ZERO BRINE

D4.2 Regeneration and performance of reverse osmosis membranes from desalination plants

July 2018

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Deliverable lead	CTM
Author(s)	Anna Casadellà, Sandra Meca
Reviewer	LENNTECH
Contact(s)	sandra.meca@ctm.com.es
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[1] **R**=Document, report; **DEM**=Demonstrator, pilot prototype; **DEC**=website, patent fillings, videos, etc.; **OTHER**=other

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

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Glossary

BEC	brine excellence center
BW	brackish water
BW-RO	brackish water reverse osmosis membrane
EC	electrical conductivity
H-1	hydrating solvent 1
H-2	hydrating solvent 2
IQE	Industrias Químicas del Ebro, S.A.
LMH	$L/m^2 \cdot h$
MF	microfiltration
NF	nanofiltration
OA	oxidative agent
PA	polyamide
ppm	part per million, mg/L
ppm·h	part per million per hour
RO	reverse osmosis
SD	standard deviation
SW	seawater
SW-RO	seawater reverse osmosis membrane
TFN	thin-film nanocomposite
TIC	total inorganic carbon
WP4	work package 4 of Zero Brine project

Executive summary

Zero Brine means to apply Circular Economy in various process industries by developing necessary concepts, technological solutions and business models. The purpose is 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 effluents generated by process industries, while eliminating wastewater discharge and minimising environmental impact of industrial operations thorough brines.

The objective of Task 4.1.4 of WP4 is to produce regenerated tailor-made membranes from end-of-life reverse osmosis (RO) elements from desalination plants. These produced membranes will be used at the silica factory IQE in Zaragoza to treat saline wastewater from the production line. As the wastewater is treated with the regenerated membranes two effluents are going to derive: permeate and concentrate. Permeate with high quality is going to be reused in the productive process and concentrate with a high salinity is going to be fed into a crystallization process so to obtain high quality water and solid salts.

To achieve the aimed tailor-made membranes, two types have been defined regarding permeability and rejection of salts. Type I has permeability higher than commercial SW-RO membranes and a rejection similar to BW-RO membranes. Type II has permeability higher than commercial NF membranes and a rejection above 85% which is the lower limit for permeate to be reused at IQE (Table 1). Tests carried out have been standard tests with NaCl and $MgSO_4$ in order to compare with commercial membranes.

Table 1. Definition of targeted tailor-made membranes

	Permeability ($L/m^2 \cdot h \cdot bar$)	Salt rejection (%)
Type I	> 1.98	> 99.0
Type II	> 3.31	> 85.0

Regeneration has been divided in two steps: hydration and oxidation. To hydrate membranes, at lab-scale, three different solvents have been studied - distilled water, H-1 and H-2 – being H-1 the solvent that gave higher increases on permeability and rejection to the end-of-life membranes. At pilot-scale, immersion and recirculation were studied as contact mode for hydration. Both methodologies gave similar results although time frame required for immersion is superior to the one for recirculation.

Relevant parameters have also been used to study the optimal conditions for oxidize the membrane, such as: pH, concentration of oxidative agent (OA), doses of OA and performance with synthetic solution. Oxidation of the membrane elements and thus higher permeability and lower rejection (within the set limits) were achieved under basic pH and a concentration C2 of OA. Regarding doses, results differed from the lab and the pilot plant which can be explained considering the difference on surface area between both cases. For example, to achieve a membrane Type II, in the lab it was required a dose of 6,000ppm·h whilst in the pilot plant around 20,000 ppm·h. Tests with synthetic solution and standard tests with sulphate gave satisfactory results on the membrane performance. In both cases, permeability and rejection comply with the limits established for their proper operation at IQE.

Both types of regenerated membranes, I and II, are suitable to be operated at the pilot plant that is going to be installed at the silica factory IQE. There, the type of membrane with the best performance for real effluents is going to be evaluated.

1. Introduction

ZERO BRINE project aims to facilitate the implementation of the Circular Economy package and the SPIRE roadmap in various process industries. To do so, it is focused on 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 effluents generated by process industries, while eliminating wastewater discharge and minimising environmental impact of industrial operational brines.

One of the four demonstration sites of the project will be located at Industrias Químicas del Ebro S.A. (IQE) in Spain. Due to IQE productive activity, high amounts of waste streams with high salinity are produced. Figure 1 presents the water cycle at IQE.

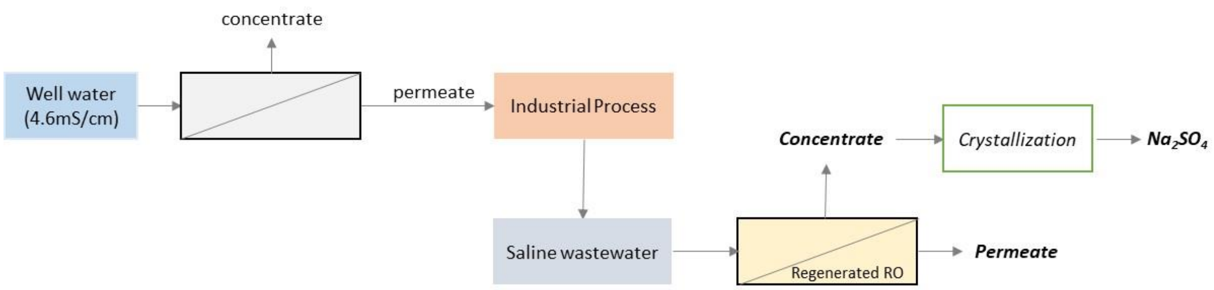

Figure 1. Water cycle in the production process at IQE.

Firstly, well water is extracted and pre-treated to be brought into a reverse osmosis (RO) system. Osmotic water produced is then used into the production process where saline wastewater streams are generated. Deliverable 4.1 from ZERO BRINE includes a deep characterization of the different waste streams generated at IQE. Table 2 shows the composition of the main wastewater stream generated at IQE.

Table 2. Characterization of the target aqueous waste streams. (n/a = not applicable; SD =standard deviation; n=number of samples).

		Filtration + Washing wastewater (n=6)	
Parameter	Units	Value	SD
pH	upH	4.8	1.3
EC	mS/cm	27.3	5.9
Turbidity	NTU	67.4	133
Cl	mg/L	1,760	498
NO_3	mg/L	11.8	0.61
SO_4	mg/L	16,470	4,450
K	mg/L	434	11
Na	mg/L	7,320	2,060
Ca	mg/L	38.5	35.3
Mg	mg/L	213	235

			Filtration + Washing wastewater (n=6)
TIC	mg/L	<5	n/a
Al	µg/L	2,270	2,880
Si total	mg/L	80.5	22.8
Si reactive	mg/L	77.1	23.0
Mn	µg/L	278	182
Fe	µg/L	855	712
Sr	µg/L	495	431
Ba	µg/L	49.2	16.4

The management of these streams has a high environmental impact and an elevated cost is associated to it. This cost is related to the discharge of these streams that must be treated in a wastewater treatment plant. In this context, ZERO BRINE, and specifically WP4, aims to evaluate an innovative treatment process for saline wastewater in order to recover reagents and water to further valorize them either in the production process at IQE or in other industries. The implementation of the new treatment process should allow to achieve a reduction of costs derived from water consumption and wastewater management.

The innovative treatment is based in a first RO stage where regenerated membranes will be used to make the process more sustainable. In order to produce regenerated membranes suitable to treat wastewater from silica process, in subtask 4.1.4 the regeneration process of reverse osmosis membranes from desalination plants will be investigated.

a. Membrane regeneration

Desalination of seawater (SW) and brackish water (BW) by reverse osmosis (RO) is abundantly applied and established in the municipal and industrial sector for freshwater production and salt concentration. Essentially, a RO membrane system involves three streams: the effluent to be treated (feed), permeate and concentrate. The feed is filtered through the membrane by applying pressure, that must be greater than the osmotic pressure of the feed and a high-quality permeate is generated as well as a high-conductivity concentrate containing the rejected salts (Figure 2).

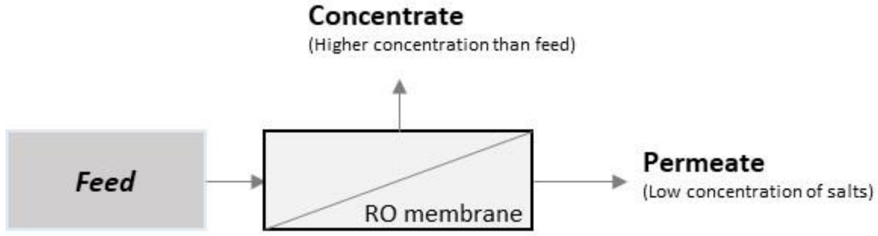

Figure 2. Effluents of a RO system.

Most RO membranes are made of three layers: (i) an ultra-thin, dense, active or selective layer of aromatic polyamide; (ii) a microporous support layer of polysulfone; and (iii) a thicker base made of polyester. The membrane performance is determined by selectivity which is often calculated by the rejection coefficients and by the permeation rate given by the volume filtered by the membrane per area and time [2]. The performance of RO desalination membranes is dependent on the composition of the membrane, which determines main salt rejection, fouling susceptibility and water permeability [2].

RO membranes are roughly divided in seawater (SW-RO) and brackish water (BW-RO) membranes regarding their permeability and their salt rejection. SW-RO membranes present higher salt rejections than BW-RO but lower permeability. For both sorts of membranes, besides physical damage and compression during performance, the main reason that sets their lifespan is fouling, causing membranes to become waste. Membranes are replaced at the end-of-life stage, which is when their performance is not suitable for a specific task anymore, regarding permeability (<15% of the initial) and rejection coefficients. This derives, together with the continuous growth of RO technologies, to a vast accumulation of end-of-life modules that are disposed in landfills [3], classified as inert solid waste. It has been reported that in brackish water treatment facilities there is an average replacement of modules between 10-20% per year, depending on the pre-treatment. In addition, in industrial and tertiary wastewater treatment facilities, the replacement is around 30% per year [4].

