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Study of Electrodialysis with Bipolar Membranes

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References

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Abstract

Electrodialysis with the bipolar membrane is a process that allows recovery acid and base from corresponding salt. Produced acid and base is possible to reuse back in the source of the waste salt technology. Due to this fact, it is possible to decline the OPEX and also decrease the environmental impact of many chemical technologies. The present thesis focuses on the recovery of acid and base from the solution of a strong electrolyte salt. During the experimental part, five different stack configurations were measured and compared with each other. Based on the data obtained, the basic migration effects in the membrane stack were described. The effects of current density and product concentration (acid and hydroxide) on the purity and quantity of both acid and base produced was studied in the three-compartment configuration. Obtained data were analyzed and used to make a statistical prediction model. Furthermore, the volt-ampere characteristics of the bipolar membrane were determined and correlated between the co-ion migration through the bipolar membrane and the value of the first plateau of U-I curve. The results show that the coordinate values of the first plateau can preliminarily predict the quality of the products of electrodialysis with the bipolar membrane.

Abstrakt

Elektrodialýza s bipolárními membránami umožňuje vyrábět z odpadních roztoků solí odpovídající zředěnou kyselinu a hydroxid. Tyto produkty je následně možné začlenit zpět do zdrojové technologie a alespoň částečně snížit provozní náklady a ekologickou zátěž řady realizovaných procesů. Předkládaná disertační práce se zabývá experimentálním studiem tohoto procesu zaměřeným na využití heterogenních bipolárních a monopolárních membrán při zpracování solí silných elektrolytů. V rámci experimentální části práce bylo proměřeno a porovnáno pět různých konfigurací svazku elektrodialyzační jednotky s bipolární membránou. Na základě provedených měření byly poté popsány vnitřní migrační děje. Pro tříkomorovou konfiguraci svazku byl detailně studován vliv koncentrace produktů a proudové hustoty na množství a čistotu produkované kyseliny a hydroxidu. S využitím získaných experimentálních dat byl navržen statistický regresní model procesu, který umožňuje predikci předpokládaného množství a čistoty vyráběných produktů pro kombinace jak koncentrací kyseliny a hydroxidu, tak i proudové hustoty. Dále byly proměřeny voltampérové charakteristiky bipolárních membrán a hledány jejich vazby na procesní charakteristiky elektrodialýzy s bipolární membránou. Bylo prokázáno, že poloha prvního inflexního bodu na U-I křivce v symetrickém i asymetrickém uspořádání je mírou průniku koiontů vrstvami BPM a lze ji využít pro prvotní kvalitativní odhad znečištění produktů EDBPM při provozu reálného membránového svazku.

Keywords

Bipolar Membrane, Electrodialysis, Sodium Sulfate, Sulfuric Acid, Sodium Hydroxide, Voltage-Ampere Characteristics

Klíčová slova

bipolární membrána, elektrodialýza, síran sodný, kyselina sírová, hydroxid sodný, volt-ampérové charakteristiky

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Introduction

Worldwide, large amounts of inorganic salts are discharged into the recipient every year as a part of wastewater. Nowadays, many legislative regulations and decrees try to limit the amount of the wastewater, both on the production side and the treatment process side (discharging limits). Due to this fact, new separation processes are playing a more important role in the wastewater treatment plant.

One of the modern approaches is the use of various modifications of electrodialysis with ion-exchange membranes. Electrodialysis is an electrochemical separation process by which ionic species are transported from one solution to another by crossing one or more selective permeability membranes, under the influence of an electrical current. Among the newly developed ion-exchange membranes also belongs to a bipolar membrane (BPM). In its simplest form, BPM is a cation-exchange membrane laminated together with an anion-exchange membrane, through an intermediate layer. The intermediate layer is the most important part of the membrane, which allows the electro-dissociation of water. The products are H^+ and OH^- ions. [3] Based on the specific configuration of anion, cation exchange membrane, and bipolar membrane into the stack, it is possible to produce acid and hydroxide from corresponding inorganic or organic salt. [4 – 6]

The requirements for a bipolar membrane in practical applications are low electrical resistance, high water dissociation rates, low co-ion transport rate, high ion-selectivities, and good chemical and thermal stability in strong acids and bases. Heterogeneous ion-exchange membranes generally have a higher electrical resistance due to the longer pathway of the mobile ion in the heterogeneous membrane structure and the higher probability of leakage of co-ions through water-filled gaps in the membrane matrix which results in lower permselectivity. On the other hand, the cost of heterogeneous membrane structures is substantially lower (2–4 times) in comparison with homogeneous BPMs. Due to this fact, the BPMs can be used in electro-membrane processes where the purity of the acids and bases does not play a significant role, and the use of homogeneous BPMs is limited due to their high cost. Simultaneously, a larger membrane area can be used in the industrial set up with heterogeneous membranes allowing for mild operating conditions which reduce membrane fouling and increase useful membrane life.

Since the emergence of BPMs is readily available as commercial products, a large number of electrodialysis with bipolar membrane (EDBPM) applications have been studied in a laboratory or pilot plant scale [7-10]. However, large-scale industrial plants remain relatively rare. The main reasons for the inadequate use of EDBM relate to shortcomings in the BPMs, which can result in a short useful membrane life, lower output product concentrations, and higher product contamination. Because the basic potential of EDBM applications is assumed to be a part of complex treatment systems, a thorough analysis of such systems is also still missing.

The author of this Ph.D. thesis participated in the project (TAČR TH01031077) solving the implementation of electrodialysis with bipolar membrane to the already existing treating process in the o.z GEAM DIAMO s.p. in Dolní Rožínka, Czech Republic, where large amounts of salt streams (mainly Na_2SO_4) were produced as a byproduct of the alkaline leaching of uranium ore. This work is focused on the basic research of selected parts of the electrodialysis process with the heterogeneous bipolar membrane. The model material is an aqueous solution of sodium sulfate.

1 Aims of the thesis

Based on a detailed literature search and the author's experimental experience, the presented doctoral thesis is focused on the basic research of electrodialysis with the heterogeneous bipolar membrane. The research was carried out mainly in the areas of :

1) effects of the membrane stack configuration (2,3, and 4 compartment configuration) on the quality and quantity of produced acid and hydroxide; the study and description of migration transports in the electrodialysis stack, evaluation of the effect of each migration mechanism,
2) a detailed study of the effect of products concentration (both acid and hydroxide) and current density on the purity of products in the three-compartment configuration of electrodialysis with the bipolar membrane,
3) the correlation between the volt-ampere characterization of bipolar membrane and process characterization parameters of electrodialysis with the bipolar membrane.

