

1 INTEGRATION OF MONOPOLAR AND BIPOLAR ELECTRODIALYSIS FOR VALORIZATION
2 OF SEAWATER REVERSE OSMOSIS DESALINATION BRINES: PRODUCTION OF STRONG
3 ACID AND BASE

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8

9 **Abstract**

10 Water scarcity in the Mediterranean basin has been solved by using seawater
11 desalination reverse osmosis technology (SWD-RO). This technology produces brine
12 which is discharged back into the sea resulting in an environmental impact on marine
13 ecosystems. Under the circular economy approach, the aim of this work is to recover
14 resources from NaCl-rich brine (~60-70 g/L), e.g. in the form of NaOH and HCl, by
15 integration of two ion exchange-based membrane technologies and quantify the
16 electrical energy consumption. Electrodialysis (ED) incorporating monovalent selective
17 cation exchange membranes as divalent ions purification and concentration of the NaCl
18 present in the SWD-RO brine, was integrated with bipolar membrane ED (EDBM) to
19 produce NaOH and HCl. Current densities of 0.30–0.40 kA/m² at two temperature
20 ranges simulating different seawater temperature regimes (15-18 °C and 22-28°C) were
21 tested and a pure NaCl solution was used as starting concentrate stream. NaCl-rich
22 brines with 100 or 200 gNaCl/L were obtained by ED and then introduced in the EDBM
23 stack producing HCl and NaOH up to 2 M, depending on the initial concentrations. A
24 minimum energy consumption of 1.7 kWh/kgNaOH was calculated when working by
25 EDBM with initial concentrations of 104 g NaCl/L and 0.24 M HCl and NaOH.

26

27 Keywords: Desalination brines; Acid-base production; Electrodialysis; Bipolar
28 membrane

29

1 **1. Introduction**

2 Water scarcity in the Mediterranean basin has been solved by using seawater and
3 reverse osmosis as desalination technology (SWD-RO). The process produces brine
4 which is discharged back into the sea resulting in an environmental impact on marine
5 ecosystems [1]. Initially, managing the generated brines was considered as an
6 environmental problem, but it has recently been identified as an opportunity to develop
7 circular economy concepts to transform a waste (the brine) to a resource for materials
8 production [2]. Any medium to large SWD-RO plant drives so large amount of
9 dissolved elements that may be considered as a mine and then, the waterworks site
10 could be seen not only as a “water factory” but also as a potential chemicals production
11 site. Although revalorization of SWD-RO brines represents a promising and sustainable
12 alternative it has been applied so far only on a limited scale because of the large number
13 of technological gaps to be covered for making it economically feasible [3].

14 Seawater contains almost all elements in the periodic table [4]. However, only a few are
15 nowadays profitable extracted conventionally by evaporation: sodium chloride,
16 potassium chloride, magnesium and bromide salts. Several extraction schemes for a list
17 of eight elements have been identified as being potentially economically and technically
18 viable (Na, K, Mg, Rb, P, Cs, In, Ge) [5]. Valorization approaches of SWD-RO brine to
19 produce salts through different concentration/precipitation technologies have been
20 widely reviewed by Kim [6], Van der Bruggen et al. [7] and Pérez-González et al. [8] in
21 an attempt to attain the zero liquid discharge (ZLD) objectives [9]. Due to the high
22 salinity and consequently high ionic conductivity, electrically driven membrane
23 processes such as electrodialysis (ED) based on the selective passage of some
24 constituents through an ion-exchange membrane (IXM) have been widely researched.
25 Several studies have been oriented to the brine reuse by the chlor-alkali industry from
26 SWD-RO brines [10–14]. This industry uses NaCl-rich brines to produce Cl_2 , NaOH
27 and H_2 by means of ED as a salt valorization option. It was demonstrated that ED
28 technology concentrates NaCl from SWD-RO brines with competitive electrical
29 consumptions around 0.20 kWh/kg NaCl to produce 200 g NaCl/L.

30 Such solutions could be also used as raw materials to produce chemical commodities as
31 HCl and NaOH if bipolar membranes (BM) are integrated. However, ED combination
32 with bipolar membranes (EDBM) has been only applied successfully for chemical and

1 biochemical applications, food processing and in less extension for waste management
2 of metallurgical industries [1,15–19]. When electric current is applied between the
3 electrodes of the EDBM stack, water splitting is produced in the BM. Therefore, the
4 produced H^+ and OH^- ions can be used to generate acid (HX) and base (MOH) from
5 salts (MX), for example NaCl from the chemical industry to produce HCl and NaOH,
6 without production of hydrogen, oxygen or undesirable products. Another of the main
7 features of EDBM process is that water dissociation is accelerated up to 50 million
8 times compared to the rate of water dissociation in aqueous solutions. Moreover,
9 EDBM has low voltage drop, maximal energy utilization, space saving, easy installation
10 and operation, low start-up and running costs and last but not least it can provide
11 products of high quality. However, one of the drawbacks of EDBM, when applied to
12 waste valorization, is that it is not as economically competitive as other membrane
13 separation technologies, due to the electrodes and ion exchange membranes cost and
14 the capital cost. Despite this economical limitation, all the features previously
15 commented have made EDBM an environmentally friendly technology for valorization
16 and management of industrial brines [1,20–22]. A clear application is, thus, the salt-rich
17 waste valorization for the production of acids and bases and a growth number of
18 applications with industrial brines are reported [1,16,17,23,24]. However more limited
19 applications are devoted to SWD-RO brines to produce acid and base with EDBM at lab
20 or pilot scale [15,25]. These studies have concluded that the economic and technical
21 feasibility will be improved if the electrical consumption could be reduced with the
22 increase of brine concentration and with the reduction of scaling compounds in the
23 brines (HCO_3^- , Ca^{2+} , Mg^{2+}). In our previous study [26], SWD-RO brines (60 g/L NaCl)
24 were purified in divalent elements by using NF membranes and 1M HCl and 1 M
25 NaOH were produced by using EDBM with electrical consumptions of 2.6 kwh/kg
26 NaOH. However, scarce data and studies could be found on the influence of the brine
27 concentration (e.g. NaCl) on the process efficiency in terms of the production of the
28 highest NaOH and HCl concentrations and the specific electrical consumption.

29 The aim of this work is to quantify the performance and the electrical energy
30 consumption of: a) the concentration and purification of NaCl from SWD-RO brines by
31 using monovalent selective ion exchange membranes to avoid the presence of divalent
32 metal ions (Ca, Mg) in ED cells; and b) the integration of an EDBM system for in-situ
33 production of HCl and NaOH from concentrated NaCl brine (e.g. 100-200 g NaCl/L).

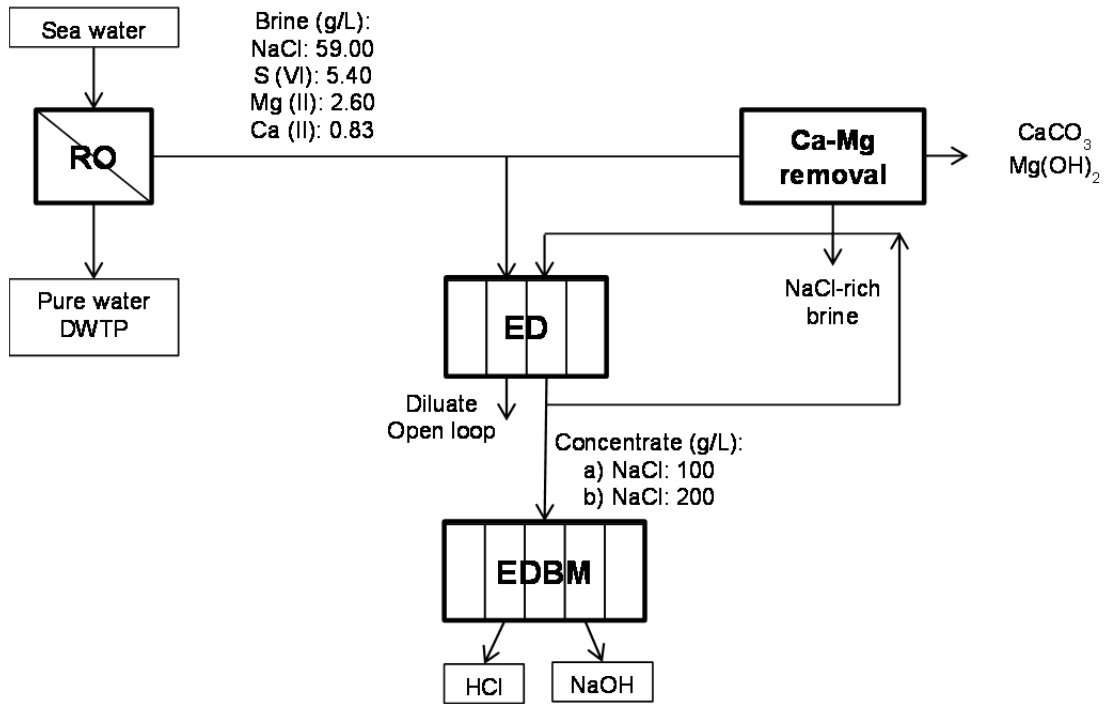
1 The specific objectives are to find optimal operation conditions of the integrated
2 processes of ED and EDBM to achieve the lowest specific electrical consumption and
3 the highest acid and base concentrations.

