

Modified bipolar membrane for electro dialysis processing of highly concentrated sodium nitrate and boric acid solution

Nazar Romanyuk ^{a*} , Julia Loza ^a , Sergey Loza ^a , Nikita Kovalchuk ^{ab} , Victor Zabolotsky ^a

a: Department of Physical Chemistry, Kuban State University, Krasnodar 350040, Russia

b: Department of Chemical Engineering, Platov South-Russian State Polytechnic University, Novocherkassk 346428, Russia

* Corresponding author: romanyuknazar@mail.ru



Abstract

We studied the characteristics of two membranes: the industrial bipolar membrane MB-3, consisting of two layers, i.e., an anion exchanger with quaternary ammonium groups and a cation exchanger with phosphonate groups, and the membrane MB-3M, modified on the cation exchange side with a 100 μm thick layer of perfluorosulfonic acid. The analysis of the selectivity of the initial and modified membranes in a wide range of current densities (0.25–4 A/dm²) showed that the application of a perfluorosulfonic acid layer leads to a decrease in the transport of nitrate anions by 18–40 times, depending on the current density, compared to the initial industrial membrane MB-3. Experiments on electro dialysis processing of a mixed 0.5 M NaNO₃ and 0.75 M H₃BO₃ solution showed that the use of a bipolar membrane modified with a perfluorosulfonic acid, at a sodium nitrate processing degree of 75%, allows obtaining a 1.01 M NaOH solution with a low impurity content (0.08 M sodium nitrate and 0.09 M boric acid) and 1.17 M HNO₃ (sodium nitrate content 0.09 M, boric acid 0.09 M). When using the initial MB-3 membrane under the same conditions, 0.77 M NaOH with a high content of impurities (0.25 M sodium nitrate and 0.08 M boric acid) and 1.03 M HNO₃ (containing 0.09 M sodium nitrate and 0.09 M boric acid) are obtained. The energy consumption for processing is comparable to that for the initial bipolar membrane MB-3 and amounts to 0.15 kW·h/mol.

Key findings

- Application of a layer of perfluorosulfopolymer to the MB-3 bipolar membrane leads to a decrease in the acid anions flux.
- The use of MB-3M in the processing of highly concentrated salt solutions increases the obtained alkali purity by 4 times.
- Application of a layer of perfluorosulfopolymer to the MB-3 bipolar membrane affects the water flux during bipolar electro dialysis.

© 2024, the Authors. This article is published in open access under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Boric acid is used as a neutron absorber at nuclear power plants in the boron cycle of excess reactivity control of nuclear reactors [1,2]. As a result, highly mineralized liquid wastes are formed at nuclear power plants, the main components of which, after decontamination, are boric acid and sodium nitrate [3]. Such waste, purified from radionuclides, is considered chemically toxic industrial waste [4]. According to the regulatory documents in force in Russia

[5], chemically toxic industrial waste containing water-soluble components is supposed to be converted into solid form and buried in reinforced concrete waterproof containers at special landfills equipped with soil insulation, drainage systems, etc. This leads to an increase in the number of territories occupied by landfills, accumulation of hazardous waste, and loss of valuable components. Reusing components through the implementation of zero liquid discharge technologies (ZLD) is a possible solution to this problem.

Accompanying information

Article history

Received: 14.11.24

Revised: 13.12.24

Accepted: 21.12.24

Available online: 28.12.24


Keywords

ion exchange membranes; selectivity; bipolar electro dialysis; nitric acid; sodium hydroxide; sodium nitrate

Funding

This work was supported by the Russian Science Foundation (22-13-00439, <https://rscf.ru/project/22-13-00439/>).

Supplementary information

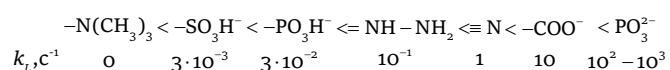
Transparent peer review: 

Sustainable Development Goals



A promising method for processing boron-containing solutions is electro dialysis with bipolar membranes [6–10]. A bipolar membrane is composed of cation-exchange and anion-exchange layers. When an electric current flows through such a membrane, a region with a high electric field strength arises near the bipolar junction, which leads to an increase in the rate of electro-dissociation of water into protons and hydroxyl ions [11], Figure 1. In this case, the resulting H^+ and OH^- ions are transported from the bipolar junction to the acid and alkaline tracts, respectively. Using electro dialysis with bipolar membranes, it is possible to regulate the pH of technological solutions and fruit juices [12–14], obtain ultrapure water [15, 16], synthesize substances [17–19] and purify wastewater [20–23].

As established in the works [24, 25], the water dissociation rate is greatly influenced by ion-exchange groups that are the part of bipolar membranes. The series of catalytic activity for the reaction of dissociation of water molecules can be represented as follows [24, 25]:



where k_L – effective rate constant for water electro-dissociation.

According to this series, phosphonate groups have the highest catalytic activity. The bipolar membrane MB-3 (Shchekinoazot LLC, Tula, Russia) consists of two layers: an anion exchange with quaternary ammonium groups and a cation exchanger with phosphonate groups.

When using the bipolar membrane MB-3, a high rate of water electro-dissociation reaction is ensured, making one of the best Russian commercial bipolar membranes at the moment. However, in the process of using the MB-3 membrane and its analogues, when the cation exchange layer is in contact with a strong acid, the dissociation of phosphonate ionogenic groups is suppressed. In this case, the permeability of the cation exchange layer for co-ions dramatically increases.

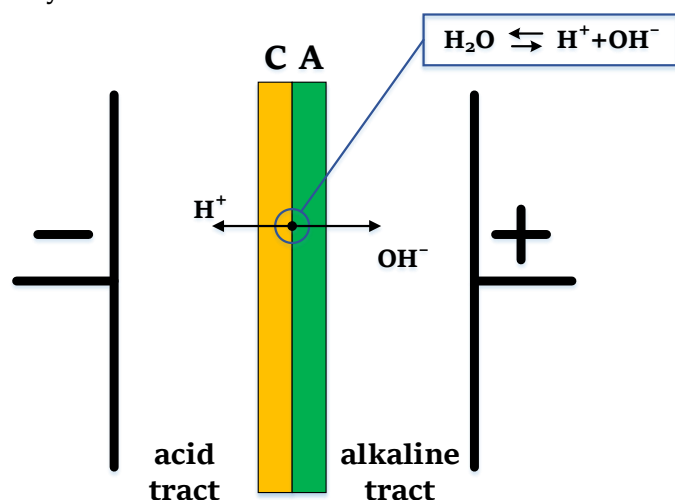


Figure 1 Scheme of a bipolar membrane operation in an electro dialysis cell, (C) cation exchange side, (A) anion exchange side.

