



Acid and Base Production through Electrodialysis with Bipolar Membranes at Semi-Industrial Scale: Study of Multi-Ionic Transport

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Electrodialysis with Bipolar Membranes (EDBM) has recently attracted considerable interest in advancing the production of acid and base solutions from waste saline streams utilizing water and electricity. Although multiple studies on EDBM have been conducted at the laboratory scale, there is a lack of knowledge on its application at larger scales and in real-world environments. This work aimed at investigating energetic performance and ion transport in a semi-industrial EDBM unit. This work produced promising results for the achieved Current Efficiency (CE), which was approximately 89%, and the Specific Energy Consumption (SEC), which was 1.25 kWh kg⁻¹NaOH at the target concentration of 0.5 mol L⁻¹ of NaOH. Moreover, the alkaline solution reached a high purity of 97% in OH⁻ and 95% in Na⁺, thus demonstrating the effectiveness of EDBM in real-world applications, particularly for the in-situ production of acid and alkaline solutions.

1. Introduction

The contemporary ideals driving research in the field of industrial wastewater treatment promote the concepts of circularity, energy saving, and waste minimization. In this context, one of the most globally underestimated raw materials is seawater. Indeed, seawater represents a widely available source of critical elements such as magnesium, lithium, caesium, cobalt, etc., which are highly important for the European economy but are at a high risk of supply issues.

The European Horizon 2020 SEArcularMINE project has developed an innovative treatment chain in Trapani, Sicily (Italy), for the valorisation of concentrated waste brines collected from local saltworks (www.searcularmine.eu), using Minimum Liquid Discharge (MLD) approaches. Typically, bitterns are collected in swallow basins, and downstream of the sodium chloride precipitation, the remaining concentrated solution is discharged back into the sea, potentially causing significant problems for the marine environment (Fernandez-Gonzales et al., 2016). However, with the innovative ideas of the SEArcularMINE project, almost all the elements present in the brine can be recovered and, thus, provide economic value. In this context, Electrodialysis with Bipolar Membranes (EDBM) is an electro-membrane process of crucial relevance due to its ability to produce the acid and alkaline reactants required in the same situ by other equipment adopting the same saline solution, thus guaranteeing circularity in the treatment chain.

The EDBM system consists of a stack of Ion Exchange Membranes (IEMs) separated by spacers and organized in different repetitive units, namely triplets, with each one made up of an Anion Exchange Membrane (AEM), a Cation Exchange Membrane (CEM), and a Bipolar Membrane (BPM). A concentrated saline solution is fed between the AEM and the CEM, while freshwater is fed into the other compartments. When a voltage difference is applied in DC by a power supply to the electrodes, the electron flux is converted into an ionic flux by electrochemical reactions in the electrodic rinse solution, allowing the ionic migration through the monopolar membranes. Specifically, cations and anions migrate from the brine towards the acid and alkaline channels, respectively. Meanwhile, water molecules diffuse inside the different charged layers of the BPM and are

dissociated into protons and hydroxide ions, which migrate toward the acid and base channels. In this way, hydrochloric acid and sodium hydroxide are produced and isolated in different compartments (Pourcelly, 2002). Most previous studies in literature have been conducted at the laboratory scale, with the goal of identifying the most suitable membranes or exploring the influence of different operating conditions on the process. Only a few studies have investigated the application of this process at larger scales. For example, Filingeri et al., 2025 examined the influence of differential pressures inside the channels on the water transport between the solutions, but using synthetic saline solutions containing only NaCl. Consequently, a comprehensive study of the influence of multi-ionic saline solutions is currently missing at the pilot scale. To fill this gap, the present work aims to investigate the application of EDBM to processing real, pre-treated saline solutions from saltworks using a semi-industrial scale unit, the largest investigated so far.

