

Feed and Bleed Bipolar Membrane Electrodialysis Process

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Abstract: In this study, a bipolar membrane electro dialysis process (BPMED) is applied to regenerate nitric acid and ammonia by splitting ammonium nitrate. Firstly, we have proved the process feasibility in batch mode. Secondly, using the same operating conditions, we have proposed to extend the study to a continuous (feed and bleed) operating mode. Forecast calculations, derived from the balance material equations, and using the batch mode results, allowed the estimation of the continuous functioning parameters for both acid and salt. There is a good agreement between the performances of the two functioning modes. The acid and ammonia current efficiencies reached respectively 85 and 83 % in batch processing, and 83 and 80 % in continuous processing.

Introduction

The nuclear fuel processing industry generates large volumes of wastewaters containing ammonium nitrate. These wastewaters are produced during the conversion of uranyl nitrate to uranium oxide. Thus, ammonium nitrate is produced at a concentration around 1 or 2 mol L⁻¹. Due to the presence of traces of uranium, ammonium nitrate solutions are not suitable for use in agriculture fertilizer production. For economic and environmental reasons, splitting of ammonium nitrate to ammonia and nitric acid is advantageous. Membrane electrolysis ¹⁻³ and bipolar membrane electro dialysis (BPMED) ⁴⁻⁶ were used to treat solutions containing ammonium nitrate. BPMED has been investigated in many studies ⁷⁻¹⁰. The principle of this operation lies in the use of a bipolar membrane where water splitting to H⁺ and OH⁻ is performed. The bipolar membrane is associated to homopolar ion-exchange membranes to produce acid and base from a salt. [Figure 1](#) illustrates the principle of the operation. A three-compartment cell is used. The bipolar membrane is associated to an anion-exchange membrane and a cation-exchange membrane. The salt solution containing NH₄NO₃ is fed to the central compartment between the two homopolar membranes. Nitrate ion NO₃⁻ migrates through the anion-exchange membrane and enters the

acid compartment to generate nitric acid with proton produced by the bipolar membrane. On the other side, ammonium ion NH₄⁺ migrates through the cation-exchange membrane to the base compartment to generate ammonia with hydroxide ion produced by the bipolar membrane.

Other authors ^{4,11} studied the splitting of ammonium nitrate solutions by BPMED in order to regenerate nitric acid and ammonia. The authors concluded that this technique was not suitable for direct treatment of ammonium nitrate waters due to the low current efficiency linked to ammonia production.

They proposed to operate in two steps. First, addition of sodium hydroxide to salt solution and stripping of ammonia and, in a second step, the sodium nitrate solution obtained is treated by BPMED to regenerate nitric acid and sodium hydroxide. In this work, direct treatment of ammonium nitrate is carried out by coupling bipolar membrane electro dialysis and continuous in situ stripping of ammonia. Selection of homopolar ion-exchange membranes to use with the bipolar membrane was achieved. Then, with the selected membranes, the production of nitric acid and ammonia was studied. These productions were carried in batch and continuous mode.

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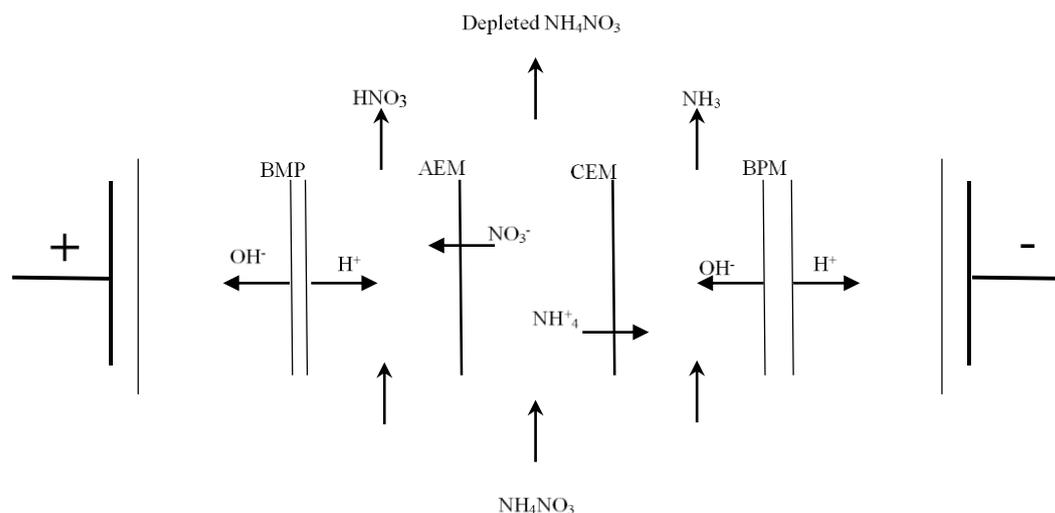


Figure 1. Principle of ammonium nitrate splitting by bipolar membrane electrodesalination.

Experimental details

Ion-exchange membranes

The membranes used are listed below:

- Bipolar membrane: BP1 (Tokuyama Soda).
- Cation-exchange membrane: CMB (Tokuyama Soda), Nafion 117 (Dupont de Nemours), CRA (Solvay).
- Anion-exchange membrane: AW (Solvay)¹², ACM (Tokuyama Soda), AAV (Asahi Glass).

The electrochemical cell stack

The cell stack supplied by Eurodia Industrie (Wissous, France) was used with four cells. Active area was 200 cm² per cell. Solutions were pumped through the cell compartments continuously from recirculation tanks. The compartment width was about 0.8mm and the flow rate was about 20 L h⁻¹ per cell (liquid velocity ~6 cms⁻¹). Manometers placed at the cell inlet of each circuit provided 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 (Fig. 2).

Operating conditions

Relatively high solution conductivity is required to operate at the usual current densities under reasonable voltage. Referring to Figure 1, the base circuit is free of ions and presents a small conductivity. In order to enhance the conductivity, sodium hydroxide was added. No separation problem is induced. Moreover, ammonia stripping is more efficient in alkaline conditions.