1.1 Studied configurations

All configurations were designed to get a concentration of acid and hydroxide products as high as possible. Also, the purity of products was an important parameter for process optimization. The basic stack configuration is the three-compartment configuration (Fig. 1). This configuration is built upon regularly recurring cation exchange membrane (CEM), anion exchange membrane (AEM), and BPM. The configuration allows the production of both acid and base. In the two-compartment configuration (Fig. 2), only one “pure“ product is obtained; the second one is always contaminated with the feed salt. [11]

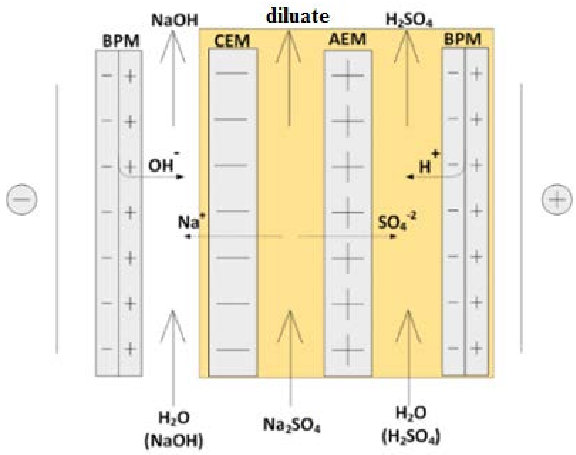

Fig. 1 Three-compartment configuration

Fig. 2 Two-compartment configurations with anion or cation exchange membrane

Four compartment configurations are used only in some special cases. In this study, three different four-compartment configurations were designed (Fig. 3).

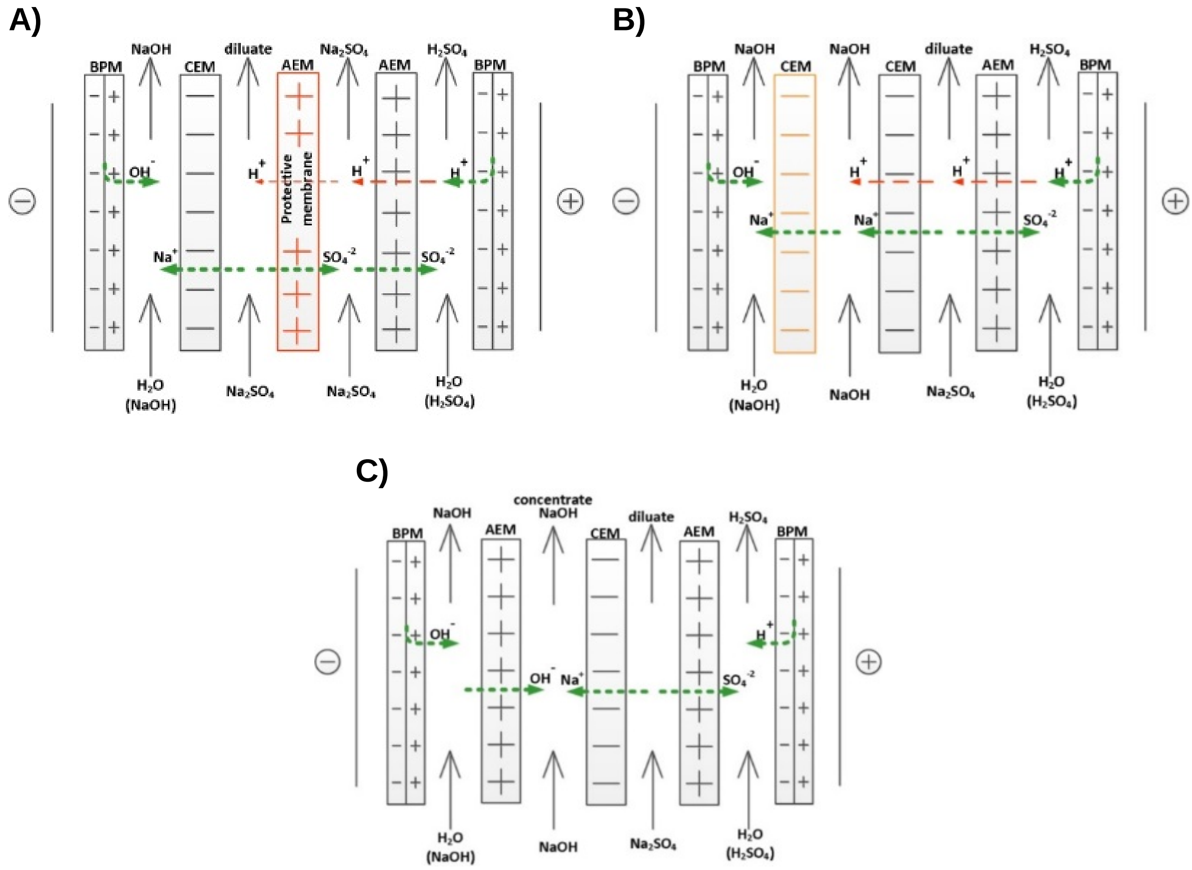

Fig. 3 Four compartment configurations

Fig. 3 A) shows the four-compartment configuration, which has one more AEM in comparison with the basic three-compartment configuration. The main idea of integrating this extra AEM into the stack was to prevent the migration of H^+ through the stack (red arrow in Fig 3A). The duplicated AEM works as a barrier for H^+ ions and due to this fact, the concentration of produced hydroxide should be higher compared to the basic three-compartment configuration.

Fig. 3 B) presents another four-compartment configuration, which includes one more CEM. This CEM helps to create one extra process stream containing NaOH. This sacrificed NaOH solution acts only as a barrier for migration of H^+ ions. As a result, the concentration of produced hydroxide should be higher in comparison with the three-compartment configuration.

Fig. 3 C) describes the four-compartment configuration in which again one more AEM is placed. Nevertheless, in comparison with the configuration mentioned above and described in Fig. 3A), this configuration combines in one stack the standard electrodialysis and EDBPM. An extra AEM doesn't create the barrier as it was described in the previous case but creates a supported process stream, where NaOH is concentrated.

2 Experimental

2.1 Membranes and model waters

Membranes used in the experiments included cation-exchange (CEM) heterogeneous membrane Ralex CM(H)-PP (Mega, Czech Republic), anion-exchange (AEM) heterogeneous membrane Ralex AM(H)-PP (Mega, Czech Republic), and heterogeneous BPM Ralex BM 3.1 (MemBrain, Czech Republic). Experiments were performed using model wastewater containing sodium sulfate at concentrations from 10 to 32 g/l. The solutions were prepared from analytical reagent grade powder received from Ing. Petr Švec – PENTA s.r.o., CZ and RO water. Chemicals used for analytical titration measurements were prepared from standardized 0,1M HCl and 0,1M $NaOH$ solution from Lach-Ner s.r.o., CZ.

2.2 Experimental unit description

Electrodialysis experimental tests were carried out using laboratory unit P EDR-Z/4x from MemBrain s.r.o. company (see Fig. 4). This unit allows to control and regulate all necessary electrodialysis parameters (current, flow, conductivity, pH, temperature, etc.).

