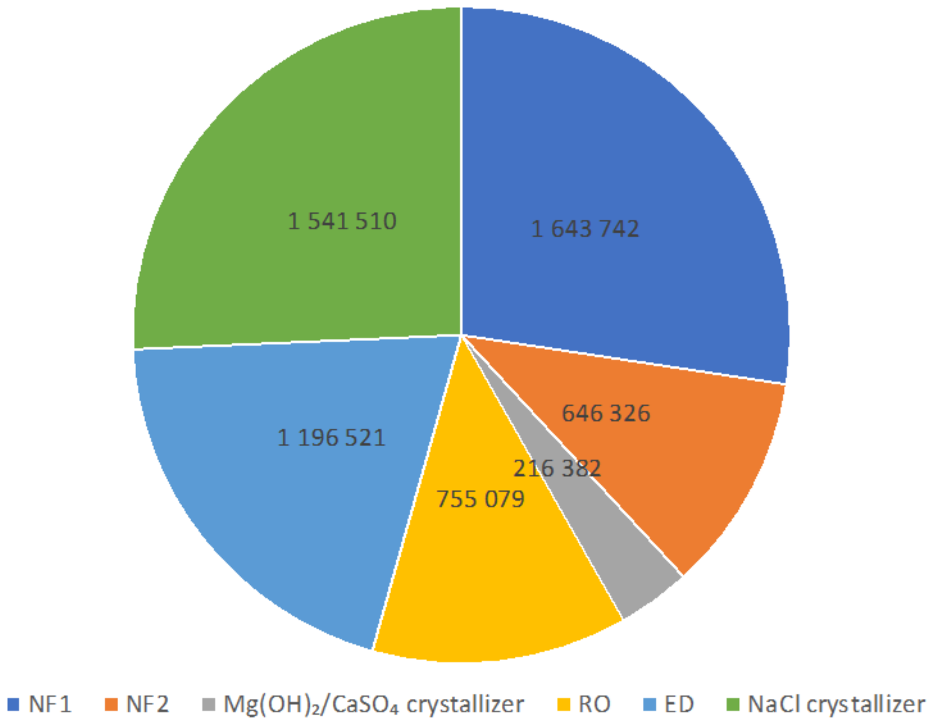


Figure 4-6. *Breakdown of OPEX [$/y] for ZERO BRINE technology*

Table 4-7. *Breakdown of annual expenses and revenue stream*

	Electricity costs [$/y]	Other OPEX (excluding rock salt) [$/y]	Mg(OH)2 revenue [$/y]	CaSO4 [$/y]	Salt revenue [$/y]
ZOD (current state)	4211219	N/A	0	0	8004034
NF-ZOD	4499492	1878278	6918907	69469	10081802
ZEROBRINE	3653401	2346159	6918907	69469	10086008

A simple comparison of capital costs and generated revenue stream – see Table 4-8 – shows that the costs of retrofitting the NF pretreatment into the existing ZOD technology (NF-ZOD) is returned within 2 years; in the case of full-scale ZERO BRINE implementation, it takes 4 years for the initial investment to pay for itself.

Table 4-8. *Prediction of the return of the investment*

Year	Balance (Revenue – Investment) [$]		
	ZOD	NF-ZOD	ZEROBRINE
0 (initial investment)	0	-12,329,357	-23,108,389
1	3,792,816	-1,636,949	-12,033,566
2	7,585,631	9,055,458	-958,742
3	11,378,447	19,747,865	10,116,081

Year	Balance (Revenue – Investment) [$]		
	ZOD	NF-ZOD	ZEROBRINE
4	15,171,262	30,440,273	21,190,904
5	18,964,078	41,132,680	32,265,727

To investigate the effect of price fluctuations on the economic viability of the ZERO BRINE replication study, a sensitivity analysis was performed – see Table 4-9. It shows that a 50% drop in evaporated salt production makes the existing ZOD technology no longer economically sustainable. On the other hand, the 50% increase in evaporated salt price would make the investment return time of ZERO BRINE very long; a simultaneous 50% increase in salt price and 50% decrease in magnesium hydroxide price would weaken ZERO BRINE business case. Assuming no $Mg(OH)_2$ revenue stream, the full-scale ZERO BRINE implementation would still break even within 6 years, but it would never generate more revenue than continuous usage of the existing plant. Conversely, the increase in magnesium hydroxide prices strengthens the ZERO BRINE business case. However, these calculations assume the existing ZOD technology can be used indefinitely, which is not really the case. According to the PGWiR management, the equipment they use was installed in the early 1990s and starts to reach the end of life; in a few years, they will have no choice but to build a new one. When that happens, the ZERO BRINE offers clear advantages in terms of lower energy consumption, increased salt production, and increased revenue streams.

Table 4-9. *Influence of price and costs fluctuations on the years it takes the ZERO BRINE to outperform existing ZOD technology*

	Electricity costs		
	-50%	0%	50%
Salt price -50%, Magnesium hydroxide price -50%	6*	5*	5*
Salt price 0%, Magnesium hydroxide price -50%	7	7	6
Salt price +50%, Magnesium hydroxide price -50%	never	never	never
Salt price -50%, Magnesium hydroxide price 0%	3*	3*	3*
Salt price 0%, Magnesium hydroxide price 0%	4	4	4
Salt price +50%, Magnesium hydroxide price 0%	12	10	9
Salt price -50%, Magnesium hydroxide price +50%	3*	2*	2*
Salt price 0%, Magnesium hydroxide price +50%	3	3	3
Salt price +50%, Magnesium hydroxide price +50%	5	4	4

* ZOD technology no longer breaks even

4.5. Conclusions

The results of techno-economic simulations show that the ZERO BRINE technology has a potential for commercialization when applied for the treatment of coal mine waste waters. The economic analysis shows that the initial investment can be returned within a few years and the full-scale implementation could be profitable. The business case of ZERO BRINE is significantly strengthened by its circular economy approach: the recovery of magnesium hydroxide from coal mine water, something that is not being done in the industry right now, generates a large portion of revenue. Without the $Mg(OH)_2$

revenue stream, the full-scale ZERO BRINE implementation will return the investment cost within 6 years, whereas recovering the Mg(OH)2 shortens this time to just 4 years and makes the investment in new technology competitive with continuous use of unmodified, old technology.

The company running the only salt production plant in Poland, PGWiR, is considering the implementation of membrane-based Zero Liquid Discharge (ZLD) systems and has confirmed the interest in the results of the ZERO BRINE project. As their current technology approaches the end of life, there is a strong possibility they will invest in the presented solution, either directly or by applying for external funding.

5. Spanish Replication Case Study

5.1. Brine selection and presentation of the case study

5.1.1. Status of brine production in Spain

A total amount of 354 hm^3/year of desalinated water was produced in Spain in 2018, according to the last data available from the Spanish Association of Desalination and Reuse (AEDyR) (Table 5-1).

***Table 5-1.** Desalinated water produced in Spain between 1988 and 2017. Data source: aquastat (accessed during 2020).*

Period	1988-1992	1993-1997	1998-2002	2003-2007	2008-2012	2013-2017
Desalinated water produced volume (10^9m^3/year)	0.1002	0.1002	0.1002	0.1002	0.1002	0.364

In Table 5-2 a summary of the most important locations with desalination plants and their capacity is shown. As can be seen, the Mediterranean region including different provinces (Castellón, Valencia, Alicante, Murcia, Almería and Málaga) is a highlighted area in the peninsula in Spain. This is related to the higher water stress that corresponds to the East and South of Spain, compared to the rest of the country.

***Table 5-2**. Desalination plants in Spain. Data source: AEDyR, 2018*

Desalination plant	Basin	Region	Capacity (hm^3/year)
Oropesa	Júcar	Castellón	18
Moncófar	Júcar	Castellón	10
Sagunto	Júcar	Valencia	8
Mutxamel	Júcar	Alicante	18
Torrevieja	Segura	Alicante	80
Valdelentisco	Segura	Murcia	48
Águilas	Segura	Murcia	60
Bajo Almanzora	Sur	Almería	15
Carboneras	Sur	Almería	42
Campo Dalías	Sur	Almería	30
Marbella	Sur	Málaga	20
Atabal	Sur	Málaga	60
		Total	**409**

According to the last data retrieved, the highest increase in desalination practices occurred between 2015-2016, as shown in Figure 5-1. After this year, also, the main destination of this source is agriculture and not urban supply (see Figure 5-2). This highlights again the strong dependence on the water of the country. During 2017 a total amount of 237 hm^3 was produced, which corresponds to 66% of the current capacity of Spain for desalination water production. Although the industrial application of desalination water is lower than the others, it also corresponds to high volumes. This scenario is also translated into the generation of high amounts of brine that must be managed accordingly.

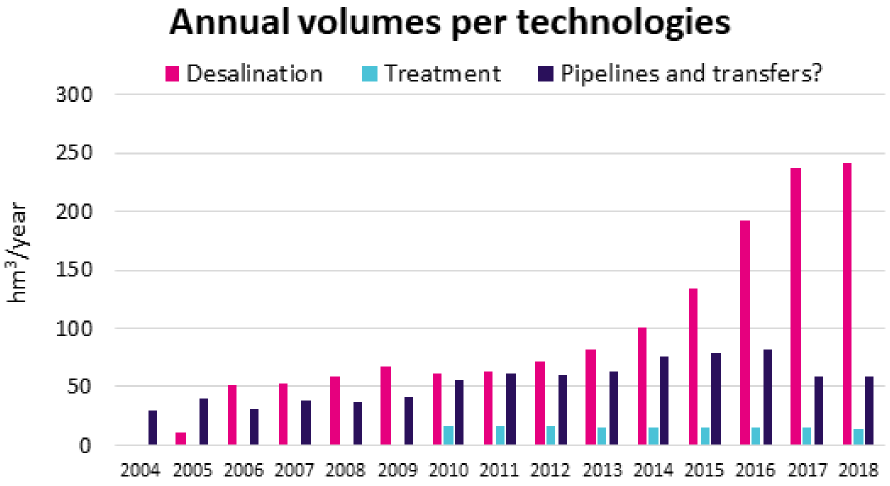


Figure 5-1. *Annual volumes per technologies produced in desalination plants in Spain. Source: AEDyR, 2018.*

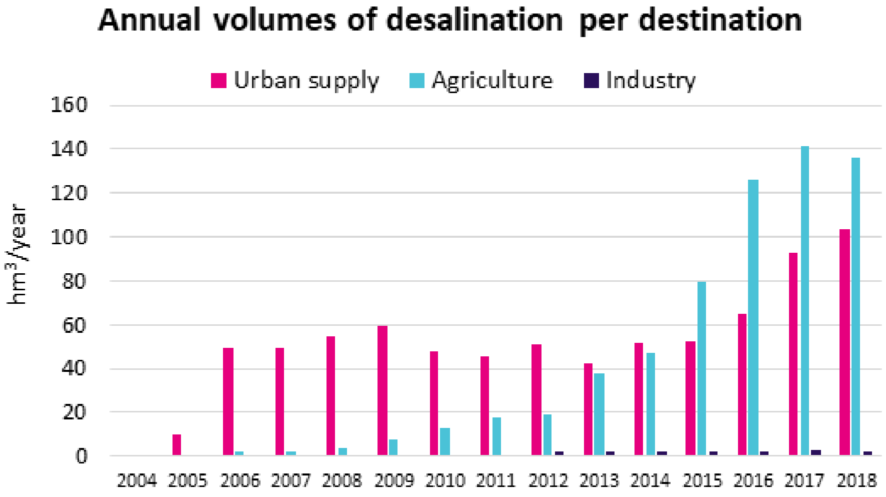


Figure 5-2. *Volume destinated of desalinated water per destination in Spain. Source: AEDyR, 2018.*

Industrial Brines

The main industry in Spain that generates waste effluents with brine (among other residues) is the agri-foodstuff for food preservation. The most important industries of this type are those of:

- Pickles
- Fish processing
- Preserves
- Dairy products
- Olives (these are the most important ones)

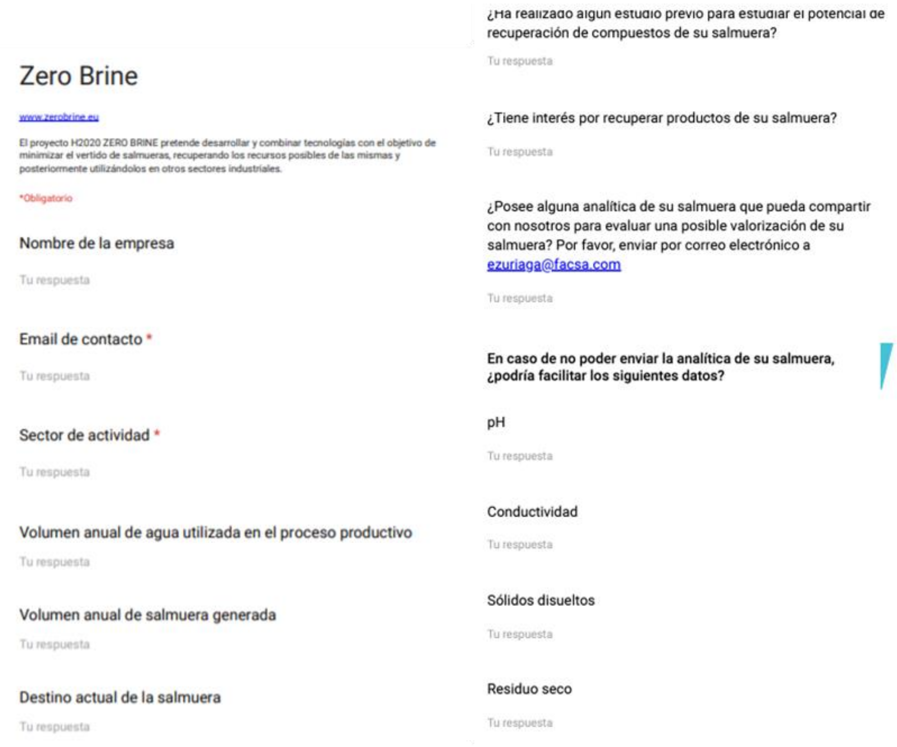
The main limitation of these type of brines is their associated high organic matter content that must be reduced to ensure appropriate management and implement recovery of high-value products from brines. Regarding inorganic brines generated in industries, Spain is the fifth country in the world with the largest number of desalination plants. In addition, there is another important industry in the generation of this waste, the one of Chlor-alkali production, which needs a saline solution to submit it to electrolysis and finally obtain Cl_2, NaOH and KOH. Table 5-3 summarizes the different brine producing industries in Spain:

Table 5-3. *Industries producing brines in Spain.*

Brines with organic content	Inorganic brines
– **Agro-food industry** – **Refineries**	– Desalination plants – Chlor-alkali industry – Glass and ceramics industry – Silica industry – Textile industry

5.1.2. Brine evaluation and selection for replicability study

FACSA and SITRA have evaluated more than 40 brines to choose the most suitable for the replication study in coordination with EURECAT and DLR partners. For this task, a questionnaire to the main customers of both companies and other stakeholders and brine owners operating in Spain have been contacted. The requested information regarding brine characteristics was retrieved in the following form (Figure 5-3)



Zero Brine

www.zerobrine.eu

El proyecto H2020 ZERO BRINE pretende desarrollar y combinar tecnologías con el objetivo de minimizar el vertido de salmueras, recuperando los recursos posibles de las mismas y posteriormente utilizándolos en otros sectores industriales.

*Obligatorio

Nombre de la empresa

Tu respuesta

Email de contacto *

Tu respuesta

Sector de actividad *

Tu respuesta

Volumen anual de agua utilizada en el proceso productivo

Tu respuesta

Volumen anual de salmuera generada

Tu respuesta

Destino actual de la salmuera

Tu respuesta

¿Ha realizado algún estudio previo para estudiar el potencial de recuperación de compuestos de su salmuera?

Tu respuesta

¿Tiene interés por recuperar productos de su salmuera?

Tu respuesta

¿Posee alguna analítica de su salmuera que pueda compartir con nosotros para evaluar una posible valorización de su salmuera? Por favor, enviar por correo electrónico a ezuriaga@facsa.com

Tu respuesta

En caso de no poder enviar la analítica de su salmuera, ¿podría facilitar los siguientes datos?

pH

Tu respuesta

Conductividad

Tu respuesta

Sólidos disueltos

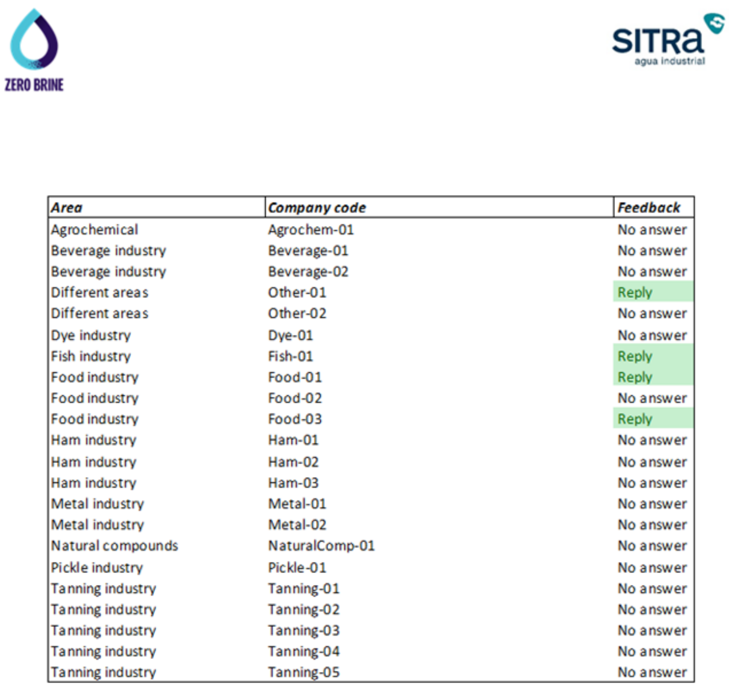
Tu respuesta

Residuo seco

Tu respuesta

Figure 5-3. *Form sent to stakeholders and brine generators to compile information and locate brine generators*

Figure 5-4, shows SITRA contact forms recovered from industries in Spain interested in the project.



