

Regeneration of hydrochloric acid and sodium hydroxide with bipolar membrane electrodialysis from pure sodium chloride

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In this work an electrodialysis process with bipolar membranes was used to generate HCl and NaOH from pure NaCl and Algerian rock salt from Hamraya. The current efficiency of this process was limited by the proton leakage through the anion exchange membrane: diffusion of HCl, NaOH, Na^+ and Cl^- through bipolar membranes. In this work two low-proton-leakage membranes, AAV and ACM, were used. NaOH and HCl solutions of high purity were obtained. The experimental values of the HCl and NaOH fluxes are compared with the values that could be calculated after integrating the Nernst–Planck electrodiffusion equations. This calculation required several parameters that were experimentally determined: ion diffusion coefficients, membrane conductance and amount of sorbed electrolytes.

Regeneration de l'acide chlorhydrique et de la soude par électrodialyse avec une membrane bipolaire à partir du chlorure de sodium. Dans ce travail, nous avons utilisé l'électrodialyse avec une membrane bipolaire pour régénérer l'acide chlorhydrique à partir du chlorure de sodium pur et du mineral de sel d'Hamraya. Le rendement faradique de ce procédé est limité par la fuite en protons au travers des membranes échangeuses d'anions: la diffusion de HCl, NaOH, Na^+ et Cl^- à travers les membranes bipolaires. Dans ce travail, nous avons utilisé les membranes AAV et les membranes ACM qui sont des membranes à faibles fuites en proton. Nous avons obtenu des solutions de HCl et de NaOH à haute pureté. Les valeurs expérimentales des flux de HCl et NaOH sont comparées avec les valeurs calculées à partir de l'intégration des équations d'électrodifusion de Nernst–Planck. Ce calcul nécessite la connaissance de plusieurs paramètres qui ont été déterminés expérimentalement: coefficients de diffusion des ions, conductance de la membrane et quantités d'électrolytes sorbés.

Electrodialysis recovery of raw materials from wastes and industrial effluents has achieved wide application over the past decades. Electrodialysis units are directly connected to industrial equipment in closed circuits to recycle recovery products, thus preventing environmental pollution.

Recent progress in ion exchange membranes has enabled the manufacture of new bipolar membranes (BPM) to produce the corresponding acid and base from a salt. The main property of these membranes (composed of a cation exchange and an anion exchange layer joined together) is to dissociate water when submitted to an electric field.^{1–6} Several advantages are offered by using bipolar membranes: no gas generated, no mercury pollution compared to the mercury cathode process and low initial cost (only two electrodes are needed for a series of cells with bipolar membranes).

The purpose of this work is to analyze transport phenomena occurring in ion exchange membranes and to study the feasibility of this process with pure salts and natural rock salt from Hamraya in southern Algeria.

Fig. 1 shows the regeneration process of HCl and NaOH from sodium chloride solutions with bipolar membrane electrodialysis. In compartments II and V under the influence of an electric field, chloride anions and sodium cations move in opposite directions to cross the anion exchange membranes (AEM) and the cation exchange membranes (CEM), respectively. Under the influence of an electric field, diffusing water molecules reaching this interface are dissociated into protons and hydroxide ions. Protons cross the cation exchange layer

of the BPM to enter compartment III in which they meet chloride anions to form hydrochloric acid. Hydroxide ions cross the anion exchange layer of the BPM to enter compartment IV containing NaOH molecules formed with sodium ions coming from compartment V. Proton leakage through the AEM membranes^{7–10} is one of the main factors that limit the current efficiency of this process. Anion exchange membranes with a low proton leakage were used during the experiments. In this work we used the following four membranes:

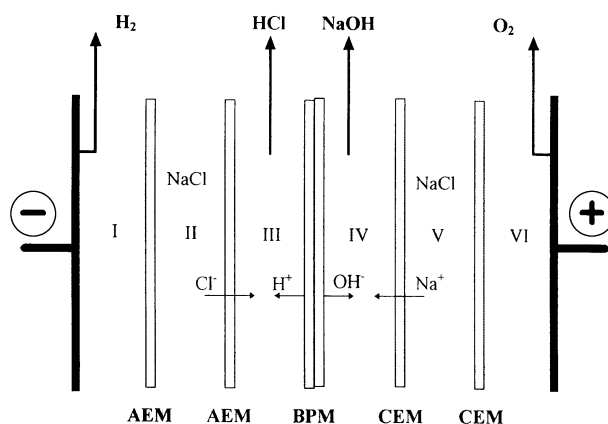


Fig. 1 The six-compartment electrodialysis cell used to produce HCl and NaOH

AAV Selemion is an AEM manufactured by Asahi Glass (Japan); ACM Neosepta is an AEM manufactured by Tokuyama Soda (Japan); CMV Selemion is a CEM manufactured by Asahi Glass (Japan) and WSI is a BPM manufactured by WSI technologies (USA).

Experimental

The electrodialysis cell

The polymethacrylate electrodialysis (ED) cell (Fig. 1) consists of two electrode compartments at each end separated by four other compartments that are 8 mm thick. The active surface of the membrane separating the compartments is 12 cm². The area of the electrodes made of platinized titanium is 20 cm². Silicone gaskets between the compartments prevent leakage.

The six compartments were filled with different solutions at different initial concentrations: NaCl in compartments I, II and V, HCl in compartment III, NaOH in compartment IV and Na₂SO₄ in compartment VI. The initial volumes were 800 mL in compartments I and VI, 250 mL in compartments II and V and 100 mL in compartments III and IV. Sodium chloride and sodium sulfate were maintained at 0.2 M in compartments I and VI. Experiments were performed with different initial concentrations in the four other compartments.

Watson-Marlow peristaltic pumps delivered a 3.6 L h⁻¹ flow in each compartment loop. The constant electric field between the electrodes was provided by a Fontaine stabilized DC generator. Voltage and intensity were measured with a multimeter. All experiments were performed at 25 °C.

Laboratory reagent grade NaCl, HCl and NaOH were used. For the last experiment we used Hamraya NaCl rock salt, which is a natural salt of high purity. Concentration variations were followed by different titrations: HCl and NaOH by acid–base titrations; Na⁺, K⁺, Ca²⁺ and Mg²⁺ by spectrophotometry; SO₄²⁻ by turbidimetry and Cl⁻ by AgNO₃ titration.

The current efficiency is given by:

$$C_e = \frac{96500(V_i C_i - V_f C_f)}{I S t}$$

in which $V_i C_i$ and $V_f C_f$ are the initial and final equivalent quantities for HCl in compartment III and for NaOH in compartment IV, respectively; I is the current density; S is the active surface of the membrane and t is the time during which the experiment was performed. Volume variations between V_i and V_f were taken into account with the intermediate concentrations.

Membrane stabilization

Before use, a pretreatment was carried out to expel impurities and to stabilize the membranes. The AEM and CEM membranes were immersed for one hour in 1 N HCl and rinsed in bidistilled water. After rinsing the CEM was immersed for one hour in 1 N NaOH and rinsed. Then the membranes were immersed in 0.1 N NaCl. This cycle was repeated twice. Thus the AEM were conditioned in the chloride form and the cation exchange membranes in the sodium form.

The same treatment was adapted to the anion and cation exchange layers of the BPM. However, the anion exchange layer remained conditioned in the hydroxide form and the cation exchange layer in the proton form.

The membranes were then equilibrated for 24 h in the salt, acid or basic solutions before sorption measurements. HCl and NaOH solutions (200 mL) and 1 L of water and NaCl solution were used for 1 g of dry membrane.

Table 1 Weight of dry membranes, exchange capacity and thickness of the utilized membranes

Membrane	AAV	ACM	CMV
Dry membrane weight/g	0.1024	0.1006	0.1052
Exchange capacity/mmol g ⁻¹	0.54	1	2.4
Thickness/μm	112.5	120	140

Table 2 Volume variation in mm³ for the different membrane samples

Membrane	Water	HCl or NaOH solution concentration/M			Maximum volume variation
		0.1	1	3	
AAV ^a	88.6	88.6	89	90.6	2.25%
ACM ^a	63.7	63.5	63.9	64.4	1.1%
CMV ^b	107	108	108	111	3.7%

^a HCl solution. ^b NaOH solution.

