



Ammonium nitrate wastewater treatment by coupled membrane electrolysis and electro dialysis

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Received 17 January 2002; accepted in revised form 1 May 2002

Key words: ammonium nitrate, electrochemical splitting, electro dialysis, membrane electrolysis, stripping

Abstract

A process coupling membrane electrolysis and electro dialysis is implemented to treat ammonium nitrate wastewater. Membrane electrolysis produces ammonia and nitric acid while electro dialysis reconcentrates the depleted salt solution. Ammonia is removed continuously by *in situ* stripping; thus allowing gas production with a constant current efficiency (about 70%). Nitric acid up to 8 mol L⁻¹ is obtained. The current efficiency of acid production depends on nitric acid concentration. When this concentration varies from 1 to 8 mol L⁻¹ the average current efficiency is about 58%. Electro dialysis produces a rejected stream containing less than 3 × 10⁻³ mol L⁻¹ of ammonium nitrate.

1. Introduction

Natural water contamination by nitrogen compounds is an increasing problem, essentially related to intensive agriculture and industrial activity. For instance, in the nuclear fuel cycle, ammonium nitrate wastewater is produced when ammonium diuranate precipitates during uranyl nitrate conversion into uranium oxide. Among the various processes used in salt wastewater treatment, electromembrane techniques constitute an interesting field of investigation, particularly those techniques in which the salt is converted to the conjugated acid and base (bipolar membrane electro dialysis and membrane electrolysis).

Bipolar membrane electro dialysis (BPMED) uses water splitting to regenerate acid and base from a salt [1].

Membrane electrolysis (ME) combines the permselective ion transport across an ion exchange membrane and electrochemical reactions at electrodes. Figure 1 gives a schematic description of the ME principle with a three compartment cell. The catholyte and anolyte compartments are respectively separated from the central compartment by a cation (CEM) and an anion (AEM) exchange membrane. Ammonium nitrate solution is fed into the central compartment. Thus, NO₃⁻ migrates through the anion exchange membrane and enters the anolyte compartment to generate nitric acid with protons produced by water oxidation at the anode.

On the other side, NH₄⁺ migrates through the cation exchange membrane to the catholyte compartment to

form ammonia with hydroxyl ions produced by water reduction at the cathode. Nitric acid concentration increases in the anolyte compartment while ammonium nitrate concentration decreases in the salt compartment.

The main industrial application of this technology is found in chlor-alkali production [2, 3]. During the last ten years ME was studied to generate concentrated phosphoric [4], sulfuric [5, 6], formic [7] and hydrochloric acid [8].

Membrane processes applied to treatment of industrial effluents are more recent. Processes devoted to ammonium nitrate wastewater treatment by BPMED were investigated [9, 10]. Unfortunately, this technique is limited to the production of about 2 mol L⁻¹ nitric acid because of bipolar membrane lifetime. Membrane electrolysis was also investigated by Sawa et al. [11, 12]. 6 mol L⁻¹ nitric acid and up to 8 mol L⁻¹ ammonia solutions were obtained. Hitachi and Japan Nuclear Fuel Companies took out a European patent [13] for the coupling of membrane electrolysis and electro dialysis to treat wastewater containing neutral salts like ammonium nitrate. The main claims concern the way the different cells are combined and how the various streams flow in the process.

The scope of the present paper is to report an environment friendly process to split ammonium nitrate in order to recycle nitric acid and ammonia. The first part deals with membrane electrolysis and the second part provides electro dialysis results.

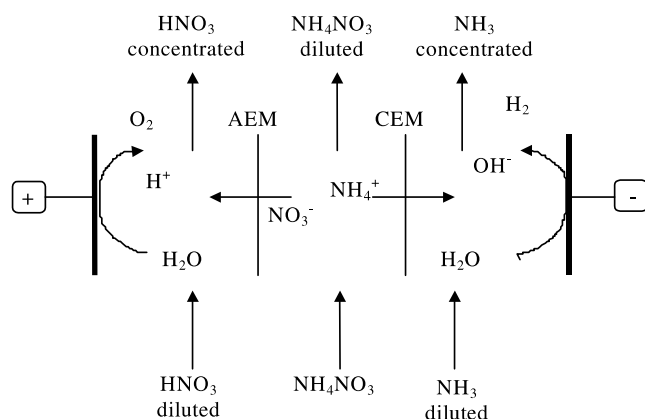


Fig. 1. Cell schema for the production of HNO₃ and NH₃ from NH₄NO₃.