4 **2. Materials and methods**

5 SWD-RO brine from the seawater desalination plant of El Prat (Barcelona, Spain) was
6 used as feed solution for the ED system. Mainly, this brine was rich in NaCl (65.1 ± 6.1
7 g NaCl/L), although it also contained other major components such as sulfate (5.4 ± 0.2
8 g/L), Mg^{2+} (2.6 ± 0.2 g/L), and Ca^{2+} (0.7 ± 0.04 g/L). Two different ranges of brine
9 temperature were evaluated: 15 to 18 °C from a spring season and 22 to 28 °C from a
10 summer season. Moreover, a pure NaCl solution was used as initial solution for the
11 concentrate loop.

12 In a previous study, Casas et al. [27] evaluated the removal of Ca^{2+} and Mg^{2+} as a
13 potential valorization pathway for seawater desalination brines. Treated brines
14 contained concentration of Ca^{2+} and Mg^{2+} below 10 mg/L. For practical purposes and
15 taking into account that the Ca-Mg purification process was evaluated previously, fresh
16 pure NaCl brines simulating the composition of the feed concentrated brines to be used
17 in the valorization as HCl and NaOH by EDBM were prepared in the present study.
18 Figure 1 shows also this procedure were pure NaCl was used as input brine for the ED
19 concentrated loop.

20 Then, the ED cell was working with an open diluate loop and a NaCl recirculated
21 concentrate stream. Sequentially, the NaCl-rich concentrated solution produced by the
22 ED system was introduced in the EDBM cell which was used to produce NaOH and
23 HCl. Details on the operation conditions are described as follows.



1

2 Figure 1. Schematic illustration of the evaluated seawater desalination brine valorization
 3 process. Stream concentrations are indicated on the arrows.

4

5 **2.1 Experimental description and operation of the ED plant.**

6 An ED pilot using an Eurodia Aqualizer SV-10 stack (620x450x313 mm) with 50 cell
 7 pairs made of Neosepta cation-exchange membranes (CIMS) and anion-exchange
 8 membranes (ACS) (0.1 m² effective surface area per membrane) was used [13,14,28].
 9 The main characteristics of the membrane are listed in Table 1.

10

11 Table 1. The main characteristics of the ED and EDBM membrane used.

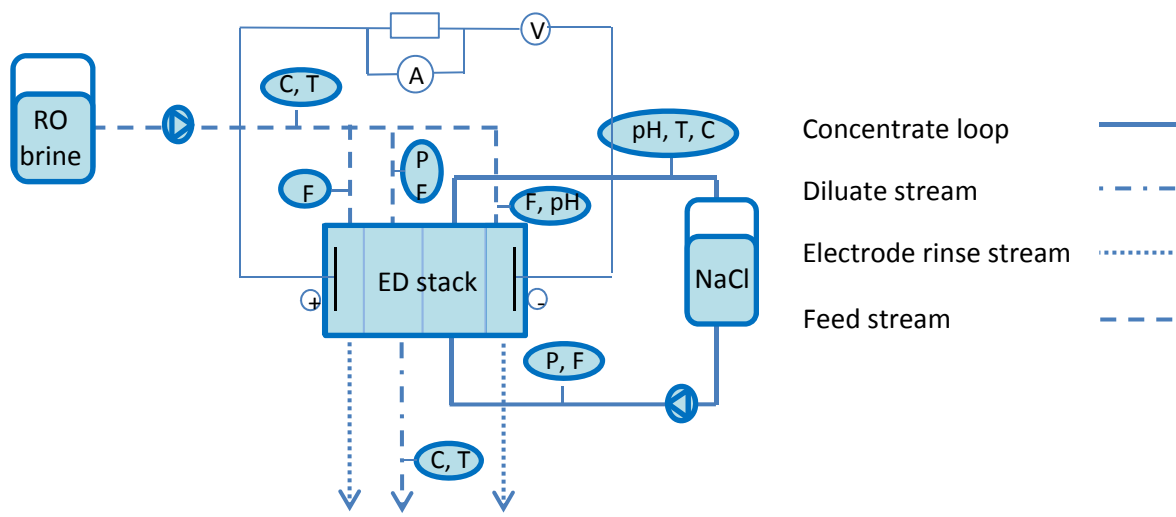
	ED		EDBM		
	ACS	CIMS	PC Acid 60	PC SK	PC BP
Type	Strongly basic anion permeable	Strongly acidic cation permeable	Strongly alkaline (ammonium)	Strongly acidic (sulfonic acid)	Water splitting efficiency > 95 %
General use	Monoanion permselective (Cl-form)	Monocation permselective (Na-form)	Monovalent acid (HCl/HNO ₃ /HF)	Standard desalination	
Electric	3.8	1.8	~ 2	~ 2.5	

resistance ($\Omega \text{ cm}^2$)					
Burst strength (MPa)	0.15	0.10	0.4 – 0.5	0.4 – 0.5	
Thickness (mm)	0.18	0.15	0.16 – 0.20	0.16 – 0.20	0.20 – 0.35

1

2 The intermembrane distance was 0.43 mm and linear flow velocity at the inlet of
3 desalting and concentrating cells was 11 cm/s. The feeding and the electrolyte circuits
4 were operated in a single-pass design to achieve higher current densities and minimize
5 the problems of the increase of temperature in the cell. The concentrate (divalent-free
6 NaCl-rich) stream was re-circulated to reach the maximum NaCl concentration with
7 sustainable electrical specific consumption (e.g. current densities $<0.4 \text{ kA/m}^2$ and
8 specific electric consumption $<0.3 \text{ kWh/KgNaCl}$) under the two given brine temperature
9 ranges evaluated. The SWD-RO brine flow rate through the stack was $0.5 \text{ m}^3/\text{h}$ in both
10 the feeding and the concentrating stream compartments and $0.15 \text{ m}^3/\text{h}$ in the electrodes
11 chambers. HCl was added to keep the pH below 4 for the cathodic circuit, below 7 in
12 the feeding circuit and below 5.5 in the concentrate circuit.

13 Two temperature ranges simulating different seawater temperature regimes ($15\text{-}18 \text{ }^\circ\text{C}$
14 and $22\text{-}28^\circ\text{C}$) were tested and current densities were varied between 0.3 and 0.40 kA/m^2
15 in order to obtain a NaCl-rich brine with the lower specific electrical consumption (less
16 than 0.3 kWh/kg NaCl). The SWD-RO brine concentration process was monitored by
17 in-line measurements of temperature, flow-rate, pressure, current intensity, voltage,
18 electrical conductivity and pH as it can be seen in Figure 2.