This in turn leads to contamination of the alkali with acid anions, which is a negative factor [26]. A promising method for ensuring the selectivity of the phosphonate cation-exchange layer is to apply a surface layer of cation-exchanger with strong acidic groups, the dissociation of which does not depend on the pH of the solution and ensures selectivity with respect to anions. Perfluorosulfonic acid is most suitable for this purpose, since it contains cation-exchange sulfonic groups and is chemically stable. In addition, perfluorosulfonic acid has proven itself well in modifying monopolar ion-exchange membranes to impart specific selectivity to them [27–29] as well as for creating asymmetric bipolar membranes [30, 31]. In these studies, a relationship between the concentration of co-ions in the processed solution, the intensity of their transport, and the thickness of the modifying layer of perfluorosulfonic acid was established. A 30 μm thick layer appears to be sufficient to effectively contain the flux of co-ions in dilute solutions with a concentration of about 0.01 mol/L, while in more concentrated solutions (0.5 mol/L) effective containment is achieved by applying a thicker layer, >80 μm [30].

It should be considered that applying a thick modifier layer leads to an increase in membrane resistance and, accordingly, energy consumption during the electro dialysis process, as well as to an overconsumption of the modifier, which has a high expense. The aim of this work is to study the electrochemical characteristics of bipolar membranes with a phosphonate cation exchange layer modified with a perfluorosulfonic acid and the process of acid and alkali recovery from a solution simulating liquid waste from the nuclear industry using them.

2. Experimental part

2.1. Materials

The object of the study is a heterogeneous bipolar membrane MB-3, manufactured by Shchekinoazot LLC, Tula, Russia. The membrane MB-3 consists of an anion-exchange layer with quaternary ammonium groups and a cation-exchange layer with phosphonate groups, Table 1.

Another object of the study is the MB-3 membrane, surface-modified with the cation exchange perfluorosulfonic layer with (hereinafter referred to as MB-3M), the thickness of the modifying layer is 100 μm .

SEM images of the cross-sections of MB-3 and MB-3M membranes are presented in Figure 2.

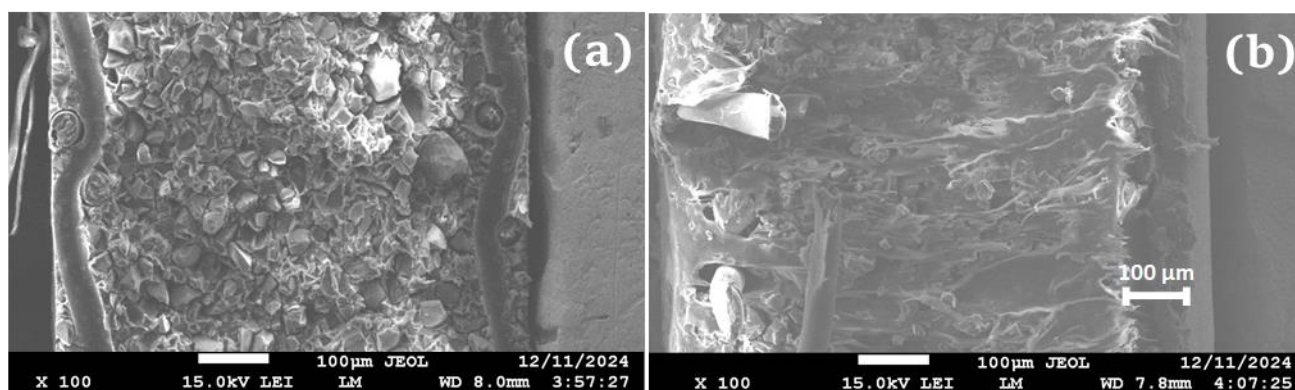
2.2. Method of modifying a bipolar membrane with a perfluorosulfonic acid

Modification of the cation-exchange layer of the MB-3 membrane was carried out with a 10% solution of perfluorosulfonic acid in dimethylformamide, according to the procedure described in [31].

Before modification, the original MB-3 membrane was equilibrated with deionized water for 1 day, and then dried at the room temperature to a constant weight.

Table 1 Structure of layers of bipolar membrane MB-3 and perfluorosulfopolymer.

cation exchange layer of MB-3	$\left[\begin{array}{c} -\text{CH}-\text{CH}_2- \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{O}=\text{P}-\text{O}^-\text{H}^+ \\ \\ \text{O}^-\text{H}^+ \end{array} \right]_n$	$\left[\begin{array}{c} -\text{CH}-\text{CH}_2- \\ \\ \text{C}_6\text{H}_4 \\ \\ -\text{CH}-\text{CH}_2- \end{array} \right]_m$
anion exchange layer of MB-3	$\left[\begin{array}{c} -\text{CH}-\text{CH}_2- \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{CH}_2-\text{N}^+(\text{CH}_3)_3 \text{Cl}^- \end{array} \right]_n$	$\left[\begin{array}{c} -\text{CH}-\text{CH}_2- \\ \\ \text{C}_6\text{H}_4 \\ \\ -\text{CH}-\text{CH}_2- \end{array} \right]_m$
perfluorosulfonic acid	$-(\text{CF}_2-\text{CF}_2)_n-\text{CF}-\text{CF}_2- \\ \\ \text{O}-(\text{CF}_2-\text{CF}(\text{CF}_3)-\text{O})_m-\text{CF}_2-\text{CF}_2-\text{SO}_3^-\text{H}^+$	

**Figure 2** Scanning electron microscopy image of the bipolar membrane MB-3 (a) and the modified membrane MB-3M (b).

The modified surface of the cation-exchange layer was treated with glacial acetic acid for 10 min before applying the modifier to activate the surface. Then a known volume of the modifier was applied to the membrane from the side of the cation-exchange layer (0.245 ml of modifier per 1 cm² of the modified membrane area). The membrane was dried for 8 h at 70 °C. After drying, the modified membrane was successively immersed in sodium nitrate solutions with different concentrations for 12 hours: saturated, 5 M, 2.5 M, 1.2 M, 0.5 M, 0.25 M, 0.125 M, and then in deionized water.

Six membrane samples with a modifying layer thickness of 100±5 μm were made (1 sample of 2x2 cm² for studying effective transport numbers and 5 samples of 5x20 cm² in size for electrodialysis processing of solutions), as well as

samples with a thickness of 150±7 and 200±6 μm, 2x2 cm² in size.

2.3. Method for studying effective transport numbers of co-ions in bipolar membranes

The effective transport numbers of nitrate anions through bipolar membranes MB-3 and MB-3M were investigated with the cell described previously [26, 30] in the “0.5 M HNO₃ – 0.5 M NaOH” systems at current densities of 0.25–4 A/dm² with a solution feed rate of 1 ml/min. In the same system, the general current-voltage characteristics of the MB-3 and MB-3M membranes were studied. Heterogeneous cation-exchange membranes Ralex CMH PES and anion-exchange membranes Ralex AMH PES, manufactured by

MEGA a.s., Czech Republic, were used as auxiliary ion-exchange membranes. Constant current density was provided using a constant current source AKTAKOM APS-7316 manufactured by CJSC SPE "ELIKS" Russia, the potential drop on the membrane was measured using Luggin-Haber capillaries connected to the membrane with silver chloride electrodes ESr-10101, as well as an Expert 001 liquid analyzer of EKONIKS-EXPERT LLC, Russia.

