



ZERO BRINE

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 filings, videos, etc.; OTHER=other

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

Executive summary

This deliverable includes results from Task 4.1. 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 (EDBM). On the one hand, regenerated membranes provided two effluents: water for reuse (permeate) and concentrated brine (concentrate) to be further treated by crystallization technologies to recover salts. On the other hand, the EDBM process is meant to obtain NaOH and H₂SO₄ as valuable reagents out of the brine considered wastewater.

Technologies can be combined in order to establish the two different treatment schemes To assess technical feasibility of the processes KPI have been defined. Treatment schemes, KPI objective and achievement of them are presented in Table 1.

Table 1: Treatment schemes evaluated at bench scale. Technical objectives (KPI).

	Technologies	Technical objectives (KPI)	Achieved
Scheme 1	Pre-treatment	Turbidity <2NTU [Al ³⁺] <50 µg/L [Fe ³⁺] <200 µg/L	✓
	RO regenerated membranes	Water recovery >70% Water quality (<4.6mS/cm)	✓
	Crystallization	Na ₂ SO ₄ purity > 98% Water quality (<4.6mS/cm)	✓
Scheme 2	Pre-treatment	Turbidity <2NTU	✓
	EDBM	Water quality (<6mS/cm)	✗
		NaOH >2mol/L H ₂ SO ₄ >2mol/L	

Pre-treatment step

The scheme for the pre-treatment of the effluent for membrane technologies 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.

Scheme 1: Pre-treatment, regenerated membranes coupled to crystallization

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 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 compared 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.

Regarding EFC technology, A conservative recovery of 42% salt and 55% ice was obtained. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ with purity 99% was produced showing that recovered salt can be sold directly to the market without any treatment. Ice product contained 7.7wt% of salt impurities, indicating that washing step should be required. A higher recovery rate could be expected with an advance harvesting equipment.

Treatment scheme 1 shows promising results thanks to the combination of concentration step using regenerated membranes and EFC technology. On the one hand, regenerated membranes allow water recoveries > 70%. The permeate presented a conductivity adequate to provide water for further reuse that is below 4.6mS/cm. On the other hand, the concentrate achieved a concentration factor of 2.17 and could be treated with EFC to produce high purity $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. However, long-term performance should be necessary to demonstrate technology robustness. This treatment scheme will be validated at pilot scale in the framework of task 4.3. The energy requirements for this treatment will be estimated during pilot plant operation period.

Electrodialysis with bipolar membranes

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. Several tests have been performed in order to establish the optimal conditions to treat wastewater from IQE. Results obtained indicates that for desalinating 1m^3 of IQE effluent, 214 L of 0.05M H_2SO_4 and 214L of 0.10 M NaOH would be needed. At the end, it would be obtained 1m^3 of treated effluent that can be reused at IQE production process. Regarding acid (0.37 M H_2SO_4 (72% of purity)) and base (0.82 M NaOH (94% of purity)) its concentration

is too low to be reused at IQE production process. Additional concentration steps of these reagents would be needed.

Under defined conditions, the electricity consumption was 135 kWh/m³, meaning an electrical cost of 13.5 €/m³ (assuming a cost for electricity of 0.1 €/kWh). The cost associated to the initial NaOH and H₂SO₄ solutions would be around 1,4 €/m³ and 1,6 €/m³, respectively (supposing a cost of 200€ /t for each, NaOH solid and H₂SO₄ 96%).

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1. Overview of the project

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.

2. Objectives

WP4 aims to demonstrate circular economy in the chemical sector, specifically in the silica industry IQE. To do this, an innovative process based on high pressure membrane filtration (NF/RO) using regenerated membranes and a crystallization stage, will be applied to treat saline wastewater generated in this industry. Water and Na_2SO_4 will be recovered from the wastewater. Alternatively, electrodialysis using bipolar membranes (EDBM) will be evaluated at bench scale in order to recover water and reagents, NaOH and H_2SO_4 , that could be recirculated in the production process. 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 evaluate at bench-scale technologies to treat wastewater from silica industry in order to recover water, sodium sulphate, acids and alkalis. Two treatment schemes have been defined by combining different processes: pre-treatment step, filtration step with membranes (regenerated and EDBM) and a crystallization step (Eutectic Freeze Crystallization - EFC) for the final recovery of salts. In Table 2 the two treatment schemes and the technical objectives for each of them are showed.

Table 2: Treatment schemes evaluated at bench scale. Technical objectives (KPI).

Technologies		Technical objectives (KPI)
Scheme 1	Pre-treatment	Turbidity <2NTU [Al ³⁺] <50 µg/L [Fe ³⁺] <200 µg/L
	RO regenerated membranes	Water recovery >70% Water quality (<4.6mS/cm)
	Crystallization	Na ₂ SO ₄ purity > 98% Water quality (<4.6mS/cm)
Scheme 2	Pre-treatment	Turbidity <2NTU Water quality (<6mS/cm)
	EDBM	NaOH >2mol/L H ₂ SO ₄ >2mol/L

It is worth to mention, that Scheme 1 is the most promising one and will be demonstrated at pilot scale in Task 4.3. Bench-scale experiments results will be used as starting point for experimental plan design during pilot plant operation. Regarding EDBM, the objective of bench scale experiments is to explore the potentiality of this technology.

3. Introduction

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. In the following table, existing technologies described in the BREF LVIC¹⁾ and other available in the market are described.

Table 3: Example Current available technologies for silica wastewater treatment.

Treatment	Disadvantages	By-product	Cost (€/t silica)	Market value sulphate compounds (€/t)
Spray dryer¹⁾	High energy consumption	Na ₂ SO ₄	280* - 700	60
Gypsum precipitation¹⁾	Energy consumption and CaO consumption	CaSO ₄ ·2H ₂ O	170* - 225	<10
Evaporation and crystallization**	High energy consumption Uneconomic when salt present is very low	Anhydrous Na ₂ SO ₄	145**	60

*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, all existing management strategies are cost-intensive. In the case of gypsum precipitation, management costs are split for energy consumption (50%), supply of calcium oxide (25%) and disposal costs (25%). In the case of spray dryer and evaporation, energy

consumption represents more than 40% of management costs, while around 60% are due to disposal costs. In this sense, valorisation of sulphate compounds is crucial to eliminate disposal costs. According market prices for recovered products, and estimating that for each tone of silica, 0.75 tone of Na_2SO_4 or 0.9 tone of $\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ can be recovered, turnover from Na_2SO_4 or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is lower than management costs. Based on that, the recovery of sulphate with existing technologies is not economically feasible.

In this context, ensuring market for recovered products is not enough. Energy consumption must be reduced. In the case of spray dryer or evaporation if the stream would be more concentrated energy consumption could be reduced making more economically feasible the management. In addition, new technologies that requires less energy would allow to reduce management cost too.

ZERO BRINE aims to develop innovative processes for treating wastewater from silica industry based on the concept of circular economy and promoting the resource efficiency by recovering resources. To do that, innovative technologies have been tested at bench-scale in order to evaluate its performance previous its demonstration at pilot scale. 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. Figure 1 presents the technological scheme proposed at bench-scale for the optimization of the pilot plant operation at IQE.

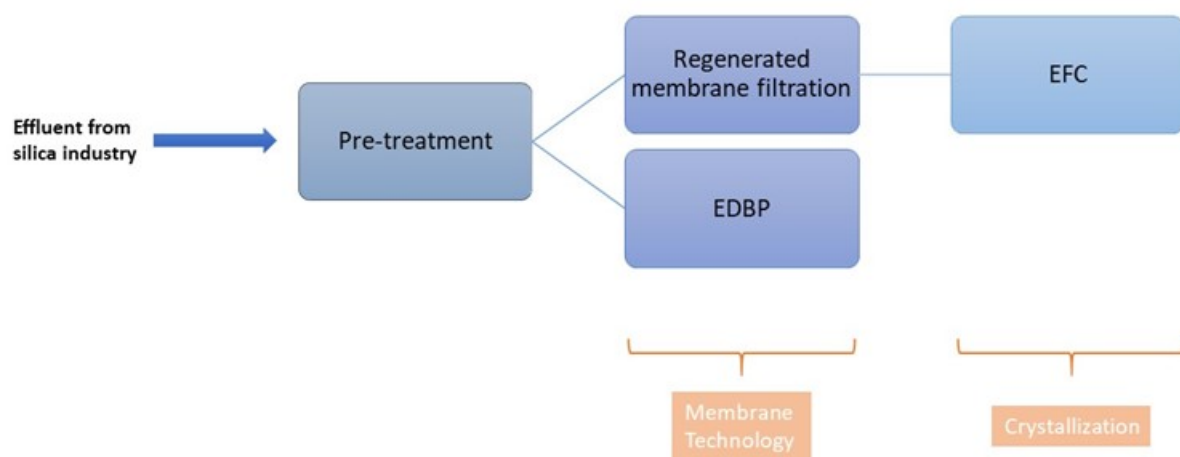


Figure 1: Technological scheme developed at bench-scale for the treatment of brine from IQE.

Specifically, membrane technologies tested are pressure-driven filtration with regenerated membranes (Deliverable D4.2) and Electrodialysis with bipolar membranes (EDBM). 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 EDBM process is meant to obtain NaOH and H_2SO_4 as valuable reagents out of the brine considered wastewater.

One of the innovative crystallization processes assessed in this project is Eutectic Freeze Crystallization (EFC). The driving force for this process is temperature. For EFC, cooling is required as a difference with more conventional crystallization technologies based on evaporation that 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.

Technologies can be combined in order to establish the two different treatment schemes presented previously in Table 2.

Scheme 1: Pre-treatment + Regenerated membranes + Crystallization

Applying this scheme, water and sodium sulphate will be recovered by concentrating wastewater 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 was evaluated in order to reduce costs. For crystallization, innovative EFC technology was investigated at bench-scale.

This treatment scheme 1 will be validated at pilot scale in “task 4.3 Validation of sodium sulphate recovery process”.

Scheme 2: Pre-treatment + EDBM

This scheme aims to recover water, NaOH and H₂SO₄ 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. For this scheme 2, the objective of bench scale experiments was to explore the potentiality of this technology.

The technological schemes 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.

4. 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 4 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.

Table 4: Process wastewater composition from IQE to be treated in ZERO BRINE.

Feed			
Parameter	Value	Parameter	Value
Ca (mg/L)	58	SO ₄ (mg/L)	11,950
Mg (mg/L)	6.00	Cl (mg/L)	1,520
Na (mg/L)	6,615	HCO ₃ (mg/L)	1.00
K (mg/L)	27	NO ₃ (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		

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) during operation. The software is usually used to predict scaling potential of the membrane surface, thus it considers possible concentration polarization. Nevertheless, the software can also be used to detect scaling tendency of a solution prior to membrane. 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 trend to precipitate.

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 ZERO BRINE. 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 20 bar at 20 °C and at different recoveries to assess its effect in the precipitation.

In Table 5 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.

Table 5: Saturation index of the concentrate

Expected scaling in the concentrate (%)			
60% recovery	70% recovery	75% recovery	80% recovery
505 % BaSO ₄	701 % BaSO ₄	868 % BaSO ₄	1137 % BaSO ₄
50% CaSO ₄	77% CaSO ₄	103% CaSO ₄	149% CaSO ₄
50 % SrSO ₄	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

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. pH effect on Al, Fe and Si solubility was evaluated using OLI software. As it can be observed in Figure 2, Al and Fe present their minimum solubility at pH between 6.0 and 8.5. In the case of Si, its solubility increases with pH increase.

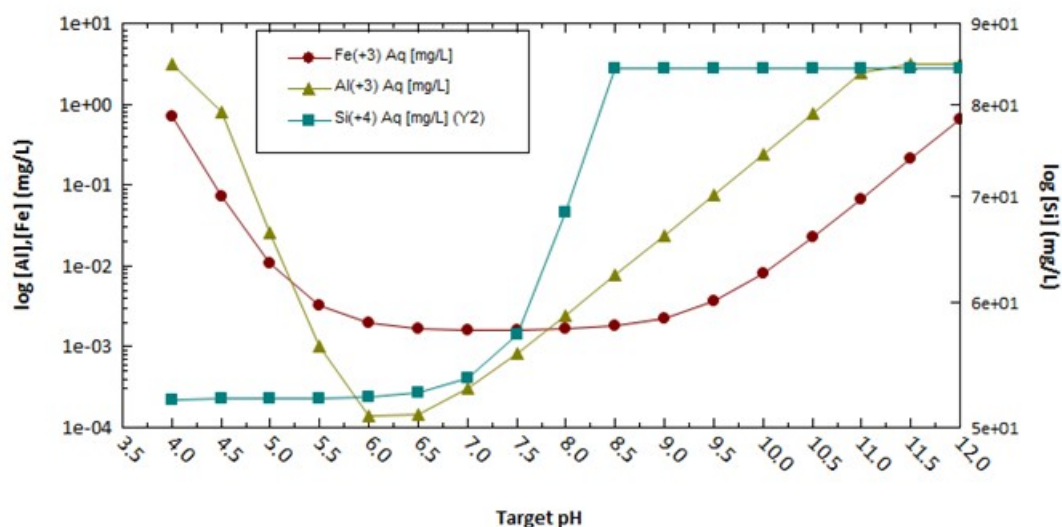


Figure 2: Solubility of Al, Fe and Si as a function of pH.

