Short Communication

Electrodialysis of Ammonium Nitrate Solution in Intensive Current Regimes

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Electrodialysis of ammonium nitrate solution with the use of different membrane pairs MK-40/MA-41, MK-41/MA-41 by UCC Szechkinoazot (Russia), Ralex CM(H)-PP / Ralex AM(H)-PP by Mega a.s. (Czech Republic) was carried out. It was demonstrated that the highest degree of desalination can be achieved with the use of the membranes Ralex CM(H)-PP / Ralex AM(H)-PP in electrodialysis cell. A membrane pair (MK-41/MA-41) was established, whose application will allow conducting a reagent-free acidification of solutions in the concentration compartment in order to prevent the precipitate formation on the surface of the anion exchange membranes in the desalination compartment.

Keywords: electrodialysis, ammonium nitrate, precipitate formation, cation exchange membranes, anion exchange membranes, current-voltage characteristic of ion exchange membranes.

1. INTRODUCTION

Ammonium nitrate is the main component of the waste water of nitrogenous mineral fertilizer production [1]. Discharge of such waste water into reservoirs is strictly regulated [1, 2]. Nitrate accumulation in open reservoirs can lead to active growth of algae, suppression of living organism activity [3]. Currently, for the treatment of nitrogenous waste water the stripping method, biochemical purification, waste water incineration, ion exchange, reverse osmosis are used [4-10]. The disadvantage of the stripping method is the high consumption of chemicals and the formation of a large amount of secondary waste water. The ion-exchange method involves the periodic regeneration of ion-exchange resins. During waste water incineration containing ammonia the formation of hydrogen cyanide, hydrazine and other highly toxic substances are possible. The effectiveness of biological purification depends on the uniformity of waste water income: volley discharges lead to the microflora destruction and disruption of the process. Currently, there are other options for the
treatment of waste water of mineral fertilizer production, such as electrocoagulation. This paper [11] represents the method for removing the mixture of phosphates and nitrates. In the research [12] the method for removing nitrates from water as a result of their recovery on the modified nickel-containing electrode is suggested.

A promising electrochemical method for the treatment of nitrogen-containing saline solutions can be electrodialysis [13-16]. This will make it possible to create non-waste industrial technologies (“green” chemistry), since the concentrate and diluate obtained by electrodialysis can be reused in technological cycle.

Currently, for the intensification of desalination process electrodialysis is carried out in so called “overlimiting” current regimes [17-19]. The use of such intensive current regimes is one of the promising directions in the development of electrodialysis process. However, under such conditions at “membrane-solution” interphase boundaries the dissociation of water molecules occurs, which leads to a change in pH of the solutions in membrane channels. For this reason, the application of electrodialysis in the treatment of the solutions – mineral fertilizer production wastes – is limited by the formation of precipitation on anion exchange membranes in concentration compartment due to alkalinization of the concentrate during the process in intensive current regimes, since the waste water from such production contains ions of iron, magnesium, calcium, copper.

The activity of dissociation of water molecules depends on the nature of electrolyte and the type of the membranes used. It is therefore of interest to search for the membranes the use of which in the electrodialyzer will afford to carry out reagent-free steady acidification of the solution concentration section in the exorbitant current modes.

Therefore, a comparative analysis of the behavior of ion exchange membranes during electrodialysis of ammonium nitrate solution carried out in intensive current regimes, the establishment of specific features of the generation of hydrogen ions by membranes of different types is a topical scientific problem, the solution of which can contribute to improving the electrodialysis process of nitrogen-containing saline solutions.