Effective numbers of nitrate ion transport through a bipolar membrane ($T(\text{NO}_3^-)$) were determined as:

$$T(\text{NO}_3^-) = \frac{C(\text{NO}_3^-)VF}{It}, \quad (1)$$

where $C(\text{NO}_3^-)$ – concentration of nitrate ions in the alkaline tract sample, mol/L; V – sample volume, L; F – Faraday constant, 96485 C/mol; I – current strength, A; t – time of the sampling, s.

Nitrate ion flux ($J(\text{NO}_3^-)$, mol·m⁻²·h⁻¹) determined by the formula 2:

$$J(\text{NO}_3^-) = \frac{C(\text{NO}_3^-)V}{St}, \quad (2)$$

where $S = 4 \text{ cm}^2$ – working area of the membrane.

2.4. Procedure for studying electro dialysis processing of a solution containing boric acid and sodium nitrate

The processing of a solution simulating nuclear industry waste, consisting of 0.75 M boric acid and 0.5 M sodium nitrate with pH = 4.5 [3,8], in order to obtain nitric acid and sodium hydroxide, was carried out with a laboratory-scale electro dialyzer-synthesizer with a membrane working area of 1 dm². The scheme of the unit cell of the apparatus is shown in Figure 3. The experiments to obtain nitric acid and sodium hydroxide were carried out in a circulation hydraulic mode at a constant current density of 2 A/dm². This value is optimal, since at a lower current density results in a low intensity of the process, and at a higher current density there is a high risk of burnout of the electro dialysis apparatus and its failure [32]. A constant current value was maintained using a GPR 7510HD direct current source manufactured by GW Instek, Taiwan, with a built-in voltmeter-ammeter for measuring voltage and current. The circulation of solutions was provided by a Heidolph Pumpdrive 5101 peristaltic multichannel pump, Germany. The volumetric flux rate of the solution through each chamber was 8.57 L/h (linear velocity 0.013 m/s through one tract of the apparatus).

Two experiments were conducted using MB-3 and MB-3 M membranes. Ralex CMH PES cation-exchange membranes and Ralex AMH PES anion-exchange membranes were used as auxiliary membranes. The apparatus consisted of 5 elementary cells consisting of one salt, one alkaline and one acid tracts. The salt tract tank initially contained 4 liters of a solution containing 0.75 M boric acid and 0.5 M sodium nitrate. The alkaline tract tank initially

contained 0.2 M sodium hydroxide solution, and the acid tract tank - 0.2 M nitric acid solution. The electrode tract tank contained 4 liters of 1 M sodium nitrate solution. The acid and alkaline tract tanks are graduated cylinders with a volume of 2 liters, which allows recording of the solution volume. During the experiments, the concentration of sodium nitrate and boric acid in all the tract tanks, as well as the concentration of nitric acid and sodium hydroxide in the tanks of the acid and alkaline tracts, respectively, were determined once per hour. The concentration of sodium nitrate was determined by Na⁺ and NO₃⁻ ions using a Stayer ion chromatograph manufactured by Aquilon JSC, Russia. The content of boric acid was determined by potentiometric titration using a Mettler Toledo EasyPlus automatic titrator, Switzerland. Depending on the acidity, a sample of the analyzed solution was adjusted to pH 7.0 with 0.1 M sodium hydroxide or nitric acid; then, an excess of sorbitol was added to convert boric acid into a stronger acid [33], which was titrated with 0.1 M NaOH. The concentration of nitric acid and sodium hydroxide was determined by potentiometric titration with 0.1 M NaOH or 0.1 M HNO₃, respectively, using a Mettler Toledo EasyPlus automatic titrator.

Based on the obtained primary data, the degree of sodium nitrate processing α was determined:

$$\alpha = \frac{C^0(\text{NaNO}_3) - C^t(\text{NaNO}_3)}{C^0(\text{NaNO}_3)} \cdot 100\%, \quad (3)$$

where $C(\text{NaNO}_3)$ – initial concentration of sodium nitrate in the salt tract tank, mol/L; $C^t(\text{NaNO}_3)$ – concentration of sodium nitrate in the salt tract tank at time t , mol/L.

Current efficiency of sodium nitrate, as well as acid and alkali in the corresponding tracts, were calculated according to:

$$\eta(i) = \frac{\Delta C(i)\Delta V F}{I\Delta t}, \quad (4)$$

where $\Delta C(i)$ – change in the concentration of the i -th component in the corresponding tank, mol/L; ΔV – change in the volume of the corresponding tank, L; Δt – the time during which the change in solution volume and concentration occurred of i -th component, s.

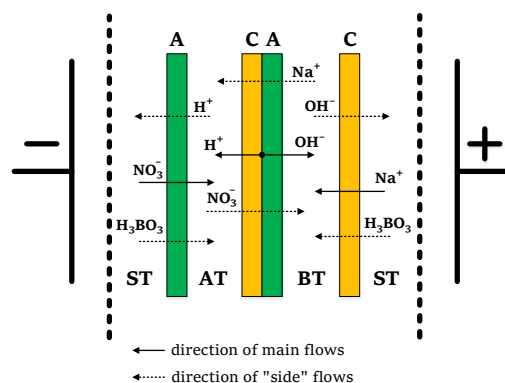


Figure 3 The scheme of the elementary cell of the electro dialyzer-synthesizer, consisting of a bipolar (CA), cation exchange (C), anion exchange (A) membranes, salt (ST), acid (AT) and alkaline (BT) tracts.

The flux density of boric acid into the alkaline and acidic tract was calculated using equation 5 for a desalination degree of 70%:

$$J(\text{H}_3\text{BO}_3) = \frac{3600\Delta C(\text{H}_3\text{BO}_3)}{S_i\Delta V\Delta t}, \quad (5)$$

where $J(\text{H}_3\text{BO}_3)$ – boric acid flux, $\text{mol}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, $\Delta C(\text{H}_3\text{BO}_3)$ – change in the concentration of boric acid in the corresponding tank over time Δt , mol/L ; S_i – total area of cation or anion exchange membranes, m^2 .

Energy consumption for processing 1 mol of sodium nitrate (W , $\text{kW}\cdot\text{h/mol}$) was calculated using equation 6:

$$W = \frac{I \int_0^{t_{\text{fin}}} U dt}{\Delta C(\text{NaNO}_3)\Delta V_s'}, \quad (6)$$

where U – voltage drop on electro dialyzer, V ; t_{fin} – electro dialysis processing time, h ; $\Delta C(\text{NaNO}_3)$ – change in sodium nitrate concentration during electro dialysis processing, mol/L ; $\Delta V_s'$ – change in the volume of the salt tract capacity, L .

3. Results and discussion

3.1. Study of effective transport numbers through the bipolar membrane MB-3 and the membrane MB-3M modified with a layer of perfluorosulfonic acid

Figure 4 shows the current-voltage characteristics (CVCs) of the initial (1) and modified (2) bipolar membranes. The data analysis shows that the application of perfluorosulfonic acid to the bipolar membrane from the side of the cation exchange layer leads to an increase in membrane resistance, and the same current density is achieved with a higher voltage on the membrane.