19

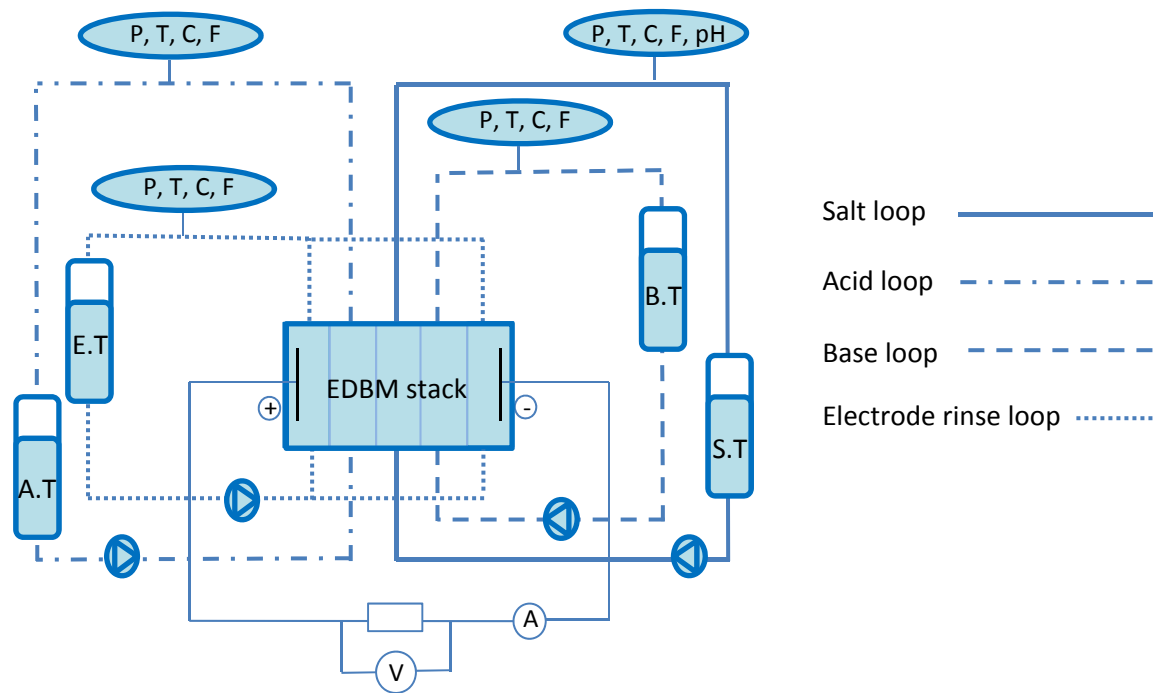
1 Figure 2. ED pilot plant scheme. (P: pressure sensor, T: temperature sensor, C:
2 conductivity sensor, F: flow-meter, pH: pH-meter, A: ammeter, V: voltmeter).

3

4 **2.2 Experimental description an operation of the EDBM plant.**

5 A lab-scale pilot incorporating an EDBM stack PCCell ED 64-004 (PCCell GmbH,
6 Germany) was used. The dimension of the cell was 0.11x0.11m. A scheme of the
7 EDBM stack is shown in Figure 3. It was a 4 chamber system (electrode rinse, acid,
8 base and salt) with an active membrane area of 64 cm² per membrane. The stack
9 configuration was composed of three cell triplets; each cell triplet had one cationic
10 exchange membrane (CEM) (PC-SK), one anionic exchange membrane (AEM) (PC
11 Acid 60) and one bipolar membrane (BM). The main characteristics of the membrane
12 are listed in Table 1. The EDBM cell worked under close loop configuration for the four
13 streams. Two electrodes rinse compartments formed a single circuit located at the cell
14 ends.

15 Four pumps were used to impulse each stream into the EDBM unit. All the
16 performances were carried out at constant voltage (9 V) until the conductivity in the
17 feed tank was almost zero (values around 2 or 3 mS/cm). Some other parameters were
18 constant during the experiments, such as pressure drop differences between
19 compartments (0.3 bar) and the flow rates (ranged from 15 to 20 L/h for the acid, base
20 and salt stream and around 100 L/h in the electrode rinse stream). Several parameters,
21 such as, pressure, temperature, flow rate, electrical current, voltage and electrical
22 conductivity were monitored for all the circuits, while pH of the diluted solution was
23 also recorded.



1

2 Figure 3. EDBM pilot plant scheme. (P: pressure sensor, T: temperature sensor, C: conductivity sensor, F: flow-meter, pH: pH-meter, A: ammeter, V: voltmeter, S.T: salt tank, A.T: acid tank, B.T: base tank, E.T: electrode rinse tank).

5 Taking into account that high voltage and/or current density values implies higher acid and base final concentrations [1,15,25,26], the maximum stack voltage that could be applied (9 V) due to the membrane stack configuration was used. To apply this voltage threshold an initial acid and base solution had to be introduced in the corresponding tank.

10 Preliminary experiments were carried out with synthetic HCl, NaOH solutions. Also, NaCl solutions at two different concentration levels mimicking the concentrate solution obtained as ED brines were used with a nominal concentration of 100 and 200 g NaCl/L (1.71 and 3.42 M NaCl). Initial HCl and NaOH concentration were needed to avoid a high resistance in the power supply. HCl and NaOH feed solution for the acid and base compartment respectively were also prepared with different concentrations (0.05, 0.10 and 0.50 M). For the electrode rinse compartment, a salt solution of nominal concentration of 45 gNa₂SO₄/L (0.32 M Na₂SO₄) was prepared.

18 Different experiments were carried at a) different initial nominal NaCl concentration (100 g NaCl/L and 200 gNaCl/L) and b) different initial acid and base concentration (about 0.05, 0.10 and 0.50 M) to evaluate the effect of these parameters on the final

1 concentration of HCl and NaOH produced. The experimental conditions used are
 2 collected in Table 2.

3

4 Table 2. Nominal experimental conditions including voltage, current density and initial
 5 concentrations of the different EDBM stack circuits used.

Constant voltage (V)	Current density (kA/m ²)	Electrode (Na ₂ SO ₄)	Salt (NaCl)	Acid (HCl)	Base (NaOH)
		C _{ini} E (g/L)	C _{ini} S (g/L)	C _{ini} AB (M)	C _{ini} AB (M)
9	0.5	45	100	0.05	0.05
			200		
			100	0.10	0.10
			200		
			100	0.50	0.50
			200		

6

7 2.3 Analytical methodologies and chemical analysis

8 Samples from ED cell: samples from feed, diluate and concentrate streams were taken
 9 every 2 hours. Chloride (Cl⁻) concentration was measured potentiometrically through
 10 precipitation with AgNO₃ and an AgCl electrode by a Metrohm 721 instrument. Sulfate
 11 (SO₄²⁻) concentration was measured by ionic chromatography using a Metrohm 761
 12 Compact IC equipped with an Anion Dual 2–6.1006.100 column. Ca²⁺ and Mg²⁺ were
 13 determined by atomic absorption spectrophotometry using a Perkin Elmer Analyst 300.
 14 Finally, pH of all the samples was also measured using a glass electrode (Crison pH
 15 Basic 20).

16 Samples from EDBM cell: samples from salt, acid, base and electrode rinse streams
 17 were taken before and during the experiments. HCl and NaOH samples were analyzed
 18 potentiometrically by acid-base titration (Titration Excellence T-70). Na⁺ cations and
 19 Cl⁻ and SO₄²⁻ anions concentration on the salt circuits were measured by ionic
 20 chromatography (Dionex ICS-1100 and ICS-1000, respectively).

21

1 **2.4 Optimization of the energy consumption of the EDBM by response surface**
2 **methodology (RSM)**

3 Response surface methodology (RSM) was used to determine the optimal initial salt,
4 acid and base concentrations to obtain the minimum specific energy consumption by
5 EDBM. A Central Composite Design (CCD) was used to determine the optimal
6 conditions (e.g. production of concentrated NaOH and HCl solutions with the minimum
7 energy consumption) for the critical factors (initial salt, acid and base concentrations). A
8 response surface (Y) was built by fitting a second-order polynomial equation described
9 by Equation 1:

$$Y = \beta + \sum_{i=1}^2 \beta_i X_i + \sum_{i=1}^2 \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^2 \beta_{ij} X_i X_j \quad (1)$$

10 where X_i and X_j represent the measured values of the independent variables, Y is
11 measured response values or dependent variable and β_i s are model coefficients
12 calculated from experimental data by using a fitting approach [29].

13 In this case study, the independent variables were the initial salt concentration (C_{iniS})
14 and the initial acid and base concentration (C_{iniAB}), while the response was the energy
15 consumption ($Ec_{(EDBM)}$) in the EDBM stack. Therefore, the specific energy consumption
16 ($Ec_{(EDBM)}$) describing the system could be described by Equation 2:

$$Ec_{(EDBM)} = \beta - \beta_1 \cdot C_{iniAB} + \beta_2 \cdot C_{iniS} + \beta_3 \cdot (C_{iniAB})^2 + \beta_4 \cdot (C_{iniS})^2 + \beta_5 \cdot C_{iniAB} \cdot C_{iniS} \quad (2)$$

17 where C_{iniS} is the initial salt concentration (gNaCl/L) and C_{iniAB} is the initial acid and
18 base concentration (M).