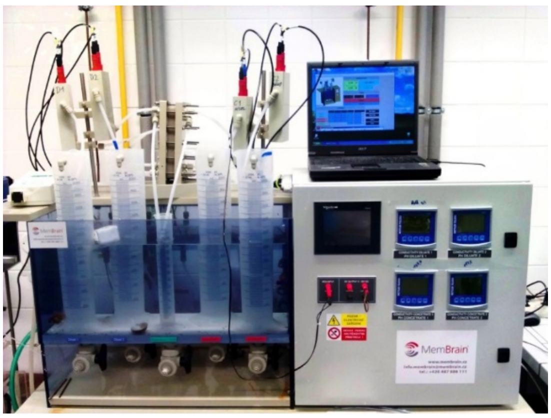

Fig. 4 P EDR-Z/4x experimental unit

Voltage-current tests were carried out using the testing cell with potentiostat unit. The cell was designed in the four-compartment configuration. As a result, it was possible to simulate the conditions of real EDBPM process. The cell was produced by PlastService s.r.o. based on drawing proposal from the MemBrain company. The potentiostatic unit used was Autolab PGSTAT 128N.

2.3 Feed and bleed mode

The main part of the experimental studies was carried out in the feed and bleed operation mode. In this mode, it is possible to run the experiments in the steady-state. The schematic drawing of feed and bleed mode is shown in fig. 5. The system is operated at a constant concentration of acid, hydroxide, and salt solution. Nevertheless, during the electrodialysis, the concentration of both produced acid and hydroxide continuously increase, and the concentration of salt solution decreases. Therefore, it is necessary to add the demi water continuously to acid and hydroxide solution produced to regulate (decrease) the product concentration to the concentration required. For feed salt solution, it is necessary to add a high concentrated solution of salt to keep the system in a steady-state system.

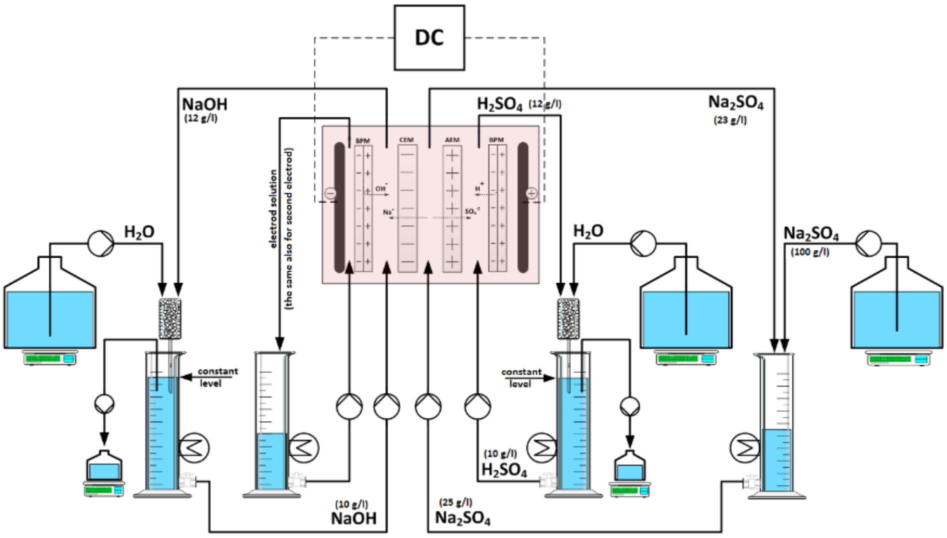

Fig. 5 Feed and bleed mode set up

2.4 Design and analysis of experiments

To obtain the maximum amount of information from a least or optimal number of experiments, the methodology of design of experiments (DoE) was used. The main application of DoE methodology was in experiments focused on the study of the effect of selected factors such as current density and both acid and base concentration on maximum concentration and purity of products. A central composite design was used for building a model for the response variable without needing to use a complete three-level factorial experiment. The results obtained (responses) were statistically analyzed using Fischer tests of analysis of variance (ANOVA) with software Statistica 12.0 (StatSoft). Using this approach, it was possible to identify what is an order of the effects of factors on the responses, and are there mutual effects of factors. The experimental data were fitted with the polynomial of the second order.

3 Results and discussion

3.1 Effect of stack configuration

Fig. 6 shows the maximum achievable concentration of sodium hydroxide in four different stack configurations. The highest concentration of sodium hydroxide was obtained in the four-compartment configuration BCCA (58 g/l), which was about 30% higher compared to the value in the standard three-compartment configuration (45 g/l). In the four-compartment configuration, BCAA has measured slightly lower hydroxide concentration (50 g/l), while in the case of two-compartment configuration the concentration of sodium hydroxide was approximately 40 g/l, which is similar to the value in the three-compartment configuration. Four compartment configurations have a positive effect on increasing the maximum achievable hydroxide concentration.

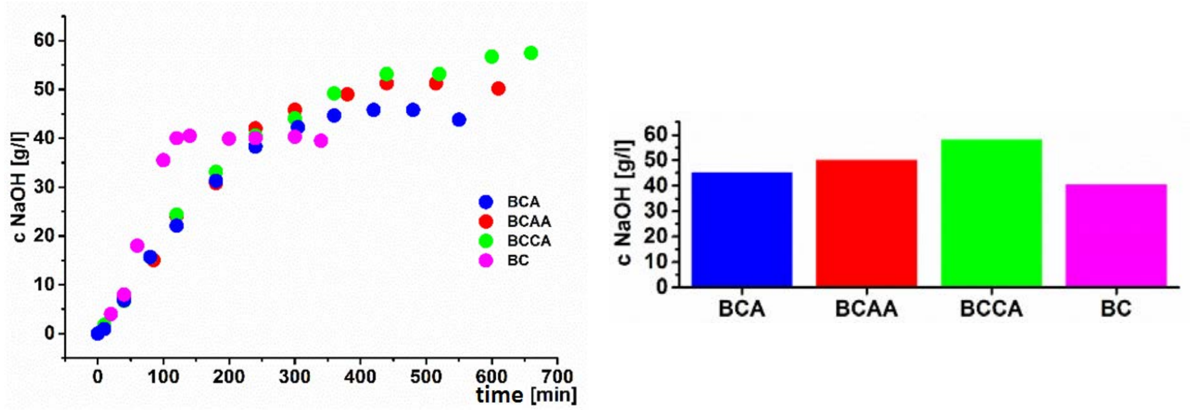

Fig. 6 Changes of NaOH concentration and maximum achievable concentration

To explain the results measured the Fig. 7 summarizes possible transports of ions through the membrane stack. The green color represents desirable transports; orange + red colors represent undesirable transports of ions through the stack. It is known that the H^+ ions are quite small, and their mobility is minimal of one order higher than the mobility of other ions. Due to this fact, H^+ ions pass quickly through AEM and can easily migrate to the stream of produced NaOH, where the H^+ ions react with OH^- ions.