Figure 5 shows the dependences of the flux density (a) and effective transport numbers (b) of nitrate anions through bipolar membranes MB-3 and MB-3M on the density of the electric current fluxing in the electromembrane system. The analysis of the data in Figure 5 a shows that with increasing density of the applied current, there is an increase in the flux density of nitrate anions both through the initial and the modified membrane. At the same time, an increase in the current density leads to a decrease in the effective transport numbers of co-ions, Figure 5 b. This is due to the fact that with an increase in the current density, an increase in the intensity of the water electro-dissociation at the bipolar junction inside the membrane occurs. The H^+ and OH^- migrate to the cation-exchange and anion-exchange parts of the bipolar membrane, respectively, entering into competitive transport with nitrate anions.

With an increase in the current density, the effective transport numbers of H^+ and OH^- will increase, and those of nitrate anions will decrease. The increase of the driving force at t at high current densities leads to an increase in nitrate anions leakage, which results in a small decrease in

the effective transport numbers of nitrate anions at the later stage, Figure 5 b.

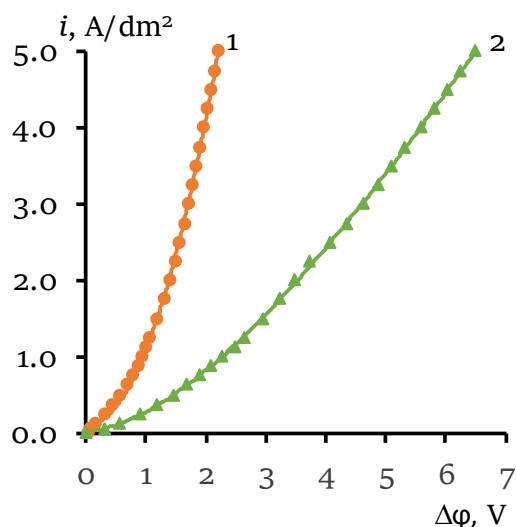


Figure 4 CVCs of the bipolar membrane MB-3 (1) and MB-3M (2).

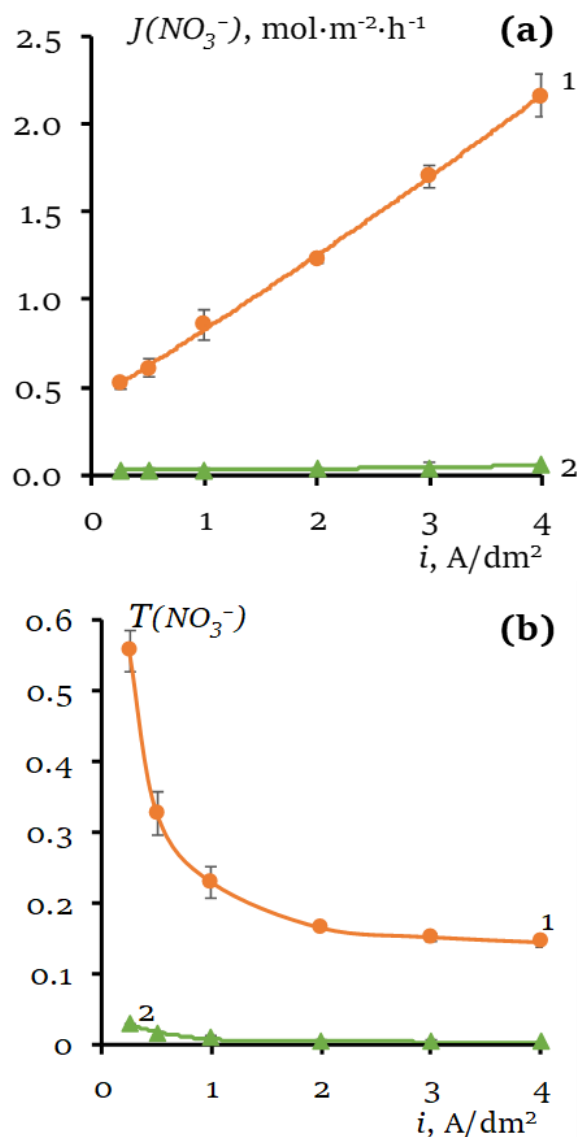


Figure 5 Dependences of flux density (a) and effective transport numbers (b) of nitrate anions through the membrane MB-3 (1) and MB-3M (2).

Modification of the bipolar membrane surface from the side of the cation-exchange layer with a perfluorosulfonic acid with strong acidic groups whose dissociation is not very sensitive to pH leads to a decrease in the transport of nitrate anions. The flux density and effective transport numbers of nitrate anions through the modified bipolar membrane MB-3M are reduced by an average of 18–40 times compared to the initial industrial membrane MB 3, depending on the current density, as seen in Figure 5 b.

3.2. Study of processing of a solution containing sodium nitrate and boric acid by bipolar electro dialysis

Since the modified bipolar membrane MB-3M showed low values of nitrate ion transport numbers compared to the initial membrane, these membranes have been chosen for use in processing a solution simulating nuclear industry waste. Figure 6 shows the concentration dependences of sodium hydroxide, sodium nitrate, boric acid, as well as the current efficiency and solution volume in the alkaline tract tank on the degree of sodium nitrate processing (α).

Analysis of the data in Figure 6 a shows that the dependence of the alkali concentration in the alkali tract tank on the degree of sodium nitrate processing is initially increasing, then the rate of concentration change slows down and reaches a plateau. This effect is associated, firstly, with a decrease in the sodium nitrate concentration in the salt tract tank, from which the acid and alkali are converted. Secondly, with the fact that part of the hydroxide anions, which have an abnormally high mobility, is transported through the cation-exchange membrane from the alkali tract to the salt tract by diffusion and migration mechanisms. At sufficiently high alkali concentrations >0.75 M (Figure 6 a, b), current transport through the cation-exchange membrane is provided mainly by co-ions (hydroxide anions) and not by counterions (sodium cations), the concentration of which in the alkaline chamber is 2 times lower and decreases over time. Application of a perfluorosulfonic acid layer to the cation-exchange layer of the MB-3 bipolar membrane results in a 4-fold decrease in alkali contamination with nitrate anions at a sodium nitrate conversion rate of 70% and is 0.08 mol/L, Figure 6 c, and a 1.6–6-fold decrease in the sodium nitrate current efficiency depending on the conversion rate (α), Figure 6 d. At the same time, an increase in the alkali concentration and current efficiency is observed at high sodium nitrate conversion rates ($>30\%$), Figure 6 a, b. An increase in the NaOH concentration in the alkaline tract when using the modified MB-3M membrane is associated with the suppression of nitrate anion transport to the alkaline tract; the nitrate anions firstly, enter into competitive transport with hydroxide anions in the anion-exchange layer of the bipolar membrane, and, secondly, transport water to the alkaline tract as part of hydrate shells. The volume increase slows down in the alkaline tract tank, which was observed when using modified

membranes, Figure 6 e. Modification of the bipolar membrane with a perfluorosulfonic acid does not affect the transport of boric acid into the alkaline tract, Figure 6 f. Its flux into the alkaline tract tank when using MB-3 and MB-3M membranes is the same and is $0.37 \text{ mol}\cdot\text{m}^{-2} \text{ h}^{-1}$. At this pH value of the solution in the salt tract tank (pH = 4.5–1.1), boric acid is in molecular form [34, 35] and cannot participate in electrical mass transport. Boric acid is transported into the alkaline tract tank through the cation-exchange membrane by a diffusion mechanism. Figure 7 shows the concentration dependences of nitric acid, sodium nitrate, boric acid, as well as the current efficiency and solution volume on the degree of sodium nitrate processing (α) in the acid tract tank using the initial and perfluorosulfonic acid modified bipolar membranes.

