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Pilot module for electrodialysis–metathesis protected against shunt currents

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ABSTRACT

Electrodialysis–metathesis is electromembrane process working with two diluting and two concentrating streams. Cations from the first diluate combine with anions from the second diluate and form the first concentrate stream, and, vice versa, cations from the second diluate combine with anions from the first diluate and form the second concentrate stream. Due to the presence of ion-exchange membranes in sealing area and high concentration differences and diluate conductivity lower than membrane's, there occurs shunt current capable of "burning the membranes" and decreasing the total current effectivity. In pilot module for electrodialysis–metathesis, a part of ion-exchange membrane around distribution channels was replaced by electrically non-conductive insert. This module was tested in the application of potassium nitrate production from ammonium nitrate and potassium chloride solutions. In parallel, the same tests were performed using standard pilot module without these treatments to be able to evaluate their impact on process performance. The module with protective treatments achieved almost 6% higher total current efficiency and 6% lower energy consumption in comparison with standard module.

Keywords: Electrodialysis; Metathesis; Shunt currents; Insulated membrane

1. Introduction

The function of standard electrodialyzers (ED) is limited to desalination and concentration of electrolyte solutions. However, there is a wide spectrum of ED with extraordinary structure of membrane stack or hydraulic streams composed of the same or similar components and working on the base of the same mass transfer principles. Such devices are possible not only to desalt or concentrate solutions, but also to change the chemical matter of substances. The device that keeps standard structure of membrane stack but works with two diluates and two concentrates is used for metathesis. Cations from the first diluate combine with anions from the second diluate and form the first concentrate stream, and, vice versa, cations from the second diluate combine with anions from the first diluate and form the second concentrate stream. This process is called electrodialysis–metathesis (EDM) [1]. EDM was successfully applied, e.g., in zero discharge desalination technology for brackish groundwater treatment to achieve maximum possible water recovery [2], to produce revalued materials from waste material, such as magnesium sulfate [3] or potassium nitrate [4], or to prepare ionic liquids [5]. In most applications, it is desirable to produce by-product salts of as high concentration as possible which allows salt reuses. Bond et al. [6] use EDM to producing technical grade quality $MgCl_2$ salt. The second concentrate contains mixture of Na_2SO_4 and NaCl. EDM prevents $MgSO_4$ precipitation in concentrate stream in conventional electrodialysis, as in reference [7].

Therefore, high concentration differences occur in the stack and diluate conductivity is often lower than conductivity of ion-exchange membranes. It is well known that such stack conditions favor the formation of shunt currents. Shunt currents may significantly decrease current efficiency of the

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process and lead to module burning – irreversible damage of module components by their local overheating. Shunt currents (also called shortcut, parasitic or leakage currents) are caused by ionic transport through the feed and drain channels and along membrane in sealing area that act as salt bridges between compartments [8]. Decreased current efficiency can be used as shunt current indicator, but it may be negatively affected by other factors, mainly by imperfect permselectivity of ion-exchange membranes, water splitting due to exceeding of limit current density, back diffusion or inner leakages from concentrate to diluate compartments [9,10].

There are several approaches to minimize shunt currents and most of them concern the design of ED cells. For instance, shunt currents in electrodialysis stack with bipolar membranes may be restricted by appropriate design of manifold area (small cross-section and long feeding channels), decreasing the number of membrane cells or by increasing the effective membrane area [11]. Authors dealing with reverse electrodialysis claim that shunt currents may be reduced by the increase of the ratio between feed and drain channel resistance and the cell resistance [8] or by the decrease of diluate cell resistance (lower intermembrane distance and spacer geometry) [12]. The evaluation of the use of various chemicals to neutralize the ion-exchange capacity of the membrane surrounding feed and drain channels to minimize shunt currents was described in reference [13]. In this paper, similar treatment was chosen to protect module against shunt currents. A part of membrane around distribution manifolds was replaced by electrically non-conductive insert and, moreover, spacers were covered by thin plastic film to insulate liquid distribution system from ion-exchange membranes.

In our pilot module for EDM, a part of ion-exchange membrane around distribution channels was replaced by electrically non-conductive insert. Moreover, spacers were covered by thin plastic film in order to completely insulate distribution system of liquid from membranes. In experiments, the same membranes were used in both modules and no changes of inner leakages were observed, so that total current efficiency on salt transport was used to assess the contribution of treatments to module protection against shunt currents.

