# Generation of sulfuric acid and sodium hydroxide from the sodium sulphate salt by electro-electrodialysis (EED)

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**Abstract:** The electro-electrodialysis process (EED) is used to generate $H_2SO_4$ and NaOH from sulphate sodium salt $Na_2SO_4$. The key phenomenon limiting the current efficiency of this process is the proton leakage through the anion selective membrane was not observed. The electro-electrodialysis was carried out with a three-compartment cell with two platinum-coated titanium electrodes separated by three compartments. The couple membrane used in this work is AFN and CMX. The experiments were carried out for four current densities 8.33 mA.cm$^{-2}$ 11.11mA.cm$^{-2}$, 13.88mA.cm$^{-2}$ and 27.77 mA.cm$^{-2}$. For each current density, a voltage variation of cell and concentrations of $H_2SO_4$ and NaOH in the two compartments with the current density was used. The concentration of $H_2SO_4$ and NaOH increases with current density and with time, but higher for NaOH. The current efficiency increases with the current applied to the cell. The request for the electro-electrodialysis operation power was calculated in terms of the electrical energy consumed to produce $H_2SO_4$ and NaOH for 6 hours of electro-electrodialysis and it was found floating with the current applied and concentration sodium sulphate used and the concentration of $H_2SO_4$ and NaOH products, but is comparable for both initial concentrations of sodium sulfate.

**Keywords:** Electro-Electrodialysis, Sodium Sulphate, Sulfuric Acid, Sodium Hydroxide

## 1. Introduction

One of the main applications of ion exchange membranes is electrodialysis and its various amendments. One possible application is the concentration and / or recovery of acids or their separation. Must include an attempt to separate the strong acids (sulfuric acid from nitric acid) and separation of weak organic acids (acetate, formic acid, lactic acid and succinic acid) on the basis of the differences dissociation constants [1]. The aim of this work is to use the electro-electrodialysis (EED) [2] to obtain NaOH and $H_2SO_4$ from the salt sodium sulphate. The electro-electrodialysis process can be conducted with different types of cells. Generally the electro-electrodialysis cells (EED) consist of two compartments, separated by three or four of the anion exchange membranes (AFN) or cation exchange (CMX). In this case to produce sodium hydroxide and sulfuric acid from solution of $Na_2SO_4$ three compartments are used (Fig.1). EED is an electro-membrane technique that is easy to use and clean. The compartments are separated by ion exchange polymer membranes and electrodes are chemically passive. The most important limiting phenomenon is the proton leakage through anion exchange membranes. This present work is done by AFN and CMX (both manufactured by Tokuyama Soda, Japan). Due to the low selectivity of conventional anion exchange membranes due to proton leakage, electro-electrodialysis has rarely been used in industry for the production of acid and base. In this work the main objective is to study the influence of physico-chemical parameters (the initial concentration and the current density) on the production of acid and base. The sodium sulphate salt was used in the electro-electrodialysis wherein protons and hydroxide ions are generated at the electrodes.

## 2. Methods and Materials

### 2.1. Electro-Electrodialysis Cell

To produce $H_2SO_4$ and NaOH simultaneously the cell consists of three compartments separated alternately by an

anion exchange membrane and a cation exchange membrane (Fig. 1). The three compartments are filled with different solutions: sodium hydroxide in the compartment I, sodium sulphate in the compartment II and sulfuric acid in the compartment III. The initial volumes are 500mL for the three compartments. The flow in the compartments I and III is $65 dm^3.h^{-1}$ and $73 dm^3.h^{-1}$. The experiments were performed at two initial concentrations of sodium sulphate (100g / l and 150g / l). The initial concentration of 0.01M for the compartments I and III.
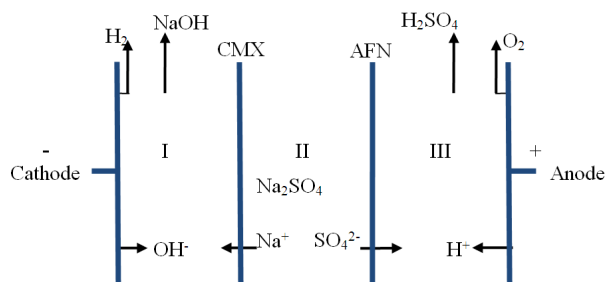