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 where the solution was brought to the established pH using sodium hydroxide. As aluminum and iron content in silica wastewater presents fluctuations, a wastewater sample with a high concentration of these elements was used to perform these experiments. 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 6 the percentage of removal of each metal ion for three pH adjustments (6.0, 6.5 and 7.0) is detailed.

Table 6: Removal of metals by pH adjustment.

	Turbidity (NTU)	Al (mg/l)	Si (mg/l)	Fe (mg/l)	Removal (%)			
					Turbidity	Al	Si	Fe
Initial (pH 5.2)	33	3.20	84	1.60	-	-	-	-
pH 6.0	0.8	1.84	88	0.34	97.6	42.5	0	78.8
pH 6.5	0.9	0.87	86	< 0.2	97.3	72.9	0	>87.5
pH 7.0	0.6	0.66	84	< 0.2	98.2	79.4	0	>87.5

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 due to the presence of silica in colloid form. When the solution increased pH, precipitate was formed and after removal of this precipitate, turbidity was 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 was the one providing higher removal rates of Al and Fe whilst Si was not affected by these pH ranges, as already expected according modelling. Thus,

it was established that a step of pre-treatment would be to adjust its pH to pH 7.0 to have Al and Fe in their precipitate form and thus remove them by ultrafiltration.

After the removal of Al and Fe, it was necessary to establish another step to minimize Si precipitation. Looking again to Figure 2 pH over 8.5 is favorable to dissolve Si in its form of SiO_2 and not derive into scaling. Thus, it was set that the feed to the module of regenerated membrane to be adjusted to 9.0 in order to avoid fouling.

Besides Fe, Al and Si, salts such as BaSO_4 , CaSO_4 and SrSO_4 were considered as well. Thus, simulation with the software PermCare provided from NALCO (antiscalant provider) were again conducted without introducing Al and Fe in the system and by introducing pH 9.0 as the pH of the feed to membrane stage. 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 3. 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 SiO_2 followed by the addition of antiscalant at the given concentration of the prediction (1.65 mg/L) to prevent SiO_2 , BaSO_4 , SrSO_4 and CaSO_4 to precipitate.



Figure 3: Pre-treatment scheme for the regenerated membrane unit.

5. 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 water and two reagents, NaOH and H₂SO₄, of value to be further reused in the production process.

a. Regenerated membranes

A regenerated membrane is an end-of-life membrane that has been regenerated for tailor-made purposes. End-of-life membranes are those membranes that doesn't comply with specifications and are then managed as a waste. 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. Membranes regeneration was evaluated in subtask 4.1.4 and results are described in Deliverable 4.2.

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 3) 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

1. Wastewater characterization

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

2. Regeneration membrane tests

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 4 and described briefly hereafter.

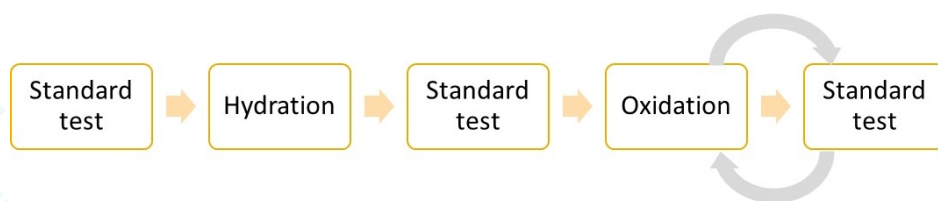


Figure 4: General methodology to regenerate membranes.

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. Hydration is as well key in the regeneration process, prior to the use of the oxidation agent (OA) on membrane surfaces, hydration of membranes is an enhancing factor in the recycling process. Some of the methods that manufacturers recommend to hydrate membranes include pressurization to 10 bar with permeate valve closed, immersion in a solution of ethanol or propanol in water at 50% or immersion in HCl at 1%.

For experiments in a lab-scale, coupons of a membrane element were required to test membranes as flat sheets. These coupons were achieved by cutting open one the RO membrane so the inner sheets of the element that form the spiral wound were accessible (Figure 5). Once opened, coupons of membrane and carriers of the middle sheets (140 cm²) were cut to fit the testing cell (Figure 6). 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.



Figure 5: Membrane element opened to access the membrane sheets.



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

Membrane performance was tested in the set-up shown in Figure 7.

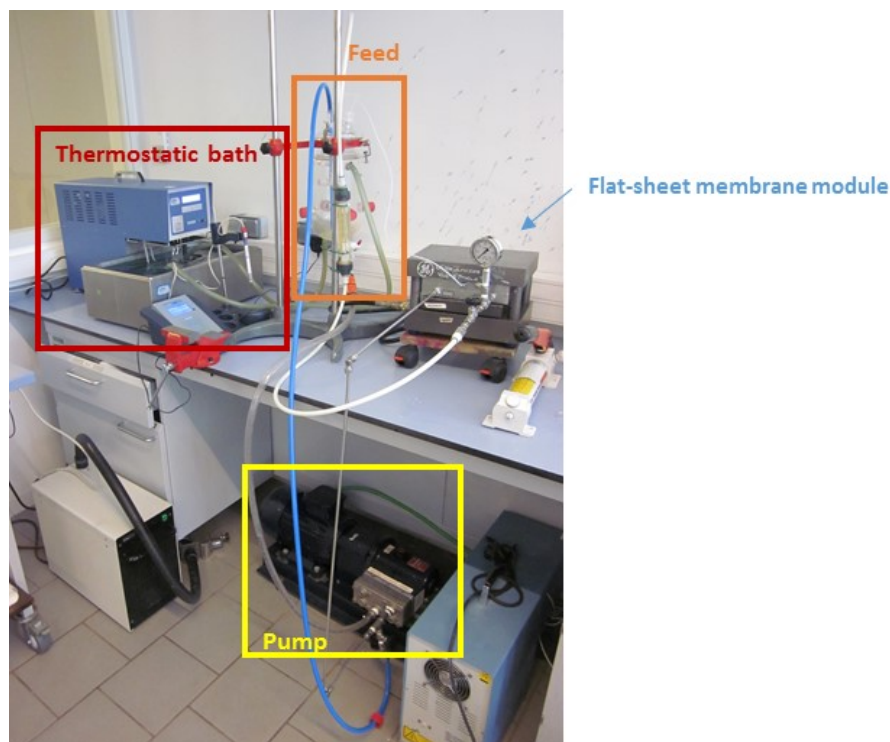


Figure 7: Experimental set-up for membrane testing at lab-scale (BP-2 from Spanish BEC)

The experimental set-up included: SEPA II membrane test cell, pump, pressure gauges, balance, temperature probe, tubing and valves. Experiments were conducted in a way that the concentrated was recirculated to the feed water while the permeate was collected monitoring recovered weight. Since the permeate was not recirculated, feed concentration increased over time and pressure was increased to maintain permeate flow constant. 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.

Membrane regeneration consisted in: 1) hydrating the membrane by immersing it in a solution of alcohol; 2) oxidizing the polyamide layer of the hydrated 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.

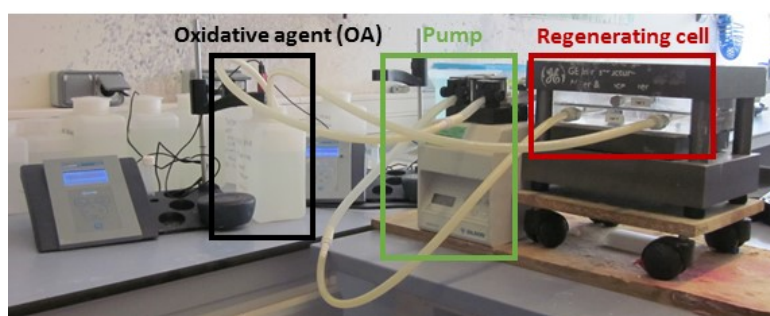


Figure 8: Experimental set-up for oxidizing the membrane at lab-scale (BP-12 from Spanish BEC).

In subtask 4.1.3 membrane regeneration process was investigated and results were presented in Deliverable 4.2. Based on regeneration results two different tailor-made membranes were selected 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. The dose is the concentration of oxidative agent (ppm) applied for a specific time (h).

ii. Results and discussion

In Table 7 Results on the standard test with NaCl provided are shown while in Table 8 performance of regenerated membranes using synthetic wastewater is showed.

Table 7: Results of standard test with NaCl for the chosen membranes (extracted from Deliverable 4.2).

	Permeability (LMH/bar)	Rejection NaCl (%)
Membrane 4,000ppm·h	4.25	98.3
Membrane 6,000ppm·h	5.02	96.7

From NaCl standard test it can be observed differences in rejection and permeability of both membranes depending on the dose applied. The membrane with the highest oxidizing degree is the one with highest permeability and lowest rejection as it is the one with the most degraded polyamide active layer.

Table 8: Performance of regenerated membranes selected when synthetic wastewater is treated (extracted from Deliverable 4.2).

	4,000 ppm·h	6,000 ppm·h
Feed flux (L/min)	1.0	1.0
Temperature (°C)	25	25
Permeability (L/(m ² ·h·bar))	1.25	1.25
Working pressure (bar)	24	20
Recovery (%)	75.9	74.6
Rejection in conductivity (%)	90.8	86.4
Final permeate conductivity (mS/cm)	2.82	4.18

These two oxidation doses were chosen as they provided a quality of the permeate within the requirements defined by IQE (conductivity <4.6mS/cm) at the lowest operation pressure 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.

Real brine was used to assess the proposed technological scheme prior to its application in the pilot plant. In Table 9, operational performance of the regenerated membranes is showed. In Table 10 results on the composition and quality of each of the technological steps are presented.

Table 9: 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

Table 10: Physicochemical results of the technological scheme with regenerated membranes for real brine.

Parameter	Unit	Initial	Adj. to pH 7.0	UF + Adj. to pH 9.0 + antiscalant addition	Membrane 4,000ppm·h		Membrane 6,000ppm·h	
					Permeate	Concentrate	Permeate	Concentrate
pH	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				
Cl	mg/l	1,336			106	2,760	108	2,754
NO₃	mg/l	9.30			< 5.0	< 5.0	< 5.0	< 5.0
SO₄	mg/l	12,645			394	27,540	408	27,528
K	mg/l	24.0			1.0	61.7	1.1	62.0
Na	mg/l	6,643			262	14,777	266	14,789
Ca	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
Al	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
Ba	µg/l	54.0	53	51	0.6	100	0.6	100

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 10 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 SiO_2 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. Pressure was adjusted during the experiment to maintain the flux constant. The membrane that was most oxidized required a pressure of 16 bar to maintain this flux whilst the other membrane, a pressure of 18 bar (Table 9). From the quality point of view, electrical conductivity of each of the effluents (permeate and concentrate) proves that the rejection of the most oxidized membrane is lower (Table 9), fact that was already established from the standard tests (Table 7). This fact is due to the higher conductivity of the permeate for the most oxidized membrane compared 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 lower energy for a suitable quality of permeate and concentrate. No scaling was observed on the membrane surface. As the tests were done in lab scale, fouling tendency cannot be correctly assessed as the module is not operating in the usual spiral-wound configuration. This is usually assessed in pilot plant. Even though, no precipitates were observed on the membrane surfaces after treatment. The permeate presented a conductivity adequate to provide water for further reuse that is below 4.6 mS/cm. The concentrate achieved a concentration factor of 2.17.

In Table 11 defined KPI and achieved results are showed. Provided all results achieved, regenerated membranes prove to be a suitable process for the concentration of Na_2SO_4 (IQE's brine) as they allow water recovery of good quality for internal reuse.

Table 11: KPIs expected and achieved for pre-treatment and regenerated membrane stage applied to treat the IQE real effluent.

KPI	Expected values	Achieved values
Turbidity after pre-treatment (NTU)	<2	0.9 ± 0.1
$[\text{Al}^{3+}]$ ($\mu\text{g/L}$) after pre-treatment	<50	<10
$[\text{Fe}^{3+}]$ ($\mu\text{g/L}$) after pre-treatment	<200	200
Water recovery (%)	>70	71-73
Water quality (mS/cm)	<4.6	1.34-2.50

b. Electrodialysis with 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. At an extreme pH difference (*i.e.*, a catholyte at approximately pH 0 versus anolyte at approximately pH 14), a voltage of 0.83 V should be applied for dissociation of water in the BM. When non-extreme pH are used, the total membrane voltage depends on the pH difference in the electrolytes ($\varphi = 0.0591 \Delta\text{pH}$, where ΔpH is the pH difference in the electrolytes). Besides, the Bm voltage also depends on the salt type/concentration, flow rate and current density⁸⁾.

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)⁹⁾.

The efficiency of the process depends on 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.

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).

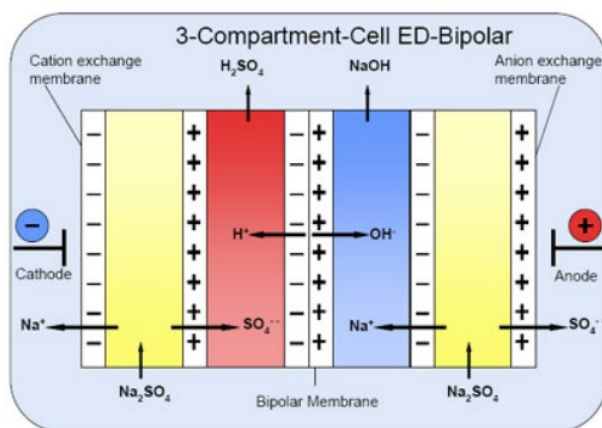


Figure 9: Flat-sheet membrane module used for regenerated membrane tests. Composition of a 3-compartment cell in the electrodialysis process with BM. Figure obtained from Fumatech¹⁰⁾.