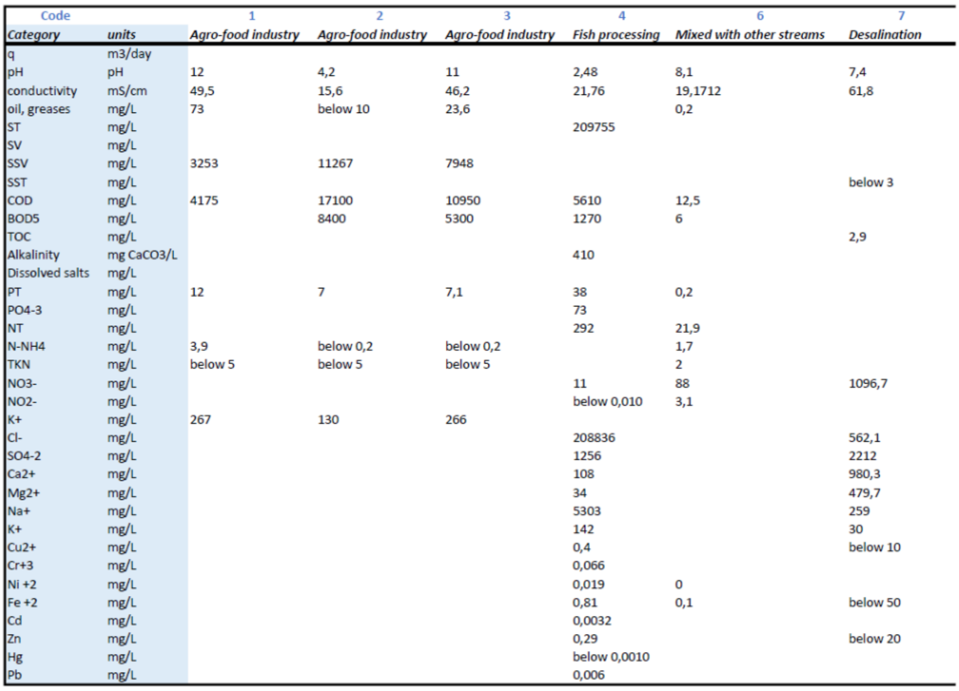
Area	Company code	Feedback
Agrochemical	Agrochem-01	No answer
Beverage industry	Beverage-01	No answer
Beverage industry	Beverage-02	No answer
Different areas	Other-01	Reply
Different areas	Other-02	No answer
Dye industry	Dye-01	No answer
Fish industry	Fish-01	Reply
Food industry	Food-01	Reply
Food industry	Food-02	No answer
Food industry	Food-03	Reply
Ham industry	Ham-01	No answer
Ham industry	Ham-02	No answer
Ham industry	Ham-03	No answer
Metal industry	Metal-01	No answer
Metal industry	Metal-02	No answer
Natural compounds	NaturalComp-01	No answer
Pickle industry	Pickle-01	No answer
Tanning industry	Tanning-01	No answer
Tanning industry	Tanning-02	No answer
Tanning industry	Tanning-03	No answer
Tanning industry	Tanning-04	No answer
Tanning industry	Tanning-05	No answer

Figure 5-4. *Report after SITRA contact compilation for industrial brine generators in Spain*

The results from the questionnaire were later analyzed and evaluated between EURECAT, FACSA and SITRA partners and can be observed in Table 5-4. The chosen brine for replicability study was number 35, which is an inorganic brine produced in an urban environment. Organic brines were evaluated for replicability but their high content in solids and organic matter presented a risk for the technology treatment proposed in this replicability study. Thus, the inorganic brine generated in a municipality of Spain was selected for bench test experiments and model validation.

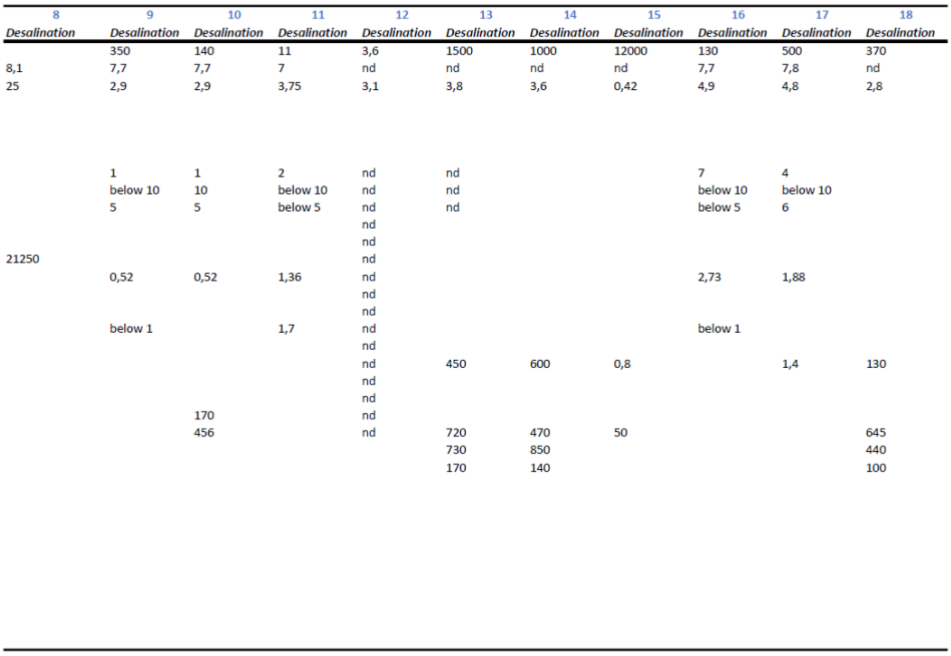
Urban inorganic brines evaluated for replicability study

Figure 5-5 to Figure 5-8 show the characteristics of all the urban brines evaluated during the project for choosing the most suitable location to implement the replication study. Brine 35 was selected due to its highest potential for Mg and Ca recovery using the proposed technology in this case study.



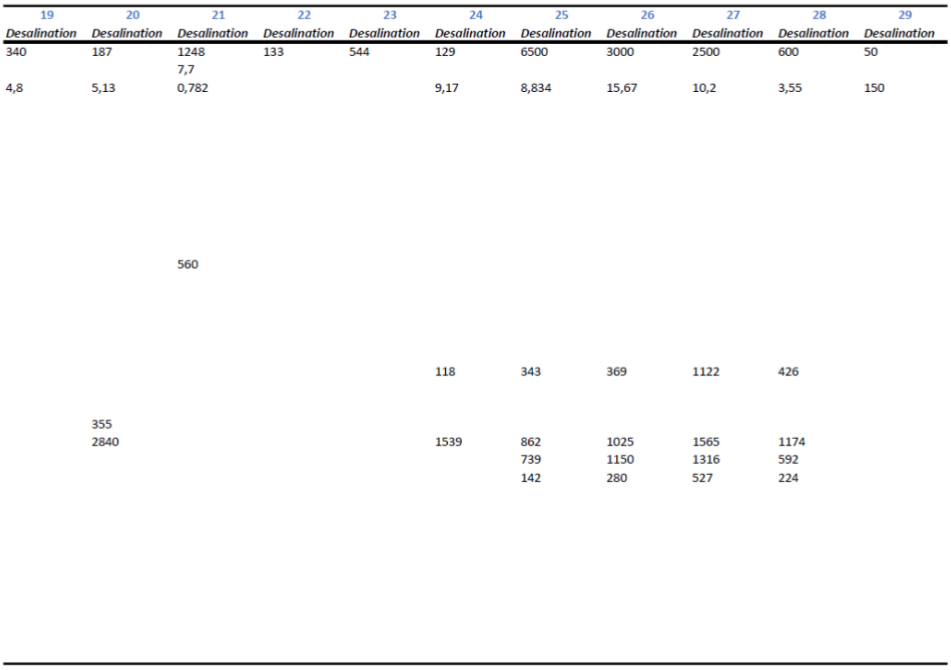
Code		1	2	3	4	6	7
Category	*units*	*Agro-food industry*	*Agro-food industry*	*Agro-food industry*	*Fish processing*	*Mixed with other streams*	*Desalination*
q	m3/day						
pH	pH	12	4,2	11	2,48	8,1	7,4
conductivity	mS/cm	49,5	15,6	46,2	21,76	19,1712	61,8
oil, greases	mg/L	73	below 10	23,6		0,2	
ST	mg/L				209755		
SV	mg/L						
SSV	mg/L	3253	11267	7948			
SST	mg/L						below 3
COD	mg/L	4175	17100	10950	5610	12,5	
BOD5	mg/L		8400	5300	1270	6	
TOC	mg/L						2,9
Alkalinity	mg CaCO3/L				410		
Dissolved salts	mg/L						
PT	mg/L	12	7	7,1	38	0,2	
PO4-3	mg/L				73		
NT	mg/L				292	21,9	
N-NH4	mg/L	3,9	below 0,2	below 0,2		1,7	
TKN	mg/L	below 5	below 5	below 5		2	
NO3-	mg/L				11	88	1096,7
NO2-	mg/L				below 0,010	3,1	
K+	mg/L	267	130	266			
Cl-	mg/L				208836		562,1
SO4-2	mg/L				1256		2212
Ca2+	mg/L				108		980,3
Mg2+	mg/L				34		479,7
Na+	mg/L				5303		259
K+	mg/L				142		30
Cu2+	mg/L				0,4		below 10
Cr+3	mg/L				0,066		
Ni +2	mg/L				0,019	0	
Fe +2	mg/L				0,81	0,1	below 50
Cd	mg/L				0,0032		
Zn	mg/L				0,29		below 20
Hg	mg/L				below 0,0010		
Pb	mg/L				0,006		

Figure 5-5. *Summarizing the analytical data of the brines produced in Spain retrieved by FACSA forms*



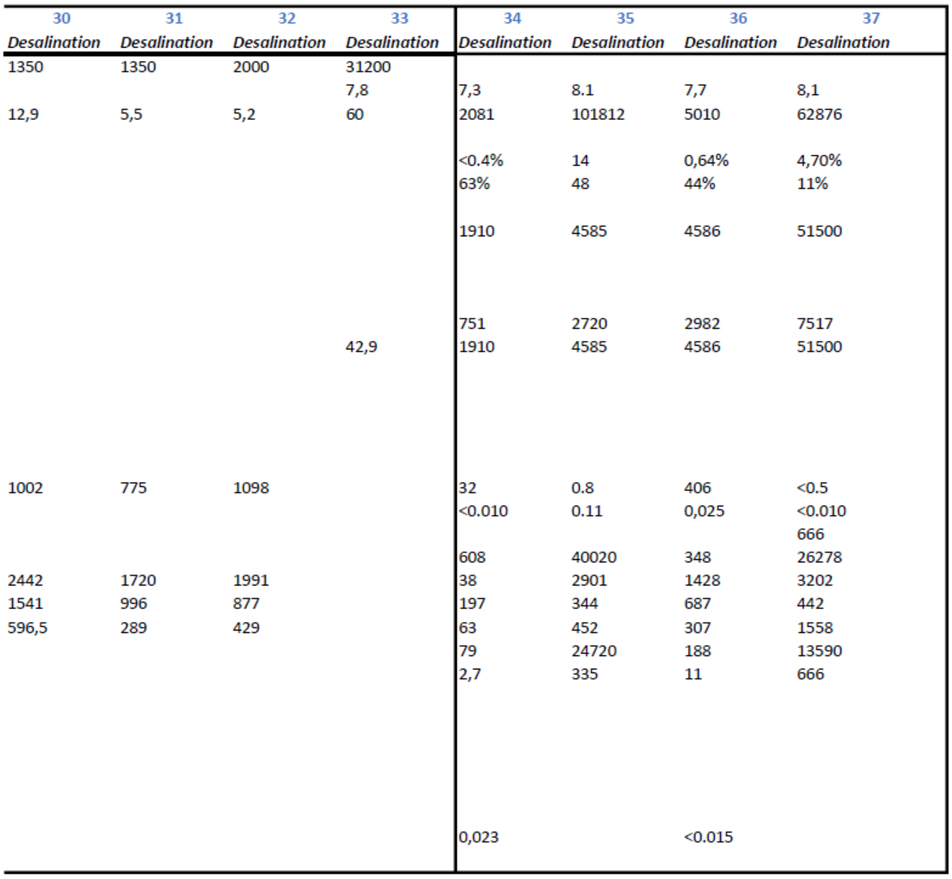
8	9	10	11	12	13	14	15	16	17	18
Desalination	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*
	350	140	11	3,6	1500	1000	12000	130	500	370
8,1	7,7	7,7	7	nd	nd	nd	nd	7,7	7,8	nd
25	2,9	2,9	3,75	3,1	3,8	3,6	0,42	4,9	4,8	2,8
	1	1	2	nd	nd			7	4	
	below 10	10	below 10	nd	nd			below 10	below 10	
	5	5	below 5	nd	nd			below 5	6	
				nd						
				nd						
21250				nd						
	0,52	0,52	1,36	nd				2,73	1,88	
				nd						
				nd						
	below 1		1,7	nd				below 1		
				nd						
				nd	450	600	0,8		1,4	130
				nd						
				nd						
		170		nd						
		456		nd	720	470	50			645
					730	850				440
					170	140				100

Figure 5-6. *Summarizing the analytical data of the brines produced in Spain retrieved by FACSA forms*



19	20	21	22	23	24	25	26	27	28	29
Desalination	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*	*Desalination*
340	187	1248	133	544	129	6500	3000	2500	600	50
		7,7								
4,8	5,13	0,782			9,17	8,834	15,67	10,2	3,55	150
		560								
					118	343	369	1122	426	
	355									
	2840				1539	862	1025	1565	1174	
						739	1150	1316	592	
						142	280	527	224	

Figure 5-7. *Summarizing the analytical data of the brines produced in Spain retrieved by FACSA forms*



30 *Desalination*	31 *Desalination*	32 *Desalination*	33 *Desalination*	34 *Desalination*	35 *Desalination*	36 *Desalination*	37 *Desalination*
1350	1350	2000	31200				
			7,8	7,3	8.1	7,7	8,1
12,9	5,5	5,2	60	2081	101812	5010	62876
				<0.4%	14	0,64%	4,70%
				63%	48	44%	11%
				1910	4585	4586	51500
				751	2720	2982	7517
			42,9	1910	4585	4586	51500
1002	775	1098		32	0.8	406	<0.5
				<0.010	0.11	0,025	<0.010
							666
				608	40020	348	26278
2442	1720	1991		38	2901	1428	3202
1541	996	877		197	344	687	442
596,5	289	429		63	452	307	1558
				79	24720	188	13590
				2,7	335	11	666
				0,023		<0.015	

Figure 5-8. *Summarizing the analytical data of the brines produced in Spain retrieved by FACSA forms*

Finally, brines number 35-36-37 were further characterized to evaluate the concentration of metals that could interact with the process or be of interest for future recovery of high-value products. The results are shown in Table 5-4.

Table 5-4. *Extended characterization for final selection of brine in replicability study*

	Facility code	35	36	37
Category	*units*			
q	m3/day	500	30	6100
pH	pH	8.1	7,7	8,1
conductivity	mS/cm	101812	5010	62876
oil, greases	mg/L			
ST	mg/L	14	0,64%	4,70%
SV	mg/L	48	44%	11%
SSV	mg/L			
SST	mg/L	4585	4586	51500
COD	mg/L			
BOD5	mg/L			

	Facility code	35	36	37
Category	*units*			
Alkalinity	mg/L	2720	2982	7517
Bicarbonates	mg/L	386	1000	172
Carbonates	mg/L	<20	<20	<20
Total sulfur	mg/L	>0.50	<0.050	<0.5
Al	µg/L	<100	<25	<100
Ab	µg/L	<50	<50	<50
Ar	µg/L	<50	<25	<50
S	mg/L	991	549	1087
Ba	µg/L	<50	121	<50
Be	µg/L	<10	<10	<10

	Facility code	35	36	37
TOC	mg/L			
Alkalinity	mg CaCO3/L	2720	2982	7517
Dissolved salts	mg/L	4585	4586	51500
PT	mg/L			
PO4-3	mg/L			
NT	mg/L			
N-NH4	mg/L			
TKN	mg/L			
NO3-	mg/L	0.8	406	<0.5
NO2-	mg/L	0.11	0,025	<0.010
K+	mg/L			666
Cl-	mg/L	40020	348	26278
SO4-2	mg/L	2901	1428	3202
Ca	mg/L	344	687	442
Mg	mg/L	452	307	1558
Na	mg/L	24720	188	13590
K	mg/L	335	11	666
Cu	mg/L			
Cr	mg/L			
Ni	mg/L			
Fe	mg/L			
Cd	mg/L			
Zn	mg/L			
Hg	mg/L		<0.015	
Pb	mg/L			

	Facility code	35	36	37
Bo	µg/L	2153	142	4515
Cd	µg/L	<10	<2	<10
Cr	µg/L	<10	<2	<10
Co	µg/L	<5	<5	<5
Cu	mg/L	<0.10	<0.015	<0.1
Sn	µg/L	<50	<15	<50
Sr	µg/L	11	8,9	15
Fe	µg/L	29	<5	<10
Li	mg/L	1.8	0,26	0,52
Mn	µg/L	113	<5	<10
Mo	µg/L	<10	<5	14
Ni	µg/L	<25	<5	<25
Ag	µg/L	<100	<25	<100
Pb	µg/L	<50	<15	<50
Se	µg/L	<50	61	73
Si	mg/L	8	20	0,28
Ta	µg/L	<25	<25	<25
Ti	µg/L	<10	<10	<10
Va	µg/L	<10	<10	<10
Zn	µg/L	<25	<15	<25

* nd is not detected

Finally, brine number 35 was selected for the trial presented in this deliverable because of the best combination of ions and the most suitable characteristics for the proposed treatment. The results are presented in the following sections.

