

1 **SELECTRODIALYSIS AND BIPOLAR MEMBRANE ELECTRODIALYSIS**
2 **COMBINATION FOR INDUSTRIAL PROCESS BRINES TREATMENT:**
3 **MONOVALENT-DIVALENT IONS SEPARATION AND ACID AND BASE**
4 **PRODUCTION**

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13 **ABSTRACT**

14 Chemical industries generate large amounts of wastewater rich in different chemical
15 constituents. Amongst these, salts at high concentrations are of major concern, making
16 necessary the treatment of saline effluents before discharge. Because most of these rejected
17 streams comprise a combination of more than one salt at high concentration, it is reasonable
18 to try to separate and revalorize them to promote circular economy at industry site level. For
19 this reason, ion-exchange membranes based technologies were integrated in this study:
20 selectrodialysis (SED) and electrodialysis with bipolar membranes (EDBM). Different
21 process brines composed by Na₂SO₄ and NaCl at different concentrations were treated first by
22 SED to separate each salt, and then by EDBM to produce base (NaOH) and acids (HCl and
23 H₂SO₄) from each salt. The optimum of both electrolyte nature and concentration of the SED
24 stack streams was evaluated. Results indicated that it was possible to separate Cl⁻ and SO₄²⁻
25 depending on the anionic membrane, initial electrolytes and concentrations of each stream.
26 Pure NaOH and a mixture of HCl and H₂SO₄ with different purities could be obtained. Energy
27 consumption evolutions were plotted and an optimal zone work was found where the
28 consumption values were acceptable.

29 **Keywords:** *Divalent-monovalent ion fractionation, Acid-base production, Monovalent ion*
30 *selectivity, High and low concentration, Valorization, Circular economy*

1. INTRODUCTION/BACKGROUND

Process industries (e.g., chemical, metallurgical, mining, petrochemical, food and beverage, etc.) use established wastewater treatments to reduce the organic load by using biological technologies. However, treated waters are still characterized by high total inorganic dissolved solids (sodium chloride (NaCl), sodium sulfate (Na₂SO₄), calcium chloride (CaCl₂), sodium nitrate (NaNO₃), etc.) and direct discharge to the medium is not a disposal option. These brines formed during processing or especially by neutralization of acid/base streams contain high strong electrolytes concentrations and therefore their treatment and disposal routes are limited and new treatment technologies are need. Traditionally, the industrial concentrates are discharged into natural water bodies (with or without dilution depending on the discharge regulations) [1–2] although this method is not environmentally friendly due to the needs to fulfill the higher requirements on water quantities and quality [3]. Then, under the fact that environmental protection and industrial sustainability has become a priority worldwide, considerable efforts have been made to develop new brine management technologies with the aim to avoid or at least minimize any discharge of high salinity streams into the environment when possible.

Brine management reviews [4–6] show that thermal processes (e.g., evaporation and distillation) have been widely researched for water recovery and brine volume reduction. These solutions allow brine volume reduction after water recovery for reuse and generation of a dry salt waste, when a zero liquid discharge (ZLD) scheme is reached, or a wet salt waste, when a ZLD scheme is not achieved. However, the high associated capital expenditures (CAPEX) and operating expenditures (OPEX) of these treatment solutions make them limited [4,7]. Moreover, under the new paradigm of circular economy, postulated through, the sustainable process industry resource and energy efficiency (SPIRE) program of the European union industry, resource recovery is the objective to be achieved [8]. Solutions pursued are focused not only on the recovery of water but also on the recovery of the salts present in the brines as pure byproducts. Successful production of pure salts will be achieved only if tailor-made separation processes are implemented.

Ion exchangers, widely used in industrial applications for decades, accomplish the separation of salts by exhibiting different affinity towards the salts to be separated [9,10]. However, for the case of the couple chloride/sulfate most of the anion exchange resins commercialized give

1 limited possibilities. Alternatively, membrane technologies have become a key separation
2 process when salinity removal is the target objective. Their applications, particularly of
3 reverse osmosis (RO) and nanofiltration (NF), have increased significantly compared to other
4 water treatment technologies. Both are widely used to produce water with low salinity content
5 [11] and to improve the quality of process waters. However, RO use is limited when the
6 objective is the selective recovery of a given target species. In this case, the alternative
7 separation process is directed to the use of schemes where only a given component or group
8 of components are removed specifically. When the selected or target group are charged
9 species (anions and cations) ion-exchange materials and processes as electrodialysis (ED) are
10 the most appropriate options [4]. ED and its related technologies are electrochemical
11 membrane separation processes in which ions are transferred through selective ion-exchange
12 membranes from one solution to another using an electric field as the driving force [12].
13 Under the influence of an electrical potential difference, the overall result is an enrichment of
14 ions in a concentrate stream and a depletion of ions in a diluate stream. The major application
15 of conventional ED has historically been concentration of NaCl from seawater prior to
16 evaporation to produce table salt in Japan for decades [13–16]. Nowadays, ED and RO are
17 competing techniques for the production of potable water from brackish water sources
18 [12,17]. In addition, ED is having a growth implementation in bio-based process industries to
19 purify, separate and concentrate byproducts (e.g. whey demineralization [18] and
20 deacidification of fruit juice [19]).

21 If selective ion separation is the objective, a conventional ED stack presents limitations for
22 ions with the same size and charge sign. However, a new combination of membranes referred
23 to as electrodialysis (SED) can be used to separate monovalent from divalent ions as it was
24 postulated by Zhang et al. [20]. This membrane configuration has an anionic monovalent
25 membrane between the standard cationic and anionic membranes [21]. Then, once the
26 monovalent and divalent streams have been separated, an ED system including a bipolar
27 membrane (EDBM) between the two standards cationic and anionic can be used to produce
28 acid and base chemicals. A bipolar membrane is formed by an anionic exchange membrane
29 and a cationic one, and when current density is applied in the electrodes, water splitting takes
30 place. Under such arrangement, EDBM is able to produce acid and base from the feed salt due
31 to the water splitting in the bipolar membrane during the EDBM process [22]. EDBM has

1 shown successful applications, mainly situated in the biotechnology and chemical process
2 industries. The largest potential application includes the recovery of organic acids and bases
3 from salts obtained in synthesis steps, e.g., the recovery of aminoacids, tartaric acid and
4 succinic acid from fermentation broths [23–25], which is accompanied by the production of
5 NaOH as a byproduct, which is in turn recycled to the fermenter to control the pH of the
6 process. However, the main challenge on EDBM application is the recycling of salt brines as
7 acids and bases to avoid a waste disposal problem. Moreover, the on-site production of
8 chemicals could be economically beneficial as the market prices of the raw materials are
9 gradually increasing.