The most recent references related with the use of this type of BM are compiled in the Table 12.

Table 12: State of the art (SoA) related with EDBM process using Fumatech bipolar membranes.

Properties	Ghyselbrecht <i>et al.</i> (2014) ¹⁴⁾	Yang, <i>et al.</i> (2014) ¹⁶⁾	Herrero-González, <i>et al.</i> (2018) ¹⁷⁾
Type of membranes	Fumasep from Fumatech	Fumatech	Fumasep from Fumatech
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 HCl	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

In the ZERO BRINE project, electrodialysis with bipolar membranes (EDBM) was tested at bench-scale aiming to desalinate IQE effluent to an electric conductivity (EC) minor than 6 mS/cm and to obtain two concentrated effluents corresponding to NaOH and H₂SO₄, looking for a zero liquid discharge objective. The KPIs pursued are the following:

Table 13. KPIs for the EDBM process applied to desalinate the IQE effluent.

KPI	Expected values
Salt removal from IQE effluent (%)	> 60% (final EC < 6 mS/cm)
Acid concentration	> 2 mol/L
Base concentration	> 2 mol/L

i. Experimental methodology

1. Wastewater to be treated

Three types of effluents were used to study the EDBM process.

- First of all, the EDBM process was performed using synthetic brine with ten times higher concentration of the salts than the real IQE effluent, *i.e.*, 0.3M NaCl and 1M Na₂SO₄, to deeper evaluate the influence of several operation parameters (specified in the section 4.2.1.3).
- Under the most appropriated operational conditions, the EDBM process was performed with a synthetic IQE effluent composed by 0.03M NaCl and 0.1M Na₂SO₄.

c. And finally, the real saline wastewater from IQE company.

2. Selection of bipolar membranes

Different commercially available bipolar membranes were evaluated and theoretically compared in order to select the most suitable for the application. Several providers have been contacted, such as FUMATECH GmbH¹¹⁾, PCCell GmbH (before called PCA - PolymerChemie Altmeier GmbH)¹²⁾ and ASTOM Co¹³⁾.

Ghyselbrecht *et al.* (2014)¹⁴⁾ 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)¹⁵⁾ 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.

Although the effluent from IQE is a saline wastewater, Eurecat decided to select Fumasep® FBM single film bipolar membrane from FUMATECH based in previous own experience and since they present better electrical and mechanical properties, and a higher acid/base purity is achieved compared with the other membranes. Every Fumasep® FBM 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 14 and its appearance, together with the spacer used, are photographed in Figure 10.

Table 14: Technical specifications of Fumasep® FBM membrane.

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

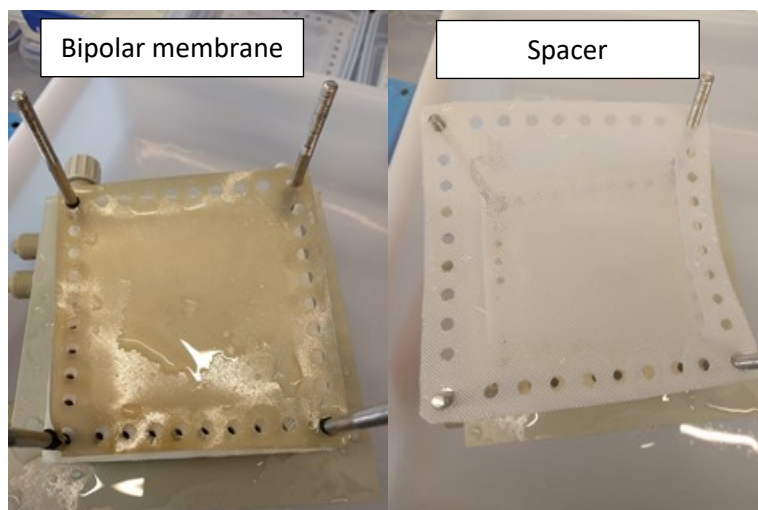


Figure 10: Spacer (left) and Fumasep® FBM membrane used during the EDBPM process (right).

Regarding CEM and AEM membranes. These were provided by Fujifilm.

3. Experimental setup and 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 11.

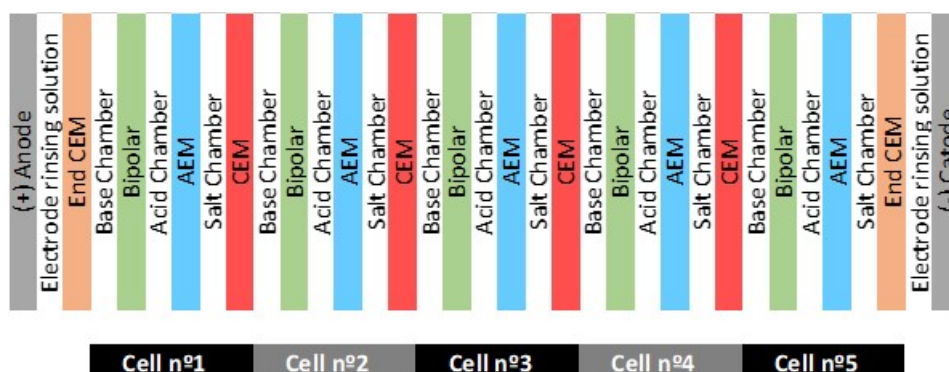


Figure 11. Diagram of the configuration of the EDBM stack.

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



Figure 12: EDBM 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 15.

Table 15: Specifications of the EDBM stack.

Properties	Values
Cell characteristics	Effective area of the membranes = 64 cm ² Membrane size = 100 x 100 mm Spacer thickness: 1 mm
Type of cationic exchange membrane (CEM)	Fujifilm CEM Type 10
Type of anionic exchange membrane (AEM)	Fujifilm AEM Type 10
Type of bipolar membranes	Fumasep® FBM membrane
Number of cell triplets	1 stack containing 5 cell triplets (see Figure 11)

The EDBM experiments were carried out at amperometric conditions (constant electrical current density) and measuring the voltage through the time.

First of all, the EDBM process was performed using synthetic brine with ten times higher concentration of the salts than the real IQE effluent, *i.e.*, 0.3M NaCl and 1M Na₂SO₄, to deeper evaluate the influence of several operation parameters such as the following ones:

- The initial concentration of the acid: 0.25 M, 0.10 M and 0.05 M H₂SO₄.
- The initial concentration of the base: 0.10 M or 0.25 M NaOH.
- The influence of the electrical current density applied to the system: 75%, 50% or 25% of the limiting current density ($I_{\max} = 10 \text{ A}$; $j = 156 \text{ mA/cm}^2$).
- The influence of the ratio $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$

For each experiment, desalination efficiency, applied electrical charge, and energy consumption were determined. During the experiments, potential and electrical current of the system, conductivity, pH, flowrate, temperature, and pressure of each stream were monitored.

Under the most appropriated operational conditions, the EDBM process was performed with a synthetic IQE effluent (composed by 0.03M NaCl and 0.1M Na₂SO₄).

Finally, the EDBM process was tested to treat the real IQE effluent to analyze the treatment performance with a real effluent and the influence of some species, such as silicon, on the efficiency. As commented before, the EDBM process aims to achieve a desalination percentage higher than 60% from the IQE effluent obtaining at the same time concentrated solutions of acid and base.

The operational conditions followed for the set of EDBM experiments are summarized in Table 16.

Table 16: Experimental design of EDBM process for the desalination of IQE effluents.

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 synthetic IQE brine	Experiment with real IQE wastewater
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	Synthetic 0.03M NaCl 0.1M Na ₂ SO ₄	Real IQE wastewater
Initial acid concentration and volume	a) 0.25M H ₂ SO ₄ b) 0.1M H ₂ SO ₄ c) 0.05M 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	The best H ₂ SO ₄ concentration previously found
Initial base concentration and volume	0.1M NaOH	0.25M NaOH	The best NaOH concentration previously found	The best NaOH concentration previously found	The best NaOH concentration previously found	The best NaOH concentration previously found
Final acid concentration	To be determined	To be determined	To be determined	To be determined	To be determined	To be determined
Final base concentration	To be determined	To be determined	To be determined	To be determined	To be determined	To be determined
Electrode rinsing solution concentration	0.3 M Na ₂ SO ₄	0.3 M Na ₂ SO ₄	0.3 M Na ₂ SO ₄	0.3 M Na ₂ SO ₄	0.3 M Na ₂ SO ₄	0.3 M Na ₂ SO ₄
Acid dissolution volume	1L	1L	1L	1,5L	The best of tested before	The best of tested before
Base dissolution volume	1L	1L	1L	1,5L	The best of tested before	The best of tested before
Diluate volume	1L	1L	1L	0,5L	The best of tested before	The best of tested before
Electrode rinsing solution volume	1L	1L	1L	1L	1L	1L
Applied current density (j)	j = 25% of limiting current density	j = 25% of limiting current density	b) j = 75% of limiting current density c) j = 50% of limiting current density	The best of tested before	The best of tested before	The best of tested before
Desalination efficiency goal	> 60 %	> 60 %	> 60 %	> 60 %	> 60 %	> 60 %

ii. Results and discussion

This section presents the results obtained for the EDBM process. First of all, the influence of several parameters on the performance of the EDBM treatment was evaluated to define the best operational conditions to apply this process to a synthetic and real IQE effluent.

1. Influence of the initial concentration of acid

Sulfuric acid was selected to perform the EDBM process. Three different initial concentrations of acid were tested: 0.25 M, 0.10 M and 0.05 M H_2SO_4 . A dissolution of 0.10 M NaOH was chose as initial base stream. Electrolyte (0.3M Na_2SO_4) was continuously recirculated throughout the cathodic and anodic compartments.

The first EDBM experiment was carried out by using a 0.25 M H_2SO_4 solution at a constant current density of 39 mA/cm^2 (2.5 A).

1L of a synthetic solution with ten times higher concentration of the salts than the real IQE effluent (0.3M NaCl and 1M Na_2SO_4 ; $\text{EC}_{\text{initial}} = 113 \text{ mS/cm}$) was used to be desalinated up to an $\text{EC} < 6 \text{ mS/cm}$. Volumes of acid, base and electrolyte solution were also of 1L.

The pressure of the 4 streams was kept at 0.3 bar, measuring the resulting flowrate of each one.

A summary of these operational conditions for the first experiment can be observed in Table 17.

Table 17: Summary of the operational parameters during the EDBM test to evaluate the influence of the acid concentration (0.25 M H_2SO_4).

I (A) / j (mA/cm ²)	Electrolyte	Effluent to be treated	Acid	Base	V electrolyte (L)	V diluate (L)	V acid (L)	V base (L)
2.5 / 39	Na_2SO_4 0.3M	Synthetic 0.3M NaCl 1M Na_2SO_4	0.25M H_2SO_4	0.1M NaOH	1	1	1	1
Q electrolyte (L/h)	P electrolyte (bar)	Q diluate (L/h)	P diluate (bar)	Q acid (L/h)	P acid (bar)	Q base (L/h)	P base (bar)	KPI diluate
80	0.3	15	0.3	15	0.3	10	0.3	< 6 mS/cm

A relative electrical charge of 1250 Ah/m^3 was applied to the electrochemical system. However, low effect on desalination of the effluent was observed. Only a 1.5 % of salt was removed from the synthetic effluent under these conditions, even though acid and base solution was concentrated. The EC of the acid solution was increased from 111 mS/cm to 169 mS/cm, whereas the pH was decreased from 0.6 to 0.3. The CE and the pH of the base was also raised from 25 mS/cm to 99 mS/cm, and from 12.5 to 13.0, respectively, indicating in both cases the good performance of the bipolar membranes.

The EC, pH and electrical consumption throughout the applied charge obtained during this experiment for acid, basic and salt streams were depicted in Figure 13.

