



Ions transfer modeling through monopolar and bipolar membranes: Treatment of wastewater containing ammonium nitrate by electrodialysis

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Abstract: In this study, a mathematical model is proposed to illustrate the different transport modes contributing to the transfer of all involved species through anion, cation and bipolar membranes. This study was carried out on wastewater containing ammonium nitrate treated by bipolar membrane electro dialysis (BPMED). Different species are involved in this electro dialysis, namely ammonium ions NH_4^+ , nitrates NO_3^- , ammoniac NH_3 , water H_2O and protons H^+ . Calculations made with the material balance sheets equations obtained in batch mode, allowed to validate the proposed transfer model and to check the balance sheets material on all involved species during electro dialysis.

Keywords: Bipolar membrane electro dialysis; material balance sheets; ions and water transfer.

Introduction

The nuclear fuel processing industry generates large volumes of wastewater containing ammonium nitrate. This wastewater is produced during the conversion of uranyl nitrate into uranium oxide. A precipitation of ammonium diuranate by the addition of ammonia is performed during this process. Thus, ammonium nitrate is produced at a concentration of around 1 or 2 mol L^{-1} . Due to the presence of uranium traces, ammonium nitrate solutions are not suitable for agricultural fertilizer production. For economic and environmental reasons, the splitting of ammonium nitrate to ammonia and nitric acid is advantageous. These products may be recycled in an upstream process (ammonia) or reused elsewhere after further concentration by evaporation (nitric acid).

Membrane electro dialysis^{1,2} and bipolar membrane electro dialysis (BPMED)^{3,4} were used to treat solutions containing ammonium nitrate. BPMED has been investigated in many studies^{5,6}. The principle of this operation lies in the use of bipolar membrane where water splitting to H^+ and OH^- is performed. The

bipolar membrane is associated to a homopolar ion-exchange membrane to produce acid and base from salt. Figure 1 illustrates the principle of operation. A three-compartment cell is used. The bipolar membrane is associated to an anion-exchange membrane and cation-exchange membrane. The salt solution containing NH_4NO_3 is fed into the central compartment between the two homopolar membranes. Nitrate ion NO_3^- migrates through the anion exchange membrane and enters the acid compartment to generate nitric acid with proton production by the bipolar membranes. On the other side, ammonium ion NH_4^+ migrates through the cation-exchange membrane to the base compartment to generate ammonia with the hydroxide ion produced by the bipolar membrane.

In this paper, a study has been carried out on the transfer of the different species involved in the treatment of wastewater containing ammonium. These species include ammonium ions NH_4^+ , nitrates NO_3^- , ammoniac NH_3 , water H_2O and protons H^+ . For that purpose, material balance sheets equations, obtained in batch mode, will be checked on all involved species during electro dialysis.

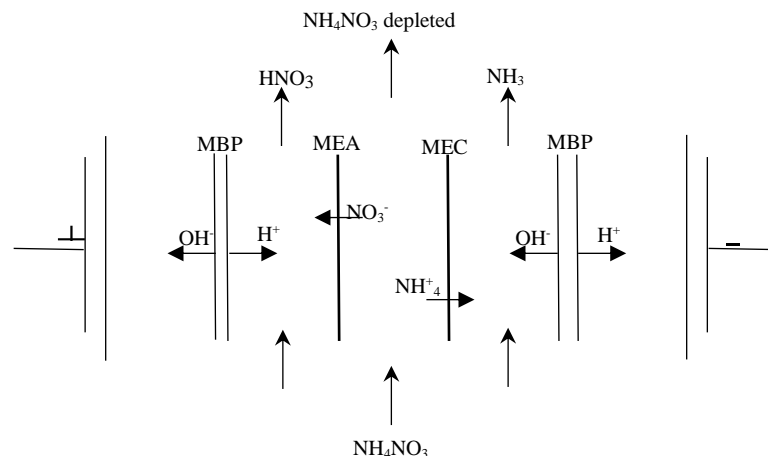


Figure 1. Principle of ammonium nitrate splitting by bipolar membrane electrodesis

Membranes

A membrane is a selective barrier separating two phases. Under a driving force and depending on their properties, some components could cross the membrane, and others are rejected. When an electrical current is applied as a driving force, selective membranes separate ions into two species: anions and cations.

Ions exchange membranes

Homopolar membrane consists of a set of macromolecular chains containing ion exchange sites. Placed in solution, the membrane behaves as a polyelectrolyte. Cation exchange membranes (CEM) are consisted of positive charged sites, and anions exchange membranes (AEM) are consisted of negative charged sites⁷.

Table 1. Illustrates the most useful ionic functional fixed sites in ions exchange membranes.

Membrane	Ionic functional fixed sites	Membrane character	
		Acid	Basic
CEM	Sulfonic: $-\text{SO}_3^-$	++	
	Carboxylic: $-\text{COO}^-$	+	
AEM	Quaternary alkyl ammonium: $-\text{NR}_3$		++
	Tertiary alkyl ammonium: $-\text{NR}_2^+$		+
	Secondary alkyl ammonium: $-\text{NH}_2\text{R}^+$		+
	Vinylpyridium: $-\text{C}_5\text{H}_4\text{NH}^+$		+

Ionic functional fixed sites used in ions exchange membranes (++: strong acid or strong base, +: weak acid or weak base).