2. Experimental details

2.1. Membrane electrolysis

2.1.1. Experimental set-up

The ME device, an electro-MP-cell supplied by Electro-cell AB, was a three compartment cell. The operation was carried out in batch mode. Each liquid circuit was equipped with a circulation tank, a pump and a flowmeter. A manometer was placed near each compartment inlet to adjust the pressure within the cell (Figure 2).

The working area of membranes and electrodes was 100 cm². The anode was a DSA[®] (dimensionally stable anode) and the cathode was made of stainless steel.

An AW membrane (a low proton leakage anion exchange membrane) supplied by Solvay, and a Nafion[®] 350 membrane (cation exchange membrane) supplied by DuPont de Nemours were used.

The current was supplied using a Lambda EMS-40-50 power source.

2.1.2. Ammonia stripping

NH₃ produced in the catholyte compartment was extracted from the recirculation tank heated to 50–60 °C and maintained under reduced pressure. Stripping

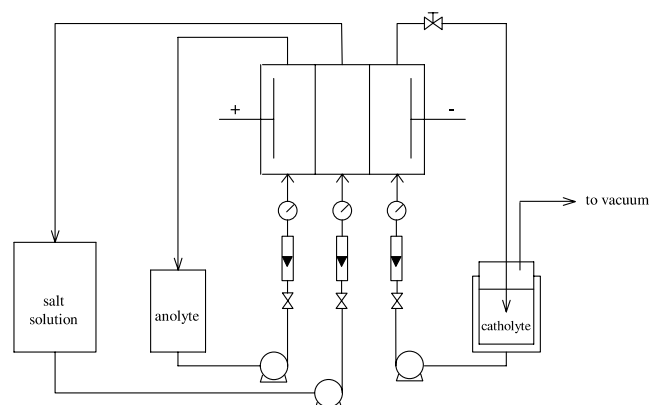


Fig. 2. Experimental set-up.

avoids current efficiency decrease due to ammonia back-diffusion through the cation exchange membrane. The low pressure (between 30 and 50 kPa) was applied only to the recirculation tank; the liquid pressure at the inlet of the three compartments of the cell was maintained at the same value (about 130 kPa).

For analytical purposes, the stripped ammonia was trapped in bubblers containing sulfuric acid.

2.1.3. Experimental conditions

All chemicals used were analytical reagents, except for the ammonium nitrate solution used in the long time experiment, which was an industrial wastewater supplied by Cogema. The main impurity contained in this solution was traces of uranium (60 μg L⁻¹). Volumes of electrolyte solutions were about 1.5 L for anolyte, 1 L for catholyte and 10 L for salt solution.

Initial acid concentration varied between 0.5 and 8 mol L⁻¹ depending on the type of experiment. Initial salt concentration varied within the range 0.25–2.5 mol L⁻¹.

Before starting operation, sodium hydroxide was added to the catholyte solution in order to ensure current transport through this compartment. The NaOH concentration was about 1 mol L⁻¹. The ammonia concentration was chosen to be close to its saturation under the operating conditions.

Solution flow-rates varied between 150 and 200 L h⁻¹ (velocities between 7 and 9 cm s⁻¹) and were adjusted in order to maintain the same constant pressure in the three compartments. The current was maintained at 20 A, which corresponds to a current density of 2000 A m⁻².

During the electrolysis, samples of anolyte, salt solution and catholyte were withdrawn at regular intervals, in order to measure (by acido-basic titration) the concentrations of HNO₃, NaOH, NH₃ and NH₄⁺. Volume variations were measured for each solution.