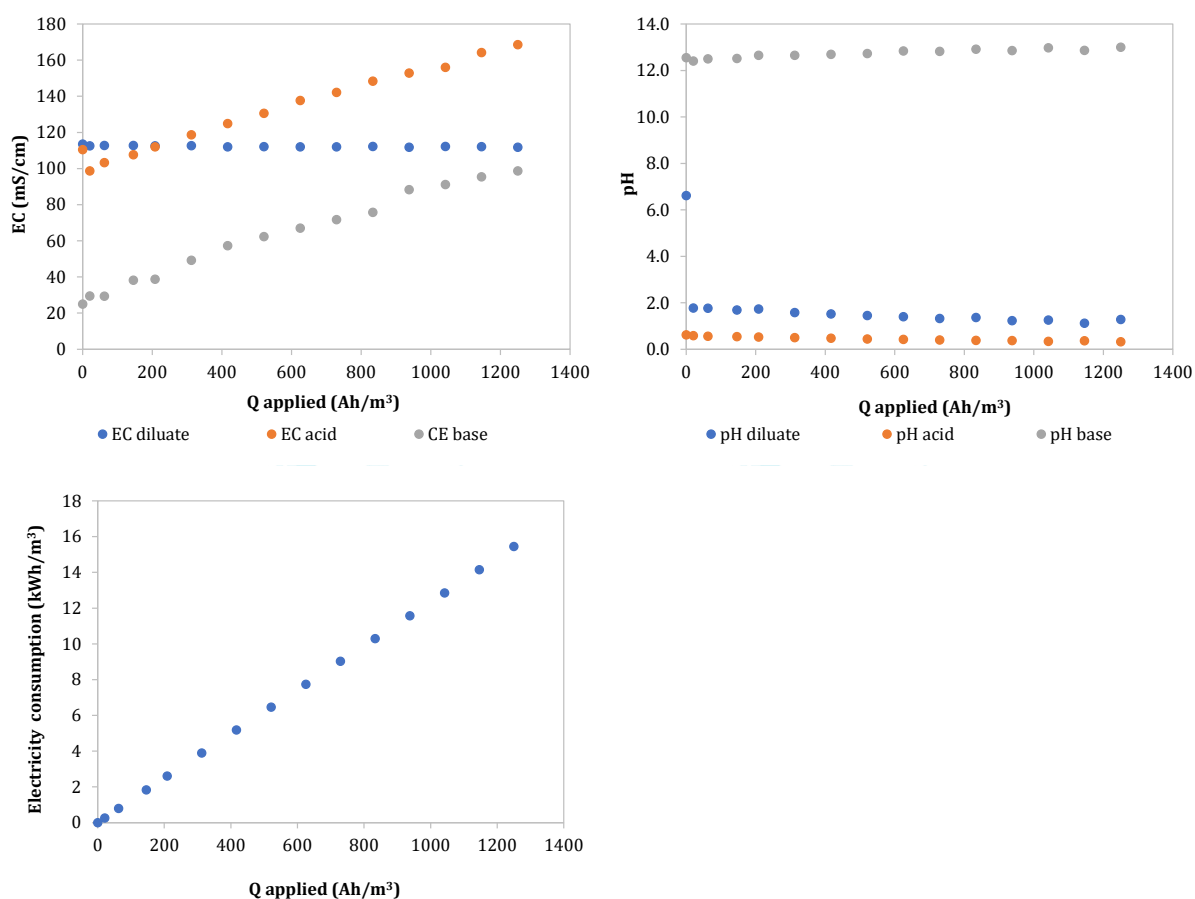


Figure 13: Evolution of the electrical conductivity, pH, and electricity consumption throughout the applied charge during the EDBM test to evaluate the influence of the acid concentration (0.25 M H_2SO_4).

To improve desalination efficiency of the EDBM process, a lower initial concentration of the acid than 0.25 M H_2SO_4 was evaluated. In this case, 0.10 M H_2SO_4 was utilized, working at the same conditions than in the before experiment. Table 18 summarized the operation conditions of this experiment.

Table 18: Summary of the operational parameters during the EDBM test to evaluate the influence of the acid concentration (0.1 M H_2SO_4).

I (A)	Electrolyte	Effluent to be treated	Acid	Base	V electrolyte (L)	V diluate (L)	V acid (L)	V base (L)
2.5	Na_2SO_4 0.3M	Synthetic 0.3M NaCl 1M Na_2SO_4	0.10M H_2SO_4	0.1M NaOH	1	1	1	1
Q electrolyte (L/h)	P electrolyte (bar)	Q diluate (L/h)	P diluate (bar)	Q acid (L/h)	P acid (bar)	Q base (L/h)	P base (bar)	KPI diluate
80	0.3	15	0.3	15	0.3	10	0.3	< 6 mS/cm

Figure 14 depicts the evolution of the EC, pH, and electricity consumption throughout the applied charge during the experiment performed with 0.10 M H_2SO_4 .

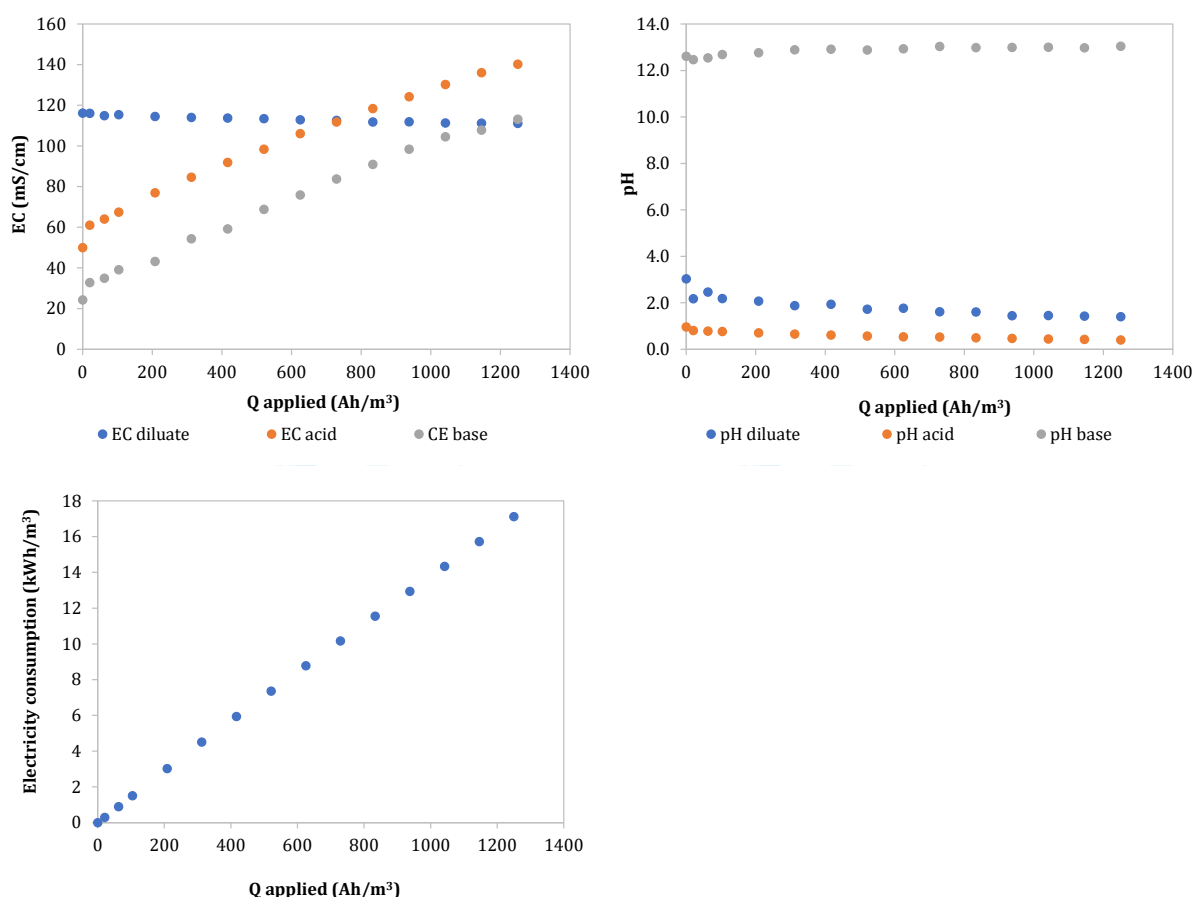


Figure 14: Evolution of the electrical conductivity, pH, and electricity consumption throughout the applied charge during the EDBM test to evaluate the influence of the acid concentration (0.10 M H_2SO_4).

Results show no significant improvement on desalination efficiency, achieving a 4.3 % of the EC removal of the salt stream when 0.10 M H_2SO_4 was used as initial concentration of the acid stream and 1250 Ah/m^3 was applied.

Also, in this case, the acid and base streams were highly concentrated, increasing the EC of both solutions almost 3 and 5 times, respectively. The pH of acid was diminished from 1.0 to 0.4; whereas the pH of the base solution was slightly increased from 12.6 to 13.0.

Since a slightly effect on desalination efficiency was observed during this last experiment, another test was performed by reducing the initial concentration of acid to 0.05 M H_2SO_4 . However, in this case, it was also modified another parameter aiming to produce a higher effect on the desalination efficiency than the only modification of the acid concentration. Therefore, the current intensity was increased from 25% to 50% of limiting intensity, *i.e.*, from 2.5 A to 5.0 A, meaning that the total electrical charge applied to the system was the double than before. The rest of operational parameters were kept as before.

Table 19 summarizes the operational conditions of this experiment and the Figure 15 depicts the results obtained.

Table 19: Summary of the operational parameters during the EDBM test to evaluate the influence of both the acid concentration (0.05 M H₂SO₄) and the electrical current density applied to the system (I = 5A; j = 59 mA/cm²).

I (A)	Electrolyte	Effluent to be treated	Acid	Base	V electrolyte (L)	V diluate (L)	V acid (L)	V base (L)
5.0	Na ₂ SO ₄ 0.3M	Synthetic 0.3M NaCl 1M Na ₂ SO ₄	0.05M H ₂ SO ₄	0.1M NaOH	1	1	1	1
Q electrolyte (L/h)	P electrolyte (bar)	Q diluate (L/h)	P diluate (bar)	Q acid (L/h)	P acid (bar)	Q base (L/h)	P base (bar)	KPI diluate
80	0.3	15	0.3	15	0.3	10	0.3	< 6 mS/cm

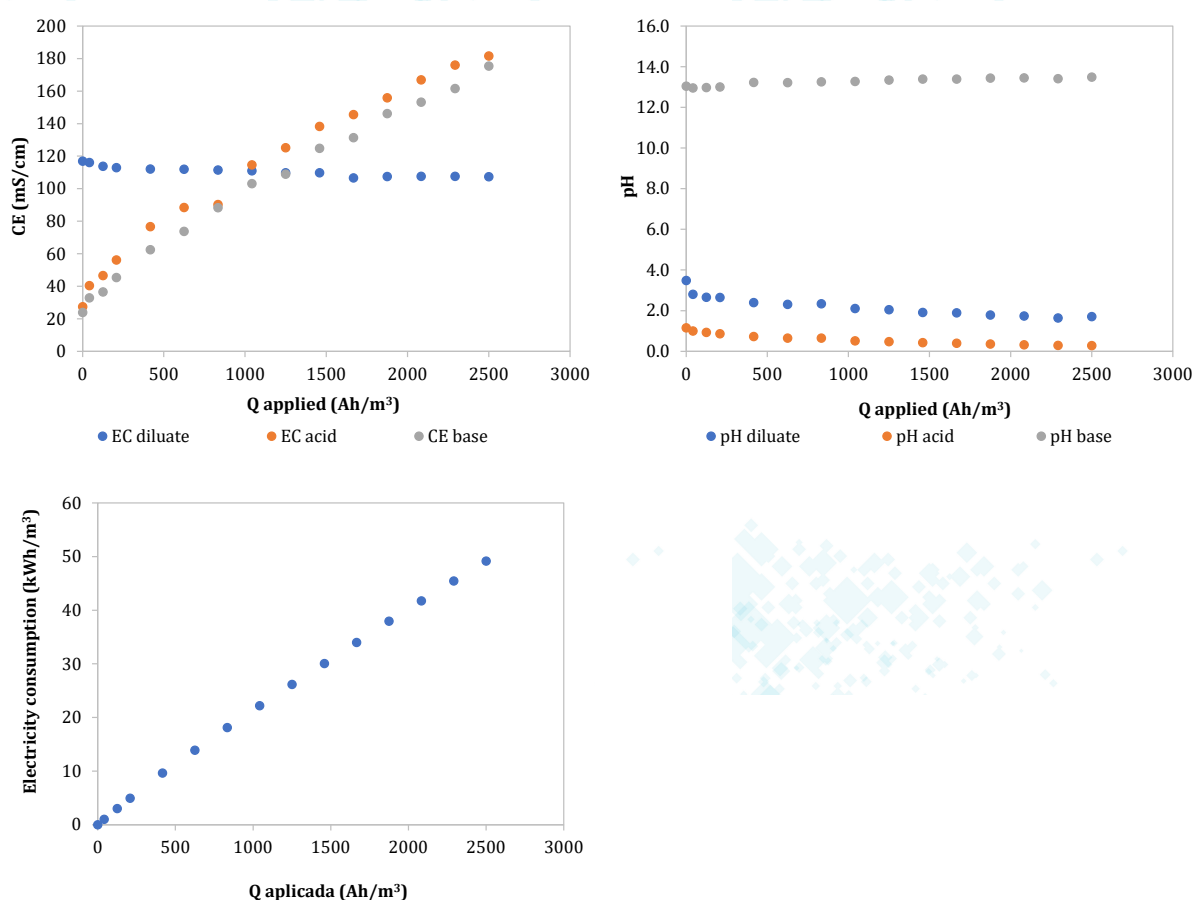


Figure 15: Evolution of the electrical conductivity, pH, and electricity consumption throughout the applied charge during the EDBM test to evaluate the influence of both the acid concentration (0.05 M H₂SO₄) and the electrical current density applied to the system (I = 5A; j = 59 mA/cm²).

Although an 8.2% of desalination was achieved by applying 2500 Ah/m³ and both acid and base solutions were suitably concentrated (around 7 times in EC), both operational parameters tested in this experiment (initial acid concentration and current density) seem to have a poor effect on the desalination of the synthetic brine, so indicating two main aspects:

- An acid solution with a low initial concentration can be used since it has no important contribution to the yield of the EDBM process under the tested conditions; but, moreover, it

is economically priority to prepare the acid and basic solutions with relatively low concentrations.

