

D4.3 Innovative technologies for recovering compounds in the precipitated silica industry

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¹ **R**=Document, report; **DEM**=Demonstrator, pilot prototype; **DEC**=website, patent fillings, videos, etc.; **OTHER**=other ² **PU**=Public; **CO**=Confidential, only for members of the consortium (including the Comission Services), **CI**=Classified

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Executive summary

This deliverable includes results from Task 4.1. This task started in June 2017 (M1) and had to be finalized in May 2020 (M36). Most of the tasks have been finalized except Subtask 4.1.3 lasted from Jun2019 to May 2020. This task involves laboratory experiments, some of them scheduled for March-May 2020. Due to COVID-19 laboratories at EURECAT were closed and it was not possible to finalize experimentation. For this reason, this deliverable has been submitted as a draft in May 2020 according the Grant Agreement, and a final version of this deliverable including EDBP final results will be submitted in December 2020.

Task 4.1 focused on the evaluation at laboratory-scale of innovative processes for treating wastewater from silica industry based on the concept of economy circular and promoting the resource efficiency by recovering resources. These recovery processes involve a pre-treatment of the effluent, membrane technologies for the separation and concentration of salts from water and thus water recovery, and crystallization processes for the recovery of salts.

Specifically, membrane technologies tested are pressure-driven filtration with regenerated membranes (Deliverable D4.2) and Electrodialysis with bipolar membranes (EDBP). Regenerated membranes provided two effluents: water for reuse (permeate) and concentrated brine (concentrate) to be further treated by crystallization technologies to recover salts. The EDBP process is meant to obtain NaOH and H₂SO₄ as valuable reagents out of the brine considered wastewater. Crystallization processes assessed in this project include eutectic freeze crystallization (EFC) and evaporation. The driving force of both processes is temperature however for EFC cooling is required whilst evaporation benefits from high temperatures. In the EFC process precipitated salt and highly pure ice are achieved providing thus water for reuse and highly pure salt for production processes. During evaporation, salt is as well recovered which can also be applied in production processes. Pros and contras of each technology will be evaluated during the project.

The scheme for the pre-treatment of the effluent for the regenerated membrane module is based on bringing the effluent to pH 7 for the removal of Al and Fe and then separating the effluent by ultrafiltration to remove suspended solids including the precipitates of Al and Fe. The product from the UF process was then brought to pH 9.0 to solubilize SiO₂ followed by the addition of antiscalant at the given concentration of the prediction (1.65 mg/L) to prevent SiO₂, BaSO₄, SrSO₄ and CaSO₄ to precipitate.

Two different tailor-made membranes were chosen to assess the performance of the technological scheme and the quality of the real effluents generated: membranes oxidized at 4,000ppm·h and 6,000ppm·h at bench-scale. According to Deliverable D4.2, these two membranes were expected to provide high concentration of brine, water for reuse at a suitable quality, high permeability at low energy and economic costs. Regarding membrane performance, a flux of 20 LMH was fixed for both membranes as it is a common flux for nanofiltration membranes, which present similar flux and rejection. The membrane that was most oxidized requires a pressure of 16 bar to maintain this flux

ZERO BRINE – Industrial Wastewater – Resource Recovery – Circular Economy



whilst the other membrane, a pressure of 18 bar. Electrical conductivity of each of the effluents (permeate and concentrate) proofed that the rejection of the most oxidized membrane is lower, fact that was already established from the standard tests. This fact is due to the higher conductivity of the permeate for the most oxidized membrane comparted to the less oxidized one. When considering the concentration of the ions, this difference turns out not to be considered as high as most of the ions are in similar concentrations in the effluents generated from both membranes, even though the rejection proportions occur accordingly. Due to the low difference in effluents quality when comparing both membranes, a membrane with similar properties to the most oxidized one was considered for the start-up of the pilot plant as it would require low energy for a suitable quality of permeate and concentrate. The permeate presented a conductivity adequate to provide water for further reuse that is below 4.6mS/cm. The concentrate achieved a concentration factor of 2.17.

Provided all results achieved, regenerated membranes proof to be a suitable process for the concentration of Na_2SO_4 (IQE's brine) as they present low energy demands (pressure), high fluxes, adequate rejections and low acquisition costs.

In the ZERO BRINE project, electrodialysis with bipolar membranes (EDBM) was tested at bench-scale to recover NaOH and H_2SO_4 from IQE effluents looking for a zero liquid discharge objective. The bipolar membrane selected for the project were the Fumasep[®] FBM single film bipolar membrane from FUMATECH. It consists of an anion exchange layer and a cation exchange layer manufactured using a patented multilayer-coating production technology. EDBM experiments have been carried out at amperometric conditions (constant current density) and measuring the voltage through the time. Different experiments have been performed in order to determine optimal density applied, optimal ratio $V_{acid}/V_{base}/V_{diluate}$ and composition of water, NaOH and H2SO4 in each stream. For each experiment, desalination and current efficiencies and energy consumption have been determined. As it has been explained, due to COVID-19 situation, Spanish BEC should reduce its activity and consequently some results from this experimentation are pending. It is expected to have final results in December 2020.

Lastly, to recover Na₂SO₄ crystals and water with a high quality from the concentre of the regenerated membranes, Eutectic Freeze Crystallization (EFC) was tested at bench-scale with synthetic wastewater. The synthetic 5 wt.% solution of Na₂SO₄·10H₂O when submitted to EFC conditions provided a clear separation of both solid phases (crystals and ice). When high subcooling (>0.25°C) was applied, the ice formed too rapidly causing ice scaling in the crystallizer. To the same, an excessive agitation (>25 rpm) caused crystals agglomeration. These undesirable EFC phenomena enhanced the difficultness of harvesting the formed ice and salt. However, when the subcooling was set at 0.25°C and agitation at 25rpm, the stable process performance was obtained, thus permitting successful product recovery. A conservative recovery of 42% salt and 55% ice was obtained. The recovered products were almost pure, with less than 1 wt.% impurities for salt and 7.7wt% for ice. EFC proof to be a robust process to produce quality crystals with different crystallization stages. In other words, steady quality salt and ice products are promised throughout the EFC process.



The technological scheme proposed provided solutions to closing a circular economy loop regarding the wastewater generated at IQE by implementing innovative management strategies more sustainable from an environmental and economical point of view.



Content

1.	Introduction	3					
2.	Objective						
3.	Pre-treatment12	2					
4.	Membrane technology1	7					
	a. Regenerated membranes17						
	i. Experimental methodology1	7					
	ii. Results and discussion	Э					
	b. Bipolar membranes21						
	i. Experimental methodology2	3					
	ii. Results and discussion	7					
5.	Crystallization of sodium sulphate 28	3					
	a. Fundaments on sodium sulphate crystallization.28						
	b. Eutectic Freeze Crystallization (EFC)29						
	i. Optimization of EFC process for sodium sulphate	2					
	ii. Recovery of sodium sulphate from synthetic RO						
	concentrate	8					
6.	Conclusions 42	2					
7.	References	3					
8.	Annex 4	5					
	Annex I	5					
	Annex II	5					



List of Figures

Figure 1. Technological scheme developed at bench-scale for the treatment of brine from IQE9
Figure 2. Solubility diagrams of Al and Fe614
Figure 3. Solubility diagram of Si 8 15
Figure 4. Pre-treatment scheme for the regenerated membrane unit 16
Figure 5. General methodology to regenerate membranes17
Figure 6. Flat-sheet membrane module used for regenerated membrane tests
Figure 7. Experimental set-up for membrane testing at lab-scale (BP-2 from Spanish BEC)
Figure 8. Experimental set-up for oxidizing the membrane at lab-scale (BP-12 from Spanish BEC) 19
Figure 9. Flat-sheet membrane module used for regenerated membrane tests. Composition of a 3-
compartment cell in the electrodialysis process with BM. Figure obtained from Fumatech ⁹
Figure 10. Diagram of the configuration of the EDBM stack
Figure 11. Spacer (left) and Fumasep® FBM membrane used during the EDBPM process (right) 25
Figure 12. EDBPM stack (left) and global system for the EDBM process used (right) (BP-6 from Spanish
BEC)
Figure 13. Phase diagram of sodium sulphate ¹⁷ . The solid lines are equilibrium phase boundaries, and
the dashed line is the metastable extension of thenardite-solution boundary and therefore represents
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solution compositions in metastable equilibrium with thenardite but supersaturated with respect
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solution compositions in metastable equilibrium with thenardite but supersaturated with respect mirabilite
solution compositions in metastable equilibrium with thenardite but supersaturated with respect mirabilite