2. Materials and methods

2.1. Modules

For experiments, pilot module for EDM with 15 membrane quadruplets composed of heterogeneous ion-exchange membranes Ralex® was used (both module and membranes made by MEGA a.s., Stráž pod Ralskem, Czech Republic). Effective membrane area was 0.6 m^2, and spacer thickness was 0.8 mm. Such module (in further text called "standard module") was compared with module modified by two protective systems against shunt currents (hereinafter referred as "innovated module"). The first one was non-conductive plastic insert (low-density polyethylene + ethylene-vinyl acetate, 0.65 mm) into membrane feed and drain channels with the same thickness as swollen membrane (Fig. 1). The second treatment was thin plastic cover (polyethylentereftalate, 0.07 mm) of spacers (Fig. 2). The both treatments completely insulate the membranes from feeding channels and distributors and should prevent shunt current occurrence and subsequent module damages as it is depicted in Fig. 3. If diluate conductivity is lower than conductivity of ion-exchange membranes, a part of electric current can pass through membranes rather than through diluate compartments in a direction perpendicular to desired current flow. Consequently, current passes through concentrate distribution channels and, at the end of the membrane stack, it has to reach the electrode. The only way is to pass through membranes near electrode, where damages due to local overheating occur most frequently.

The expectation of this treatment is to increase the module effectivity due to lowering shunt currents and increase the immunity against sealing's area Joule heat membrane burning effect.

2.2. Apparatus and chemicals

There were used analytical grade chemicals potassium chloride (KCl) and ammonium nitrate (NH_4NO_3) produced by Lachner s.r.o., Neratovice, Czech Republic. The water was demineralized of conductivity <0.01 mS cm^{-1}. The EDM test was held on four circuit P1 Pilot unit made by MEGA a.s. The conductivity was measured using Mettler-Toledo meter m300 using ISM InPro® 7108i probes. The product concentration and purity were determined using inductively coupled plasma–optical emission spectroscopy (ICP–OES).

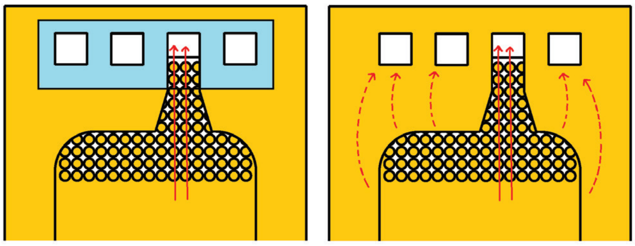

Fig. 1. Left: Illustration of shunt current path in innovated membrane with non-conductive inset (blue) and separator in order to electrically insulate the membrane active area from liquid distribution system (feeding channels). Right: Illustration of shunt current path in the standard membrane with separator.

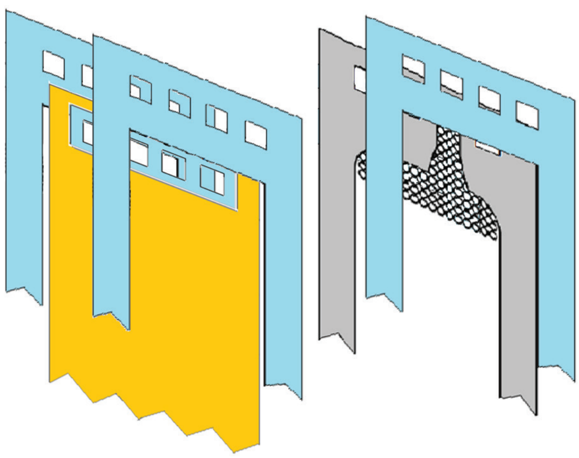

Fig. 2. Spacer (gray) with thin plastic cover (blue) on both sides in order to insulate feed and drain channels from ion-exchange membranes and membrane (yellow) by inset and thin plastic cover (blue) completely insulated from distribution system.

2.3. Experiment

Both standard and innovated modules were tested under the same conditions in the process of potassium nitrate (KNO_3) production from potassium chloride (KCl) and ammonium nitrate (NH_4NO_3) solutions (Fig. 4). Experiments were conducted in batch operation mode with constant temperature 25°C and constant stack voltage 22.5 V. Both diluates (D1 – potassium chloride solution 14.9 g L^{-1} and D2 – ammonium nitrate solution 10.2 g L^{-1}) had initial volume 65 L and conductivity 25 mS cm^{-1}. In both concentrate tanks, there were 5 L of demineralized water at the beginning of each test. During test, there was in concentrate stream C1 formatted ammonium chloride (NH_4Cl). All solutions were circulated at flow rate of 215 L h^{-1}. The electrode rinse solution was 5 L of 20 g L^{-1} Na_2SO_4 at 300 L h^{-1} flow rate.