An important phenomenon occurring under electrodialysis is concentration polarization: at “solution – membrane” boundary there appears a diffusion flux directed to the interphase boundary and a decrease in electrolyte concentration near the membrane takes place. The concentration polarization results in an irreversible dissociation of water molecules at the “membrane-solution” boundary, the transfer of H\(^+\) and OH\(^-\) ions across the membrane and the increase in the electrical resistivity of the system. The maximum of ion transfer across the membrane corresponds to the limiting current density. The limiting state on the membranes is reached when the electrolyte concentration near the membrane is practically zero. The current density corresponding to such a state is called a limiting diffusion density \(i_{\text{lim}}\) [20]:

\[
i_{\text{lim}} = \frac{z_i F D_i C_0}{(T_i - t_i) \delta},
\]

where \(z_i\) is a charge number of a counterion, \(F\) is the Faraday constant, \(D_i\) is the ion diffusion coefficient in the solution, \(C_0\) is the bulk solution concentration, \(T_i\) and \(t_i\) the transport numbers of counter ions in the membrane and solution, respectively, \(\delta\) the thickness of a boundary layer.
The purpose of this work is to assess the impact of the type of a membrane pair on the efficiency of electrodialysis of ammonium nitrate solutions; to select the membranes capable of preventing alkalization of the solution in concentration compartments at current densities exceeding the limiting diffusion densities.

2. EXPERIMENTAL

In this work the ion exchange membranes MK-40, MK-41 and MA-41 (UCC Szchekinoazot, Russia) [21]; Ralex CM(H)-PP/Ralex AM(H)-PP (by Mega a.s., Czech Republic) [22] were used. Russian membranes are made by hot pressing a mixture of powders of polyethylene and ion exchange resins; Czech membranes are produced using roller technology. All membranes are heterogeneous: they consist of an ion exchange component, polyethylene and reinforcing fabric. A distinctive feature of Czech counterparts is a higher degree of grinding of the ion exchanger, which is part of the samples. The fraction of the surface occupied by ionite granules for heterogeneous ion exchange membranes Ralex is 25-30%, for MK and MA it is two times less. The radius of the sections of ion exchange grain exit to the surface for cation exchange membranes Ralex CM(H) is 0.5-7.0 μm; for MK-40 - 1-12 μm; for anion exchange membranes Ralex AM(H) and MA-41 – 0.6-7.0 μm and 1-17 μm, respectively [15, 23, 24].

Pretreatment of membranes for the work and determination of their characteristics was performed using the standard techniques [25, 26]. Some characteristics of the studied membranes are presented in table 1.

Table 1. Characteristics of heterogeneous ion-exchange membranes

<table>
<thead>
<tr>
<th>Index</th>
<th>MK-40</th>
<th>MK-41</th>
<th>MA-41</th>
<th>RalexCM(H)-PP</th>
<th>RalexAM(H)-PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional groups&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-SO&lt;sub&gt;3&lt;/sub&gt;H</td>
<td>-PO&lt;sub&gt;3&lt;/sub&gt; &lt;sub&gt;2&lt;/sub&gt;H</td>
<td>-N&lt;sup&gt;+&lt;/sup&gt;(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-SO&lt;sub&gt;3&lt;/sub&gt;H</td>
<td>-N&lt;sup&gt;+&lt;/sup&gt;(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Binder&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td></td>
<td></td>
<td>polyethylene</td>
<td></td>
</tr>
<tr>
<td>Reinforcing fabric&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>capron</td>
<td></td>
<td>polypropylene</td>
<td></td>
</tr>
<tr>
<td>Membrane thickness, mm</td>
<td>0.41±0.04</td>
<td>0.72±0.07</td>
<td>0.61±0.06</td>
<td>0.60±0.06</td>
<td>0.60±0.06</td>
</tr>
<tr>
<td>Total exchange capacity, mmole / g (NaOH or HCl with concentration 0.1 mole / dm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>2.2±0.22</td>
<td>2.8±0.28</td>
<td>1.6±0.16</td>
<td>2.1±0.21</td>
<td>1.6±0.16</td>
</tr>
<tr>
<td>Working exchange capacity&lt;sup&gt;b&lt;/sup&gt;, mmole / g</td>
<td>1.2±0.12</td>
<td>0.5±0.05</td>
<td>1.0±0.01</td>
<td>1.2±0.12</td>
<td>0.9±0.09</td>
</tr>
<tr>
<td>Moisture contents, %</td>
<td>40.0 ± 5.0</td>
<td>30.0±5.0</td>
<td>40.0 ± 5.0</td>
<td>30.0±5.0</td>
<td>28.0±5.0</td>
</tr>
<tr>
<td>Transport number&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&gt;0.8</td>
<td>&gt;0.8</td>
<td>&gt;0.94</td>
<td>&gt;0.95</td>
<td>&gt;0.95</td>
</tr>
</tbody>
</table>