2.2. Electrodialysis

The electrodialysis stack consisted of 10 cells (EUR-2P-10 supplied by Eurodia Industrie). CMV-AMV membranes from Asahi Glass Company were used. The cell active area was 2 dm². The diluate and concentrate circuits were initially fed with the same solution of ammonium nitrate.

3. Results and discussion

3.1. Membrane electrolysis results

3.1.1. Influence of acid concentration on current efficiency
Short time experiments (between 30 and 60 min) were carried out in order to evaluate the influence of salt and acid concentrations on the current efficiency of the process.

The differential current efficiency, η , of acid production is defined as

$$\eta = \frac{d(VC)F}{Idt} \quad (1)$$

where F is the faradaic constant, I the current. V is the volume of anolyte and C the nitric acid concentration.

During these short time experiments, all the concentrations varied to a small extent. Measuring small variations of nitric acid amount allows the determination of differential current efficiency (i.e., the current efficiency for given conditions). The main factor affecting η is the nitric acid concentration in the anolyte. Figure 3 reports this effect.

As expected, the current efficiency of acid production decreases as the nitric acid concentration increases. The relationship is linear. For 1 mol L⁻¹ nitric acid solution, η is about 87%, whereas it is only 36% for 8 mol L⁻¹. This is due to proton leakage through the anion exchange membrane, which increases with concentration [14, 15].

Salt concentration in the range 0.25–2.5 mol L⁻¹ does not change the current efficiency of acid production. In these experiments the catholyte ammonia concentration was 2 mol L⁻¹. The current efficiency of ammonia production remains constant and equal to about 85%. *In situ* ammonia stripping limits current efficiency loss due to ammonia diffusion through the cation exchange membrane.

3.1.2. Experiments at variable concentrations

Experiments were carried out to produce concentrated nitric acid (8 mol L⁻¹ starting from a 1 mol L⁻¹ solution) and to determine performances of the operation during this production.

(a) *Water transfer.* Volume variations were observed in the three circuits during electrolysis. The salt solution volume decreases while the anolyte and catholyte volumes increase. For membranes used in these experiments average volume variations are reported in Table 1.

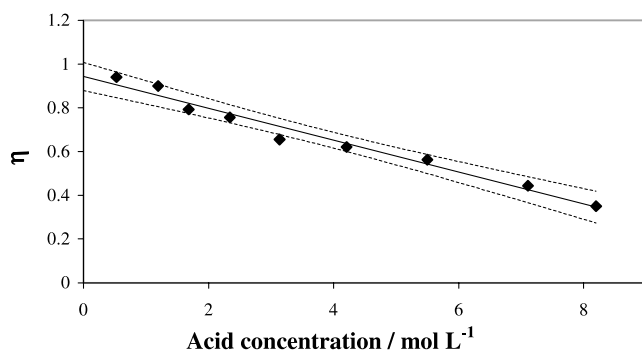


Fig. 3. Effect of acid concentration on current efficiency. Parameters: $I = 20$ A, $[\text{NH}_3] = 2$ mol L⁻¹, $[\text{NH}_4\text{NO}_3] = 2.5$ mol L⁻¹, $[\text{NaOH}] = 1$ mol L⁻¹. Key: (—) linear fitting, $\eta = -0.073 C + 0.94$; (---) confidence bands (95%).

Table 1. Volume variations in the three solutions
Stripping conditions: $T = 60$ °C, $P = 35$ kPa.