List of Tables

Table 1. Current available technologies for silica wastewater treatment. 8
Table 2. Process wastewater composition from IQE to be treated in ZERO BRINE. 12
Table 3. Saturation index of the concentrate
Table 4. Removal of metals by pH adjustment14
Table 5. Results of standard test with NaCl for the chosen membranes 19
Table 6. Physicochemical results of the technological scheme with regenerated membranes for real
brine
Table 7. Operation conditions and results of the regenerated membranes with real brine
Table 8. SoA related with EDBM process using Fumatech bipolar membranes. 23
Table 9. Technical specifications of Fumasep® FBM membrane 24
Table 10. Specifications of the EDBM stack 25
Table 11. Experimental design of EDBP process for the desalination of IQE effluents
Table 12. Existing crystallization processes for industrial production of sodium sulphate ¹⁸
Table 13. EFC key parameters for process optimization. 35
Table 14. Compositions of the synthetic experimental solutions 39
Table 15. Recorded eutectic freeze point of different solutions 40
Table 16. Description of the used analytical methods 45
Table 17. Performance of one H-1 hydrated membrane with synthetic solution. 46
Table 18. Removal of Cl and SO4 from the synthetic solution with oxidized membranes at different
doses



1. Introduction

ZERO BRINE project aims to facilitate the implementation of the Circular Economy package and the SPIRE roadmap in various process industries by developing necessary concepts, technological solutions and business models to redesign the value and supply chains of minerals and water while dealing with present organic compounds in a way that allows their subsequent recovery. This is achieved by demonstrating new configurations to recover these resources from saline impaired effluents generated by process industries, while eliminating wastewater discharge and minimising environmental impact of industrial operations thorough brines.

One of the four demonstration sites of the project is located at Industrias Químicas del Ebro S.A. (IQE) in Spain. IQE Group is an industrial chemical group composed by three companies: DESILSA, SIMAL and Industrias Químicas del Ebro, S.A. IQE, which has its headquarters in Zaragoza, began its business activity in 1958. It is specialized in basic inorganic chemistry and manufactures sodium and potassium silicates, metasilicate, zeolites, sodium and potassium aluminates, aluminum sulphate, precipitated silica, aluminum silicate and amorphous aluminum hydroxide.

In the silica production process high amounts of water and reagents (NaOH, H₂SO₄, sand) are consumed and high amounts of waste streams with high salinity are produced. These streams contain high concentration of sodium sulphate and are normally discharged to natural watercourses (rivers, sea) after passing through wastewater treatment plants, with a high cost and environmental impact associated. The recovery of sulphate with existing technologies is not economically feasible³. In the following table, existing technologies described in the BREF LVIC and other available in the market are described.

Treatment	Disadvantages	By-product	Cost (€/t silica)	
Spray dryer ¹	High energy consumption	Na ₂ SO ₄	280*-700	
Gypsum precipitation ¹	Energy consumption and CaO consumption	CaSO ₄ .2H ₂ O	170* -225	
Evaporation and crystallization**	High energy consumption Uneconomic when salt present is very low	Anhydrous Na ₂ SO ₄	57,4*	

Table 1. Current available technologies for silica wastewater treatment.

*disposal costs not included if there is a market for by-product; ** Data obtained from technology provider

As it can be seen in the previous table, valorisation of sulphate compounds is crucial, as disposal costs in landfill represents a high percentage of the management cost. In the case of spry dryer and



evaporation, the energy consumption is related with salts concentration. Based on that, as much concentrated is the waste stream lower energy consumption.

ZERO BRINE aims to develop innovative processes for treating wastewater from silica industry based on the concept of economy circular and promoting the resource efficiency by recovering resources. To do that innovative technologies have been evaluated at bench-scale in order to evaluate its performance previous its demonstration at pilot scale. These recovery processes involve a pretreatment of the effluent, membrane technologies for the separation and concentration of salts from water and thus water recovery, and crystallization processes for the recovery of salts. Figure 1 presents the technological scheme proposed at bench-scale for the optimization of the pilot plant operation at IQE.



Figure 1. Technological scheme developed at bench-scale for the treatment of brine from IQE

Specifically, membrane technologies tested are pressure-driven filtration with regenerated membranes (Deliverable D4.2) and Electrodialysis with bipolar membranes (EDBP). Regenerated membranes will provide two effluents: water for reuse (permeate) and concentrated brine (concentrate) to be further treated by crystallization technologies to recover salts. The EDBP process is meant to obtain NaOH and H₂SO₄ as valuable reagents out of the brine considered wastewater.

Crystallization processes assessed in this project include eutectic freeze crystallization (EFC) and evaporation. The driving force of both processes is temperature however for EFC cooling is required whilst evaporation benefits from high temperatures. In the EFC process precipitated salt and highly pure ice are achieved providing thus water for reuse and highly pure salt for production processes. During evaporation salt is as well recovered which can also be applied in production processes. Pros and contras of each technology will be evaluated during the project.

Technologies can be combined in order to establish two different treatments:



- 1. Concentration using membrane technology and crystallization of the concentrate produced. Membrane based separation processes have gradually become an attractive alternative to evaporation for the treatment of wastewater when salt concentration is too low. The application of membrane filtration processes not only enables high removal efficiencies, but also allows reuse of water. By concentrating wastewater using membranes, high concentrations of sodium sulphate are achieved in the rejected stream making economically feasible its treatment using crystallization. For membrane stage, the use of regenerated membranes will be evaluated in order to reduce costs. For crystallization the innovative EFC technology will be investigated at bench-scale, while evaporation will be tested at pilot scale, considering that is more mature technology.
- 2. Recovery of water, NaOH and H_2SO_4 by electrodialysis using bipolar membranes. In this case, reagents and water could be reused in the silica production process. The process will be evaluated only at bench scale.

The technological scheme proposed provides solutions to closing a circular economy loop regarding the wastewater generated at IQE by implementing innovative management strategies more sustainable from an environmental and economical point of view.

In the coming sections of this report, results on each of the technological steps assessed is described.



2. Objective

The study of the technologies at a bench-scale prior to their application in a pilot plant is crucial so to assess and optimize relevant operational parameters and thus identify possible challenges and benefits during the operation and investigate them at a smaller scale.

The main objective of Task 4.1 "Bench-scale optimization of recovery processes" is to demonstrate the technical feasibility of implementing a circular economy scheme in the precipitated silica industry to recover water, sodium sulphate, waste heat, acids and alkalis. The technical processes have been based on the definition of a pre-treatment step, the performance assessment of the filtration step with membranes (regenerated and EDBP) and a crystallization step (EFC and evaporation) for the final recovery of salts.



3. Pre-treatment

A pre-treatment step was considered in order to provide membranes with a suitable composition of effluent to be treated to minimize scaling and thus reduce operation drawbacks. These drawbacks could involve time as cleaning processes would be required every short periods of time but also could involve economic aspects as membranes could break or the production could be diminished significantly.

In order to assess the optimal pre-treatment, the feed composition detailed in Table 2 was used as it was representative for the wastewater that would be treated in the pilot plant of ZERO BRINE. This wastewater is rich in sulphate, sodium and chloride from the industrial process of IQE but it also contains Al, Fe, Si, Ba and other trace elements that need to be taken into account during the operation of the plant as they could contribute to inorganic fouling given their low solubility.

Feed							
Parameter	Value	Parameter	Value				
Ca (mg/L)	58	SO4 (mg/L)	11,950				
Mg (mg/L)	6.00	Cl (mg/L)	1,520				
Na (mg/L)	6,615	HCO₃ (mg/L)	1,00				
K (mg/L)	27	NO₃ (mg/L)	14				
Ba (mg/L)	0.01	Si (mg/L)	66,6				
Sr (mg/L)	1.10						
Fe (mg/L)	0.03						
Al (mg/L)	0.30						
Mn (mg/L)	0.0						

Table 2. Process wastewater composition from IQE to be treated in ZERO BRINE.

To minimize precipitation and scaling, it is important to establish well-designed scale control measures and avoid exceeding the solubility limits of soluble salts. The most critical salts in narrow-pore membrane systems (RO and NF) are CaSO₄, CaCO₃ and silica. Other salts creating a potential scaling problem are CaF₂, BaSO₄, SrSO₄, and Ca₃(PO₄)₂².