2. Methodology

The following section describes the i) material and setup (section 2.1), ii) experimental procedure (2.2), iii) analytical techniques (2.3) and iv) performance analysis (2.4) related to the EDBM experimental campaign. The unit was tested using a real brine collected from the Margi pond of the Trapani saltworks, which was pre-treated and utilized to feed the saline compartment.

2.1 Materials and Setup

The experiments presented in this work were conducted using a semi-industrial-scale EDBM stack (ED-STACK 3CBPED), supplied by SUEZ and made up of 50 triplets containing IEMs with an active area of 0.325 m². The unit was equipped with three regenerative turbine pumps (Teorema PTM 3X9) and three gear pumps to feed the solutions. Various measurement instruments were placed along the hydraulic circuit: three flow meters (OPTIFLUX 4100 Krohne, Germany) to measure the outlet volumetric flowrates of the three solutions, three pressure transducers (OPTIBAR P 1010 C, Krohne, Germany), and six conductivity meters (OPTISENS IND 1000, Krohne, Germany) for inlet and outlet solutions. For the electrical connection, a power supply from Giussani s.r.l. was installed, with a usable voltage up to 100 V and a maximum current of 200 A. The EDBM unit was fed with a concentrated saline solution to the saline compartment and two dilute acid and base solutions to the acid and alkaline compartments, respectively. Specifically, for the acid and alkaline compartments, two synthetic solutions were prepared by adding either 0.05 mol L⁻¹ of HCl (ACS 37%, Honeywell, Fluka) or 0.05 mol L⁻¹ of NaOH (technical grade, Inovyn), respectively, to softened water.

The natural brine underwent different pre-treatment steps: (i) ultrafiltration to remove the organic matter, (ii) ion exchange to remove boron, (iii) reactive crystallization for the precipitation of magnesium in hydroxide form, and (iv) ion exchange for the removal of the residual hardness. The inlet composition of the obtained saline solution fed to the salt channel is reported in Table 1.

Table 1: Composition of the pre-treated brine from Margi.

Brine composition	Na ⁺	Cl ⁻	SO ₄ ²⁻	K ⁺	Br ⁻
Concentration [g L ⁻¹]	12.569	15.306	5.437	1.141	0.214

2.2 Experimental procedure

The test was conducted using a batch mode, namely closed-loop configuration, which involved the recirculation of the three solutions inside the EDBM channels. This process increases the concentrations of NaOH and HCl in the alkaline and acid compartments and gradually depletes the ions in the saline compartment over time. Three tanks with a capacity of 1 m³ were used to contain the feed solutions. During the first part of the test, the main turbine pumps were started in order to allow the solutions to flow and to reach a pseudo steady-state condition inside the pipes and the stack. The system was run with the application of a pressure control strategy to avoid possible pressure gradients which can lead to water transport between channels. After the hydraulic start-up procedures were initiated, the EDBM power supply was turned on, and a voltage limit was applied in order to guarantee system safety. Samples were collected every 30 or 60 minutes, and the key process variables were recorded (voltage, current, conductivity, temperature, flowrates, volume levels).

The test was carried out with the following set of operating conditions:

- initial volumes of 550 L (0.550 m³) for acid, base, and salt;
- inlet pressures of 1 barg;
- maximum applied voltage of 75 V.

When the electrical conductivity of the saline solution dropped below 10 mS cm⁻¹, indicating significant ion depletion, the test was discontinued.

2.3 Analytical techniques

The collected samples were analyzed through volumetric acid-base titrations to assess the molar concentrations of protons and hydroxide ions in the acid and base solutions, respectively. A solution of 0.05 mol L⁻¹ Na₂CO₃ and standard 0.1 mol L⁻¹ HCl were used as the titrants for the acid and base samples, respectively. Ethyl orange was used as an indicator to observe the pH turning point of the solutions.

Ion chromatography (IC) was employed to measure the concentration of the different ions present in the solutions. The samples were firstly diluted with ultrapure water, and then analyzed with Metrohm 930 compact 45 IC plus, using Metrosep A Supp 5 – 250/4.0 as anionic column and Metrosep C 4 – 250/4.0 as cationic column.