19 The range and levels of experimental variables (salt, acid and base concentrations) used
20 in this study are collected in Table 3.

21

22

23

24

1 Table 3. Coded levels and range of independent variables for experimental design

Level	Coded level	Factors	
		C _{ini} S	C _{ini} AB
Low	-1	50*	0.05
Mid	0	100	0.1
High	1	200	0.5

2 * A 50 gNaCl/L solution was used in order to compare between three initial NaCl
3 concentrations levels.

4 **2.5 Determination of energy consumption and current efficiency of NaCl** 5 **concentration in the ED process**

6 The energy consumption ($E_{c(ED)}$) for the NaCl concentration by ED was calculated as
7 the energy necessary to increase the NaCl concentration in the tank. It was calculated
8 according to Equation 3:

$$E_{c(ED)} \left(\frac{kWh}{kg NaCl} \right) = \frac{U_{cell} \cdot I \cdot t}{v_{tank} \cdot C_{ini}S} \quad (3)$$

9

10 Where U_{cell} (V) is the mean membrane stack potential, I (A) is the applied current
11 intensity, t (h) is the operation time, v_{tank} (L) is the NaCl solution volume of the
12 concentrate tank and $C_{ini}S$ (gNaCl/L) is the sodium chloride concentration obtained at
13 the end of the performance.

14

15 **2.6 Determination of energy consumption and current efficiency in the EDBM** 16 **process**

17 Energy consumption ($E_{c(EDBM)}$) and current efficiency (I_e) in the EDBM stack were
18 calculated by means of Equations 4 and 5, respectively.

$$E_{c(EDBM)} \left(\frac{kWh}{kg product} \right) = \frac{(U \cdot I \cdot t)/1000}{m_{final product}} \quad (4)$$

19 Where U (V) and I (A) are the voltage and current applied in the EDBM stack,
20 respectively, t (h) is the time of the operation and $m_{final product}$ (kg) is the acid or base
21 produced.

$$I_e = \frac{F \cdot (V_t \cdot C_t - V_i \cdot C_i)}{I_d \cdot S \cdot t \cdot n} \quad (5)$$

1 Where F (96500 C/mol) is the faraday constant, V (L) and C (M) are the volume and
2 concentration of the desired product at time “ t ” or at initial time “ i ”, I_d (A/cm²) is the
3 current density, S (64 cm²) the membrane surface, t (s) is the operational time and n is
4 the cell triplets of the EDBM stack (3 in this study).

5

6 **3. Results and discussion**

7 **3.1 Concentration of NaCl brines by ED**

8 The NaCl concentration profiles for different current densities (from 0.30 kA/m² to 0.4
9 kA/m²) at two different temperature ranges: a) 15 - 18 °C and b) 22 - 28 °C, are plotted
10 in Figure 4. Both temperature ranges provided the expected temperature regimes for
11 SWD-RO brines as consequence of the seasonal variation on the Mediterranean Sea.
12 Current densities were limited to values below 0.4 kA/m² to reduce the specific
13 electrical consumption. For the two temperature scenarios the concentration of NaCl in
14 the concentrate tank increased gradually with time (from an initial 60-70 g NaCl/L)
15 until a plateau was reached by the end of the experiment at concentrations between 185
16 and 205 g NaCl/L for the low temperatures and between 105 to 135 g NaCl/L for the
17 high temperatures, depending on the current density applied: the higher the intensity
18 applied, the higher the final concentration of NaCl reached (Figure 4).

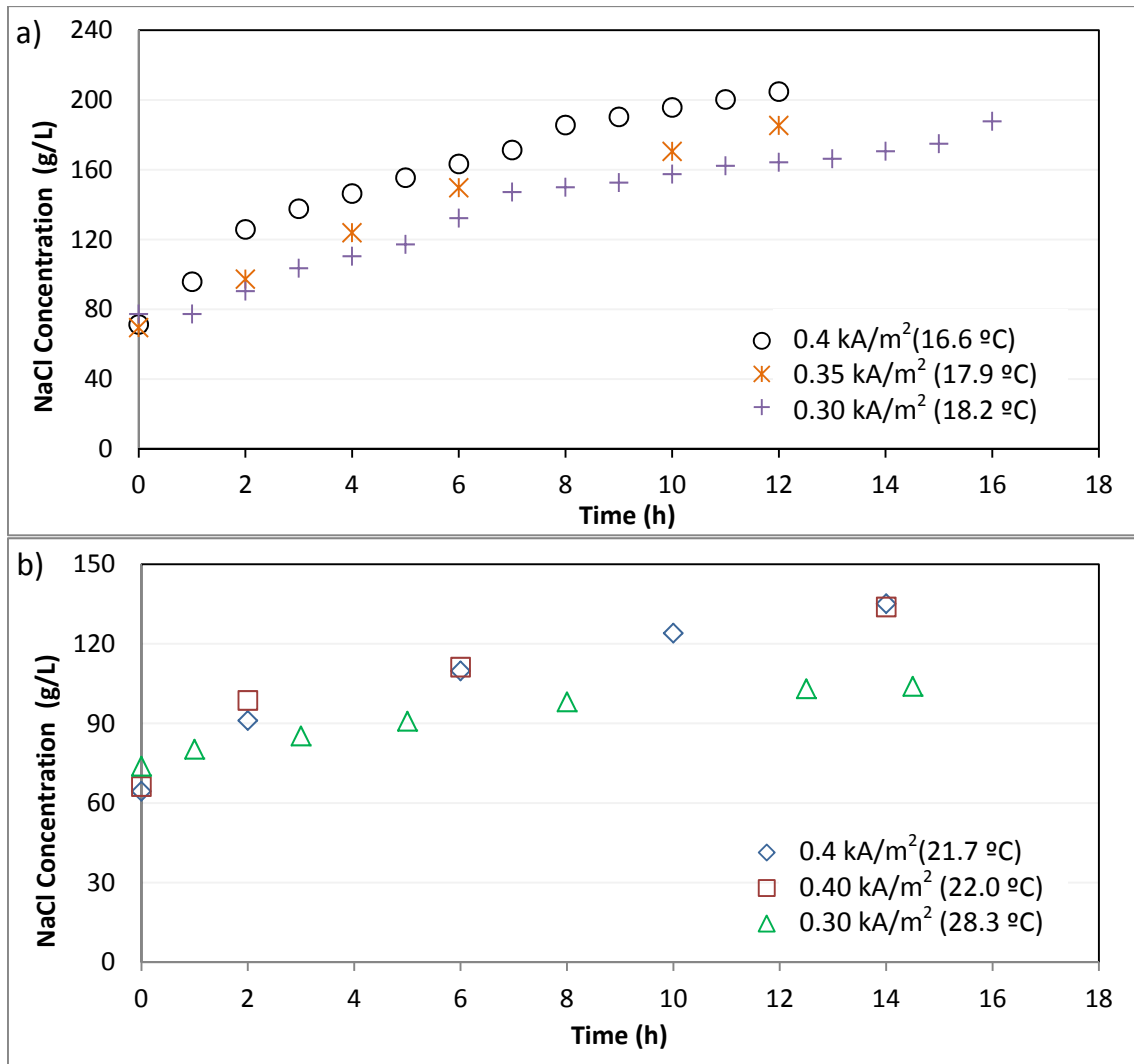


Figure 4. Evolution of NaCl concentration by ED. a) Experiments at 15 – 18 °C, b) Experiments at 22 – 28 °C.

Firstly, the applied electrical potential favored the ion migration flux and the electro-osmosis flux. However, the NaCl concentration gradient between the diluate and the concentrate circuits had an increase of 30 to 130 g/L NaCl, depending on the intensity and temperature conditions. This NaCl concentration gradient promoted two new mass transport phenomena: diffusion of NaCl from the concentrate compartment to the diluate compartment and osmotic flux whereby water was transported from the diluate compartment to the concentrate one. These two mass transfer phenomena diminished the desired effect of increasing the NaCl concentration on the concentrate tank and increased the energy requirements of the process. Then, concentration experiments were limited to the point where these phenomena were important. As seen in Figure 4, at the low temperature range (15 - 18 °C), NaCl concentrations between 185 and 205 gNaCl/L

1 were achieved after 12 hours of operation, whereas only between 105 and 135 gNaCl/L
2 at the high temperature range (22 - 28 °C). Lengthening the experiment time did not
3 provide any substantial increase in the NaCl concentration (increase differences less
4 than approximately 1 g/L) after 12 hours of additional concentration.