Given the physicochemical characterization of the effluents detailed in deliverable D4.1 and former presented, a software provided by an antiscalant provider (PermaCare by NALCO) was used to model the operation of the membranes and thus predict the possible formation of inorganic fouling (scaling). Predictive methods for scale precipitation and deposition provide numerous scaling index³. In this report, saturation index is used which is related to the solubility constant for the salt being 100% the saturation concentration of the salt and thus its precipitation.



The prediction was carried out considering the operation of a RO membrane, specifically a membrane destined to filter brackish water as it is like the regenerated ones that would be used in the pilot plant. The properties of BW-RO were considered as the worse scenario in the pilot plant as regenerated membrane would have a maximum rejection similar rejection to BW-RO (98%) and thus being the conditions in which scaling is more likely. The operation conditions of the membrane in which the prediction was based were 20bar at 20°C and at different recoveries to assess its effect in the precipitation.

In Table 3 the results of the prediction are presented where percentages above 100% represent a certainty that the indicated elements will precipitate under the given conditions as their solubility is far surpassed. It is noteworthy that BaSO₄ and SiO₂ precipitate under the four conditions and that CaSO₄, SrSO₄, Al and Fe are only of concern at the highest recoveries. In any case, these salts need to be treated prior to enter the membrane modules to avoid membrane damage and operation drawbacks.

Expected scaling in the concentrate (%)							
60% recovery	70% recovery	75% recovery	80% recovery				
505 % BaSO ₄	701 % BaSO ₄	868 % BaSO ₄	1137 % BaSO₄				
50% CaSO ₄	77% CaSO ₄	103% CaSO ₄	149% CaSO ₄				
50 % SrSO₄	91 % SrSO ₄	134 % SrSO ₄	147 % SrSO ₄				
6.30% CaCO ₃	$14 \% CaCO_3$	19.2% CaCO ₃	25.3% CaCO ₃				
68% Fe ³⁺	91% Fe ³⁺	110% Fe ³⁺	136% Fe ³⁺				
68% Al ³⁺	89% Al ³⁺	107% Al ³⁺	134% Al ³⁺				
30% Mn ²⁺	41% Mn ²⁺	49% Mn ²⁺	60% Mn ²⁺				
139% SiO ₂	185% SiO ₂	222% SiO ₂	278% SiO ₂				

Table 3. Saturation index of the concentrate

One of the most critical compounds present in the targeted effluent is SiO₂ also known as silica. Silicic acid is a weak acid and it is mostly in the undissociated form at or below a neutral pH. Supersaturated silicic acid can further polymerize to form insoluble colloidal silica or silica gel, which can cause membrane scaling. The maximum allowable SiO₂ concentration in the concentrate stream is based on the solubility of SiO₂.

The precipitation of silicic acid and the occurrence of silica scaling is mostly correlated with the presence of aluminum and/or iron⁴. It has been reported that, when Al³⁺ and Fe³⁺ coexist in the pretreated feedwater, silica is precipitated even below its saturation⁵. Frequent physicochemical determinations of these ions are thus needed. Fouling with metal silicates may occur from a chemical



reaction and precipitation process (scaling), and from colloidal fouling with submicron particles entering the membrane system.

Therefore, the first step considered in the pre-treatment was the removal of Al and Fe from the feed wastewater. These metal ions present their minimum solubility at pH around 6.0 an 8.5 (Figure 2), respectively. Thus, so to remove them from the feed of the pilot plant, it was established that a step of pre-treatment would be to adjust its pH to pH 7.0 to have both metal ions in their precipitate form and thus remove them by ultrafiltration.



Figure 2. Solubility diagrams of Al and Fe6

Given the range of pH provided by the predictive tools, bench-scale tests were conducted with real water in order to confirm the optimal pH to remove Al and Fe from the effluent at the entrance of the pilot plant.

Jar tests were conducted were the solution was brought to the established pH using sodium hydroxide. After the addition of the base, the solution was stirred for 2 minutes and then allow it to settle for 5 min. The mixture was then filtered, and metals were determined by ICP-MS (Annex I). In Table 4 the percentage of removal of each metal ion for three pH adjustments (6.0, 6.5 and 7.0) is detailed.

					Remov	al (%)		
	Turbidity (NTU)	Al (µg/l)	Si (mg/l)	Fe (µg/l)	Turbidity	AI	Si	Fe
Initial (pH 5.2)	33	3200	84	1600		-	-	-
pH 6.0	0.8	1840	88	340	97.6	42.5	0	78.8
pH 6.5	0.9	870	86	< 200	97.3	72.9	0	>87.5
pH 7.0	0.6	660	84	< 200	98.2	79.4	0	>87.5

Table 4. Removal of metals by pH adjustment

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Turbidity is a representative parameter of the effect of the pH adjustment in the solution. Initially is 33NTU at a pH of 5.2 being the solution milky-like whereas when the solution increases pH, precipitate is formed and after removal of this precipitate, turbidity is reduced to below 1 NTU in all three cases. Metal ions of Al, Si and Fe were monitored to assess the effect of the pH change. The adjustment to pH 7.0 is the one providing higher removal rates of Al and Fe whilst Si has not been affected by these pH ranges, as already expected. It was concluded in this step that the effluent had to be adjusted to pH 7.0 before entering the pilot plant in order to minimize the effect of Al and Fe precipitated and thus effect negatively the operation of the pilot plant.

After the removal of Al and Fe, it was necessary to stablish another which pH is favorable to dissolve Si in its form of SiO₂ and not derive into scaling. According to the solubility diagram of Si (Figure 3), its solubility increases at pH 9.0, where silicates are starting to form. Thus it was set that the feed to the module of regenerated membrane to be adjusted to 9.0 in order to avoid fouling.





In addition, salts such as BaSO₄, CaSO₄ and SrSO₄ are to be considered as well. Thus, simulation with the software provided from NALCO (antiscalant provider) were again conducted without introducing AI and Fe in the system and by introducing pH 9.0 as the pH of the feed to the brackish water membrane. Results showed that to prevent scaling in the regenerated membranes, antiscalant (PC-391T) needed to be dosed at a concentration of 1.65 mg/L.

Therefore, the scheme for the pre-treatment of the effluent for the regenerated membrane module is the one depicted in Figure 4. The effluent is firstly brought to pH 7 for the removal of Al and Fe and thus the effluent is separated by ultrafiltration to remove suspended solids including the precipitates of Al and Fe. The product from the UF process is then brought to pH 9.0 to solubilize SiO₂ followed by the addition of antiscalant at the given concentration of the prediction (1.65 mg/L) to prevent SiO₂, BaSO₄, SrSO₄ and CaSO₄ to precipitate.





Figure 4. Pre-treatment scheme for the regenerated membrane unit



4. Membrane technology

Two different membrane processes are considered in this project: pressure-driven filtration with regenerated membranes and electrodialysis with bipolar membranes (EDBP). Each of these processes provides a different outcome for the project. Filtration with regenerated membranes provides water that can be reused as well as a high concentrated brine from which sodium sulphate can be recovered. On the other hand, EDBP provides two reagents of value to be further reused in the production process: NaOH and H_2SO_4 .

a. Regenerated membranes

A regenerated membrane is a membrane that was considered at its end-of-life and has been regenerated for tailor-made purposes. Properties of the tailor-made membrane are given by the permeability and the rejection defined. An increase of permeability will allow to reduce working pressure, and consequently the energy consumption. On the other hand, rejection is defined considering the conductivity of the wastewater used as feed for the regeneration membrane and the permeate conductivity. Generally, membrane regeneration is based on applying an oxidative agent (OA) in order to oxidize the polyamide active layer of the membrane.

In order to assess the overall technological scheme (Figure 1) real saline wastewater from IQE was acquired. The scheme followed was pre-treatment scheme (Figure 4) and the "recovery compound technology" was the filtration of the effluent by regenerated membranes to assess the quality of the permeate and the concentrate so they can be further reused in the production process.

i. Experimental methodology

Wastewater characterization

Brine provided by IQE was assessed for its physiochemical parameters using the analytical methods detailed in Annex I.

Membrane regeneration

Membrane regeneration and membrane performance assessment carried out at bench-scale was performed as described in D4.2.

In short, the overall methodology followed to obtain tailor-made membranes is presented in Figure 5 and described briefly hereafter.