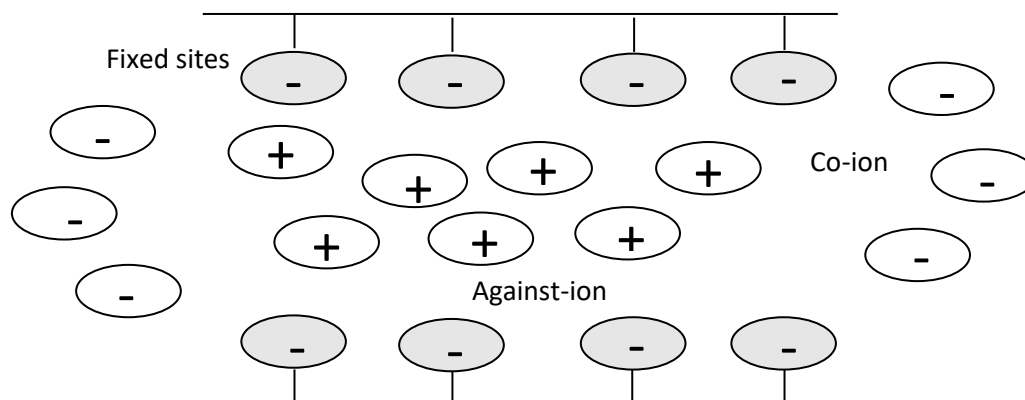


Figure 2. Schema of cation exchange membrane

Bipolar membranes

A bipolar membrane is a juxtaposition of anion and cation exchange membranes. Under an electrical current, the water contained in the bipolar membrane and coming from adjacent compartments is split into

proton H^+ and hydroxyl OH^- . The obtained products are then transported through each membrane layer towards the corresponding solutions in the adjacent compartments.

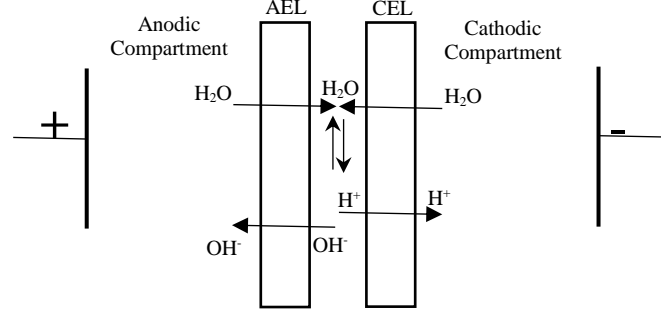


Figure 3. Principle of water splitting in a bipolar membrane

Modelling of species transfer

The molar flow is defined as a quantity of species transferred by unit of time and by unit area ($mol \cdot m^{-2} \cdot s^{-1}$):

$$N_i = \frac{1}{S} \cdot q_i \cdot C_i = U_i C_i \quad (3.1)$$

q_i : a species volumetric flow ($m^3 \cdot s^{-1}$)
 C_i : concentration ($mol \cdot m^{-3}$)
 U_i : speed ($m \cdot s^{-1}$)
 S : considered area (m^2)

The individual speed (U_i) of species i , is difficult to determine. The global average volumetric flow \bar{q} of the fluid is the only greatness accessible to the experiment (and thus the average speed \bar{U})

$$\bar{q} = \frac{\sum q_i C_i}{\sum C_i} \quad (3.2)$$

Yet

$$\bar{U} = \frac{\sum U_i C_i}{\sum C_i} \quad (3.3)$$

-Flow J_i modelisation

In most cases, and by some approximations, the flow expression J_i most used in diluted electrolytic solutions is expressed by:

$$J_i = -\frac{D_i C_i}{RT} \text{grad} \mu_i \quad (3.8)$$

Where

C_i : species concentration ($mol \cdot l^{-1}$)
 D_i : species diffusion coefficient ($m^2 \cdot s^{-1}$)
 μ_i : Electrochemical potential (V)

Because

$$\mu_i = \mu_i^0 + RT \ln(a_i) + z_i F \phi_S \quad (3.9)$$

The average molar flow is defined as:

$$\bar{N}_i = \bar{U} \cdot C_i \quad (3.4)$$

\bar{N}_i corresponds to the quantity of the species i transported by the global movement of the electrolytic solution. This transport is due to convection contribution (natural or forced).

The flow J_i defined as:

$$J_i = N_i - \bar{N}_i = (U_i - \bar{U}) C_i$$

J_i corresponds to all transport mechanisms contribution, except convection. This is an intrinsic characteristic of species contained in electrolytic solutions under applied electrical current.

We note that:

$$\sum J_i = 0 \quad (3.6)$$

Indeed,

$$\sum J_i = \sum (N_i - \bar{N}_i) = \sum U_i C_i - \sum \bar{U}_i C_i = \sum U_i C_i - \bar{U} \sum C_i = 0 \quad (3.7)$$

We deduce

$$J_i = -D_i C_i \text{grad}(\ln a_i) - \frac{D_i C_i}{RT} z_i F \text{grad} \phi_S \quad (3.10)$$

The first term corresponds to the diffusional contribution (molecular or turbulent) under the gradient of concentration. The second translates the contribution of the ionic migration of species under electrical current.