- It is important to test higher current intensities than tested up to now ($I > 50\%$ of I_{limit}) to evaluate the effect of the high values of this parameter onto the yield of the process but also combining it with the modification of the ratio of the volumes of the several streams.

Considering the abovementioned aspects, the following section was dedicated to investigate the effect of increasing the current density above $I > 50\%$ of I_{limit} , as well as the $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio.

2. Influence of the electrical current density applied to the system combined with the $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio

In this experiment, a current intensity of 7.5 A (75% of I_{limit}) was studied, keeping the initial concentration of acid at 0.05 M H_2SO_4 . However, the volume of the salt solution used in this experiment was also reduced to the middle in order to study its influence on the desalination yield ($V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}} = 0.5/1/1$).

The operational conditions employed during this experiment are collected in Table 20.

Table 20. Summary of the operational parameters during the EDBM test to evaluate the influence of the electrical current density applied to the system ($I = 7.5\text{A}$; $j = 117\text{ mA/cm}^2$).

$I \text{ (A)} / j \text{ (mA/cm}^2\text{)}$	Electrolyte	Effluent to be treated	Acid	Base	V electrolyte (L)	V diluate (L)	V acid (L)	V base (L)
7.5 / 117	Na_2SO_4 0.3M	Synthetic 0.3M NaCl 1M Na_2SO_4	0.05M H_2SO_4	0.1M NaOH	1	0.5	1	1
Q electrolyte (L/h)	P electrolyte (bar)	Q diluate (L/h)	P diluate (bar)	Q acid (L/h)	P acid (bar)	Q base (L/h)	P base (bar)	KPI diluate
80	0.3	15	0.3	15	0.3	10	0.3	< 6 mS/cm

Figure 16 shows the evolution of EC, pH and electricity consumption throughout the applied charge for this experiment.

Results demonstrate that applying 4700 Ah/m^3 , the desalination efficiency was increased to 38% by using the operational conditions summarized in Table 17. The ECs of acid and base solutions were concentrated around 7.5 and 8.4 times, respectively. The acid pH was diminished from 1.2 to 0.3; whereas the base pH was increased from 13.0 to 13.4., indicating a better performance of the process than the before experiments.

To distinguish the effect of the electrical current density, from the $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio, it can be considered the desalination efficiency achieved at 2500 Ah/m^3 (the same value than that obtained when $I = 5\text{ A}$ was applied). So, in this last experiment, at 2500 Ah/m^3 , a 20% of desalination yield was obtained. This value is more than the double of the obtained when $I = 5\text{A}$ was applied (desalination yield = 8.2%).

Therefore, this indicates that the major effect on EDBM process comes from the $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio.

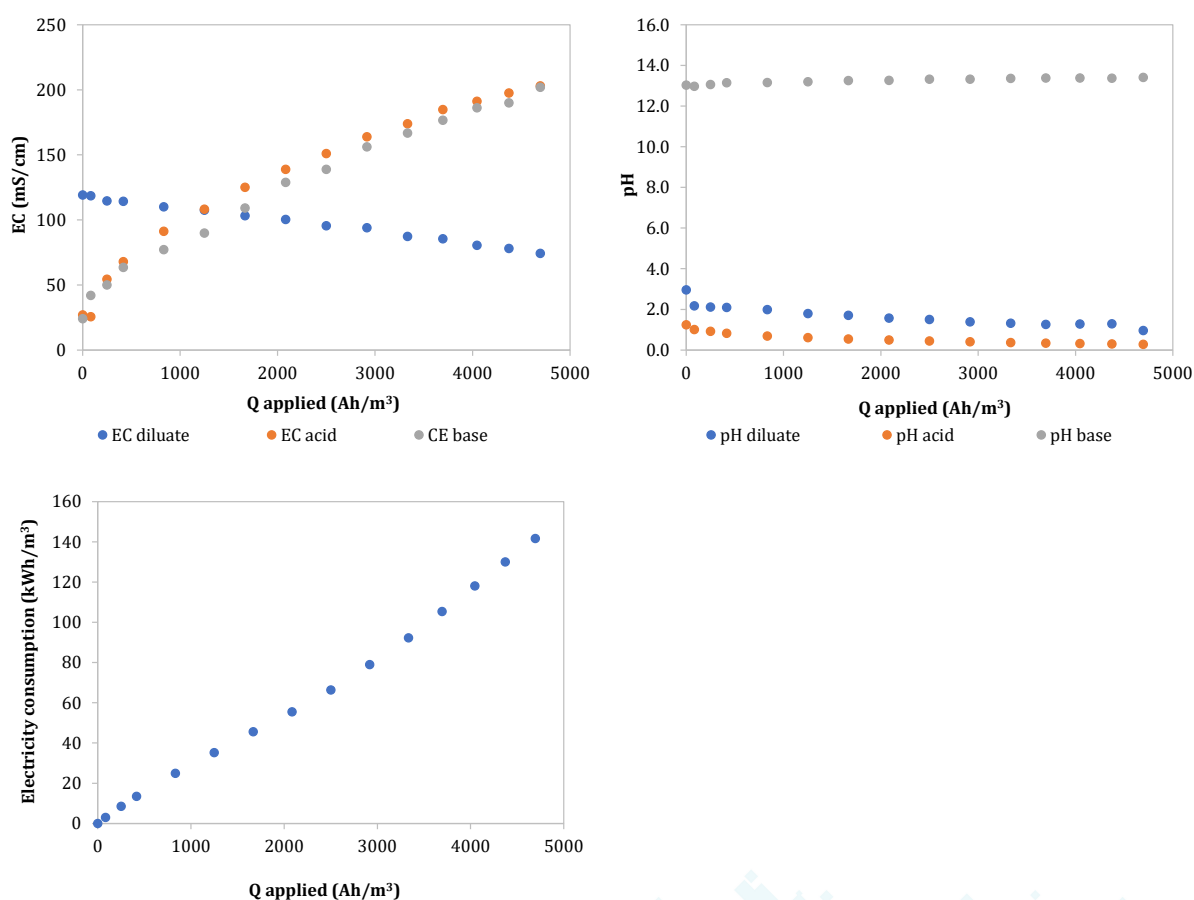


Figure 16: Evolution of the electrical conductivity, pH, and electricity consumption throughout the applied charge during the EDBM test to evaluate the influence of the of the current density applied to the system ($I = 7,5\text{A}$; $j = 117\text{ mA/cm}^2$).

3. Influence of the initial concentration of base

Considering the conclusion reached during section 4.2.2.2, that indicates that the major effect on EDBM process comes from the $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio, it is considered that the effect on the initial concentration of NaOH on the EDBM is not as significant as the $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio. Therefore, taking into account that the number of mols of H^+ is equal to the number of OH^- in the initial acid and basic solutions, and these values are economically feasible as starting solutions, it was decided to keep the NaOH concentration at 0.1M.

4. The influence of the $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio

After evaluating a $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio of 0.5/1/1 (section 4.2.2.2), this parameter was diminished by keeping the volume of synthetic effluent at 0.5L, and increasing the volume of both the acid and base solutions to 1.5 L. To compare the results with those obtained in the experiment of Table 17, the intensity applied to the system was the same, *i.e.*, 7.5 A (117 mA/cm^2).

Table 21 summarizes the operational conditions of this experiment and Figure 17 depicts the results obtained.

Table 21: Summary of the operational parameters during the EDBM test to evaluate the influence of the $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio.

$I \text{ (A) } / j \text{ (mA/cm}^2\text{)}$	Electrolyte	Effluent to be treated	Acid	Base	V electrolyte (L)	V diluate (L)	V acid (L)	V base (L)
7.5 / 117	Na_2SO_4 0.3M	Synthetic 0.3M NaCl 1M Na_2SO_4	0.05M H_2SO_4	0.1M NaOH	1	0.5	1.5	1.5
Q electrolyte (L/h)	P electrolyte (bar)	Q diluate (L/h)	P diluate (bar)	Q acid (L/h)	P acid (bar)	Q base (L/h)	P base (bar)	KPI diluate
80	0.3	15	0.3	15	0.3	10	0.3	< 6 mS/cm

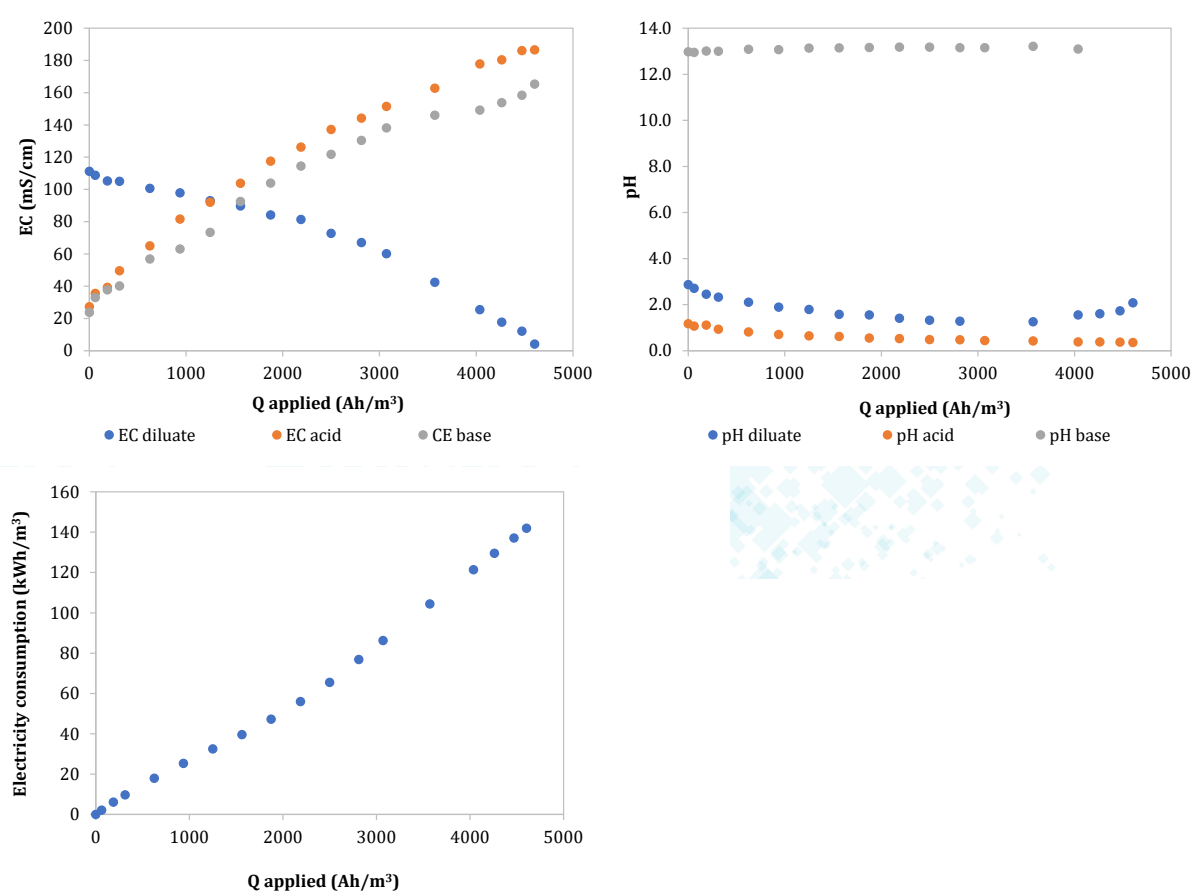


Figure 17: Evolution of the electrical conductivity, pH, and electricity consumption throughout the applied charge during the EDBM test to evaluate the influence of the $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio.

As it can be seen, the conductivity of the synthetic effluent was reduced to 4 mS/cm by applying 4600 Ah/m³, achieving a 96% of desalination yield.

Under these conditions, the acid and basic solutions were concentrated 7 times from the initial solutions. This implies a final pH of 0.3 and 13.3 for the acid and basic solutions, respectively.

The electricity consumption was around 140 kWh/m³. Thus, assuming an electrical cost of 0.1 €/kWh, this would imply an electricity cost of 14 €/m³.

Therefore, a ratio $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}} = 0.5/1.5/1.5$ was selected as a baseline to study the EDBM process applied to the synthetic and real effluent from IQE company, as detailed in the following sections.

5. Synthetic effluent from IQE

Synthetic effluent from IQE was composed by 0.03 M NaCl and 0.10 M Na₂SO₄.

0,5 L of this effluent was desalinated by applying 5 A (78 mA/cm²) instead of 7.5 A in order to decrease the electrical consumption compared to the last experiment. 1,5L of both acid and basic solution was used.

To concentrate as maximum as possible the acid and base solutions, a total of 12 cycles were performed, using in every cycle new salt solution. Therefore, the total volume of the salt solution consumed during the whole experiment was 6 L (0,5L/cycle x 12 cycles). The Table 22 summarized the operational conditions for the synthetic effluent treatment by EDBM process.

Table 22. Summary of the operational parameters during the EDBM test to treat a synthetic effluent from IQE company.