<sup>a</sup>Measured in 0.012 mol/dm<sup>3</sup> NH₄NO₃
<sup>b</sup>Information taken from products brochure
The experiment was conducted in a seven-compartment electrodialysis cell, which is a set of consecutively alternating cation and anion exchange membranes (Fig. 1). Three types of membrane pairs were considered: MK-40/MA-41; MK-41/MA-41; Ralex CM(H)-PP/Ralex AM(H)-PP. Intermembrane distance was estimated by the thickness of polyethylene gaskets and was equal to 1 mm. The area of the working surface of the membrane was 14.4 cm², the solution feed rate was 0.046 cm/s. The galvanostatic mode of electrodialysis was provided by a direct current source AKIP-1137-200-1.

![Figure 1. Seven-compartment electrodialysis cell](image)

Ammonium nitrate solution with the concentration of 0.012 mol/dm³ was used as a model solution. Under the action of electric current, ammonium ions migrated to the cathode across the cation exchange membrane. Their further migration was restricted by the anion exchange membrane. A similar process took place with respect to nitrate ions. Thus, upon application of a potential difference the desalination (2, 4, 6) and concentration (3, 5) compartments were formed. At low current densities the experimental conditions provided a laminar hydrodynamic regime. Mass transfer in the desalination compartment of the cell under these conditions can be described by a convection-diffusion model [27], which allows one to calculate the limiting current values for the membrane system in the absence of concentration polarization effects by the formula:

\[
\frac{i_{lim}}{i_{0,lim}} = 1.47 \frac{FD_i C_0}{h(T - t_i)} \left( \frac{h^2 V}{LD_i} \right)^{1/3}, \tag{2}
\]

where \( h \) is intermembrane distance, \( L \) is desalination path length, \( V \) is an average linear solution flow rate.

Efficiency criteria of the treatment of ammonium nitrate solution by electrodialysis – energy consumption, degree of desalination – were determined by the formulas shown in Table 2.
Table 2. Formulas for the calculation of the main parameters of the process

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formula for the calculation</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of desalination, %</td>
<td>$F_{\text{des}} = \Delta C/C_0$</td>
<td>$\Delta C$ – concentration difference inlet and outlet of the desalination compartment (mol/dm$^3$), $C_0$ – initial solution concentration (mol/dm$^3$)</td>
</tr>
<tr>
<td>Energy consumption, kW·h/kg</td>
<td>$W = I \cdot U \cdot \tau / m$</td>
<td>$I$ – current (A), $U$ - voltage (V), $\tau$ - time (h), $m$ – mass of transferred NH$_4$NO$_3$ (kg)</td>
</tr>
</tbody>
</table>

Figure 2. Current-voltage curve of the ion exchange membrane under electrodialysis

To characterize the processes taking place on the membranes during electrodialysis, the current-voltage curves (CVC) of the membranes were estimated. For this purpose, in the adjacent compartments of the electrodialysis cell on both sides of the membrane under investigation two silver probe electrodes connected to a voltmeter were installed V7-22A. CVC was got by the static method: before registering of the potential difference the membrane was held for 30 minutes at the fixed value of the current density. Under such conditions in the system "membrane / solution" the steady state was achieved. Then the voltmeter data recording was carried out.

Fig. 2 shows specific CVC with three sections differing in slope with respect to the current density axis: a linear section of ohmic resistance (I), a limiting current plateau (II); section (III) is characterized by the appearance in the solution of additional current carriers - ions H$^+$ and OH$^-$ formed as a result of heterolytic reaction of water dissociation.