5.1.3. Proposed treatment train for replicability case study

As commented in the previous sections, the selected brine is an inorganic brine produced in an urban environment that presents high Mg and Ca recovery potential. The proposed treatment train to be studied in this replicability case is presented in Figure 5-9. The first step is the chemical precipitation of Ca in form of $CaCO_3$, with addition of Na_2CO_3. This precipitation step is followed by an ultrafiltration (UF) step, which acts as pretreatment for the next step that is a nanofiltration (NF) to recover the purified brine in the permeate – that can be reused – and recover Mg and SO_4 in the concentrate. The last step is the chemical precipitation of Mg in the concentrate as $Mg(OH)_2$ with addition of NaOH. This treatment could also include a last step of evaporation to recover the SO_4 in form of Na_2SO_4, but this step is only proposed theoretically and was not studied by means of laboratory experiments nor with the RCE model.

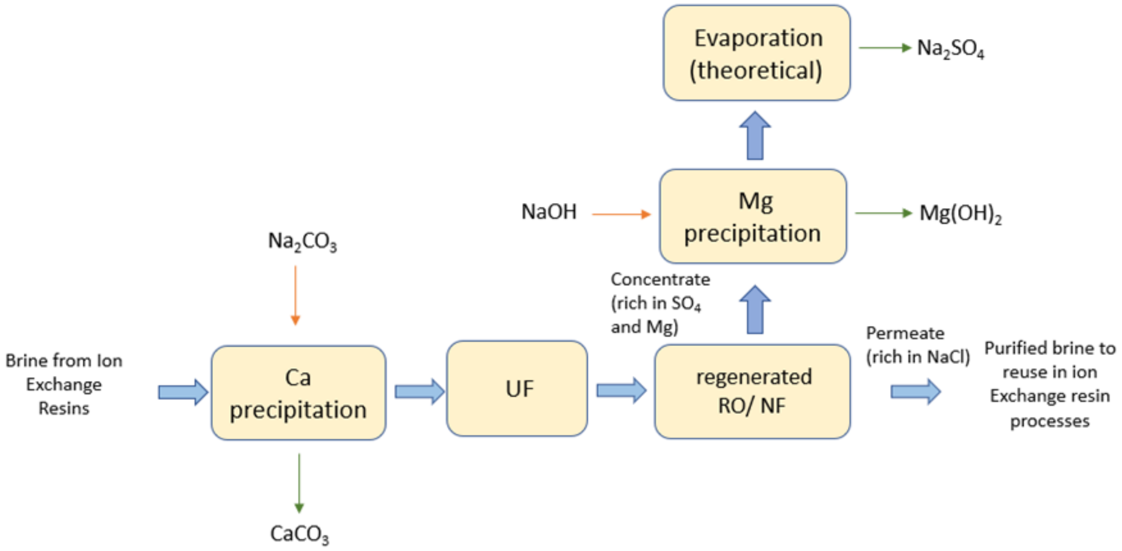

Evaporation (theoretical)
Na2SO4
NaOH
Mg precipitation
Mg(OH)2
Na2CO3
Concentrate (rich in SO4 and Mg)
Permeate (rich in NaCl)
Brine from Ion Exchange Resins
Ca precipitation
UF
regenerated RO/ NF
Purified brine to reuse in ion Exchange resin processes
CaCO3

Figure 5-9. *Diagram of the proposed treatment train for exhausted brine from ion exchange resins regeneration processes*

5.2. Presentation of the modelling platform

The treatment chain has been simulated using DLR's RCE (Remote Component Environment) software platform, which is an open-source software that allows the project partners remote access to the Tools to be able to use them in their own workflow implementations. Under the ZERO BRINE project several technology Tools for significant processes in a treatment chain, for example, nanofiltration, Ca, precipitation, etc. have been modelled in Python and then made available on the RCE platform as Tools[3] . These Tools, implemented at DLR, have been published using RCE's Component Publishing option to RCE users at several project partners that have been authorized a project-specific access by DLR's IT department. The partners have the possibility to import these published Tools in a workflow to implement any desired treatment chain or modify the existing ones. Based on a modelled treatment chain, the RCE Scripts need to be modified which may have different functions including unit conversion, reading the output from one Tool and making it available to the next Tool in the desired form, performing global economic calculations for the entire treatment chain, etc.

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[3] For a more detailed understanding of the RCE-specific terms, please refer to the RCE documentation on https://rcenvironment.de/

Once the Tools and Scripts are modified and connected to each other and appropriate Input Providers and Output Writers, executing the RCE workflow provides two excel sheets as output: I) the outputs of individual technology tools are simply merged, ii) a global economic output that cost estimation for the entire treatment chain. The global output result generally consists of the annual quantity of mineral and water recovery, capital and operating expenditures for each technology. The annual expenditures are also indicated in terms of the Levelized Cost of the chain's main product. For example, in the Spanish replicability case study the main product could be the NaCl-rich permeate leaving the NF unit, which is then recirculated to the ion exchange plant. In the global economic output, it will be expressed as Levelized brine cost (LBC) in USD/tonNaCl.

5.3. Bench test experiment required for model validation assumptions

5.3.1. Chemical precipitation of $CaCO_3$

The first step of the treatment train to be studied in the replicability case is the chemical precipitation of calcium (Ca) in form of calcium carbonate ($CaCO_3$) by addition of sodium carbonate (Na_2CO_3). In the following section, we present the methodology and results regarding the bench-scale test of Ca precipitation.

Methodology

To define the quantity of reactant (Na_2CO_3) needed for the precipitation of the amount of Ca contained in the brine to be treated, we developed a model for the precipitation process using the Software OLI (OLI Studio. Version 10.0.2.1. Copyright 1997-2020 OLI Systems, Inc.). The characterization of the brine to be treated that was used for the modelling of the precipitation of Ca is presented in Table 5-5 and was provided by Facsa.

Table 5-5. *Characterization of exhausted brine from ion exchange resins regeneration processes*

Parameter	Unit	Values
pH	pH	8.1
Conductivity	µS/cm	101812
TS	mg/L	14%
VS	mg/L	48%
Dissolved salts	mg/L	4585
NO_3^-	mg/L	0.8
NO_2^-	mg/L	0.11
Cl^-	mg/L	40020
SO_4^{-2}	mg/L	2901

Parameter	Unit	Values
Ca^{2+}	mg/L	344
Mg^{2+}	mg/L	452
Na^{+}	mg/L	24720
K^{+}	mg/L	335
Total hardness	mg/L	2720
Bicarbonates	mg/L	386
Carbonates	mg/L	<20
Total sulphides	mg/L	>0.50
Al^{+3}	µg/L	<100
Sulphur	mg/L	991
Boron	µg/L	2153
Strontium	µg/L	11
Iron	µg/L	29
Lithium	mg/L	1,8
Manganese	µg/L	113
Silicium	mg/L	8
Zinc	µg/L	<25

The model considered the addition of NaOH besides Na_2CO_3. As a result, we obtained the graphs presented in Figure 5-10 and Figure 5-11.

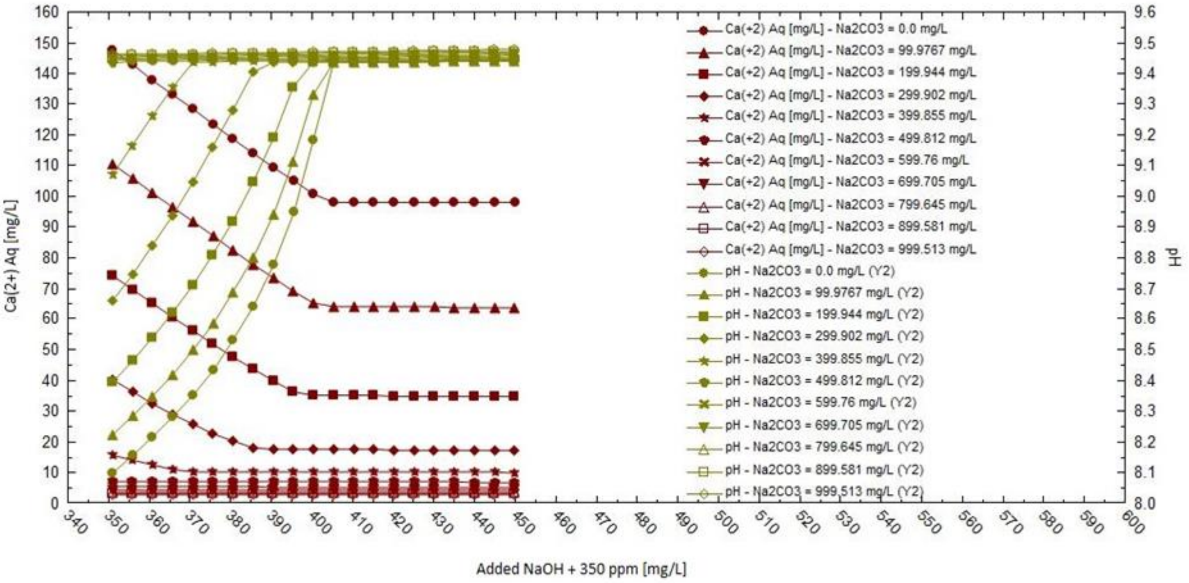

Figure 5-10. *Modelling of calcium precipitation with addition of Na_2CO_3 and NaOH - Ca and pH for different Na2CO3 and NaOH concentrations*

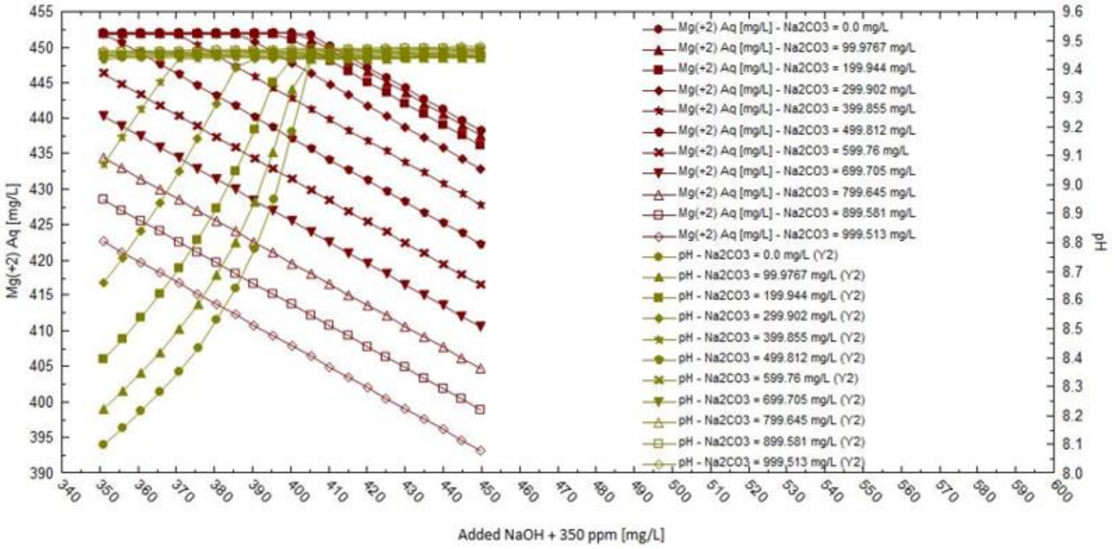

Figure 5-11*. Modelling of calcium precipitation with addition of Na2CO3 and NaOH - Mg and pH for different Na2CO3 and NaOH concentrations*

The model indicates several equilibrium points regarding Ca concentration and pH that can be achieved by adding different amounts of Na_2CO_3/NaOH. We also modelled the precipitation of Mg, to ensure no Mg is precipitated during the Ca precipitation step. We decided to perform a first bench-scale test by adding 0.5 g/L brine of Na_2CO_3; this amount of reactant should allow to precipitate Ca until a concentration of less than 10 mg/l and produce no precipitation of Mg, according to the model. Concentrations lower than 0.5 g/L brine of Na_2CO_3 do not allow to reach Ca concentrations less than 10 mg/l in the brine, according to the model.

The precipitation assay was done by adding brine sample (0.5 L) and reactant into a beaker with magnetic agitation (see Figure 5-12). Samples were collected at different times, and the last sample was taken after a reaction time of approximately 3 hours. Collected samples were filtered with a 0.2 µm filter (simulating an ultrafiltration step) before analysis. The assay was done at room temperature (22 ± 1 ºC).

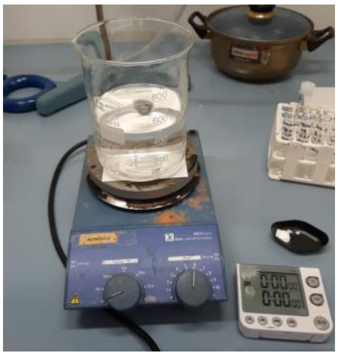

Figure 5-12. *Calcium precipitation assay with 0,5 L of brine*

Results

Final Ca concentration in the brine achieved by adding 0.5 g/L of Na_2CO_3 was 94 mg/l. This final concentration was still high, so we decided to perform a second beaker tests with a higher concentration of Na_2CO_3. The second precipitation assay was performed as the first one (as described in the “Methodology” section) but with addition of 0.8 g/L brine of Na_2CO_3 and addition of NaOH to correct the pH to the value indicated by the model for the concentration of Na_2CO_3. This concentration of Na_2CO_3 could produce the precipitation of Magnesium – which is not desired in this step -, but not more than 15 mg/L according to the model (see Figure 5-11). According to the model, in case of adding 0.8 g/L brine of Na_2CO_3 the pH should be around 9.5 (see Figure 5-10), so NaOH was added to achieve this value. A resume of the experimental conditions and results of both assays is presented in Table 5-6.

Table 5-6. *Results for calcium precipitation assays with 0,5 L of brine by addition of 0,5 g/L and 0,8 h/L of* Na_2CO_3

Parameter	Ca precipitation with 0,5 g/L of Na_2CO_3	Ca precipitation with 0,8 g/L of Na_2CO_3 and pH correction with NaOH
Added Na_2CO_3 [g/L]	0.5	0.8
Initial Ca concentration in brine [mg/L]	233	233
Final Ca concentration in brine [mg/L]	94	< 25

The second precipitation assay had better results in terms of Ca precipitation (no Ca was detected in the brine after the precipitation process, with a limit of detection of 25 mg/L), so we selected these precipitations conditions (addition of 0.8 g/L brine and correction of pH to 9.5 with NaOH) as the optimal ones to precipitate the Ca contained in the brine. To be able to perform the bench-scale tests of the following steps of the treatment train, we applied these optimal Ca precipitation conditions to a higher amount of brine (5 L, see Figure 5-13). The precipitation was done following the same methodology as with the previous experiments. The amount of NaOH needed for pH correction to 9.5 at the beginning of the precipitation process was 0,42 g NaOH/L of brine. After the precipitation process, the sample was filtered with an 0.2 µm filter. In Table 5-7 we present the composition of the brine sample before and after the precipitation process.

Table 5-7. *Results for calcium precipitation assay with 5 L of brine, by addition of 0,8 g/L of Na2CO3 and pH correction with NaOH*

Parameter	Initial brine sample	Brine after Ca precipitation with 0,8 g/L of Na_2CO_3 and pH correction with NaOH
pH	8.13	9.3
CE [mS/cm]	104.2	103
STD [g/L]	87	87.3
Turbidity [NTU]	0.37	0.32
TIC [mg/L]	242	350
Ca [mg/L]	233	<50
Mg [mg/L]	441	417
K [mg/L]	296	287
Na [mg/L]	30100	29800
Cl [mg/L]	33500	35300
SO_4 [mg/L]	6330	7050

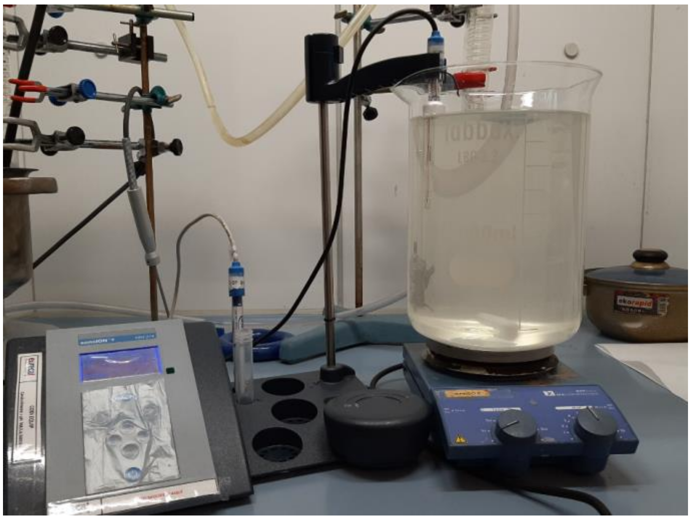

Figure 5-13. *Calcium precipitation assay with 5 L of brine*

5.3.2. Nano-Filtration (NF)

The second step of the treatment train to be studied in the replicability case is the Nanofiltration (NF) step, to separate the monovalent ions (Na, Cl) from divalent ions (Mg, SO_4). This step will allow to recover salt in the permeate and produce a concentrate with higher concentrations of Mg and SO_4, which in turn can be subjected to further separation processes to recover $Mg(OH)_2$ and Na_2SO_4. In the following section, we present the methodology and results regarding bench-scale test of NF.