I (A) j (mA/cm ²)	Electrolyte	Effluent to be treated	Acid	Base	V electrolyte (L)	V diluate (L)	V acid (L)	V base (L)
5.0 78	Na ₂ SO ₄ 0.3M	Synthetic 0.03M NaCl 0.1M Na ₂ SO ₄	0.05M H ₂ SO ₄	0.1M NaOH	1	6 (12 cycles with 0.5L)	1.5	1.5
Q electrolyte (L/h)	P electrolyte (bar)	Q diluate (L/h)	P diluate (bar)	Q acid (L/h)	P acid (bar)	Q base (L/h)	P base (bar)	KPI diluate
80	0.3	15	0.3	15	0.3	10	0.3	< 6 mS/cm

Figure 18 shows the results obtained for this experiment. In the cycle 8, the EC concentration kinetics for the acid and base solutions were decayed around the 25% and 18%, respectively, compared to kinetics of cycle 1; whereas in the cycle 12, both decays were increased up to 45%. Therefore, taking into account this increase in the decays of the EC concentration kinetics from the cycle 8 to the cycle 12, it was preferable to consider the final conditions of the test at the end of cycle 8 instead of the cycle 12.

At that moment, 3600 Ah/m³ was applied, achieving a 75% of desalination yield and an effluent with an EC < 4-5 mS/cm. The acid pH was decrease from 1.2 to 0.5, whereas the base pH was increase from 12.7 to 13.4. The final EC for acid and base were 150 mS/cm and 144 mS/cm, respectively. The final compositions of acid and base at the end of the cycle 8 are represented in the Table 23, showing high purity of the base solution and a mixt of acid (HCl + H₂SO₄) in the acid solution.

Table 23: Acid and base composition after the cycle 8 of the EDBM process with the IQE synthetic effluent.

	Acid			Base		
	Initial concentration	Final concentration	Concentration factor	Initial concentration	Final concentration	Concentration factor
NaOH	-	-		0.1 M	0.75M	7.5
H ₂ SO ₄	0.05 M	0.29 M	5.8	-	-	
HCl	-	0.09M		-	-	

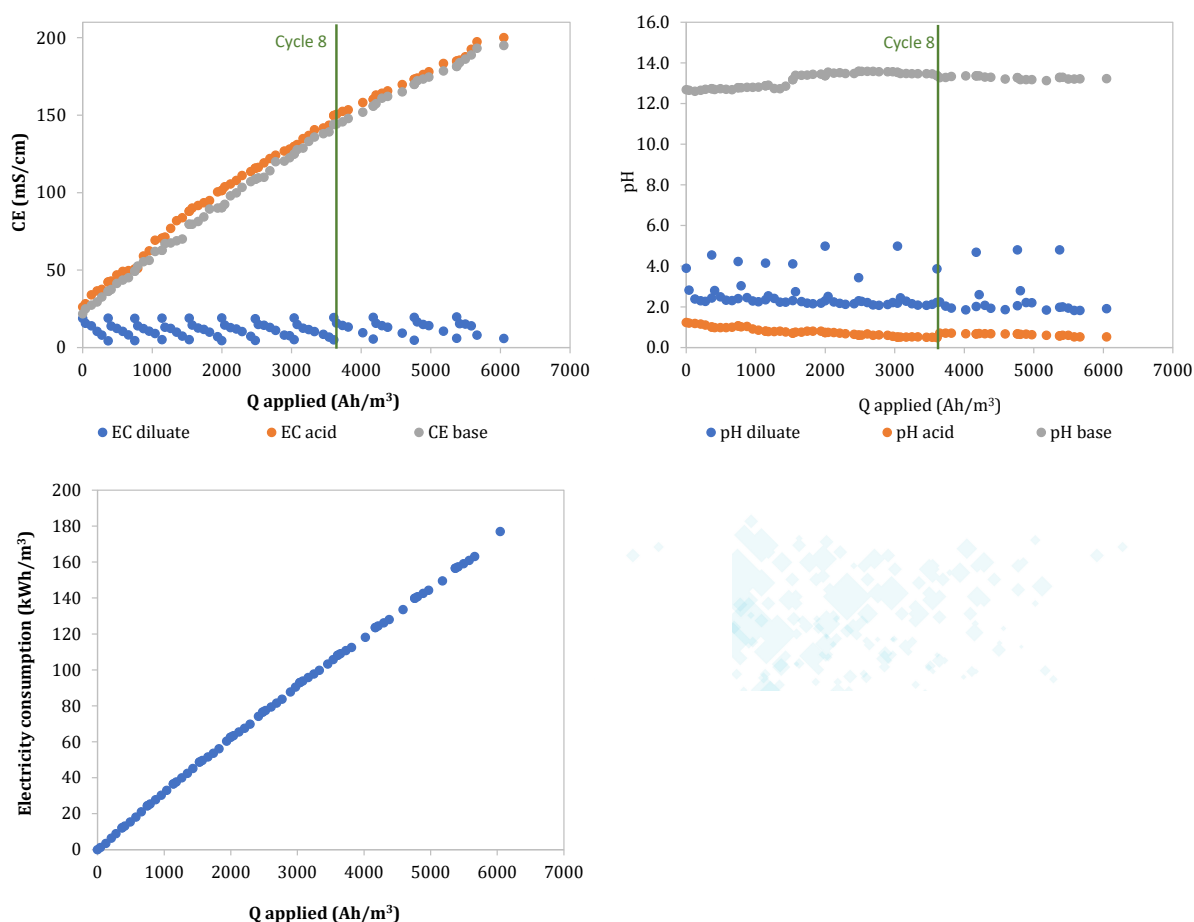


Figure 18: Evolution of electrical conductivity, pH, and electricity consumption throughout the applied charge during the EDBM test to treat a synthetic effluent from IQE company.

At the end of the cycle 8, the electrical consumption was around 108 kWh/m³, indicating an approximated cost of 10.8 €/m³ to treat the synthetic effluent from IQE by EDBM process (if 0.1 €/kWh was assumed).

The operational conditions, compiled in Table 22 at the end of the cycle 8, were selected to be applied to the real effluent from IQE, which results were specified in the section 4.2.2.6.

6. Real effluent from IQE

As commented before, the real effluent coming from the silica precipitation process of IQE was chosen to be treated by EDBM process. The composition of this effluent previously filtered at 0.45µm is collected in the Table 22. It should be highlighting that the supernatant contains mainly NaCl (0.01M) and Na₂SO₄ (0.08M) with a high concentration of silicon (around 1.2M).

This effluent was filtered at 0.45 µm to remove any colloid or particulate solid. The EDBM procedure was the same than when synthetic effluent is used, but in this case, the total numbers of cycles performed were 16, representing a total volume of effluent of 8 L.

The Table 24 summarizes the operational conditions of this test and the Figure 19 depicts the results obtained during the 16th cycles performed (it should be reminded that in every cycle, the whole volume of the salt effluent was substituted by a new one, whereas the acid and base solutions were not substituted).

Table 24: Summary of the operational parameters during the EDBM test to treat the real effluent from IQE company.

I (A)	Electrolyte	Effluent to be treated	Acid	Base	V electrolyte (L)	V diluate (L)	V acid (L)	V base (L)
5.0	Na ₂ SO ₄ 0.3M	Real effluent from IQE previously filtered at 0.45 µm	0.05M H ₂ SO ₄	0.1M NaOH	1	8 (16 cycles with 0.5L)	1.5	1.5
Q electrolyte (L/h)	P electrolyte (bar)	Q diluate (L/h)	P diluate (bar)	Q acid (L/h)	P acid (bar)	Q base (L/h)	P base (bar)	KPI diluate
80	0.3	15	0.3	15	0.3	10	0.3	< 6 mS/cm

Every cycle was performed up to the EC of the salt stream was minor to 6 mS/cm. Table 25 summarized the composition of the initial and final salt streams as well as the removal obtained for the several parameters analyzed.

Table 25: Composition of real effluent from silica precipitation process from IQE before and after the EDBM process.

Parameter	Units	Initial values	Final values	Removal (%)
pH	-	6.5	2.3	-
CE	mS/cm	14.4	5.5	62%
Cl ⁻	mg/L	845	119.0	86%
PO ₄ ³⁻	mg/L	2.3	n.a.	-
NO ₃ ⁻	mg/L	7.3	1.7	77%
SO ₄ ²⁻	mg/L	6980	1254.0	82%
Ca ²⁺	mg/L	< 10	< 10	-
Mg ²⁺	mg/L	< 5	< 5	-
K ⁺	mg/L	49	3.9	92%
Na ⁺	mg/L	3640	19.6	99%
Total iron	mg/L	0.15	<100	-
Al	µg/L	<100	<100	-
Ba	µg/L	41	6	85%
Mn	µg/L	27	9	67%
Si	µg/L	33700	33420	1%
Sr	µg/L	126	18	86%

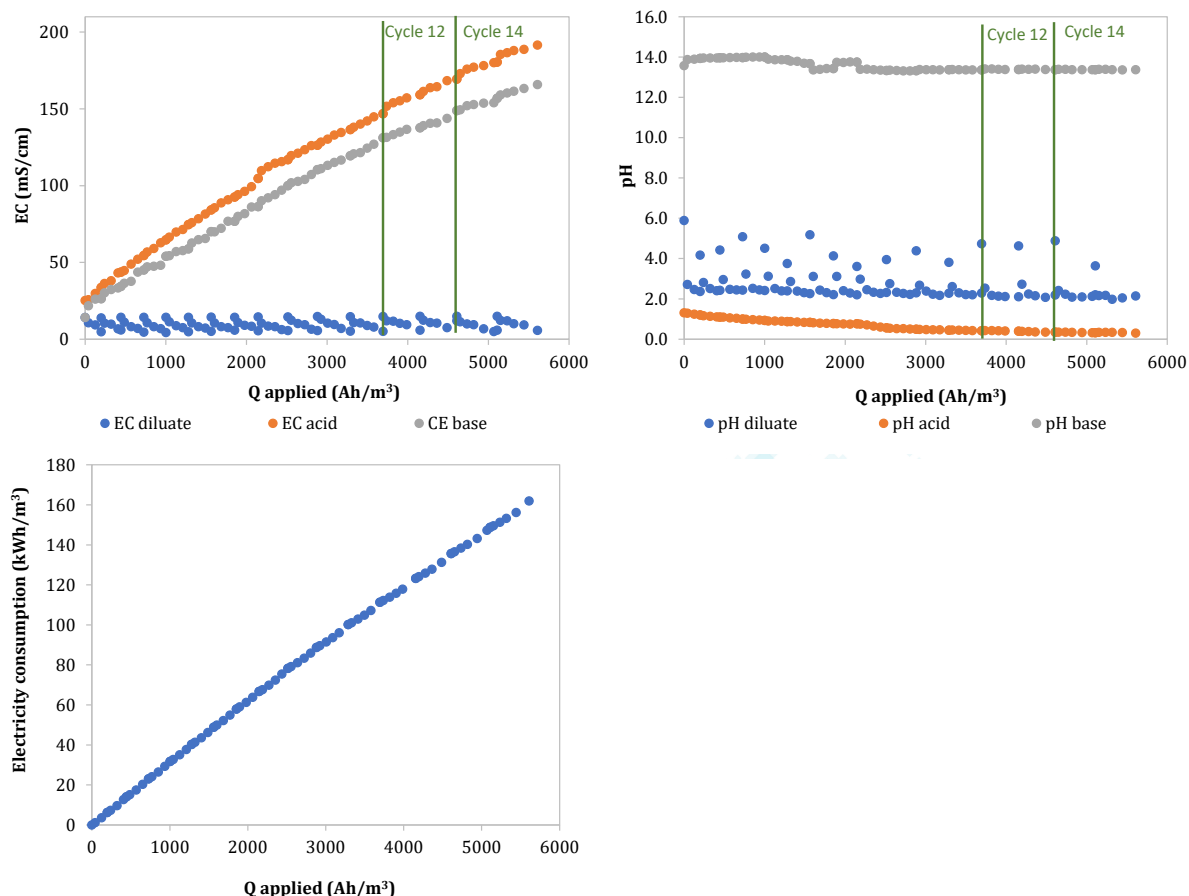


Figure 19: Evolution of the electrical conductivity, pH, and electricity consumption throughout the applied charge during the EDBM test to treat the real effluent from IQE company.

As can be observed, good removals were achieved for monovalent and divalent cations and anions. Metals such as Ba, Mn and Sr were also efficiently removed. Instead, the dissolved silicon was remained in the salt stream, probably due to it was part of the SiOx structures which have a higher size than the porous of membranes, so its movement throughout them is no possible. It must be also highlighted that no precipitation of the Si-compounds was observed on the membranes, remaining this concentration practically equal before and after the EDBM treatment. As this treated effluent has an EC < 6 mS/cm, it can be directly discharged to the sewer or, alternatively, SiOx can be recovered if the remained quantity can provide some economic benefit for the IQE company.

An electrical charge of 3600 Ah/m³ was applied during the EDBM process with synthetic effluent under the selected conditions (8th cycle). Therefore, to compare real with synthetic IQE effluents, the same value of the applied electrical charge must be considered. So, in the real effluent, the 3600 Ah/m³ were applied after the 12th cycle, instead of the 8th cycle of the EDBM treatment of the synthetic effluent. This means that with the same electrical charge, it can be treated 6 L of real IQ effluent instead of 4 L (obtained with the synthetic one). Thus, the $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio was increased form 4/1.5/1.5 (synthetic effluent) to 6/1.5/1.5 (real effluent), contributing to increase the benefit of the EDBM since more volume of wastewater can be treated by the same acid or base volumes.