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

- Acid circuit: nitric acid ≈1 mol L⁻¹ (membranes should not withstand strongly acidic media)
- Salt solution: NH₄NO₃ 2 mol L⁻¹
- Base circuit: NH₃ and NaOH 1 mol L⁻¹ each (the ammonia concentration in the base circuit is equal to the equilibrium value in the stripping conditions, for example [NH₃] = 1 mol L⁻¹ for 14.5 kPa, 45 °C and [NaOH] = 1 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 and continuous feed and bleed operation were carried out. Acid and ammonia concentrations were determined by titration. Volume variations for each solution were determined by means of a measuring scale on the recirculation solution tank. Due to the limited chemical resistance of the bipolar membrane nitric acid concentration was kept lower than 3 mol L⁻¹.

Ammonia stripping

During electrodesalination, produced ammonia was extracted continuously from the recirculation tank. This was achieved by exerting a reduced pressure (generally 14.5 kPa unless other value specified) and by heating to 45 °C (the temperature must not exceed this value for thermal stability of the bipolar membrane). The temperature was controlled by circulation of thermostated water in the jacketed recirculation tank. During the tests, small variations of the temperature were observed (no more than 1 or 2 °C)¹³.

In our case, the extracted ammonia was absorbed in nitric acid in order to determine the produced quantity. Otherwise, ammonia must be absorbed in water to give ammonia solution. Figure 2 represents the ammonia stripping and absorption device.

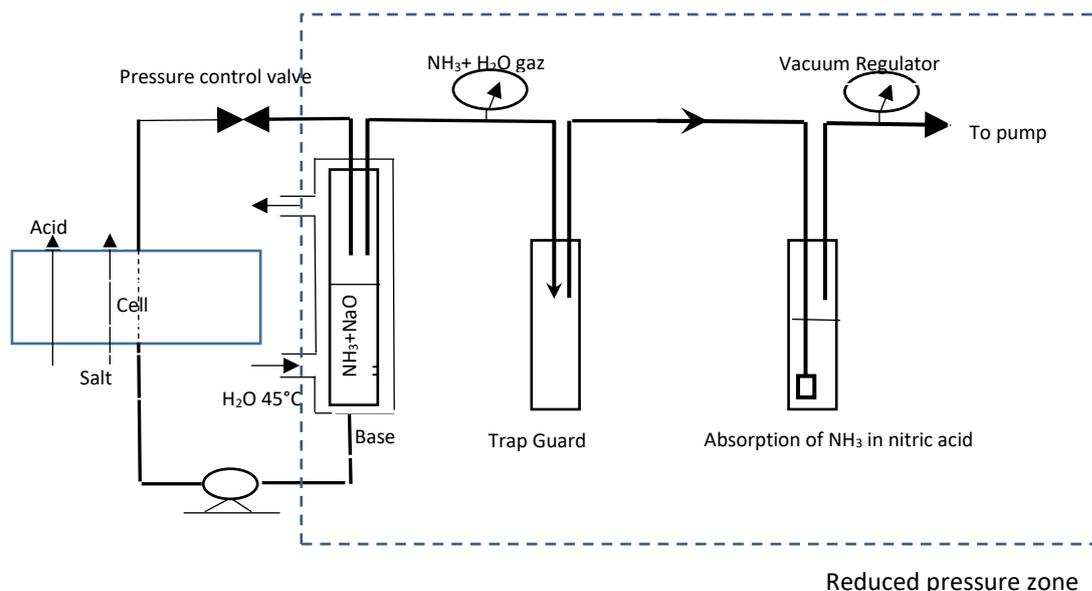


Figure 2. Ammonia stripping and absorption device (nitric acid is used here only for quantitative determination of ammonia).

Batch mode results and discussion

First, the production of nitric acid and ammonia was tested successfully. Then, selection of membranes was achieved and the effect of different parameters studied in batch mode.

Nitric acid and ammonia production

The current efficiency (%) is a measure of the system's ability to use the current advisedly. The current efficiency CE (%) for production of component C during a time Δt is the ratio between the moles of C produced during Δt and the theoretical moles corresponding to the quantity of charge involved during Δt .

$$CE = \frac{P}{P_{theoretical}} = \frac{\Delta(CV)}{nJS\Delta(t)}$$

$$= \frac{\Delta(CV)F}{nJS\Delta(t)} \quad (\text{section Volume variations})$$

During a 2 h reaction where acid concentration increased from 1 to 2 mol L⁻¹, the average CE for nitric acid is near 85%. The average CE for ammonia

production during this experiment is 83%, a value close to that for acid if all the produced ammonia is simultaneously stripped from the base circuit.

Effect of acid concentration

The differential current efficiency (DCE) is given by the relation:

$$DCE = \frac{d(VC)F}{JSdt} = \frac{(VdC + CdV)F}{JSdt}$$

V and C are the volume and concentration of nitric acid solution, J the current density, S the membrane surface area and F is the Faraday constant: 96485 As mol⁻¹. The term dV/dt is known (Section *Volume variations*) and the term dC/dt is obtained from a 120-min experiment (the slope of the tangent to the curve at the considered point). The DCE varies with acid concentration as reported in Figure 3. The change in DCE is linear in the investigated range, dropping from 90% to 1 mol L⁻¹ concentration to 77% for 2 mol L⁻¹. The decrease of the DCE is explained by proton leakage through the anion-exchange membrane, which is greater when acid concentration increases¹⁴.