Finally, the flow N_i is expressed by:

$$N_i = -D_i C_i \text{grad}(\ln a_i) - \frac{D_i C_i}{RT} z_i F \text{grad} \theta_S + \bar{U} C_i \quad (3.11)$$

Diffusion Ionic Migration Convection

Remarks

1- The diffusion coefficient D_i depends on the absolute mobility m_{i0} ($\text{m}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) by the Stokes-Einstein relation de ⁸.

$$D_i = R \cdot T \cdot m_{i0} \quad (3.12)$$

In diluted electrolytic solutions, the activity a_i is confused with concentration C_i .

The flow is expressed: $(J_i)_{\text{diff}} = -D_i \text{grad } C_i$

When the electrolytic solution is hydrodynamically stagnant or in laminar flow, the diffusion is molecular and governed by the Fick law. The diffusion coefficient D_i depends only on the system (nature of species, temperature and pressure).

In turbulent flow, the diffusion coefficient D_i depends especially on hydrodynamics.

3- The migration ionic flow, under electrical current, is expressed:

$$(J_i)_{\text{migr}} = -D_i \frac{C_i}{RT} z_i F \text{grad } \phi \quad (3.14)$$

The current density J is defined by:

$$J = F \sum z_i J_i \quad (3.15)$$

Yet,

$$J = -F^2 \left(\sum \frac{D_i}{RT} C_i (z_i)^2 \right) \text{grad } \phi \quad (3.16)$$

$$J = -k \text{grad } \phi \quad (3.17)$$

Where

$k = F^2 \left(\sum \frac{D_i}{RT} C_i (z_i)^2 \right)$ is the conductivity of the electrolytic solution, depending on ionic the mobility (m_{i0}) of species?

Water transfer through membranes

Osmosis appears when there is a difference of concentration between two solutions separated by a membrane. A transfer of water, from a diluted compartment to a concentrated one, is then observed. This transfer tends to cancel out the osmotic pressure difference. In electrodialysis, this effect tends to limit the concentration of the solution.

However, in electrodialysis, the water transfer is mainly due to the migration through ion exchange membranes. This is called electro-osmosis. When an ion crosses a membrane under an electrical current, it takes a quantity of the solvent. It means that it is impossible to obtain an ionic solution concentration superior than the ionic species concentration in the solvation process during their migration.

To quantify the water accompanying an ion during its migration through a membrane, we define the water transport number of ion. When this ion crosses the membrane alone, its water transport number is expressed in the following way⁹:

2- Diffusional contribution $(J_i)_{\text{diff}}$ is expressed:

$$(J_i)_{\text{diff}} = -D_i C_i \text{grad}(\ln a_i) \quad (3.13)$$

$$t_{\text{H}_2\text{O}} = \frac{\Delta V \cdot \rho}{n_i \cdot M_{\text{H}_2\text{O}}} \quad (4.18)$$

Where:

ΔV : volume variation of the solution to which the ionic species migrates (l)

$M_{\text{H}_2\text{O}}$: water molar mass ($\text{Kg} \cdot \text{mol}^{-1}$)

n_i : mole number of the species transferred

This number varies according to the ionic species nature and depends on the ion membrane exchange used. Okada et al⁹ showed that for a cation exchange membrane Nafion 350, the water transport number is equal to 7 for the ammonium ion (NH_4^+). On the other side, Robbins et al¹⁰ showed that for an anion exchange membrane AW, the water transport number is equal to 3.5 for one nitrate ion (NO_3^-) and 1 for one transferred proton H^+ .

Generally, the cation water transport number is superior than the anion water transport number¹¹. Gieneeste¹² showed that, in NaCl solution concentrated to 3.5 mol L^{-1} , the water transport number for Na^+ is equal to 3 and equal to 1 for Cl^- ion.

Experimental validation: treatment of wastewater containing ammonium nitrate by bipolar membrane electro dialysis

Ion-exchange membranes

The membranes used are listed below:

- Bipolar membrane: BP1 (Tokuyama Soda)
- Cation-exchange membrane: CMB (Tokuyama Soda),
- Anion-exchange membrane: AW (Solvay)

The electrochemical cell stacks

The cell stack supplied by Eurodia Industrie (Wissous, France) was used with four cells. Active area was 200 cm^2 per cell. Solutions were continuously pumped from recirculation tanks through the cell compartments. Each compartment width was about 0.8 mm and the flow rate was about 20 Lh^{-1} per cell (liquid velocity $\sim 6 \text{ cm s}^{-1}$). Manometers placed at the cell inlet of each circuit provided the information required to properly control the working pressure. The adjustment of pressure in the different compartments to the same value was achieved by varying the flow rate of solutions and by means of the pressure valve in the base circuit.

Operating conditions

Relatively high solution conductivity is required to operate at usual current densities and under reasonable voltage.

The experiments were achieved under the following conditions, named “standard conditions”; otherwise, any nonstandard parameter is specified:

- Acid circuit: nitric acid $\approx 1 \text{ mol L}^{-1}$;
- Salt solution: NH_4NO_3 2 mol L^{-1} acidified to $\text{pH} < 3$ (this is necessary to avoid blocking the anion exchange membrane).