An alternative to landfill management is recycling end-of life membranes by conditioning them for their reuse that can be indirect or direct. On one hand, indirect reuse implies deconstructing the membrane element and reusing its parts for other membranes [5]. On the other hand, direct reuse consists of cleaning the membranes and recovering their commercial properties. Research has shown that cleaning process are dependent on the storage conditions of the modules [6]. Cleaning processes of dry membranes only allows to achieve partial recovery. Membrane producers typically recommend soaking the membrane in a sodium bisulphite solution at 1% and then store it in a sealed bag to maintain membrane hydration and to preserve performance by reducing bio-fouling formation [7]. Another direct reuse or recycle of membrane modules is to chemically modify with an oxidative agent (OA) the membrane polymeric active layer leading to a membrane with new properties and uses. ZERO BRINE project is focused on direct reuse or recycle of membrane modules after treating it by an OA to grant them with new uses. This process is also known as membrane regeneration.

Generally, membrane regeneration is based on applying an OA in order to oxidize the polyamide active layer of the membrane. However, many factors such as membrane hydration, type of oxidizing agents (OA), concentration of the solutions, contact mode (immersion or recirculation), operating pressure and treatment time are crucial for the resulting performance of the regenerated membrane [9].

Hydration is as well key in the regeneration process, prior to the use of OA on membrane surfaces, hydration of membranes is an enhancing factor in the recycling process [6]. Therefore, the storage of membranes is crucial for their further reuse. Dried polyamide membranes are a disadvantage on the membrane-water interactions (diffusion mechanism), causing a relevant decrease in the permeate flowrate. Some of the methods that manufacturers recommend to hydrate membranes include pressurization to 10bar with permeate valve closed, immersion in a solution of ethanol or propanol in water at 50% or immersion in HCl at 1% [7]. Several authors indicated that the method with best results, in terms of permeability, in the later regeneration is pre-soaking the dry aromatic polyamide membranes in short-chain aliphatic alcohols [9] [10] [8].

Research on membrane regeneration started with removing the polyamide (PA) layer to achieve a microfiltration membrane (MF). It is worth mentioning that membranes under study were previously washed with bisulphite solution in recirculation for 18h, so membranes should be hydrated. Conditions assessed involved different OA, concentration, exposure time and different methods of contact. Oxidizing agents that gave best results were sodium hypochlorite (NaClO) and potassium permanganate ($KMnO_4$) when they were recirculated for 1-2 at 5-10bar. Newly obtained membranes presented similar properties regarding MF membranes, with salt rejection almost zero and rejection of suspended solids around 97% [11] [12]. Other authors have tested the same OA further. For example, these three OA were tested at different doses (in ppm·h), so the concentration of OA remained constant whilst the exposure time varied. A higher concentration can contribute to reduce the amount of time required for the degradation but most importantly it is crucial for controlling the degrading process. According to the state-of-art, NaOCl gave the best results in terms of an increase of permeability (4-175 $L/m^2 \cdot h \cdot bar$) and decrease of rejection (>4%) in all studied cases [13] [14] [8]. Besides the three presented OA, other reagents such as acetone or *N*-methyl-2-pyrrolidone (NMP) have been tested but did not give better results [15]. The parameter of pH also needs to be considered as chemical modifications is dependent on the pH. Studies show that when comparing different pH conditions (pH 3, 7 and 10.5), alkaline conditions give the highest increase in permeability [13] [15]. Acid pH could lead to hydrolysis of the PA active layer and therefore oxidation processes not be favorable.

Thus, the choice of the best operation conditions relies on the targeted properties of the recycled membrane which is, actually, tailor-made.

b. Tailor-made membranes properties

In ZERO BRINE project, regenerated membranes will be used to treat wastewater from a silica industry (IQE) which has a high conductivity. The properties of the regenerated membranes will be set in order to produce a permeate with a suitable quality to be reused and reducing the working pressure of the RO process.

Permeate obtained from the RO treatment using these membranes will be reused at IQE. Depending on the permeate composition (conductivity), different reuse strategies within the production process can be considered as it can be seen in Figure 3 :

- Low conductivity, similar to permeate from RO used to treat well water: direct reuse.

- Conductivity around 4.6 mS/cm, which is the conductivity of well water. In that case water could be mixed with well water to be treated in the RO and/or used as washing water in the production process.

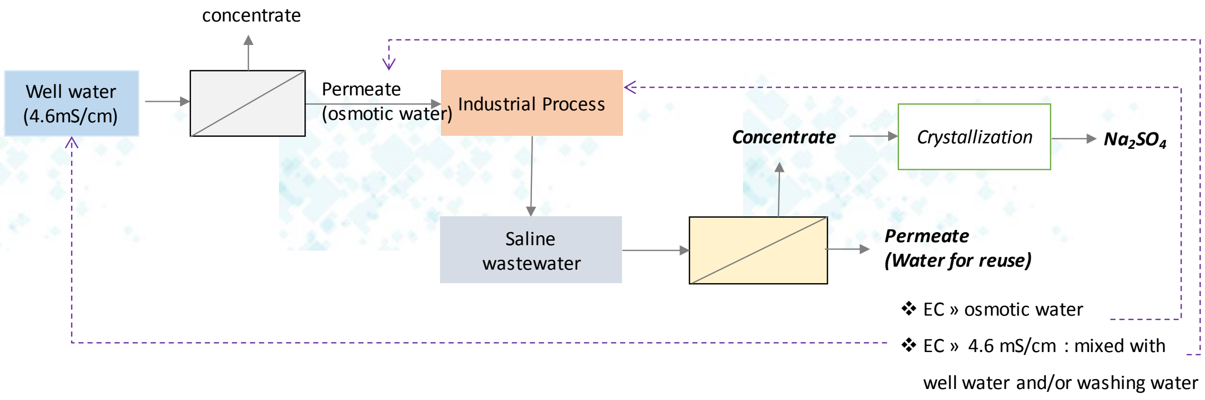

Figure 3. Water cycle in the production process together with reuses of regenerated RO effluents.

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 taking into account the conductivity of the wastewater used as feed for the regeneration membrane and the permeate conductivity. As already stated in Deliverable D4.1, the wastewater from IQE has a conductivity around 27 mS/cm. Therefore, to obtain a permeate with a conductivity lower than 4.0 mS/cm (well water), the minimum total salt rejection measured in conductivity should be around 85%.

According the previous requirements, the targeted regenerated membrane should present the following properties:

- Higher permeability than SW-RO membranes: its increase will allow to reduce working pressure and energy consumption.
- Permeate quality adapted to the water uses at IQE. For that, a minimum rejection of 85% has been defined.

Based in these properties two different tailor-made membranes will be produced in ZERO BRINE project. In *Table 3*, rejection coefficients for these membranes and of commercial membranes of SW, BW-RO and NF are showed. These values are based on sodium chloride (NaCl) rejection for SW and BW membranes and on magnesium sulphate ($MgSO_4$) for NF membranes. The rejection coefficients described for commercial membranes will serve as guidance to compare properties of regenerated membranes with the commercial.

Table 3. Permeability and salt rejection of commercial membranes.

	Permeability (L/m^2·h·bar)	Rejection (%)

	Permeability (L/m^2·h·bar)	Rejection (%)
Commercial SW-RO[a]	1.98	> 99.7[b]
Commercial BW-RO[a]	2.81	> 99.0[b]
Commercial NF[a]	3.31	> 97.0[c]
Tailor-made membrane Type I	>1.98	> 99.0
Tailor-made membrane Type II	>3.31	> 85.0

[a]commercial specifications for LG SW 440 GR, BW30-400 and NF270-400/34i; [b]Rejection of NaCl; [c]Rejection of $MgSO_4$

As a result of the set properties of the tailor-made membrane, end-of-life SW-RO and BW-RO membranes from desalination plants (little biofouling) are proper starting membranes to achieve our target membrane. In this project, we aim to achieve two types of membranes to later evaluate their performance with real effluent from IQE. Type I of these membranes is based on a permeability between SW and RO membranes and a rejection similar to BW RO membranes. Type II is based on a permeability above NF membranes with a rejection above 85%.

2. Objective

WP4 from ZERO BRINE project aims to demonstrate the technical and economic feasibility of implementing a circular economy scheme in the silica industry (IQE) to recover water, sodium sulphate, waste heat, acids and alkalis. In particular, in subtask 4.1.4 the regeneration process of reverse osmosis membranes from desalination plants will be investigated in order to define the regeneration conditions to obtain a tailor-made membrane which allows the recovery of water (permeate) with a suitable quality to be reused at IQE production process.

In this context, the main objective of this report is to evaluate the regeneration process and to optimize it to obtain specific membranes with tailor-made properties. These properties are defined based on a reduction of energy consumption by requiring lower working pressure and on the production of an effluent that can be reused in the production process (permeate).

Table 4 shows the target properties of the aimed tailor-made membranes. Type I membranes have a permeability higher than commercial SW RO membranes and a rejection similar to BW RO membranes (*Table 3*). Type II have a permeability higher than commercial NF membranes (*Table 3*) and the rejection corresponds to the minimum rejection stablished by the possible water reuses at IQE.

Table 4. Target properties of the tailor-made membranes.

	Permeability (L/m^2·h·bar)	Salt rejection (%)
Type I	> 1.98	> 99.0

	Permeability ($L/m^2 \cdot h \cdot bar$)	Salt rejection (%)
Type II	> 3.31	> 85.0

3. Regeneration methodology

To recover water with a quality suitable for its reuse in the production process of IQE (permeate), regeneration process for SW and BW membranes has been investigated. It was also relevant to achieve high permeability and lower pressure requirements so to save energy and time. Thus, the aimed membranes had properties corresponding to membranes of Type I or II.

End-of-life SW-RO and BW-RO membranes were provided by two desalination plants located in Spain. These membranes correspond to commercial SW-RO membranes fabricated by LG Chem and to commercial BW-RO membranes fabricated by Dow Filmtec (Table 5).

Table 5. Specifications of the commercial SW-RO and BW-RO membrane used for regeneration.