Methodology

The testing set-up for the evaluation of membrane performance is shown in Figure 5-14 and consisted of a: testing cell (Figure 5-15) a thermostatic bath (DIGIT-COOL, HAAKE (EK20)) and a pump (Hydra-cell, G03X). The testing cell was made of stainless steel so it could resist pressure, which was regulated using a needle valve at the concentrate, and it was continuously monitored by a pressure meter. To monitor the flow of the feed a flowmeter was used. The set-up was all connected with a series of tubes, gauges, and valves. The nanofiltration membrane used for the test at bench scale was a NF270 membrane cupon (FilmTecTM). The pH of the NF inlet brine sample (resulting brine from the previous Ca precipitation step) was adjusted to 6.5 to prevent any precipitation of solids on the membrane. The filtration assay was done at a recovery of 75% and a filtration pressure of 15 bar.

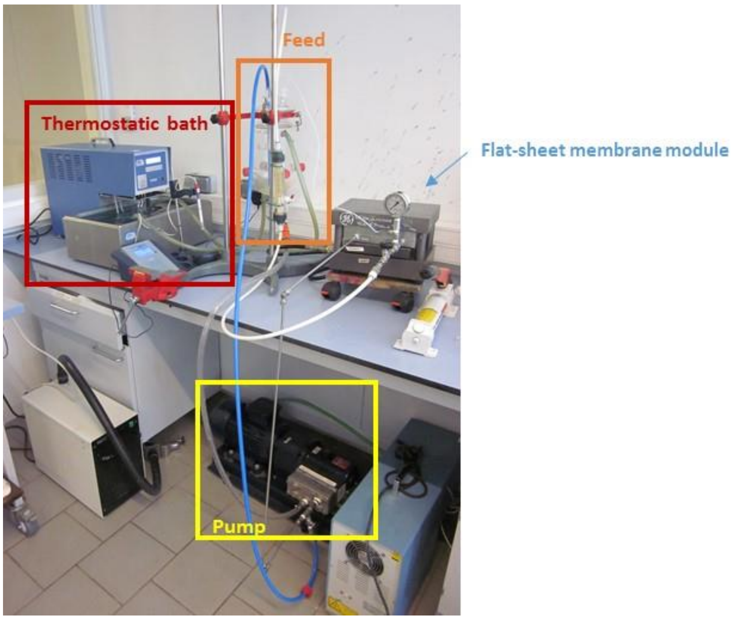

Figure 5-14. *Experimental set-up for membrane filtration testing at bench-scale*

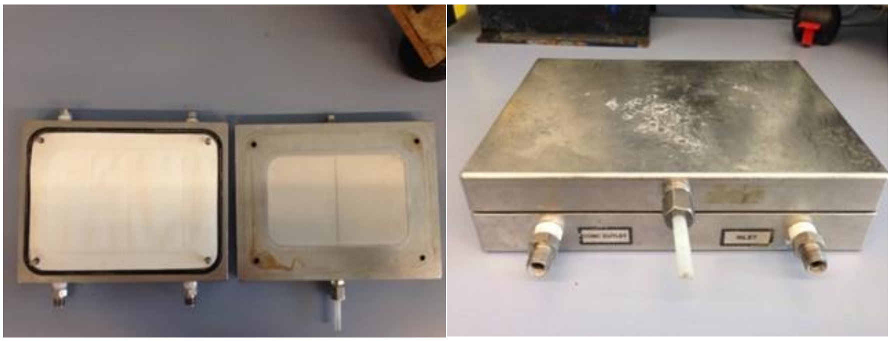

Figure 5-15. *Flat-sheet testing cell used for membrane filtration assays at bench-scale*

Results

The results regarding inlet brine, permeate and concentrate composition are presented in Table 5-8. The results regarding ion rejection are presented in Table 5-9. Magnesium rejection was not as high as expected for a nanofiltration process. Rejection of salt (indicated by Cl rejection) was very low, which favors the recovery of salt in the permeate. The rejection of SO_4 was quite high, which favors the recovery of sodium sulfate in the concentrate. The flux was 44 LMH and the membrane permeability was 2.9 LMH/bar.

Table 5-8. *Results for the brine nanofiltration assay at bench-scale*

Parameter	Brine before NF	NF Permeate	NF concentrate
pH	6.5	7.8	8.0
CE [mS/cm]	103	98.7	115
STD [g/L]	87.3	76	116
Turbidity [NTU]	0.32	<0.20	2.4

Parameter	Brine before NF	NF Permeate	NF concentrate
TIC [mg/L]	350	166	463
Ca [mg/L]	<50	<50	<50
Mg [mg/L]	417	152	1070
K [mg/L]	287	254	354
Na [mg/L]	29800	26600	38100
Cl [mg/L]	33500	35000	37400
SO_4 [mg/L]	6330	<80	25800

__Table 5-9__. Rejection of main components in brine sample for the nanofiltration assay

Parameter	NF rejection
Mg [%]	63.5
Cl [%]	0.8
SO_4 [%]	98.9
K [%]	11.5

5.3.3. Chemical precipitation of $Mg(OH)_2$

The third step of the treatment train to be studied in the replicability case is the chemical precipitation of Magnesium (Mg) in form of Magnesium hydroxide ($Mg(OH)_2$) by addition of sodium hydroxide (NaOH). In the following section, we present the methodology and results regarding the bench-scale test of Mg precipitation.

Methodology

To define the quantity of reactant (NaOH) needed for the precipitation of the amount of Mg contained in the brine to be treated in form of Brucite ($Mg(OH)_2$) , we developed a model for the precipitation process using the Software PhreeqC (Versión 3.7.1. United States Geological Survey (USGS) 2021). The characterization of starting brine used for the modelling of the precipitation of Mg is the one presented in Table 5-8 for NF concentrate. For the modelling, we considered two scenarios: one that considers the precipitation of magnesite ($MgCO_3$) besides brucite and one that does not. The results can be seen in Figure 5-16 and Figure 5-17.

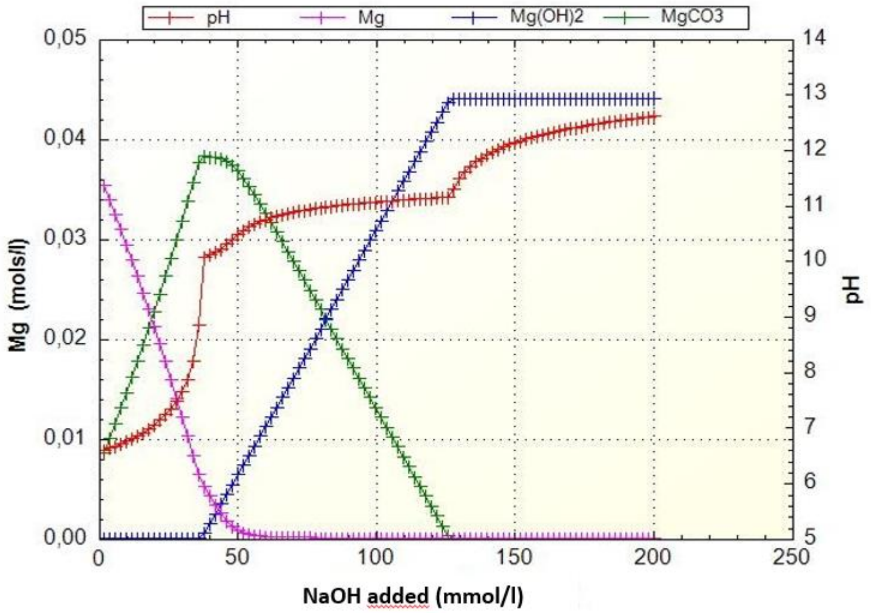

__Figure 5-16__. Modelling of magnesium precipitation by addition of NaOH - considering Magnesite precipitation

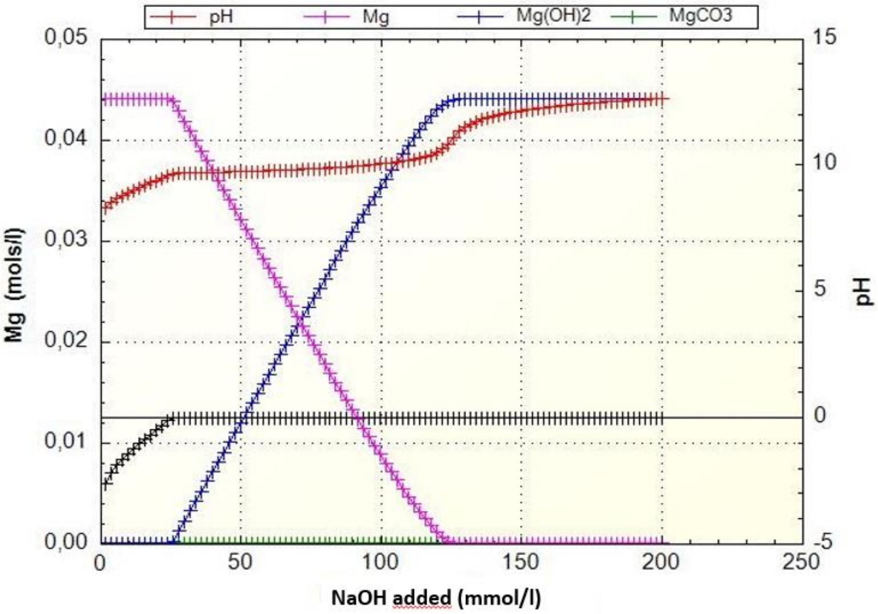

__Figure 5-17__. Modelling of magnesium precipitation by addition of NaOH - not considering Magnesite precipitation

If we consider the precipitation of magnesite besides brucite, the addition of 50 mmol of NaOH/L of brine would be enough to precipitate Mg up to a concentration of less than 0.001 mol/L brine, according to the model. If we consider that magnesite does not precipitate, this amount increases up to approximately 125 mmol/L brine.

Therefore, we decided to test at bench-scale 3 different NaOH concentrations: 50 mmol/L brine (2 g/L brine), 100 mmol/L brine (4 g/L of brine) and 150 mmol/L brine (6 g/L of brine). The results are presented in Table 5-10.

Table 5-10. *Results for magnesium precipitation assays at three different NaOH concentrations*

Parameter	Brine before Mg precipitation	Brine after Mg precipitation with 2 g/L brine of NaOH	Brine after Mg precipitation with 4 g/L brine of NaOH	Brine after Mg precipitation with 6 g/L brine of NaOH
pH	8.0	10	10.4	12
CE [mS/cm]	115	107	109	113
STD [g/L]	116	106.1	106.9	107.8
Turbidity [NTU]	2.4	0.5	0.31	0.4
TIC [mg/L]	463	259	285	379
Ca [mg/L]	<50	<100	<100	<100
Mg [mg/L]	1070	554	73	<50
K [mg/L]	354	382	382	387
Na [mg/L]	38100	39200	40800	40600
Cl [mg/L]	37400	37000	37400	36600
SO_4 [mg/L]	25800	26000	26300	25800

The optimal condition for Mg precipitation was the addition of 6 g/L of brine of NaOH, that resulted in a final Mg concentration in the brine of <50 mg/l. These results are closer in line with the modelling that does not consider magnesite precipitation than with the modelling that does. Nevertheless, further analysis would be needed to confirm the composition of the generated precipitate. In this case, we will assume that all Mg is precipitated in form of brucite.

5.3.4. Evaporation for Na_2SO_4 precipitation (theoretical analysis)

The evaporation step (last step of the treatment train) could not be modelled by the RCE platform; therefore, no bench-scale experiments were done to determine operational parameters for the process. Nevertheless, a simple calculation can be done to estimate the recovery of Na_2SO_4 through evaporation, as the amount of sulfate determines the amount of Na_2SO_4 that can be recovered. The amount of sulfate contained in the brine after Mg precipitation is 25,800 mg/L, which corresponds to 0.27 mol/L. Therefore, a maximum of 0.27 mol/L of Na_2SO_4 could be recovered from the brine. This corresponds to 38.2 g/l of Na_2SO_4.

5.4. Simulation campaign

5.4.1. Description of the modelled treatment chain

For the simulation of the current treatment chain on DLR's RCE platform, the following Tools have been used: nanofiltration (NF), Ca precipitation and Mg precipitation. The techno-economic modelling of NF and the precipitators is discussed in the previous works of this project (Micari, Cipollina, et al., 2019; Micari, Moser, et al., 2019). The modelled treatment chain is shown in Figure 5-18. Comparing with Figure 5-9, it is seen that pH adjustment, ultrafiltration (UF) and evaporator for Na_2SO_4 precipitation have not been modelled. Thus, the global economic calculations to determine the LBC (USD/tonNaCl) do not reflect the costs for these components as well as the revenue from the recovery of Na_2SO_4.

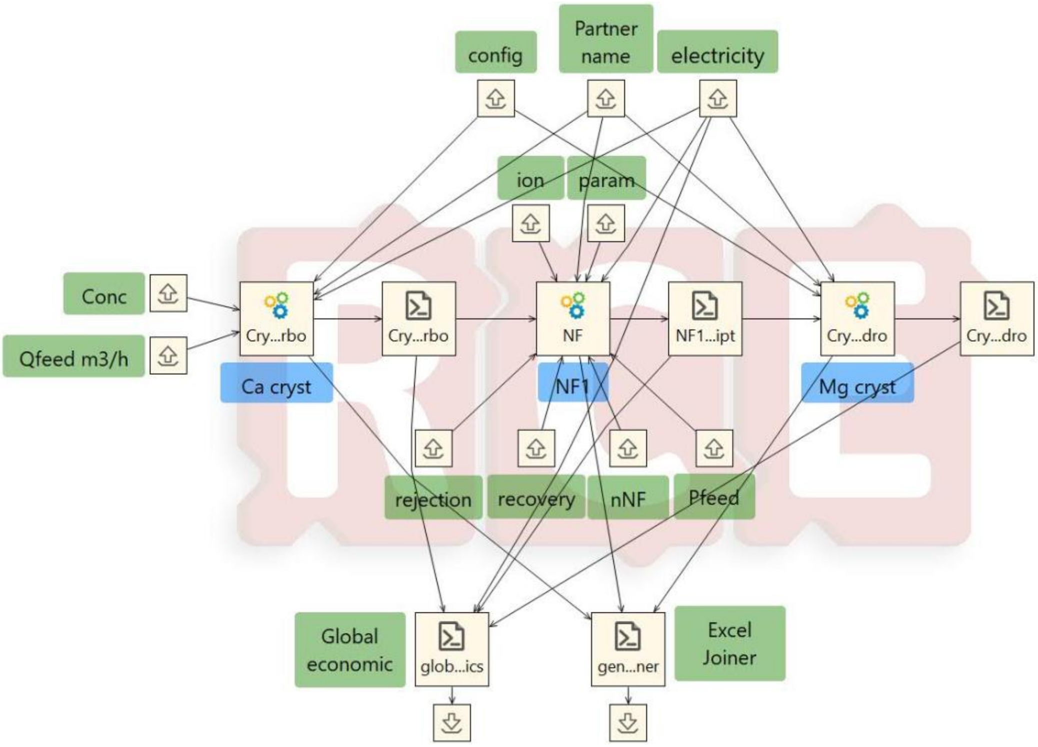

Figure 5-18. *Modelled treatment chain on RCE*

As seen in the figure, Ca precipitator is the first *Tool* in the modelled treatment chain which takes the ion concentration and volumetric flow rate as an input. After $CaCO_3$ is precipitated in this tool, the effluent which is free of Ca ions is sent to the *NF Tool*. Using a feed pressure of 20 bar, a recovery rate of ~79% and the experimentally determined rejection rate, the *Tool* separates divalent ions like Mg and SO_4 from the feed. The retentate rich in these divalent ions is sent to another precipitator where Mg is precipitated in the form of $Mg(OH)_2$.

For the economic evaluation of the treatment chain, the annualized capital (CAPEX) and operating (OPEX) expenditures are computed assuming an interest rate of 6% and technology-specific depreciation periods. The Levelized cost of the product (in this case that of NF permeate or brine) is computed using the following equation, which also accounts for the potential revenues from $CaCO_3$ and $Mg(OH)_2$.

$$LBC\left[\frac{USD}{m^3{}_{brine}}\right] = \frac{CAPEX + OPEX - Revenue_{CaCO_3 + Mg(OH)_2}\left[\frac{USD}{year}\right]}{NF\ permeate\ or\ brine\left[\frac{m^3_{brine}}{year}\right]}$$

The general economic assumptions used to simulate the treatment chain are summarized in Table 5-11 below and are based on the previous work of (Micari et al., 2020).