- Base circuit: NH_3 and NaOH 1 mol L^{-1} each (the ammonia concentration in the base circuit was equal to the equilibrium value in the stripping conditions, for

example $[\text{NH}_3] = 1 \text{ mol L}^{-1}$ for 14.5 kPa, 45 C° and $[\text{NaOH}] = 1 \text{ mol L}^{-1}$);

- The starting volume of each solution is about 2 L;
- The current density is held constant at 500 A m^{-2} .

Batch operation were carried out. Acid and ammonia concentrations were determined by titration. Volume variations for each solution were determined by means of a scale on the recirculation solution tank. Due to limited chemical resistance of the bipolar membrane, nitric acid concentration was kept lower than 3 mol L^{-1} .

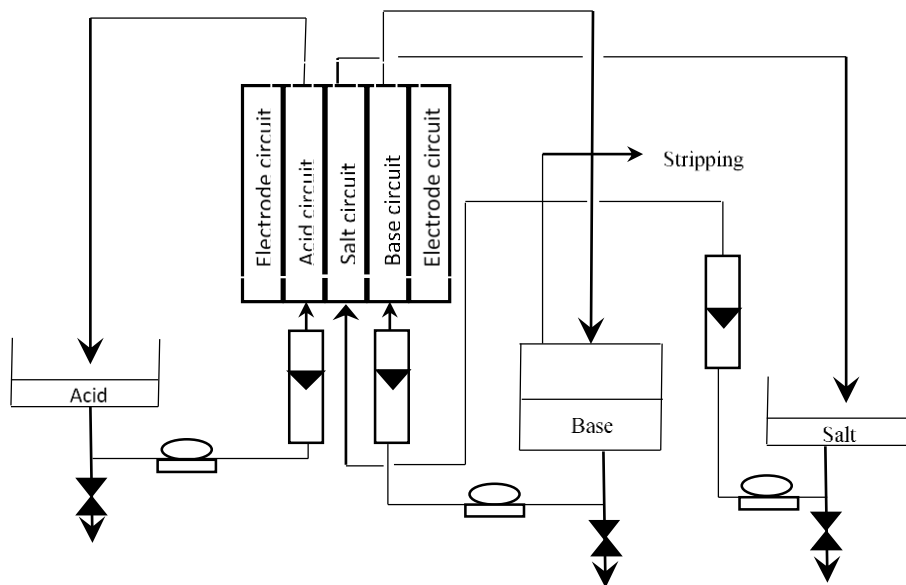


Figure 4. BP MED Set-up for nitric acid and ammonia production in batch mode

Material Balance sheets

We suggest verifying the balance sheets of electro dialysis in batch mode operation. The experiments were run for two hours. To do this, we

had to analyze the ionic and molecular exchanges between the different solutions. These ionic exchanges are represented on Figure 5.

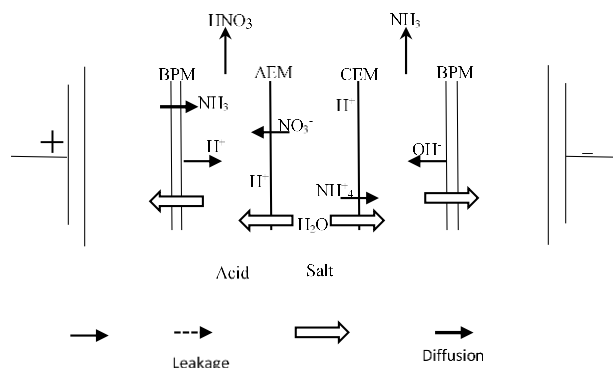


Figure 5. Transport of the different species through membranes

Nitrate balance sheet

The ions present in the salt solution are H^+ , NH_4^+ and NO_3^- . The electroneutrality of the solution is expressed by the following equations:

$$n(\text{NO}_3^-)_{s,\text{initial}} = n(\text{NH}_4^+)_{s,\text{initial}} + n(\text{H}^+)_{s,\text{initial}}$$

$$n(\text{NO}_3^-)_{s,t} = n(\text{NH}_4^+)_{s,t} + n(\text{H}^+)_{s,t}$$

where

“s” : index for salt solution
 “initial” : index for starting time
 N(X) : species mole number

$$\Delta n(\text{NO}_3^-)_s = n(\text{NO}_3^-)_{s,\text{initial}} - n(\text{NO}_3^-)_{s,t} = n(\text{NH}_4^+)_{s,\text{initial}} - n(\text{NH}_4^+)_{s,t} + n(\text{H}^+)_{s,\text{initial}} - n(\text{H}^+)_{s,t}$$

The ions present in the acid solution are H^+ , NH_4^+ and NO_3^- . The electroneutrality of the solution is expressed by the following equations:

$$n(\text{NO}_3^-)_{a,\text{initial}} = n(\text{NH}_4^+)_{a,\text{initial}} + n(\text{H}^+)_{a,\text{initial}}$$

$$n(\text{NO}_3^-)_{a,t} = n(\text{NH}_4^+)_{a,t} + n(\text{H}^+)_{a,t}$$

Where

“a” : index for acid solution
 “initial”: index for starting time
 N(X) : species mole number

Both greatnesses in the second member of the 2 previous equations are measurable.