Element model	LG SW 440 GR	BW30-400
Configuration	8-inch spiral wound	8-inch spiral wound
Membrane polymer	Thin-film nanocomposite (TFN) polyamide	Thin-film nanocomposite (TFN) polyamide
Permeate flow rate (m^3/dia)	31.2	40.0
NaCl rejection (%)	> 99.7	> 99.0
Active membrane area (m^2)	41	37

c. Membranes characterization

Six end-of-life membranes were used for this task: one BW-RO and five SW-RO. The BW-RO membrane was used at lab-scale and the SW-RO membranes: one at lab-scale and four at pilot plant scale.

For each membrane a standard test was performed to assess its performance, allowing to compare initial properties of delivered membranes with the properties of regenerated membranes. The standard test used is showed in (Table 6). This test consisted in assessing and comparing the permeability and the rejection of NaCl at the standard conditions.

Table 6. Standard test conditions and expected permeability and salt rejection.

Standard conditions for membrane evaluation	
NaCl solution (ppm)	1500
Pressure (bar)	16
Recovery (%)	15
Temperature (ºC)	25

Standard conditions for membrane evaluation	
Commercial BW[a] membrane permeability (L/m^2.bar.h)	2.81
Commercial BW[a] membrane NaCl rejection (%)	> 99.0
Commercial SW[b] membrane permeability (L/m^2.bar.h)	*1.94*
Commercial SW[b] membrane NaCl rejection (%)	*> 99.7*

[a] BW30-400, DOW Filmtec; [b] LG SW 440 GR, LG Chem

This test was performed recirculating a dissolution containing 1500 ppm of NaCl, returning the permeate and the concentrate to the feed tank. However, a modification of the standard test was performed during pilot plant operation. Instead of setting a given recovery, a performance time was established: 30min. Standard tests would run for 30 min and then membrane performance in terms of recovery, permeability and rejection were measured.

Besides this test, a test to evaluate the rejection of sulphates was as well conducted The standard method based on magnesium sulphate ($MgSO_4$) which is the standard test for NF membranes is presented in Table 7. The same methodology than NaCl test is used.

Table 7. Operating conditions of pilot plant for standard tests of NF.

Operating conditions – NF standard test	
Mg_2SO_4 solution (ppm)	2,000
Pressure (bar)	16
Recovery (%)	variable
Temperature (ºC)	25
Feed flux (m^3/h)	8-10

Finally, in order to evaluate the membrane performance treating the wastewater from IQE, tests using synthetic solution with similar composition of real wastewater were performed at laboratory scale. The synthetic solution was composed of Na_2SO_4 at 24.4g/L and NaCl at 2.97g/L. pH was adjusted with sodium hydroxide to pH 9 accordingly the pre-treatment conditions before reaching the regenerated RO system, and that had been stablished to reduce scaling problems during RO process. To evaluate the full performance of the produced membranes, first of all a P vs Q curve was performed. Permeability (Q) is measured for each of the membranes at given pressures. Via this plot, a starting working pressure to achieve 20 LMH (1.25 $L/m^2\cdot bar\cdot h$) can be decided. During the full experiment, this pressure was increased in time in order to maintain the permeate flux constant as the feed got more concentrated due to recirculation of the concentrate.

d. Laboratory-scale regeneration

The overall methodology followed to obtain tailor-made membranes is presented in **Figure 4**.

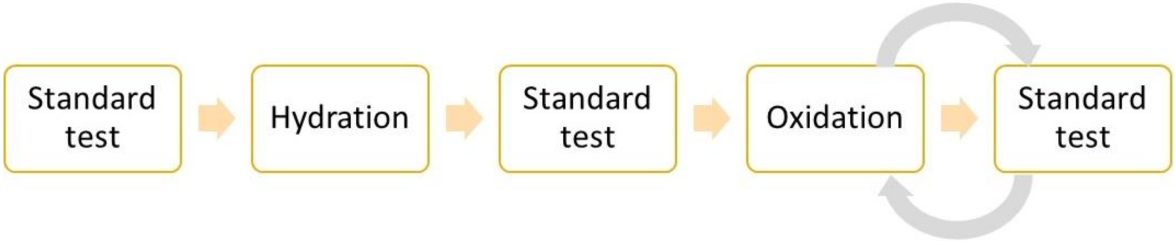

Figure 4. General methodology to regenerate membranes.

After assessing end-of-life membranes properties with the standard NaCl test, regeneration was carried out. The process of regeneration was conducted in two steps: hydration and oxidation. Firstly, the regeneration process was conducted in the lab with membrane coupons to evaluate the optimal conditions to achieve a membrane that fulfils the aimed requirements by the silica factory. The effect of each of the regenerating steps on the membranes was measured with the NaCl standard test for, so permeability and rejection for NaCl were measured.

For experiments in a lab-scale, coupons of a membrane element are required to test membranes as flat sheets. These coupons were achieved by cutting open one of each of the RO membranes so the inner sheets of the element that form the spiral wound are accessible (**Figure 5**). Once opened, coupons of membrane and carriers cut of the middle sheets (140 cm^2) were cut to fit the testing cell (Figure 7). 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. BW-RO membrane element opened to access the membrane sheets.

i. Testing set-up (Spanish BEC BP-2)

The testing set-up for the evaluation of membrane performance is shown in Figure 7 and consisted of a: testing cell (Figure 6), a thermostatic bath (DIGIT-COOL, HAAKE (EK20)) and a pump (Hydra-cell, G03X).

The testing cell was made of stainless steel so it could resist pressure, which was regulated using a needle valve at the concentrate, and it was continuously monitored by a pressure meter. To monitor the flow of the feed a flowmeter was used. The set-up was all connected with a series of tubes, gauges and valves. This set-up was used for standard tests with NaCl and also for tests with synthetic wastewater at higher recoveries.

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

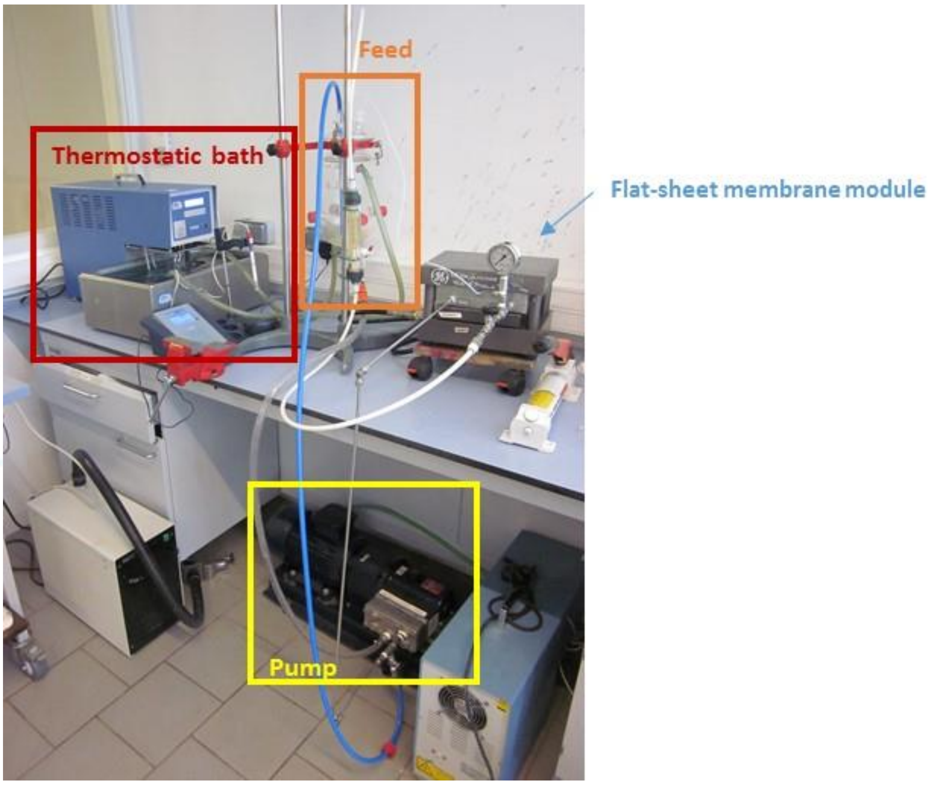

Figure 7. Experimental set-up for membrane testing at lab-scale.

Standard tests (Table 6) were carried out at a working pressure of 16 bar for 30 minutes, permeate was collected until a 15% of recovery. Recovery was monitored by a scale and the concentrate was recirculated. The overall operating conditions are detailed in Table 8.

Table 8. Operating conditions of the testing cell (flat-sheet membrane module) for standard tests of BW-RO.

Operating conditions – testing cell	
NaCl solution (ppm)	1500
Pressure (bar)	16
Recovery (%)	15
Temperature (ºC)	25
Feed flux (L/min)	1.0
Cross-flow velocity (m/s)	0.27

Besides, standard NaCl tests, tests with synthetic solution, based on assessing the membrane performance at maximum recovery, were conducted.

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.

ii. Regeneration set-up (Spanish BEC-BP-12)

The process of membrane regeneration consisted in two different steps: hydration and oxidation. Regeneration study involved the evaluation of the membrane performance under the effect of: different hydrating solvents, different concentrations of the OA, different oxidative doses and pH (Table 9).

Table 9. Description of the tested conditions during regeneration studies.

Parameters tested	Conditions
Hydrating solvents	Distilled water, H-1 and H-2
Concentration of OA (ppm)	C1, C2, C3
Doses of OA (ppm·h)	1,000, 2,000, 4,000, 6,000, 7,000, 10,000
pH (upH)	5.0, 6.5, 9.0, 12

Three different solvents were assessed for their hydrating properties of end-of-life RO membranes. One of the solvents was distilled water and due to confidentiality matters, hereafter we will name the other two hydrating solvents H-1 and H-2. The hydrating process was passive, so the membrane coupon was immersed in the corresponding solvent: 24 hours in distilled water, 15 minutes in H-1 and 48 hours in H-2. After each hydrating process, a standard test was conducted to evaluate its effect on permeability and rejection of the membrane coupon.