2.4 Equations and Performance Parameters

Two Key Performance Indicators (KPIs) have been calculated in order to evaluate the performance of the EDBM process, in terms of the amount of sodium hydroxide produced. Regarding the Current Efficiency, CE (%), Eq(1) estimates the amount of electric current converted into the OH⁻ flux for the production of NaOH, as a percentage of the total electric current applied to the system.

$$CE = \frac{(c_{b,OH^-,t} * V_{b,t} - c_{b,OH^-,0} * V_{b,0}) * F}{I * N * t} * 100 \quad (1)$$

where I (A) is the current, N (-) the number of triplets, t (s) the time passed since the test started, $c_{b,OH^-,t}$ and $c_{b,OH^-,0}$ (mol L⁻¹) are the molar concentrations of OH⁻ in the base and $V_{b,t}$ and $V_{b,0}$ (L) the volume of base, respectively at the current time and at the start of the test.

For the Specific Energy Consumption, SEC (kWh kg⁻¹), Eq(2) represents the energy spent to produce 1 kg of sodium hydroxide.

$$SEC = \frac{I * \int_0^t V * dt}{3,600 * M_{NaOH} * (c_{b,OH^-,t} * V_{b,t} - c_{b,OH^-,0} * V_{b,0})} \quad (2)$$

where V (V) is the applied external voltage and M_{NaOH} (g mol⁻¹) the molar weight of sodium hydroxide.

The purity (P_i) of the two EDBM products was estimated based on the anionic and cationic purities at the target alkaline concentration of 0.5 mol L⁻¹ of OH⁻ as shown in Eq(3) and Eq(4), respectively.

$$P_{a^*,sol} = \frac{c_{a^*,sol}}{\sum_i c_{a_i,sol}} * 100 \quad (3)$$

where $c_{a_i,sol}$ and $c_{a^*,sol}$ (mol L⁻¹) are the molar concentration of a generic anion and of the desired anion in a solution, respectively.

$$P_{c^*,sol} = \frac{c_{c^*,sol}}{\sum_i c_{c_i,sol}} * 100 \quad (4)$$

where $c_{c_i,sol}$ and $c_{c^*,sol}$ (mol L⁻¹) are respectively the molar concentration of a generic cation and of the desired cation in a solution.

3. Results and discussion

The test was carried out in potentiostatic mode, meaning that the external applied voltage was kept constant (Figure 1a) and the electric current varied based on the global electrical resistance of the stack (Figure 1b). The current density increased during the first half of the test due to the reductions in the ohmic resistance, which, in turn, resulted from the rising conductivities in the acid and alkaline compartments. Conversely, the current density decreased in the second half of the test due to reductions in the saline solution conductivity.

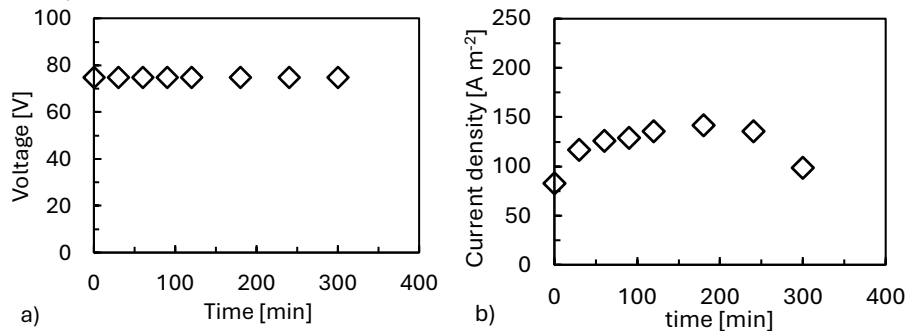


Figure 1: a) Voltage and b) current density profiles over time.