The nitrate mole number variation in salt solution is then:

$$\Delta n(\text{NO}_3^-)_s = \Delta n(\text{NH}_4^+)_s + \Delta n(\text{H}^+)_s \quad (5.19)$$

Thus, the nitrate mole variation in acid solution:

$$\Delta n(\text{NO}_3^-)_a = \Delta n(\text{NH}_4^+)_a + \Delta n(\text{H}^+)_a$$

Ammonium balance sheet

In the salt solution, we obtain ammonium concentration directly by titration. This ion crosses the cation exchange membrane to the base compartment where it is converted into NH_3 . The balance sheet spells:

$$\Delta n(\text{NH}_4^+)_s = n(\text{NH}_4^+)_{s,\text{initial}} - n(\text{NH}_4^+)_{s,t} = \Delta n(\text{NH}_3) + n(\text{NH}_4^+)_{a,t} - n(\text{NH}_4^+)_{a,\text{initial}}$$

$$\Delta n(\text{NH}_4^+)_s = \Delta n(\text{NH}_3) + \Delta n(\text{NH}_4^+)_a \quad (5.20)$$

$\Delta n(\text{NH}_3)$: total ammoniac mole variation

Greatness evaluation Salt solution

Figures 6 and 7 illustrate both the evolution of NH_4^+ concentration in the salt compartment and the volume of the salt solution according to time:

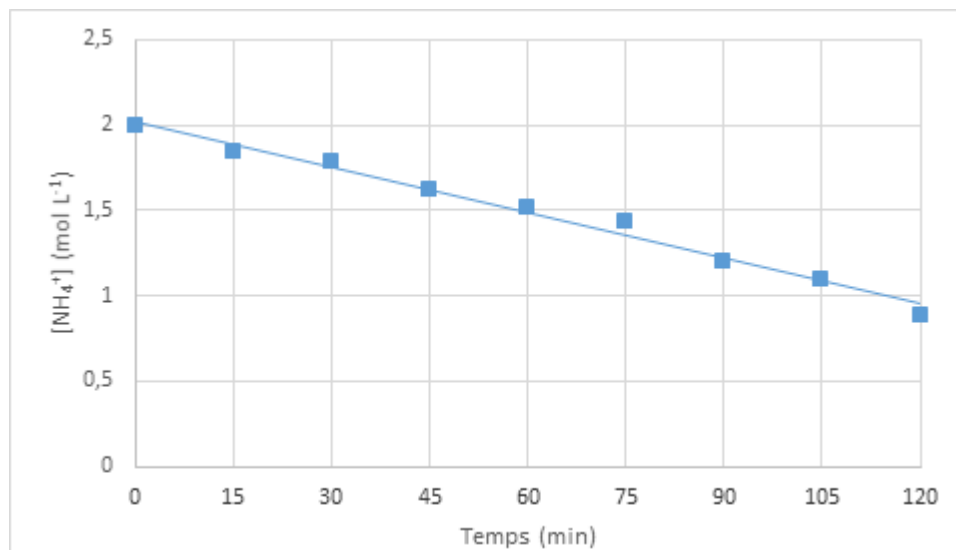


Figure 6. Evolution of NH_4^+ concentration in salt compartment versus time

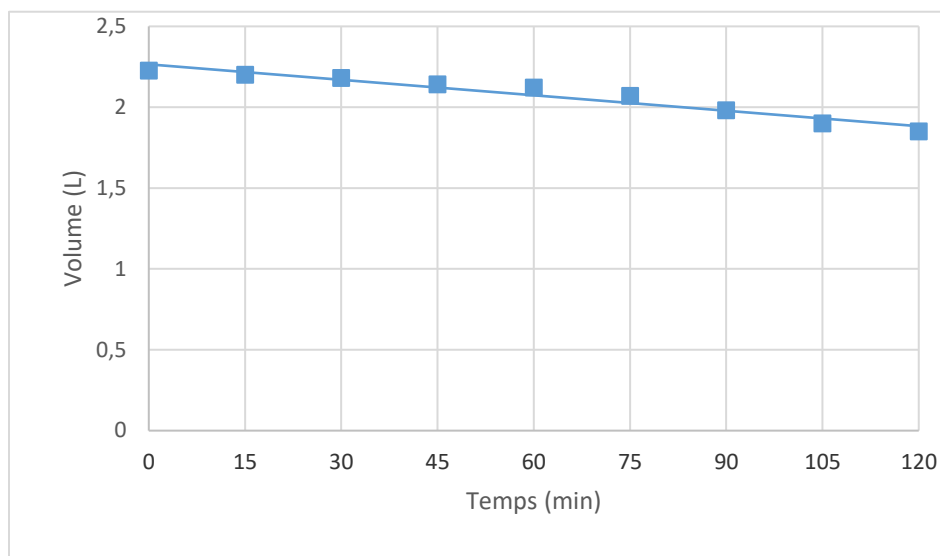


Figure 7. Evolution salt compartment volume versus time

NH_4^+ concentration and volume in the salt compartment decrease linearly. We deduce the NH_4^+ number mole variation in the salt compartment. Figure 8 illustrates this variation according to time.