After the hydrating process, membranes were oxidized by an oxidative agent (OA) to increase their permeability and obtain the desired salt rejection. The oxidizing process involved a decrease on the salt rejection which was the limiting parameter that set the end of oxidizing doses. 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. The recirculation was carried out during set periods of times which were given by the dose (ppm·h) under study and the used concentration of oxidative agent. As well as for hydration, after each oxidative step, a standard test was carried out on the coupon to evaluate the effect of oxidation on its performance.

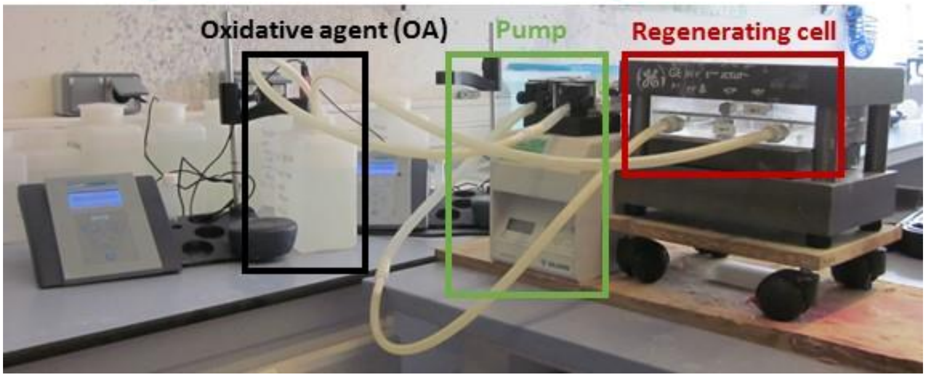

Figure 8. Experimental set-up for oxidizing the membrane at lab-scale.

e. Pilot plant-scale regeneration

As mentioned above, the sub-objective of experimentation by pilot plant is to obtain membranes with properties of Type I and Type II. The pilot plant is meant to provide elements with the suitable properties that can be transported to the silica factory for further use in this project.

Once the optimal lab-scale conditions to produce Type I and II membranes were defined, regeneration at pilot scale was evaluated (Figure 4). At pilot plant scale, as in lab-scale, hydration was combined with oxidation of the membrane elements in a sequential way in order to find the most optimal regeneration conditions. For other two elements, the effect of no hydration was assessed. The used methodology is the same as at lab-scale (Figure 4). Tests on regenerated membrane performance with real effluent are going to be carried out at the site.

To evaluate membrane regeneration process at pilot scale two equipment have been used: one for hydrating and one to carry out the oxidation of the membrane.

iii. Equipment to carry out hydration

To hydrate membrane elements, two different methodologies were followed. One consisted on immersing the element in H-1 during 48h and the other one to recirculate H-1 during 4h with a peristaltic pump. For both methodologies, elements were placed into a PVC case (Figure 9) with an exit valve on the bottom.

Figure 9. PVC case for membrane elements to be hydrated.

iv. Pilot plant for testing and oxidizing

A pilot plant has been constructed (BEC-BP-10) to produce regenerated membrane modules. It consisted mainly of a pressure tube for reverse osmosis membranes type 8040, a low pressure pump and a high pressure pump. Figure 10 presents a 3-D model of the pilot plant, Figure 11 shows pictures of the pilot plant in reality and in Table 10 the different components are summarized.

Figure 10. 3-D model of the pilot plant used for oxidation and tests on membrane performance.

The constructed pilot plant can be used to test membranes and to regenerate membranes by recirculation the oxidizing solution. As it can be seen in Table 10, the pilot plant has 3 feed tanks: one tank of 1,000L, which contains the solution to make the different brine test; another one tank of 500L, which contains water to perform the different flushing operations and the last one of 250L, which contains the oxidizing solution. Once the feed has been selected (opening/closing the different valves) the effluent enters the system by first passing through the low pressure pump, then by the safety filter (to avoid that possible external agents could damage the membrane), then by the high pressure pump and finally by the reverse osmosis module. The evaluation of the membrane performance can be regulated by the manometers installed as well as by monitoring flux of the feed, permeate and concentrate together with their conductivity.

Table 10. Relation of the equipment of the pilot plant to oxidize the membranes.

Element	Description	Element	Description
1	First concentrate	11	Maximum concentrate pressure sensor 1
2	Second concentrate	12	Maximum concentrate pressure sensor 2
3	First permeate	13	Valve
4	Second permeate	14	Bypass valve high pressure pump
5	Recirculation	15	Permeate flowmeter
6	First feed	16	Concentrate flowmeter
7	Second feed	17	Filter
8	Third feed	18	High pressure pump
9	Minimum feed pressure sensor	19	Pressure tub for reverse osmosis
10	Maximum permeate pressure sensor	20	Low pressure pump

Figure 11. Pictures of the regeneration pilot plant used for oxidation and tests on membrane performance.

Oxidation procedure

In the same way that in the experimentation at laboratory scale, to perform an oxidation or a standard test, a flushing with water is performed to drag possible precipitated agents and to clean the membrane.

Regeneration was carried out by the low pressure pump (4 bar) whereas the high pressure pump was dodged to avoid possible corrosion damage within the pump. However, when a NaCl or $MgSO_4$ standard test was being carried out, the plant was operated at 16 bars using the high pressure pump. To oxidize, OA at C2 was recirculated continuously with the low pressure pump and dodging the high pressure pump for a certain time. In the first 15 minutes of each regeneration was taken a sample of the solution to verify that the concentration continues to be established initially. In case a concentration decrease, the concentration is readjusted to maintain the concentration fixed (if the concentration was less than 75% of the established past the first 15 minutes, within 30 minutes of starting the test the concentration was re-checked and readjusted if necessary). At the end of each regeneration, the OA concentration was re-measured to ensure proper oxidation in the specified conditions.

f. Analytical determinations

To evaluate the membrane performance, the analytical methods described in Table 11 were used.

Table 11. 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
Cations (K, Na, Ca, Mg)	Aquion, Dionex	Ionic Chromatography
Anions (Cl, NO_3, SO_4)	ICS 2100, Dionex	Ionic Chromatography

4. Regeneration results

a. End-of-life membranes characterization

End-of-life received membrane elements of SW-RO and BW-RO were tested with the NaCl standard test to evaluate its performance. Tests were performed using an existing pilot plant property of CTM (BEC-BP3) as when membranes were received the regeneration plant was not constructed yet.

In Table 12, results from the tests performed to end-of-life SW-RO membranes modules are presented as well as a test with a brand new membrane of the same model. In addition, specifications from commercial membranes are showed also for its comparison. BW-RO elements were not tested at pilot scale.

Table 12. Comparison of the performance of end-of-life SW-RO membranes with commercial membranes at pilot-scale.

	Permeability ($L/m^2 \cdot h \cdot bar$)	Rejection NaCl (%)
SW-E1[a]	0.64	99.8
SW-E2[a]	0.71	99.7
SW-E3[a]	0.73	99.7

	Permeability ($L/m^2 \cdot h \cdot bar$)	Rejection NaCl (%)
SW-E4[a]	0.82	99.7
SW-E5[a]	0.75	99.8
New SW-RO[a]	1.60	99.7
Commercial SW-RO[b]	1.98	> 99.7

[a]used in pilot plant test, n=1; [b]commercial specifications for LG SW 440 GR

As it can be seen, the tested end-of-life elements (coded as SW-E*X*) presented a lower performance comparing to the one of their corresponding commercial membranes. The acquired new SW-RO element and the commercial specifications differ slightly although rejection remains the same. Elements of end-of-life SW-RO tested have more than 50% difference in permeability from commercial membranes but rejection is similar.

An end-of-life BW-RO membrane together with the SW-E1 module were cut open in order to obtain membrane coupons. Two different sorts of coupons were then tested in order to evaluate the effect of regeneration for each sort. Standard tests with NaCl were conducted to several coupons of each sort to assess the membrane properties. Results are shown in Table 13.

Table 13. Evaluation of end-of-life SW and BW coupons at lab-scale.

	Permeability ($L/m^2 \cdot h \cdot bar$)	Rejection NaCl (%)
End-of-life BW-RO[a]	0.33 ± 0.06	93 ± 1
End-of-life SW-E1[a]	0.99 ± 0.14	93 ± 4
Commercial SW-RO[b]	1.98	> 99.7
Commercial BW-RO[b]	2.81	> 99.0
Commercial NF[b]	3.31	> 97.0

[a]used at lab-scale, n=3; [b]commercial specifications for LG SW 440 GR, BW30-400 and NF270-400/34i.

End-of-life BW-RO coupon presents 80% difference in permeability from a commercial membrane and around 6% difference in rejection. This fact indicates a relevant effect of the fouling on the membrane performance.

Regarding end-of-life SW-RO membranes tested in the lab and in the pilot plant present different rejections of NaCl although permeability is the same. The difference in rejection can be explained by distribution of the fouling in the element. The coupon tested in the lab corresponds to a fraction of a sheet of the element and the membrane tested in the pilot plant is the whole element.

b. Lab-scale regeneration

Regeneration at lab-scale was based on researching the optimal conditions in terms of hydration and oxidation to apply to the end-of-life membranes (BW and SW) to obtain a membrane with the properties defined in Table 4, suitable for IQE's production.

Parameters assessed were hydration agents, pH, OA concentrations and OA doses. The coupon obtained with the optimal regeneration conditions was used to treat synthetic wastewater with a composition similar to the real effluent.

i. Effect of hydration

One of the causes of the low permeability obtained for end-of-life membranes is a low membrane hydration. This hydration is based on making the polyamide chains (polymeric active layer) swallow by creating van der Waals forces in-between these chains. End-of-life membranes, should be stored maintaining hydration, but sometimes it is difficult. So, the first step to recover the permeability is membrane hydration.

Effect of hydrating solvent

Three different solvents were used to hydrate the membrane: distilled water, H-1 and H-2. The hydration solvent effect was tested for both BW and SW membranes.

Figure 12 shows the effect of the hydrating solvents on the end-of-life BW-RO membrane.