Analysis of the data in Figure 7 a and b shows that, as in the case of alkali, the rate of increase in the acid concentration slows down with increasing α . This is also due to a decrease in the concentration of sodium nitrate in the salt tract tank as well as the ability of hydrogen cations to be transported through anion-exchange membranes by the electrodiffusion mechanism. In this case, the current efficiency of nitric acid (Figure 7 b) during electromembrane processing is much less than the output of the sodium hydroxide flux (Figure 6 b). This is due to the total electrodiffusion transport of acid from the acid to the salt tract being greater than the total transport of alkali from the alkali to the salt tracts. This is confirmed by a decrease in the pH of the salt tank solution during electro dialysis processing from 4.5 to 1.1. When modifying the bipolar membrane on the surface of the cation-exchange layer, the perfluorosulfonic acid forms a continuous film that covers the pores present in the heterogeneous cation-exchange layer. This leads to a decrease in the concentration of sodium nitrate in the acid tract (Figure 7 c), the intensity of electrodiffusion transport of sodium cations from the alkaline tract to the acid tract (Figure 7 d).

Also, clogging of large pores and applying a layer of hydrophobic perfluorosulfonic acid [36], along with a decrease in the transport of water molecules in the hydration shell of nitrate anions, can lead to a decrease in the diffusion transport of water molecules to the bipolar junction region, where the water electro-dissociation occurs. This is confirmed by the decreasing rate of decrease in the volume of the acid tract (Figure 7 e) when using MB-3M membranes. At the same time, modification of the cation exchange layer leads to an insignificant increase in the concentration of acid in the acid tract (Figure 7 a), as well as an increase in the current efficiency for nitric acid, Figure 7 b. Modification of the MB-3 bipolar membrane with a perfluorosulfonic acid does not affect the transport of boric acid into the acid tract, despite the fact that the concentration of boric acid in the acid tract when using MB-3M membranes is lower than that when using MB-3, Figure 7 f.

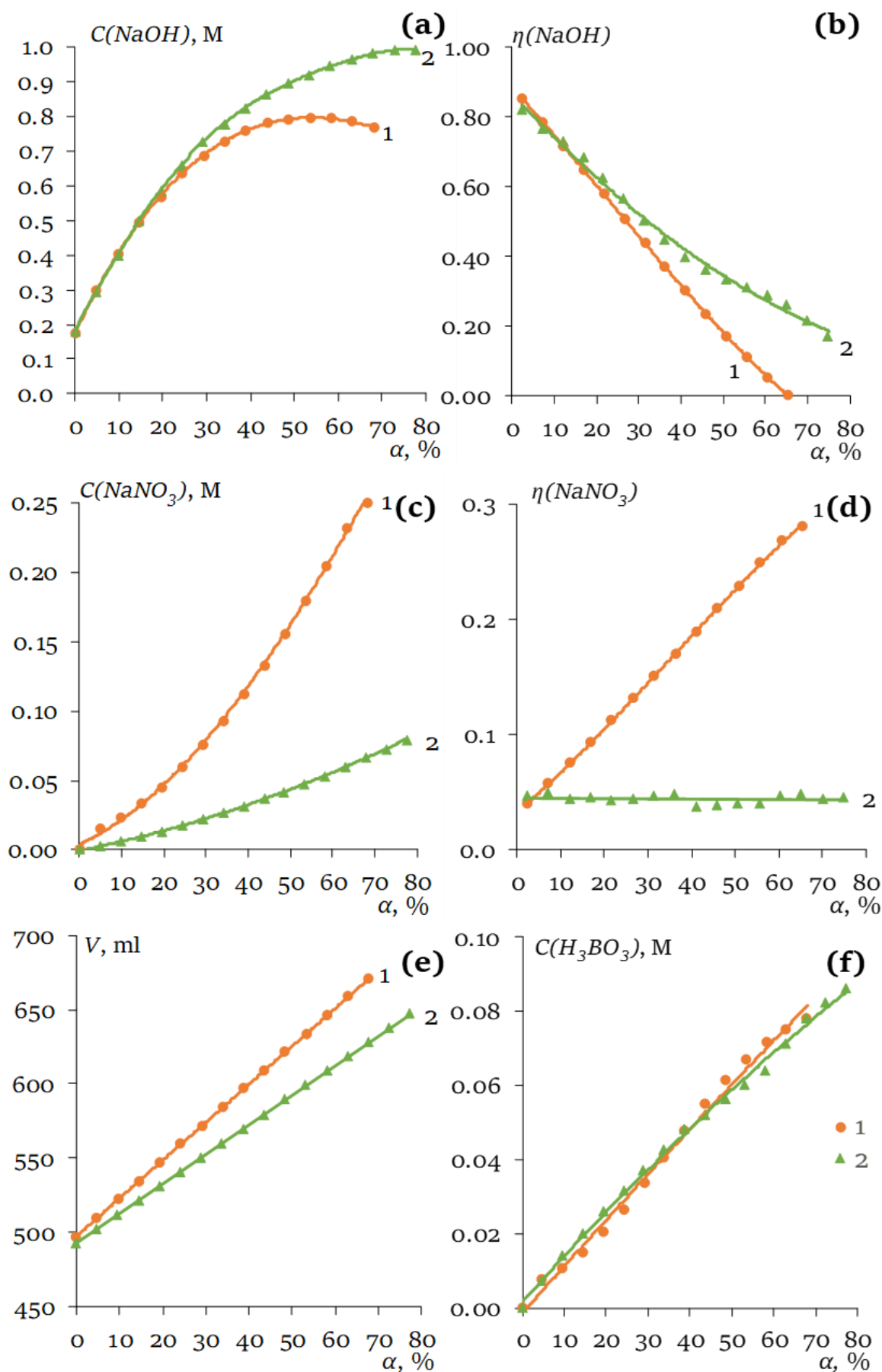


Figure 6 Dependence of sodium hydroxide concentration (a), sodium hydroxide current efficiency (b), sodium nitrate concentration (c), sodium nitrate current efficiency (d), volume (e), boric acid concentration (f) on the degree of sodium nitrate processing α in the alkaline tract tank using MB-3 (1) and MB-3M (2) membranes.