5 Experiments at both temperature regimes have shown the temperature influence on ED
6 mass transport processes and properties of the brine (electrical conductivity and
7 density), solvent (molecular diffusivity) and membrane (resistance and electrical
8 conductivity) [30,31]. The temperature influence on the concentration process in ED is
9 more complex than that exerted by the current intensity because the different mass
10 transfer processes involved (e.g., it may be because the osmosis transport of NaCl) are
11 temperature dependent. Although theoretical models to describe this dependence are
12 still lacking, Tanaka et al. [32] have recently developed a model for the concentration of
13 seawater to produce salt. This model was based on analysis of a large data base
14 containing experimental results of ion transport through ion exchange membranes
15 where the correction of temperature for physical parameters, such as density, electrical
16 conductivity and membrane resistance was considered.

17 Experiments also showed that it was possible to produce a NaCl-rich concentrate stream
18 from SWD-RO brine by means of an ED pilot plant. Due to the single-pass design
19 circuit for the diluate stream, and the recirculated NaCl-rich concentrate loop, a final
20 divalent free solution containing concentrated NaCl was obtained. Moreover, as it was
21 reported previously [14], the rejection of divalent minor ions, such as Ca^{2+} , Mg^{2+} and
22 SO_4^{2-} , was favored in the concentrate stream due to the selectivity of the ion exchange
23 membranes used. In this study, final concentration of Ca^{2+} and Mg^{2+} were 0.31 and 0.30
24 g/L, respectively for the high temperature experiments and 0.55 g Ca^{2+} /L and 0.49 g
25 Mg^{2+} /L for the low temperature experiments. Then, it can be stated that the divalent ions
26 migration flux was insignificant in the concentrate loop. Yang et al. [15] also used a
27 pre-treatment of the seawater RO concentrate to reduce Ca^{2+} and Mg^{2+} ions and avoid
28 scaling using Na_2CO_3 and NaOH to precipitate Ca^{2+} as CaCO_3 and Mg^{2+} as Mg(OH)_2 .
29 After precipitation, the pH of the RO concentrate was adjusted with HCl to prevent
30 organic and inorganic fouling on the anion exchange membranes of the EDBM stack.

31 Recently, the integration of nanofiltration (NF) and EDBM for the valorization of
32 SWD-RO brine has been evaluated [26], where NF was applied for the removal of

1 divalent ions from the SWD-RO brine. NF rejected 20% of NaCl, resulting in an
 2 undesired dilution of the NaCl in the treated brine. In the present study, the application
 3 of ED allowed not only to avoid the presence of divalent ions in the treated brine but
 4 also to increase the nominal NaCl concentration from 65 g/L up to 100 and 200 g/L,
 5 depending on the operation conditions. With this increase of NaCl concentration, it was
 6 possible to achieve higher HCl and NaOH concentrations when compared with those
 7 obtained using NF as purification step.

8

9 **3.2 Energy consumption on the concentration of NaCl ($E_{C(ED)}$)**

10 The energy consumption ($E_{C(ED)}$) raised gradually in all the experiments until the
 11 concentration in the tank reached its maximum concentration depending on the
 12 operation conditions (temperature and current density). Experiments were stopped when
 13 the energy consumption increased dramatically because osmosis and ion diffusion
 14 fluxes inside the stack reached a maximum due to the concentration gradient between
 15 the diluate and the concentrate compartments (data not shown). A summary of the
 16 energy consumption for continuous operation ($E_{C(ED)}$) for different operation conditions
 17 evaluated is shown in Table 4.

18

19 Table 4. NaCl concentration achieves and energy consumption calculated depending on
 20 experimental conditions

Temperature (°C)	Current density (kA/m ²)	NaCl concentration, C_{iniS} (g/L)	Energy consumption $E_{C(ED)}$ (kWh/kg NaCl)
16.6	0.40	204.8	0.217
17.9	0.35	185.4	0.154
18.2	0.30	187.7	0.148
21.7	0.40	135.1	0.096
22.0	0.40	133.9	0.055
28.3	0.30	104.0	0.161

21

22 The energy consumption increased if working with higher current density, thus,
 23 0.4kA/m² was confirmed as the maximum operable point. The temperature affects the
 24 product flow rate, and lower flow rates were obtained at higher temperatures.

1 An average of 0.17 kWh/kg NaCl was calculated when around 200 gNaCl/L were
2 produced, while lower values around 0.10 kWh/kg NaCl were achieved when only
3 approximately 100 gNaCl/L were concentrated by ED. The values obtained in our pilot
4 plant were within the range of the published results. For laboratory scale studies [33],
5 the energy consumption with NaCl solutions up to approximately 100 g/L ranged
6 between 0.18 and 0.33 kWh/kg with 80% solute recovery and current densities of 0.20
7 to 0.30 kA/ m² were reported. Besides, it was reported that an ED industrial target in
8 Japan was to produce 200 g NaCl/L from seawater with an energy consumption lower
9 than 0.12 kWh/kg NaCl [34].

10 It can be concluded that concentration of NaCl brines by ED is dependent on the
11 temperature and current density applied. Higher current density and low temperature
12 lead to higher NaCl concentration. For this reason, in order to achieve 200 gNaCl/L by
13 ED with specific electrical consumption below 0.2 kWh/kg NaCl, it was preferable to
14 work during winter-spring seasons (when temperatures are below 20°C) and at high
15 current densities. However, during summer season (when temperatures are above 21°C)
16 NaCl brines between 100 to 130 g/L were obtained at specific electrical consumption
17 around 0.1 kWh/kg when using current densities of 0.30 and 0.40 kA/m².

18

19 **3.3 Evaluation of HCl and NaOH production from NaCl brines by means of** 20 **EDBM**

21 EDBM (Figure 5) experiments using NaCl brines (nominal concentration of 100-200
22 gNaCl/L) as feed solution indicated that the desalinating process and the production of
23 NaOH and HCl occurred efficiently as was previously reported [16,17]. For both brines
24 100 and 200 gNaCl/L, NaCl concentrations at the end of the experiments were around
25 20 mgNaCl/L. It is important to point out that conductivity of the electrode rinse stream
26 (Na₂SO₄) was constant along the whole experiment. This fact indicated that no leak or
27 non-desired ion transport occurred between the electrode rinse compartment and their
28 adjacent compartments. Figure 5 also shows the final NaOH and HCl concentrations
29 obtained with an initial nominal NaCl concentration of 100 g/L (1.71 M NaCl) (Figure
30 5a) and 200 g/L (3.42 M NaCl) (Figure 5b) as a function of the initial concentrations
31 evaluated for the acid and base circuits (from 0.05 to 0.5 M).