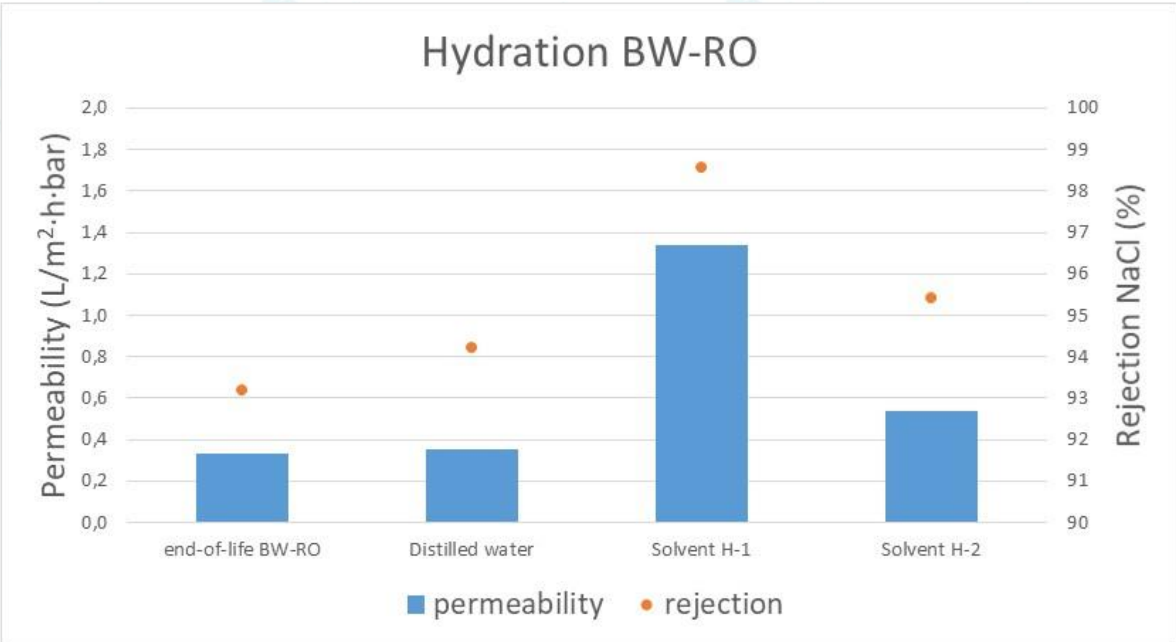

Figure 12. Effect of the hydrating solvents on end-of-life BW-RO at lab-scale (n=1).

In terms of increase of permeability and rejection, solvent H-1 gave the best results, increasing the permeability of end-of-life membrane more than 4-fold. Solvent H-2 also increase the permeability but only a 20% more, while rejection is increased 2%. Distilled water had not significant effect on permeability and rejection. In any case, permeability is lower than the corresponding to commercial BW-RO (2.81 L/m^2·h·bar).

Figure 13 shows the effect of the hydrating agent on performance of SW-RO membranes. As in the case of BW-RO membranes, H-1 is the solvent that provides the highest hydration to the membrane whereas distilled water and H-2 present similar hydration efficiency. Regarding these results, hydrating solvent H-1 was chosen for later tests involving an oxidative agent.

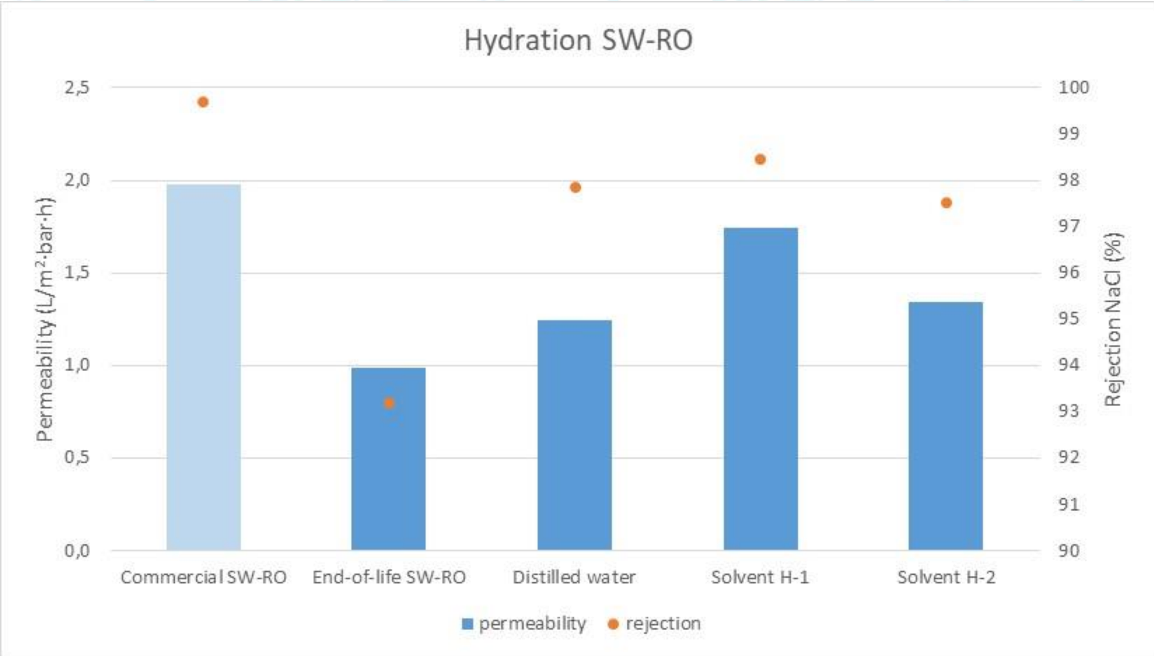

Figure 13. Effect of the hydrating solvents on end-of-life SW-RO at lab-scale (n=1).

However, hydrated SW-RO coupons with H-1 did give similar results to commercial SW-RO (1.98 L/m^2·h·bar). From the previous results it can be concluded that H-1 showed the best results for both type of membranes. But the effect of water and H-2 is different depending on the membrane. This could mean that the efficiency of water and H-2 will depend of the fouling and scaling in the membranes.

Effect of hydration on the oxidative process

Once effect of different hydrating solvents was evaluated, the effect of hydration on the oxidation was studied on BW-RO coupons. Figure 14 shows the resulting permeability and rejection of several BW-RO coupons hydrated with two solvents H-1 and H-2 and oxidized at C2 of OA.

The tested solvents presented relevant differences in terms hydration, as detailed previously. During oxidation, the difference still persisted and the effect of degrading the active layer is proportional to the difference in hydration. Both types of coupons (H-1 and H-2) increased their permeability 2-fold. Therefore, hydrating assisted on removing fouling and thus H-1 solvent was more efficient for the tested membranes.

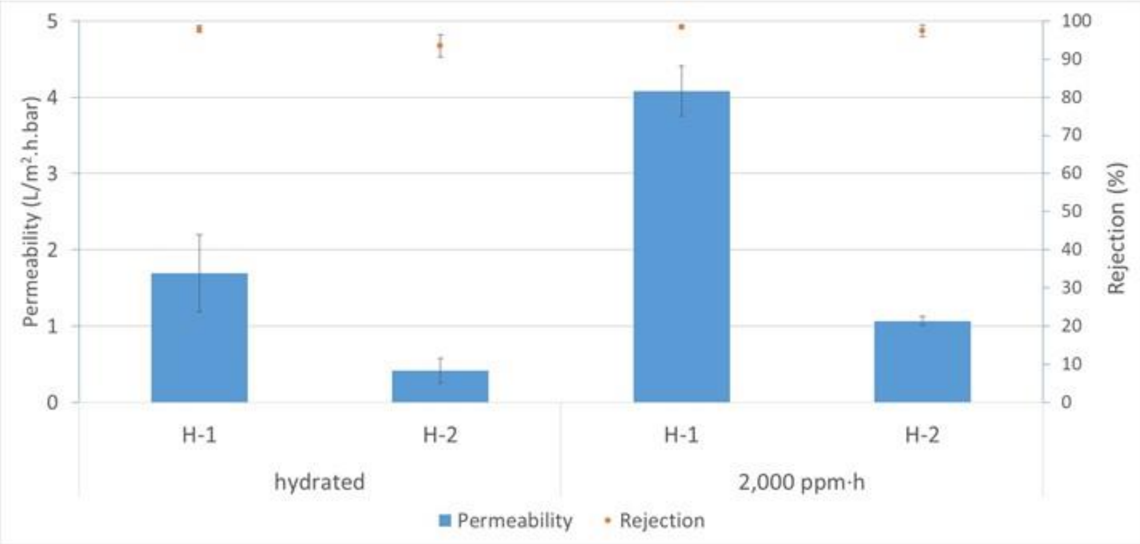

Figure 14. Effect of hydrating solvents on oxidative process of end-of-life BW-RO coupons.

ii. Effect of pH

The effect of the pH was tested using coupons of a BW-RO element. The objective of the study was to validate the information from state of the art that indicates basic pH favors the regeneration of membranes over neutral or acid pH [15].

Four different pH (12, 9, 6.5 and 5) were tested during the oxidation of four coupons at the same OA conditions (C1, 2000ppm·h). All the BW-RO coupons used for this test were first hydrated with H-1 before testing. Figure 15 presents the effect of the different pH on the regeneration process.