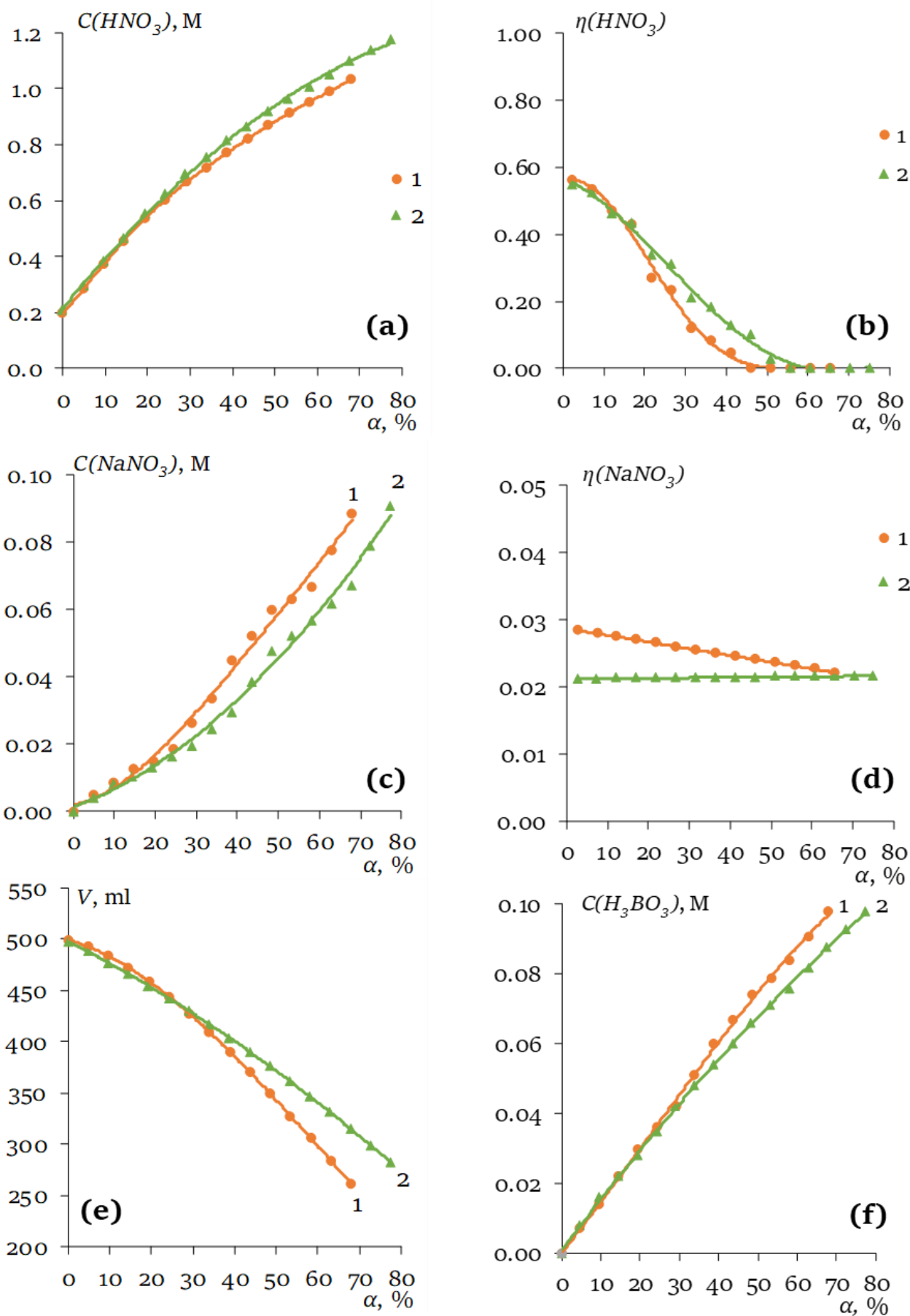


Figure 7 Dependence of nitric acid concentration (a), nitric acid current efficiency (b), sodium nitrate concentration (c), sodium nitrate current efficiency (d), volume (e), boric acid concentration (f) on the degree of sodium nitrate processing α in the acid tract tank using MB-3 (1) and MB-3M (2) membranes.

This is explained by the difference in the volumes of the acid tract capacities; if we recalculate, the amount of boric acid in the acid tract using the initial and modified membranes has almost the same value and differs by no more than 3%, and the boric acid flux is $0.19 \text{ mol}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. Low flux of boric acid is related to the fact that it is in molecular form at a given pH value and cannot participate in electrical mass transport but is transferred by the diffusion mechanism.

The application of a perfluorosulfonic acid layer to the cation exchange side of the MB-3 membrane affects the transport of water molecules during bipolar electro-dialysis. When using modified MB-3M membranes, the rate of change of the capacity volumes of the alkaline and acidic tracts decreases. This is explained, firstly, by a decrease in the flux of nitrate anions, which are capable of transporting water molecules in the hydrate shells from the acidic to the alkaline path and to the bipolar boundary region. Secondly, by clogging large pores of the initial cation-exchange layer and creating a more hydrophobic layer on the surface of the cation-exchange side of the bi-polar membrane, which affects the diffusion transport of water molecules from the acid tract to the zone of water electro-dissociation reaction.

Thus, modification of the cation exchange layer of the MB-3 membrane with a perfluorosulfonic acid leads to an increase in the purity and concentration of alkali at the same degree of sodium nitrate conversion level due to a decrease in the transport of nitrate anions. In this case, the energy consumption for processing 1 mol of sodium nitrate (at $\alpha = 70\%$) remains practically unchanged and amounts to $0.14 \text{ kW}\cdot\text{h}/\text{mol}$ when using MB-3 membranes and $0.15 \text{ kW}\cdot\text{h}/\text{mol}$ when using the MB-3M membrane. This shows the potential of processing highly concentrated solutions of sodium nitrate and boric acid by the method of bipolar electro-dialysis using bipolar membranes modified with perfluorosulfonic acid.

4. Limitations

Since [30] showed that a perfluorosulfonic acid film with a thickness of $80 \mu\text{m}$ effectively restrained co-ions in solutions with a high concentration, several samples of MB-3M membranes with different thicknesses of the perfluorosulfonic acid were manufactured: 100 ± 5 , 150 ± 7 , $200\pm 6 \mu\text{m}$. However, when placing the MB-3M membrane samples after modification in sodium nitrate solutions, the modifier film with a thickness of 150 and $200 \mu\text{m}$ peeled off from the MB-3 substrate membrane, while the MB-3M membrane with a modifier thickness of $100 \mu\text{m}$ was a solid composite. We assume that the peeling of sufficiently thick layers of perfluorosulfonic acid from the MB-3 membrane can be explained by different degrees of swelling of the perfluorosulfonic acid and the membrane material. The measured changes in the linear dimensions of the perfluorosulfonic acid ionomer during swelling in deionized water are 14.8% in length and 24.1% in width, while for the MB-3

membrane, which contains a reinforcing mesh in its structure, it is much smaller and is 8.3% in length. At the same time, the force of the osmotic pressure of water, which tends to increase the linear dimensions of the perfluorosulfonic acid, when applying sufficiently thick layers (150 , $200 \mu\text{m}$) is greater than the adhesion forces between the perfluorosulfonic acid ionomer and the cation-exchange side of the MB-3 membrane.