**Figure 1.** *Three compartments electro-electrodialysis to produce $H_2SO_4$ and NaOH*

A report that no significant volume change was detected in the three compartments. The flow solutions in the three compartments were produced by three peristaltic pumps ASTI. Beaker, used as a reservoir, was included in the loop of each compartment. Production of NaOH and $H_2SO_4$ from $Na_2SO_4$ was performed in batch system using an electro-electrodialysis cell. The electric current is applied through two platinized titanium electrodes connected to a generator type P. FONTAINE with varied electrical potential. The current and voltage were measured by two multimeters Metrix kind. The electro-electrodialysis cell (EED) consists of two platinized titanium electrodes separated by three compartments. The active surface of the membrane separating the compartments is of $36 cm^2$. Rubber seals between the compartments help prevent leaks. The intermembrane distance is 10mm, Chemical reagents used $Na_2SO_4$, $H_2SO_4$ and NaOH are laboratory quality. $Na_2SO_4$ salt is dissolved in distilled water before being introduced into the electro-electrodialysis cell water. Changes in concentration of $H_2SO_4$ and NaOH were followed by acid-base titration. From the solution of $Na_2SO_4$ (Compartment II) cations $Na^+$ migrate through the cation exchange membrane (CMX) to the catholyte compartment to form sodium hydroxide solution with the hydroxide ions which comes from the reduction of water to the cathode (Compartment I). The Sulphates which comes from the solution of $Na_2SO_4$ (Compartment II) migrate through the anion exchange membrane (AFN) to the anolyte compartment to form the solution of $H_2SO_4$ with the proton $H^+$ which comes from the oxidation of water to the anode (compartment III). Therefore the concentrations of NaOH and $H_2SO_4$ increase while the concentration of $Na_2SO_4$ decreases (measured by the decrease in conductivity of the solution of $Na_2SO_4$ (Compartment II).

The average current efficiency for the compartments I and III for the generation of $H_2SO_4$ and NaOH was calculated using the equation:

$$C_{eff} = \frac{\Delta M F}{Q} \qquad (1)$$

Where $\Delta M$ is the increasing amount of moles in compartments I and III.

$$\Delta M = (C_f - C_i) V_{sol} \qquad (2)$$

$C_f$ is the final concentration of the anolyte / catholyte, $C_i$ is the initial concentration of the anolyte / catholyte and $V_{sol}$ the volume of the anolyte / catholyte, F is the Faraday constant (equal to 96485.34 C / mol), and Q is the total charge (in Coulombs). The total charge passed during the electro-electrodialysis can be calculated as follows:

$$Q = \int I dt \qquad (3)$$

Where I is current, and t the time of the electro-electrodialysis.

### 2.2. Membrane Stabilizing

Before using the membranes, they were subjected to a pretreatment for conditioning. AFN membrane was immersed in a solution of 1M $H_2SO_4$ for 1 hour and rinsed with distilled water. Then the CMX membrane was immersed in a solution of 1M NaOH for 1 h. Then the two membranes were immersed in a solution of 0.1M $Na_2SO_4$.

### 2.3. Characteristics of Membranes

The characteristics of the ion exchange membranes AFN and CMX used in this work are given in Table 1, these characteristics are provided by Tokuyama Soda, Japan.

**Table 1.** *Characteristics of membranes CMX and AFN*

| Membrane type | CMX | AFN |
|---|---|---|
| Character conferred on the membrane | Strong acid | Strong base |
| Electrical resistance /$\Omega.cm^2$ | 2.5-3.5 | 0.4-1.5 |
| Transport number | 0.98 | 0. 98 |
| Exchange capacity /méq. g$^{-1}$ | 1.7 | 2.75 |
| Thickness /mm | 0.18 | 0.18 |

# 3. Results and discussion

### 3.1. Influence of Current Density on the Effectiveness of Electro-Electrodialysis (EED)

To assess the effectiveness of the influence of current density on the efficiency of electro-electrodialysis (EED), H2SO4 and NaOH were regenerated from solutions of initial concentration 100g/l and 150g/l corresponding to 1.05M and 0.7M of $Na_2SO_4$, using four current densities: 8.33, 11.11, 13.88 and 27.77 mA.cm$^{-2}$. All experiments were carried out for 360 min. Figures 2 (a) and 2 (b) give for the pair of membrane CMX AFN the current efficiency against current density.
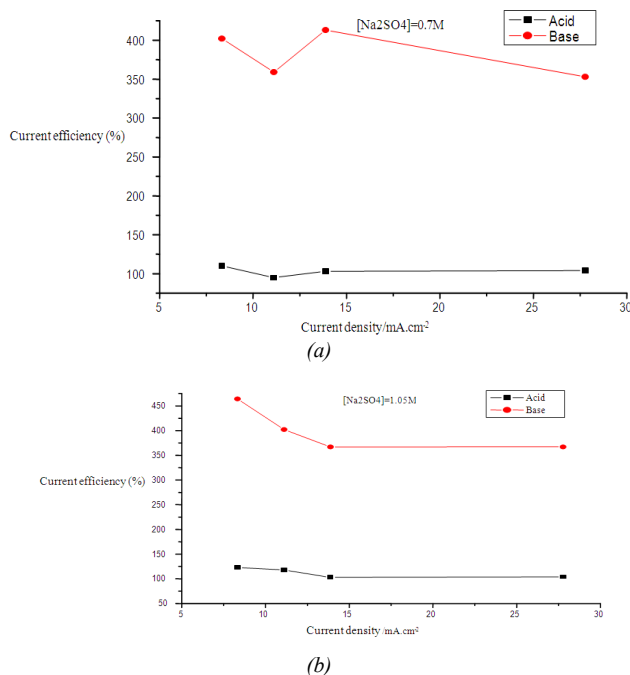
*(a)*