10 In this study, a mixture of NaCl and Na₂SO₄ have been treated by a combination of SED, to
11 achieve the separation of chloride /sulfate, and EDBM, to produce acid and base from the
12 SED products. A three-compartment configuration has been used to produce acid and base
13 from the feed salt due to the water splitting in the bipolar membrane during the EDBM
14 process.

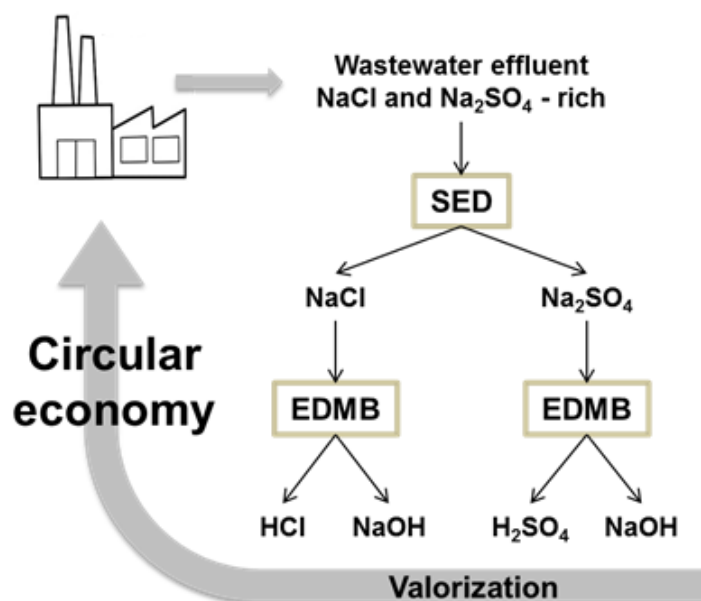
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17 **2. EXPERIMENTAL**

18 The proposed valorization scheme (Figure 1) consists in the conversion of residual salty
19 wastewater effluent (rich in NaCl and Na₂SO₄) into value-added products (HCl, H₂SO₄ and
20 NaOH) ready to be used in the same industrial plant. The proposed scheme aims thus to fully
21 address the principles of a circular economy by: a) brine minimization, b) reduction of solid
22 wastes production and c) increase of reusability and recyclability of waste through chemical
23 production (acids and bases) for in-plant uses [26,27].

24



1
2 Figure 1. Schematic illustration of the wastewater effluent valorization by ED processes

3
4 Sodium chloride- and sodium sulfate-rich industry process brines were obtained from a
5 chemical company, kept anonymous by a confidentiality agreement. These brines were
6 generated in a dye synthesis step where initially sodium chloride and sodium thiosulfate
7 brines were produced. After a chemical oxidation process using sulfuric solutions, thiosulfate
8 was oxidized to sulfate producing a precipitated elemental S(s) byproduct, which was
9 removed by filtration.

10 Experiments with feed solutions consisting of different concentration wastewater effluents
11 from the chemical company were conducted by a lab-scale SED stack to produce two separate
12 streams (NaCl-rich stream and Na₂SO₄-rich stream) followed by EDBM to produce HCl and
13 H₂SO₄ as it is shown in Figure 1.

14
15 **2.1 Experimental set-up description and operation**

16 The ED set-up used was a PCCell ED 64-004 (PCCell GmbH, Germany) with a cell of 11 x
17 11 cm. The stack consisted of a 4 chambers system with 3 cell triplets with an active
18 membrane area of 64 cm² per membrane. By means of this equipment it was possible to
19 perform the SED and also the EDBM experiments only by changing the membranes
20 employed in each case. Main characteristics of the membrane as functional group type,

1 electrical resistance, burst strength and thickness are listed in Table 1.

2

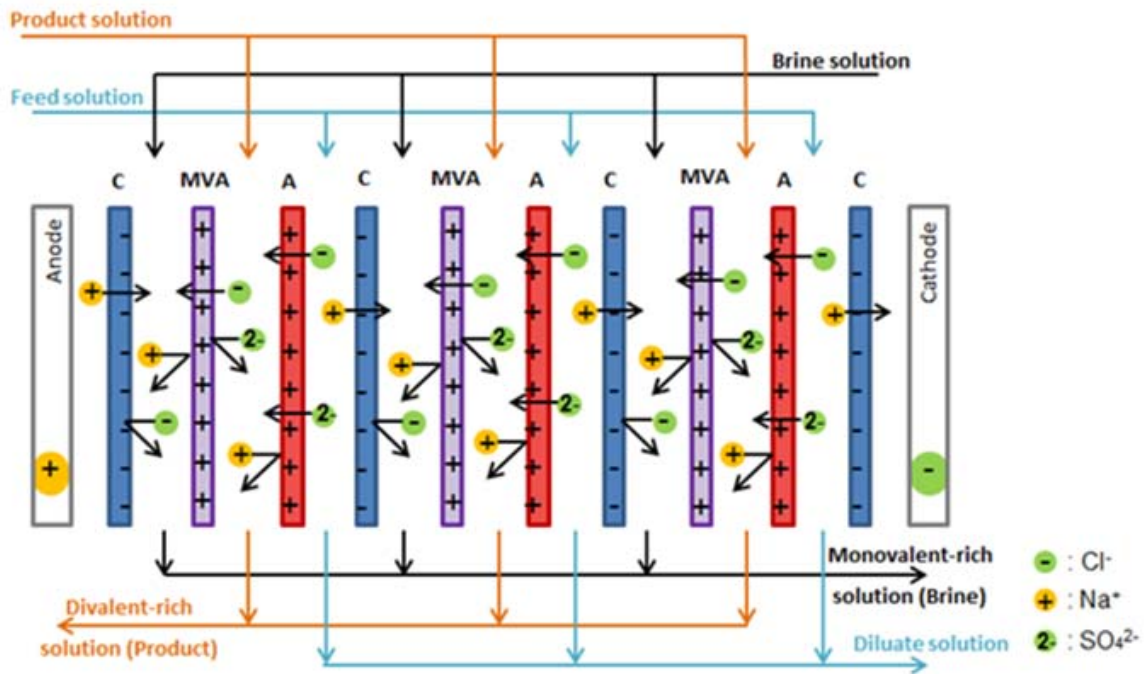
3 Table 1. Main characteristics of the SED and EDBM membrane used