Figure 5. General methodology to regenerate membranes

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End-of-life membranes properties were firstly assessed with the standard NaCl test and then the regeneration step was carried out. The process of regeneration was conducted in two steps: hydration and oxidation. Coupons (140 cm²) from a RO membrane element at its end-of-life were used for bench-scale tests. The middle sheets were considered so to have representative coupons of the fouling of the membrane, which is more abundant in the inner sheets and very little in the outer sheets. Membrane performance was tested in the set-up shown in Figure 6 and Figure 7.



Figure 6. Flat-sheet membrane module used for regenerated membrane tests



Flat-sheet membrane module

Figure 7. Experimental set-up for membrane testing at lab-scale (BP-2 from Spanish BEC)

For all tests, permeability was calculated by the time needed to reach the set recovery and it was expressed as $L/m^2 \cdot h \cdot bar$. Salt rejection was determined by conductivity differences between the feed and the permeate and it was expressed as a percentage.

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Membrane regeneration consisted in hydrating and oxidizing the polyamide layer of the coupons with an oxidative agent (OA) to increase their permeability and obtain the desired salt rejection. To oxidize, a similar cell as the testing cell was used (Figure 8) although this one was made of methacrylate to prevent its degradation by the OA. This process consisted in recirculating with a peristaltic pump the oxidative solution on the active layer of the membrane, so the layer made of polyamide.



Figure 8. Experimental set-up for oxidizing the membrane at lab-scale (BP-12 from Spanish BEC)

ii. Results and discussion

Two different tailor-made membranes were chosen to assess the performance of the technological scheme and the quality of the effluents generated: membranes oxidized at 4,000ppm·h and 6,000ppm·h at bench-scale. These two oxidation doses were chosen as they were the highest doses tested during the assessment of membrane regeneration (Deliverable D4.2) that provided a quality of the permeate within the limits (<4.6mS/cm) at the lowest operation pressure (24 and 20 bar, respectively) when filtering synthetic brine. Thus, these two membranes were expected to provide high concentration of brine, water for reuse at a suitable quality, high permeability at low energy and economic costs. Results on the membrane performance of these membranes can be found in Annex II of this document. Results on the standard test with NaCl provided in Table 5 show the difference in rejection and permeability of both membranes being the membrane with the highest oxidizing degree the one with highest permeability and lowest rejection as it is the one with the most degraded polyamide active layer.

Table 5. Results o	f standard	test with	NaCl for t	he chosen	membranes
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	Permeability (LMH/bar)	Rejection NaCl (%)
Membrane 4,000ppm·h	4.25	98.3
Membrane 6,000ppm·h	5.02	96.7

As mentioned, real brine was used to assess the proposed technological scheme prior to its application in the pilot plant. In Table 6 results on the composition and quality of each of the technological steps



are presented and in Table 7, on the operational performance of the regenerated membranes. In this sampling campaign the initial composition of the effluent presents low concentration of Fe in comparison to other sampling campaigns and Al was found below the detection limit of the analytical method. This variability is directly associated to the production process at IQE and thus representative of the overall process. Pre-treatment tests with higher concentration of both metal ions were already evaluated and detailed in the previous section.

The pre-treatment step for both membranes is common, having the pre-treated effluent split in two for the tests with the regenerated membranes. In Table 6 it is shown that turbidity increases significantly after the adjustment of pH to 7.0, being this fact related to the formation of precipitates of Fe which is derived also by its reduction in concentration, as it is not soluble anymore. The rest of the chemical parameters and ions remain unaffected by this pH adjustment. Next step was UF followed by pH adjustment to 9.0 and the addition of the antiscalant. This step derived into a great reduction of the conductivity due to the filtration of the precipitates and also a stabilization of SiO₂ as it remained in solubility throughout the step and thus together with the antiscalant not likely to precipitate on top of the membrane when operating. Also, from these steps no significant changes of the other ions occurred. Cations and anions were not determined in these two steps as their concentration was not expected to present any changes.

Regarding membrane performance, a flux of 20 LMH was fixed for both membranes as it is a common flux for nanofiltration membranes, which present similar flux and rejection. The membrane that was most oxidized requires a pressure of 16 bar to maintain this flux whilst the other membrane, a pressure of 18 bar (Table 7).

From the quality point of view, electrical conductivity of each of the effluents (permeate and concentrate) proofs that the rejection of the most oxidized membrane is lower (Table 7), fact that was already established from the standard tests (Table 5). This fact is due to the higher conductivity of the permeate for the most oxidized membrane comparted to the less oxidized one. When considering the concentration of the ions, this difference turns out not to be considered as high as most of the ions are in similar concentrations in the effluents generated from both membranes, even though the rejection proportions occur accordingly.

Parameter	Unit	Initial	Adj. to pH 7.0	UF + Adj. to pH 9.0 + antiscalant addition	Membrane 4,000ppm·h Permeate Concentrate		Membrane	e 6,000ppm·h
					renneute	concentrate	renneute	concentrate
рН	upH	6.6	6.8	8.95	9.3	9.3	9.3	9.3
Conductivity	mS/cm	24.9	25.0	24.3	1.34	51.4	2.50	46.7
Turbidity	NTU	2.4 ± 0.1	10 ± 0.1	0.9 ± 0.1				
CI	mg/l	1,336			106	2,760	108	2,754
NO ₃	mg/l	9.30			< 5.0	< 5.0	< 5.0	< 5.0

Table 6. Physicochemical results of the technological scheme with regenerated membranes for real brine

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Parameter	Unit	Initial	Adj. to pH 7.0	UF + Adj. to pH 9.0 + antiscalant addition	Membrane 4,000ppm·h Permeate Concentrate		Membrane Permeate	e 6,000ppm·h Concentrate
SO ₄	mg/l	12,645			394	27,540	408	27,528
к	mg/l	24.0			1.0	61.7	1.1	62.0
Na	mg/l	6,643			262	14,777	266	14,789
Са	mg/l	< 12.5			< 12.5	< 12.5	< 12.5	< 12.5
Mg	mg/l	< 12.5			< 12.5	< 12.5	< 12.5	< 12.5
AI	μg/l	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0
Si	mg/l	51	52	50	2.2	72	2.3	75
Mn	μg/l	65.0	69	66	1.2	160	1.1	160
Fe	μg/l	230	207	200	< 10.0	701	12.0	690
Sr	μg/l	190	190	190	2.3	433	2.6	430
Ва	μg/l	54.0	53	51	0.6	100	0.6	100

Table 7. Operation conditions and results of the regenerated membranes with real brine

	Flux (LMH)	Rejection conductivity (%)	Pressure (bar)	Recovery (%)
Membrane 4,000ppm·h	20	94.5	18	73
Membrane 6,000ppm·h	20	89.5	16	71

Due to the low difference in effluents quality when comparing both membranes, a membrane with similar properties to the most oxidized one was considered for the start-up of the pilot plant as it would require low energy for a suitable quality of permeate and concentrate. The permeate presented a conductivity adequate to provide water for further reuse that is below 4.6mS/cm. The concentrate achieved a concentration factor of 2.17.

Provided all results achieved, regenerated membranes proof to be a suitable process for the concentration of Na_2SO_4 (IQE's brine) as they present low energy demands (pressure), high fluxes, adequate rejections and low acquisition costs.

b. Bipolar membranes

Bipolar membranes (BM) are integrated by both a cation exchange layer (with negative charges fixed) and an anion exchange layer (with positive charges fixed). This configuration offers several advantageous properties such as the simultaneous separation of mono- and/or divalent cations from anions, anti-deposition, anti-fouling, water dissociation, etc. Specifically, water splitting for the conversion of a salt into its corresponding acid and base is the most important application of BM, when



exceeding a potential difference between electrodes of approximately 0.8 V. Due to its unique structure and same swelling properties in both anion and cation exchange layers, the BM possess both excellent mechanical and chemical stability⁷. Moreover, the electro-catalytically forced water dissociation produces – in contrast to the classical electrolysis of water – no reaction gases. Therefore, one mol of OH⁻ and H⁺ can be achieved at an energy value of approximately 22 Wh (electrolysis: 55 Wh/mol)⁸.

Bipolar membranes are usually combined with cationic and anionic exchange membranes for performing the electrodialysis process, as represented in Figure 9. When this type of configuration is used, the electrodialysis process is composed by several 3-compartment cell integrated by a bipolar membrane, a cation exchange membrane and an anion exchange membrane, where acid, base and diluate are generated. This process is called electrodialysis with bipolar membranes (EDBM).



Figure 9. Flat-sheet membrane module used for regenerated membrane tests. Composition of a 3-compartment cell in the electrodialysis process with BM. Figure obtained from Fumatech⁹.