Table 5-11. *Results for magnesium precipitation assays at three different NaOH concentrations*

Parameter	Value
Capacity factor of the plant [-]	0.94
Interest rate [%]	6
Electricity cost [USD/kWh$_{el}$]	0.1035
Na_2CO_3 [USD/ton]	275
$CaCO_3$ [USD/ton]	300
NaOH [USD/ton]	350
$Mg(OH)_2$ [USD/ton]	1200

5.4.2. Technical results of the RCE model

Results obtained by the RCE model regarding technical process parameters are summarized in Table 5-12. There is overall a good agreement between the experimental results and the results obtained with the model. The initial values for the initial brine do not agree exactly, because the RCE model requires a correction considering the principle of electroneutrality. The values corresponding to the experimental part are based on empirical analysis of the samples with inherent variability and do not always reflect exactly this principle.

For the nanofiltration unit, the RCE model results indicate rejection values of 54.3% in case of Mg, 97.9% in case of SO_4 and 0% for Cl. Mg rejection obtained in experimental nanofiltration tests was slightly higher (63.5%), but Cl and SO_4 rejection values are very close to those obtained with the model (0,8% for Cl and 98.9% for SO_4).

These results indicate that the RCE model can be a very effective tool to estimate the technical outcomes of this process.

***Table 5-12.** Technical results obtained by RCE model and laboratory experiments*

		Initial brine	After Ca precipitation	NF permeate	NF concentrate	After Mg precipitation
RCE model	Na [mg/L]	23057	23181	21178	33046	29926
	Cl [mg/L]	31608	31430	32750	32726	26962
	Ca [mg/L]	222	3,8E-14	8,5E-15	1,5E-13	1,2E-13
	Mg [mg/L]	416	414	189	1346	1,5E-13
	SO_4 [mg/L]	6045	6011	124	27253	22728
Lab experiments	Na [mg/L]	30100	29800	26600	38100	40600
	Cl [mg/L]	33500	35300	35000	37400	36600
	Ca [mg/L]	233	<50	<50	<50	<100
	Mg [mg/L]	441	417	152	1070	<50
	SO_4 [mg/L]	6330	7050	<80	25800	25800

5.4.3. Economical results of the RCE model

RCE model results are shown in Table 5-13 highlighting the revenue of the two main products that can be recovered from the treatment chain proposed in this study: $CaCO_3$ and $Mg(OH)_2$. The LBC value for this treatment is 38,81€/m^3. This value was calculated according to the corresponding formula shown above which already considers the market cost of both products commercialization. For these products, high quality and full standard requirements have been considered in this study. However, these aspects should be further explored.

The CAPEX and OPEX cost related to the treatment for brine valorization are 25.95€/m^3 and 12.86€/m^3, correspondingly.

***Table 5-13.** CAPEX and OPEX results from replication study*

Model input/output	Parameter	Units	Global (USD)	Global (EUR)
capex cryst_NaCarbo_CaCarbo	CAPEX Crystalization 1	$/y	$ 15,432.49	€ 13,117.62
opex cryst_NaCarbo_CaCarbo	OPEX Crystalization 1	$/y	$ 2,136.16	€ 1,815.74
revenue $CaCO_3$	Revenue $CaCO_3$	$/y	$ 2,096.12	€ 1,781.70
capex NF1	CAPEX Nanofiltration	$/y	$254,983.39	€ 216,735.88
opex NF1	OPEX Nanofilstration	$/y	$149,761.40	€ 127,297.19

Model input/output	Parameter	Units	Global (USD)	Global (EUR)
capex cryst_NaOH_ MgHydro	CAPEX Crystalization 2	\$/y	\$ 20,546.30	€ 17,464.35
opex cryst_NaOH_ MgHydro	OPEX Crystalization 2	\$/y	\$ 5,062.39	€ 4,303.03
revenue Mg(OH)2	Revenue $Mg(OH)_2$	\$/y	\$ 10,666.02	€ 9,066.11
CAPEX	Global CAPEX	\$/m^3	\$ 30.53	€ 25.95
OPEX	Global OPEX	\$/m^3	\$ 15.13	€ 12.86
LBC TOTAL	Total LBC	\$/m^3	\$ 45.65	€ 38.81

5.4.4. Sensitivity analysis of process profitability performances

A sensitivity analysis for all profits estimated from the experimental results is summarized below (Figure 5-19). The four end-products of interest, $CaCO_3$, $Mg(OH)_2$, Na_2CO_3 and NaOH, showed up no differences in terms of sensitivity analysis considering -50, -25, +25 and +50% deviation ranges. Therefore, it can be concluded that the estimations obtained after the analysis are confident and future investment to get any of the abovementioned products would have no risk as soon as the proposed scheme for their recovery from brines is maintained.

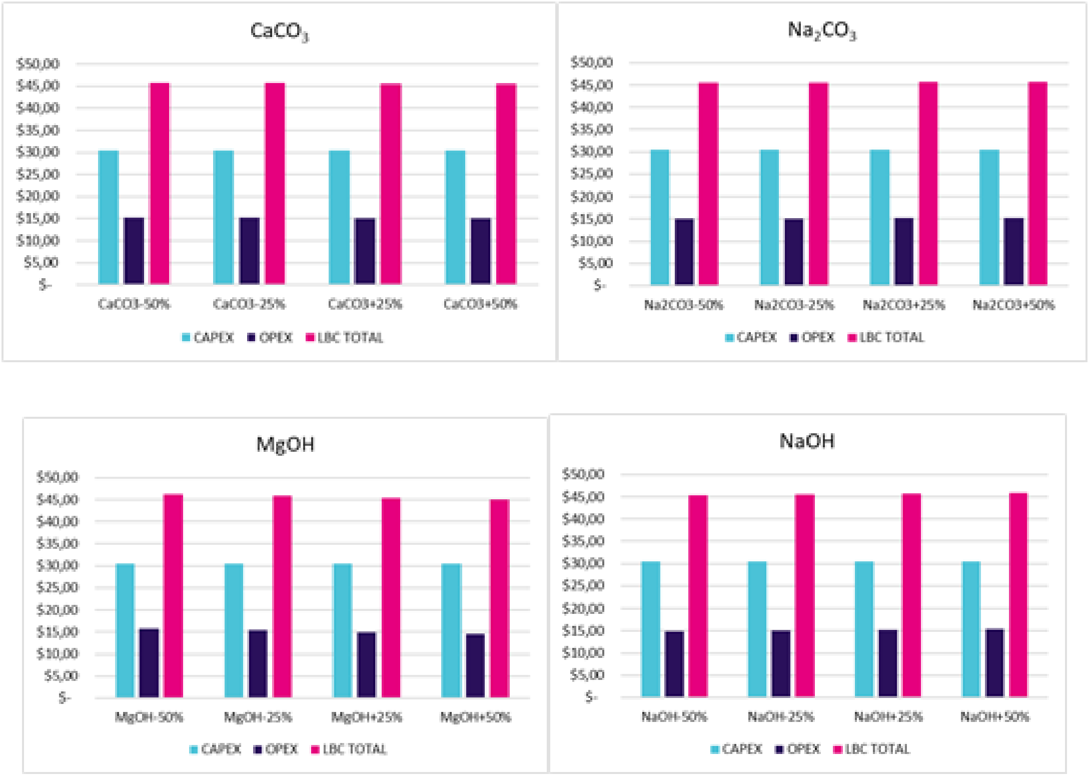

***Figure 5-19**. Cost sensitivity analysis for products with high value recovered from brine.*

5.5. Final discussion and overview of implementation potentials

According to data retrieved from FACSA and SITRA for status of desalination technologies in Spain, depending on the selected technology the exploitation cost for drinking water generation from high-salt concentration influents ranges from 0.111-0.134€/m^3. The lowest price is related to nanofiltration plants (0.111€/m^3), then inverse osmosis (0.129€/m^3) and finally electrodialysis (0.129€/m^3) (see Table 5-14). Considering these values, we can observe that further treatment of brine to recover products of interest would require a good balance in between revenue and the costs related to the technology since the costs are feasible and low from an economic viability point of view and in terms of drinking water production.

***Table 5-14.** Costs related to the produced volume of desalinated water (2020, AEDYR)*

	Units	Inverse Osmosis	Nanofiltration	Electrodialysis
CAPEX	€/m^3	150	160	170
OPEX	€/m^3	0.0066	0.0078	0.0215
Exploitation cost	**€/m^3**	**0.134**	**0.111**	**0.129**

As it can be seen in the following figures, when considering brine management from BWRO a related electrical consumption of 0.05 kW/h is commonly required while for SWRO is 0.27 kW/h. The distribution of the highest to the lowest electrical requirement for both kinds of water sources is shown in Figure 5-20. A reduction in terms of this cost would be required to ensure the feasibility of the proposed treatment for brine in this study to maintain the balance. However, the proposed scheme should include the cost of the recovered products, as expressed in the LBC value, to make feasible the coupling of the Zero Brine proposed scheme for brine management and salts recovery.

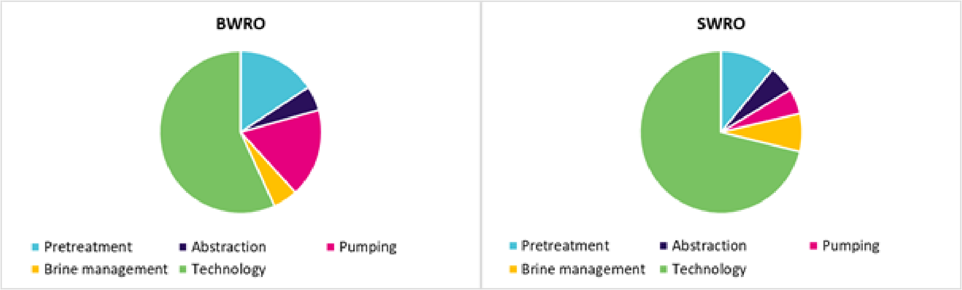

***Figure 5-20.** Distribution of electrical costs and requirements for BWRO and SWRO production, including brine management.*

Currently, the most common method for brine management is surface water discharge, as shown in Figure 5-21. The related cost to this method is mainly related to the pumping requirements and maintenance of the infrastructure. The cost for this strategy is estimated to be 5-15 € mm. According to the replicability study from the Zero Brine project, the proposed scheme has a higher exploitation cost compared to the conventional brine management practice: 38.81€/m^3. However, there is an indirect environmental benefit that is not reflected in the cost. Related to this, a penalty cost based on environmental protection measurements could modify the final cost of conventional brine management methods. The 13-39% increase in the cost when moving from the current scenario to the Zero Brine proposed scheme might not be feasible from a purely economic point of view. However, compared to other known brine management methods such as evaporation ponds might be a promising alternative. In this case, the cost ranges 34-136 for BWRO and SWRO, respectively which is +88% and +350% more expensive compared to the Zero Brine proposed treatment. Also, evaporation ponds do not allow direct recovery of salts and their consequent valorization for the market product.

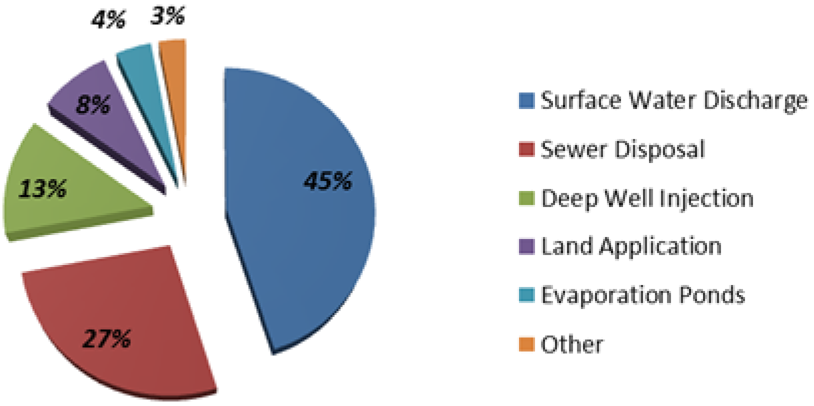

Figure 5-21. *Destination distribution for brine management (Katal et al. 2020)*

Table 5-15. *Average values for each brine treatment according to Katal et al. (2020)*

	€/mm average values	
	BWRO	**SWRO**
Surface water discharge	5,10	15,51
Sewer discharge	1,06	3,40
Deep well injection	5,10	17,00
Evaporation ponds	34,00	136,00
Land application	7,65	29,75

6. Dutch Replication Case Studies

6.1. Presentation of the Case Studies

To investigate the feasibility of using Eutectic Freeze Crystallization (EFC) for two replication industrial case studies, TU Delft conducted the transportation and experimental evaluation of the solutions proposed by Solvay and Grace companies.

Solvay is an international chemical company founded in 1863 to produce sodium carbonate by the Solvay process, the company has diversified into two main sectors of activity: chemicals and plastics. The Company produces soda ash, hydrogen peroxide, functional polymers, silica, surfactants, food and fragrance flavours, and other specialty polymers.

Grace is recognized as the global leader in specialty inorganic catalysts used in energy and refining, polyolefin and plastics, as well as petrochemical, and other chemical manufacturing applications. Grace entered the catalyst market in 1942 with the introduction of silica gel-based catalysts for fluid cracking. And since then, their product portfolio and the applications they serve have broadened with their core materials science focused around silica, alumina and silica-alumina chemistry. Grace is one of the few catalyst manufacturing leaders with the ability to produce both catalysts and supports.

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. EFC is a promising low-temperature desalination technique that can retrieve salt and water in pure form from the saline waste streams, at a relatively low energy demand compared to conventional evaporation based separation processes. It is a fairly recent technology that has been studied and applied mainly for the recovery of water and salts from wastewater.

In this report, a technical analysis of the sodium sulphate recovery process using the EFC technique at the pilot scale for the aqueous brine solution provided by Grace and Solvay companies is reported.

6.2. Pilot test experiment for two replication case studies

6.2.1. Experimental setup

For the purpose of performing pilot-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.

6.2.2. Crystallizer

For the pilot-scale EFC experiments, a triple-wall, cylindrical, glass vessel with a capacity of 5L is 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.

6.2.3. 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 poly-ethylene (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.

6.2.4. 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 400Ncm 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.

Figure 6-1 shows the 5L scraped cooled triple wall glass crystallizer used in this study for conducting batch crystallization experiments.

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.

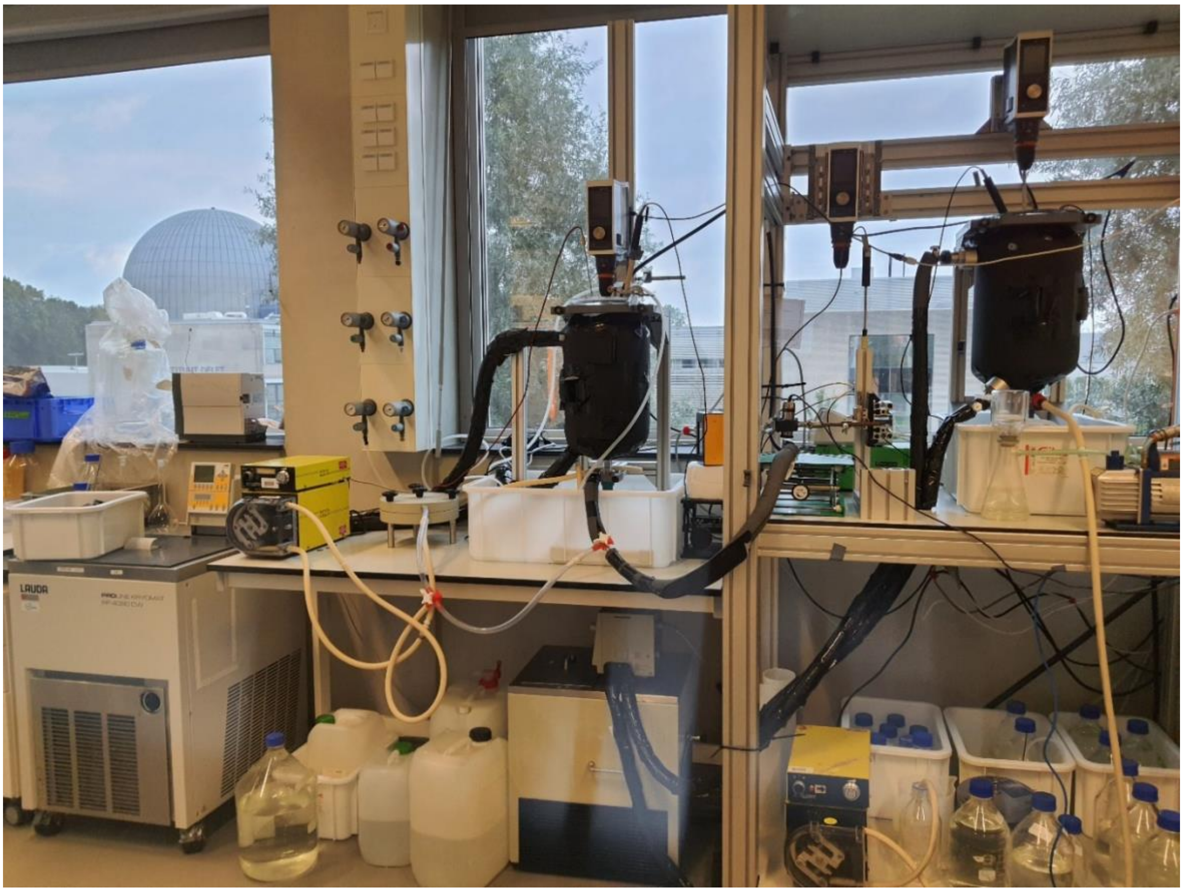

__Figure 6-1.__ Setup used for the EFC tests

6.3. Brine solution composition

The compositions of the brine solution provided by Solvay and Grace companies, for the EFC test, were analysed using IC (ion Chromatography, 883 Basic IC plus, Metrohm, Switzerland) and ICP-MS (Plasma Quant MS, Analytik Jena, Jena, Germany) setups. IC and ICP-MS were applied for the determination of the anions ($SO4^{-2}$ and Cl^{-}) and the cations (Ca^{+2}, K^{+}, Mg^{+2}, Na^{+}), respectively.