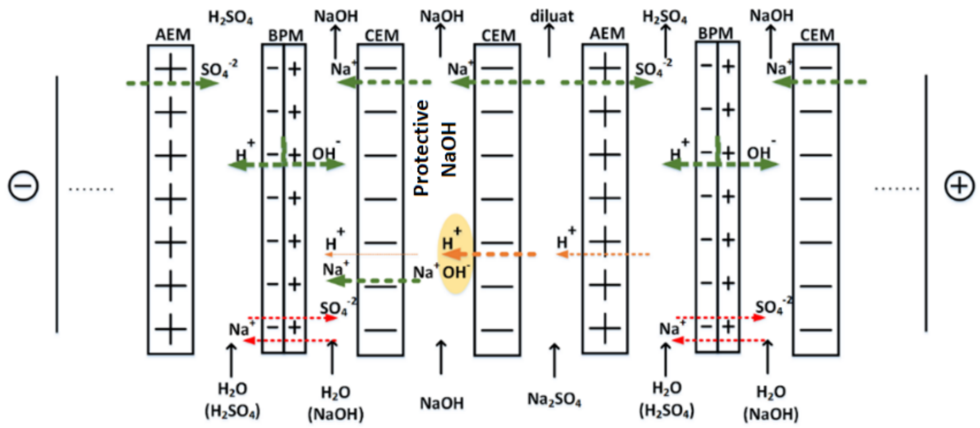

Fig. 7 Ion transport through the BCCA EDBPM stack

Fig 8 shows time changes in the concentration of protective NaOH (green color). It is evident that with increasing concentration of acid, the concentration of hydroxide in the protective stream decreases. Furthermore, the results show that the decline of hydroxide concentration is lower for low concentrations of acid, while if the concentration of acid gets more then 38 g/l the negative slope characterizing the decreasing of hydroxide concentration is higher, which means that under these conditions more H^+ ions pass through the AEM.

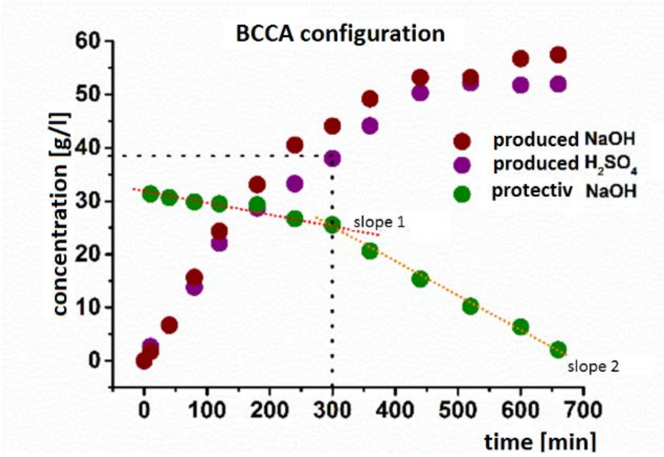

Fig. 8 Concentration of all stream in BCCA configuration

In the case of sulfuric acid, the highest concentration of produced acid was obtained in the three-compartment configuration BCA (60 g/l), as it is shown in Fig. 9. Four compartment configurations allowed concentration 52 g/l (BCCA) and 54 g/l (BCAA), respectively. The sulfuric acid concentration in the two-compartment configuration was only 15 g/l. Explanation, why the four-compartment configurations give a lower concentration of sulfuric acid in comparison with the three-compartment configuration should be the fact, that both duplicated membranes (CEM, AEM) don't stop the increased migration of H^+ ions. As a result, there is an imbalance of ions in the acid stream and the migration of SO_4^{-2} ions take place.

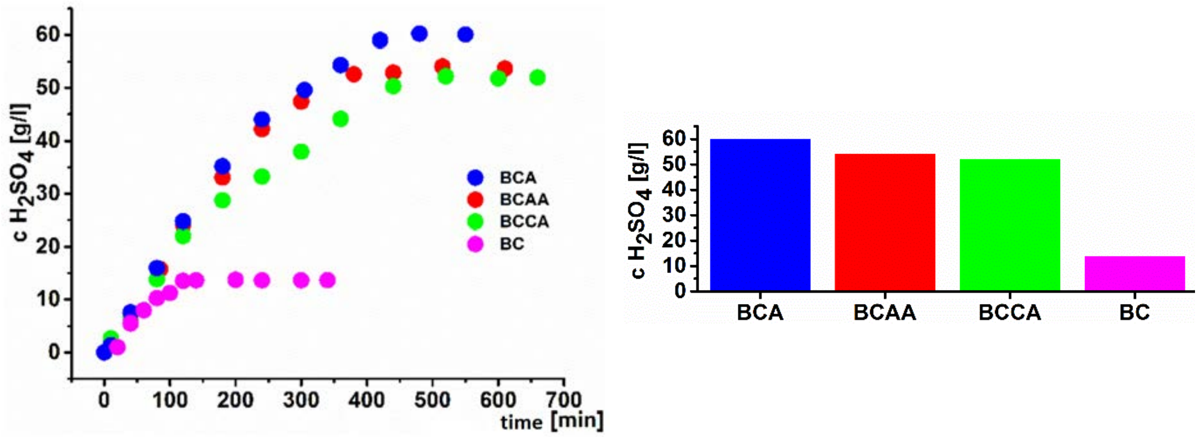

Fig. 9 The maximum achievable concentration of sulfuric acid

Fig 10 shows the consumption of electricity for the three-compartment (CBA) and four compartment configurations. The three-compartment configuration has the lowest energy consumption. It is because the three-compartment configuration stack has less membrane in total, so the electrical resistance of the stack is lower compared to the four-compartment configurations.

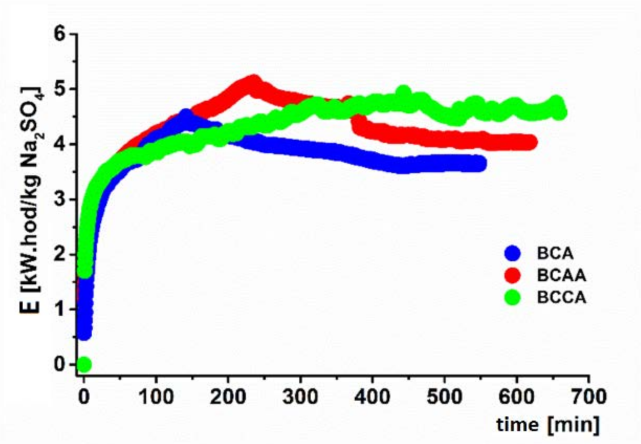

Fig. 10 Comparison of the electrical consumption of various EDBPM configurations

3.2 Effect of concentration and current density on quantity and quality

Fig. 11 shows the contour plot of the production of both acid and hydroxide independence on the concentration of the products. The production of acid and hydroxide depends mainly on the concentration of acid. The graph also shows that lower concentration has a positive impact on the quantity of products. The difference in product quantity at high and low concentration is significant. From this point of view, it is better to produce both acid and hydroxide with lower concentration.