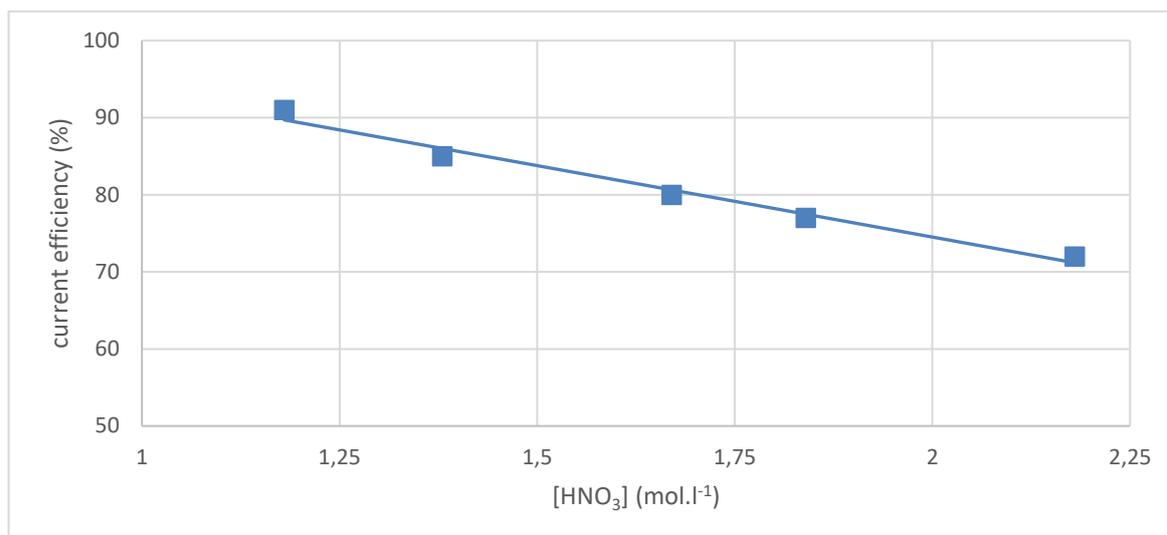


Figure 3. Nitric acid differential current efficiency vs. acid concentration

Homopolar membranes selection

The objective here is to select the pair of homopolar membranes which, in association with the bipolar membrane BP1, leads to the highest current efficiency.

Anion-exchange membrane

We have tested the three anion-exchange membranes (Section *Ion-exchange membranes*) together with the CMB membrane. These anion-exchange membranes are known to have a small proton leakage and are suitable for working with acids.

Table 1. HNO₃ and NH₃ 120 min average current efficiencies (CE, %) for different pairs of anion and cation-exchange membranes under our standard conditions.

	AW-CMB	ACM-CMB	AAV-CMB	AW-N117	AW-CRA
HNO ₃ average CE (%)	83	61	52	81	79
NH ₃ average CE (%)	84	64	50	72	57

Table 1 reports the acid and base average current efficiency for different sets of membranes in the standard conditions for a 120-min experiment. Final acid concentrations are respectively 2, 1.7 and 1.6 mol L⁻¹, for AW, ACM and AAV membranes. Ammonia concentration in the base circuit remains constant at about 1 mol L⁻¹. Under the experimental conditions, acid and ammonia current efficiencies are close for each set of membranes. The AW membrane exhibits the highest current efficiency value. This is probably linked to its small water content. This membrane was chosen for the remainder of this study ¹⁵.

Cation-exchange membrane

The three cation-exchange membranes (Section *Ion-exchange membranes*) were each tested with the AW membrane.

The acid current efficiency is nearly the same for the three cation-exchange membranes tested. The cation-exchange membrane has only a small effect on the production of nitric acid. In contrast, the ammonia

production is different with each cation-exchange membrane tested. The ammonia current efficiency varies from 84% for the CMB membrane to 57% for the CRA membrane. This is probably due to the ammonia diffusion through these membranes from the base compartment to the salt one. During these experiments, the pH of the salt solution decreased slightly with the CMB membrane but it increased significantly for the two-other cation-exchange membranes. Since the CMB membrane seems to prevent ammonia diffusion, the AW and CMB pair of membranes are used for all other experiments.

Volume variations

Volume variations occur during the mass transfer between the different solutions and must be taken into account to establish the material balance and accurately calculate current efficiencies.

Figures 4 and 5 illustrate both the evolution of acid compartment and salt compartment volumes according to time:

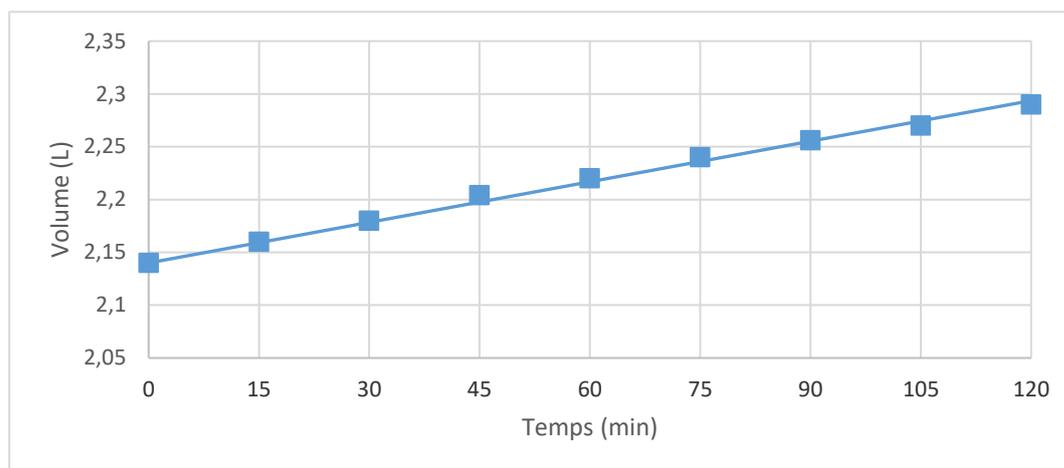


Figure 4: Evolution acid compartment volume versus time

The acid solution volume increases as the salt volume decreases. These changes are due to the transfer of solvated (water) ions through the membranes. The volume of base solution should also increase but due to water evaporation under the reduced pressure required for ammonia stripping it remains practically constant. The volume variation in the salt compartment is about 230 ml h^{-1} , compared to the total variation in the acid and stripping compartments ($75 + 140 = 215 \text{ ml h}^{-1}$)¹⁶.