	Standard anionic and cationic membranes (AEM, CEM)		Selective membrane (MVA)	Bipolar membrane (BP)
	PC SA	PC SK	PC MVA	PC BP
Type	Strongly alkaline (ammonium)	Strongly acidic (sulfonic acid)	Strongly alkaline (ammonium)	Water splitting efficiency > 95 % Water splitting voltage: 0.8 – 1 V
General use	Standard desalination	Standard desalination	Monovalent anion selective	
Electric resistance ($\Omega \text{ cm}^2$)	~ 1.8	~ 2.5	~ 20	
Burst strength (MPa)	0.4 – 0.5	0.4 – 0.5	0.2	
Maximum operating temperature ($^{\circ}\text{C}$)	60	50	40	40
Thickness (mm)	0.18 – 0.22	0.16 – 0.20	0.11	0.20 – 0.35

4

5 The membrane configuration in the SED stack was based on a conventional ED but
6 incorporating one monovalent selective anion exchange membrane (MVA) between a
7 standard anion exchange membrane (AEM) and a standard cation one (CEM). All the
8 membranes were supplied by PCCell. CEM and AEM were regarded as having no selectivity
9 to their counter-ions (they were assumed to be an ideal non-selective CEM and an ideal non-
10 selective AEM, respectively) whereas the MVA had a limited selectivity to monovalent
11 anions, i.e., monovalent anions (e.g., Cl^-) have a higher transport number than multivalent
12 anions (e.g., SO_4^{2-}). The proposed configuration for the $\text{Cl}^-/\text{SO}_4^{2-}$ separation is shown in
13 Figure 2, the feed and the product streams comprised a $\text{Cl}^-/\text{SO}_4^{2-}$ mixture with cation Na^+ . The
14 purpose of such configuration was to enrich SO_4^{2-} while removing Cl^- in the product
15 compartment. The MVA was a monovalent selective anion exchange membrane with a
16 selective factor of “n”. Selective factor (n) is a simplified parameter to reflect membrane
17 selectivity, which is calculated by the ion molar amount ratio which two types of ions are
18 transported through the membrane. This MVA–AEM–CEM unit was a repeating membrane
19 trio in the SED stack which had three compartments (denoted as feed, product and brine). By
20 applying an electrical potential, Cl^- and SO_4^{2-} anions were attracted to the anode whereas Na^+
21 cations were attracted to the cathode. In the feed compartment, cations were transported

1 through the CEM membrane to the brine compartment, while anions were transported through
 2 the AEM to the product compartment. Since the AEM was an ideal non-selective membrane,
 3 the same molar amount (m) of anion Cl^- and SO_4^{2-} was transported through the AEM to the
 4 product compartment. Meanwhile, due to the electroneutrality in the feed solution, $3m$ of Na^+
 5 passed through the CEM to the brine compartment. Due to the MVA membrane, only Cl^- ions
 6 passed through it achieving a NaCl concentrated stream in the brine compartment and a
 7 Na_2SO_4 concentrated stream in the product compartment. Then, SED system consisted of 4
 8 streams: electrode rinse, salt (diluted), brine (monovalent anions-rich) and product (divalent
 9 anions-rich).



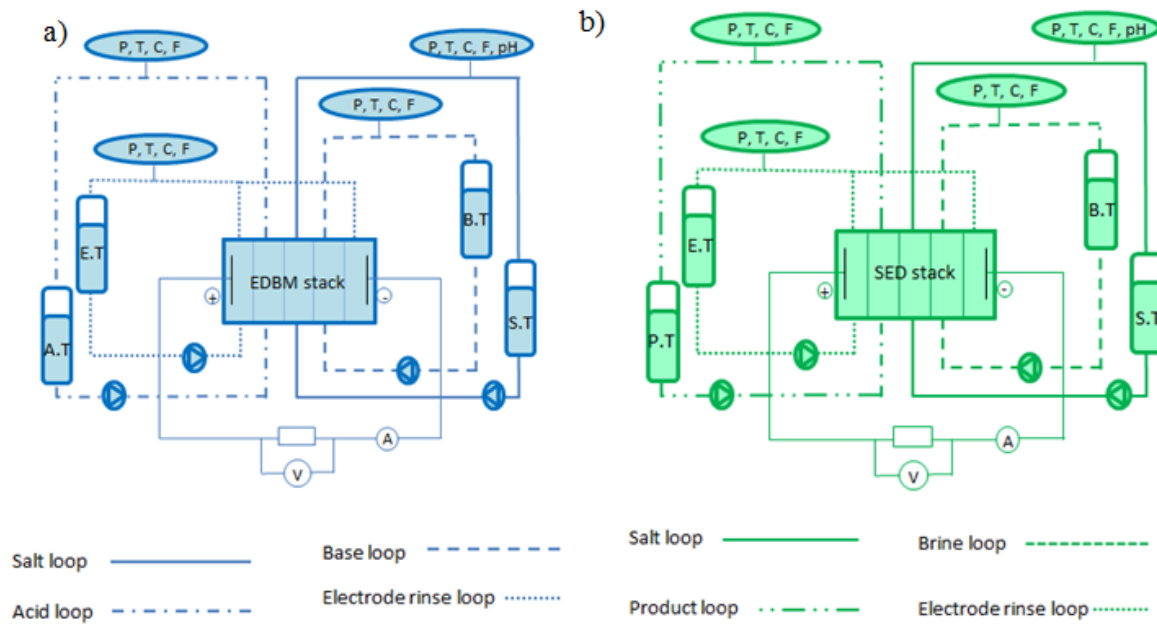
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11 Figure 2. Selectrodialysis (SED) stack scheme including membranes arrangement and
 12 definition of stacks streams.

13

14 On the other hand, the EDBM system was also composed by 4 streams: electrode rinse, salt
 15 (diluted), acid and base (which increase its concentration). In this case, each cell triplet was
 16 composed of one CEM, one AEM and one bipolar membrane (BM).

1 The set-up scheme for the EDBM and the SED systems operated under a recirculation
 2 configuration is shown in Figure 3.