With the same applied charge, the final concentrations of acid and base streams were similar for the real and synthetic IQE effluents, achieving a final concentration of 0.30-0.29 M H₂SO₄ and 0.72 – 0.75 M NaOH.

For the acid stream, small quantities of other acids (0.06 M HCl and 0.0006 M HNO₃) and some salts (such as 0.02M NaCl and 0.0006 M KCl) were also present. Minimum quantities of metals were detected. This implies a 73% of purity of the H₂SO₄ solution.

For the base stream, low quantities of other bases (0.004 M KOH) and other salts (0.0008 NaCl) were found. Ba and Sr were preferably removed from the salt stream toward the base solution. Mn was present in both acid and base solutions. This implies a 99% of purity of the NaOH solution.

The Table 26 summarizes the values obtained after the cycle 12 of the EDBM process with real effluent.

Table 26: Acid and base composition after the cycle 12 of the EDBM process with the IQE real effluent.

	Acid			Base		
	Initial	Final	Concentration factor	Initial	Final	Concentration factor
NaOH	-	-		100 mM	721.4 mM	7.2
KOH	-	-		-	3.6 mM	
H₂SO₄	50 mM	304.6 mM	6.1	-	-	
HCl	-	59.1 mM		-	-	
HNO₃	-	0.6 mM		-	-	
NaCl	-	23.2 mM		-	0.8 mM	
KCl	-	0.6 mM		-	-	
Na₂SO₄	-	-		-	2.2 mM	
Si	-	< 89 µM		-	< 89 µM	
Al	-	< 3.7 µM			<3.7 µM	
Fe		< 0.003 µM			< 0.003 µM	
Mn	-	0.30 µM		-	0.25 µM	
Ba	-	0.09 µM		-	0.66 µM	
Sr	-	0.66 µM		-	3.29 µM	
Acid /base Purity		73 %			99%	

The increase on the concentration of acid and base streams was observed up to the end of cycle 14. After that, both concentrations were practically kept constant. At the end of the cycle 14, 4610 Ah/m³ were applied and the final concentration of acid and base solutions were increase up to 0.37 M H₂SO₄ and 0.82 M NaOH. In this last case, the quantity of other species in both streams was slightly raised, being found 0.07 M HCl, 0.0007 M HNO₃, 0.03M NaCl and 0.0007 M KCl in the acid solution, being the purity of the H₂SO₄ solution (72%) similar than the 12th cycle (73%). In the base solution, 0.001 M KOH and 0.001 NaCl were determined, implying a decrease on the purity of the NaOH solution (94%). The Table 27 summarizes the values obtained after the cycle 14 of the EDBM process.

Table 27: Acid and base composition after the cycle 14 of the EDBM process with the IQE real effluent.

	Acid			Base		
	Initial	Final	Concentration factor	Initial	Final	Concentration factor
NaOH	-	-		100 mM	825.1 mM	8.3
KOH	-			-	1.3 mM	
H₂SO₄	50 mM	369.2 mM	7.4	-	-	
HCl	-	70.8 mM		-	-	
HNO₃	-	0.7 mM		-	-	
NaCl	-	31.3 mM		-	12.6 mM	
KCl	-	0.7 mM		-	-	
Na₂SO₄	-	-		-	35.4	
Si	-	< 89 µM		-	< 89 µM	
Mn	-	0.32 µM		-	0.20 µM	
Ba	-	0.07 µM		-	0.75 µM	
Sr	-	0.67 µM		-	3.97 µM	
Acid /base Purity		72 %			94%	

Taking into account that a) the purity of acid is more or less the same in the cycle 12 than the cycle 14; b) the purity of base solution only decreases a 5%; and c) the acid and base final concentrations increased a 20% and 14%, respectively, compared to cycle 12, it seems reasonable to choose the operational conditions of the cycle 14 as the best ones. This is important, especially considering that in most part of the industrial processes no so high purities are needed. However, if a base stream with high purity was needed, it would be also the possibility to stop the EDBM at the cycle 12.

These results demonstrate the efficient performance of the EDBM process up to the 14th cycle. Considering the option to treat the effluent up to the conditions of the cycle 14, the best $V_{\text{diluate}}/V_{\text{acid}}/V_{\text{base}}$ ratio found for treating the real IQE effluent was 7/1.5/1.5. Under these conditions, the KPI proposed are achieved, as summarized in the Table 28.

Table 28: KPIs expected and achieved for the EDBM process applied to desalinate the IQE real effluent.

KPI	Expected values	Achieved values
Salt removal from IQE effluent (%)	> 60% (final EC < 6 mS/cm)	> 60% (final EC < 6 mS/cm)
Acid concentration	> 2 mol/L	0.37
Base concentration	> 2 mol/L	0.82

This means that for desalinating 1m³ of IQE effluent, 214 L of 0.05M H₂SO₄ and 214L of 0.10 M NaOH would be needed. At the end, it would be obtained 1m³ of treated effluent that can be reused at IQE production process. Regarding acid (0.37 M H₂SO₄ (72% of purity)) and base (0.82 M NaOH (94% of purity)) its concentration is too low to be reused at IQE production process. Additional concentration steps of these reagents would be needed.

Under defined conditions, the electricity consumption was 135 kWh/m³, meaning an electrical cost of 13.5 €/m³ (assuming a cost for electricity of 0.1 €/kWh). The cost associated to the initial NaOH and H₂SO₄ solutions would be around 1,4 €/m³ and 1,6 €/m³, respectively (supposing a cost of 200€ /t for each, NaOH solid and H₂SO₄ 96%).

Finally, it should be mentioned that fouling on membranes was not monitored during the lab-scale tests, since this is a phenomenon specially observed when working at long experimental times. Moreover, to well determine the fouling, it should be also considered the polarity reversal that permits a self-cleaning mechanism to remove scaling, colloidal deposition, and charged organics from the ion exchange membranes, but during the lab-scale tests no polarity reversal was applied. Therefore, severe irreversible fouling mainly due to DOC and associated metal ion complexes should be specially monitored during pilot scale experiments that work with EDBM process with polarity reversal. *In-situ* and *ex-situ* cost-effective cleaning steps should be also then defined.

6. Crystallization of sodium sulphate

a. Fundamentals 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 20. The equilibrium solubility is given for mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), anhydrous thenardite (Na_2SO_4), metastable anhydrous thenardite i.e. heptahydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$).

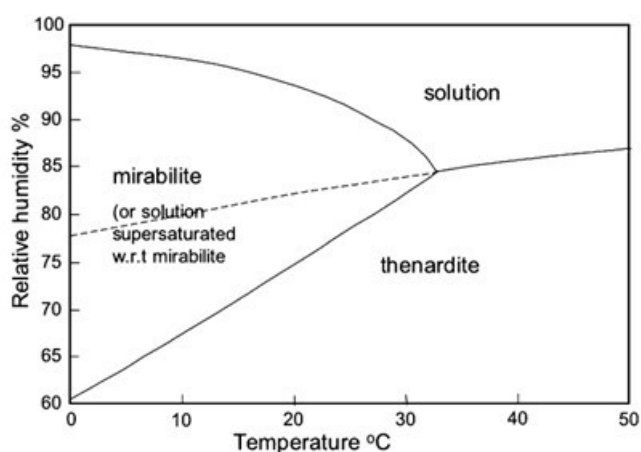


Figure 20: Phase diagram of sodium sulphate¹⁸. The solid lines are equilibrium phase boundaries, and the dashed line is the metastable extension of thenardite-solution boundary and therefore represents solution compositions in metastable equilibrium with thenardite but supersaturated with respect mirabilite.

The mechanisms for generating supersaturation rely on the changes in solubility of the crystallizing 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.

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

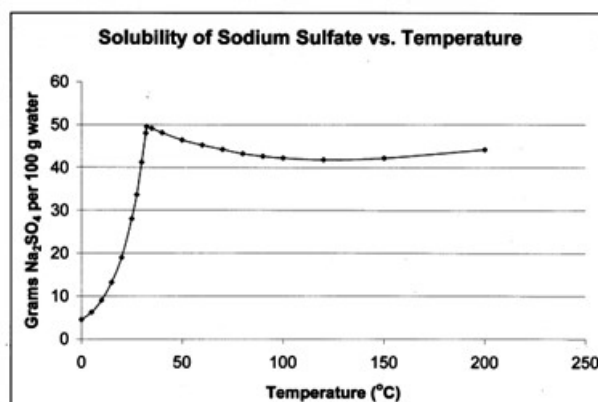


Figure 21: Sodium sulphate solubility.

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

Table 29: Existing crystallization processes for industrial production of sodium sulphate¹⁹.

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 vacuum	by
sodium sulphate (anhydrous)	salt purification	30% Na ₂ SO ₄	crystals	crystallization evaporation	by

As it has been mentioned in the Introduction section, in ZERO BRINE 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 was evaluated at bench scale. The objective of bench-scale test is to determine eutectic-point and evaluate the effect of impurities on this point.

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 22.

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.

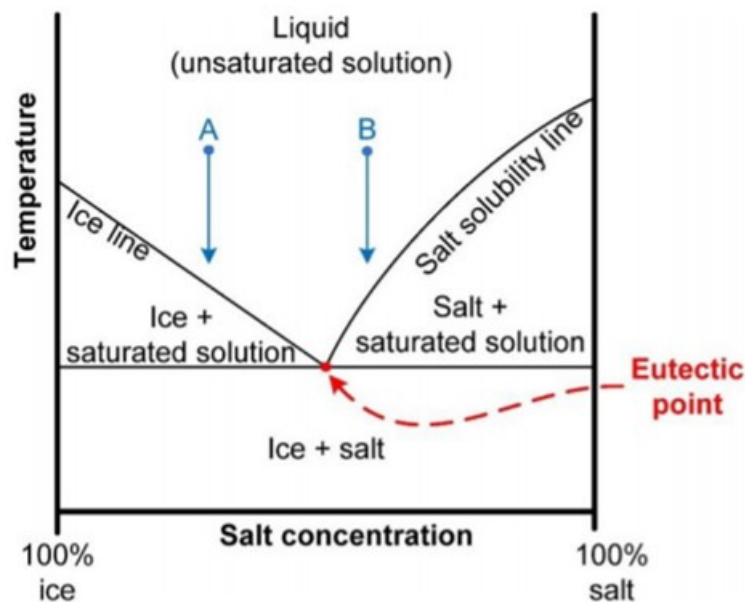


Figure 22. A typical phase diagram for aqueous salt solutions showing the eutectic point²³.

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/cm^3) and salts (e.g. $\text{NaCl } 2.17 \text{ g/cm}^3$)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 23 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 Na_2SO_4 till 44%) can be used exactly as that of Figure 22. The value of 44% represents the concentration of pure Na_2SO_4 in the hydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, i.e. $(\text{MW of } \text{Na}_2\text{SO}_4)/(\text{MW of } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}) = 0.44$ where MW stands for molecular weight. The other two new areas (“solid Na_2SO_4 + saturated solution” and “solids $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ”) are again areas where two phases coexist, and the lever rule applies.

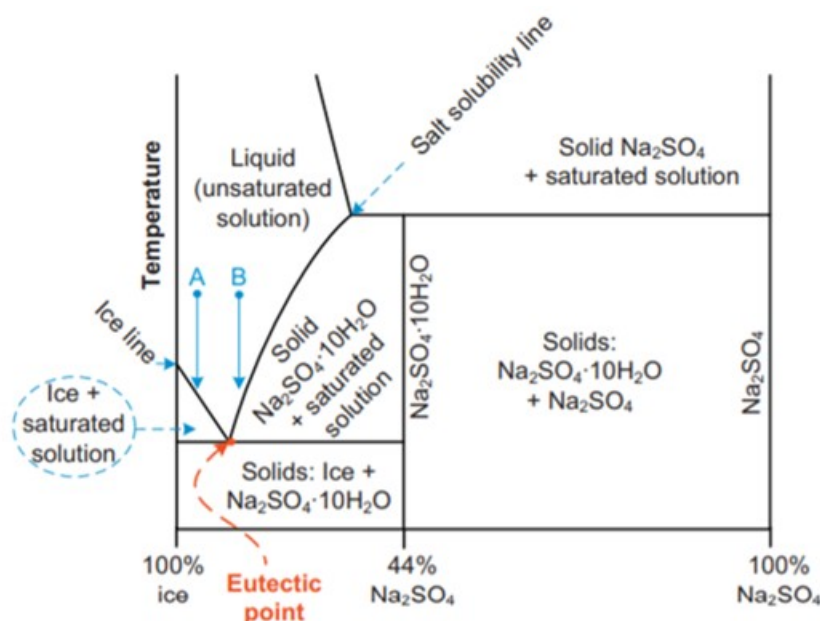


Figure 23. Binary phase diagram for sodium sulphate-water system²¹.

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 CuSO_4 , MgSO_4 , Na_2SO_4 and a $\text{KNO}_3\text{-HNO}_3$ ternary system. Nevertheless, the ability to use EFC to separate multiple salts from multicomponent brine has not been fully investigated²²). A research conducted by Randall *et al.*²³) on RO brine using EFC resulted in a 97% water recovery as well as recovery of pure Na_2SO_4 (96.4% purity) and pure CaSO_4 (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 HCO_3^- and Na^+ . The application of EFC crystallizer to this solution resulted in the formation of ice and 5.8 wt.% NaHCO_3 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 multi-step evaporation.