Exchange capacities and volume variations

The exchange capacities of homopolar membranes were determined by acid–base titration.¹¹ Membrane weights were determined with sodium counter ions for the CMV and chloride counter ions for the AAV and the ACM after appropriate conditioning in 0.1 M NaCl, Table 1. The membrane thickness was determined with a micrometer, the membrane being placed between two glass slides. The thickness is obtained from the difference of the two measurements with and without the membrane. The length and width of the membrane samples were measured with an optical micrometer.

Table 2 gives the volume variations from pure water up to 3 M solutions. When soaked in water or solutions, maximum volume variations do not exceed 3.7%. So taking an average volume, supposed to remain constant, volume variations can be considered as experimental errors that do not exceed 2% for the CMV, 1.15% for the AAV and 0.6% for the ACM.

Determination of the sorbed HCl, NaOH and NaCl quantities in AEM and CEM

The AEM equilibrated with Cl⁻ counter ions was immersed for 24 h in HCl at different concentrations. After removal from the equilibrating solutions, the membrane was dried with blotting paper and immersed in stirred bidistilled water for 24 h to desorb. After quantitative analysis the amount of sorbed chloride is divided by the number of fixed sites for comparison purposes with the other membranes.

The same method was used with the CEM, which was equilibrated with Na⁺ counter ions by immersing in NaOH solutions.

The same process was also used with 0.5 M NaCl in which the AEM and CEM membranes were immersed for 24 h.

Resistance measurements

To measure the membrane resistances we have used a polymethacrylate clip cell. The membrane was pressed between two platinum electrodes (covered with black platinum), which were separated from the membrane by a small cylindrical volume of solution.

The surface of the disk electrodes and of the measured membrane was 1 cm². The resistance of the membrane is the difference between the measurements with and without the membrane. After 24 h of conditioning in a solution, the electric resistance was measured at 25 °C with a Tacussel CD60 conductimeter at 1000 Hz.¹²

Results and Discussion

Figures showing current efficiencies or fluxes are concerned with ion transfer into compartment III for HCl or compartment IV for NaOH. The amount of transferred ions was calculated from concentrations and volume measurements.

The influence of initial HCl and NaOH concentrations on current efficiency

The experiments were performed for 4 h with a current density of 40 mA cm^{-2} using initial concentrations of 0.1, 0.5, 1 and 1.5 M for HCl and NaOH and 0.5 M for NaCl.

Fig. 2 shows the decreasing current efficiencies with the two AEM membranes for acid as well as for base regeneration as the initial concentrations increase. This is a limiting phenomenon because high concentrations are difficult to reach with satisfactory current efficiency. This limiting effect can be attributed to the low selectivities of the AEM, CEM and BPM that decrease with increasing HCl and NaOH concentrations, which increases the proton and hydroxide ion leakages.

This figure also shows that the current efficiency is higher for NaOH than for HCl. This phenomenon is due to the proton leakage through the AEM, which is as expected more important than the OH^- leakage through the CEM.¹³

Influence of current density on ED efficiency

In order to evaluate the influence of the current density on the ED efficiency, HCl and NaOH were regenerated from initial concentrations of 0.1 and 0.5 M NaCl by using three current densities: 40, 80 and 120 mA cm^{-2} . All experiments were performed for 3 h.

Fig. 3 shows current efficiencies *vs.* current densities. With higher current densities, concentrations increase more rapidly, which induces increasing co-ion leakage and diffusion of HCl and NaOH through the BPM and proton leakage through the AEM. These three factors explain the decreasing current efficiency with increasing current densities between 40– 120 mA cm^{-2} .

Sodium and chloride leakage through the bipolar membrane

Fig. 4 shows the variations of the transfer current efficiency of Na^+ and Cl^- through the WSI bipolar membrane *vs.* HCl or NaOH concentrations. Co-ion leakage through the BPM will limit the current efficiencies for the production of protons and hydroxide ions by this membrane. The current efficiency for Cl^- reaches a value of 1.4% when the HCl or NaOH concentration is 1.5 M. The current efficiency for Na^+ is always lower than 0.2%.