$\Delta V/\Delta n$ /mL faraday ⁻¹	Anolyte	Salt	Catholyte
	20	-170	70

The anolyte, salt solution and catholyte volume variations correspond, respectively, to 1, -9 and 4 moles of water per faraday. Variations of salt volume are only due to water transfer by electroosmosis. Anolyte volume variations are the balance between water transfer through the anion-exchange membrane and water consumption by electrolysis. Catholyte volume variations are due to water transfer through the cation-exchange membrane, water consumption by electrolysis and evaporation with the stripped ammonia. The water transference coefficient $t_{\text{H}_2\text{O}}$ is defined as the number of moles of water transported per faraday through a membrane. In our experiments the sum of the water transference coefficients in the two ion-exchange membranes is given by salt solution volume variations (i.e., 9 mol faraday⁻¹). Okada et al. [16] report that $t_{\text{H}_2\text{O}}$ for ammonium ions in a Nafion[®] 115 membrane is 7 mol faraday⁻¹. If we assume the same behaviour for Nafion[®] 350, the water transference coefficient in the anion-exchange membrane is thus about 2 mol faraday⁻¹. Robbins and Field [17] report an analysis of water transfer through an AW membrane used for nitric acid concentration: the nitrate ions are transported with about 3.5 molecules of water per molecule of NO₃⁻ while protons are transported in the opposite direction with a single water molecule.

The value of 2 for water transference coefficient in an AW membrane deduced from our experiments results from the competition of nitrate and proton transfer.

(b) *Concentration evolution.* Changes in the concentrations of nitric acid, salt, ammonia and acid in salt during electrolysis are reported in Figure 4. The mass balance was calculated for nitrate and ammonium, taking into account the variations of each solution volume (see below). It was checked within 2%.

During these experiments acid concentration increases from 1 to 8 mol L⁻¹. Ammonia concentration in the

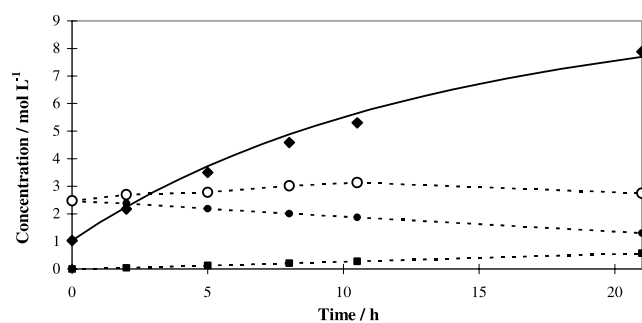


Fig. 4. Change in concentrations during electrolysis. Parameters: $I = 20$ A, $P = 53$ kPa, $T = 55$ °C. Key: (◆) $[\text{HNO}_3]$ in anolyte; (●) $[\text{NH}_4\text{NO}_3]$ in salt; (■) $[\text{H}^+]$ in salt; (○) $[\text{NH}_3]$ in catholyte; (—) $[\text{HNO}_3]$ calculated (Section 3.1.2 (c)).

catholyte solution is almost constant. The value (about 2.8 mol L^{-1}) corresponds to ammonia solubility under fixed temperature and pressure conditions (Section 3.1.3). This figure also shows an increase in proton concentration in the salt compartment, due to proton leakage through the anion exchange membrane.

The current efficiency of base production varies in the range 69–77%. These values are lower than those obtained for short time experiments (about 85%). This can be explained by the increase in proton concentration in the salt compartment, as shown in Figure 4. The protons cross the cation exchange membrane and neutralize the base produced in the catholyte compartment. A pH adjustment allows avoidance of this effect.

(c) *Modelling*. Knowing the differential current efficiency of acid production the objective is to calculate an integral current efficiency when nitric acid concentration varies from C_i to C_f and to compare these values to experimental ones. The integral current efficiency is given by

$$\bar{\eta} = \frac{(V_f C_f - V_i C_i) F}{I(t_f - t_i)} \quad (2)$$

where V_i and V_f are, respectively, the initial and the final anolyte volume, t_i and t_f are the initial and the final time of experiment.

Referring to Equation 1 the integral current efficiency may be expressed as

$$\bar{\eta} = \frac{(V_f C_f - V_i C_i)}{\int_{C_i}^{C_f} \frac{dV C}{\eta}} \quad (3)$$

η is a function of C (Figure 3):

$$\eta = -0.073 C + 0.94 \quad (4)$$

Considering a moderate volume variation and using the mean value of anolyte volume, Equations 3 and 4 give

$$\bar{\eta} = \frac{(C_f - C_i)}{\int_{C_i}^{C_f} \frac{dC}{-0.073 C + 0.94}} = 0.073 \times \frac{(C_f - C_i)}{\ln\left(\frac{-0.073 C_i + 0.94}{-0.073 C_f + 0.94}\right)} \quad (5)$$

When acid concentration increases from 1 to 8 mol L^{-1} the integral current efficiency would be about 58%.