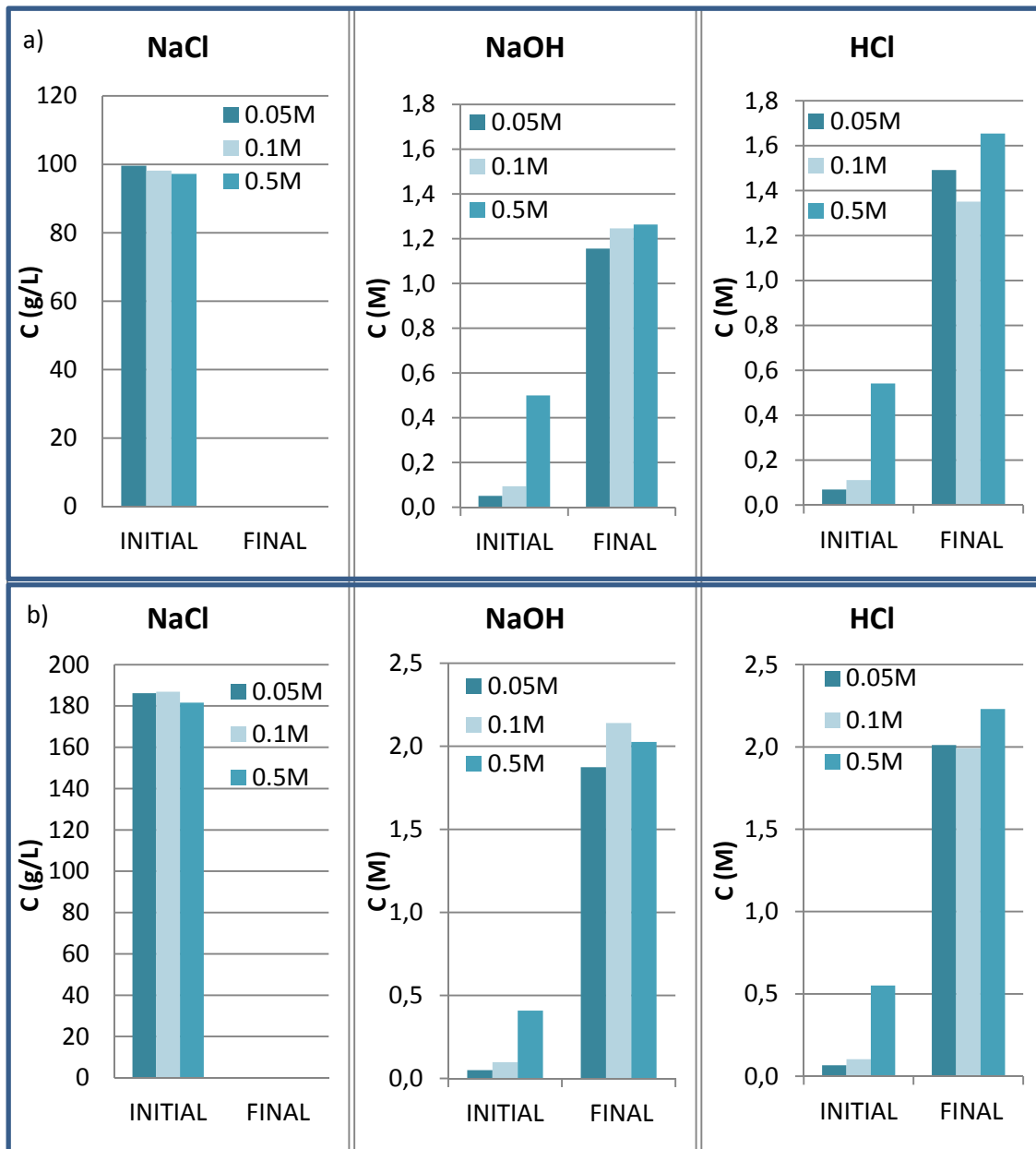


Figure 5. Salt, acid and base concentration at the initial and final experimental time under different initial concentration of HCl and NaOH (0.05, 0.10 and 0.50 M). Using initial nominal NaCl concentration of a) 100 g/L and b) 200 g/L.

Figure 5 demonstrates that the initial acid and base concentration had no significant effect on their final concentration, in contrast with initial NaCl concentration, which appeared to effect the final concentration of NaOH and HCl. In fact, working with initial NaCl 100 g/L (1.71 M) allowed to concentrate NaOH and HCl concentrations up to 1.26 M and 1.65 M, respectively, whereas using the concentrate stream of ED of 200 g NaCl/L (3.42 M) allowed to achieve final concentrations of NaOH and HCl around 2 M.

1 The NaCl percentage that was converted into NaOH and HCl for the different
 2 experiments is shown in Table 5. When current is applied between the electrodes,
 3 proton ions have higher mobility than hydroxyl ones, then, conversion percentage to
 4 HCl could be higher than the NaCl percentage that was converted into NaOH.

5

6 Table 5. NaCl percentage that was converted into NaOH and HCl in the first set of
 7 EDBM experiments.

Initial HCl and NaOH concentration	Initial salt concentration: 100 g NaCl/L		Initial salt concentration: 200 g NaCl/L	
	NaOH	HCl	NaOH	HCl
0.05	65 %	84 %	57 %	61 %
0.10	69 %	75 %	64 %	59 %
0.50	46 %	68 %	52 %	54 %

8 As it can be seen in Table 5, the higher conversion percentage was achieved working
 9 with the nominal 100 g NaCl/L solution and 0.05 M HCl and NaOH. In general, higher
 10 percentages were obtained with 100 gNaCl/L solutions and higher conversion ratios to
 11 HCl than to NaOH reaching a maximum of 84 %.

12 The influence of the initial NaCl concentration (~100 and 200 gNaCl/L) on the final
 13 acid and base concentrations for 0.05M HCl and NaOH initial solutions is shown in
 14 Figure 6. In order to make a better comparison, some experiments using 50 g NaCl/L
 15 (approaching the SWD-RO brine composition) as feed solution were conducted. Then,
 16 the results are also shown in Figure 6 comparing the initial and final concentrations
 17 obtained.

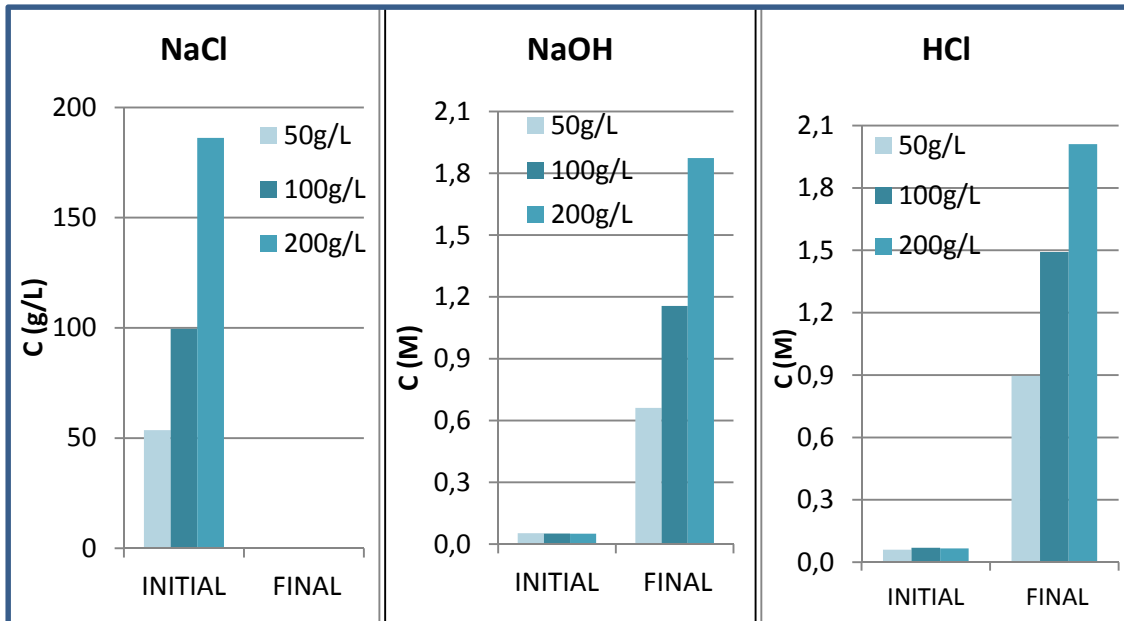


Figure 6. Salt, acid and base concentration at the initial and final experimental time under different initial concentration of NaCl

Figure 6 shows that working with an initial NaCl concentration of 50 g/L it was possible to obtain NaOH 0.66 M and HCl 0.90M. These results are in agreement with those reported by Ibañez et al. [25], who obtained very similar HCl and NaOH concentrations (0.71 and 0.91M, respectively) under the same current density (0.5 kA/m²) and initial NaCl concentration of 50 g/L. The higher concentration values obtained for HCl in comparison with those for NaOH were associated to the higher exchange capacity of the anionic membranes and the lower co-ion transport through them.

It should be pointed out that it was possible to raise the final HCl and NaOH concentration by increasing the initial NaCl concentration. As it is shown in figure 6, by using a more concentrated NaCl feed (~100 g/L) the NaOH and HCl concentrations obtained were 1.2 and 1.5 M, respectively, and for NaCl solutions of 200 g/L, it was possible to concentrate NaOH up to 1.9 M and HCl up to 2.0 M. Thus, higher HCl and NaOH concentrations can be obtained by working at high current density and high initial NaCl concentration. As described previously, Yang et al. [15] used a pretreated seawater RO concentrate as feed solution using a similar EDBM configuration and reached 0.4 M NaOH, whereas Ibañez et al. [25] obtained NaOH up to 1 M working with synthetic SWD-RO concentrate.