Fig 12 shows similar contour plot of production value not only in dependence on the concentration but also on current density. It is obvious that current density has a significant effect, dominantly in the case of production of sodium hydroxide. If it is necessary to increase the production of acid and hydroxide, the higher current density can help to reach this goal.

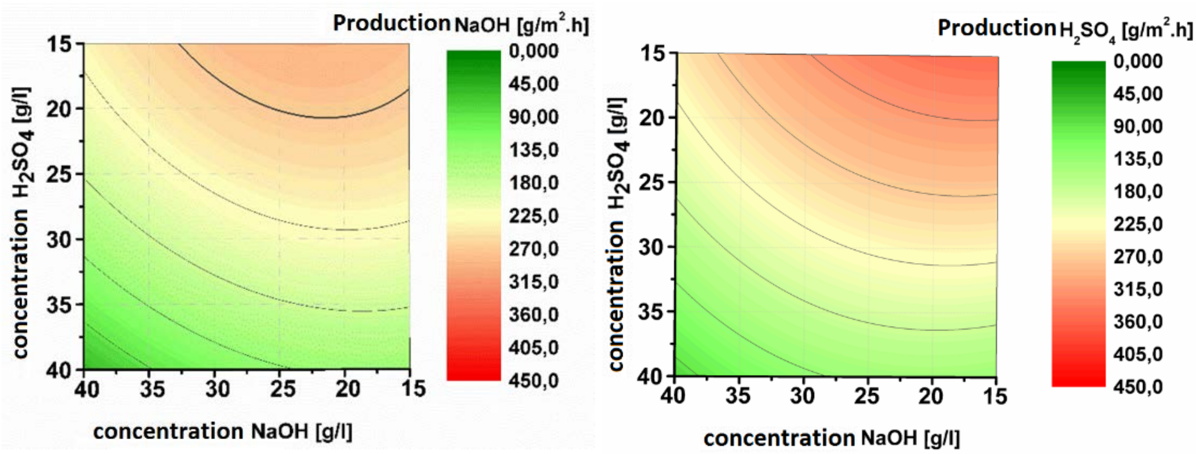

Fig. 11 Effect of concentration on the quantity of produced acid/hydroxide

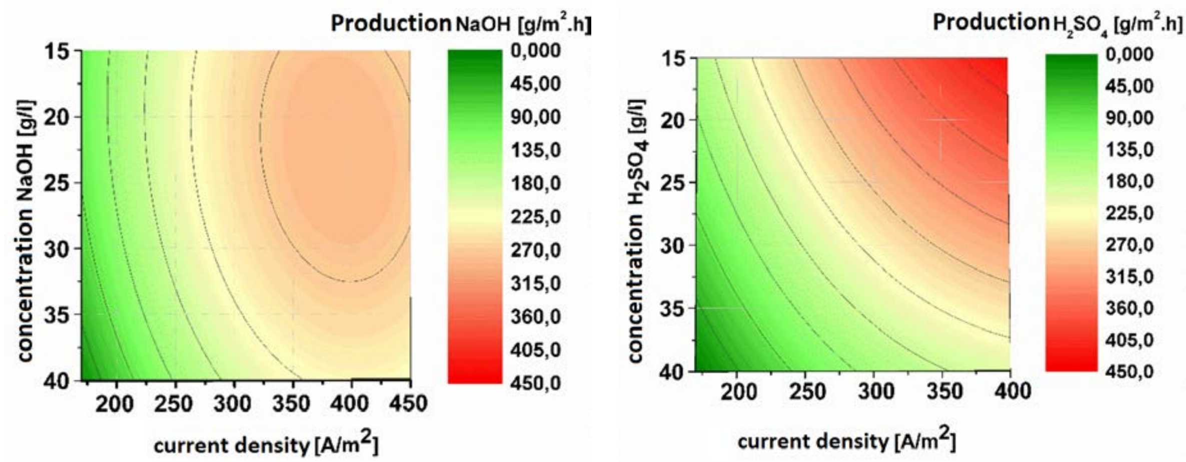

Fig. 12 Effect of current density and products concentration on produced quantity

Above described experimental results were modeled by the second-order polynomial equation using response surface methodology. The level of the confidence was set at 95% for all responses, and the probability was expressed as p-value at the significance level of 0.05. The regression coefficients were calculated, employing the least square method. Still due to certain variations in both, the predicted response and the coefficients estimates, it was made ANOVA tests of analysis of variance to show that hypothesis was valid. The model was taken as satisfactory when the regression was significant, and the lack of fit is non-significant for the confidence interval. As a result of the prediction of the produced quantity of acid J_{acid} and hydroxide J_{hydrox}, the following equations were obtained

$$J_{acid} = 249{,}549 - 137{,}471 \cdot C_{H_2SO_4} - 35{,}204 \cdot C_{NaOH} + 84{,}367 \cdot \rho_I \qquad \textbf{(2)}$$

$$J_{hydrox} = 244{,}677 - 90{,}864 \cdot C_{H_2SO_4} - 24{,}878 \cdot \rho_I^2 + 61{,}992 \cdot \rho_I \qquad \textbf{(3)}$$

where ρ_I is current density and C_i is concentration.

Another important parameter for the description of EDBPM is the quality (purity) of produced acid and base. Fig 13 shows the results of unsteady EDBPM experiments in the three-compartment setup. The concentration of both produced acid and hydroxide play an important role from the point of view of purity as well as the time necessary to reach the steady-state. It was found that it is necessary to perform tests minimally 18 -20 hour, to be sure that the final measured value is the steady-state value.

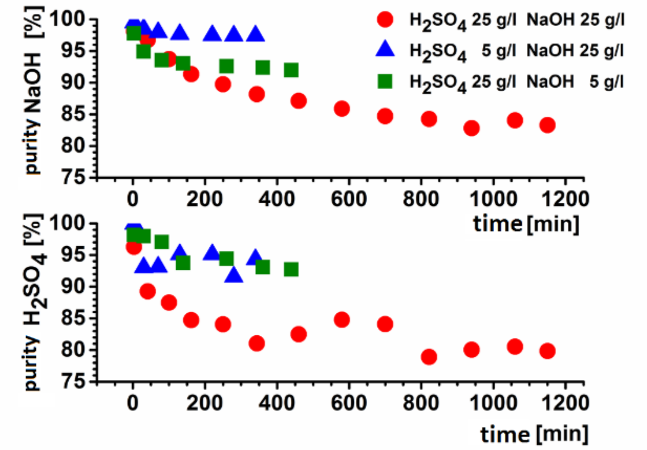

Fig. 13 Three compartment EDBPM - changes in products purity in time

Fig 14 and Fig 15 show contour plots of purity (acid, hydroxide) dependence on the concentration of produced acid (base) and current density. It is evident that the produced acid has higher purity in comparison with the produced hydroxide. Furthermore, the produced acid concentration play an important role in the purity of hydroxide. It is mainly due to the fact, that H^+ ions pass easily through AEM as it was described in Fig. 7. As a result, there should be charge imbalance and the higher concentration of SO_4^{-2} ions, which can pass through BPM to hydroxide stream.