Experimental values obtained were compared with values calculated by Equation 5. Table 2 summarizes the

results. The agreement is good. Moreover, Equation 5 and volume variations allow the calculation of the nitric acid concentration against time. An example is given in Figure 4. The calculated curve (solid line) is very close to experimental points, showing the accuracy of the current efficiency model.

3.1.3. Ammonia stripping at different conditions

The ammonia concentration in the catholyte solution remains almost constant in each experiment. Its value depends on the stripping conditions. For fixed temperature and pressure values, ammonia solubility can be calculated [18]. The calculation takes into account the effect of NaOH concentration, hydrogen pressure and water vapour pressure (see Appendix). For various stripping conditions experimental ammonia solubility has been measured and compared to the calculated values as reported in Table 3. The agreement is good.

To obtain low ammonia solubility in order to reduce ammonia backdiffusion, the stripping pressure must be low and the temperature high. Moreover, for experiments carried out under low stripping pressure, the increase in catholyte volume was reduced.

This *in situ* stripping represents an original way of ammonia recovery. This differs from the process proposed by Sawa et al. [11, 12] where ammonia is recovered in a subsidiary chemical operation, with a subsequent sodium sulphate production.

3.1.4. Nitric acid purity

Ammonium nitrate wastewater to be treated by the membrane electrolysis process may contain some impurities that can be transferred through the ion exchange membranes and pollute the acid or the catholyte obtained, particularly uranium, which is present in ammonium nitrate as uranyl ions. Experiment showed that uranium may cross the anion exchange membrane and pollute nitric acid. If this minor pollution is unwanted pretreatment is necessary.

Table 3. Comparison of ammonia solubility (experimental and calculated)

Stripping pressure/kPa	32	33	51	52
Temperature/°C	60	51	55	52
[NaOH]/mol L ⁻¹	0.8	0.9	0.9	0.8
[NH ₃] calc./mol L ⁻¹	0.9	1.81	2.54	3.6
[NH ₃] exp./mol L ⁻¹	0.97	1.93	2.25	3.35

Table 2. Comparison of experimental and calculated integral current efficiency of acid production
 $I = 20 \text{ A}$, $[\text{NH}_3] = 2 \text{ mol L}^{-1}$, $[\text{NH}_4\text{NO}_3] = 2.5 \text{ mol L}^{-1}$, $[\text{NaOH}] = 1 \text{ mol L}^{-1}$

Experiment duration/h	3	3.5	4	5	5	9	10	21
C^i /mol L ⁻¹	2.71	0.94	0.95	0.95	1.00	4.27	1.02	1.04
C^f /mol L ⁻¹	3.52	2.19	2.24	2.48	2.86	6.84	5.00	8.23
Average anolyte volume/L	1.92	1.78	1.92	1.97	1.60	1.44	1.26	1.20
$\bar{\eta}$ experimental/%	69	85	83	81	80	55	67	55
$\bar{\eta}$ calculated/%	72	83	83	82	80	53	71	56

Ammonium ions NH_4^+ are able to cross the anion exchange membrane by diffusion. NH_4^+ may thus be present in the anolyte compartment as an impurity in the nitric acid produced. For this reason, the NH_4^+ concentration has been measured in nitric acid for different experiments by a colorimetric method. A maximum value of $1.7 \times 10^{-4} \text{ mol L}^{-1}$ was determined for experiments where an 8 mol L^{-1} acid was reached starting from 1 mol L^{-1} and with an ammonium nitrate initial concentration of 2.5 mol L^{-1} . The concentration ratio $[\text{NH}_4^+]/[\text{NO}_3^-]$ in nitric acid is lower than 2×10^{-5} . Then pollution of nitric acid by NH_4^+ diffusion can be considered negligible.