EFC has been commercialised by several companies internationally. Cool Separations (The Netherlands) have developed single stage EFC that can handle multicomponent systems and multi-stage 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/m³ ²⁷. The cost of this treatment technology is approximately US\$1.42/m³ of freshwater produced²⁸.

The objective of this sub-task was to evaluate the crystallization process in terms of different combinations of subcooling and agitation using EFC for a binary sodium sulphate solution as well as to determine the purity of the recovered valuables. To achieve the objective, experimental studies were performed by EURECAT, SEALEAU and Delft University of Technology.

i. Optimization of EFC process for sodium sulphate

1. Experimental methodology

a. Preparatory actions

▪ Preparation of brine

A synthetic 5 wt.% binary solution of Na₂SO₄·10H₂O was prepared by dissolving analytical-grade Na₂SO₄·10H₂O from Scharlau (>99% purity) in 3kg of ultra-pure water (18MΩ/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 Na₂SO₄ at 0°C was prepared by dissolving analytical-grade Na₂SO₄ (>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.

b. Experimental set-up

The experimental set-up used throughout this study is shown in Figure 24. 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 Julabo Easy Temp Professional 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 25). 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

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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 Electrode 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 Julabo Easy Temp Professional and NI LabVIEW 2016 software were used.

2. Experimental procedure

In order to observe the performance of the system and the recovery of Na_2SO_4 crystals, an EFC experiment of the synthetic 5 wt.% solution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (aq) was performed using the 5L setup. Before a precooled solution was transferred in a crystallizer, a cooling unit was turned on and Julabo Easy Temp Professional 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 Na_2SO_4 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.

3. Results and discussion

a. 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 30.

Table 30. EFC key parameters for process.

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

After performing various EFC experiments of the synthetic 5 wt.% solution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and different subcooling-agitation combinations, a clear performance tendency based on key parameters was observed.

Effect of sub-cooling temperature

When high subcooling ($>0.25^\circ\text{C}$) was applied, the ice formed too rapidly causing ice scaling (Figure 26). That enhanced the difficultness of harvesting the formed ice and trapped part of the salt crystals onto the scaling (Figure 27) 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 28) 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. When subcooling was set at 0.25°C and agitation at 25 rpm, 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.



Figure 26: Scaling due to high subcooling.

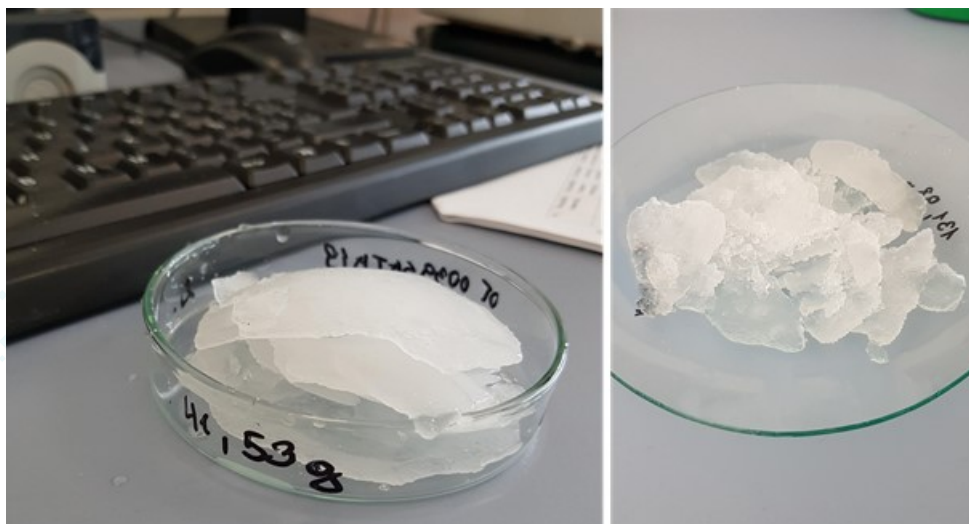


Figure 27: Salt trapped onto the scaling.

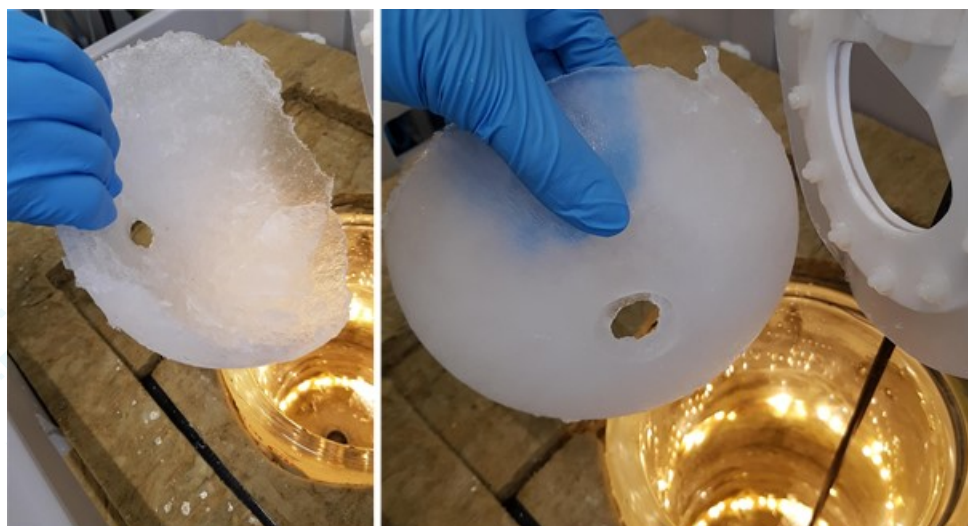


Figure 28: Block of ice from the bottom of the crystallizer.

Effect of agitation rates

When synthetic solution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was agitated rapidly (>25 rpm), undesirable crystallization phenomenon – agglomeration was observed (Figure 29). 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: 9.56 mS/cm) and salt (recovery yield 1.1-2.3 %) given that the phases were mixed.



Figure 29: Agglomeration phenomenon.

b. 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 30).



Figure 30: 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. As this study was performed in Netherlands, synthetic solutions should be used as real solution was not stable and precipitations occurred during transport of the sample.

1. Experimental methodology

For this study four synthetic RO solutions with different compositions were prepared (Table 31). 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. $\text{Na}_2\text{SO}_4 - \text{NaCl} - \text{MgCl}_2$ system is a solution without any suspected insoluble compounds (Ca^{2+} , Sr^{2+} , Ba^{2+} , SiO_2). 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.

Table 31: Compositions of the synthetic experimental solutions.

Ion	8wt% sodium sulphate solution with 1% sodium bicarbonate		Na ₂ SO ₄ – NaCl – MgCl ₂ 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

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 31). 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 scraper 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 found 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. Note all tubing was 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. Note the washing was conducted without stirring the crystal products.

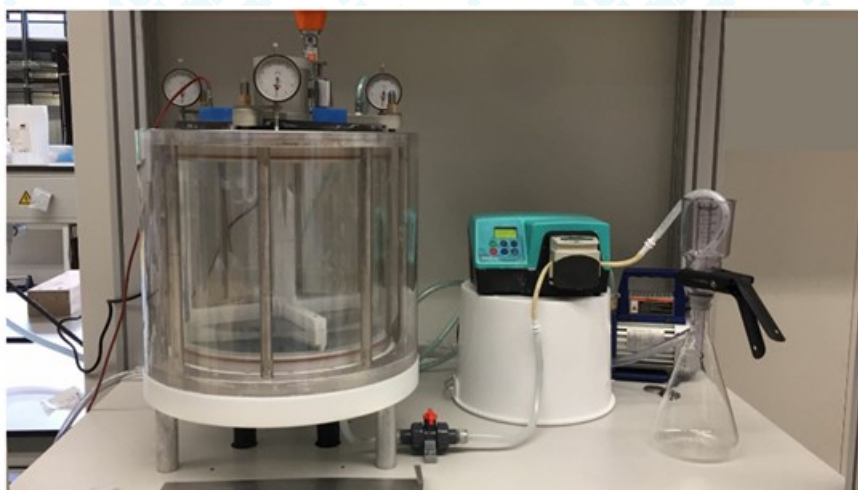


Figure 31: 15L reactor for EFC process.

2. Results and discussion

Depressions of the eutectic freeze point due to impurities were observed in different solutions, as shown in Table 32. A more impure solution was observed to encounter a deeper depression.

Table 32: Recorded eutectic freeze point of different solutions.

Na ₂ SO ₄ system (value from literature)	Eutectic freeze point recorded (°C)			
	Na ₂ SO ₄ – NaHCO ₃ system	Na ₂ SO ₄ – NaCl – MgCl ₂ 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 can be concluded that the technology is able 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.

7. Conclusions

Several technologies have been evaluated at bench-scale in order to define technical feasibility of two treatment schemes for management of saline wastewater produced at IQE. These treatment schemes 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. The two treatment schemes evaluated as well as technical objectives established are showed in Table 33.

Table 33: Treatment schemes and KPI for the evaluation of its technical feasibility.

	Technologies	Technical objectives (KPI)	Achieved
Scheme 1	Pre-treatment	Turbidity <2NTU [Al ³⁺] <50 µg/L [Fe ³⁺] <200 µg/L	✓
	RO regenerated membranes	Water recovery >70% Water quality (<4.6mS/cm)	✓
	Crystallization	Na ₂ SO ₄ purity > 98% Water quality (<4.6mS/cm)	✓
Scheme 2	Pre-treatment	Turbidity <2NTU	✓
	EDBM	Water quality (<6mS/cm) NaOH >2mol/L H ₂ SO ₄ >2mol/L	✗

- An effective pre-treatment scheme was established comprising pH adjustment and ultrafiltration for metal and suspended solids removal. 1.65 mg/L of anti-scalant must be added to prevent SiO₂, BaSO₄, SrSO₄ and CaSO₄.
- Treatment scheme 1 shows promising results thanks to the combination of concentration step using regenerated membranes and EFC technology. On the one hand, regenerated membranes allow water recoveries > 70%. The permeate presented a conductivity adequate to provide water for further reuse that is below 4.6mS/cm. On the other hand, the concentrate achieved a concentration factor of 2.17 and could be treated with EFC to produce high purity Na₂SO₄·10H₂O. However, long-term performance should be necessary to demonstrate technology robustness. This treatment scheme will be validated at pilot scale in the framework of task 4.3. The energy requirements for this treatment will be estimated during pilot plant operation period.
- The treatment scheme 2, based on the application of EDBM process to the IQE effluent, allow to achieve a desalinated stream (KPI = 60% desalination) with an EC < 6 mS/cm able to be reused in the IQE facilities. For each m³ of wastewater treated, 214L of acid and base are produced. Acid stream was concentrated up to 0.37 M H₂SO₄ (72% of purity; concentration factor = 7.4) and the base stream was concentrated up to 0.82 M NaOH (94% of purity; concentration factor = 8.3). Even high concentration factors are achieved, more concentrated reagents are required for internal reuse at IQE. The electricity consumption was 135 kWh/m³, meaning an electricity cost of 13.5 €/m³ (assuming a cost for electricity of 0.1 €/kWh).

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9. Annex

Annex I

Table 34. Description of the used analytical methods.

Parameter	Equipment	Standard/Method
pH	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.

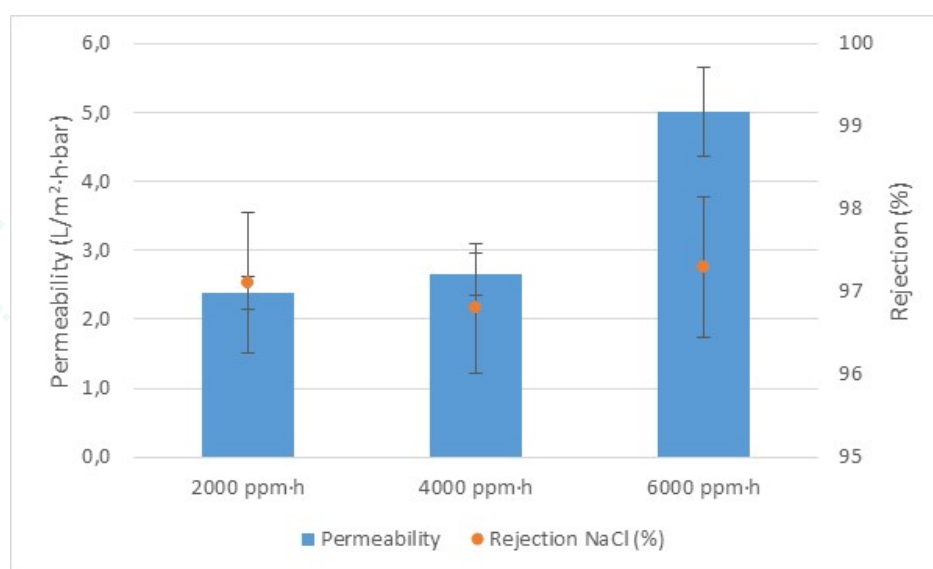


Figure 32: Effect of OA doses on SW-RO coupons (n=2).

Table 35: Performance of one H-1 hydrated membrane with synthetic solution.

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

n=1	H-1		2000 ppm·h		4000 ppm·h		6000 ppm·h	
	Cl (ppm)	SO ₄ (ppm)	Cl (ppm)	SO ₄ (ppm)	Cl (ppm)	SO ₄ (ppm)	Cl (ppm)	SO ₄ (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