5. Conclusions

In the course of the work, the cation exchange layer containing phosphonate ion exchange groups of the bipolar membrane MB-3 was modified with a $100 \mu\text{m}$ thick perfluorosulfonic acid layer. The study of the selectivity of the initial and modified membranes showed that the transport number of co-ions in the cation exchange layer of the modified membrane was reduced by 18 – 40 times compared to the initial membrane, depending on the density of the applied current.

In the study of electro-dialysis processing of a highly concentrated solution simulating nuclear waste containing boric acid and sodium nitrate, it was shown that the use of modified MB-3M membranes allows reducing the contamination of alkali with sodium nitrate by 4 times and acid by 1.5 times with a degree of processing of the original solution of 70% .

Also, the application of a perfluorosulfonic acid layer to the cation exchange side of the MB-3 membrane affects the transport of water molecules during bipolar electro-dialysis.

Modification of the bipolar membrane with perfluorosulfonic acid does not affect the transport of boric acid during bipolar electro-dialysis in the acid and alkaline tanks, since it is transported through the cation- and anion-exchange membranes by a diffusion mechanism.

Supplementary materials

No supplementary materials are available.

Acknowledgments

Scanning electron microscopy images of the membranes were obtained at the Scientific and Educational Center "Diagnostics of the Structure and Properties of Nanomaterials" of the Center for Collective Use of Scientific Equipment of the FGBVO "Kuban State University" by the engineer Sergei Ivanin.

Author contributions

Conceptualization: V.Z., N.R.
Data curation: N.R., N.K.
Formal Analysis: N.R., S.L.
Funding acquisition: V.Z.
Investigation: N.R., N.K.
Methodology: N.R.
Project administration: V.Z.
Resources: V.Z., N.R., S.L., N.K.
Software: V.Z., N.R., S.L., N.K.
Supervision: V.Z.
Validation: V.Z., S.L.
Visualization: N.R., N.K., J.L.
Writing - original draft: N.R., S.L.

Writing – review & editing: N.R., S.L.

Conflict of interest

The authors declare no conflict of interest.

Additional information

Author IDs:

Nazar Romanyuk, Scopus ID [57211329938](https://orcid.org/0000-0002-5721-1329);
 Julia Loza, Scopus ID [58201875600](https://orcid.org/0000-0002-5820-1875);
 Sergey Loza, Scopus ID [6603644690](https://orcid.org/0000-0002-6603-6446);
 Nikita Kovalchuk, Scopus ID [58028060800](https://orcid.org/0000-0002-5802-8060);
 Victor Zabolotsky, Scopus ID [7003668542](https://orcid.org/0000-0002-7003-6685).

Websites:

Kuban State University, <https://inter.kubsu.ru/>;
 Platov South-Russian State Polytechnic University,
<https://edurussia.ru/university/platov-south-russian-state-poly-technic-university/>.