Similar to quantity measurements the prediction equations for the purity of produced acid ($\%\, acid\, purity$) and base ($\%\, hydroxid\, purity$) were obtained by statistical evaluation as

$$\%\, hydroxid\, purity = 80{,}577 - 30{,}511 \cdot C_{H_2SO_4} + 3{,}077 \cdot \rho_I \quad \textbf{(4)}$$

$$\%\, acid\, purity = 90{,}596 - 10{,}816 \cdot C_{H_2SO_4} - 12{,}404 \cdot C_{NaOH} - 2{,}295 \cdot \rho_I^2 + 4{,}118 \cdot \rho_I - 5{,}621 \cdot C_{H_2SO_4} \cdot C_{NaOH} \quad \textbf{(5)}$$

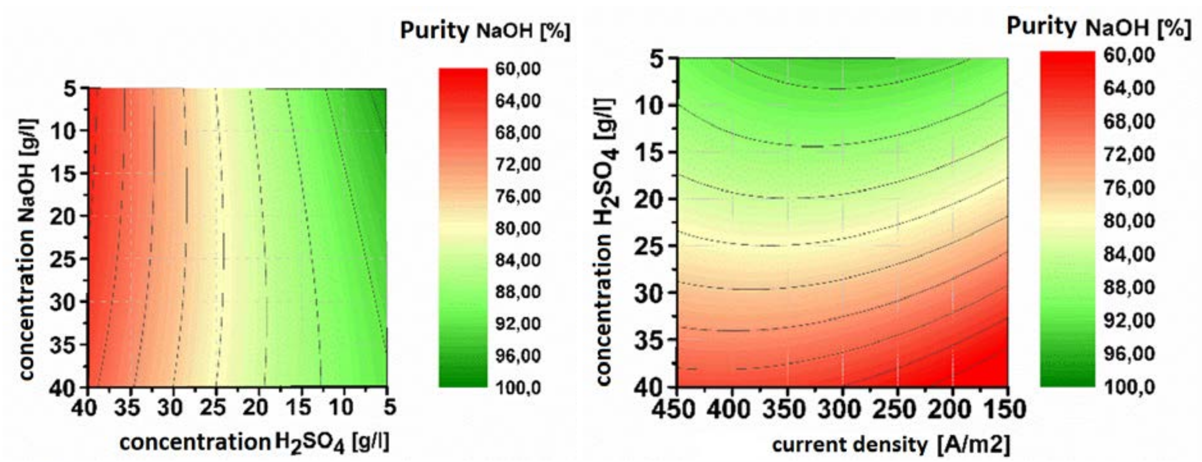

Fig. 14 Effect of products concentration and current density on the purity of hydroxide

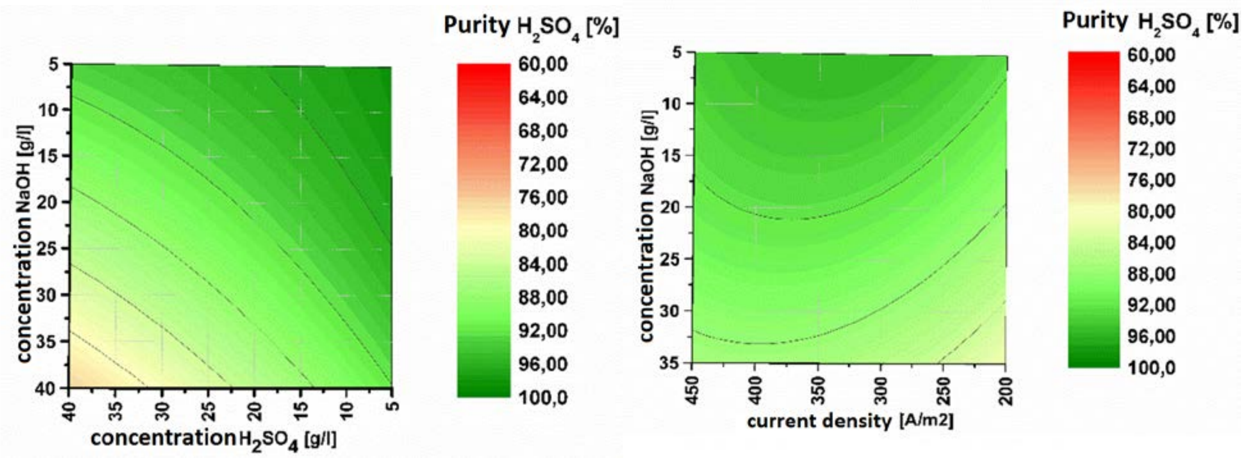

Fig. 15 Effect of products concentration and current density of purity of acid

3.3 Voltage-ampere characterization of bipolar membrane

The current density across a bipolar membrane was also measured as a function of the applied potential drop. As a result, an inflection point can be observed in the obtained current-voltage curve at a certain voltage value. This inflection point indicates the start of the extra electro-dissociation (splitting) of water. The results should be obtained in a few seconds (minutes). Nevertheless, the standard volt-ampere tests are used mainly to compare different membranes in the system with the same salt solution on both sides of BPM as shows Fig. 16 (red curves).

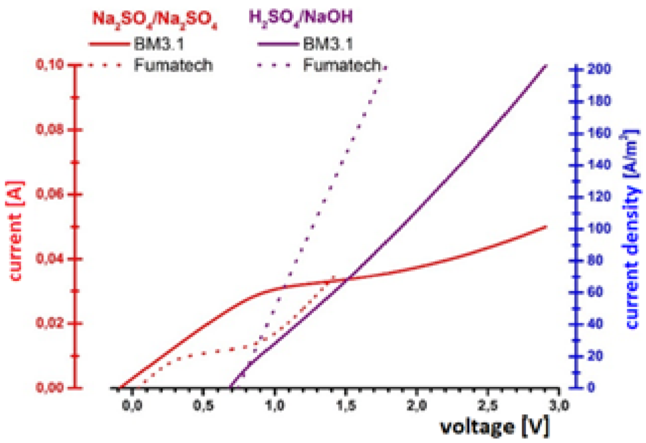

Fig. 16 Comparison of U-I curves between heterogeneous bipolar membrane BM3.1 homogeneous bipolar membrane Fumatech in two different combinations of solutions

It is evident from Fig. 16 that heterogenous bipolar membrane gives worse result in comparison with homogeneous one. Splitting water voltage is lower for homogeneous (three times); also the current density in inflection point is lower, which means that fewer co-ions can pass through the homogeneous membrane, and the final purity of produced acid and hydroxide should be higher compared to the heterogeneous membrane. Fig 16 also shows that the asymmetric combination of solutions (acid-

BPM-hydroxide) causes that the classic shape of the U-I curve almost disappears. In the case of the heterogeneous membrane, it is possible to find some inflection point (basic plato), but homogeneous membrane doesn´t have. Because the heterogeneous membrane has some inflection point, it was possible to make preliminary measurements focused on the effect of concentration of acid and base on both sides of BPM on the shape of U-I curve. The results are shown in Fig. 17. Based on this data, inflection points were evaluated, and values of current density at inflection points were determined.