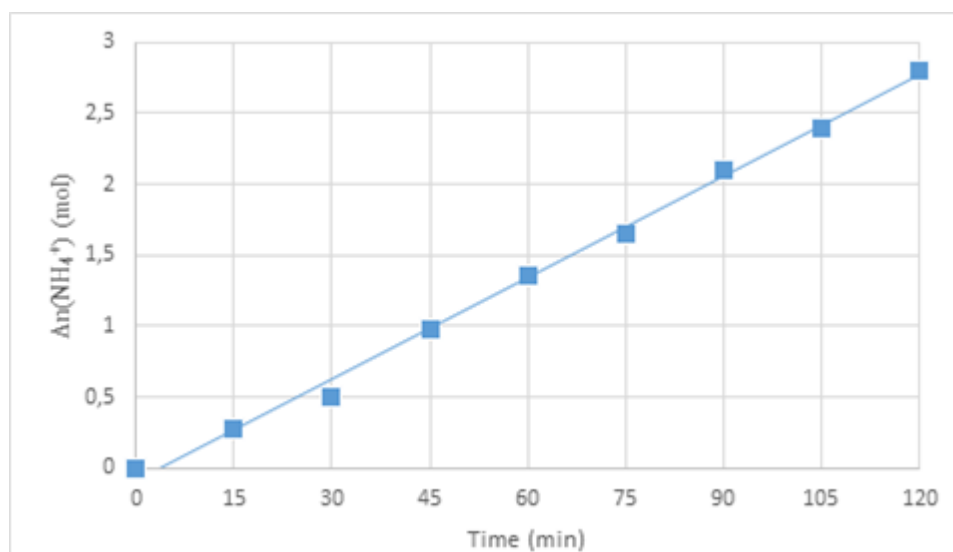


Figure 8. NH_4^+ number mole variation in salt compartment versus time

The obtained slope gives the ammonium speed disappearance from the salt solution. This speed is equal to 1.37 mol h^{-1} .

Proton leakage towards the salt compartment

Figure 9 illustrates the evolution of the H^+ concentration variation in the salt compartment according to time.

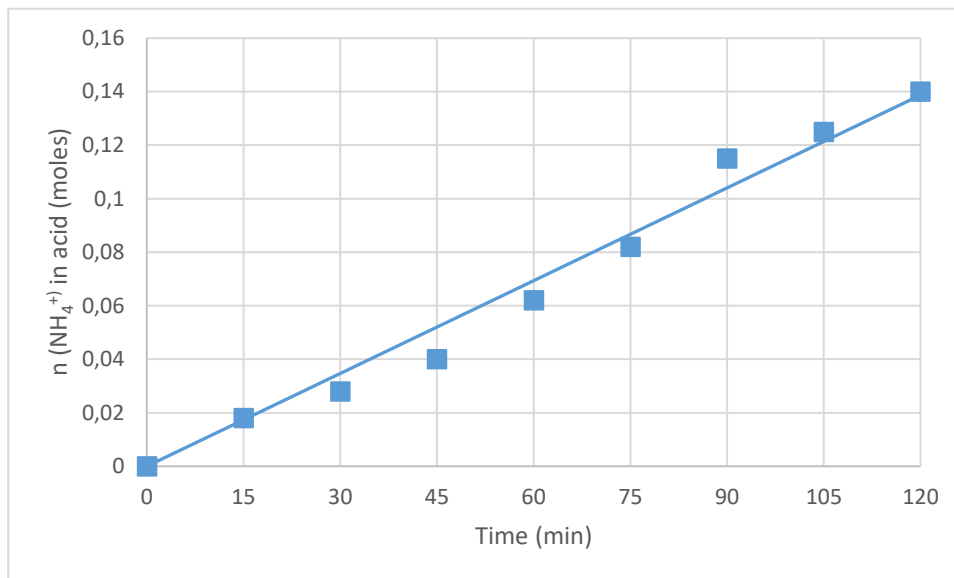


Figure 9. H⁺ concentration variation in the salt compartment

The slope appearing on the right in figure 9 corresponds to the H⁺ speed accumulation in the salt solution. It is equal to 0.025 mol L⁻¹.min⁻¹.

Part of the ammonia produced in the base compartment, diffuses through the bipolar membrane to the acid compartment, where it is converted into ammonium ion.

NH₃ diffusion in acid compartment

Figure10 illustrates the variation of NH₄⁺ mole number in the acid compartment according to time.