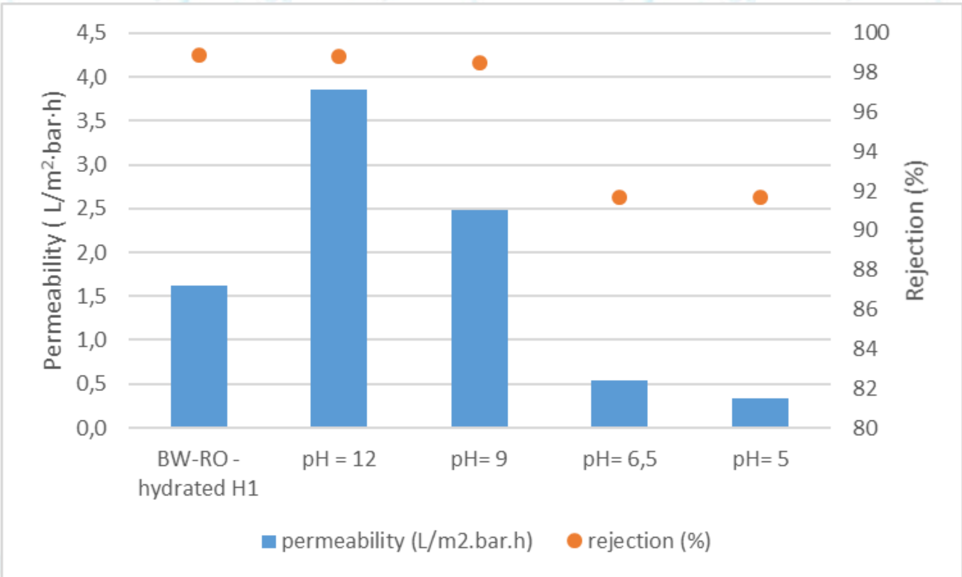

Figure 15. Effect of pH on the regeneration process of BW-RO coupons at lab-scale (n=1).

As it was expected, basic pH gave the best results in terms of permeability and rejection increase of the hydrated coupons, in particular pH 12. It can be observed, as well, that at pH 12 already Type II membrane has been achieved. Acid pH resulted in lower permeability and rejection than hydrated coupons. These could be explained by the chemical modification that acid conditions could bring to the polyamide active layer which can make the polymer blocked to diffusion.

According the obtained results, all the other experiments where performed at pH 12 so to achieve the best regenerating conditions.

iii. Effect of OA concentration

Concentration of OA renders effect on the kinetics of the oxidative process, therefore, two different studies were conducted using BW-RO and SW-RO membranes respectively. For BW-RO coupons, 3 different OA concentrations (C1, C2 and C3) at the same dose, 2000ppm·h were tested. For SW-RO, the study was focused on two concentrations of OA (C1 and C2).

Effect of OA concentration on end-of-life BW-RO coupons

Three concentrations C1, C2 and C3 were tested at the same dose, 2000ppm·h, to evaluate if the kinetics of the oxidative process were affected. This study was carried out for BW-RO coupons and performance of the modified coupons was conducted by NaCl standard test.

Figure 16 presents the effect of the three concentrations tested as well as the membrane performance at its end-of-life and after hydration with H-1.

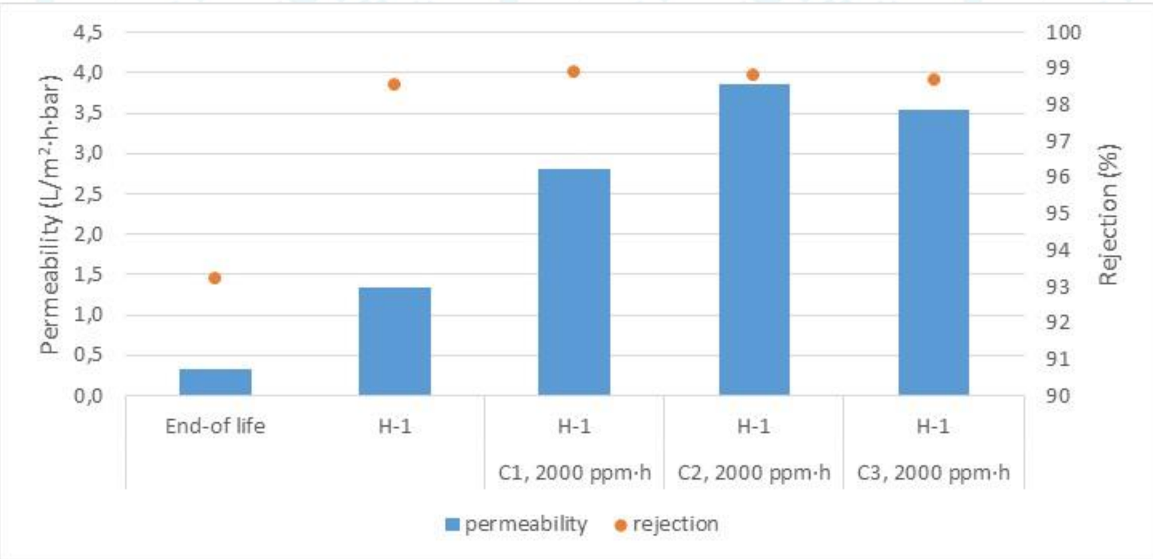

Figure 16. Effect of OA concentration on end-of-life BW-RO coupons (n=1)

For the three different OA concentrations, no effect on the rejection is observed, as it is the same than the hydrated membrane. However, permeability is affected. The oxidative process increases more than 2-fold permeability of membranes compared to hydrated membranes. Among concentrations, and increase on OA concentration has a positive effect comparing C1 and C2, permeability increases as the concentration increases. However, the difference between C2 and C3 is not relevant as the increase is around 0.3 L/m^2·bar·h which could be with the error. Therefore, C2 was the chosen concentration in further experiments as it gives the maximum kinetic effect and the minimum reagent consumption.

Effect of OA concentration on end-of-life SW-RO coupons

Coupons of end-of-life membrane SW-RO hydrated with H-1 (n=3) were thus put in contact with an oxidizer so to chemically modify the active polymeric surface. Two different concentrations (C1 and C2) of the oxidative agent (OA) were used at the same dose (2000ppm·h) to evaluate, with the standard NaCl test, the effect of the OA concentration (kinetics). Figure 17 shows the properties of SW membranes after regeneration at 2,000 ppm·h using different concentration of OA.

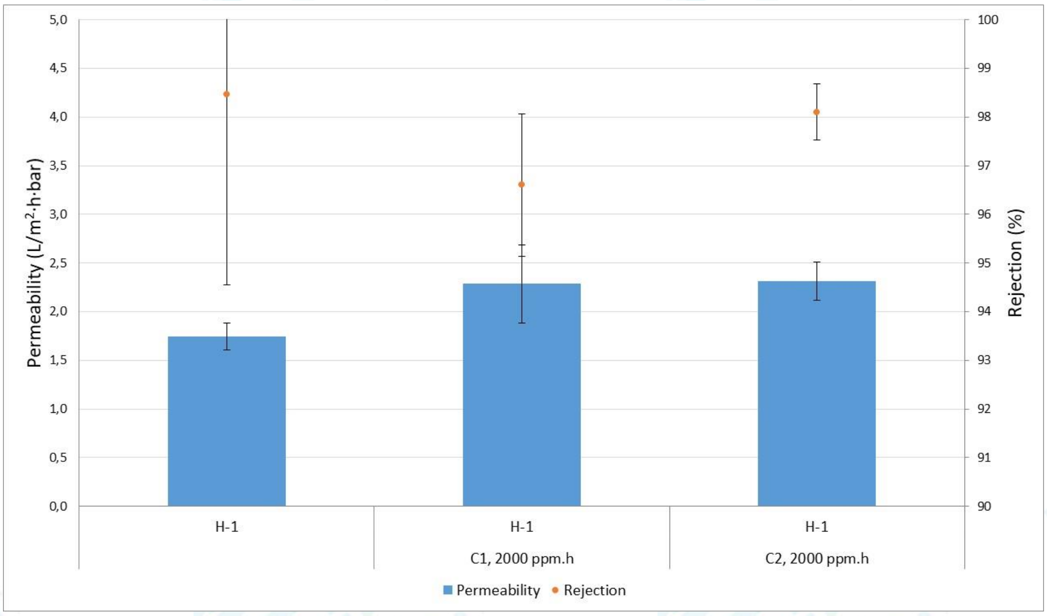

Figure 17. Effect of OA concentration on hydrated SW-RO membranes (n=3) using a dose of 2,000ppm·h.

It can be observed that oxidation resulted in an increase on permeability and in a decrease on rejection on the two membranes tested at C1 and C2. The two different concentrations, they both give similar results thus kinetics, in principle, is not influenced by the difference of these two solutions. This fact is consistent with results obtained for BW-RO coupons, as there is a maximum concentration that is kinetically more suitable as it consumes less reagent. In the case of BW, effect of AO concentration is observed in arrange of concentration (C1 and C2). This fact is most likely fouling-related as BW-RO membranes presented more fouling that implies also AO consumption. Once membrane fouling is removed, no effect of the concentration is observed as in the case of SW-RO becasuse the active layer to oxidize is the same organic polymer.

iv. Effect of dose

Concentration C2 was chosen for BW-RO and SW-RO to further oxidize the polyamide active layer of the end-of-life membrane coupons. The effect of the dose was studied for the hydrating solvent H-1 at C2. Figure 18 presents the effect of doses on BW-RO coupons.

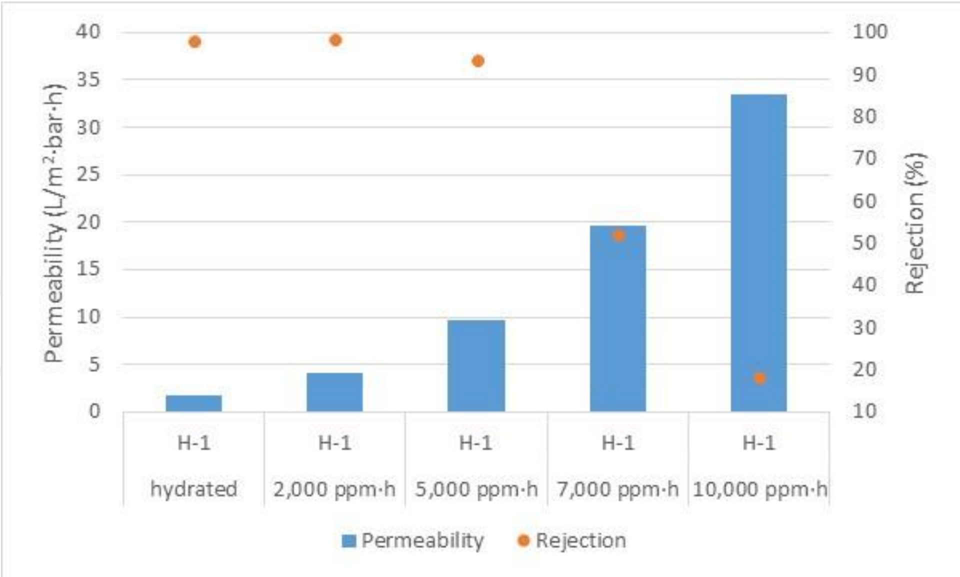

Figure 18. Effect of OA doses on BW-RO coupons with two different hydrating solvents, H-1 (n=3).