3
 4 Figure 3. Pilot plants scheme a) EDBM configuration and b) SED configuration. (P: pressure
 5 sensor, T: temperature sensor, C: conductivity sensor, F: flow-meter, pH: pH-meter, A:
 6 ammeter, V: voltmeter, S.T: salt tank, A.T: acid or product tank, B.T: base tank (EDBM) and
 7 brine tank (SED), P.T: product brine, E.T: electrode rinse tank).

8
 9 The operation of SED and EDBM systems started once electrical current was applied. In order
 10 to do not damage the membranes, some initial salt concentration was needed in each tank. For
 11 this reason, different initial salts (NaCl , Na_2SO_4 or a mixture of both) and concentration levels
 12 in each stream were tested to achieve the maximum separation of monovalent and divalent
 13 anions by SED under constant voltage conditions of 9 V and several chemical industrial
 14 effluents.

15 Then, both streams obtained by SED (one monovalent-rich and the other divalent-rich salty
 16 current) were treated separately by EDBM to obtain the corresponding acid and base products
 17 while desalting the feed salt. In the EDBM system, NaOH was introduced initially in the base
 18 tank, but for the acid species, again several acids (HCl , H_2SO_4 or a mixture of both) and
 19 concentrations of them were tested to achieve a better separation at constant voltage of 9 V.

1 For both SED and EDBM systems, 1 L of initial solution was introduced in each tank. All
2 reagents used were of quality analysis (PA-ACS-ISO reagent, PANREAC). For the electrode
3 rinse compartment, 0.42 M Na₂SO₄ was used in all the tests. Flow rates were set at 100 L/h in
4 the electrode rinse stream and 15-20 L/h in the others. As it can be seen in Figure 3, pressure,
5 temperature and conductivity were monitored during the experimentation by means of sensors
6 located in each stream of the ED set-up. Besides, the pH in the salt stream and the electrical
7 current and voltage for all the system were also monitored. Samples of each tank were taken
8 during the performance until the conductivity in the feed tank was almost zero and then
9 analyzed to know the concentration of each stream.

11 **2.2 Experimental protocols and methodologies**

12 Separation of Cl⁻/SO₄²⁻ mixtures was carried out by SED. Three feed solution qualities were
13 assessed, namely: low concentrated effluent (with 63 mM Cl⁻ and 26 mM SO₄²⁻), medium
14 concentrated effluent (with 151 mM Cl⁻ and 230 mM SO₄²⁻) and high concentrated effluent
15 (with 497 mM Cl⁻ and 840 mM SO₄²⁻). Process NaCl/Na₂SO₄ brines used in this study were
16 characterized by very low levels of divalent cations e.g., Mg(II) and Ca(II) as water used in
17 the synthesis process was demineralized water. Values of both metals were always below 3
18 mg/L (0.075 mM Ca²⁺; 0.123 mM Mg²⁺).

19 For the brine compartment an initial pure NaCl solution was used, since this compartment it
20 would become the monovalent-rich during the experiment because of the membrane disposal.
21 The product loop was initially filled with a NaCl, a Na₂SO₄ or a mixture of both solutions.
22 The product compartment would become the divalent-rich with the experimental time, and
23 due to the membrane disposal the Cl⁻ ions could pass through the MVA and led the
24 compartment without monovalent ions. For this reason, several experiments were carried out
25 to determine the initial salt that offered the best Cl⁻/SO₄²⁻ separation (Table 2). Once the
26 optimal initial salt was determined to be pure NaCl, more experiments were carried out to
27 determine its optimal concentration to achieve the maximum monovalent/divalent anions
28 separation. In this case, the initial brine and product streams concentration were varied. Table
29 2 collects the experimental design for the SED tests for both, product electrolyte and
30 composition selection.

1 Table 2. Experimental concentrations used for $\text{Cl}^-/\text{SO}_4^{2-}$ separation by SED configuration

	Feed	Brine	Product
Product electrolyte selection (low concentration)	63 mM Cl^- 26 mM SO_4^{2-}	31 mM Cl^-	31 mM Cl^-
		31 mM Cl^-	13 mM SO_4^{2-}
		31 mM Cl^-	15 mM Cl^- 6 mM SO_4^{2-}
Product electrolyte selection (medium concentration)	151 mM Cl^- 230 mM SO_4^{2-}	76 mM Cl^-	76 mM Cl^-
		76 mM Cl^-	115 mM SO_4^{2-}
		76.0 mM Cl^-	38 mM Cl^- 58 mM SO_4^{2-}
Product composition selection (medium concentration)	151 mM Cl^- 230 mM SO_4^{2-}	76 mM Cl^-	76 mM Cl^-
		151 mM Cl^-	151 mM Cl^-
		302 mM Cl^-	302 mM Cl^-
Product composition selection (high concentration)	497 mM Cl^- 840 mM SO_4^{2-}	497 mM Cl^-	497 mM Cl^-
		995 mM Cl^-	995 mM Cl^-

2

3 Production of acid and base solutions was carried out by EDBM. Once the SED experiments
 4 were done, two separate streams were obtained: a NaCl-rich solution in the brine stream and a
 5 Na_2SO_4 -rich solution in the product stream. These two streams were treated separately by
 6 EDBM. However, firstly the acid selection between HCl, H_2SO_4 or a mixture of both in the

1 acid compartment was carried out using the low concentration feed solution (Table 3).
 2 Secondly, once the optimal option was determined, the EDBM experiments with the two SED
 3 solutions (monovalent-rich and divalent-rich) obtained were conducted. In all the EDBM
 4 tests, NaOH was used as initial base, since the main cation in all streams was Na⁺. Table 3
 5 summarizes the experimental concentrations for each EDBM experiment.

6

7 Table 3. Experimental concentrations used for acid and base solutions production by EDBM
 8 configuration.

	Feed	Base	Acid
Acid selection (low concentration)	63 mM Cl ⁻ 26 mM SO ₄ ²⁻	50 mM NaOH	50 mM HCl
			50 mM H ₂ SO ₄
			25 mM HCl
			25 mM H ₂ SO ₄
Experiments from SED	1477 mM Cl ⁻	100 mM NaOH	100 mM HCl
	485 mM SO ₄ ²⁻	100 mM NaOH	100 mM H ₂ SO ₄

9

10 2.3 Analytical methodologies and chemical analysis

11 Ion chromatography (Dionex ICS-1000 and ICS-1100) was used to quantify the ion
 12 concentration on each stream (Na⁺, Cl⁻ and SO₄²⁻). Besides, it was possible to determine the
 13 calcium and magnesium concentration by atomic absorption (Varian, SpectrAA-640). Finally,
 14 automatic acid-base titration system (Titration Excellence T-70) was employed to determine
 15 the HCl, H₂SO₄ and NaOH concentrations.