3.1.5. Long duration experiment

A 1000 h experiment with industrial wastewater was carried out to confirm the industrial feasibility of the process, in terms of current efficiency and also to check over the chemical resistance of membranes and electrodes. The experimental apparatus was the same as that used in previous experiments. This long time experiment was carried out by 24 h cycles. During one cycle, the acid concentration increased from 1 to 8 mol L^{-1} and the salt concentration decreased from 1.5 to about 0.5 mol L^{-1} . At the end of each 24 h cycle, electrolysis was stopped. Ammonium nitrate was replaced by a more concentrated solution and nitric acid was withdrawn and replaced by 1 mol L^{-1} solution.

(a) *Electrolysis cell voltage.* The cell voltage was recorded during the experiments. For each 24 h cycle, the same cell voltage evolution was observed. An example is presented in Figure 5. The plateau value is rather high ($>7 \text{ V}$) due to the large width of the compartment in the laboratory cell (6 mm). In an industrial cell, the voltage would be about 5 V at the same current density (2000 A m^{-2}).

Figure 6 represents the variations of cell voltage (plateau value) measured during the 1000 h experiment. This value remains almost constant.

(b) *Current efficiency of acid and base production.* Figure 7 represents the change in the integral current efficiency (as $[\text{HNO}_3]$ varies from 1 to 8 mol L^{-1}) with time, for acid and base production. In both cases a slight decrease is observed, the magnitude of which is of the same order as the experimental errors (about 3% for 1000 h).

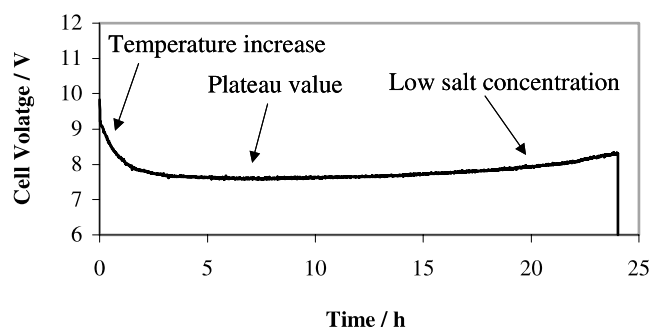


Fig. 5. Cell voltage change during a 24 h cycle.

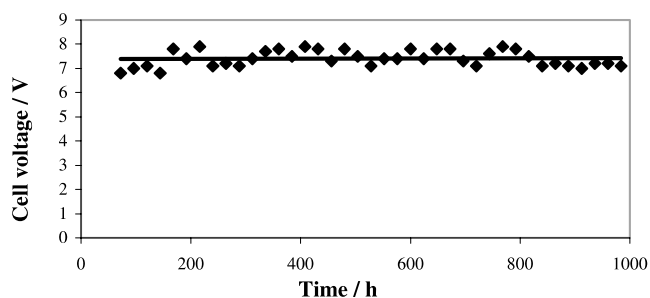


Fig. 6. Change in cell voltage with time. $I = 20 \text{ A}$.

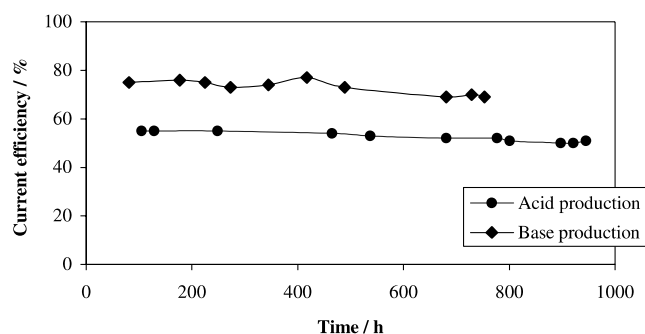


Fig. 7. Change in current efficiency of acid and base production with time. Parameters: $I = 20 \text{ A}$, $[\text{HNO}_3]$ initial = 1 mol L^{-1} , $[\text{NH}_3] = 2 \text{ mol L}^{-1}$, $[\text{NaOH}] = 1 \text{ mol L}^{-1}$.