After regeneration, these coupons achieve similar properties of Type II (3.31 L/m^2·bar·h, > 97.0%) at 2,000ppm·h. The higher the dose of OA applied, the lower the rejection of NaCl is and the higher the permeability. Thus, for our target, membranes hydrated BW-RO coupons with H-1 at 2,000ppm·h with C2 are already suitable, moreover, this study provides data on how to develop other tailor-made membranes with different targets than the production at IQE.

Effect of OA doses on SW-RO

To further optimize the regeneration process, SW-RO coupons were tested with three different doses (2,000 ppm·h, 4,000 ppm·h and 6,000ppm·h) to membranes already hydrated with H-1. Figure 19 gives the results of the standard tests on the oxidized membranes. It is noticeable that doses of 2,000ppm·h and of 4,000ppm·h give membranes of Type I. Their permeability is close to the one of a BW-RO (2.81 L/m^2·bar·h) membrane although their rejection is lower (< 99.0%). The oxidizing dose of 6,000ppm·h leads to a membrane of Type II with a higher permeability than a NF membrane and very similar rejection (3.31 L/m^2·bar·h, >97.0%). For this project, membrane regenerated with a dose of 6,000ppm·h is optimal for the purpose at IQE regarding a high permeability and a sufficient rejection. However, rejection is only measured with NaCl thus performance with synthetic water was conducted.

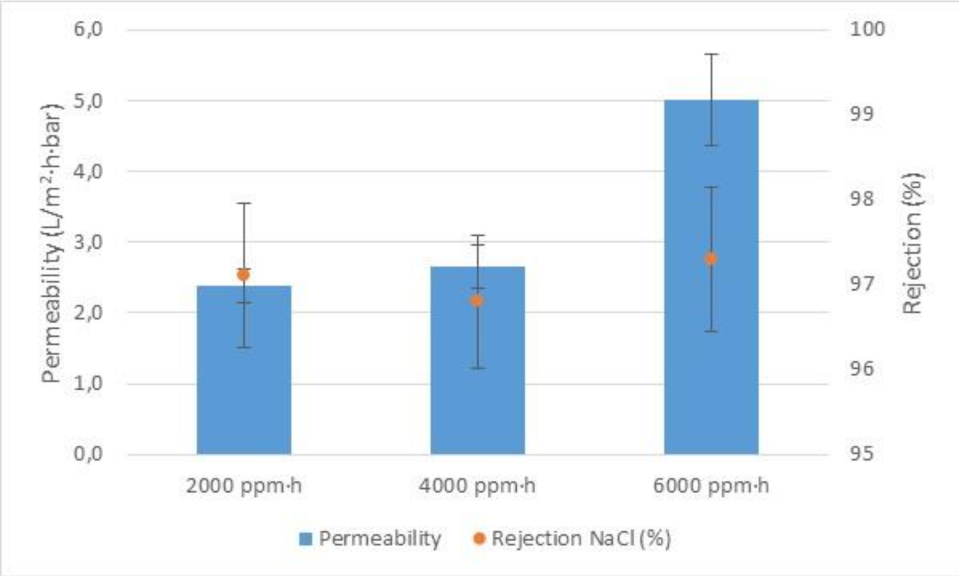

Figure 19. Effect of OA doses on SW-RO coupons (n=2) .

v. Optimal conditions for tailor-made membranes

To further produce tailor-made membranes, even though BW-RO coupons gave good performances, end-of-life SW-RO were used due to their broader availability in the region. SW-RO coupons were assessed with synthetic solution that is similar to the one at the silica factory IQE.

The hydrated coupon with H-1 was tested using synthetic wastewater to assess the performance in terms of operational conditions and the resulting quality of both permeate and concentrate and therefore conclude if the end-of-life membrane required further treatment. First of all, a P vs Q curve was performed in order to select the working pressure. In Figure 20 curves performed with the different coupons are presented.

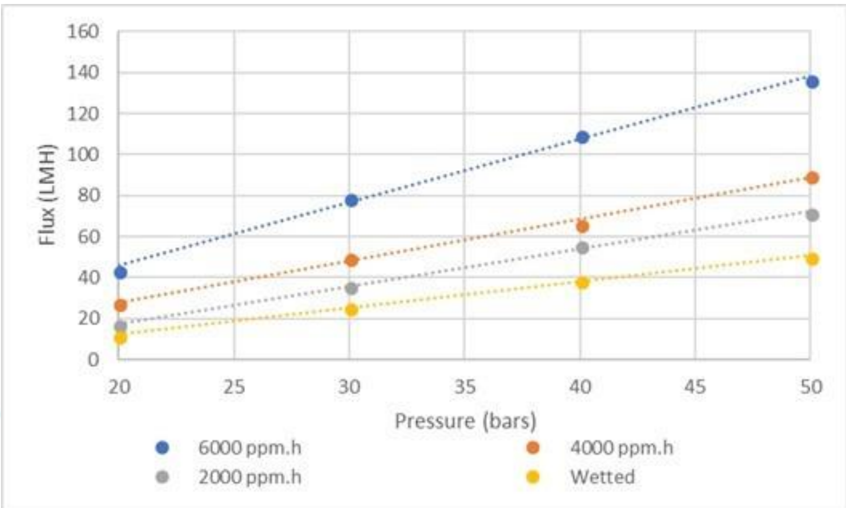

Figure 20. P vs Q curves for the SW-RO regenerated membranes at lab-scale with synthetic water.

Working pressure was selected in order to achieve a permeate flux of 20 LMH. For example, for coupons regenerated at 6,000 ppm·h, the starting working pressure was 24 bar. This pressure increased during time in order to maintain the permeate flux constant as the feed gets more concentrated due to recirculation of the concentrate. Table 14 shows the results obtained by testing the hydrated membrane and the oxidized membranes with the synthetic solution. At 71% of recovery, the hydrated membrane provides a permeate with a conductivity of 0.75mS/cm, which is lower than the maximum limit to be used in the silica factory (4.6 mS/cm). Therefore, the performance of the membrane in terms of quality is satisfactory. However, as it has been explained it is desirable reduce the working pressure to reduce the cost in terms of energy. Thus, an oxidative treatment was assessed to achieve a membrane with satisfactory rejection, high permeability and lower working pressure.

Thus, fully regenerated end-of-life SW-RO coupons were then assessed with the synthetic solution at also 20LMH to evaluate the quality of the effluents as well as the pressure required (Table 14). All three tests were performed at a recovery of around 75%, the maximum the system could afford. Rejection decreased when membranes were more oxidized, however, the final conductivity of the permeate was acceptable in all three cases as it is below 4.6mS/cm. Another tendency of the degree of oxidation was the pressure requirement. The more oxidised the membrane was, lower are the pressure requirements.

Table 14. 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
Temperature (ºC)	25	25	25	25
Permeability (L/m²·h·bar)	1.25	1.25	1.25	1.25
Working pressure (bar)	38	38	24	20
Recovery (%)	71.0	75.1	75.9	74.6
Rejection in conductivity (%)	97.6	94.1	90.8	86.4
Final permeate conductivity (mS/cm)	0.75	1.80	2.82	4.18

Besides conductivity to evaluate rejection, it was important to assess the specific rejection for chloride and sulphate (Table 15). Rejection of both anions decreases as the membrane oxidized status increases. Chloride is smaller than sulphate; therefore, rejection is lower compared to the one of sulphate.

Table 15. 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

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)
Permeate	56.4	278.4	134.8	764.5	174.1	1,095	347.6	1,502
Concentrate	477	60,170	5,050	60,880	4,550	60,260	4,330	61,450
Rejection (%)	*96.8*	*98.3*	*92.4*	*95.3*	*90.2*	*93.3*	*80.3*	*90.9*

Therefore, lab-scale optimal conditions that produce a membrane that fulfil the requirements established of permeability and rejection Type II were the oxidation of end-of-life SW-RO membrane at a dose of 6,000ppm·h with a solution of OA at C2.

c. Pilot plant regeneration

Based on the results obtained in the laboratory, it was decided to regenerate SW-RO membrane elements because of the availability to obtain SW-RO membranes in the region. The target was to obtain 2 membranes with the properties defined for membranes Type I and Type II (Table 4).

i. Regenerated membranes: type I.

First, the hydration process was performed using the equipment showed in Figure 9. Two different methodologies were conducted to evaluate the effect of the contact mode: immersion and recirculation of H-1. In Table 16, test results from hydrated elements are showed.

Table 16. Effect of hydrating contact mode on end-of-life SW-RO elements

	Contact mode	End-of-life		Hyrated	
		Permeability (L/m^2·h·bar)	Rejection NaCl (%)	Permeability (L/m^2·h·bar)	Rejection NaCl (%)
SW-RO-E2	Immersion 48h	0.6	99.8	1.3	99.8
SW-RO-E3	Recirculating 4h	0.9	99.8	1.1	99.8

As it was demonstrated at laboratory scale, hydrating the membrane elements improved the membrane performance compared to end-of-life membranes in terms of permeability, while hydration process has no effect on rejection. Regarding the hydration methodology, it can be concluded that both methodologies gave the same results. Thus, the most efficient method is to recirculate H-1 as it is less time consuming.

After hydrating, both membrane elements were oxidized with OA at C2 concentration. Different doses were applied and NaCl standard test conducted until the regenerated membranes gave permeability and rejection similar to Type I. Results from standard tests with NaCl for SW-RO-E2 are shown in Figure 21. It can be observed that the increase on permeability from the element hydrated to the element oxidized at 2,000ppm·h is negligible. However, for the rest of doses, as dose increased, permeability increased although rejection remained constant. A Type I membrane was considered to be achieved at 16,000 ppm·h.