The wanted product potassium nitrate (KNO_3) was formed in C2 stream. The experiments were terminated when conductivity of both diluates decreased below 10 mS cm^{-1}. The data of electrical current and conductivities were recorded regularly in 5 min intervals. Experiments were made in triplicates.

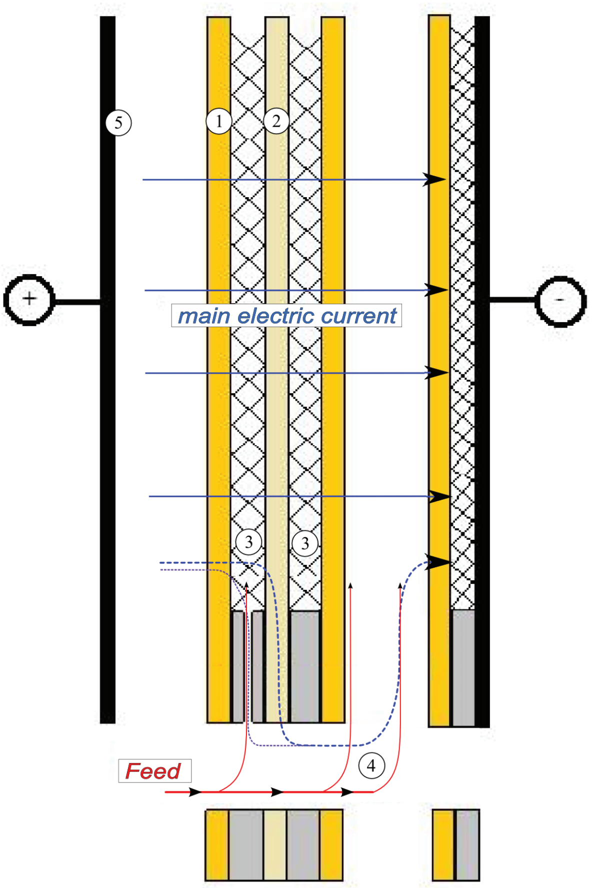

Fig. 3. Stack cross-section: pathway of shunt current in membrane and distributors area (standard electrodialysis stack). 1 – CM membrane, 2 – AM membrane, 3 – separator/manifold with oriented distributor, 4 – feeding channel and 5 – electrode.

3. Results and discussion

From gathered data, following desalination characteristics was evaluated: current efficiency of potassium nitrate production, mass flux, specific energy consumption and product purity. Current efficiency was calculated using Eqs. (1) and (2):

$$Q = \int_{t0}^{t} I(t)dt \tag{1}$$

$$\eta = \frac{v_C z_C F \Delta n}{NQ} 100\% \tag{2}$$

Average mass flux over experiment was calculated using Eq. (3). The specific energy consumption was calculated according to Eq. (4):

$$J = \frac{\Delta m}{Nwl\Delta t} \tag{3}$$

$$E_m = \frac{U\ Q}{3600\Delta m} \tag{4}$$

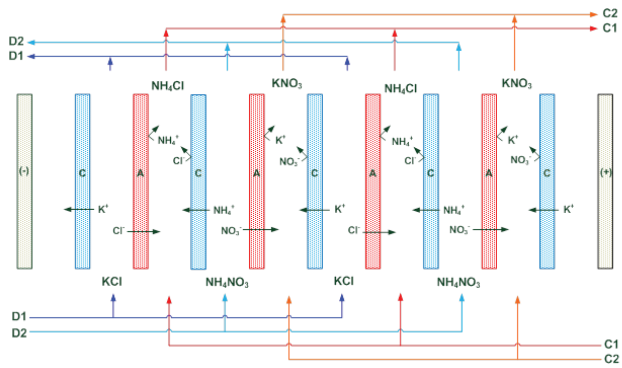

Fig. 4. Principle of potassium nitrate production by electrodialysis–metathesis.