(c) *Resistance of materials.* At the end of the 1000 h experiment the cell was disassembled. Electrodes and membranes did not show any change except for traces of uranium detected in the cation-exchange membrane.

3.2. Electrodialysis results

As stated previously electro dialysis is carried out to reconcentrate ammonium nitrate withdrawn from the membrane electrolysis salt circuit. It also produces a diluate containing very low nitrate concentration. Figure 8 reports the variation of ammonium nitrate concentration with time, in the diluate and the concentrate streams. The solid line represents the concentrate concentration calculated from the diluate results and mass balance. Good agreement with experimental measurements is observed.

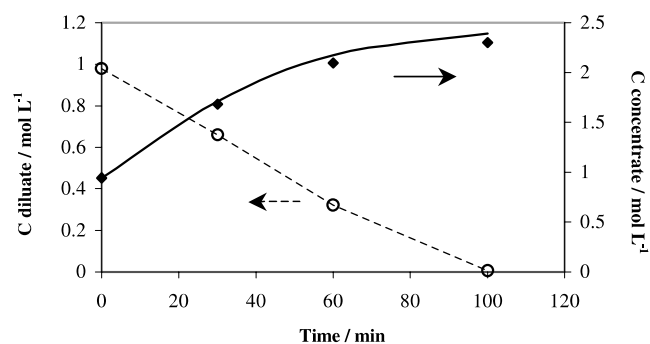


Fig. 8. Change in ammonium nitrate concentration during ED operation. Parameters: $U_{\text{max}} = 20 \text{ V}$, I varies from 10 to 1 A/10 unit cells; (solid line) calculated from diluate concentration and mass balance.

The integral current efficiency was about 95%. The final salt concentration in the concentrate solution was relatively high (about 2.3 mol L^{-1}) and water transfer through membranes was about $13 \text{ mol faraday}^{-1}$.

The electro dialysis results demonstrate the possibility of reducing ammonium nitrate concentration to a residual concentration lower than $3 \times 10^{-3} \text{ mol L}^{-1}$.

3.3. Coupled process: membrane electrolysis and electro dialysis

The whole process is schematized on Figure 9. Acid is preferably produced in batch mode for efficiency reasons. During each cycle, acid concentration increases progressively from an initial value of about 1 mol L^{-1} to a final value of about 8 mol L^{-1} . The ammonia produced in the catholyte is extracted continuously from the recirculation tank. The ammonia concentration remains nearly constant and is equal to the ammonia solubility for the operating conditions. Sodium hydroxide concentration also remains nearly constant. The variations are related to the volume increase due to water transfer. The catholyte volume must be kept constant by withdrawing the excess solution.

Continuous processing in the feed and bleed mode seems to be the most suitable for the salt solution. Ammonium nitrate wastewater is introduced continuously to the salt recirculation tank.

During membrane electrolysis, the salt solution becomes increasingly acid because of proton leakage if no pH adjustment is operated. The overflow of the catholyte solution may be used to adjust the salt solution pH value to about 3. Sodium ions are then introduced into the salt compartment but without any consequence on the process because they will return to the catholyte solution by crossing the cation exchange membrane. A purge is also done to avoid impurity accumulation.

Salt solution is extracted from the recirculation tank and fed to electro dialysis operation. For this step a

batch mode is suitable. The concentrate is reintroduced into the tank to increase salt concentration and the diluate constitutes the final rejection of the process. The ammonium nitrate concentration in this stream must be as low as possible (a value of $3 \times 10^{-3} \text{ mol L}^{-1}$ is reached).

Salt concentration in the recirculation tank varies during each electro dialysis cycle. The average value may be chosen so to minimize electrolysis and electro dialysis costs.