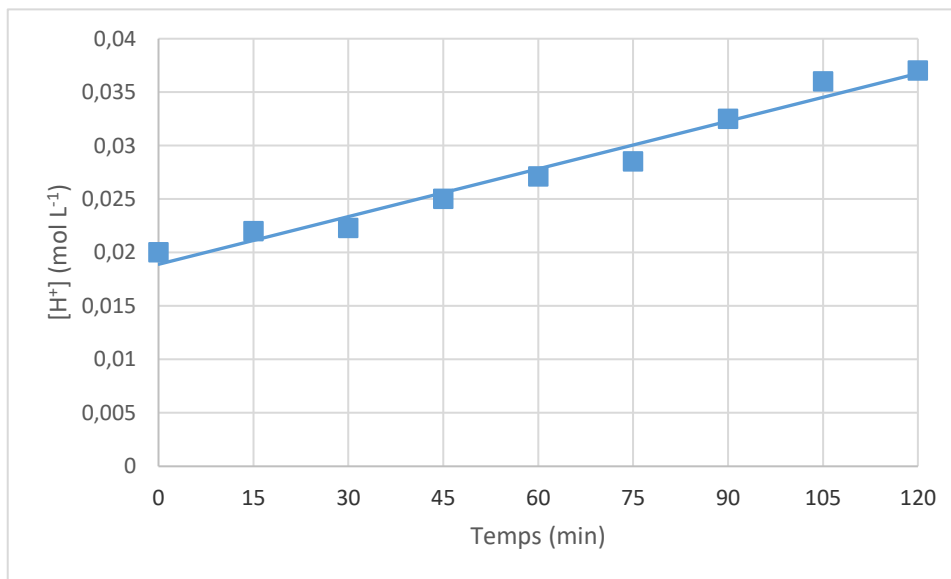


Figure10. NH₄⁺ mole number in acid compartment versus time

Material balance sheets verification

The following table recapitulates the values of production of acid and ammonia as well as the

variations of mole number of ammonium nitrate and protons in the salt and acid solutions.

Table 2. Greatnesses for balance electro dialysis

$\Delta n (\text{H}^+)_{\text{acide}} (\text{mol h}^{-1})$	1,30
$\Delta n (\text{NH}_3) (\text{mol h}^{-1})$	1,25
$\Delta n (\text{NH}_4^+)_{\text{sel}} (\text{mol h}^{-1})$	1,37
$\Delta n (\text{H}^+)_{\text{sel}} (\text{mol h}^{-1})$	-0,025
$\Delta n (\text{NH}_4^+)_{\text{acide}} (\text{mol h}^{-1})$	0,07

Applying the relations (5.19 and 5.20), we calculate the values included in the following Table:

Table 3. Comparative degree of material balance sheets

$\Delta n (\text{NO}_3^-)_{\text{sel}} (\text{mol h}^{-1})$	1,35
$\Delta n (\text{NO}_3^-)_{\text{acide}} (\text{mol h}^{-1})$	1,37
$\Delta n (\text{NH}_4^+)_{\text{sel}} (\text{mol h}^{-1})$	1,37
$\Delta n (\text{NH}_3) (\text{mol h}^{-1}) + \Delta n (\text{NH}_4^+)_{\text{acide}} (\text{mol h}^{-1})$	1,32

The following relation expresses the preservation of nitrates balance sheets:

$$\Delta n (\text{NO}_3^-)_{\text{sel}} = \Delta n (\text{NO}_3^-)_{\text{acide}}$$

We notice that the nitrate balance sheet is verified at less than 2 %. The value is the same for ammonium balance sheet, which is verified at less than 4 %.

Water transfer

Water transfer through anion exchange membrane

To determine the water transport accompanying every ion, we have to write the preservation equations mass taking into account all the transfers and reactions

that are susceptible to occur in the system. To overcome this problem, we are going to make some simplifying hypotheses. In fact, the mass variation in the acid compartment is due:

- To transfer of solvated ions through the anions membrane exchange and the bipolar membrane
- To the water diffusion and splitting in the bipolar membrane
- To the diffusion of other species towards acid compartment (ex NH_3)

Neglecting the variations of volume (denials) due to the water diffusion and its splitting and variations due to transfers of ionic species (positive variations), the variation of the volume is assimilated to the quantity of water crossing the anions exchange membrane.

By knowing the variation of volume in the acid compartment and the produced mole number of acid, we can deduct the values of water transport number for NO_3^- , in the following way:

$$t_{\text{H}_2\text{O}:\text{NO}_3^-} \approx \frac{V_1 \cdot \rho}{M_{\text{H}_2\text{O}} \cdot n_{\text{NO}_3^-}}$$

Where

$t_{\text{H}_2\text{O}/\text{NO}_3^-}$: H_2O mole number accompanying NO_3^-

$n_{\text{NO}_3^-}$: Produced acid mole number (mol h^{-1})

$M_{\text{H}_2\text{O}}$: Water molar mass (g mol^{-1})

V_1 : volume variation in the acid compartment, 75 ml h^{-1} (ref. figure11)

ρ : water volumetric mass (1 Kg l^{-1})

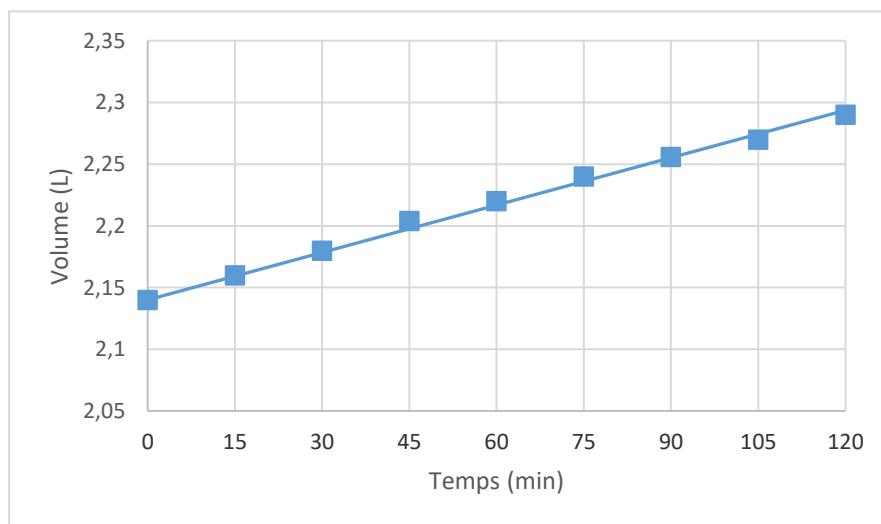
**Figure 11.** Volume acid evolution versus time