Table 1
Summary of the results achieved with standard and innovated pilot module for electrodialysis–metathesis

KNO_3	Standard module	Innovated module
η, %	83.9327	89.5
	σ = 0.0084	σ = 1.5
J, kg m^{-2} h^{-1}	0.6662	0.6633
	σ = 0.0071	σ = 0.0027
E_m, W h kg^{-1}	526.41	493.7
	σ = 0.52	σ = 8.4
c KNO_3 in product, g L^{-1}	104.2 σ = 4.3	111.6 σ = 1.8
P (NO_3^-/anions), %	97.990	97.856
	σ = 0.074	σ = 0.045
P (K^+/cations), %	99.27	99.28
	σ = 0.16	σ = 0.34

Table 2
Summary of ion composition in product

	Standard module	Innovated module	Method
NH_4^+, mol L^{-1}	4.87×10^{-4}	2.90×10^{-4}	UV–VIS
	$\sigma = 3.8 \times 10^{-5}$	$\sigma = 0.29 \times 10^{-5}$	
K^+, mol L^{-1}	1.224	1.340	ICP-OES
	$\sigma = 0.049$	$\sigma = 0.076$	
Na^+, mol L–1	0.0086	0.0094	ICP-OES
	$\sigma = 0.0023$	$\sigma = 0.0040$	
Cl^-, mol L^{-1}	0.0212	0.0242	Ion chromatography
	$\sigma = 0.0017$	$\sigma = 0.00012$	
NO_3^-, mol L^{-1}	1.031	1.105	Ion chromatography
	$\sigma = 0.042$	$\sigma = 0.018$	

Using laboratory analysis, there was determined concentration of ions in product stream C2 in the end of experiments (Table 1). Potassium nitrate purity was calculated according to Eq. (5):

$$P = \frac{c_{NO_3^-}}{c_{Cl^-} + c_{NO_3^-}} 100\% \tag{5}$$

Table 1 includes evaluated results gained with both modules – the standard one and the innovated one. Since experiments were made in triplicate, presented results are average values. Innovated module for EDM achieved almost the same mass fluxes, but 5.6% higher current efficiency and 6% lower specific energy consumption in comparison with standard module. These results confirm the positive effect of innovations on module resistance to shunt currents. In electrodialysis modules, current efficiency decrease could have various causes, e.g., shunt currents, imperfect perm-selectivity of ion-exchange membranes or internal leakages. However, current efficiency increase in the case of innovated module is obviously a result of shunt current restriction, as the same membranes were used and internal leakages were negligible in both modules. Moreover, no significant differences in produced potassium nitrate purity were observed, which confirms similar internal leakages in standard and innovated module. Table 2 informs about quality of product – molar concentration of ions in stream C2.

The product composition (stream C2, Table 2) was tested under our own laboratory instrumental methodology. The ammonia concentration was tested using UV–VIS spectroscopy on "PhotoLab 6100 VIS", the sodium and potassium concentration were tested using ICP-OEM on "iCAP 7400 Duo" and chloride and nitrate concentration were tested using ion chromatography on "Dionex ICS-500+ HPIC SYSTEM". The molar concentration total sum inhomogeneity is caused probably due to using three different methods and their individual deviations. The product content was calculated from nitrate concentration.

4. Conclusions

In order to restrict the appearance of shunt currents in the EDM module, the liquid distribution system of module was completely electrically insulated from membrane effective area. This was carried out by the means of thin plastic film placed on both side of non-active membrane area and non-conductive insert into ion-exchange membranes in the area around distribution channels. These treatments helped to optimize pilot batch production of potassium nitrate by EDM as the current efficiency of the process increased by 5.6% and specific energy consumption decreased by 6% while mass flux remained almost the same. Moreover, it was confirmed that these improvements could appear only as a result of shunt currents restriction since the same ion-exchange membranes were used in both standard and innovated modules, internal leakages were negligible in both cases and product purity was comparable.

Acknowledgments

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Symbols

$c_{NO_3^-}$	—	Concentration of nitrates, mol L^{-1}
E_m	—	Specific energy consumption, W h kg^{-1}
F	—	Faraday constant, 96,485.3 C mol^{-1}
I	—	Electric current, A
J	—	Mass flux, kg m^{-2} h^{-1}
l	—	Length of effective membrane area, m
Δm	—	Mass of produced substance, kg
Δn	—	Amount of produced substance, mol
N	—	Number of membrane pairs
t	—	Time, s
Δt	—	Duration of experiment, s
P	—	Product purity, %
Q	—	Electric charge, C
U	—	Applied voltage, V
w	—	Width of effective membrane area, m
z_C	—	Valence of cation in compound
η	—	Current efficiency, %
υ_C	—	Stoichiometric coefficient of cation
σ	—	Standard deviation

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