A variation in volume was observed over time (Figure 2), with an increasing trend for the acid and alkaline solutions and a decreasing trend for the saline solution. This phenomenon is primarily attributed to water transport across the membranes, mainly driven by electro-osmosis. As ions migrate from the saline channel to the other two compartments, they are surrounded by water molecules, which inevitably leads to an increase in the volume of the products, 9.1 % for the base and 12.7 % for the acid compared to their initial values.

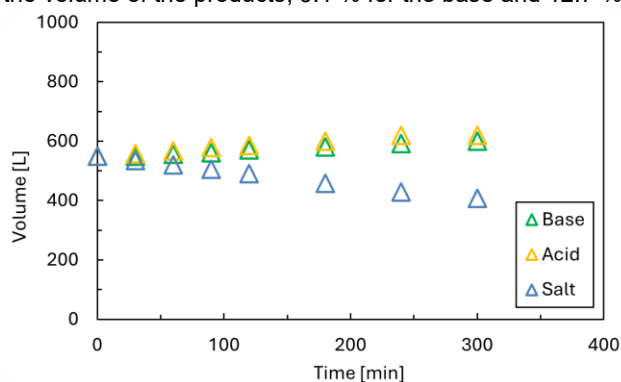


Figure 2: Volume trends during the test.

The concentrations of base and acid were periodically measured through titrations, revealing an increasing trend over time due to the migrative transport of ions. The final concentrations reached 0.50 mol L⁻¹ for hydroxide ions (Figure 3a) and 0.46 mol L⁻¹ for protons (Figure 3b). However, a slight decrease in the slope of OH⁻ curve was observed, attributed to the undesired diffusion of protons and hydroxide ions from the acid and base channels, respectively, to the saline compartment. For the saline solution, electrical conductivity was used as an indirect measure of ion concentration (Figure 3c), showing a linear decreasing trend, with a final conductivity of 5.7 mS cm⁻¹, meaning that a high level of depletion of ions in the salt compartment was reached.

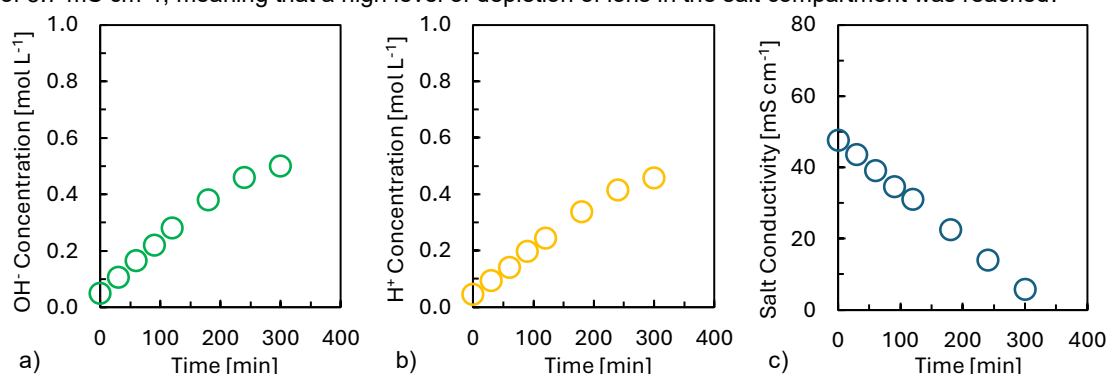


Figure 3: a) OH⁻ concentration in the alkaline solution, b) H⁺ concentration in the acid solution and c) electrical conductivity in the saline compartment during the test.

Regarding the calculated KPIs, the observed trends align with literature data at the laboratory scale. Current Efficiency (Figure 4a) decreased over time due to undesired diffusion phenomena, which are more pronounced at higher product concentrations. Conversely, Specific Energy Consumption (Figure 4b) increased over time with a variable slope, as it is inversely proportional to Current Efficiency. In the first phase of the test, the slope was lower because the increasing current density led to a high production rate of sodium hydroxide. In the second phase, it increased more rapidly due to the reduction in the sodium hydroxide production rate, further influenced by the decreasing current efficiency.