16

17 2.4 Evaluation of the monovalent/divalent anion separation and energy consumption

18 The purity of each anion was calculated according to Equation 1 and thus the selectivity and
 19 the separation efficiency between two anions *a* and *b* for the MVA membrane were assessed:

$$P_a = \frac{(Ca_t - Ca_i)}{(Ca_t - Ca_i) + (Cb_t - Cb_i)} \cdot 100 \quad \text{Equation 1}$$

20

21 Where C denotes the concentration of each ion (M) at time “t” or at initial time “i”. According
 22 to this estimation, the purity value ranges between 0 and 100, values close to 100 meaning a

1 high retention of ion b ion in the diluate side and a high selectivity of ion a ; and values close
2 to zero meaning the opposite case [28].

3 For the SED experiments, the purity was calculated as the percentage of each ion in the
4 product and brine streams. For the EDBM tests, Equation 1 was used to determine the anions
5 behavior in the acid compartment to obtain the maximum separation. The separation of both
6 anions (Cl^- and SO_4^{2-}), the MVA membrane efficiency, the quality of the solutions produced
7 and the separation in the feed stream for both ED systems were evaluated by using the purity
8 value.

9 Another important parameter to determine was the energy consumption (E_c) in the ED stack,
10 and it was calculated by means of Equation 2.

$$E_c \left(\frac{kWh}{kg \text{ product}} \right) = \frac{(U \cdot I \cdot t)/1000}{m_{\text{final product}}} \quad \text{Equation 2}$$

11 Where U (V) and I (A) are the voltage and current applied in the ED stack, respectively, t (h)
12 is the operation time of the operation and $m_{\text{final product}}$ (kg) is the mass obtained of the desired
13 product (NaCl and Na_2SO_4 concentrate solutions achieved in the SED study or the acid and
14 base produced by EDBM).

15

16 3. RESULTS

17 Conductivity values measured during the tests were used to confirm that both systems were
18 working as expected. The conductivity of the electrode rinse stream remained constant during
19 each experiment, since there was not any interaction with the others streams. Indeed, the
20 conductivity in the feed solution decreased with time as ions migrated to the brine or product
21 compartments once SED was put in operation or to the base and acid compartments when
22 EDBM was employed. For these last two streams (brine/base and product/acid), the
23 conductivity evolution was different depending on whether SED or EDBM was used. For the
24 SED experiments, the concentration of NaCl in the brine stream increased due to the transport
25 of both Cl^- through the MVA membrane and Na^+ through the CEM from the feed solution to
26 this compartment. The Na_2SO_4 -rich product stream kept almost constant its concentration, as
27 both Cl^- and SO_4^{2-} anions crossed the AEM from the feed solution, but Cl^- leaved this
28 compartment through the MVA. For the EDBM system, acid and base streams increased its

1 conductivity, due to the water splitting produced in the BP membrane and the CEM and the
 2 AEM disposal in the stack.

3 4 **3.1 Chloride/sulfate separation by SED configuration**

5 On the basis of the process stream composition (e.g., concentration values of both
 6 electrolytes), four sets of experiments were carried out in order to find the optimal electrolyte
 7 composition to be introduced in the product stream, and then its optimal initial concentration
 8 that provides the highest $\text{Cl}^-/\text{SO}_4^{2-}$ separation factors. First, NaCl, Na_2SO_4 and a mixture of
 9 both solutions were tested by using electrolyte streams in the low (63 mM Cl^- and 26 mM
 10 SO_4^{2-}) and medium concentration range (151 mM Cl^- and 230 mM SO_4^{2-}).

11 Table 4 collects the final Cl^- and SO_4^{2-} concentrations in the brine compartment and the
 12 electrolyte purity reached (Equation 1) with the low concentration effluent (26 mM Cl^- and 63
 13 mM SO_4^{2-}) when using different initial salts in the product tank and NaCl (31 mM Cl^-) in the
 14 brine tank.

15

16 Table 4. Brine composition and separation percentage obtained in each SED experiment

	Initial product composition	Final brine composition			
		Cl^-		SO_4^{2-}	
		Final concentration (mM)	P_{Cl^-} (%)	Final concentration (mM)	$P_{\text{SO}_4^{2-}}$ (%)
Product electrolyte selection (Low concentration)	31 mM Cl^-	68 ± 4	93 ± 1	3 ± 1	7 ± 5
	13 mM SO_4^{2-}	45 ± 2	61 ± 4	9 ± 1	39 ± 2
	15 mM Cl^- + 6 mM SO_4^{2-}	55 ± 3	75 ± 1	8 ± 1	25 ± 5
Product electrolyte selection (Medium concentration)	76 mM Cl^-	232 ± 12	49 ± 1	162 ± 17	51 ± 4
	115 mM SO_4^{2-}	214 ± 11	34 ± 2	273 ± 29	66 ± 3
	38 mM Cl^- + 58 mM SO_4^{2-}	264 ± 14	42 ± 2	264 ± 28	58 ± 3
Product composition selection (Medium concentration)	76 mM Cl^-	232 ± 12	49 ± 1	162 ± 17	51 ± 4
	151 mM Cl^-	316 ± 17	57 ± 1	122 ± 13	43 ± 4
	302 mM Cl^-	532 ± 28	78 ± 1	65 ± 7	22 ± 5
Product composition selection (High concentration)	497 mM Cl^-	1439 ± 77	65 ± 1	498 ± 52	35 ± 5
	995 mM Cl^-	1477 ± 79	72 ± 1	186 ± 20	28 ± 5

1 The objective was to obtain a brine stream as pure in NaCl as possible after the SED trials. As
2 can be seen in Table 4, by using only NaCl as initial product it was possible to achieve a 93 %
3 purity of Cl⁻ in the brine compartment when low concentration feed solution was used. Lower
4 Cl⁻ purity values (61 and 75 %) were reached only if Na₂SO₄ or a mixture of both salts (NaCl
5 and Na₂SO₄) were initially used as product solutions, thus obtaining lower anions separations
6 than the one achieved when using NaCl as initial product.