To confirm the electro dialysis results obtained in batch mode, we propose to study the electro dialysis in continuous mode (feed and bleed)

Electrodialysis Study in continuous (feed and bleed) operating mode

The objective of this study is to produce a nitric acid solution with constant flow rate and

concentration, as well as gaseous ammonia with constant flow rate. Starting from any initial conditions, a steady-state was reached.

For continuous operation, a feed and bleed mode were utilized. An adjustable flow rate pump introduced pure water into the acid recirculation tank maintaining the desired acid concentration. Ammonium nitrate solution was similarly pumped into a salt recirculation tank. For the base circuit, the operation was performed in the same way than in batch mode taking into account that volume change in this circuit was negligible and that a quasi-stationary state was reached.

For acid and salt solution constant volume of the circuit was insured by an overflow. Their volume value was about 3L.

Figure 6 shows a diagram of the experimental device suitable for a continuous mode operating.

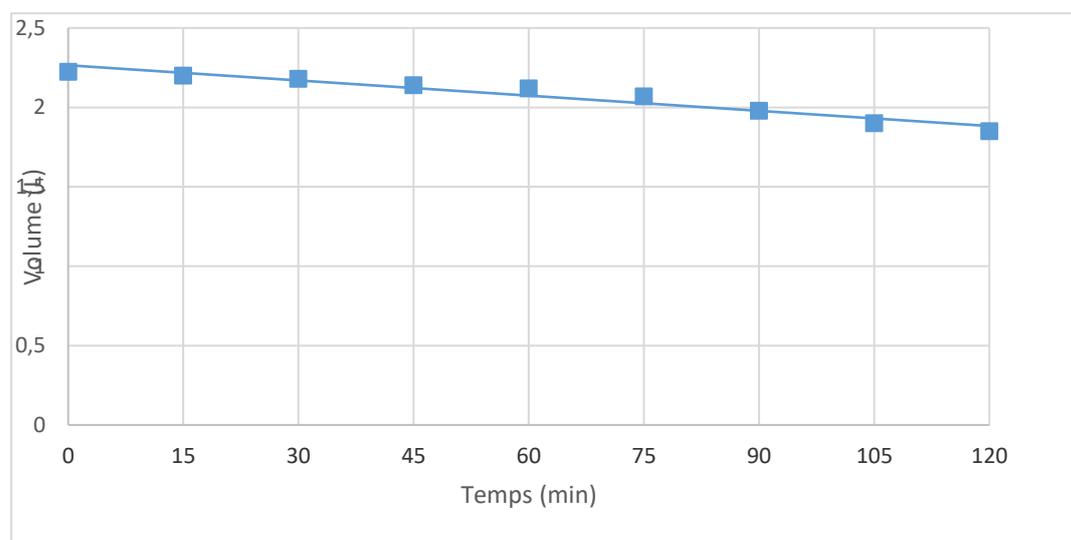


Figure 5. Evolution salt compartment volume versus time

The acid solution volume increases as the salt volume decreases. These changes are due to the transfer of solvated (water) ions through the

membranes. The volume of base solution should also increase but due to water evaporation.

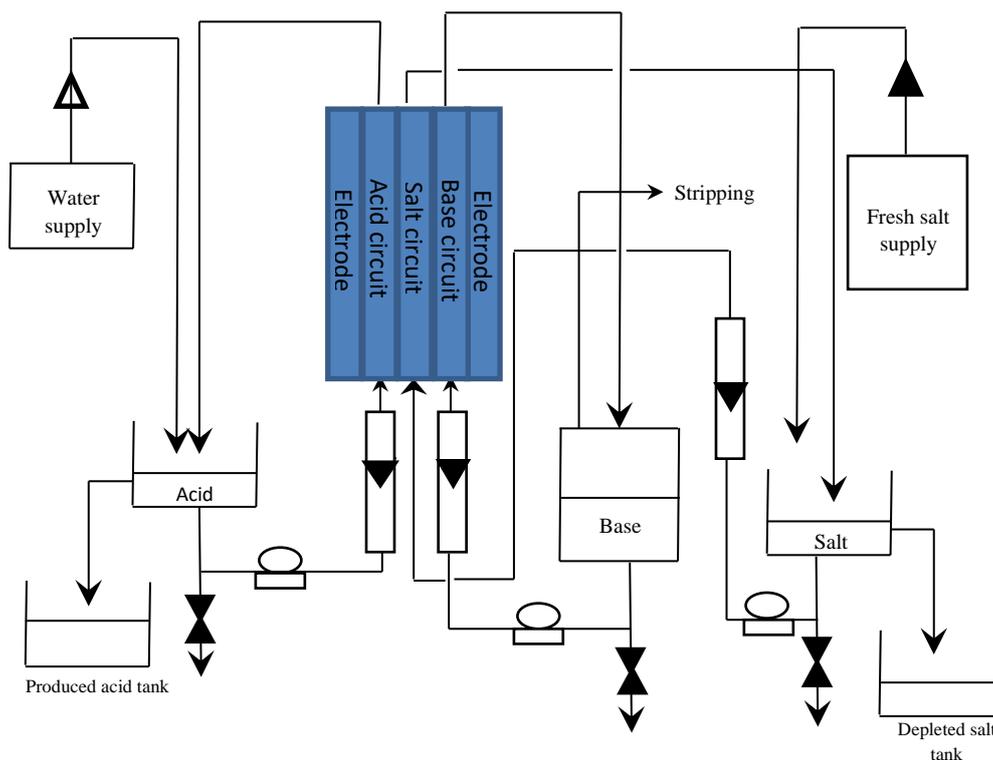


Figure 6. Scheme of the experimental device

Forecast of continuous operating mode

The approach is to write the balance material equations and to give the methodology to predict the operating points of electro dialysis when operating conditions are set.