The following CVC parameters were analyzed: the value of the limiting current density ($i_{\text{lim}}$); the potentials corresponding to the achievement of a limiting state ($E_{\text{lim}}$, the transition from section I to section II) and overlimiting state ($E_{\text{cr}}$, the transition from section II to section III); the length of the limiting current plateau ($dE$).
3. RESULTS AND DISCUSSION

The theoretical limiting current value \( i_{\text{lim\ theor}} \), calculated from the convection-diffusion model according to equation (2) for cation exchange membranes is 0.67 mA/cm\(^2\), for anion exchange membranes 0.92 mA/cm\(^2\). Fig. 3 - 5 show CVC of the studied membranes obtained at various steps of the polarization during electrodialysis of ammonium nitrate solution. Tables 3 and 4 present the results of the CVC analysis and parameters of the process calculated when the limiting diffusion current is exceeded.

![Figure 3](image)

**Figure 3.** Current - voltage curves of the membranes MK-40 (a) and MA-41 (b) during electrodialysis of NH\(_4\)NO\(_3\) solution (0.012 mol/dm\(^3\)) with a membrane pair MK-40/MA-41 and the change in pH of the solution in the concentration compartment

![Figure 4](image)

**Figure 4.** Current - voltage curves of the membranes MK-41 (a) and MA-41 (b) during electrodialysis of NH\(_4\)NO\(_3\) solution (0.012 mol/dm\(^3\)) with a membrane pair MK-41/MA-41 and the change in pH of the solution in the concentration compartment
Figure 5. Current - voltage curves of the membrane Ralex CM(H)-PP (a) and Ralex AM(H)-PP (b) during electrodialysis of NH₄NO₃ solution (0.012 mol/dm³) with a membrane pair Ralex CM(H)-PP/Ralex AM(H)-PP and the change in pH of the solution in the concentration compartment.

The investigation of the current-voltage curves of the membranes (Table 3) showed that for the membranes MK-40 and Ralex CM(H)-PP $i_{lim}^{exp}$ coincides with $i_{lim}^{theor}$. This may occur when the formation of the diffusion layer and its development is due only to electrodiffusion and forced convection of the electrolyte in the intermembrane space [28].

Ralex membranes have CVC with a more clearly defined limiting current plateau. For the Russian membranes, whose surface is less homogeneous, the conjugated effects of concentration polarization, accompanying the achievement of the limiting state, are revealed with different force in different sections [29], which leads to the degradation of the limiting current plateau.

The conjugated convection of the pre-membrane solution for the samples of Ralex CM(H)-PP/Ralex AM(H)-PP is revealed at sufficiently low values of $E_{cr}$; this membrane pair is characterized by the least intensive generation of medium ions which is shown by the value of the limiting current plateau. Besides, for Ralex samples the limiting current region is shifted towards lower values of the voltage drop on the membrane, resulting in the increase of the mass transfer of salt ions across the membranes and, consequently, allows obtaining a high degree of desalination at low energy consumption.

Table 3. Results of the analysis of current-voltage curves of the membranes

<table>
<thead>
<tr>
<th>Membrane pair</th>
<th>Membrane</th>
<th>$i_{lim}^{exp}$, mA/cm²</th>
<th>$E_{lim}$, V</th>
<th>$E_{cr}$, V</th>
<th>dE, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK-40/MA-41</td>
<td>MK-40</td>
<td>0.8</td>
<td>0.05</td>
<td>0.55</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>MA-41</td>
<td>2.0</td>
<td>0.20</td>
<td>2.80</td>
<td>2.60</td>
</tr>
<tr>
<td>MK-41/MA-41</td>
<td>MK-41</td>
<td>1.6</td>
<td>0.40</td>
<td>8.40</td>
<td>8.00</td>
</tr>
<tr>
<td></td>
<td>MA-41</td>
<td>2.7</td>
<td>0.28</td>
<td>4.40</td>
<td>4.10</td>
</tr>
<tr>
<td>Ralex CM(H)-PP /</td>
<td>Ralex C</td>
<td>0.7</td>
<td>0.20</td>
<td>1.60</td>
<td>1.44</td>
</tr>
<tr>
<td>Ralex AM(H)-PP</td>
<td>Ralex A</td>
<td>1.0</td>
<td>0.15</td>
<td>1.80</td>
<td>1.35</td>
</tr>
</tbody>
</table>
Table 4. Parameters of the electrodialysis process of ammonium nitrate solution ($i = 5 \text{ mA/cm}^2$)