*(b)*

**Figure 2.** *Influence of current density on the current efficiency at the initial concentration (0.01M) for the acid and base*

The production of NaOH is generally higher than that of H$_2$SO$_4$. This difference may be explained by the fact that the number of transport of sodium ion in the CMX membrane is greater than that of the sulfate ion in the membrane AFN. In this experimental range of current densities, the current efficiency decreases gradually until the current density of 13.88 mA.cm-2 and then remains practically constant and this is more remarkable when the initial concentration of sodium sulfate increases.

### 3.2. Influence of Current Density on the Production of H$_2$SO$_4$ and Naoh

Figures 3 (a) and 3 (b) show the relationship between the production of NaOH and H$_2$SO$_4$ and the current density applied in the electro-electrodialysis (EED) for both initial concentrations of sodium sulphate operation.

In the experimental range of current density, the concentration of NaOH and H$_2$SO$_4$ generally follows a linear growth and this is especially remarkable for NaOH. These two figures also show that increasing the current density leads to an increase in concentration of NaOH and H$_2$SO$_4$ but this increase is not very significant. The concentration of NaOH is higher than that of H2SO4 for both initial concentrations of Na$_2$SO$_4$; this can be explained by the leakage of hydroxide ion through the membrane CMX.

### 3.3. Cell Voltage

Figures 4 (a) and 4 (b) show the relationship between the cell voltage, current density and time of the operation of electro-electrodialysis (EED) to 300K temperature of solutions of the three compartments.
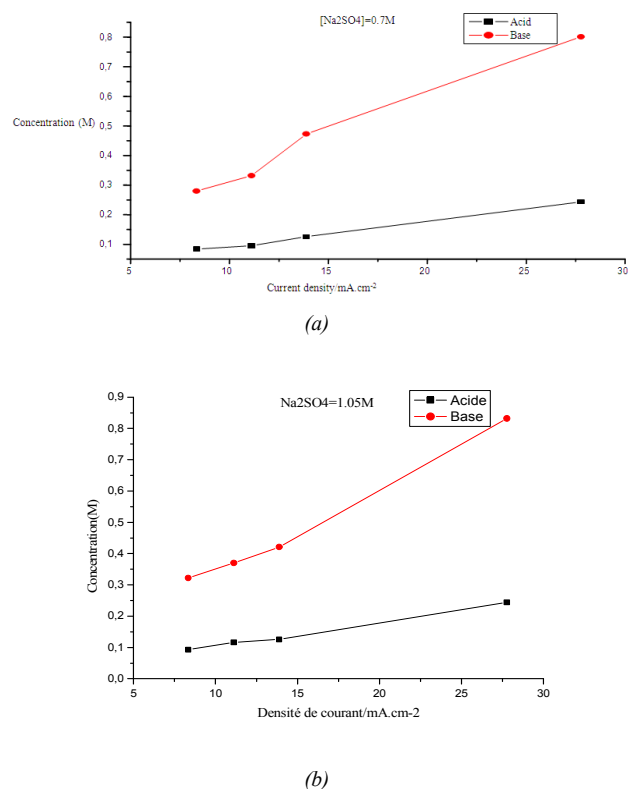

*(a)*


*(b)*

**Figure 3.** *Influence of current density on the production of H$_2$SO$_4$ and NaOH*

In the results of the electro-electrodialysis operation, the voltage of the cell decreases rapidly for 60 minutes for four applied current densities, the concentration of the catholyte and anolyte changed by electro-electrodialysis and the difference concentration between anolyte and catholyte and the reduction of the electrical conductivity of Na$_2$SO$_4$ solution led to a decrease in the cell voltage. For 6 hours of the electro-electrodialysis and initial concentrations of both sodium sulphate operation, the cell voltage decreased progressively after 60 min as shown in Figures 4 (a) and 4 (b). The difference between the cell voltages for the four current densities and for two concentrations of sodium sulphate is not very significant, which means that the initial concentration of sodium sulphate does not have a great effect on the voltage cell and this in the range of concentration of sodium sulphate studied. The electrical energy required is simply calculated by the following equation [3]:

$$W = \Sigma \ (VIt) \qquad (4)$$

Where W is electric power, the voltage V, the electric current I and time t.