Problem data:

$[\text{NH}_3] = 1 \text{ mol l}^{-1}$, $[\text{NaOH}] = 1 \text{ mol l}^{-1}$,
 $[\text{NH}_4\text{NO}_3] = 2 \text{ mol l}^{-1}$, $J = 500 \text{ A m}^{-2}$,
 number of cells = 4

The target is:

- A fixed final acid concentration C_{fa}
- A fixed depleted salt concentration C_{fs}

Nitric acid balance

In steady state, the material balance on nitric acid is written:

$$Q_{0a} \cdot C_{0a} + P = Q_{Fa} \cdot C_{Fa} \quad (1)$$

Where:

C_{0a} : Initial concentration of nitric acid in the supply (zero) (mol l^{-1})
 C_{Fa} : final concentration of acid (mol l^{-1})
 P : actual acid production (mol h^{-1})
 Q_{Fa} : flow rate of withdrawal acid (l h^{-1})
 Q_{0a} : input flow rate of the supply (l h^{-1})

That's why:

$$Q_{fa} = \frac{P}{C_{fa}} \quad (2)$$

To know the acid production P , simply use the results of tests conducted in batch mode (section *Effect of acid concentration*)¹⁰. In fact, for a fixed concentration of C_{fa} and assuming that all conditions remain unchanged, the current efficiency η_a is well known.

$$P = P_{theoric} \cdot \eta_a \quad (3)$$

$$P_{theoric} = \frac{n_c \cdot I}{F} \quad (4)$$

Where:

n_c : number of electro dialysis cells
 I : current intensity (A)
 F : Faraday number ($96500 \text{ C} \cdot \text{mol}^{-1}$)

Assuming that the densities are constant, we can write the following equation:

$$Q_{Fa} = Q_{0a} + q_a \quad (5)$$

Where:

q_a : volume variation in acid compartment, expressed in $\text{l} \cdot \text{h}^{-1}$ (this quantity does not depend on the operating mode)

By replacing Q_{Fa} and P by their values, equation (5) is then written:

$$Q_{0a} = \frac{\eta_a \cdot n_c \cdot I}{F \cdot C_{fa}} - q_a \quad (6)$$

Ammonium nitrate balance

Similarly, we have established a material balance on the salt, assuming that the stationary regime is reached

$$\text{Incoming flow} = \text{Output flow} + \text{transferred flow} \quad (7)$$

$$Q_{0s} \cdot C_{0s} = Q_{fs} \cdot C_{fs} + T \quad (8)$$

Whence

$$Q_{0s} = \frac{Q_{fs} \cdot C_{fs} + T}{C_{0s}} \quad (9)$$

Where:

C_{0s} : Initial salt concentration (mol l^{-1})

C_{fs} : final salt concentration (mol l^{-1})

T: quantity of salt transferred to acid and base compartment (mol l^{-1})

Q_{fs} : withdrawal salt flow rate (l h^{-1})

Q_{0s} : fresh salt supply flow rate of (l h^{-1})

To determine the number of moles of transferred salt, simply knowing the current efficiency of ammonium ions. We will assume that the current efficiency of ammonium ions is little different from the acid one.

We write:

$$T = P_{\text{theoric}} \cdot \eta_a \quad (10)$$

By replacing P theoretical by its value, equation (10) then becomes:

$$T = \eta_a \cdot \frac{n_c \cdot I}{F} \quad (11)$$

We also have:

$$Q_{fs} = Q_{0s} - q_s \quad (12)$$

Where:

q_s : measurable volume variation of salt solution expressed in l h^{-1} (section *Volume variations*). It is independent of operating mode. According to the results obtained in the batch mode, this volume is equals to 230 ml.h^{-1} (section *Volume variations*).

By replacing Q_{fs} and T by their values, equation (12) becomes:

$$Q_{0s} = \frac{\eta_a \cdot n_c \cdot I - F \cdot q_s \cdot C_{fs}}{F \cdot (C_{0s} - C_{fs})} \quad (13)$$

Equations 5, 6, 12 and 13 allow the calculation of the inlet and outlet flow rates, in order to obtain products with specified concentration. These values will be confronted with the experimental ones.

Experimental results and comparison with forecasts

Acid compartment

The steady state is reached when the concentrations and flows are constant. The concentrations of solutions used during the starting can be advantageously chosen equal to those of steady-state mode, in order to reduce the transitional period.

Two continuous experiments were conducted, for which the targeted acid concentrations were 1,25 and 2 mol l^{-1} . The experimentally obtained values are shown in Figure 7.