Figure 12. Illustrates the evolution of water transfer accompanying NO_3^- crossing the anion

exchange membrane as water solvated ions.

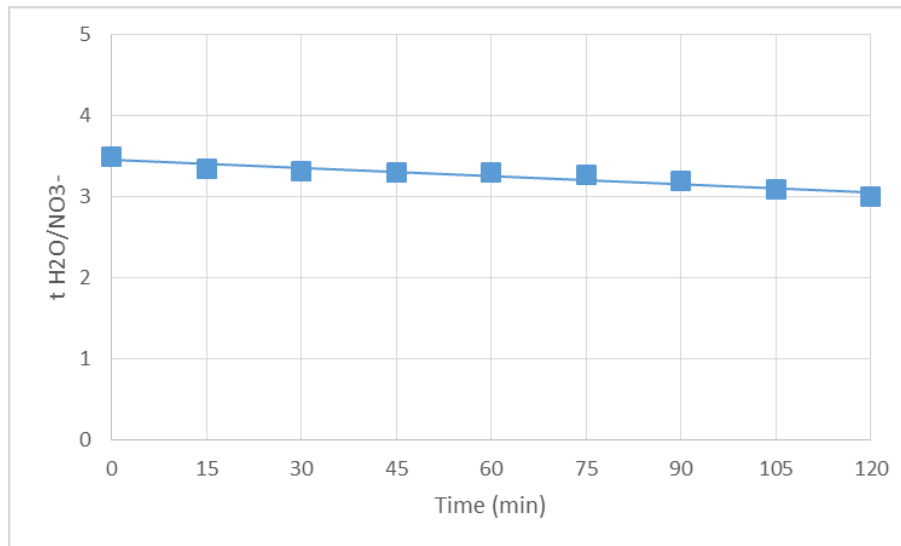


Figure 12. Water transport number for NO_3^- versus time

We notice that by using AW anion exchange membrane, the water transport number is 3. This value complies with the literature [9, 10].

Water transfer through cation exchange membrane

The same hypothesis used in the previous paragraph with the anions exchange membranes was maintained with the cation exchange membranes. The transfer of water through the cation exchange membrane will be thus assimilated to the increase of volume in the compartment base.

By knowing the volume variation in the basic solution and in the stripping circuit as well as the basic produced mole number, we can deduce the water transport number for NH_4^+ as water solvated ions.

$$t_{\text{H}_2\text{O}:\text{NH}_4^+} \approx \frac{V_2 \cdot \rho}{M_{\text{H}_2\text{O}} \cdot n_{\text{NH}_4^+}}$$

Where

$t_{\text{H}_2\text{O}:\text{NH}_4^+}$: water transport number for NH_4^+

V_2 : volume variation in basic compartment (L)

$n_{\text{NH}_4^+}$: ammonium mole number (mol h^{-1})

V_2 expresses the volume variation in the base compartment and in the stripping circuit.

$$V_2 = \Delta V_{\text{base}} + \Delta V_{\text{stripping}} = 140 \text{ ml h}^{-1} \text{ (cf. Table 4)}$$

Table 4. Volume variation in base circuit

	Initial volume (L)	Final volume (L)
Base compartment	2,287	2,322
Stripping circuit	0,5	0,74

Where: $t_{\text{H}_2\text{O}:\text{NH}_4^+} = 5$

This value complies with the literature^{9,10}.

Balance sheet check in water

By knowing the volume variations of acid and base solutions, we can easily verify the preservation of the global water balance sheet. For this purpose, we have to compare the total volume variation in both compartments to the volume variation in the salt one.

According to results given in figure 5, the volume variation in the salt compartment is about 230 ml h^{-1} . By comparing this value to the total volume variation in acid and base compartments (140 + 75 = 215 ml h^{-1}), the difference between the two values could be explained by the water splitting in bipolar membrane.

Conclusion

This study allowed to validate the proposed transfer model and to check the balance sheets material on all involved species during electro dialysis. Indeed, the contribution of migration (NH_4^+ and NO_3^-) and diffusion (NH_3 and H_2O) in the transport of the various

involved species, has been illustrated in ammonium nitrate electro dialysis. Besides, we showed that the balance sheet of the nitrate and ammonium ions is verified at less than 4 %. We have also determined the water transport number through the two monopolar membranes. The values comply with the literature (3 moles of H₂O per NO₃⁻ mole and 5 moles of H₂O per NH₄⁺ mole).

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