In the ZERO BRINE project, electrodialysis with bipolar membranes (EDBM) was tested at bench-scale to recover NaOH and H₂SO₄ from IQE effluents looking for a zero liquid discharge objective. The efficiency of the process on brines depends of several factors such as a) the permselectivity of the membranes; b) back diffusion of the salts from the concentrate to the diluate; c) current leakages depending on the resistivity of the materials and solutions.

Different commercially available bipolar membranes have been evaluated and theoretically compared in order to select the most suitable for the application. Related with BM, several providers have been contacted, such as FUMATECH GmbH¹⁰, Pccell GmbH (before called PCA - PolymerChemie Altmeier GmbH)¹¹ and ASTOM Co.¹².

Ghyselbrecht *et al.* (2014)¹³ compared the electrical resistance, the current efficiency and purity of the produced acid and base streams obtained by using Fumatech bipolar membranes with those acquired by using the BM of PCA - PolymerChemie Altmeier GmbH to desalinate a NaCl industrial stream. They found that the Fumasep bipolar membranes (from Fumatech) scored slightly better for electrical resistance and current efficiency than PCA ones.



Herrero-González, *et al.* (2020)¹⁴ confirmed that bipolar membranes from PCCell and ASTOM are most frequently applied for the treatment of saline wastewater, whereas those ones from Fumatech are more implemented for the brine desalination.

Based on this context, EURECAT decided to select Fumasep[®] FBM single film bipolar membrane from FUMATECH, which specifications are detailed in the following section. The most recent references related with the use of this type of BM are compiled in the Table 8.

Properties	Ghyselbrecht <i>et al.</i> (2014) ¹³	Yang, et al. (2014) ¹⁵	Herrero-González <i>, et al.</i> (2018) ¹⁶
Type of membranes	Fumasep from Fumatech	Fumatech	Fumasep from Fumatech
Limiting current density	15 mA/cm ² for 99% of desalination using 1.8M NaNO ₃ 23 mA/cm ² for 95% of desalination using 1.8M NaNO ₃	No specified	No specified
Initial composition of the brine	75 g/L NaCl 101.9 mS/cm	0.7M NaCl	1M NaCl
Initial acid concentration and volume	0.5M HCl	No specified	1M HCl
Initial base concentration and volume	0.6M NaOH	No specified	1.5M NaOH
Final acid concentration	2M HCI	0.7M HCl	0.98M HCl
Final base concentration	2M NaOH	1M NaOH	1.64M NaOH
Electrode rinsing solution concentration	1.4M Na ₂ SO ₄	0.5 Na ₂ SO ₄	0.5 NaOH 0.5 Na ₂ SO ₄
Acid dissolution volume	2L	No specified	No specified
Base dissolution volume	2L	No specified	No specified
Diluate volume	2L	No specified	No specified
Electrode rinsing solution volume	4L	No specified	No specified
Applied current density	No specified	57	22
Desalination efficiency	99%	No specified	No specified

Table 8. SoA related with EDBM process using Fumatech bipolar membranes.

i. Experimental methodology

The EDBM lab-scale experiments were carried out with a PCCell ED 64-004 stack (manufactured by PCCell GmbH, Germany). The EDBM system installed at Eurecat was integrated by 5 cell triplets (5 three-compartment cells), each one composed by one bipolar membrane, one anion exchange membrane (AEM) and one cation exchange membrane (CEM). Therefore, for each cell, there are three chambers: a) the first one is related with the base production; b) the second one is related with the acid production; c) and the third one ("salt chamber") corresponds to the diluate. By using this three-



compartment configuration, four separate loops were resulted: acid, base, diluate and the electrode rinsing solution (continuously recirculated for anode and cathode compartments).



The assembly of the EDPM stack with the 5 three-compartment cells is represented in the Figure 10.

Figure 10. Diagram of the configuration of the EDBM stack.

The bipolar membrane selected for the Zerobrine project were the Fumasep[®] FBM single film bipolar membrane from FUMATECH. It consists of an anion exchange layer and a cation exchange layer manufactured using a patented multilayer-coating production technology. This composite membrane is chemically stable and mechanically reinforced with woven PEEK. The membrane should be operated under forward bias conditions which may cause blistering.

The specifications of the Fumasep[®] FBM membrane are detailed in the Table 9 and its appearance, together with the spacer one, are photographed in Figure 11.

Properties	Values
Colour	Brown
Thickness (dry)	130 – 160 μm
Wight per unit area (dry)	15 – 17 mg/cm ²
High water splitting efficiency	>98% at 100 mA/cm ² in 0.5 M NaCl, at 25°C
Low water splitting voltage	< 1.2 V at 100 mA/cm ² in 0.5 M NaCl, at 25°C
Mechanical properties at low thickness (0.13 – 0.16 mm)	Excellent
Maximum operation temperature	40°C

 Table 9. Technical specifications of Fumasep® FBM membrane





Figure 11. Spacer (left) and Fumasep® FBM membrane used during the EDBPM process (right).

The cell used for the EDBM as well as the general system can be observed in Figure 12.



Figure 12. EDBPM stack (left) and global system for the EDBM process used (right) (BP-6 from Spanish BEC).

The characteristics of the EDBM cell are collected in Table 10.

Table 10. Specifications of the EDBM stack

Properties	Values			
Cell characteristics	Effective area of the membranes = 64 cm Membrane size = 100 x 100 mm Spacer thickness: 1 mm			
Type of cationic exchange membrane (CEM)	Fujifilm CEM Type 10			

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Properties	Values
Type of anionic exchange membrane (AEM)	Fujifilm AEM Type 10
Number of stacks	10 (see Figure 10)

The operational conditions followed for the set of EDBM experiments are summarized in Table 11.

Properties	Influence of the initial concentration of acid	Influence of the initial concentration of base	Influence of the current density applied to the system	Influence of the volume relationship	Experiment with real brine
Initial composition of the brine	Synthetic 0.3M NaCl 1M Na ₂ SO ₄	Synthetic 0.3M NaCl 1M Na ₂ SO ₄	Synthetic 0.3M NaCl 1M Na ₂ SO ₄	Synthetic 0.3M NaCl 1M Na ₂ SO ₄	Real or representative of synthetic water.
Initial acid concentration and volume	a) 0.25M H ₂ SO ₄ b) 0.5M H ₂ SO ₄	The best H ₂ SO ₄ concentration found previously	The best H ₂ SO ₄ concentration previously found	The best H ₂ SO ₄ concentration previously found	The best H ₂ SO ₄ concentration previously found
Initial base concentration and volume	0.5M NaOH	0.25M NaOH	The best NaOH concentration previously found	The best NaOH concentration previously found	The best NaOH concentration previously found
Final acid	To be	To be	To be	To be	To be
concentration	determined	determined	determined	determined	determined
concentration	determined	determined	determined	determined	determined
Electrode rinsing solution concentration	0.5 M Na ₂ SO ₄	0.5 M Na ₂ SO ₄	0.5 M Na ₂ SO ₄	0.5 M Na ₂ SO ₄	0.5 M Na ₂ SO ₄
Acid dissolution volume	2L	2L	2L	1L	The best of tested before
Base dissolution volume	2L	2L	2L	1L	The best of tested before
Diluate volume	2L	2L	2L	2L	2L
Electrode rinsing solution volume	2L	2L	2L	2L	2L
Applied current density (j)	j = 50% of limiting current density	j = 50% of limiting current density	b) j = 75% of limiting current density c) j = 25% of limiting current density	The best of tested before	The best of tested before
Expected desalination efficiency	> 90 %	> 90 %	> 90 %	> 90 %	> 90 %

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ii. Results and discussion

EDBM experiments have been carried out at amperometric conditions (constant current density) and measuring the voltage through the time.

First of all, EDBM process has been performed using synthetic brine (0.3M NaCl and 1M Na₂SO₄) to evaluate the influence of several operation parameters such as a) the initial concentration of the acid (0.5M or 0.25M H₂SO₄); b) the initial concentration of the base (0.5M or 0.25 M NaOH); c) the influence of the current density applied to the system (75%, 50% or 25% of the limiting current density); and the influence of the ratio $V_{acid}/V_{base}/V_{diluate}$. For each experiment, desalination and current efficiencies and energy consumption have been determined. During the experiments, potential and electrical current of the system, conductivity, pH, flow rate, temperature, and pressure of each stream solution have been monitored. Membrane fouling is one of the major problems that affects the electrodialysis processes by reducing the flux, increasing the membrane resistance and energy consumption, and decreasing the ion migration yield. Thus, it was also considered during experiments.