The analysis results of the brines solution provided by Solvay and Grace are summarized in Table 6-1 and Table 6-2, respectively.

__Table 6-1.__ The composition of the brine solution used in this study, provided by Solvay.

Ions	Concentration, mg/L
Ca^{+2}	75
K^{+}	38
Mg^{+2}	4
Na^{+}	13,058
Cl^{-}	59
SO_4^{-2}	35,319

Table 6-2. *The composition of the brine solution used in this study, provided by Grace.*

Ions	Concentration, mg/L
Ca^{+2}	40
K^{+}	14
Mg^{+2}	7
Na^{+}	8,049
Cl^{-}	-
SO_4^{-2}	19,818

6.4. Methodology

6.4.1. Eutectic Freeze Crystallization

In order to study the eutectic point of the Brine solution provided by Grace and Solvay, as well as to observe the performance of the system and the recovery of Na2SO4 crystals, EFC experiments were performed using a 5L setup.

50 mL of the initial solution provided by Grace and Solvay were taken as a sample for elemental analysis with Ion Chromatography and Inductively Coupled Plasma Mass Spectrometry.

5L of the brine solutions provided by Grace and Solvay were transferred to the 5L EFC setup to observe the eutectic conditions of the brine solution, observe the system and test the salt crystals for elemental impurities. The speed of the motor was set to 80 rpm and the system was cooled down and the temperature of the coolant solution was adjusted to -10^{o}C. After reaching and maintaining eutectic conditions for about 60 minutes, the cooling was stopped. Approximately 250mL of the slurry was removed from the bottom outlet of the reactor and transferred to the filtration setup in order to filter and wash the salt crystals.

6.4.2. Filtering & Washing of crystals

The effect of washing on the purity of the salt and ice 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 250mL removed from the reactor were filtered under vacuum, using the filtration setup that was described in the previous section. 5g of the unwashed crystals that remained on the filter and 20mL of the permeate are stored for elemental analysis.

The remaining cake of Na2SO4 crystals was washed using 25mL of saturated Na2SO4 solution. The saturated solution was poured into the Buchner filter and the slurry was stirred gently for a few seconds before turning on the vacuum. After the liquid was filtered out, 5g of the washed crystals are taken as a sample for analysis.

In the same way, ice crystal samples collected from the top of the crystallizer were filtered. The washing effect on the purity of the ice crystals was also tested. Ice crystals were washed using 250 ml Milli-Q water at 0^{o}C. After the Milli-Q water was filtered out, 5g of the washed ice crystals are taken as a sample for analysis.

6.4.3. 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 5mg /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 cations concentration with ICP-MS (Plasma Quant MS, Analytik Jena, Jena, Germany), using acidified Milli-Q water as blank.

For the IC analysis, Milli-Q water was used as blank and the concentrations of SO-4 and Cl- anions were measured using the Ion Chromatography setup (883 Basic IC plus, Metrohm, Switzerland).

6.5. Results and discussion

6.5.1. EFC test on the brine solution provided by Solvay

Figure 6-2 presents the temperature cooling profile of the solution provided by Solvay company.

$T_{Set\ point}$ indicates the set point temperature that we define, $T_{Coolant}$ is the temperature of the cooling liquid inside the LAUDA cooling bath and $T_{Reactor}$ is the temperature measured by the probe inside the EFC reactor.

The figure shows that after 43 minutes of cooling there was a temperature jump from -0.123 °C to -0.00 °C indicating the supersaturation and nucleation and growth of salt crystals, where the first salt crystals were clearly visible. The working solution became turbid at this temperature indicating the production of Na_2SO_4 crystals.

Upon further cooling, the crystallization of the salt increased and as a result, the concentration of the reactant solution decreased until the ice began to crystallize simultaneously with the salt product at -1.71 ° C. The release of the crystallization enthalpy at the nucleation resulted in the sudden rise of the reactant temperature, after a short period of time the temperature of the system gradually began to rise and finally, stabilized at the eutectic conditions at a temperature of approx to −1.14 ◦C where it reached a plateau.

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 the production of ice and Na2SO4 crystals continued. Furthermore, no ice scaling was visually observed on the walls of the reactor, which is also suggested by the low torque values of the stirrer. The trial was terminated, and the temperature was increased, when the solid contents of the reactor were considerably higher, approx. 100 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.

The eutectic temperature and composition for this solution system were obtained to be −1.14 ◦C and 2.388 wt%, respectively. There is a slight deviation compared to the temperature of the binary sodium sulphate and water mixture found in our previous study (-1.019°C). This slight depression of the eutectic point can be explained due to the freezing point depression caused by the impurities that are present in the working solution.

Before the eutectic point, about 20% of the sodium sulphate salt is recovered solely by cooling precipitation without ice formation.

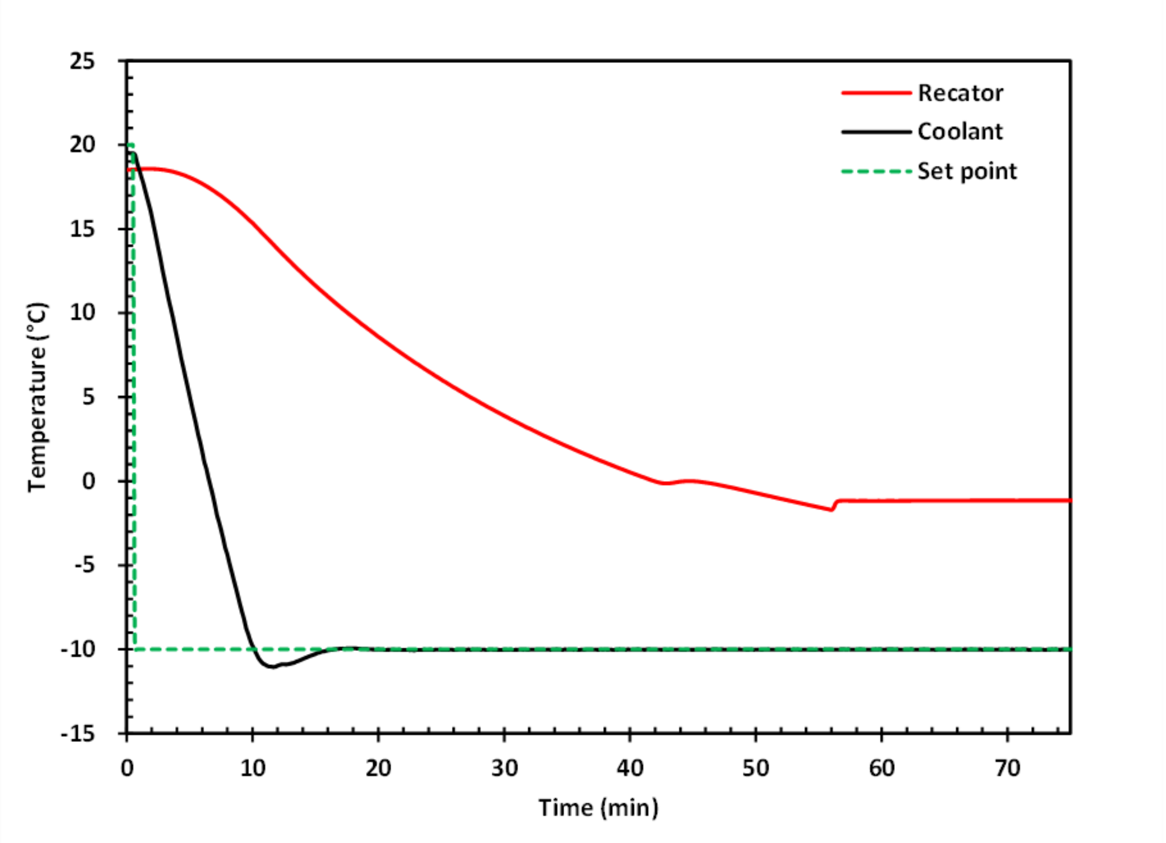

Figure 6-2. *The temperature profile for the solution provided by Solvay Company cooled from ambient to eutectic temperature.*

6.5.2. EFC test on the brine solution provided by Grace

Figure 6-3 presents the temperature cooling profile of the solution provided by Grace company. The figure shows that after 54 minutes of cooling there was a temperature jump from -2.94 °C to -0.82 °C indicating the ice nucleation and growth of ice crystals, where the first ice crystals were clearly visible.

Since the concentration of the solution provided by Grace company for the EFC tests was far less than the eutectic concentration, it was not possible to achieve the eutectic point and therefore solid and ice production simultaneously in one batch. Therefore, the solution had to be concentrated in sequential batches by separating ice formed.

The amount of ice formed determines the time of each batch. After the formation of about 10 to 15% ice in crystallizers, the cooling and stirring had to be stopped to remove the ice formed, first the concentrated salt solution had to be drained and transferred to the buffer tank, and then the ice had to be removed from the crystallizer by washing using tap water. The collected concentrated salt solutions of different batches in the buffer tank would be transferred to the crystallizer to repeat the concentration process. The concentration process had to be repeated in successive batches until the salt content in the solution approached the eutectic concentration. Cooling of the concentrated solution at the eutectic point would result in the simultaneous formation of ice and solid.

In practice, it was found that the feed concentration was too dilute for the EFC unit. Since in EFC unit in each batch solution can be concentrated up to 10 to 15%, to achieve the eutectic concentration of sodium sulphate, the sequencing batches had to be repeated several times. This was practically impossible due to the high volume of operational work.

The reason for the need for many consecutive batches was:

1. For proper separation, it was not possible to form more than about 10 to 15% ice per batch. After 10 to 15% ice had formed, the reactor had to be stopped to first remove the solution and then remove the ice from the reactor.
2. During drainage, some of the solution was lost along with the wet ice.
3. The initial volume of liquid inside the reactor for the batch should be about 5 litres. Therefore, taking into account the formed ice and the lost liquid along with the wet ice, about 3.5 to 4 liters were available for the next batch, therefore for instance four batches had to be run to feed up to about three next batches.

To solve the problem of excessive dilution of the initial solution, an evaporation system using air was installed to concentrate the feed to the EFC unit. Therefore, the EFC tests were performed on this concentrated feed. The eutectic temperature of the concentrated feed was obtained to be about -1.13^{o}C. Thereafter, simultaneous production of solid and ice occurred.

The eutectic point of the concentrated solution was close to the eutectic point of the pure sodium sulphate binary system, -1.109. This indicates that the slight presence of impurities does not have a significant effect on the eutectic temperature.

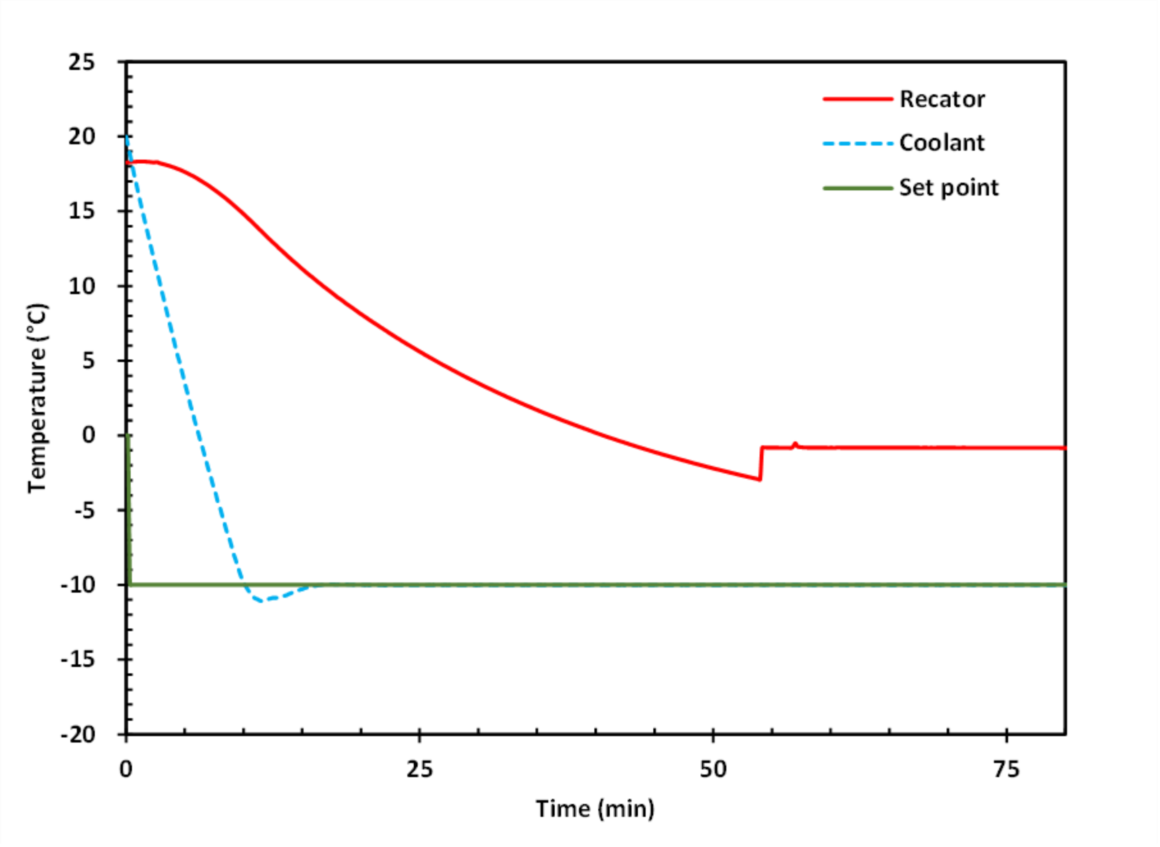

Figure 6-3. *The temperature profile for the solution provided by Grace Company cooled from ambient to Ice formation temperature.*

6.6. 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 SO_4 anions and with ICP-MS for the concentration of cations.

6.6.1. Quality of the crystal products from the brine solution provided by Solvay

For the solution provided by Solvay, before the eutectic point, about 20% of the sodium sulphate salt is recovered solely by cooling precipitation without ice formation. The purity of sodium sulphate salt obtained before the eutectic point, without rinsing with saturated sodium sulphate solution, was about 98.88%. The total sodium sulphate salt obtained after the eutectic point had a purity of 99.95%, which increased to 99.97% after one wash of saturated sodium sulphate solution.

6.6.2. Quality of the crystal products from the brine solution provided by Solvay

For the solution provided by Grace, the purity of sodium sulphate salt obtained without rinsing with saturated sodium sulphate solution was about 99.11%, which increased to 99.85% after one wash of saturated sodium sulphate solution.

6.7. Final discussion and overview of implementation potentials

There are two important advantages to using EFC as a separation technique. This technique can lead to a significant reduction in energy consumption and is usually suitable for producing highly pure products.

Pilot-scale tests for two replication industrial case studies were performed in order to study the eutectic conditions of the system and to evaluate the quality of crystalline products using a 5L EFC Setup.

The 5L EFC testes were 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 scrapper was very efficient.

The eutectic temperature of the Brine solution provided by Solvay was found to be approx. -1.14^{o}C, which is slightly lower compared to the temperature found for the binary sodium sulfate-water mixture in our previous study which was -1.019 ^{o}C. This depression of the eutectic point is caused due to the small impurities in the solution. Due to the high purity of the initial solution provided by Solvay, the quality of sodium sulphate obtained was also high and about 99.95%, which increased to 99.97% after rinsing with saturated sodium sulphate solution.

The brine solution provided by Grace for the batch EFC unit was very dilute. Therefore, before the FEC test, the brine solution was concentrated using an evaporation system. The eutectic temperature of the Brine solution provided by Grace was found to be approx. -1.13^{o}C, which is also slightly lower compared to the temperature found for the binary sodium sulphate-water mixture at -1.019 ^{o}C. The purity of the initial solution provided by the Grace was also high, so the quality of the sodium sulphate obtained was also high, about 99.11%, which increased to 99.85% after washing with saturated sodium sulphate solution.

The recommendation for the full-scale application is to design a continuous crystallizer made of stainless steel. With the possibility of separating ice and solid in place as well as using two filter belts for continuous washing of ice and solid crystals, respectively.

If a continuous system is used, the dilute solution provided by Grace can also be fed directly to the crystallizer. Of course, economic calculations can determine whether another concentration unit before the EFC is necessary or not.

7. Conclusions of the replication studies

In this deliverable, six replication case studies examined the brines originated from the following industries: one seawater desalination plant in Nisyros island, Greece, one seawater desalination plant in Pantelleria island, Italy, one coal mine (Dębieńsko) in Poland, one desalination plant in Spain and finally two precipitated silica industries, SOLVAY in France and GRACE in Germany. In Table 7-1, the brine compositions of the different replication studies are provided. We can observe that the composition varies in the different sectors, with the Total Dissolved Solids having a range from 30,000 ppm to almost 73,000 ppm.