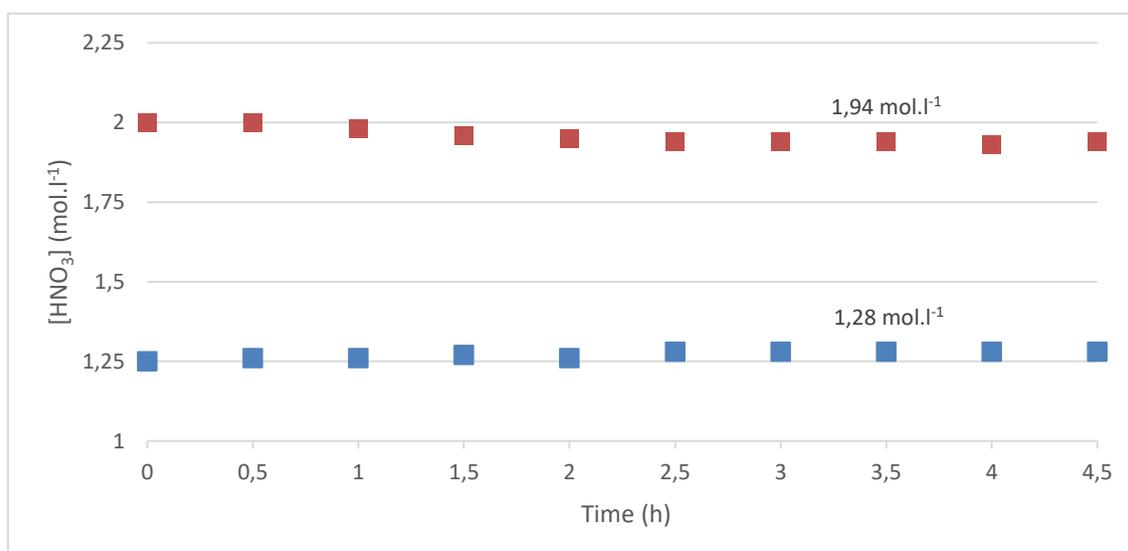


Figure 7. Evolution of the acid concentrations

It is noted that the concentrations reached in steady state are 1, 28 and 1, 94 mol l^{-1} . These are close

to the targeted acid concentration values (1, 25 and 2 mol l^{-1}).

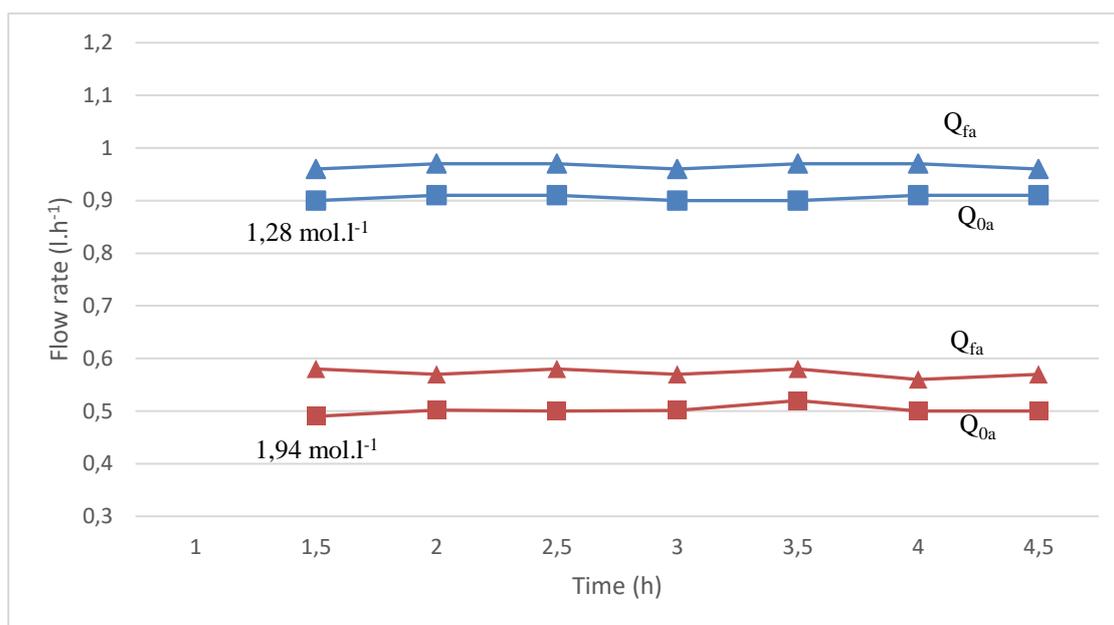


Figure 8. Evolution of water supply and outlet flow rates for the two studied acid concentrations

Figure 8 shows the variations of inlet and outlet flow rates for 2 acid concentrations. The table below

summarizes the results obtained.

Table 2. Experimental concentrations and flows obtained.

Acid concentration (mol l ⁻¹)	Inlet flow rate Q _{0a} (l h ⁻¹)	outlet flow rate Q _{fa} (l h ⁻¹)	Q _{fa} - Q _{0a} (l h ⁻¹)
1,94	0,501	0,575	0,074
1,28	0,905	0,969	0,064

The difference between Q_{fa} and Q_{0a} is about 0,07 l.h⁻¹. This value is substantially the same as determined in the batch mode (0.075 l h⁻¹) (Taking into account the volume measurement uncertainties ± 10 ml in the bath mode).

From the values of produced acid concentration, the current efficiency can be calculated by the following relation (Fig. 3):

$$\eta_a = 1,10 - 0,19[\text{HNO}_3]$$

Equation 6 is used to estimate the input flow rate. Table 3 shows the results:

Comparison with calculations:

Table 3. Comparison between calculated and experimental water supply flow rates.

Concentration (mol l ⁻¹)	Current efficiency (%)	Calculated inlet flow rate (l h ⁻¹)	Experimental inlet flow rate (l h ⁻¹)	Gap (%)
1,28	85	0,916	0,905	1,2
1,94	73	0,490	0,501	1,8

The differences between experimental and calculated water supply flow rates are very low (less than 2%) for the carried-out experiments.

Similarly, the calculated and experimental acid output rates can be compared. Equation 5 makes it possible to estimate the output flow rate. Table 4 shows the results:

Table 4. Comparison between calculated and experimental withdrawal acid flow rate.

Concentration (mol l ⁻¹)	Calculated outlet flow rate (l h ⁻¹)	Experimental outlet flow rate (l h ⁻¹)	Gap (%)
1,28	0,986	0,969	1,7
1,94	0,56	0,575	2,6

The differences between calculated and experimental acid output flow are also very low (less than 3%) for the two experiments carried out.

Determination of the acid current efficiency

The measurements carried out make it possible to obtain the values of the experimental current

efficiency for fixed and stationary acid concentrations.