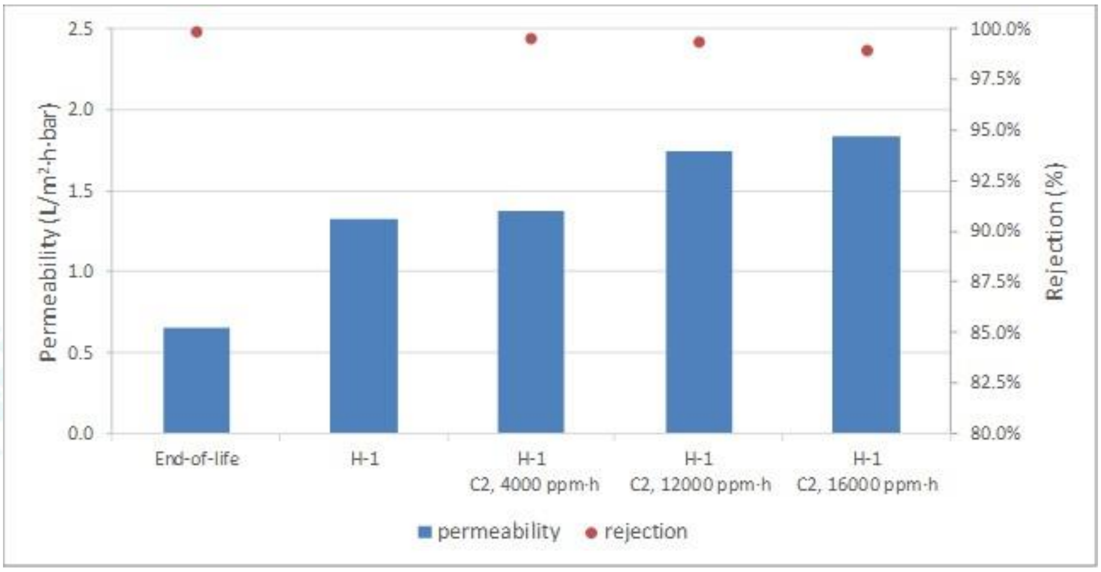

Figure 21. Effect of dose of OA on a hydrated SW-RO element. Results from NaCl standard tests.

The same dose was applied to the second element SW-RO-E3 and similar results were obtained. It is worth to mention that doses at pilot-plant scale were higher than at lab-scale. This fact can be explained by the surface to be oxidized, 140cm^2 at lab-scale and 41m^2 at pilot plant scale.

At the end of the regeneration of SW-RO-E-2 and -3, standard test of $MgSO_4$ was also performed in order to determine rejection for divalent ions. Results from both NaCl and Mg_2SO_4 tests of the obtained membranes are showed in Table 17.

Table 17. Regenerated end-of-life SW-RO elements previously hydrated to Type I membranes.

		NaCl		$MgSO_4$	
	Dose of OA at C2	Permeability (L/m^2·h·bar)	Rejection NaCl (%)	Permeability (L/m^2·h·bar)	Rejection $MgSO_4$ (%)
SW-RO-E2	16,000	1.8	98.9	3.1	98.7
SW-RO-E3	16,000	1.7	98.4	3.0	99.2

At the optimized dose, the produced Type I membranes present a rejection for NaCl slightly lower than for commercial BW-RO (>99.0%) and a permeability very close to commercial SW-RO membranes (1.98 L/m^2·h·bar). However, from these results it can be expected to produce high quality permeate suitable to be reused at the production process at IQE.

ii. Regenerated membranes: Type II.

Two other elements, SW-RO-E4 and -E5 were regenerated until their performance was equivalent to tailor-made membranes Type II. In this case, hydration was not conducted as elements already presented similar permeability as SW-RO-E2 and E3 after hydration, around 1.1 L/m^2·h·bar. Oxidation was carried out until both elements had permeability similar to NF membranes (3.31 L/m^2·h·bar), higher than Type I membranes. This point was accomplished at different doses of OA at C2. In Figure 22, the increase of permeability as function of the dose applied is presented.

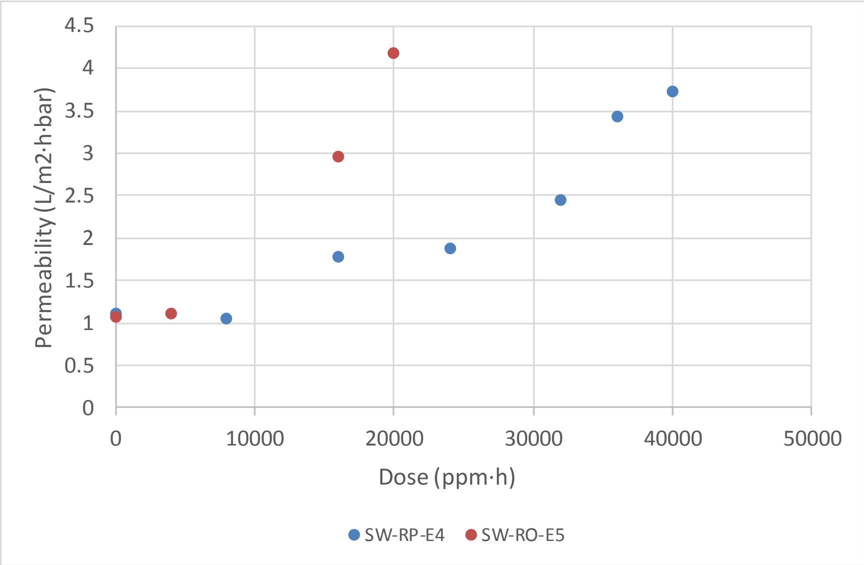

Figure 22. Effect of the dose for the two regenerated elements

As it can be seen in Figure 22, oxidative requirements differ from one membrane to the other. This fact could be explained by the lack of hydration of the membrane elements to be regenerated and thus fouling can have a different effect on the regeneration process. This fact confirms the need of hydration. Nevertheless, adapting the AO dose membranes with similar properties can be obtained.

Table 18 shows the results of the tests on the regenerated membranes regarding permeability and rejection of NaCl and $MgSO_4$ at 16 bar .

Table 18. Regenerated end-of-life SW-RO elements to Type II membranes.

		NaCl			Mg_2SO_4		
	Dose of OA at C2 ppm·h	Permeability (L/m²·h·bar)	Permeate conductivity (µS/cm)	Rejection NaCl (%)	Permeability (L/m²·h·bar)	Permeate conductivity (µS/cm)	Rejection $MgSO_4$ (%)
SW-RO-E4	40,000	3,7	249,0	91,1	3.9	156.3	94.3
SW-RO-E5	20,000	4,2	173,6	94,4	3.8	53.1	97.5

One of the aims of this task was as well to reduce the needed working pressure for the performance of the tailor-made membranes. Thus, these two Type II elements were studied at 10 bar instead of 16, which is common for NF membranes. Table 19 shows that permeability is equivalent to BW-RO membranes which is around 2.81 $L/m^2 \cdot h \cdot bar$. Rejection of NaCl and $MgSO_4$ are within the limits of the targeted quality of permeate. Rejection for $MgSO_4$ is higher than for NaCl because the size of sulphate is greater than Cl thus there is more resistance to diffuse through the polymeric active layer.

Table 19. Standard tests for regenerated end-of-life SW-RO elements Type II membranes at 10bar.

	NaCl		$MgSO_4$	
	Permeability ($L/m^2 \cdot h \cdot bar$)	**Rejection NaCl (%)**	**Permeability ($L/m^2 \cdot h \cdot bar$)**	**Rejection $MgSO_4$ (%)**
SW-RO-E4	2.4	90.5	2.6	96.4
SW-RO-E5	2.5	93.7	2.6	97.1

Both types of regenerated membranes, I and II, are suitable to be operated at the pilot plant that is going to be installed at the silica factory IQE. There, the type of membrane with the best performance for real effluents is going to be evaluated.

5. Conclusions

- Five end-of-life SW-RO membranes and one of BW-RO membrane were characterized using standard tests for BW-RO with NaCl.
- End-of-life SW-RO membranes gave permeability of less than half of the commercial corresponding membrane whilst the BW-RO gave a reduced permeability of more than 9-fold. Rejections in all cases were slightly lower than commercial standards.
- Two different tailor-made membranes have been produced: Type I membranes have a permeability >1.98 $L/m^2 \cdot h \cdot bar$ and a rejection >99%; Type II have a permeability >3.31 $L/m^2 \cdot h \cdot bar$ and the rejection corresponds to the minimum rejection stablished by the possible water reuses at IQE, >85%.
- In order to produce tailor-made membranes, hydration followed by oxidation processes have been evaluated.
- Regarding hydration, three hydrating solvents, distilled water, H-1 and H-2, were tested for BW-RO and SW-RO membranes. H-1 solvent gave the best results by increasing the permeability 3-fold and the rejection 6% of the end-of-life membranes.
- At pilot scale, the contact mode of H-1 was tested: immersion and recirculation. For both methodologies to give similar results, immersion had to have a time frame of 44h longer than recirculating.
- Hydrated membranes were successfully oxidized by the selected OA. The effect of different conditions has been evaluated: effect of pH, effect of OA concentration and effect of dose.
- Regarding OA concentration, best results were obtained with a concentration of C2. Higher concentrations did not result in better membrane performances.

- Doses increase on the hydrated membranes derived in an increase of permeability and a decrease of rejection.

- Two elements of each of types of membranes were produced. Doses were higher than at lab-scale: for Type I, 16,000ppm·h and for Type II, between 20,000 and 40,000 ppm·h. Rejections matched the objectives of each type of tailor-made membranes.
- Both types of regenerated membranes, I and II, are suitable to be operated at the pilot plant at the silica factory IQE. Once installed, the type of membrane with the best performance for real effluents is going to be evaluated.

6. References

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