Table 7-1. *Brine concentration for the different replication studies*

Ions	Brine Concentration (mg/L)						
	Greek CS (Seawater Desalination)	**Italian CS** (Seawater Desalination)	**Polish CS** (Coal Mine)		**Spanish CS** (Desalination)	**Dutch CSs** (Pr. silica)	
			Budryk	Budryk miernie		**SOLVAY**	**GRACE**
Na$^+$	13,551	21,400	43,783	10,476	24,720	13,058	8,049
Cl$^-$	24,561	39,000	43,783	19,790	40,020	59	-
Mg^{+2}	1,520	2,700	1,152	665	452	4	7
Ca^{+2}	575	880	960	524	344	75	40
SO$_4^{-2}$	2,770	5,500	1,171	356	2,901	35,319	19,818
TDS	42,907	70,000	72,682	30,802	69,401	48,553	27,928

7.1. Bench-scale Tests

For each case study, bench-scale tests were performed and the results could be summarized as follows:

7.1.1. Greek Replication Study

The results from the bench scale tests for the respective technologies were:

For the **Nanofiltration:**

- The highest possible divalent ions (Magnesium and Calcium) rejection – around **80%**
- The lowest monovalent (Sodium and Chloride) rejection – around **45%**

For the **Reverse Osmosis:**

- Rejection of divalent ions **-** more than **80%**
- Rejection of monovalent ions - more than **85%**

For the **Magnesium and calcium precipitation with crystallizer**:

- No bench-scale experiments were performed. Instead, the quantity of the recovered minerals was simulated via the RCE platform.

For the **Multiple Effect Distillation (MED)**:

- Quality and quantity of the inlet brine solution

Inlet Brine Volume (L)	Sodium (mg/L)	Chloride (mg/L)	Magnesium (mg/L)	Calcium (mg/L)	Inlet brine TDS (mg/L)
100	19,987	30,860	12	25	50,884
100	21,700	35,468	11.6	22.3	57,201

- Quality and quantity of the concentrated brine solution

Concentrated Brine Volume (L)	Sodium (mg/L)	Chloride (mg/L)	Magnesium (mg/L)	Calcium (mg/L)	Concentrated brine TDS (mg/L)
30	67,987	123,900	43.1	84.3	192,014
25	86,800	133,872	56.4	90.4	220,818

7.1.2. Italian Replication Study

The results from the bench scale tests for the respective technologies were:

For the **Nanofiltration**:

- Model equations were validated with literature information

For the **Magnesium/calcium hydroxide crystallizer (MF-PFR):**

- Magnesium hydroxide precipitation step – Magnesium recovery ranged from about **90% (test A) up to almost 99% (test C)** implying partial recovery. The recovery of the magnesium is affected by the value of the pH. Indeed, the lower recovery is obtained due to the outlet pH equal to 10.3, while the higher value of the recovery is obtained at pH equal to 10.4.
- Calcium hydroxide precipitation step - Calcium recovery ranged from about **96% (test A) down to 95% (test C)**. Nevertheless, the outlet pH was kept equal to 13, which allows the complete precipitation of calcium. However, tested brines required a reaction pH higher than 13 due to the high calcium concentration in the inlet brine.

For the **Multiple Effect Distillation (MED):**

- Results obtained from the bench scales tests in Greek Replication Studies.

For the **Sodium Chloride (NaCl) crystallizer:**

- Model equations were validated with literature information

7.1.3. Polish Replication Study

The results from the bench scale tests for the respective technologies were:

For the **Nanofiltration**:

- Model equations were validated with literature information

For the **Reverse Osmosis**:

- Model equations were validated with literature information and other projects

For the **Electrodialysis**:

- The maximum ED concentrate salinity was established as 241 g/dm^3 as NaCl (146 g/dm^3 as Cl) which was high enough for the implementation of ZERO BRINE technology at the Dębieńsko site, especially with the rock salt being added.

7.1.4. Spanish Replication Study

The results from the bench scale tests for the respective technologies were:

For the **Chemical precipitation of $CaCO_3$**

- Optimal precipitation conditions - addition of 0.8 g/L of Na_2CO_3 and pH correction to 9.5 with NaOH (5 L of brine)

For the **Nanofiltration**:

- Mg rejection – **63.5%**
- Cl rejection **- 0.8%**
- SO_4 rejection **– 98.9%**
- K rejection – **11.5%**

For the **Chemical precipitation of $Mg(OH)_2$:**

- The optimal condition for Mg precipitation was the addition of 6 g/L of brine of NaOH, which resulted in a final Mg concentration in the brine of <50 mg/l

For the **Evaporation for Na_2SO_4 precipitation:**

- Theoretical analysis**:** a maximum of 0.27 mol/L of Na_2SO_4 could be recovered from the brine. This corresponds to 38.2 g/l of Na_2SO_4.

7.1.5. Dutch Replication Studies

The results from the bench-scale tests for Eutectic Freeze Crystallization were:

For **SOLVAY**:

- Before the eutectic point, about 20% of the sodium sulphate salt is recovered solely by cooling precipitation without ice formation.
- The purity before the eutectic point was about 98.88%.
- The total sodium sulphate salt obtained after the eutectic point had a purity of 99.95%, which increased to 99.97% after one wash of saturated sodium sulphate solution.

For **GRACE**:

- The purity of sodium sulphate salt obtained without rinsing with saturated sodium sulphate solution was about 99.11%, which increased to 99.85% after one wash of saturated sodium sulphate solution.

7.2. Simulation Campaign & Estimated economic potentials

Following the bench-scale tests, the proposed treatment chains were simulated in the DLR's RCE platform for all the replication studies except the Dutch ones since the Eutectic Freeze Crystallization was not simulated in the RCE. Furthermore, the technical and economic results for each study were presented.

7.2.1. Greek Replication Study

The economic analysis showed that the proposed system has a revenue approximately equal to the CAPEX and OPEX of the proposed system. The main profit from the proposed system is coming from the $Mg(OH)_2$ and the NaCl recovery. The economic feasibility of the proposed system combined with the ZLD principle makes such systems compelling. In Nysiros especially, renewable energy can be used for the electric demand of the proposed train. Geothermal energy, solar and wind energy can be used for the operation leading to the minimization of the system operating cost. It has to be noted that for the estimation of the revenues from NaCl, it was assumed that the concentrated brine from the MED evaporator was sent into salt ponds where the water can be evaporated.

7.2.2. Italian Replication Study

The results of the techno-economic analysis for the Italian Case Study demonstrated the economic feasibility of the proposed MLD chain. Such feasibility is exclusively possible thanks to the sale of valuable goods such as $Mg(OH)_2$ and NaCl (products that mainly contribute to the total revenue of the chain). In particular, taking into account the magnesium present in the total amount of brine produced in Sicily it is possible to achieve revenues as high as 90 million €/yr. As for NaCl, revenues could amount up to 47 million €/yr, respectively. Furthermore, it was demonstrated that the applied MLD system can be a useful alternative integrated technology for the production of valuable goods and for brine disposal. As a matter of fact, it was shown that the Brine Treatment Specific Cost (BTSC) was much lower than the cost concerning conventional brine disposal methods, making the MLD system an extremely better alternative for brine treatment.

7.2.3. Polish Replication Study

The results of techno-economic simulations showed that the ZERO BRINE technology has a potential for commercialization when applied for the treatment of coal mine wastewater. The economic analysis showed that the initial investment can be returned within a few years and the full-scale implementation could be profitable. In particular that the investment of retrofitting the NF pretreatment into the existing technology is returned within 2 years and in the case of full-scale ZERO BRINE implementation, it takes 4 years for the initial investment to pay for itself. Without the $Mg(OH)_2$ revenue stream, the full-scale ZERO BRINE implementation will return the investment cost within 6 years, whereas recovering the $Mg(OH)_2$ shortens this time to just 4 years and makes the investment in new technology competitive.

7.2.4. Spanish Replication Study

Currently, the most common method for brine management is surface water discharge. The related cost to this method is mainly related to the pumping requirements and maintenance of the infrastructure. The cost for this strategy is estimated to be 5-15 €/m^3. According to the replicability study of the Zero Brine project, the proposed scheme has a higher exploitation cost compared to the conventional brine management practice and amounts up to 38.81 €/m^3. However, there is an indirect environmental benefit that is not reflected in the cost. Related to this, a penalty cost based on environmental protection measurements could modify the final cost of conventional brine management methods. The 13-39% per cent increase in the cost when moving from the current scenario to the Zero Brine proposed scheme might not be feasible from a purely economic point of view. However, compared to other known brine management methods such as evaporation ponds might be a promising alternative. In this case, the cost is up to 34€/m^3 and 136€/m^3 for BWRO and SWRO, respectively which is +88% and +350% more expensive compared to the Zero Brine proposed treatment. Also, evaporation ponds do not allow direct recovery of salts and their consequent valorization for the market product.

8. Roadmap for Replicability

ZERO BRINE aims to close the loop of the problematic brine effluents through the recovery of water and minerals. During the project, four case studies were developed to demonstrate the ZERO BRINE systems under different industrial circumstances: (1) Industry water sector in the Netherlands (WP2), (2) Coal mine sector in Poland (WP3), (3) Textile sector in Turkey (WP3) and (4) Precipitated Silica sector in Spain (WP4).

Furthermore, throughout the project implementation, five Brine Excellence Centers (BECs) have been developed; the central BEC facility has been established in the Netherlands (TU DELFT), while four satellite BECs have been developed in Poland (SUT), Spain (EURECAT), Greece (NTUA) and Italy (UNIPA). These facilities altogether comprise a fully-equipped set of bench- and pilot-scale systems covering the whole chain of innovative and enabling brine treatment technologies. This equipment was the main tool for the replication of the project results to other process industry sectors (see Figure 8-1).

Based on the research and experiments that have been done for the 4 demonstration Cases Studies (see also *D8.5 Business plans for four industrial sectors*) and the 6 replication Case Studies presented in this report, the following results can be drawn with respect to the replicability of the project outcomes:

Precipitated Silica Sector

Based on the discussions we had with key players in the precipitated silica industry such as IQE (Demonstration CS in Spain) and GRACE and SOLVAY (Dutch replication CSs - Section 6), precipitated silica producers wish to expand their business due to the strategy based on the anticipated green tyres market growth; truck tyres are of special importance for the EU. Many of the key industries in the sector are unable to meet the anticipated market demands due to local regulatory restrictions that forbid the discharge of more wastewater effluent to the surface water bodies. This is a limiting factor for their business growth.

The application of ZERO BRINE technologies allows achieving almost 80% of water recovery, promoting water reuse and reducing significantly costs derived from water consumption and wastewater management. Furthermore, ZERO BRINE aims to provide technologies for the recovery of sodium sulphate that can be sold in other markets for industrial use.

As a consequence, new, innovative technologies are urgently needed to enable a transition towards a circular economy and Zero Pollution practices. This requires systemic innovation, including not only technical but also business model and regulatory innovation, including all relevant stakeholders. The great replicability potential of this industry is shown by the decision of IQE to go for full-scale implementation. They led the preparation of a LIFE programme "Valorisation of precipitated silica wastewater through circular economy strategy for sodium sulphate and water recovery". With further pursuing follow-up activities with the stakeholders that we have established communication and collaboration, namely SOLVAY, GRACE and IQE, we can reach up to high replication potential for this sector (see also *D8.6 Business plans for participating SMEs*). More particularly, in terms the representation of the abovementioned companies is translated to 5 out of 11 precipitated plants in the EU (>45%), while in terms of capacity, the replication potential is even higher, with 290,000 metric ton of precipitated silica being produced in these plants, out of the total 597,000 tons produced in Europe (or 48.6%) (see also Table 8-1).

Table 8-1. *Replication potential for the precipitated silica sector (European Commission, 2017)*

Country	Company	Capacity (Metric tons/year)
GERMANY	EVONIK	195,000
	GRACE	40,000
ITALY	SOLVAY	25,000
POLAND	SOLVAY	85,000
FRANCE	SOLVAY	100,000
UK	PQ Corp	20,000
BELGIUM	EVONIK	10,000
SPAIN	IQE	40,000
	EVONIK	40,000
NL	PGG Europe	27,000
FINLAND	EVONIK	15,000
	Total	**597,000**

Industry Water Sector

The main conclusion for this sector, in reference to the Case Study of Evides Industriewater at the Botlek site of the Port of Rotterdam, is that for the time being, implementing a circular business around the Zero Brine technologies is not feasible, mainly due to the lack of a solid business case. This stems from different factors such as the lack of regulation about the discharge of brines, no water scarcity issues in the areas etc. (see also *D8.2 Report on the circular business model suggested for the large-scale demonstration in Rotterdam Port*).

As a result, the replication case studies focused on brines generated from the desalination sector (Greek replication CS – Section 2, Italian replication CS – Section 3, Spanish replication CS - Section 5). Based on the results of this report, it is evident that the application of ZERO BRINE systems makes the investment compelling mainly due to the profit from the recovered valuable goods such as $Mg(OH)_2$ and NaCl and the recovery of water since some areas, especially the islands, are suffering from water scarcity. An important factor to take into consideration is the application of renewable energy in the Zero Brine systems. An example is Nysiros island, in which geothermal, solar and wind energy can be used for the operation leading to the minimization of the systems operating cost.

The seawater desalination industry comprises an important target sector for the ZERO BRINE project since the composition of the seawater does not vary significantly among the different regions, making the ZERO BRINE solution widely applicable and with high replicability potential. Furthermore, traditional seawater desalination produces brine that is twice as salty as seawater, and it is energy-intensive. The replication potential is also shown by the number of desalination plants that operate in Mediterranean-EU countries (Table 8-2) and GCC countries (Table 8-3).

Table 8-2. *Replication potential (Mediterranean-EU countries) for seawater desalination sector (UNFCC, 2019)*

Country	Number of Plants	Installed Capacity (m^3/day)
Portugal	18	16,319
Spain	153	4,724,116
France	59	220,604
Italy	292	609,963
Malta	31	251,151
Greece	197	149,250
Cyprus	28	228,853
Total	**760**	**6,190,902**

Table 8-3. *Replication potential (GCC countries) for seawater desalination sector (UNFCC, 2019)*

Country	Number of Plants	Installed Capacity (m^3/day)
Bahrain	18	1,094,060
Kuwait	153	3,514,125
Oman	59	1,642,037
Qatar	292	2,174,741
Saudi Arabia	31	14,527,639
UAE	197	9,387,205
Total	**760**	**32,339,807**

It is important to note that the Greek islands have an immediate replication potential of the ZERO BRINE project. There are more than 90 desalination plants installed at the islands serving the drinking water needs of the local populations. The dependence on desalination to meet drinking water needs in islands is as high as 100%, as the only alternative is water transportation through ships that is affected by weather conditions, and it is not cost-efficient.

Coal Mine Sector

Coal production comes with a high environmental cost at the regional (or even national) level. The exploitation of hard coal mines leads to the generation of vast amounts of salty wastewater effluents (brines) which have severe environmental impacts. Several policies have been introduced by the EC that address the environmental effects of coal mining with the most important being the Water Framework Directive and the European Green Deal. The carbon neutrality path to 2050 is of essential importance for the EU. Although coal mining is being phased out in favor of alternative, cleaner sources of energy, it is still very important for the metallurgical industry. Coking coal is considered to be a critical raw material by the European Union. Deep mining of hard coal generates the problem of saline wastewater, as the mines need constant dewatering.

The demonstration case study in Poland showcased that the main reason coal mine industry is interested in new technologies such as ZERO BRINE for brine reuse and treatment is that environmental authorities require the mines to pay fines based on the total amount of chloride and sulphate ions discharged (€/kg of salt in discharged water). Currently, PGG can discharge the produced brine in the nearby river (Vistula river) by diluting it with industrial wastewater without significant costs. However, in accordance with the WFD and the EU Green Deal, it is expected that the regulations in Poland about brine discharge will be tighter and the fines will be higher. Then, there will be the need to move towards sustainable systems for the treatment of brines, like Zero Brine.

The Dębieńsko wastewater treatment plant is treating brine leading to Zero Liquid Discharge (ZLD) as well as salt recovery since the '80s. However, its main drawback is the extremely high energy consumption (approx. 720 kWh/t of salt recovered), which has a high impact on the business viability and financial outcome. Based on the Polish replication case study (see Section 4), ZERO BRINE showed that improved energy efficiency and environmental performance is possible. The new plant design offers the opportunity to recover salt, pure water, gypsum and magnesium hydroxide and the energy efficiency of the Dębieńsko plant is improved by approx. 30% (approx. 500 kWh/t of salt recovered). The company running the only salt production plant in Poland (Dębieńsko), PGWiR, is considering the implementation of membrane-based Zero Liquid Discharge (ZLD) systems and has confirmed its interest in the results of the ZERO BRINE project. As their current technology approaches the end of life, there is a strong possibility they will invest in the presented solution, either directly or by applying for external funding. With further pursuing follow-up activities with the stakeholders that we have established communication and collaboration, namely JSW, PGG, TAURON, PG SILESIA, BOGDANKA, WĘGLOKOKS which represents all the coal mines in Poland, we can reach up to high replication potential for this sector. This potential is going to be further examined through the LIFE programme "Demonstration of an advanced technique for eliminating coal mine wastewater (brines) combined with resource recovery" that the Innovation Manager of the ZERO BRINE project, Dr Dimitris Xevgenos, originated and prepared.