The acid current efficiency is given by the relation:

$$\eta_a = Q_{fa} C_{fa} \frac{F}{n_c I}$$

So for:

$C_{fa} = 1,28 \text{ mol l}^{-1}$, the current efficiency is 83%

$C_{fa} = 1,94 \text{ mol l}^{-1}$, the current efficiency is 75%

These values are to be compared with those obtained by the empirical relation and grouped in

Table 3 (85% for $1,28 \text{ mol l}^{-1}$ and 73% for $1,94 \text{ mol l}^{-1}$).

Ammonia

We assume that the operating mode in the base circuit is not stationary. **Figure 9** shows the variations of NH_3 concentration and volume in the base compartment during the measurement period.

It is seen that the concentration of ammonia is substantially constant while the total volume varies very slightly (+ 50 ml for a total volume of 2L, and during 4,5 h). It is therefore legitimate to assume that the base circuit is also in the steady state.

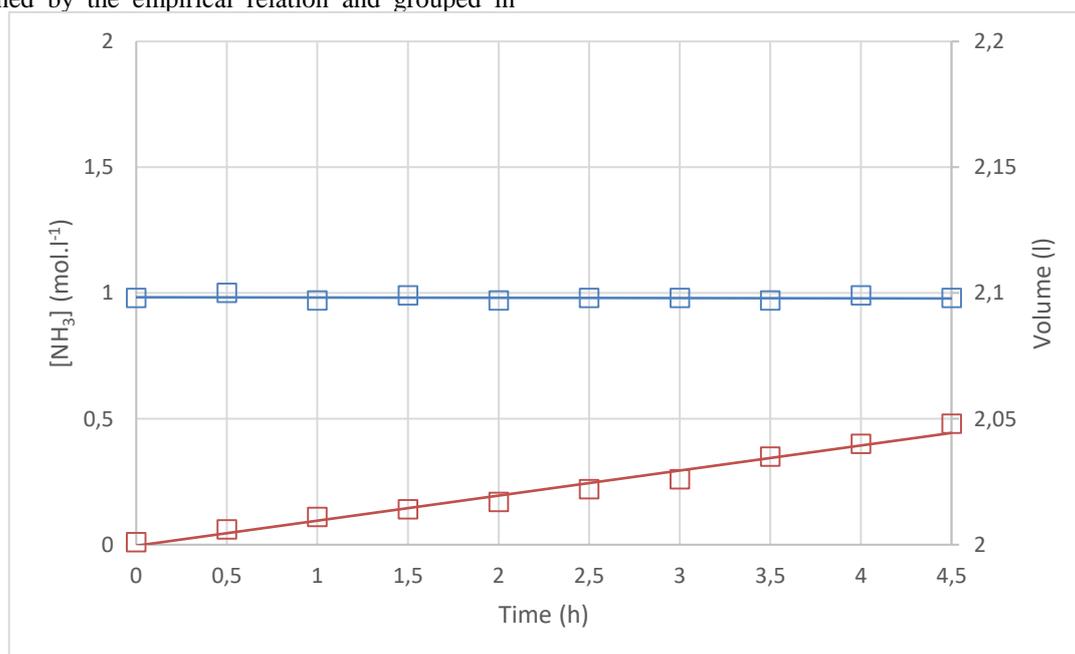


Figure 9. Evolution of volume and ammonia concentration in the circulation tank in function of time

The following table recapitulates the stripping results of the desorbed ammonia and then recovered

in the two traps designed for this purpose.

Table 5. Evolution of volume, concentration and ammonia production in the traps.

	Initial Volume (l)	Final volume (l) after 4,5 hours	Concentration (mol l ⁻¹)	Production (mol h ⁻¹)
Trap 1	0,50	0,90	3,70	0,74
Trap 2	0,50	0,73	2,71	0,44

The quantity produced ammonia is thus $0,74 + 0,44 = 1,18$ mole per hour. This corresponds to ammonia current efficiency average of 80% ($\eta_{\text{ammonia}} = \frac{P}{P_{\text{theoretic}}}$). The variation of ammonia moles number in the base circuit (less than 0.3% of the total amount of ammonia) is neglected.

Salt compartment

The concentration and flow rates of the salt compartment are shown in **Figures 10 and 11**.

The production of nitric acid produced is $1,28 \text{ mol l}^{-1}$.

The concentration of the salt solution gradually decreases to stabilize at a value $1,28 \text{ mol l}^{-1}$. The time required to reach a steady state is about 3 hours (because the starting value is different from the stationary one and that the internal volume of the salt solution is about 3 l).