7 Moreover, similar trials were carried out again, but in this case by using brine with a medium
8 initial concentration (151 mM Cl⁻ and 230 mM SO₄²⁻). Then, the initial brine composition was
9 76 mM Cl⁻, while varying the initial salt solution (NaCl, Na₂SO₄ and a mixture of both) in the
10 product tank. Table 4 also lists the results of these tests. In this second set of experiments,
11 separation was not achieved in either case. Purity values between 34 and 49 % were obtained
12 for both streams for Cl⁻ and SO₄²⁻, which are clearly lower than those achieved with the first
13 set of experiments at lower concentrations.

14 In both cases, the optimal option was using NaCl as a single salt solution in the product
15 compartment. For this reason, NaCl solutions of different concentrations were used as initial
16 product stream in the third set of experiments. Again, different process brines (medium and
17 high concentration) were used. Table 4 shows the results in the case of using 151 mM Cl⁻ and
18 230 mM SO₄²⁻ as initial (medium) concentration feed. In this case, the higher the initial NaCl
19 concentration introduced in the product and brine tanks the higher the purities obtained, with
20 purities values reaching almost 80 % Cl⁻ / 20 % SO₄²⁻ when using the double of the initial
21 NaCl concentration (302 mM Cl⁻).

22 Experiments were repeated with a higher concentrated brine stream (497 mM Cl⁻ and 840 mM
23 SO₄²⁻) as feed solution. Again, almost 80 % Cl⁻ / 20 % SO₄²⁻ was separated when working
24 with the highest initial product and brine NaCl concentration (Table 4).

25 For all the experiments commented above, Cl⁻ and SO₄²⁻ contents in the product stream were
26 analyzed. As an average, 90.5 % SO₄²⁻ and 9.5 % Cl⁻ were calculated as final purity of each
27 ion in the product stream. In comparison with the literature reviewed, Zhang et al. [20]
28 reached similar SO₄²⁻ purity values in the product stream (over 85 %) working with a SED
29 system to separate Cl⁻ and SO₄²⁻ and using monovalent selective (PC MVA) and non-selective
30 membranes (PC SK and PC SA) from PCCell GmbH, Germany. Moreover, Tanaka et al. [29]
31 also studied the Cl⁻ and SO₄²⁻ separation and values around 86 % SO₄²⁻ and 14 % Cl⁻ were

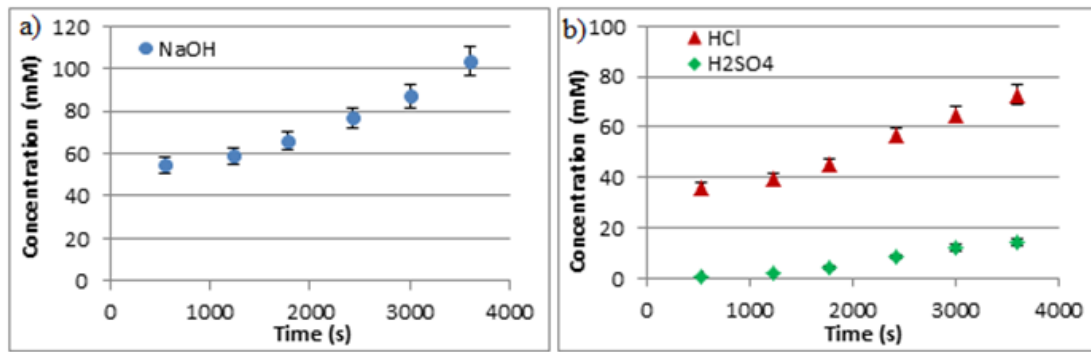
1 reported using a conventional configuration of ED where only selective monovalent ion
2 exchange resins Aciplex K172 and A172 (Asahi Chemical Co., Japan) were used .
3 Finally, it can be concluded that the optimal option to obtain the higher $\text{Cl}^-/\text{SO}_4^{2-}$ by means of
4 SED was using the higher initial NaCl brine and product concentration, in this case the double
5 than in the initial feed stream.
6 The reason of this behavior relies on the diffusion phenomena. Working with divalent anions,
7 the concentration gradient in both MVA membrane sides was high, so a decrease of their
8 selectivity was observed and, consequently, the migration of the divalent anions. If some
9 initial SO_4^{2-} concentration was introduced in the product tank a concentration gradient could
10 appear and divalent diffusion through the MVA membrane could happen. On the other hand,
11 when NaCl was introduced in the product compartment, the diffusion contribution diminished
12 due to the decrease of the concentration gradient in both MVA membrane sides, which
13 delimited the product and brine compartments. Increasing the initial chloride concentration in
14 both streams, hindered the diffusion of sulfate ions through the MVA membrane, which
15 represents a better selectivity and also that a reduced fraction of divalent ions could be
16 transported through it.

17

18 **3.2 Production of acid and base solutions by EDBM configuration.**

19 Before using the real product and brine obtained by SED, it was necessary to perform some
20 test in order to study, which was the optimal initial base and acid concentrations. Different
21 initial acid combinations were used (HCl, H_2SO_4 or a mixture of both). The least concentrated
22 brine (63 mM Cl^- and 26 mM SO_4^{2-}) was used as feed solution in this first set of EDBM
23 experiments. Indeed, a mixture of both acids was produced in the acid stream, since the initial
24 feed stream contained both anions, but an HCl-rich solution was the desired product in the
25 acid compartment. The results indicated that 83 % Cl^- / 17 % SO_4^{2-} separation was obtained
26 when using a pure initial HCl stream in the acid compartment, against 45 % Cl^- / 55 % SO_4^{2-}
27 when using pure H_2SO_4 or 55 % Cl^- / 45 % SO_4^{2-} when a mixture of both acids was employed.
28 Figure 4 shows the results when only HCl was used in the acid compartment, which was the
29 option that yielded the highest HCl purity.