Under most appropriated operational conditions, EDBM has been performed with a real IQE effluent to analyze the system performance with a real effluent and the influence of organic matter on the system.

Due to COVID-19 situation, Spanish BEC should reduce its activity and consequently some results from this experimentation are pending. It is expected to have final results in December 2020.



5. Crystallization of sodium sulphate

a. Fundaments on sodium sulphate crystallization

Concentrate stream produced during treatment using regenerated membranes will be feed to a crystallization process in order to recover sodium sulphate.

Equilibria between solid and liquid phases are the thermodynamic foundation of all crystallization processes from the melt and solution and thus of fundamental importance for the design of industrial crystallization processes. The phase diagram of sodium sulfate is given in Figure 13. The equilibrium solubility is given for mirabilite ($Na_2SO_4 \cdot 10H_2O$), anhydrous thenardite (Na_2SO_4), metastable anhydrous thenardite i.e. heptahydrate ($Na_2SO_4 \cdot 7H_2O$).



Figure 13. Phase diagram of sodium sulphate¹⁷. The solid lines are equilibrium phase boundaries, and the dashed line is the metastable extension of thenardite-solution boundary and therefore represents solution compositions in metastable equilibrium with thenardite but supersaturated with respect mirabilite.

The mechanisms for generating supersaturation rely on the changes in solubility of the crystalizing component as a function of temperature and composition. For large-scale continuous processes, the most common way to generate supersaturation is to remove the solvent selectively. In this way no residual material is created that requires further processing. Several methods have been developed for selectively removing solvent from a solution. By far the oldest, and still the most commonly used method is evaporation. Single-effect evaporation consumes a great deal of energy, and so many evaporation processes operate with multiple effects at different pressure, and the steam from each effect other than the first is used to power the subsequent effect.

Another method for removing solvent from solution is by cooling. This mechanism is best suited for systems in which the solubility of the crystallizing components decreases steeply or moderately with decreasing temperature. It is not suited for systems with flat or inverted solubility-temperature relationships.

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In the case of sodium sulphate, its solubility behavior makes cooling process suitable for its crystallization, as its solubility decreases with temperature decrease.





In fact, some of the industrial processes for sodium sulfate production is based in cooling mechanisms, i.e. Glauber salt process.

Table 12. Existing crystallization processes for industrial production of sodium sulphate¹⁸

PRODUCT	PROCESS	FEED*	END PRODUCT	TYPE OF OPERATION
- sodium sulphate (Glauber salt) cooling	salt purification	5% Na ₂ SO ₄ , 25% NaCl	crystals, 10H ₂ O	crystallization by vacuum
- sodium sulphate (anhydrous)	salt purification	30% Na ₂ SO ₄	crystals	crystallization by evaporation

As it has been mentioned in the Introduction section, in ZERO BRINE two different crystallization technologies will be considered. One of them is the innovative Eutectic Freeze Crystallization, based on freezing the solvent to drive the solution to the eutectic point, where solute crystals and ice form simultaneously. Suitability of this technology has been evaluated at bench-scale.

b. Eutectic Freeze Crystallization (EFC)

Eutectic Freeze Crystallization (EFC) is an emerging technology that operates at the eutectic temperature of the solution to enable simultaneous separation of saline solutions into ice and salt, with advantages of energy reduction, high salt purity and an absence of additional chemicals. Thereby, EFC has the potential to fulfil the requirement of sustainable development of recovery of both water and valuables from waste streams with high salinity.



The principle of the EFC concept can be described using a typical phase diagram of a binary aqueous solution, shown in Figure 15. When unsaturated aqueous solution is cooled from point "A" until the ice line is reached (vertical displacement, blue arrow), ice begins to form in the now saturated solution. A further decrease in temperature causes the system to become more concentrated due to the crystallization of ice and to eventually reach the eutectic point, the lowest possible temperature of crystallization. At this point, crystalline salt structures and ice crystals form separately and can be separated due to the large density difference between ice (0.92 g/cm³) and salts (e.g. NaCl 2.17 g/cm³)¹⁹. Similarly, for a solution with a higher starting concentration than the eutectic concentration (point "B"), the crystallization of salt will occur first, followed by ice at the eutectic point.

A brief explanation of more complicated phase diagrams such as the one shown in Figure 16 is as follows: the diagram again plots temperature vs. salt concentration for the particular case under consideration in this sub-task, sodium sulphate/water system. The left side of this figure (from 0% of Na₂SO₄ till 44%) can be used exactly as that of Figure 15. The value of 44% represents the concentration of pure Na₂SO₄ in the hydrate Na₂SO₄·10H₂O, i.e. (MW of Na₂SO₄)/(MW of Na₂SO₄·10H₂O) = 0.44 where MW stands for molecular weight. The other two new areas ("solid Na₂SO₄ + saturated solution" and "solids Na₂SO₄ + Na₂SO₄·10H₂O") are again areas where two phases coexist, and the lever rule applies.

In a continuous process, two extra separators are required, one to process the ice slurry and wash the ice with recycled pure water, and another to wash the salt with a saturated solution.



Figure 15. A typical phase diagram for aqueous salt solutions showing the eutectic point Error! Bookmark not defined.

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*Figure 16. Binary phase diagram for sodium sulphate-water system*²⁰*.*

Various studies about EFC have focused on the recovery of one salt from a simple binary or ternary system. Until today, EFC has been successfully applied to treat various binary aqueous solutions, such as CuSO₄, MgSO₄, Na₂SO₄ and a KNO₃-HNO₃ ternary system. Nevertheless, the ability to use EFC to separate multiple salts from multicomponent brine has not been fully investigated²¹. A research conducted by Randall *et al.*²² on RO brine using EFC resulted in a 97% water recovery as well as recovery of pure Na₂SO₄ (96.4% purity) and pure CaSO₄ (98% purity). Thus, the sequential removal of salts from a multicomponent mixture is apparently feasible as each salt crystallizes at its unique eutectic temperature. Salvador Cob *et al.*²³ studied the application of EFC to RO brine rich in HCO₃⁻ and Na⁺. The application of EFC crystallizer to this solution resulted in the formation of ice and 5.8 wt.% NaHCO₃ at -3.9 °C. Furthermore, it was observed the overall water recovery by the application of EFC to the RO brine was increased from 98.0% to 99.7%.

A life cycle assessment comparing EFC and evaporative crystallization indicated that EFC processes have great potential to reduce the energy consumption and carbon footprint of the crystallization units. It was found that the EFC process consumes 6–7 times less energy when compared to evaporative crystallization for a 4 wt.% model solution of sodium sulphate. Van der Ham *et al.*²⁴ found that EFC could reduce the energy required to recover sodium nitrate (from 35 wt.% aqueous solution) and copper sulphate (from 12 wt.% aqueous solution) by 30% and 65%, respectively, compared to multistep evaporation.

EFC has been commercialised by several companies internationally. Cool Separations (The Netherlands) have developed single stage EFC that can handle multicomponent systems and multistage EFC that can crystallise out the specific salts in sequence by operating a series of crystallisers at



different temperatures. In 2016, the implementation of a large-scale EFC in South Africa was reported. The facility was built at the Eskom Research and Innovation Centre in Rosherville and acts as a training platform and demonstration plant for treatment experiments²⁵. Other companies include PROXA Water (South Africa) and Prentec Pty Ltd. (South Africa). The specific energy consumption (SEC) of this technology is 43.8–68.5 kWh/m^{3 26}. The cost of this treatment technology is approximately US\$1.42/m³ of freshwater produced²⁷.

The objective of this sub-task was to optimize the crystallization process using EFC for a binary sodium sulphate solution as well as to determine the purity of the recovered valuables and evaluate overall process performance. To achieve the objective, experimental studies at EURECAT, Technological Centre of Catalonia (Spain) and Delft University of Technology (Netherlands) were performed.

i. Optimization of EFC process for sodium sulphate

Experimental methodology

Preparatory actions

Preparation of brine

A synthetic 5 wt.% binary solution of $Na_2SO_4 \cdot 10H_2O$ was prepared by dissolving analytical-grade $Na_2SO_4 \cdot 10H_2O$ from Scharlau (>99% purity) in 3kg of ultra-pure water ($18M\Omega/cm$). Dissolution was performed at room temperature under 500rpm mixing conditions for 60min. Before being transferred to the crystallizer, the sample solution was precooled to app. 3-5°C in a cooling room before starting the experiment.