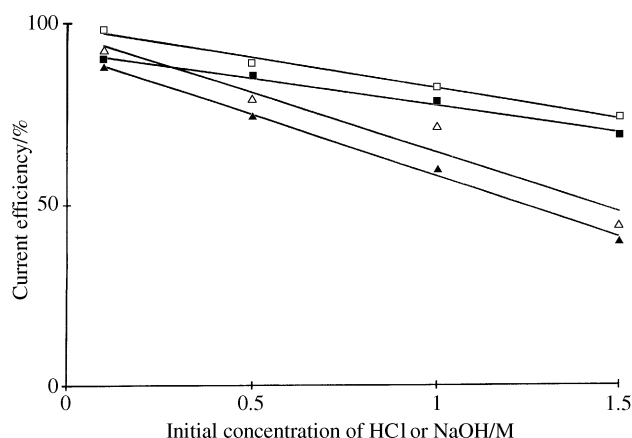


Fig. 2 Current efficiency *vs.* initial concentration of HCl and NaOH at $I = 40 \text{ mA cm}^{-2}$. (■) NaOH and (▲) HCl for AAV; (□) NaOH and (△) HCl for ACM

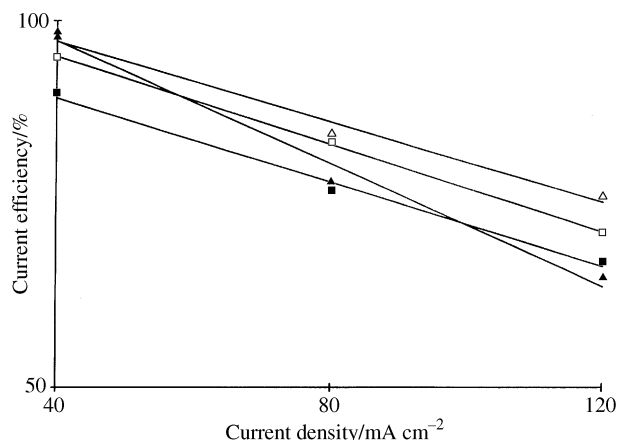


Fig. 3 Influence of current density on current efficiencies at constant initial concentrations (0.1 M HCl and NaOH). (■) NaOH and (▲) HCl for AAV; (□) NaOH and (△) HCl for ACM

tration is 1.5 M. The current efficiency for Na^+ is always lower than 0.2%.

HCl and NaOH diffusion through the bipolar membrane at zero current

Diffusion fluxes through the bipolar membrane were determined between different initial concentrations of HCl in compartment III and water in compartment IV and then different initial concentrations of NaOH in compartment IV and water in compartment III. Table 3 gives the increasing concentrations of HCl and NaOH in compartments III and IV from an initial concentration of 2 M.

Fig. 4 shows the increasing diffusion flux as the initial concentrations of HCl and NaOH increase. These flux measurements were performed during the steady state at zero current density. It can be noted that HCl diffusion through the bipolar membrane is more important than that of NaOH.

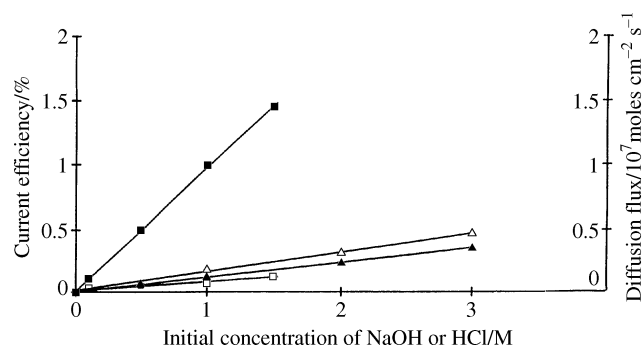


Fig. 4 WSI current efficiency of Na^+ and Cl^- transport with a 40 mA cm^{-2} current density and the HCl and NaOH diffusion fluxes *vs.* initial concentrations of HCl or NaOH. (■) Current efficiency of sodium leakage. (□) Current efficiency of chloride leakage. (▲) Diffusion flux of NaOH. (△) Diffusion flux of HCl

Table 3 Increasing concentrations of HCl and NaOH in compartments III and IV during diffusion. In both cases the concentration gradient is 2 M

Diffusion time/h	1	2	3	4
[HCl]/mmol L ⁻¹	14	28	42	56
[NaOH]/mmol L ⁻¹	10	20	31	41

By applying Fick's law to calculate the diffusion coefficients, for a membrane thickness d of 1.1×10^{-2} cm one obtains $\bar{D}_{\text{HCl}} = 1.79 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $\bar{D}_{\text{NaOH}} = 1.32 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. The diffusion process of these electrolytes can be considered as limiting factors to obtain higher concentrations for acid and base.