4. Conclusion

The ammonium nitrate treatment process based on coupling of membrane electrolysis and electro dialysis is efficient for regeneration of nitric acid and ammonia. It solves the problem posed by a salt laden effluent. The products may be of a relatively high concentration. Nitric acid 8 mol L^{-1} is obtained with an acceptable current efficiency (related to the choice of anion exchange membrane) of about 60%. Gaseous ammonia will be absorbed classically to give a pure concentrated solution. In term of economics, the treatment might appear expensive due to the relatively low current efficiency and high cell voltage. However, the cell voltage will be lower in an industrial process because the compartment width is smaller than in the laboratory cell. The estimated electrochemical energy consumption of an industrial process is about 4–5 kWh for the production of 1 kg of nitric acid and the stoichiometric amount of ammonia (0.27 kg). The quality of the products (nitric acid and stripped and absorbed ammonia) is high. The current density must be optimised considering fixed and variable costs. The economics of the process must take into account the generation of recyclable or saleable products of high purity and the credit for disposal of salt effluent.

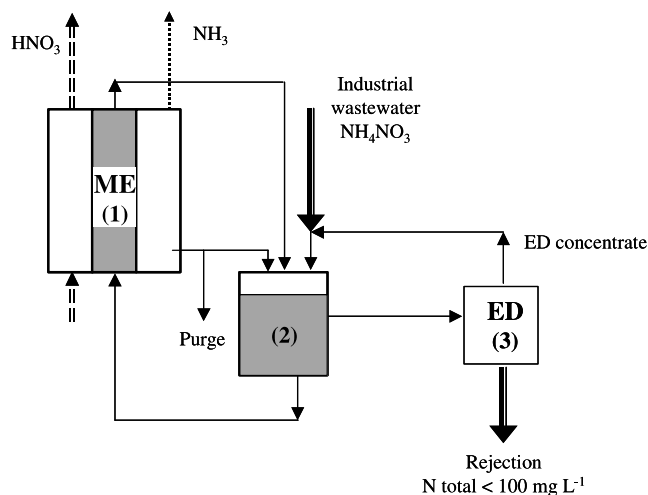


Fig. 9. Schema of the process. Key: (1) membrane electrolysis cell; (2) salt recirculation tank; (3) electro dialysis cell.

Acknowledgement

This work was supported by Cogema, Pierrelatte, France.

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Appendix: Ammonia partial pressure in the stripped gas

Experimental measurements give total pressure in the catholyte tank: P_t . The gas contains ammonia, hydrogen generated by water reaction at the cathode and water vapour. So,

$$P_t = p_{\text{NH}_3} + p_{\text{H}_2} + p_{\text{H}_2\text{O}}$$

$p_{\text{H}_2\text{O}}$ is the water vapour pressure at temperature θ . The gas is assumed to be water saturated. Thus, $p_{\text{H}_2\text{O}}$ is calculated using the following [19]:

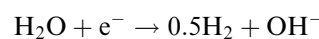
$$\log p_{\text{H}_2\text{O}} = 10.23245 - \frac{1750.286}{\theta + 235}$$

where $p_{\text{H}_2\text{O}}$ is in Pa and θ in °C.

The above equation allows the calculation of water vapour pressure over pure liquid water. This value is only slightly modified by the presence of 1 mol L⁻¹ NaOH or ammonia. Then,

$$p_{\text{H}_2} + p_{\text{NH}_3} = P_t - p_{\text{H}_2\text{O}}$$

For one faraday the amount of H₂ produced by water reduction is 0.5 mol, that is,



and the amount of NH₃ produced is η_{NH_3} mol, where η_{NH_3} is the current efficiency of base production.

The partial pressure of ammonia is given by the following relation:

$$p_{\text{NH}_3} = \frac{\eta_{\text{NH}_3}}{\eta_{\text{NH}_3} + 0.5} (P_t - p_{\text{H}_2\text{O}})$$

Given the temperature, NaOH concentration and total pressure, this equation allows the calculation of p_{NH_3} . The solubility of ammonia is then calculated [18].