Energy demand calculated for the electro-electrodialysis is shown in Tables 2 and 3:
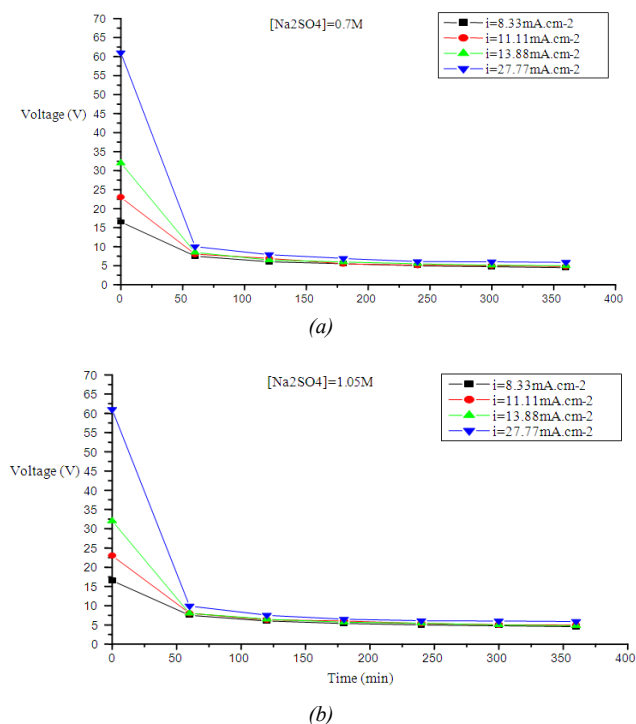
*(a)*



*(b)*

**Figure 4.** *Relationship between the current density, the cell voltage and the operation time of EED*

**Table 2.** *Electrical energy required for the electro-electrodialysis [Na$_2$SO$_4$] =0.7 M*

| Parameters | [Na$_2$SO$_4$] 0.7 M | | | |
|---|---|---|---|---|
| Current density/mA.cm$^{-2}$ | 8.33 | 11.11 | 13.88 | 27.77 |
| [Acid]/ M | 0.084 | 0.095 | 0.126 | 0.243 |
| [Base]/ M | 0.280 | 0.262 | 0.473 | 0.801 |
| Electrical energy required /KJ | 120.424 | 169.281 | 220.408 | 515.041 |

**Table 3.** *Electrical energy required for the electro-electrodialysis [Na$_2$SO$_4$]=1.05 M*

| Parameters | [Na$_2$SO$_4$] 1.05 M | | | |
|---|---|---|---|---|
| Current density /mA.cm$^{-2}$ | 8.33 | 11.11 | 13.88 | 27.77 |
| [Acid]/M | 0.093 | 0.116 | 0.126 | 0.244 |
| [Base]/M | 0.322 | 0.37 | 0.421 | 0.832 |
| Electrical energy required /KJ | 120.586 | 173.478 | 214.216 | 506.581 |

Tables 2 and 3 give the electrical energy required for the production of H$_2$SO$_4$ and NaOH from Na$_2$SO$_4$ salt by electro-electrodialysis for 6 hours of operation for the four current densities and for both initial concentrations of sodium sulphate, the cell voltage is high at the beginning of the operation of electro-electrodialysis when increasing the current applied to the cell of EED and gradually decrease during the elec-electrodialysis time (6 hours) and remains substantially the same for the applied current and in the range of concentration of sodium sulphate studied. Electrical energy required in the electro-electrodialysis operation for both initial concentrations of sodium sulphate is comparable. The power increases with the applied current.

## 3. Conclusion

This work shows that it is possible to simultaneously produce NaOH and H$_2$SO$_4$ at laboratory scale. The main limitation of this process is the proton leakage which is not achieved under the conditions of this work.

In the range of current densities chosen and for the time of operation of electro-electrodialysis of 6 hours, the concentration of H$_2$SO$_4$ and NaOH increases gradually to approximately and respectively 0.20M and 0.80M for both initial concentrations of sodium sulphate and for the current density of 27.77 mA.cm$^{-2}$ because of the low selectivity of membranes for acid and base. The concentration of the base is greater than the acid concentration in the range of current densities studied.

It is possible to envisage an industrial use of ion exchange membranes with adequate industrial cells to reach a high production capacity of acid and base. These membranes can be useful to recycle salts.

## References

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