Sorption and conductivity measurements

Fig. 5 gives the number of sorbed molecules for every site in the AAV and ACM membranes after equilibrating in different HCl solutions and in the CMV after equilibrating in NaOH solutions. This figure shows that the AAV membrane sorbs more ions than the ACM membrane. This type of curve, which exhibits an unusual shape, has already been obtained.^{10,14} For Pourcelly and coworkers,¹⁴ the experimental and theoretical curves from the Donnan relation do not present the same type of curvature because the Donnan equation does not take into account the nonhomogeneity of the fixed charge distribution. However, there is good agreement between the experimental values and the Gluekauf equation, which takes into account the nonhomogeneity.

In 0.5 M NaCl solutions, the number of sorbed molecules per fixed site is 0.18 for AAV, 0.05 for ACM and 0.069 for CMV.

From the value of the resistance of the membranes equilibrated with each counter ion in the absence of any sorbed electrolyte (Donnan exclusion), we can deduce, thanks to the Nernst-Einstein relation, the value of the diffusion coefficients for each counter ion in the membrane.¹⁵ Values of 0.7, 1.3 and 0.8 ($10^7 \text{ cm}^2 \text{ s}^{-1}$) are obtained for AAV, ACM and CMV, respectively. Fig. 6 shows the conductance curves *vs.* the number of sorbed HCl molecules per fixed site for the three membranes. As shown in Table 2, in a first approximation the

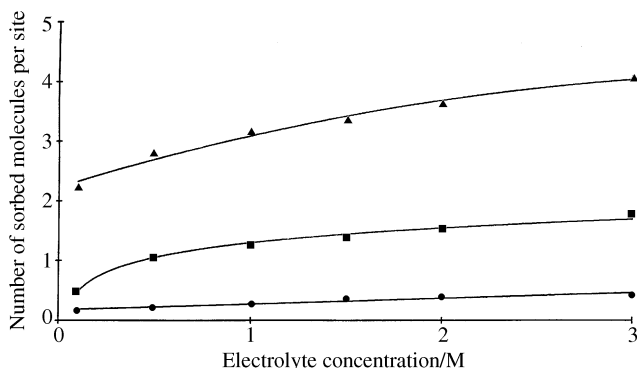


Fig. 5 Number of sorbed molecules per fixed site *vs.* external concentrations of electrolyte (HCl for AAV and ACM and NaOH for CMV). (●) CMV, (▲) AAV, (■) ACM

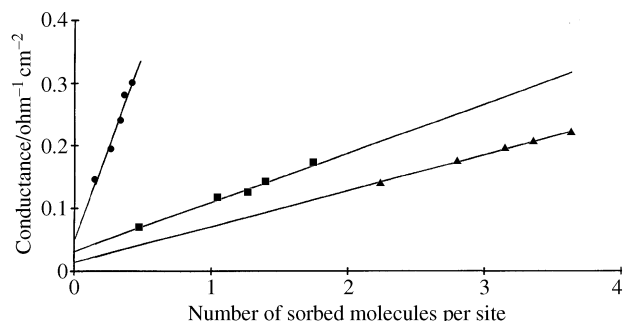


Fig. 6 Conductance variations *vs.* the number of sorbed molecules per fixed site (HCl for AAV and ACM and NaOH for CMV). (●) CMV, (▲) AAV, (■) ACM

volume variations of the membrane between water and 3 M solutions can be neglected. We are thus allowed to extrapolate conductance curves from concentrated solution to infinite dilution through the least squares method. Correlation coefficient values range from 0.99 to 0.997. From the slope and the intercept of these straight lines, the proton-to-chloride mobility ratio (and consequently the proton diffusion over the chloride diffusion coefficient ratio) were obtained.¹⁰