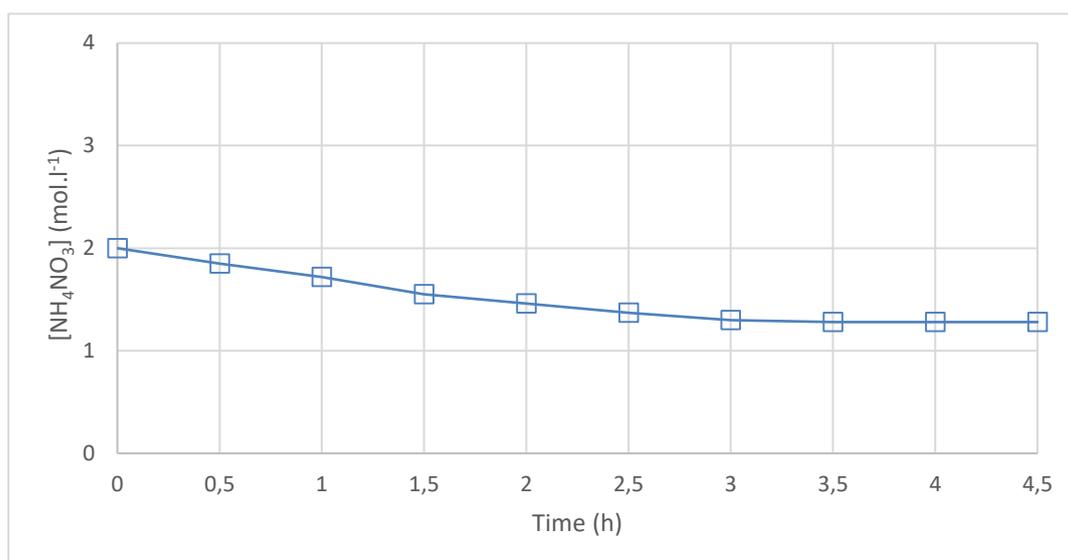


Figure 10. Evolution of salt concentration as a function of time

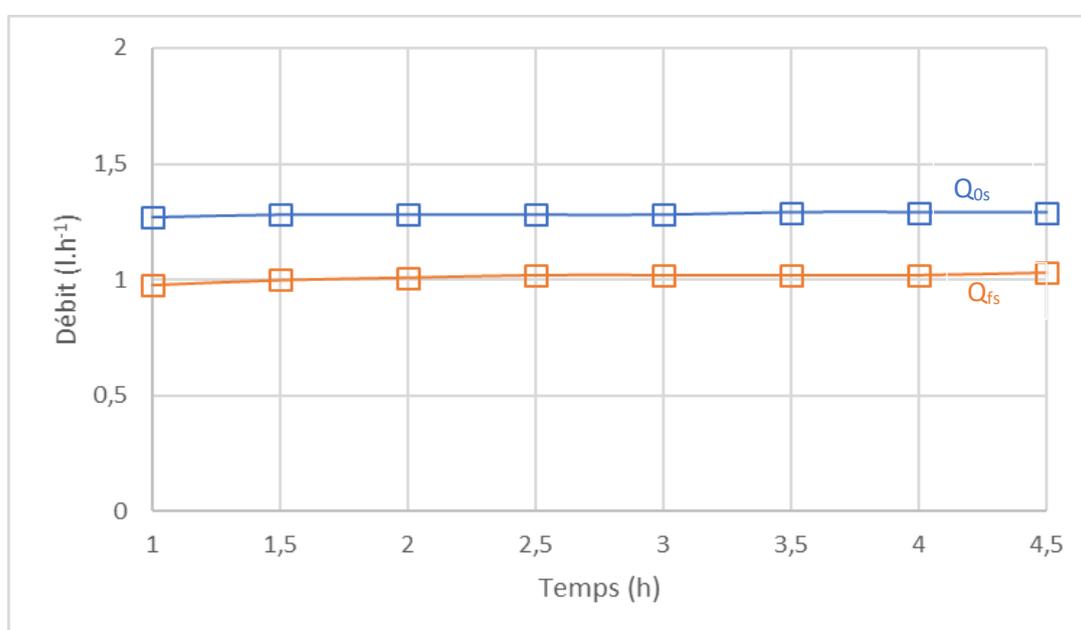


Figure 11. Evolution of inlet and outlet salt flow rates in a steady state $[\text{NH}_4\text{NO}_3] = 1,28 \text{ mol l}^{-1}$; $[\text{HNO}_3] = 1,28 \text{ mol l}^{-1}$

Table 6 shows the experimental results and compared to the expected ones made by the equations 12 and 13. For calculation, the hourly variation of salt

solution is about 230 ml h^{-1} (section *Volume variations*).

Table 6. comparison between experimental and calculated inlet and outlet salt flow rates.

$[\text{NH}_4\text{NO}_3]_{\text{feed}}$ (mol.l ⁻¹)	$[\text{NH}_4\text{NO}_3]_{\text{steady state}}$ (mol.l ⁻¹)	Experimental input flow rate (l.h ⁻¹)	Calculated input flow rate (l.h ⁻¹)	Experimental output flow rate (l.h ⁻¹)	Calculated output flow rate (l.h ⁻¹)
2,02	1,28	1,270	1,316	1,044	1,086

The gap between forecasts and experiments is about 4%. The flow variation, due to the species transfer during electrodialysis, is experimentally about 226 ml h^{-1} , in good agreement with the value obtained in batch mode study (230 ml h^{-1}).

-Comparison of flow rate variations

The following values were obtained experimentally:

$$q_s = Q_{0s} - Q_{fs} = 1,27 - 1,044 = 0,226 \text{ l.h}^{-1}$$

$$q_a = Q_{fa} - Q_{0a} = 0,070 \text{ l.h}^{-1}$$

The difference between these two values should be reflected largely in the base circuit including the stripping device. In fact, the volume changes associated with this circuit are as follows (for a period of 4,5 hours and according to [Figure 7](#) and [Table 5](#)):

Base tank: 50 ml.

Traps: 630 ml.

Approximately $151 \text{ ml}\cdot\text{h}^{-1}$, while q_s-q_a is about $156 \text{ ml}\cdot\text{h}^{-1}$. The agreement is very good. The transferred water balance is therefore identical in the two operating modes.

Conclusion

The coupling of bipolar membrane electro dialysis (BPMED) and in-situ continuous ammonia stripping enables the regeneration of nitric acid and ammonia by treating directly the wastewaters containing ammonium nitrate. This study, conducted in batch mode, allowed to determine the functioning optimal conditions:

- selection of AW (Solvay) and the CMB (Tokuyama Soda), as homopolar membranes.
 - initial nitric acid concentration 1 mol L^{-1}
 - NaOH and ammonia concentration 1 mol L^{-1}
- (This was imposed by the chosen stripping conditions at 45°C and 145 mbar).

In these conditions, the current efficiencies of acid and ammonia reached more than 80 % (to obtain a 2 mol L^{-1} nitric acid concentration).

The forecast calculations, based on the balance material equations and batch mode study results, were used to estimate the feed and bleed mode operating parameters for both acid and salt. The agreement is deemed very well (maximum deviation equal 4%). The current efficiencies obtained from feed and bleed mode are comparable to those obtained from batch mode (under the same conditions). Indeed, the acid and ammonia current efficiencies reached respectively 85 and 83 % in batch processing, and 83 and 80 % in continuous processing.

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