Preparation of washing solutions

To wash ice obtained in the crystallization experiment, jars filled with ultrapure water were stored in a refrigerator at app. 1°C. To wash salt, saturated solution of Na_2SO_4 at 0°C was prepared by dissolving analytical-grade Na_2SO_4 (>99%) in 1kg of ultrapure water. Dissolution was performed at room temperature under 500rpm mixing conditions for 3 hours. Jars filled with saturated solution were stored in a refrigerator at app. 1°C.

Experimental set-up

The experimental set-up used throughout this study is shown in Figure 17. A cooled wall crystallization reactor of 5L (VidraFOC, S.A.) was used to study the eutectic freezing process. Cooling was achieved using a Julabo C41 cooling unit using JulaboEasyTempProfessional software to control the thermostat temperature. A coolant, Thermal HY Julabo, was continuously circulated through the double wall of the reactor to affect the heat transfer. Agitation was achieved using a digital overhead stirrer Hei-TORQUE 100 connected to a paddle. A plastic paddle was designed and fabricated from high density polyethylene (HDPE), that is resistance in low temperatures, specifically for this experimental set-up (Figure 18). It had a specific "U" shape with holes (was not fully filled) to ensure good mixing, not break down ice crystals and allow the insertion of measurement probes from the top of the vessel. 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 paddle also had a silicone edge to prevent scaling on the inner crystallizer surface.



Figure 17. Experimental EFC set-up





Figure 18. Scheme of a plastic paddle.

The temperature inside the reactor was measured with the PT-100 (Julabo) probe that is connected to the cooling unit. The crystallization reactor was illuminated by LEDs for better process observation. For final products (ice and salt) filtration, cooled wall Buchner funnels (VidraFOC, S.A.) with pore size 10-26 µm and connected with cooling unit, vacuum flasks and vacuum pump Electroad model H30P3 were used. Noted all tubing were insulated by insulating foam as to minimize heat transfer with the environment. For experiment control and data record, computer with JulaboEasyTempProfessional and NI LabVIEW 2016 software were used.

Experimental procedure

In order to observe the performance of the system and the recovery of Na₂SO₄ crystals, an EFC experiment of the synthetic 5 wt.% solution of Na₂SO₄·10H₂O (aq) was performed using the 5L setup. Before a precooled solution was transferred in a crystallizer, a cooling unit was turned on and JulaboEasyTempProfessional software was played to control a cooling unit and to create a desired cooling profile with required cooling temperature (setpoint). When cooling unit reached the setpoint, 3L of a synthetic solution was transferred in a cooled wall crystallizer. The digital overhead stirrer connected to a paddle was turned on and agitation rate was set to 25rpm to ensure good mixing as well as to wipe the cooled wall surface and remove the forming ice layer, before it creates a solid crust. The synthetic solution in the crystallizer was cooled down gradually and all the operational parameters were kept constant until the solution reached the eutectic point (which corresponds to the formation of ice and salt crystal). After reaching and maintaining eutectic conditions for close to 30 minutes, the



cooling and agitation was stopped, allowing salt crystals to settle at the bottom of the crystallizer and the ice crystals to float to the top. Salt slurry was collected from the bottom valve of the crystallizer and pumped to the filtration setup in order to filter and wash the salt crystals. Ice crystals were scooped via a domestic plastic sieve and from the top of the reactor and transferred manually to the filtration setup in order to filter and wash the ice crystals.

While filtering, ice crystals were washed manually in 2-3 steps with precooled pure water with a mass ratio of 1:1 between the washing liquid and wet crystals on the filter. The washed ice crystals were placed in a tared jar with cap and let to melt in a room temperature in order to determine the impurity concentration by conductivity measurements. While filtering, salt crystals were also washed manually in 2-3 steps with saturated solution of Na₂SO₄ with a mass ratio of 1:1 between the washing liquid and wet crystals on the filter. Washed salt crystals were placed into tared Petri dishes and dried in an oven at 40 °C for 24 hours. Noted the washing was conducted without stirring the crystal products.

Results and discussion

Preliminary study on the effect of sub-cooling and agitation

One of the most important EFC process key parameters are subcooling (difference between the cooling liquid temperature and eutectic temperature) and agitation, having to ensure correct salt and ice formation in terms of purity and their separation from each other. Therefore, different combinations of subcooling and agitation were studied in order to evaluate their effect on process performance. Values of these two parameters were selected from the literature and are enclosed in Table 13.

Subcooling (°C)	Agitation (rpm)
0.25	20
0.8	25
1.4	50
2.4	100

Table 13. EFC key parameters for process optimization.

After performing various EFC experiments of the synthetic 5 wt.% solution of Na₂SO₄·10H₂O and different subcooling-agitation combinations, a clear performance tendency based on key parameters was observed.

Effect of sub-cooling temperature

When high subcooling (>0.25°C) was applied, the ice formed too rapidly causing ice scaling (Figure 19). That enhanced the difficultness of harvesting the formed ice and trapped part of the salt crystals onto the scaling (Figure 20) and further reduced the gain in salt product. Moreover, great formations of the ice on the inner side of the crystallizer wall, principally on the bottom, were also obtained (Figure 21) during the experiments of high subcooling and low agitation (<20 rpm) hindering the recuperation of salt. The yield of water recovery in form of ice was about 10%, however its purity was not high



(between 22.9mS/cm and 36.1 mS/cm), demonstrating, that lower subcooling must be applied in order to recover high-quality values.



Figure 19. Scaling due to high subcooling



Figure 20. Salt trapped onto the scaling





Figure 21. Block of ice from the bottom of the crystallizer

Effect of agitation rates

When synthetic solution of $Na_2SO_4 \cdot 10H_2O$ was agitated rapidly (>25 rpm), undesirable crystallization phenomenon – agglomeration was observed (Figure 22). It affected the separation of the precipitated salt and formed ice. Due to rapid agitation, the salt was not able to set to the bottom of the crystallizer, as well as ice was not able to float to the top. Moreover, the purity of the ice was found to be low, undoubtedly, because of the absorption of the salt on the ice crystals. Therefore, the rapid agitation also inhibited recovery of high-quality ice (experimental conductivity: 9.56mS/cm) and salt (recovery yield 1.1-2.3 %) given that the phases were mixed.



Figure 22. Agglomeration phenomenon

ZERO BRINE – Industrial Wastewater – Resource Recovery – Circular Economy



Results on the optimal operation conditions

Provided results of the preliminary study, when subcooling was set at 0.25°C and agitation at 25rpm, the stable process performance was obtained. At these conditions the salt precipitated and settled to the bottom of the crystallizer, ice crystals formed and flowed to the top. Consequently, both products were successfully recovered (Figure 23).



Figure 23. Recovered ice and salt

Results in the optimal conditions for the design reactor, derived into a high ice quality being its conductivity between 0.41 and 0.48mS/cm and a recovery yield of 9.6% and 11.2% and a sodium sulphate yield recovery of 7.2% and 11.4%. Recoveries are considered in this stage to be low and this fact is attributed to the cooling rate of the equipment as it provided slow cooling rate and thus requiring a high amount of time to reach the subcooling set-point. This fact could have been directly related to the scaling challenges faced. In further stages a new cooling equipment is required.

ii. Recovery of sodium sulphate from synthetic RO concentrate

The study of recovery of sodium sulphate from synthetic RO concentrate solution was conducted by Xevgenos, D. *et al.* (2019)²⁸ and Hon-Chuk Yu (2018)²⁹ in which the effect of the impurities was assessed.