<table>
<thead>
<tr>
<th>Membrane pair</th>
<th>MK-40/MA-41</th>
<th>MK41/MA-41</th>
<th>Ralex CM(H)-PP/ Ralex AM(H)-PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{\text{des}}(\text{NH}_4\text{NO}_3), %$</td>
<td>91.4</td>
<td>79.2</td>
<td>96.1</td>
</tr>
<tr>
<td>$W(\text{NH}_4\text{NO}_3), \text{kW} \cdot \text{h/kg}$</td>
<td>11.6</td>
<td>21.7</td>
<td>4.8</td>
</tr>
<tr>
<td>pH in the concentration</td>
<td>7.8</td>
<td>3.1</td>
<td>5.5</td>
</tr>
<tr>
<td>compartment</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The current-voltage characteristics of the membranes MK-40 and Ralex CM (H)-PP having in their composition identical functional groups are different. The surface of MK-40 has more extensive non-conductive sections (polyethylene), the larger grains of ionite emerging onto the surface, which reduces electric or thermoconvective mixing of the solution near the membrane due to fragmentation of the sections on which a local achievement of the limiting current is observed. In the case of Ralex CM (H)-PP the closeness of fine ionite grains facilitates the formation of a more homogeneous membrane surface, and its electrochemical behavior becomes similar to the behavior of homogeneous membranes, which are characterized by a longer CVC plateau in comparison with similar, with respect to functional groups, heterogeneous samples. Similar results were obtained in [30] for membranes MF-4SK (homogeneous) and MK-40 (heterogeneous).

The analysis of the change in pH in the concentration compartment showed that for all membrane pairs the acidification of the solutions is observed when the limiting diffusion current on the cation exchange membrane is reached. Further increase in the current density in the systems using cation exchange membranes with sulfonic-acid groups leads to alkalization of the solutions in concentration compartment, since the generation of hydroxyl ions at the “anion exchange membrane – solution” boundary proceeds more intensely than the generation of hydrogen ions at the “cation exchange membrane – solution” boundary [31].

The phosphonic acid membrane MK-41 is most active in terms of the generation of hydrogen and hydroxyl ions. At current densities above the limiting current density the solution in concentration compartments is acidified even when the limiting current on the anion exchange membrane is reached. This behavior of the membrane is caused by the nature of functional groups: in accordance with a series of catalytic activity with respect to the water dissociation reaction [32] phosphonic acid groups to a greater extent than the quaternary ammonium ones increase the rate of water dissociation:

$$-\text{N}^+(\text{CH}_3)_3 < -\text{SO}_3\text{H} < -\text{PO}_3\text{H}^- < \equiv\text{NH}_2 < \equiv\text{N} < -\text{COO}^- < -\text{PO}_4^{2-}$$

The membrane MK-41 has the longest limiting current plateau. However, this behavior of the membrane leads to somewhat decreased fluxes of ammonium ions due to a very active competitive transfer of hydrogen ions, which affects the degree of desalination of the solution.

4. CONCLUSIONS

In electrodialysis of ammonium nitrate solution in underlimiting current regimes in order to obtain high values of the degree of desalination in combination with low energy consumption it is
recommended to use a membrane package composed of membranes Ralex CM(H)-PP/Ralex AM(H)-PP. When using membrane pairs MK-40/MA-41 and Ralex CM(H)-PP/Ralex AM(H)-PP in electrodialysis at current densities above the limiting diffusion density a tendency to alkalize the solution in concentration compartments is revealed, and only in the case of the pair MK-41/MA-41 the solution is acidified. The use of phosphoric acid membranes MK-41 in the electrodialysis cell at a current density above the limiting diffusion density will make it possible to conduct a reagent-free acidification of the solutions in concentration compartments, which is necessary to prevent the precipitation formation of slightly soluble hydroxides on the anion exchange membrane.

References


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