The maximum NaOH concentration obtained in this work was 2 M (8% w/v), which agrees with previous published studies where the maximum NaOH concentration

1 reached by EDBM at bench- and pilot-scale ranged from 8 to 9.5% (and up to 12.5% if
 2 the electrochemical consumption was increased) [23–25]. These values reported by
 3 bench- and pilot-scale systems are, however, low compared to the one reached by the
 4 current chlor-alkali industry (32-50 % w/v depending on the technology applied).

5 The initial approach is the on-site use of the NaOH produced or the use by other
 6 industries with distances below 40 km (e.g., reagent for pH adjustment or other
 7 commodities uses). If the objective is out-side use, the production site should consider a
 8 concentration step up to 32-50% by evaporation with an electrical consumption of
 9 2400-4500 kWh/t NaOH [35].

10 **3.4 Evaluation of the energy consumption on the HCl and NaOH production from** 11 **NaCl brines by means of EDBM**

12 Table 6 summarizes the results of the different assays performed on the production of
 13 HCl and NaOH from NaCl brines by the EDBM stack including the initial and final
 14 concentrations of each stream and also the quantity of HCl produced and the energy
 15 consumption to produce NaOH under a voltage of 9 V. Although HCl and NaOH were
 16 obtained from NaCl, taking into account the lowest market prices of HCl in comparison
 17 to NaOH, energy consumption ($EC_{(EDBM)}$) was calculated as kWh per kilogram of NaOH
 18 obtained, and HCl was considered a by-product.

19 Table 6. Experimental results on the specific energy consumption on the production of
 20 NaOH and HCl from NaCl solutions (~ 50, 100 and 200 gNaCl/L) by EDBM at room
 21 temperature (21 ± 1 °C).

U_{max} (V)	\bar{I} (kA/ m ²)	Electrode (Na ₂ SO ₄)		Salt (NaCl)		Acid (HCl)		Base (NaOH)		Time (h)	kg HCl produced	$EC_{(EDBM)}$ kWh/kg NaOH produced
		C _{initial} (g/L)	C _{final} (g/L)	C _{initial} (g/L)	C _{final} (g/L)	C _{initial} (M)	C _{final} (M)	C _{initial} (M)	C _{final} (M)			
9.0	0.41	45.50	43.59	53.60	0.01	0.06	0.90	0.05	0.66	2.44	0.031	2.345
8.9	0.47	42.46	43.37	99.58	0.03	0.07	1.49	0.05	1.16	4.07	0.052	2.460
8.9	0.52	42.37	47.95	186.15	0.02	0.07	2.01	0.05	1.87	6.75	0.071	2.713
8.9	0.44	44.66	43.85	52.98	0.01	0.12	0.88	0.10	0.71	2.54	0.028	2.576
8.8	0.41	43.25	41.93	98.18	0.02	0.11	1.35	0.09	1.25	3.63	0.045	1.822
8.9	0.52	47.48	45.92	186.88	0.02	0.10	1.99	0.10	2.14	6.24	0.069	2.238
8.9	0.47	46.86	45.03	52.88	0.02	0.53	1.16	0.44	1.06	2.68	0.023	2.888
8.9	0.43	44.86	49.19	97.21	0.02	0.54	1.65	0.50	1.26	3.89	0.041	3.104
8.9	0.59	41.45	45.21	186.61	0.02	0.55	2.23	0.41	2.03	6.94	0.061	3.624

1 As it reported in the last column of Table 6, a range of $EC_{(EDBM)}$ values were achieved
 2 from 1.822 up to 3.624 kWh/kg NaOH. In order to define the initial acid, base and salt
 3 concentrations that require the minimum $EC_{(EDBM)}$, a factorial design was defined to
 4 obtain a general lineal model using the response surface methodology (RSM) and
 5 central composite design (CCD). Table 7 represents the least squares matrix (Z) with
 6 different values of initial salt, acid and base concentration and the response matrix (Y)
 7 of energy consumption.

8 Table 7. Initial matrix for the statistic model (Z) and response matrix (Y)

	Z					Y
	C_{iniAB}	C_{iniS}	C_{iniAB}^2	C_{iniS}^2	$C_{iniAB} \cdot C_{iniS}$	$EC_{(EDBM)}$
1	0.05	50	0.0025	2500	2.5	2.34
1	0.05	100	0.0025	10000	5	2.46
1	0.05	200	0.0025	40000	10	2.71
1	0.1	50	0.01	2500	5	2.58
1	0.1	100	0.01	10000	10	1.82
1	0.1	200	0.01	40000	20	2.24
1	0.5	50	0.25	2500	25	2.89
1	0.5	100	0.25	10000	50	3.10
1	0.5	200	0.25	40000	100	3.62

9

10 The model coefficients (β) in the factorial design, described by the matrix in Table 7,
 11 were estimated by Equation 6: .

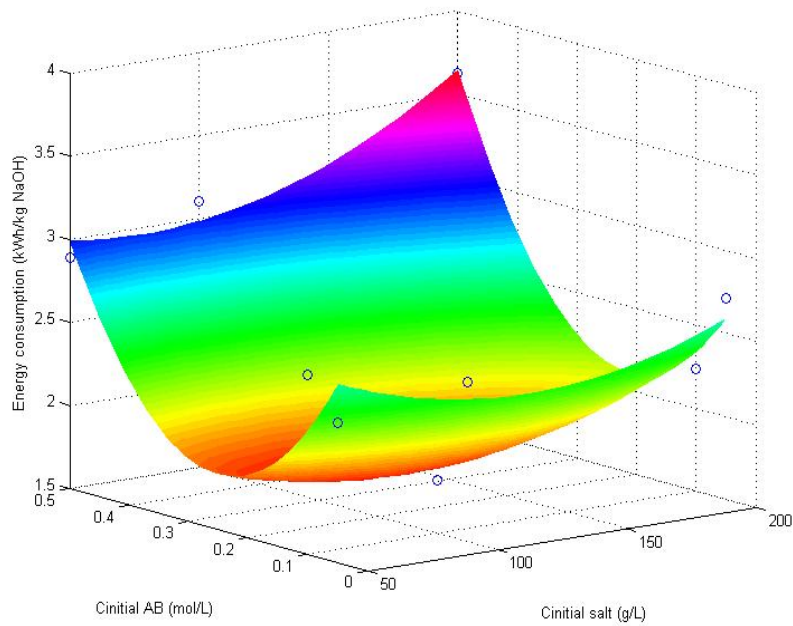
$$\beta = [(Z \cdot Z')^{-1}] \cdot [Z' \cdot Y] \quad (6)$$

12 Then, the initial salt and acid/base concentration values to obtain the minimum energy
 13 consumption could be estimated by Equation 7:

$$EC_{(EDBM)} = 3.4589 - 9.7568 \cdot C_{iniAB} - 0.0116 \cdot C_{iniS} + 18.5658 \cdot (C_{iniAB})^2 + 4.5173e - 5 \cdot (C_{iniS})^2 + 0.0094 \cdot C_{iniAB} \cdot C_{iniS} \quad (7)$$

14

15 A surface plot for $EC_{(EDBM)}$ values as a function of salt and acid/base concentrations,
 16 including both the experimental (by un-filled circles) and model predicted values, is
 17 shown in Figure 7. Figure 7 shows that for the used EDBM stack the optimum operating
 18 values yielding a minimum energy consumption of 1.7 kWh/kg NaOH, at a constant
 19 voltage of $8.9 \pm 0.1V$, can be obtained with and initial NaCl concentration of 104 ± 4 g/L
 20 and initial acid and base concentration of 0.24 ± 0.2 M.