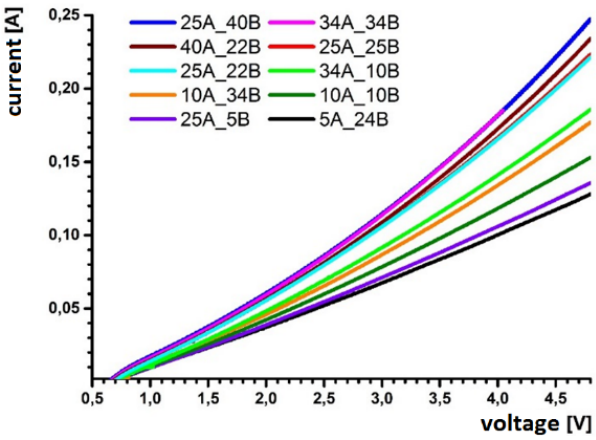

Fig. 17 Effect of acid and base concentration during asymmetric combination

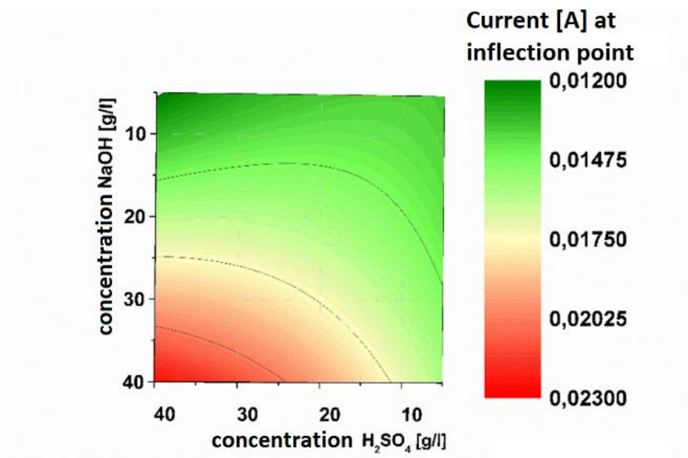

Fig. 18 Value of current in the inflection point

It follows from Fig. 18 that the increasing concentration of acid and hydroxide also increases the value of current in the inflection point. As per quality, it corresponds to previous results obtained in EDBPM unit.

4 Conclusions

The obtained data show that the membrane stack configuration has a significant effect on the maximum achievable concentration of both the acid and the base produced. Furthermore, the data obtained contributed to the description of the main migration transports in the stack. It was found that the limitation for products purity is the selectivity of BPM, while in the case of quantity, it is the selectivity of AEM.

Three compartment configuration was used to determine the effect of the concentration of acid and base on process parameters, mainly on the quality and quantity of products. All experimental dependencies were modeled by the statistical regression equations which enable to predict the quality and quantity of produced acid and hydroxide. If the requirement for a final concentration of sulfuric acid is not higher then 15 g/l, it is much more efficient to operate EDBPM at this concentration of acid, or lower. The optimum concentration of hydroxide is about 30 g/l.

The experiments focused on the volt-ampere characterization of bipolar membrane show that there is a significant difference between homogeneous and heterogeneous bipolar membrane. Also, it was found that there is a partial correlation between the result obtained by voltage-amper test and longtime tests using the standard EDBPM laboratory unit. Nevertheless obtained data cannot determine the exact effect of each ion in the solution. Due to this fact, further in-depth research on this topic is necessary.

List of references

[1] PALATÝ, Zdeněk, ed. *Membránové procesy*. Prague: Vysoká škola chemicko-technologická, 2012. ISBN 9788070808085.

[2] NOVÁK, Luboš. *Elektromembránové procesy*. Vysoká škola chemicko-technologická v Praze, 2014. ISBN 9788070808658.

[3] KROL, John Jacco. *Monopolar and bipolar ion exchange membranes*, 1997. Universiteit Twente.

[4] KROUPA, J., J. KINČL a J. CAKL. Recovery of H2SO4 and NaOH from Na2SO4 by electrodialysis with heterogeneous bipolar membrane. *Desalination and Water Treatment*. 2015, **56**(12). ISSN 19443986 19443994. doi:10.1080/19443994.2014.980972

[5] ONGWEN, Xu a Yang WEIHUA. Citric acid production by electrodialysis with bipolar membranes. Chemical Engineering and Processing: Process Intensification. 2002, 41(6), 519–524. doi:10.1016/S0255-2701(01)00175-1

[6] FERRER, J. S Jaime, S. LABORIE, G. DURAND a M. RAKIB. Formic acid regeneration by electromembrane processes. *Journal of Membrane Science*. 2006, **280**(1–2), 509–516. ISSN 03767388. doi:10.1016/j.memsci.2006.02.012

[7] KROUPA, J., J. KINČL a J. CAKL. Recovery of H2SO4 and NaOH from Na2SO4 by electrodialysis with heterogeneous bipolar membrane. *Desalination and Water Treatment*. 2015, **56**(12). ISSN 19443986 19443994. doi:10.1080/19443994.2014.980972

[8] HADDAD, Maryam, Laurent BAZINET, Oumarou SAVADOGO a Jean PARIS. Electrochemical acidification of Kraft black liquor: Impacts of pulsed electric field application on bipolar membrane colloidal fouling and process intensification. *Journal of Membrane Science*. 2017, **524**, 482–492. ISSN 03767388. doi:10.1016/j.memsci.2016.10.043

[9] TONGWEN, Xu a Yang WEIHUA. Citric acid production by electrodialysis with bipolar membranes. *Chemical Engineering and Processing: Process Intensification*. 2002, **41**(6), 519–524. doi:10.1016/S0255-2701(01)00175-1

[10] JAIMEFERRER, J, E COUALLIER, P VIERS, G DURAND a M RAKIB. Three-compartment bipolar membrane electrodialysis for splitting of sodium formate into formic acid and sodium hydroxide: Role of diffusion of molecular acid. *Journal of Membrane Science*. 2008, **325**(2), 528–536. ISSN 03767388. doi:10.1016/j.memsci.2008.07.059

[11] JAIME-FERRER, J.S., E. COUALLIER, P. VIERS a M. RAKIB. Two-compartment bipolar membrane electrodialysis for splitting of sodium formate into formic acid and sodium hydroxide: Modelling. *Journal of Membrane Science*. 2009, **328**(1–2), 75–80. ISSN 0376-7388. doi:10.1016/J.MEMSCI.2008.10.058

List of student's published works

Publications in journals with IF

KROUPA, J. – KINČL, J. - CAKL, J. Recovery of H_2SO_4 and NaOH from Na_2SO_4 by electrodialysis with heterogeneous bipolar membrane *Desalination and Water Treatment*, 2015, vol. 56, no. 12, s. 3238-3246. ISSN: 1944-3994.