30



1

2 Figure 4. EDBM experiments using 50 mM HCl as initial acid concentration.

3

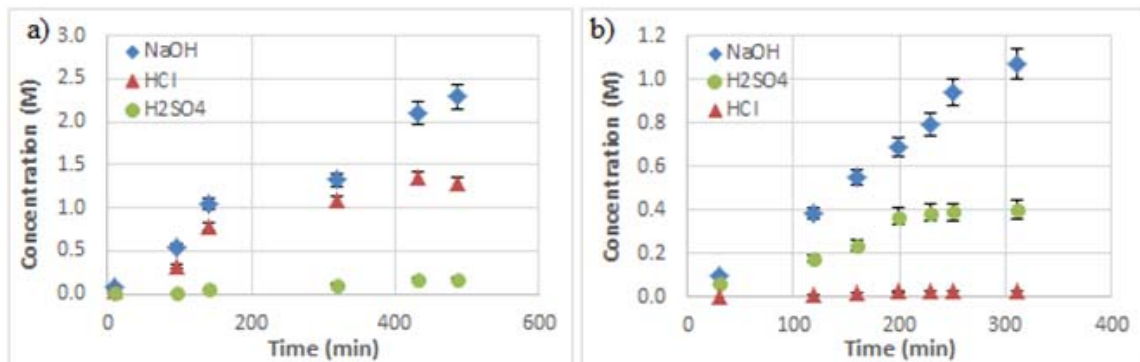
4 It is observed in Figure 4 that NaOH solution doubled its concentration during the
 5 experiments from 0.05 M to 0.10 M. An HCl-rich acid was produced in the acid
 6 compartment, in which HCl concentration increased from less than 0.05 M to above 0.07 M
 7 and final H₂SO₄ concentration was lower than 0.02 M.

8 It can be pointed out that it was better to use initial HCl if higher HCl acid purity was needed,
 9 while for a more concentrated H₂SO₄, initial H₂SO₄ is required.

10 Then, for the next set of EDBM experiments, HCl was used as initial acid solution when the
 11 SED monovalent-rich stream was treated and a pure H₂SO₄ acid was needed if treating the
 12 divalent-rich solution produced by SED. In both cases, NaOH was concentrated in the base
 13 compartment.

14 EDBM experiments were carried out with the SED brine and product streams obtained
 15 working with the higher concentration effluent as SED feed solution and higher product and
 16 brine initial concentration (Table 4). The SED monovalent-rich stream had 1477 mM Cl⁻, but
 17 also 186 mM SO₄²⁻, which was used as initial feed for the second set of EDBM experiments.
 18 Then, 0.1 M HCl and 0.1 M NaOH solutions were initially placed in the acid and base tanks,
 19 respectively. Figure 5a shows the concentration evolution for NaOH in the base stream and
 20 also for HCl and H₂SO₄ in the acid compartment. On the other hand, the divalent-rich stream
 21 from SED was also used as feed solution for the EDBM system. The solution concentration
 22 was 485 mM SO₄²⁻, but also 14 mM Cl⁻, which was used as initial feed for the third set of
 23 EDBM experiments. In this case, pure 0.1 M NaOH was used again as initial base, and pure
 24 0.1 M H₂SO₄ was employed for the initial acid, instead of HCl, because the major anion in the

1 feed stream was SO_4^{2-} . The concentration evolutions for the NaOH in the base stream and also
2 for the H_2SO_4 and HCl in the acid compartment are also plotted in Figure 5b.



3
4 Figure 5. Concentration evolution using as EDBM feed solution the a) SED Cl⁻-rich stream b)
5 SED SO₄²⁻-rich stream.

6
7 As shown in Figure 5, in both cases it was possible to obtain pure NaOH in the basic
8 compartment, since the only cation of the initial solution was Na⁺. By using either the
9 monovalent-rich stream or the divalent-rich one, it was possible to obtain almost pure HCl or
10 H₂SO₄ acid, respectively.

11 When using the Cl⁻-rich stream from SED, it was possible to obtain a pure 2.3 M NaOH in the
12 base compartment, but a mixture of 1.3 M HCl and 0.2 M H₂SO₄ was produced in the acid
13 one. Although a mixture of acids was achieved in the corresponded compartment, HCl was
14 the prevailing acid with 87 % Cl⁻ / 13 % SO₄²⁻ purity.

15 On the other hand, when the SO₄²⁻-rich stream produced by SED was introduced in the
16 EDBM system, less concentrated pure NaOH (1.1 M) and also an almost pure 0.4 M H₂SO₄
17 (with 0.03 M HCl traces) were obtained.

18 For this reason, it can be said that it was possible to valorize a non-desirable salty NaCl and
19 Na₂SO₄ solution by means of their separation and concentration into a monovalent and a
20 divalent rich solutions. Each stream could then be treated by EDBM to produce a NaOH base
21 solution and a HCl-rich or a H₂SO₄-rich solution in the acid compartment. Both base and acid
22 solutions could be reused in the same chemical industry to promote circular economy or be
23 sold in the chemical market [27].