Textile Sector

In Zorluteks (Turkish demonstration CS), the water recovery and reuse are very limited, and despite withdrawing fresh process water bears relatively low costs for Zorlu, the organization is committed to increasing sustainability and bringing its processes towards a full circular layout. Taking into consideration the ZERO BRINE results, Zorlu is currently evaluating a considerable capital investment opening to enlarge the capacity for the advanced treatment up to 100%.

However, in the case of Turkey (demonstration CS) and some countries in the EU, there are no limits of some parameters for water discharge with respect to the textile sector. As a result, companies would prioritize breakeven and profits since they are not obligated or forced to be environmentally responsible. A substantial change of mindset or the application of stricter regulation with regards to the environment in the textile sector is needed in order for ZERO BRINE to have a business case and replicability potential in this sector.

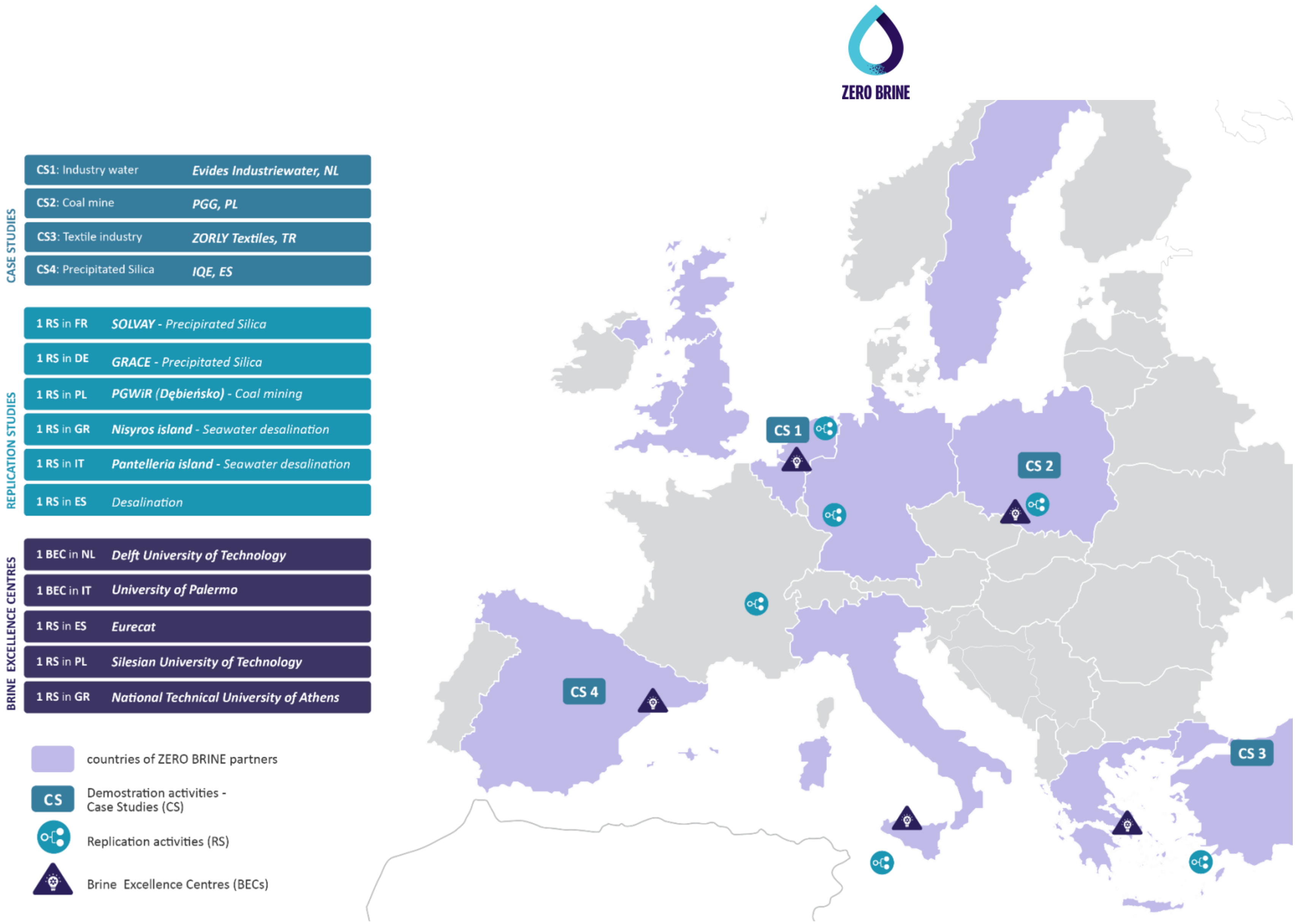
ZERO BRINE
CASE STUDIES
CS1: Industry water
Evides Industriewater, NL
CS2: Coal mine
PGG, PL
CS3: Textile industry
ZORLY Textiles, TR
CS4: Precipitated Silica
IQE, ES
REPLICATION STUDIES
1 RS in FR
SOLVAY - Precipirated Silica
1 RS in DE
GRACE - Precipitated Silica
1 RS in PL
PGWiR (Dębieńsko) - Coal mining
1 RS in GR
Nisyros island - Seawater desalination
1 RS in IT
Pantelleria island - Seawater desalination
1 RS in ES
Desalination
BRINE EXCELLENCE CENTRES
1 BEC in NL
Delft University of Technology
1 BEC in IT
University of Palermo
1 RS in ES
Eurecat
1 RS in PL
Silesian University of Technology
1 RS in GR
National Technical University of Athens
countries of ZERO BRINE partners
CS
Demostration activities - Case Studies (CS)
Replication activities (RS)
Brine Excellence Centres (BECs)
CS 1
CS 2
CS 3
CS 4

Figure 8-1. *Demonstration & Replication activities and BECs of ZERO BRINE project*

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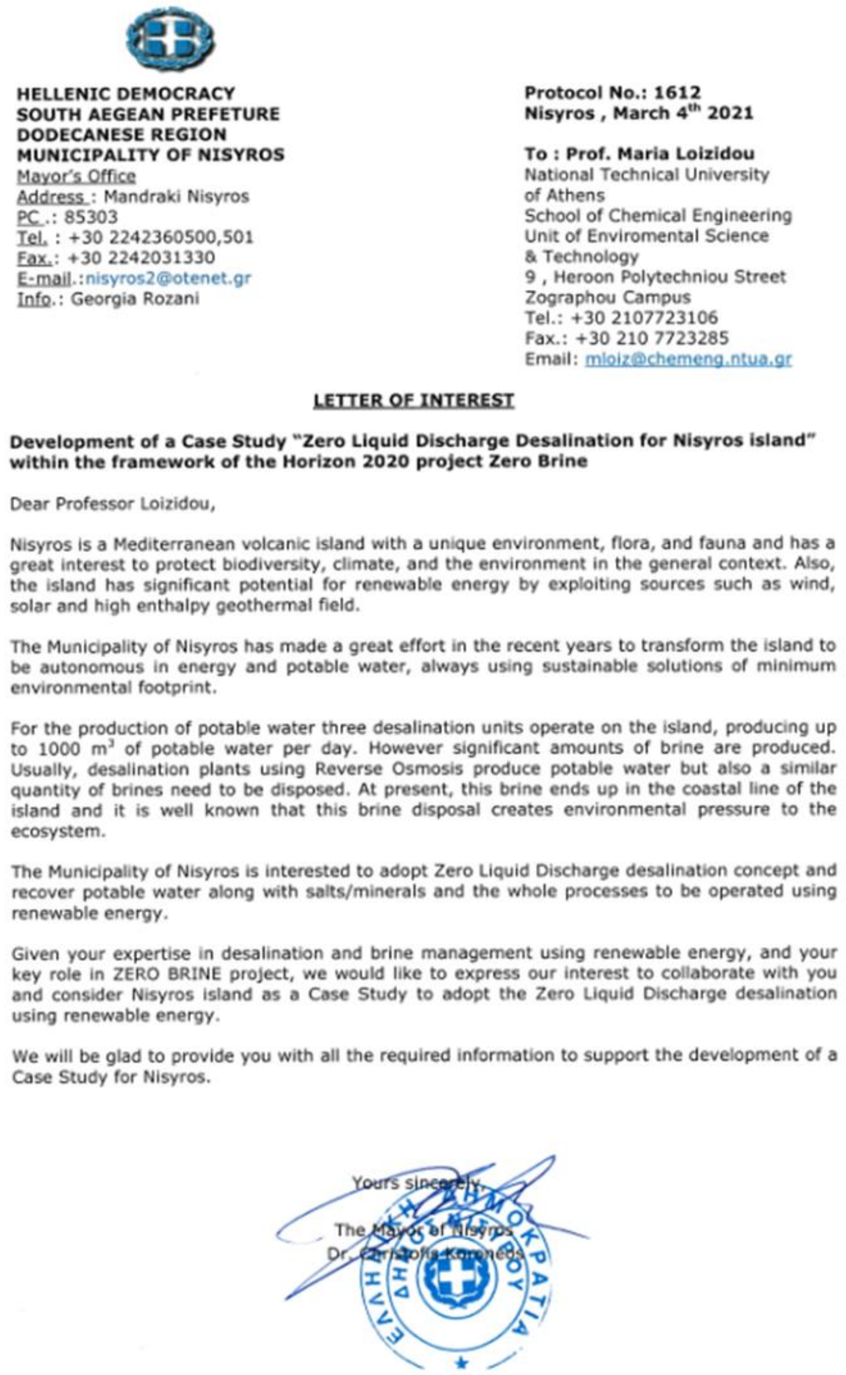
Annexes

Annex A: **Letter of interest** - *Greek Replication Case Study*



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Protocol No.: 1612
Nisyros , March 4th 2021

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LETTER OF INTEREST

Development of a Case Study "Zero Liquid Discharge Desalination for Nisyros island" within the framework of the Horizon 2020 project Zero Brine

Dear Professor Loizidou,

Nisyros is a Mediterranean volcanic island with a unique environment, flora, and fauna and has a great interest to protect biodiversity, climate, and the environment in the general context. Also, the island has significant potential for renewable energy by exploiting sources such as wind, solar and high enthalpy geothermal field.

The Municipality of Nisyros has made a great effort in the recent years to transform the island to be autonomous in energy and potable water, always using sustainable solutions of minimum environmental footprint.

For the production of potable water three desalination units operate on the island, producing up to 1000 m^3 of potable water per day. However significant amounts of brine are produced. Usually, desalination plants using Reverse Osmosis produce potable water but also a similar quantity of brines need to be disposed. At present, this brine ends up in the coastal line of the island and it is well known that this brine disposal creates environmental pressure to the ecosystem.

The Municipality of Nisyros is interested to adopt Zero Liquid Discharge desalination concept and recover potable water along with salts/minerals and the whole processes to be operated using renewable energy.

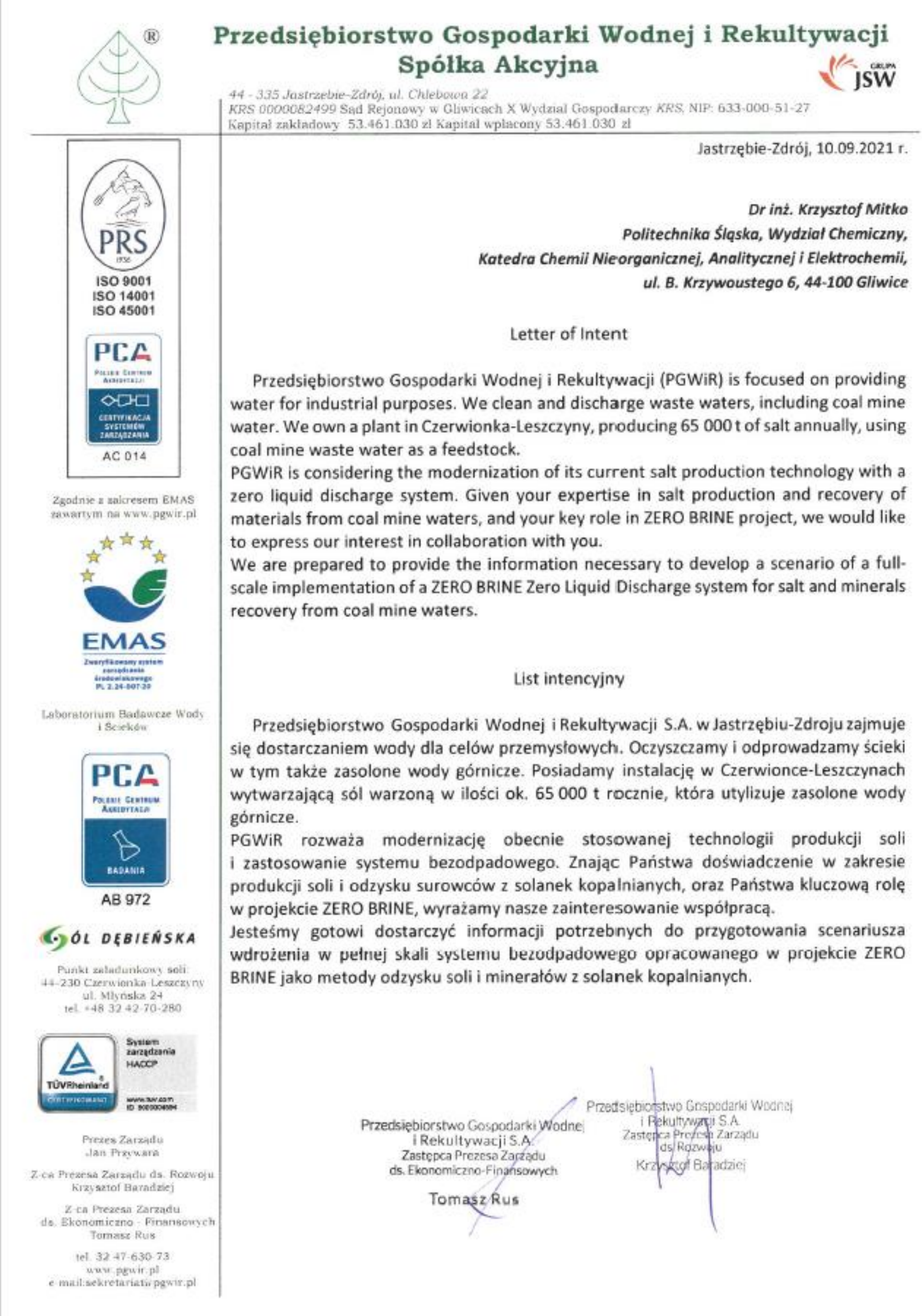
Given your expertise in desalination and brine management using renewable energy, and your key role in ZERO BRINE project, we would like to express our interest to collaborate with you and consider Nisyros island as a Case Study to adopt the Zero Liquid Discharge desalination using renewable energy.

We will be glad to provide you with all the required information to support the development of a Case Study for Nisyros.

Yours sincerely,

The Mayor of Nisyros
Dr. Christoforos Koroneos

Annex B: **Letter of intent** - *Polish Replication Case Study*



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Spółka Akcyjna

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Kapitał zakładowy 53.461.030 zł Kapitał wpłacony 53.461.030 zł

Jastrzębie-Zdrój, 10.09.2021 r.

Dr inż. Krzysztof Mitko
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Letter of Intent

Przedsiębiorstwo Gospodarki Wodnej i Rekultywacji (PGWiR) is focused on providing water for industrial purposes. We clean and discharge waste waters, including coal mine water. We own a plant in Czerwionka-Leszczyny, producing 65 000 t of salt annually, using coal mine waste water as a feedstock.

PGWiR is considering the modernization of its current salt production technology with a zero liquid discharge system. Given your expertise in salt production and recovery of materials from coal mine waters, and your key role in ZERO BRINE project, we would like to express our interest in collaboration with you.

We are prepared to provide the information necessary to develop a scenario of a full-scale implementation of a ZERO BRINE Zero Liquid Discharge system for salt and minerals recovery from coal mine waters.

List intencyjny

Przedsiębiorstwo Gospodarki Wodnej i Rekultywacji S.A. w Jastrzębiu-Zdroju zajmuje się dostarczaniem wody dla celów przemysłowych. Oczyszczamy i odprowadzamy ścieki w tym także zasolone wody górnicze. Posiadamy instalację w Czerwionce-Leszczynach wytwarzającą sól warzoną w ilości ok. 65 000 t rocznie, która utylizuje zasolone wody górnicze.

PGWiR rozważa modernizację obecnie stosowanej technologii produkcji soli i zastosowanie systemu bezodpadowego. Znając Państwa doświadczenie w zakresie produkcji soli i odzysku surowców z solanek kopalnianych, oraz Państwa kluczową rolę w projekcie ZERO BRINE, wyrażamy nasze zainteresowanie współpracą.

Jesteśmy gotowi dostarczyć informacji potrzebnych do przygotowania scenariusza wdrożenia w pełnej skali systemu bezodpadowego opracowanego w projekcie ZERO BRINE jako metody odzysku soli i minerałów z solanek kopalnianych.

Przedsiębiorstwo Gospodarki Wodnej
i Rekultywacji S.A.
Zastępca Prezesa Zarządu
ds. Ekonomiczno-Finansowych

Tomasz Rus

Przedsiębiorstwo Gospodarki Wodnej
i Rekultywacji S.A.
Zastępca Prezesa Zarządu
ds. Rozwoju

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