Experimental methodology

For this study four synthetic RO solutions with different compositions were prepared (Table 14). The 8wt% sodium sulphate solution with 1% sodium bicarbonate is a simple case which has only one type of pollutant; sodium bicarbonate was chosen as it is harmless and it can prevent scaling comparing with a pure binary system. Na₂SO₄ – NaCl – MgCl₂ system is a solution without any suspected insoluble compounds (Ca²⁺, Sr²⁺, Ba²⁺, SiO²). The third solution is the synthetic RO concentrate from filtration



with regenerated membranes, which composition is taken from a study of Casadellà & Meca (2018)³⁰ and, represents a concentrated effluent from the silica industry. The 4.5wt% sodium sulphate with doubled RO concentrate impurities is a solution that simulates a situation during a continuous EFC process with accumulation of impurities. As it is a simulation of an ongoing EFC processes, the sodium sulphate concentration in the solution was assumed to be the same as the eutectic concentration and lower than the concentration in the synthetic RO concentrate; the other concentrations were assumed doubled.

lon	8wt% sodium sulphate solution with 1% sodium bicarbonate		Na2SO4 – NaCl – MgCl2 system		Synthetic RO concentrate		4.5wt% sodium sulphate with doubled RO concentrate impurities	
	(mg/L)	wt%	(mg/L)	wt%	(mg/L)	wt%	(mg/L)	wt%
Sulphate	54103.07	5.41	54663.00	5.47	54663.00	5.47	29320.00	2.82
Sodium	28633.61	2.86	27930.30	2.79	27930.30	2.79	17769.20	1.71
Chloride			5105.83	0.51	5213.29	0.52	10741.49	1.03
Magnesium			817.00	0.08	817.00	0.08	1634.00	0.16
Silica					269.20	0.03	538.40	0.05
Calcium					60.20	0.01	120.40	0.01
Bicarbonate	7263.32	0.73						
Strontium					1.10	0.00	2.20	0.00
Barium					0.13	0.00	0.26	0.00

Table 14. Compositions of the synthetic experimental solutions

9L of synthetic solution was prepared for each experiment. A 15L cooled disk column crystallizer, which was constructed by DEMO TU Delft, was used for crystallization experiments (Figure 24). A vessel was isolated with 2 borosilicate glass and evacuated double walls to prevent condensation on the outside. The cooling of the crystallizer occurred from a copper heat exchanger plate with duplex coating, placed on the bottom of the reactor. A set of 4 scrapper blades was used to remove the forming ice layer on the heat exchanger plate. The thermostat and the agitation motor were connected to a computer, which controlled, monitored and logged measurements via their official software. More details about the EFC set-up can be find in the *Deliverable 5.1: Third plan for the shared use of BEC modules*.

Two double-walled vacuum glass filtrations, made by Prism Research Glass, were individually installed for filtering salt crystals and ice crystals. The filters' porosity was 10-26 µm. Salt crystals were collected as slurry from the bottom valve of the crystallizer and pumped by a peristaltic pump to the top of the filtration. Ice crystals were scooped via a domestic plastic sieve and transported manually to the top of the filtration; the transportation time is around 1 second. Noted all tubing were insulated by insulating foam as to minimize heat transfer with the environment.



The amount of impurities on the crystal surface were investigated via direct washing on a thermostating vacuum filtration. Washing was conducted with 20ml, 40ml, and 60ml washing solution on about 2g crystal products. For salt product, the samples were washed at room temperature; the washing solution used in each wash was saturated sodium sulphate. Similarly, for ice product, the samples were washed at 0°C; the washing solution used in each wash was 0°C Milli-Q water. Noted the washing was conducted without stirring the crystal products.



Figure 24. 15L reactor for EFC process

Results and discussion

Depressions of the eutectic freeze point due to impurities were observed in different solutions, as shown in Table 15 . A more impure solution was observed to encounter a deeper depression.

Table 15. Recorded eutectic freeze point of different solutions

Eutectic freeze point recorded (°C)							
Na₂SO₄ system (value from literature)	Na₂SO₄ – NaHCO₃ system	Na2SO4 – NaCl – MgCl2 system	Synthetic RO concentrate	Synthetic concentrated RO concentrate			
-1.27	-1.34	-1.36	-1.36	-1.49			

With a simple manual retrieving method, a conservative recovery of 42% salt and 55% ice with the 15L EFC equipment was obtained. Due to the avoidance of the stirrer blades during the manual harvesting, only part of the salt and ice from the solution were recovered, therefore the obtained value did not reflect the optimal recovery of the salt and ice; the values can be seen as the conservative estimation of the recovery via the EFC equipment. A higher recovery rate could be expected with an advance harvesting equipment.



Still, an almost pure salt was obtained, and a quality ice product was produced. The concentration of impurities was less than 1 wt.%, showing that recovered salt can be sold directly to the market without any treatment. Similar observation was found in different crystallization stages, which crystals were taken at 3°C (during freeze crystallization), eutectic point (during eutectic freeze crystallization), and 30 min after reaching eutectic point (during eutectic freeze crystallization). It is obvious that the technology is also robust to produce quality crystals with different crystallization stages. Ice product contained 7.7wt% of salt impurities, indicating that washing step should be required.

As to identify if the impurities were embedded in the crystals' structure, washing step was applied. If the impurities are not embedded, impurities can be easily washed out and the product quality will be enhanced. For both products, salt and ice, the impurities were reduced along with the washing step, indicating that the impurities were not fixed inside the crystals structure, and thus enhancing the product quality.



6. Conclusions

- A pre-treatment scheme was established through a simulation software by adjusting the effluent to pH 7.0 for the removal of Al and Fe, ultrafiltrating it to remove SST and precipitates, adjusting the pH at 9.0 to solubilize SiO₂ and by dosing antiscalant at a concentration of 1.65 mg/L to prevent the precipitation of SiO₂, BaSO₄, SrSO₄ and CaSO₄.
- A membrane with similar properties to the most oxidized one (6,000pm·h) was considered for the start-up of the pilot plant as it would require low energy for a suitable quality of permeate and concentrate. The permeate presented a conductivity adequate to provide water for further reuse that is below 4.6mS/cm. The concentrate achieved a concentration factor of 2.17.
- Regenerated membranes proof to be a suitable process for the concentration of Na₂SO₄ (IQE's brine) as they present low energy demands (pressure), high fluxes, adequate rejections and low acquisition costs.
- The synthetic 5 wt.% solution of Na₂SO₄·10H₂O when submitted to EFC conditions provided a clear separation of both solid phases (crystals and ice).
- When high subcooling (>0.25°C) was applied, the ice formed too rapidly causing ice scaling in the crystallizer. To the same, an excessive agitation (>25 rpm) caused crystals agglomeration. These undesirable EFC phenomena enhanced the difficultness of harvesting the formed ice and salt.
- When subcooling was set at 0.25°C and agitation at 25rpm, the stable process performance was obtained, thus permitting successful product recovery.
- During the EFC experiments with synthetic RO concentrate, a conservative recovery of 42% salt and 55% ice was obtained. The recovered products were almost pure, with less than 1 wt.% impurities for salt and 7.7wt% for ice.
- The impurities were reduced along with the washing step, indicating that the impurities were not fixed inside the crystals structure, and thus enhancing the product quality.
- EFC proof to be a robust process to produce quality crystals with different crystallization stages.
 In other words, steady quality salt and ice products are promised throughout the EFC process.



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8. Annex

Annex I

Table 16. Description of the used analytical methods

Parameter	Equipment	Standard/Method
рН	pHmeter, Crison GLP 22	ISO10523:2008
Conductivity	Conductimeter, Crison MM41	UNE EN 27888:1994
Turbidity	2100Qis Turbidimeter , Hach Lange	Nephelometric
Cations (K, Na, Ca, Mg)	Aquion, Dionex	Ionic Chromatography
Anions (Cl, NO ₃ , SO ₄)	ICS 2100, Dionex	Ionic Chromatography
Metals (Al, Si, Mn, Fe, Sr, Ba)	7500 CX, Agilent Technologies	ICP-MS

Annex II

Results of the performance of membranes oxidized at 4,000ppm·h and 6,000ppm·h described in Deliverable D4.2.



Figure 25. Effect of OA doses on SW-RO coupons (n=2)



	H-1 hydrated membrane	2,000 ppm∙ h	4,000 ppm∙ h	6,000 ppm∙ h
Feed flux (L/min)	1.0	1.0	1.0	1.0
Permeability (L/m²·h·bar)	1.25	1.25	1.25	1.25
Recovery (%)	71.0	75.1	75.9	74.6
Final permeate conductivity (mS/cm)	0.75	1.80	2.82	4.18

Table 17. Performance of one H-1 hydrated membrane with synthetic solution.

Table 18. Removal of Cl and SO4 from the synthetic solution with oxidized membranes at different doses.

	H-1		2000 ppm∙h		4000 ppm∙h		6000 ppm∙h	
n=1	Cl (ppm)	SO ₄ (ppm)	Cl (ppm)	SO₄ (ppm)	Cl (ppm)	SO₄ (ppm)	Cl (ppm)	SO₄ (ppm)
Feed	1,768	16,435	1,768	16,435	1,768	16,435	1,768	16,435
Concentrate	477	60,170	5,050	60,880	4,550	60,260	4,330	61,450