The Nernst-Planck equations applied to transport processes

From the Nernst-Planck equations,¹⁶ the ion electroneutrality equation (obtained by summing all the positive and negative charges in the membrane) and taking into account that in our system the current density is related to the proton and chloride fluxes, one obtains the chloride flux relation:

$$-J_{\text{Cl}^-} = \frac{-2\bar{D}_{\text{Cl}^-}}{d(1 + \bar{D}_{\text{Cl}^-}/\bar{D}_{\text{H}^+})} ([\text{Cl}^-]^0 - [\text{Cl}^-]^d) + \frac{\bar{D}_{\text{Cl}^-}[\bar{X}]}{d(1 + \bar{D}_{\text{Cl}^-}/\bar{D}_{\text{H}^+})} f(\bar{\Phi}_0 - \bar{\Phi}_d) + \frac{\bar{D}_{\text{Cl}^-}/\bar{D}_{\text{H}^+}}{1 + \bar{D}_{\text{Cl}^-}/\bar{D}_{\text{H}^+}} \frac{I}{F} \quad (2)$$

and the difference potential between the two sides of the membrane:

$$\bar{\Phi}_0 - \bar{\Phi}_d = -I \int_0^d \frac{dx}{fF\{\bar{D}_{\text{H}^+}[\bar{H}^+] + \bar{D}_{\text{Cl}^-}([\bar{X}] + [\bar{H}^+])\}} + \int_{\bar{C}_s(x=0)}^{\bar{C}_s(x=d)} \frac{(\bar{D}_{\text{Cl}^-} - \bar{D}_{\text{H}^+}) d[\bar{H}^+]}{f\{\bar{D}_{\text{H}^+}[\bar{H}^+] + \bar{D}_{\text{Cl}^-}([\bar{X}] + [\bar{H}^+])\}} \quad (3)$$

in which $[\text{H}^+]$ and $[\text{Cl}^-]$ are the concentrations of the respective ions inside the membrane; $\bar{\Phi}$ is the membrane potential, x is the abscissa in the membrane, ($0 < x < d$), d being the thickness of the membrane; $[\bar{X}]$ is the concentration of fixed exchange sites; \bar{D}_{H^+} and \bar{D}_{Cl^-} are the diffusion coefficients of the respective ions in the membrane; $f = F/RT$ in which F is the Faraday constant, R the gas constant and T the absolute temperature; \bar{C}_s is the concentration of the sorbed electrolyte.

By analogy one can write:

$$\bar{\Phi}_0 - \bar{\Phi}_d = IR_M + E_D \quad (4)$$

The first term is the potential difference due to Ohm's law and integrating the second term of eqn (3) allows one to obtain E_D , the diffusion potential.¹⁶ Then it is possible from the experimental values of R_M , concentrations and diffusion coefficients of ions inside the membrane to calculate $\bar{\Phi}_0 - \bar{\Phi}_d$ and J_{Cl^-} . These calculated values will be compared to the experimental values obtained with the following relation:

$$J_{\text{exp}} = \Delta N/St \quad (5)$$

where ΔN is the number of transferred molecules, S is the active surface of the membrane, and t is the time during which the steady state occurs (30 min, the time in which the ion fluxes through the membranes remain constant and the concentrations in compartments I and II are linearly increasing).

The Nernst-Planck equations applied to cation exchange membranes

Again using the Nernst-Planck equations and replacing $[\text{H}^+]$ and $[\text{Cl}^-]$ by $[\text{Na}^+]$ and $[\text{OH}^-]$, respectively, and performing the same calculation we obtain a similar relation for J_{Na^+} and for the diffusion potential.

These equations show that the transference flux of J_{Na^+} depends on the same factors as J_{Cl^-} . Experimental and calculated results are given in Fig. 7. The results obtained after 30 min with a current density of 120 mA cm^{-2} show that the experimental values are always higher than those calculated.