In a previous work conducted at the laboratory scale, Lopez et al., 2025 reported a Current Efficiency of approximately 89% and a Specific Energy Consumption of 1.6 kWh kg⁻¹ when reaching a NaOH concentration of 0.5 mol L⁻¹ at a current density of 300 A m⁻². These values highlight the high performance of the process at the pilot scale, as in the present study CE and SEC were 73.8 % and 1.35 kWh kg⁻¹, respectively, at the same NaOH target concentration, but with a lower current density.

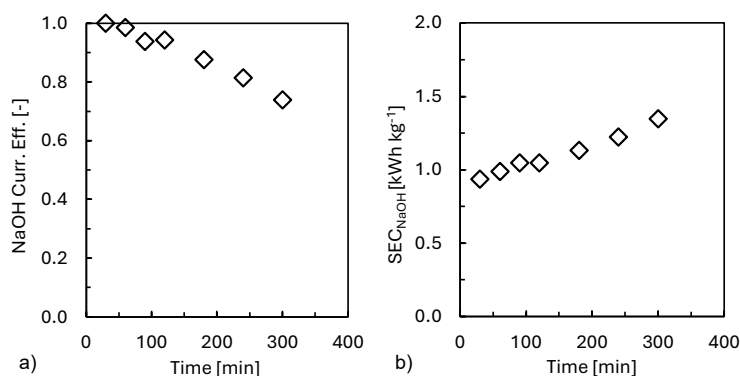


Figure 4: Trends of a) Current Efficiency and b) Specific Energy Consumption, referred to the amount of sodium hydroxide produced.

In addition to determining OH⁻ and H⁺ concentrations through titrations, the quantification of other ions via IC enabled the calculation of the final product purity. Figure 5 and Figure 6 present the initial and final compositions of the alkaline, acid, and saline solutions, including both major and minor ions.

At the end of the test, the alkaline solution was primarily composed of sodium, with a minor amount of potassium that migrated through the CEM. A small quantity of chloride ions was present as an impurity, due to the non-ideal behavior of the membranes, which partially allowed co-ions diffusion. The final composition of the acid solution mainly consisted of chlorides ions, along with smaller amounts of sulphates and sodium. In particular, the sodium concentration suggests that the apparent selectivity of the AEM is lower than that of the CEM.

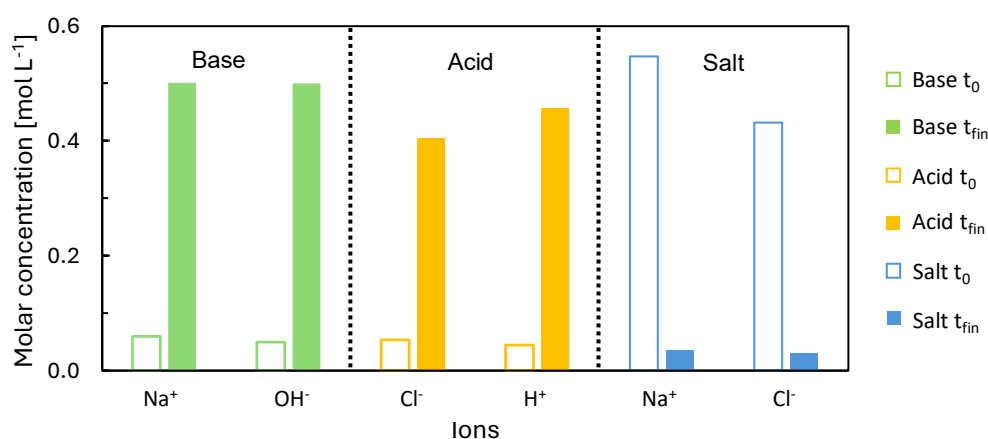


Figure 5: Ions concentration in alkaline, acid and saline solutions at the start and at the end of the test (major ions).