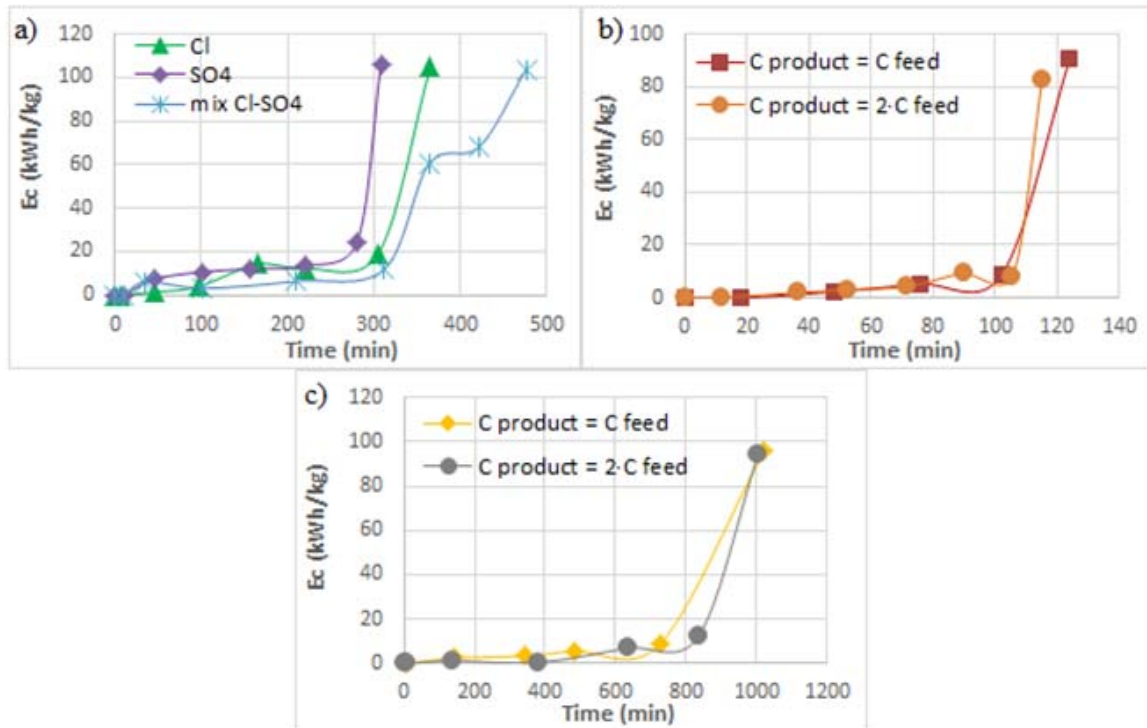
24

1 **3.3 Energy consumption**

2 Because both systems are electrical current-driven processes, energy consumption (E_c) was a
3 crucial parameter in order to decide their applicability at the industrial scale. Equation 2 was
4 used to calculate E_c in each experiment. The final mass product on Equation 2 was calculated
5 in a different way depending on the membrane configuration SED or EDBM and the desired
6 product.

7 For the SED trials, two desired products were obtained: the NaCl produced in the brine
8 compartment and the Na₂SO₄ solution obtained in the product compartment. Then, both
9 masses were taken into account considering also the initial solutions introduced in each
10 compartment.

11 For the EDBM trials, two products were obtained: acid and base. However, as it was seen in
12 Figure 5, a mixture of HCl and H₂SO₄ was achieved in the acid compartment in every EDBM
13 experiment, although pure NaOH was produced in the base tank. In the chemical market, the
14 NaOH price is higher than for HCl or H₂SO₄, and therefore this pure NaOH can be easily
15 commercialized in the industry. For this reason, the NaOH produced was the final mass
16 product used in Equation 2. E_c evolution curves obtained for SED and for EDBM systems
17 were similar. Figure 6 shows the EC evolution curves for the SED experiments. Each graph
18 represents the three main selections carried out to determine the optimal initial salt in the
19 product tank and its composition: a) electrolyte selection (Cl⁻, SO₄²⁻ or a mixture of both
20 anions) with the medium feed concentration brine, b) composition selection (with the same or
21 the double feed concentration) with the medium feed concentration brine and c) composition
22 selection (with the same or the double feed concentration) with the high feed concentration
23 brine.



1
 2 Figure 6. SED energy consumption evolution for product selection of a) electrolyte with
 3 medium feed concentration, b) composition at medium feed concentration and c) composition
 4 at high feed concentration.

5
 6 As it is observed in Figure 6, firstly, a slightly constant E_c value was obtained until the brine
 7 and product production achieved a steady value, then the E_c increased drastically. This
 8 increase was due to osmosis and ion diffusion fluxes inside the SED stack reach a maximum
 9 because of the concentration gradient between the diluate and the concentrated compartments.
 10 Once the concentration of brine and product increased really slowly, the energy applied is
 11 used to slowly increase their concentrations and then, E_c increases. It can be concluded that it
 12 is important to work in the optimal zone to maintain low E_c values. This E_c behavior was
 13 reported elsewhere [29,30]. Table 5 reports the E_c experimental values, taken into account the
 14 optimal zone work for each experiment.

15
 16
 17

1 Table 5. Compilation of electrical consumption values (E_c) values at the optimal zone work
 2 for the SED and EDBM experiments.

ED system		Initial product composition	Energy consumption (kWh/kg product)
SED	Product electrolyte selection (Low concentration)	31 mM Cl^-	0.35
		13 mM SO_4^{2-}	0.97
		15 mM Cl^- + 6 mM SO_4^{2-}	0.47
	Product electrolyte selection (Medium concentration)	76 mM Cl^-	7.9
		115 mM SO_4^{2-}	8.9
		38 mM Cl^- + 58 mM SO_4^{2-}	7.1
	Product composition selection (Medium concentration)	76 mM Cl^-	7.9
		151 mM Cl^-	5.4
		304 mM Cl^-	5.5
	Product composition selection (High concentration)	497 mM Cl^-	5.9
995 mM Cl^-		2.9	
EDBM	Acid selection (Low concentration)	50 mM HCl	1.3
		50 mM H_2SO_4	1.3
		25 mM HCl + 25 mM H_2SO_4	1.5
	Experiments from SED	100 mM HCl	4.2
		100 mM H_2SO_4	5.8

3
 4 As it reported in Table 5, working at low feed concentrations implied low E_c values, although
 5 also low final concentrations in the product and the brine tank were achieved (Table 4). For
 6 the SED experiment carried out with the medium and high concentrations effluents, an E_c
 7 average of 6.4 kWh/kg product obtained was calculated. For the EDBM experiments, lower
 8 energy consumption values (~1.4 kWh/kg NaOH) were also calculated working with the
 9 lower initial concentrations. However, higher E_c values (around 5 kWh/kg NaOH) were
 10 estimated when the obtained SED streams were treated by EDBM. These values are in
 11 accordance with the E_c values for similar systems found in the scientific literature, such as 3
 12 kWh/kg NaOH [31] or 2.6 kWh/kg NaOH [27].

1 **5. CONCLUSIONS**

2 This study demonstrated that it was possible to valorize chemical industry process brines
3 (containing NaCl and Na₂SO₄) by means of a combination of two current-driven ion-
4 exchange membrane technologies: SED and EDBM.

5 First of all, chloride and sulfate ions were separated by SED reaching purities of more than 90
6 % SO₄²⁻ in the divalent-rich stream and about 90 % Cl⁻ in the monovalent-rich stream.
7 Different initial electrolytes and several concentration values were tested in order to reach the
8 maximum separation efficiency, and the optimal result was to use an initial NaCl solution in
9 the brine and product compartments with a double concentration than the brine feed.

10 EDBM is a suitable process to produce base and acid from the SED monovalent-rich and
11 divalent-rich stream separated by SED. Pure NaOH were produced in both cases, whereas
12 HCl-rich (87 %) and H₂SO₄-rich (93 %) acids were obtained when the SED monovalent-rich
13 stream or the SED divalent-rich stream were used as EDBM feed, respectively.

14 Finally, Ec evolution curves were calculated for each experiment and it is important to point
15 out that it is better to work by SED or EDBM until the production (brine and product or base
16 and acid streams, respectively) become almost constant, because in that point the Ec increased
17 drastically.

18

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26

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