Publications in other scientific journals

KROUPA, J. - CAKL, J. - CHARAMZA, J. - KINČL, J. - JIŘÍČEK, T. Influence of Sulfate Type Waste Water Contamination on H_2SO_4 and NAOH production by Electrodialysis with Bipolar Membrane *Innovative remediation technologies - research and experience*, 2017, vol. 9, no. 1, s. 1-7. ISSN: 1805-0182.

KROUPA, J. - CAKL, J. - KINČL, J. Increasing the concentration of products from electrodialysis with heterogeneous bipolar membrane *Innovative remediation technologies - research and experience*, 2016, vol. 8, no. 1, s. 1-6. ISSN: 1805-0182.

KROUPA, J. - CAKL, J. - KINČL, J. - TOMAN, F. Integration of electrodialysis with bipolar membrane into the technology of treatment of extra wastewater containing sodium sulfate *Innovative remediation technologies - research and experience*, 2015, vol. 7, no. 1, s. 1-9. ISSN: 1805-0182.

Contributions presented at international scientific conferences

JIŘÍČEK, T. - FEHÉR, J. - AMRICH, M. - NEDĚLA, D. - TOMAN, F. - VELEN, B. - CAKL, J. - KROUPA, J. Recycling sulphuric acid and sodium hydroxide by industrial scale bipolar electrodialysis. In MELPRO 2018 : book of abstracts. Česká Lípa: Česká membránová platforma (CZEMP), 2018. s. 101 s. ISBN 978-80-906831-2-9.

KINČL, J. - JIŘÍČEK, T. - FEHÉR, J. - AMRICH, M. - NEDĚLA, D. - TOMAN, F. - VELEN, B. - CAKL, J. - KROUPA, J. Electromembrane Processes in Mine Water Treatment. In Mine Water & Circular Economy. Vol. II. Lappeenranta: Lappeenranta University of Technology, 2017. s. 1154-1162 s. ISBN 978-952-335-065-6.

KROUPA, J. - CAKL, J. - KINČL, J. - TOMAN, F. Integration of the product of waste sodium sulfate electrodialysis with bipolar membrane into the technology of uranium beneficiation. In XXXII. European membrane society summer school 2015 "Integrated and Electromembrane Processes". Česká Lípa: Česká membránová platforma (CZEMP), 2015. s. 21 s. ISBN 978-80-904517-3-5.

KROUPA, J. - KINČL, J. - CAKL, J. Recovery of H_2SO_4 and NaOH from Na_2SO_4 by electrodialysis with heterogeneous bipolar membrane. In MELPRO - International Conference Membrane and Electromembrane Processes. Book of Abstracts.. Praha: Ústav makromolekulární chemie AV ČR, 2014. s. 88 s. ISBN 978-80-85009-78-1.

KROUPA, J. – CAKL, J. – KINČL, J. A study of Co-ions Leakage in Electrodialysis with Heterogeneous Bipolar Membrane, Euromembrane 2015, Aachen, Germany 6.-10.9.2015;

KROUPA, J. - KINČL, J. - CAKL, J. Application of electrodialysis with heterogeneous bipolar membrane for recovery of Na_2SO_4 to NaOH and H_2SO_4. In EIDS 2014 – European Industrial Doctoral School – Summer Workshop 2014. Book of Abstracts.. Pardubice, 2014. s. 52 s. ISBN 978-80-7395-779-7.

Contributions presented at national scientific conferences

KROUPA, J. - CHARAMZA, J. - KINČL, J. - JIŘÍČEK, T. - CAKL, J. Vliv vybraných parametrů na množství produkované báze a kyseliny při elektrodialýze s bipolární membránou. In MEMPUR 2017 : sborník abstraktů. Česká Lípa: Česká membránová platforma (CZEMP), 2017. ISBN 978-80-904517-9-7.

KROUPA, J. - CAKL, J. - CHARAMZA, J. - KINČL, J. - JIŘÍČEK, T. Vliv znečištění odpadních síranových vod na produkci H2SO4 a NaOH při elektrodialýze s bipolární membránou. In Inovativní sanační technologie ve výzkumu a praxi IX. Chrudim: Vodní zdroje Ekomonitor, spol. s r.o., 2016. s. 53-59 s. ISBN 978-80-86832-94-4.

KROUPA, J. - CAKL, J. - KINČL, J. Zvyšování koncentrace produktů elektrodialýzy s heterogenní bipolární membránou. In Inovativní sanační technologie ve výzkumu a praxi VIII. Chrudim: Vodní zdroje Ekomonitor, spol. s r.o., 2015. s. 97-103 s. ISBN 978-80-86832-87-6.

KROUPA, J. - CAKL, J. - KINČL, J. - TOMAN, F. Effect of stack configuration of electrodialysis with the bipolar membrane on the achievable concentration of sodium hydroxide. In Proceedings of Workshop of Students‘ Presentations 2014 „Membranes and Membrane Processes“. Česká Lípa: Česká membránová platforma (CZEMP), 2014. s. "33-1"-"33-6" s. ISBN 978-80-904517-2-8.

KROUPA, J. - CAKL, J. - KINČL, J. - TOMAN, F. Začlenění elektrodialýzy s bipolárními membránami do technologie zpracování nadbilančních odpadních vod obsahujících síran sodný. In Inovativní sanační technologie ve výzkumu a praxi VII.. Chrudim: Vodní zdroje Ekomonitor, spol. s r.o., 2014. s. 4-11 s. ISBN 978-80-86832-82-1.

KROUPA, J. - CAKL, J. - KINČL, J. Výroba kyseliny sírové a hydroxidu sodného ze síranu sodného s použitím elektrodialýzy s heterogenní bipolární membránou. In Sborník - Workshop studentských prací 2013, Téma: elektromembránové a tlakové membránové procesy. Abstrakt v angličtině a CD s plnými texty. Česká Lípa: Česká membránová platforma (CZEMP), 2013. s. "36-1"-"36-9" s. ISBN 978-80-904517-1-1.