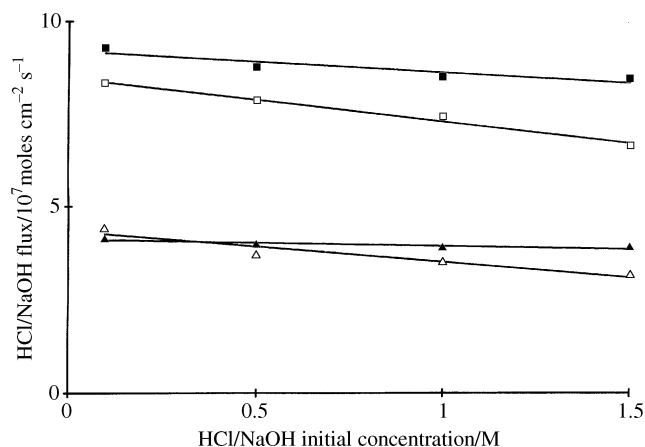


Fig. 7 Calculated and experimental transfer flux variations of HCl through AEM (AAV) and NaOH through CEM with a current density of 120 mA cm^{-2} vs. HCl or NaOH initial concentrations. (■) Experimental and (▲) calculated values through the AAV. (□) Experimental and (△) calculated values through the CMV

Both kinds of values show the same types of variations. The difference between the theoretical and experimental values can be explained because of the preliminary assumptions:

- the membranes were considered as homogeneous gels;
- the diffusion coefficients were assumed to be constant in the membrane;
- the activity coefficients in the membrane were assumed to be equal to one;
- the electrical resistance of the membrane was assumed to be equal to the resistance of the membrane equilibrated in the most conductive solution;
- the Nernst–Planck equation does not take into account the electroosmosis process;
- and the coupling between individual ion fluxes is only expressed by electroneutrality, which is itself an assumption due to neglect of Poisson's law.

Electrodialysis application to Hamraya rock salts

The results obtained with trade or laboratory salts have enabled us to perform BPM electrodialysis experiments by using natural salts from Hamraya, Southern Algeria, after filtering to eliminate insoluble components. The chemical analysis of this salt gives: 59.2% chloride, 38.7% sodium, 0.16% calcium, 0.06% magnesium, 0% potassium and 0.78% sulfates. Table 4 gives the compositions of the solutions obtained (HCl and NaOH) with the two anion exchange membranes.

From the initial concentrations of 0.1 M for HCl and NaOH and 58.5 g l^{-1} for the rock salt, under a current density of 80 mA cm^{-2} , concentrations of about 1.5 M were reached after 6 h of electrodialysis. After 6 h the current efficiency for HCl production is 65% with the ACM and 60% with the AAV. For NaOH production, the current efficiency is

Table 4 Composition of the final acid and base solutions obtained with the AAV and ACM membranes^a

Membrane	Product	$\text{Cl}^-/\text{mg L}^{-1}$	$\text{Na}^+/\text{mg L}^{-1}$	$\text{SO}_4^{2-}/\text{mg L}^{-1}$
AAV	1.42 M HCl	504 10	12	2.2
	1.57 M NaOH	23	361 10	0
ACM	1.5 M HCl	532 50	12	2.5
	1.66 M NaOH	25	381 80	0

^a The Ca^{2+} and Mg^{2+} concentrations were found to be 0 mg L^{-1} in all cases.

63% with the ACM and 58% with the AAV. The average voltage is about 45 V when using the ACM and 63 V with the AAV. The energy consumption is lower with the ACM than with the AAV.

The compositions of the solutions obtained show the high quality of the HCl and NaOH final solutions. Only 12 ppm of sodium appear in the HCl solution because of diffusing Na^+ crossing over the AEM and about 25 ppm of chloride appear in the NaOH solution because of diffusing Cl^- crossing the CEM. The small percentages of alkaline earth cations did not hinder the production process. However in the case of an industrial production it is necessary to envisage a pretreatment of the brines in order to eliminate all the ions that may precipitate.¹⁷

Conclusion

This work shows that it is possible to produce HCl and NaOH simultaneously without any pollution, the main limit of this process being the low selectivity of the membranes at high concentrations. Two AEM membranes (AAV and ACM) with low proton leakages have been tested. The AAV membrane shows a lower current efficiency than the ACM membrane. Applying this process to the Algerian rock salt of Hamraya gives, for this type of laboratory cell, satisfying results with a 60–65% current efficiency, as well as in the quality of the products obtained. Moreover, this process avoids the evolution of highly corrosive gaseous chlorine. In this batch process the concentrations of HCl and NaOH were limited to a maximum of 1.5 M because of the decrease in permselectivity of the membranes at high acid or base concentrations. A continuous process with several cells assembled in a stack between two electrodes should enable one to reach higher concentrations.

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