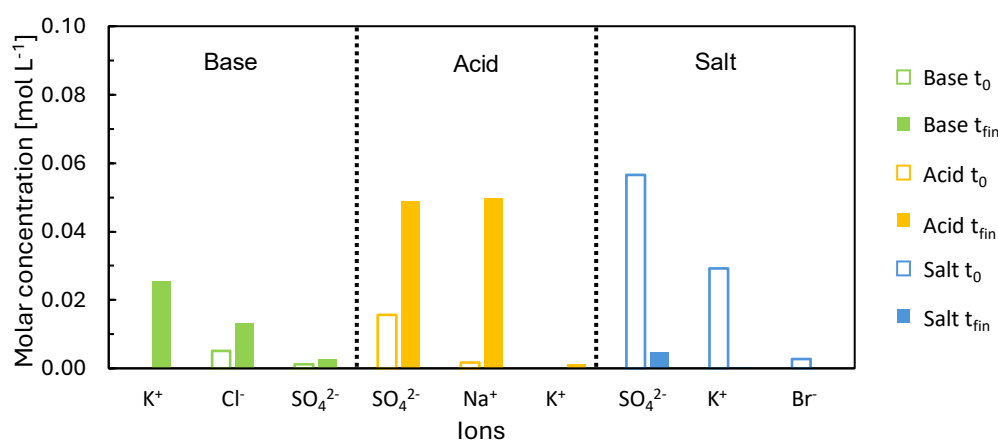


Figure 6: Ions concentration in alkaline, acid and saline solutions at the start and at the end of the test (minor ions).

For the produced solutions, purity was calculated by considering the percentage of the target cation relative to the total cation content and the percentage of the target anion relative to the total anion content.

At the end of the test, the cationic purity of sodium in the alkaline solution was 95.1%, while the anionic purity of hydroxide ions was 96.9%. In the acid solution, the anionic purity of chloride was 88.6 %, while the cationic purity of protons was 90.0 %. These results further support the previous hypothesis regarding the lower apparent selectivity of the AEM compared to the CEM.

4. Conclusions

In this study, the EDBM process was investigated using real feed solutions at the pilot scale. A pre-treated brine from saltworks, containing sodium, chloride, sulphates and smaller amounts of potassium and bromide, was fed into the stack for a closed-loop test.

The objective of producing an alkaline solution with a final concentration of 0.5 mol L⁻¹ OH⁻ was successfully achieved, with a hydroxide purity of 96.9% relative to the total anion content in the solution. Moreover, the process performance was satisfactory: at the target concentration, although the Current Efficiency reached 73.8%, slightly lower than that obtained in literature at laboratory scale (Lopez et al., 2025), a lower Specific Energy Consumption of 1.35 kWh kg⁻¹ was found.

Finally, the distribution of ions from the feed solution to the final products was analyzed, confirming the high selectivity of the membranes, as indicated by the low concentration of co-ions in the compartments.

These results demonstrate the strong potential of EDBM technology for real-world applications and pave the way for further investigations aimed at enhancing the process performance.

Nomenclature

AEM – Anion Exchange Membrane

BPM – Bipolar Membrane

CEM – Cation Exchange Membrane

IEM – Ion Exchange Membrane

$c_{a,i}$ – molar concentration of i in the acid, mol L⁻¹

$c_{b,i}$ – molar concentration of i in the base, mol L⁻¹

CE – current efficiency, -

F – Faraday constant, 96,485 C mol⁻¹

I – current, A

M_{NaOH} – molecular weight of NaOH, 40 g mol⁻¹

N – number of triplets, -

$P_{\text{cation,solution}}$ – cationic purity, %

$P_{\text{anion,solution}}$ – anionic purity, %

SEC – Specific Energy Consumption, kWh kg⁻¹

t – time, s

V – voltage, V

V_b – volume of base, L

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