References

- Myerscough PB. Eds., Nuclear physics and basic technology, Nuclear power generation, Elsevier, 1992. 110 p. doi:[10.1016/B978-0-08-040519-3.50008-1](https://doi.org/10.1016/B978-0-08-040519-3.50008-1)
- Oto B, Yıldız N, Akdemir F, Kavaz E. Investigation of gamma radiation shielding properties of various ores. Prog Nucl Energy. 2015;85:391-403. doi:[10.1016/j.pnucene.2015.07.016](https://doi.org/10.1016/j.pnucene.2015.07.016)
- Ivanenko VI, Sedneva TA, Lokshin EP, Kornejkov RI., inventors; Kola Science Center of the Russian Academy of Sciences, assignee. Method for processing liquid waste from nuclear power plants with boron regulation. Russian Federation patent RU 2652978. 2017 Apr 12. Russian.
- Dmitriev SA, Lifanov FA, Savkin AE, Lashchenov CM. Handling of the bottom residues of a nuclear power plant. Atomic Energy. 2000;89(5):884-889. doi:[10.1023/A:1011338231351](https://doi.org/10.1023/A:1011338231351)
- Ministry of Construction, Housing and Utilities of the Russian Federation, Set of rules 127.13330.2017. Landfills for the disposal and burial of toxic industrial waste. Basic design provisions. Approved 2017 Nov 14.
- İpekçi D, Kabay N, Bunani S, Altıok E, Arda M, Yoshizuka K, Nishihama S. Application of heterogeneous ion exchange membranes for simultaneous separation and recovery of lithium and boron from aqueous solution with bipolar membrane electro dialysis (EDBM). Desalin. 2020;479:114313. doi:[10.1016/j.desal.2020.114313](https://doi.org/10.1016/j.desal.2020.114313)
- Figueira M, Reig M, Luis Cortina J, Reza Moradi M, Pihlajamäki A, Valderrama C. Production of boric acid by bipolar membrane electro dialysis: Evaluation of commercial and polyelectrolyte multilayers-coated ion exchange membranes. Sep Purif Technol. 2025;354:129467. doi:[10.1016/j.seppur.2024.129467](https://doi.org/10.1016/j.seppur.2024.129467)
- Kovalev NV, Karpenko TV, Sheldeshov NV, Zabolotsky VI. Electrochemical characteristics of modified heterogeneous bipolar membrane and electromembrane process of nitric acid and sodium hydroxide recuperation from sodium nitrate and boric acid solution. Russ J Electrochem. 2021;57(2):122-133. doi:[10.1134/S1023193521020063](https://doi.org/10.1134/S1023193521020063)
- Jarma YA, Çermikli E, İpekçi D, Altıok E, Kabay N. Comparison of two electro dialysis stacks having different ion exchange and bipolar membranes for simultaneous separation of boron and lithium from aqueous solution. Desalin. 2021;500:114850. doi:[10.1016/j.desal.2020.114850](https://doi.org/10.1016/j.desal.2020.114850)
- Hung W-Ch, Horng RS, Tsai Ch-H. Effects of process conditions on simultaneous removal and recovery of boron from boron-laden wastewater using improved bipolar membrane electro dialysis (BMED). J Water Proc Engin. 2022;47:102650. doi:[10.1016/j.jwpe.2022.102650](https://doi.org/10.1016/j.jwpe.2022.102650)
- Mauro A. Space charge regions in fixed charge membranes and the associated property of capacitance. Biophys J 1962;2(2):179-198. doi:[10.1016/S0006-3495\(62\)86848-9](https://doi.org/10.1016/S0006-3495(62)86848-9)
- Pärnamäe R, Mareev S, Nikonenko V, Melnikov S, Sheldeshov N, Zabolotskii V, Hamelers HVM, Tedesco M. Bipolar membranes: A review on principles, latest developments, and applications. J Memb Sci. 2021;617:118538. doi:[10.1016/j.memsci.2020.118538](https://doi.org/10.1016/j.memsci.2020.118538)
- Bazinet L, Lamarche F, Ippersiel D. Bipolar-membrane electro dialysis: Applications of electro dialysis in the food industry. Trends Food Sci Technol. 1998;9(3):107-113. doi:[10.1016/S0924-2244\(98\)00026-0](https://doi.org/10.1016/S0924-2244(98)00026-0)
- Luo Y, Liu Y, Shen J, der Bruggen BV. Application of Bipolar Membrane Electro dialysis in environmental protection and resource recovery: A Review. Membranes. 2022;12(9):829. doi:[10.3390/membranes12090829](https://doi.org/10.3390/membranes12090829)
- Wood J, Gifford J, Arba J, Shaw M. Production of ultrapure water by continuous electrodeionization. Desalin. 2010;250(3):973-976. doi:[10.1016/j.desal.2009.09.084](https://doi.org/10.1016/j.desal.2009.09.084)
- Grabowski A, Zhang G, Strathmann H, Eigenberger G. The production of high purity water by continuous electrodeionization with bipolar membranes: Influence of the anion-exchange membrane permselectivity. J Memb Sci. 2006;281(1-2):297-306. doi:[10.1016/j.memsci.2006.03.044](https://doi.org/10.1016/j.memsci.2006.03.044)
- Raucq D, Pourcelly G, Gavach C. Production of sulphuric acid and caustic soda from sodium sulphate by electromembrane processes. Comparison between electro-electro dialysis and electro dialysis on bipolar membrane. Desalin. 1993;91(2):163-175. doi:[10.1016/0011-9164\(93\)80055-R](https://doi.org/10.1016/0011-9164(93)80055-R)
- Achoh A, Zabolotsky V, Melnikov S. Conversion of water-organic solution of sodium naphtenates into naphtenic acids and alkali by electro dialysis with bipolar membranes. Sep Purif Technol. 2019;212:929-940. doi:[10.1016/j.seppur.2018.12.013](https://doi.org/10.1016/j.seppur.2018.12.013)
- Boyaval P, Seta J, Gavach C. Concentrated propionic acid production by electro dialysis. Enzyme Microb Technol. 1993;15(8):683-686. doi:[10.1016/0141-0229\(93\)90069-E](https://doi.org/10.1016/0141-0229(93)90069-E)
- Niftaliev S, Kozaderova O, Kim K. Application of Bipolar Electro dialysis with Modified Membranes for the Purification of Chromic Wastewater from Galvanic Production. Ecology Industry Russ. 2021;25(10):4-9. doi:[10.18412/1816-0395-2021-10-4-9](https://doi.org/10.18412/1816-0395-2021-10-4-9)
- Chen T, Bi J, Ji Z, Yuan J, Zhao Y. Application of bipolar membrane electro dialysis for simultaneous recovery of high-value acid/alkali from saline wastewater: An in-depth review. Water Res. 2022;226:119274. doi:[10.1016/j.watres.2022.119274](https://doi.org/10.1016/j.watres.2022.119274)
- Ilhan F, Kabuk HA, Kurt U, Avsar Y, Gonullu MT. Recovery of mixed acid and base from wastewater with bipolar membrane electro dialysis - A case study. Desalin Water Treat. 2016;57(11): 5165-5173. doi:[10.1080/19443994.2014.1002012](https://doi.org/10.1080/19443994.2014.1002012)
- Ferrari F, Pijuan M, Molenaar S, Duinslaeger N, Sleutels T, Kuntke Ph, Radjenovic J. Ammonia recovery from anaerobic digester centrate using onsite pilot scale bipolar membrane electro dialysis coupled to membrane stripping. Water Res. 2022;218:118504. doi:[10.1016/j.watres.2022.118504](https://doi.org/10.1016/j.watres.2022.118504)
- Zabolotskii VI, Sheldeshov NV, Gnusin NP. Dissociation of water molecules in systems with ion-exchange membranes. Russ Chem Rev. 1988;57(8):801-808. doi:[10.1070/RC1988v057n08ABEH003389](https://doi.org/10.1070/RC1988v057n08ABEH003389)
- Zabolotckii VI, Gnusin NP, Sheldeshov NV. Vliianie prirody' ionogenny'kh grupp na konstanty' dissotciatcii vody' v bipolarny'kh ionoobmenny'kh membranakh. Elektrohimiia (in Russian). 1986;22:1676-1679.
- Zabolotskii V, Sheldeshov N, Melnikov S. Heterogeneous bipolar membranes and their application in electro dialysis. Desal. 2014;342:183-203. doi:[10.1016/j.desal.2013.11.043](https://doi.org/10.1016/j.desal.2013.11.043)
- Achoh AR, Zabolotsky VI, Lebedev KA, Sharafan MV, Yaroslavtsev AB. Electrochemical properties and selectivity of bilayer ion-exchange membranes in ternary solutions of strong electrolytes. Membranes Membrane Technol. 2021;3(1):52-71. doi:[10.1134/S2517751621010029](https://doi.org/10.1134/S2517751621010029)
- Zabolotsky VI, Achoh AR, Lebedev KA, Melnikov SS. Permselectivity of bilayered ion-exchange membranes in ternary

- electrolyte. *J Memb Sci.* 2020;608:118152. doi:[10.1016/j.memsci.2020.118152](https://doi.org/10.1016/j.memsci.2020.118152)
29. Yurova PA, Stenina IA, Yaroslavtsev AB. The effect of the cation-exchange membranes mk-40 modification by perfluorinated sulfopolymer and ceria on their transport properties. *Russ J Electrochem.* 2020;56(6):528–532. doi:[10.1134/S1023193520060154](https://doi.org/10.1134/S1023193520060154)
30. Zabolotskii V, Sheldeshov N, Melnikov S. Effect of cation-exchange layer thickness on electrochemical and transport characteristics of bipolar membranes. *J Appl Electrochem.* 2013;43(11):1117–1129. doi:[10.1007/s10800-013-0560-3](https://doi.org/10.1007/s10800-013-0560-3)
31. Zabolotsky VI, Sheldeshov NV, Melnikov SS. inventors; Kuban State University, assignee. Asymmetrical bipolar membrane. Russian Federation patent RU 120373 U1. 2012 Jun 08. Russian.
32. Peng Z, Cheng Y, Ma X, Hu X, Han Y, Wang H. Thermal effect of the stack in a bipolar membrane electro dialysis: Mechanism, risk, size effect and salt effect. *Desalin.* 2024;586:117838. doi:[10.1016/j.desal.2024.117838](https://doi.org/10.1016/j.desal.2024.117838)
33. Nemodruk ZK, Karalova AA, Analytical chemistry of boron, Ann Arbor: Ann Arbor-Humphrey Science Publishers, 1969. 236 p.
34. Edwards JO, Morrison GC, Ross VF, Schultz JW. The structure of the aqueous borate ion. *J Am Chem Soc.* 1955;77(2):266–268. doi:[10.1021/jao1607a005](https://doi.org/10.1021/jao1607a005)
35. Zhou Y, Fang C, Fang Y, Zhu F. Polyborates in aqueous borate solution: A Raman and DFT theory investigation. *Spectrochim. Acta Part A Mol Biomol Spectrosc.* 2011;83(1):82–87. doi:[10.1016/j.saa.2011.07.081](https://doi.org/10.1016/j.saa.2011.07.081)
36. Berezina NP, Kononenko NA, Dyomina OA, Gnusin NP. Characterization of ion-exchange membrane materials: Properties vs structure. *Adv Colloid Interface Sci.* 2008;139(1–2):3–28. doi:[10.1016/j.cis.2008.01.002](https://doi.org/10.1016/j.cis.2008.01.002)