1

2 Figure 7. Surface plot for optimal values of energy consumption versus initial salt and
3 acid/base concentration.

4 Scarce data of process performance and energy consumption for application of BM
5 stacks with brines can be found in the scientific literature. Table 8 summarizes the
6 published data on brine treatment by means of EDBM for acid and base production.
7 Different brine types had been used as feed solution with different concentrations. Most
8 of them had been pre-treated in order to be introduced in the EDBM stack by means of
9 different techniques. Also, the EDBM cell used included different dimensions, active
10 surface membrane area and membrane properties (e.g. different manufacturers). Some
11 authors had calculated the energy consumption of the EDBM process. It is important to
12 mention that it has not been found any published work on the integration of a brine pre-
13 concentration step before the EDBM, in which the total energy consumption was
14 calculated. Then, in this work apart from the reported energy consumption of the
15 production of NaOH and HCl by the EDBM process, the energy consumption of the ED
16 pre-treatment has also been taken into account: around 0.17 kWh/kg NaCl when the
17 brine was concentrated up to 200 gNaCl/L and 0.10 kWh/kg NaCl when concentrated
18 up to 100 g NaCl/L.

Table 8. Comparison of the published data on brine treatment by EDBM

Brine Type	Brine Composition (g/L)	EDBM cell (Area (m ²))	By-products	Current efficiency (%) / Current density (kA/m ²)	Energy consumption	Ref.
SWD-RO brine. Concentrated by ED	Cl (38.8), Na (20.8), SO ₄ (5.41), Mg (2.64), Ca (0.83). EDBM feed: NaCl (100;200)	PCA-SK (0.0064) PCA-Acid 60 PCA-BM	HCl 1.99 M NaOH 2.14 M (200gNaCl/L; 0.5 kA/m ²)	55-88 / 0.5	1.8-3.6 kWh/kg NaOH 1.9 - 3.8 kWh/kg HCl 0.08 - 0.23 kWh	This work
Synthetic SWD-RO concentrate	NaCl (54), K (0.7), Mg (-), Ca (-), SO ₄ (5.3), HCO ₃ (0.2)	RALEX AMH (0.02) RALEX CMH NEOSEPTA-BP1	HCl 0.6-0.8 M NaOH 0.7-1.0 M (0.25-1 KA/m ²)	80 / 0.25 50 / 1.0	n.a	[25]
SWD-RO/ Pre-treated for Ca/Mg removal	NaCl (38), K (0.4), Mg (-), Ca (-), SO ₄ (3.8), HCO ₃ (0.07), Br(0.1)	Qianqiu AEM (0.0088) Qianqiu CEM Fumatech –BPM	HCl 0.7 M (0.57 kA/m ²) NaOH 0.4 M	50-66 / 0.35-0.57	7.2-9.4 kWh/kg HCl	[15]
Sea water	n.a.	Commercial : (0.012) CMI - 7000S AMI - 7001S PSDVB – BPM Synthetic: (0.012) PSu - CEM, AEM, BPM	Commercial: HCl 0.4 M NaOH 0.5 M Synthetic: HCl 0.6 M NaOH 0.7 M	Commercial: 15-45 / 0.05 Synthetic: 35-63 / 0.05	Commercial: 0.129 kWh Synthetic: 0.14 kWh	[36]
Industrial Brine	NaCl (70), Ca (-), TIC (0.01), TOC (0.132), pH=12.6	PCA-SK (0.0064) PCA-Acid 60 Fumatech –FBM PCA-PBM	PBM: (0.572 kA/m ²) HCl 1.6 M, NaOH 1.7 M FBM: (0.523 kA/m ²) HCl 1.8 M, NaOH 2.0 M	PBM: 65 / 0.572 FBM: 81 / 0.523	n.a.	[23]
Industrial Brine	NaCl (20),SO ₄ (2.9), K (6.6), Ca (0.8), TIC (0.01), TOC (0.02), pH=7.6. Ca removal pre-treatment	PCA-SK (0.0064) PCA-Acid 60 PCA-BM	HCl 1.6 M H ₂ SO ₄ 0.12 M NaOH 1.2 M KOH 0.7 M	Cl: 64 / 0.6 SO ₄ : 10 / 0.6 Na: 47 / 0.6 K: 31 / 0.6	n.a.	[17]
Industrial Brine	SO ₄ (89), Ca(0.02), Na(45) Ni (0.01), pH=10.5 Pre-treatment: pellet reactor	Fumatech FAB (0.0064) Fumatech FKB Fumatech –FBM	0.29 – 0.59 M mix acid 0.34 – 0.68 M mix base (0.3 to 0.6 kA/m ²)	Mix acid: 60 / 0.3; 70 / 0.6 Mix base: 80 / 0.3; 90 / 0.6	5 – 6 kWh/kg mix acid 4 -5 kWh/kg mix base	[24]

1 As it can be seen in Table 8, the highest HCl and NaOH concentration was achieved in
2 this work. This was possible due to the pre-treatment concentration by ED process. The
3 initial feed for the EDBM in this case was the higher among the reviewed studies. For
4 the current efficiency, it can be stated that similar values (e.g. from 60-88%) were
5 calculated in comparison to the other studies. As discussed previously on the literature,
6 the observed trend is that the amount of electric current converted into the desired
7 product (current efficiency) decreases with increasing current density within the
8 evaluated interval working with synthetic SWD-RO concentrate [25], synthetic sea
9 water brines [37] or synthetic brackish brines [1]. High values of current density
10 increased the concentration of products more rapidly by leading to an increase of a co-
11 ion leakage. Finally, regarding the energy consumption estimation, each study took into
12 account different parameters to be referenced. For example, Venugopal et al. [36]
13 reported as total kWh consumed, and values calculated were in the same range as the
14 obtained in the present study. Besides, Yang et al. [15] stated it as kWh per each kg of
15 HCl produced. Their energy consumption values were higher (7.2 - 9.4 kWh/kg HCl)
16 than the ones calculated in this work (1.9 - 3.6 kWh/kg HCl). Also, Tran et al. [24]
17 quantified as kWh per each kg of mix acid obtained, but also as kWh per kg of mix base
18 produced. In both cases, the reported energy consumption (5 -6 kWh/kg mix acid and 4
19 - 5 kg mix base) were higher than in this study (1.9 - 3.6 kWh/kg HCl and 1.8 - 3.6
20 kWh/kg NaOH). Only, recently, Wang et al. [38], developed a mathematical model of a
21 typical three-compartment EDBM process to calculate the energy consumption and total
22 cost of the process. With an increase in the current density, the energy consumption of
23 the process increases and the total process cost decreases at first and then increases
24 gradually with a minimum cost value at a given current intensity.

25

26 **4. Conclusions**

27 ED was used in order to pre-concentrate SWD-RO brines from 60-70 g/L up to 100 or
28 200 g NaCl/L by appropriate current density and temperature control. Low temperatures
29 helped to concentrate easily the SWD-RO brines up to 200 g NaCl/L, while lower
30 concentrations (100 g NaCl/L) were achieved at higher temperatures (more than 20 °C).
31 The ED energy consumption for 0.30 - 0.40 kA/m² current densities ranged from 0.10
32 to 0.17 kWh/kg NaCl produced, depending on the final NaCl concentration achieved.

1 Moreover, by working with a NaCl initial concentrated stream it was possible to obtain
2 a NaCl-rich solution with reduced levels of divalent ions.

3 According to the EDBM results using NaCl concentrates, HCl and NaOH solutions up
4 to 2 M concentration were produced. EDBM technique requires an initial acid, base and
5 salt concentration. The initial acid and base concentrations represented no substantial
6 effect on the overall performance. Then, the minimum initial HCl and NaOH
7 concentrations are advised to be used. Moreover, concerning the effect of feed salt
8 concentration, it was reported that an increase of NaCl led to an increase of acid and
9 base concentration. Then, the ED process can be a successful pre-treatment in order to
10 have a more concentrated initial feed in the EDBM and produce a more concentrated
11 HCl and NaOH.

12 Energy consumption measured in EDBM was ranged from 1.8 to 3.6 kWh/kg NaOH.
13 Consumption values were lower to those reported in the literature for similar brines
14 (e.g., pre-treated RO concentrates). Finally, the lineal model developed identified a
15 minimum EDBM energy consumption of 1.7 ± 0.1 kWh/kg NaOH for an initial NaCl
16 concentration of 104 ± 4 gNaCl/L and for the initial concentration of HCl and NaOH
17 circuits of 0.24 ± 0.04 M. Although the energy consumption values for the production of
18 acid and base to valorize brines are above the market prices, only for in-situ waterworks
19 uses or when industries would be forced to follow more sustainable brine management
20 approaches the proposed solution would have potential interest for implementation.

21

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