

INCREASING THE CONCENTRATION OF PRODUCTS FROM ELECTRODIALYSIS WITH HETEROGENEOUS BIPOLAR MEMBRANE

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Abstract

The process of electrodialysis with bipolar membranes allows producing acid and hydroxide from the corresponding salt. The integration of this process into the technology of treatment of overbalanced wastewater from uranium ore processing in o.z. GEAM DIAMO s.p. in Dolní Rožínka (ČR) has already been described in our previous work. We have identified sub processes of the technology in which sulfuric acid and sodium hydroxide of various concentrations and purities are used. It was also found that the main limitation for greater use of sulfuric acid as well sodium hydroxide produced by means of electrodialysis with bipolar membranes is particularly maximum attainable concentration of both products. For the standard three-chamber arrangement of membrane stack it acquires values which does not exceed 5 wt%. This paper focuses on the description and evaluation of laboratory experiments aimed at searching ways to increase the maximum achievable concentrations of sulfuric acid and sodium hydroxide produced. Experiments were performed using a laboratory test unit EDR-Z/10-0.8 (MemBrain, Czech Republic) operated in a standard configuration with monopolar membranes as well as in the arrangement with bipolar membranes. In doing so, the acid and hydroxide solution produced in the three-chamber arrangement were further concentrated using standard electrodialysis and alternatively was tested a four-chamber arrangement with bipolar and protective membrane. Both studied methods allow obtaining products of higher concentration. As shown particularly preferable is to use classical electrodialysis with monopolar membranes. This method allowed up to a twofold increase in the maximum achievable concentrations of both acid and base.

Key words:

Electrodialysis, Bipolar Membrane, Sulfuric Acid, Sodium Sulfate, Sodium Hydroxide.

Introduction

Bipolar membrane (BPM) is a special ion exchange membrane which allows splitting of water into H⁺ and OH⁻ ions in the electric field. This feature can be used in combination with the selective transport through monopolar electrodialysis membranes in the production of acids and bases from corresponding organic or inorganic salts (Strathmann, 2004). Principle of electrodialysis with bipolar membrane (EDBPM) is shown in Fig. 1. The diluate circuit is fed by the treated salt solution. The loaded voltage leads to migration of ions present. These are transported through corresponding monopolar membrane (cations through CEM and anions through AEM) into the adjacent circuits. Simultaneously bipolar membrane splits water to H⁺ and OH⁻ ions, which form together with the corresponding cations or anions either acid or hydroxide solution. (Wei, Wang, Zhang, Xu 2013)

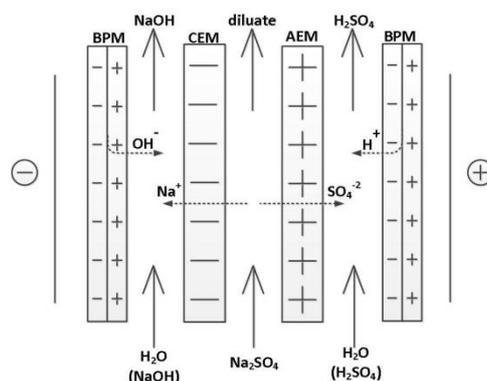


Fig. 1: Principle of electrodesalination with bipolar membrane – three compartment configuration (AEM – anion exchange membrane, CEM – cation exchange membrane, BPM - bipolar membrane)

A very common industrial waste salt is sodium sulfate. Major producer of waste sodium sulfate waters in the Czech Republic is the company o.z. GEAM DIAMO s.p. Dolní Rožínka (hereinafter only GEAM) which annually produces about 6,400 tons of solid sodium sulfate from the overbalanced wastewater resulting from the processing of uranium ore (Jez 2008). Although sodium sulfate is not toxic, its discharge into the receiving water body is limited by strict regulations. For this reason, it is necessary to treat waste water contaminated with sodium sulfate, for example using reverse osmosis, electrodesalination or evaporation followed by crystallization of the product (Kroupa, Kinčl, Cakl 2014).

Recovery production of sulfuric acid and sodium hydroxide from waste sulfate solution represents an interesting opportunity to reduce the negative environmental impact of the technology of uranium ore treatment. For this reason, previously the study has been made focused on the possible use of sulfuric acid and sodium hydroxide produced with EDBPM backward in the GEAM technology (Kroupa et al., 2014). In the study we have identified several sub processes, in which sulfuric acid and sodium hydroxide were used and for these sub processes the basic requirements for the product purity and minimal concentration were defined. The neutralization processes need dominantly concentration of the agent of about 4% by weight, i.e. concentration that is easily accessible by EDBPM with heterogeneous membranes. However, it appears that in some technological stages particular acid concentration of at least 10% by weight is required. This parameter is currently unreachable by conventional EDBPM with heterogeneous bipolar membranes (Kroupa, Cakl, Kinčl 2014). Therefore, the present paper deals with the experimental study of two ways how to increase the concentration of products in comparison with traditional EDBPM in a three-chamber arrangement. At first, by changing the configuration of membrane stack by adding protective membrane to the classic three chamber stack and, at second, using conventional electrodesalination to concentrate the acid and hydroxide previously formed in the standard three-chamber arrangement.

Methodology and Experimental

All experiments were carried out with model sodium sulfate solution prepared from analytical reagent grade powder received from Sigma-Aldrich Chemicals and deionized water. The concentration of model sodium sulfate solution was about 35 g/l which is close to the concentration of real waste water from GEAM.

Measurements were performed using an electrodesalination unit EDR-Z_FULLL_v3 (MemBrain, CZ). The device enables laboratory testing in batch, feed and bleed or continuous mode. During measurements basic operating parameters such as voltage, electrical current, process liquid conductivity, pH and temperature were controlled continually. Flows in the individual working circuits were also monitored and regulated. The membrane stack was formed from CEM – RALEX CM(H)-PP (Mega, CZ), AEM – RALEX AM(H)-PP (Mega, CZ) and developmental bipolar membrane BM1 (MemBrain, CZ). Typical arrangement of membranes in the stack is shown in Fig. 1 for basic three compartment configuration. In addition, other variants of membrane arrangements were also tested. Typical examples are four compartment configurations with two AEM (Fig. 2 a+c)) or two CEM (Fig. 2 b)). Here, A represents anion exchange, C cation exchange, and B bipolar membrane.

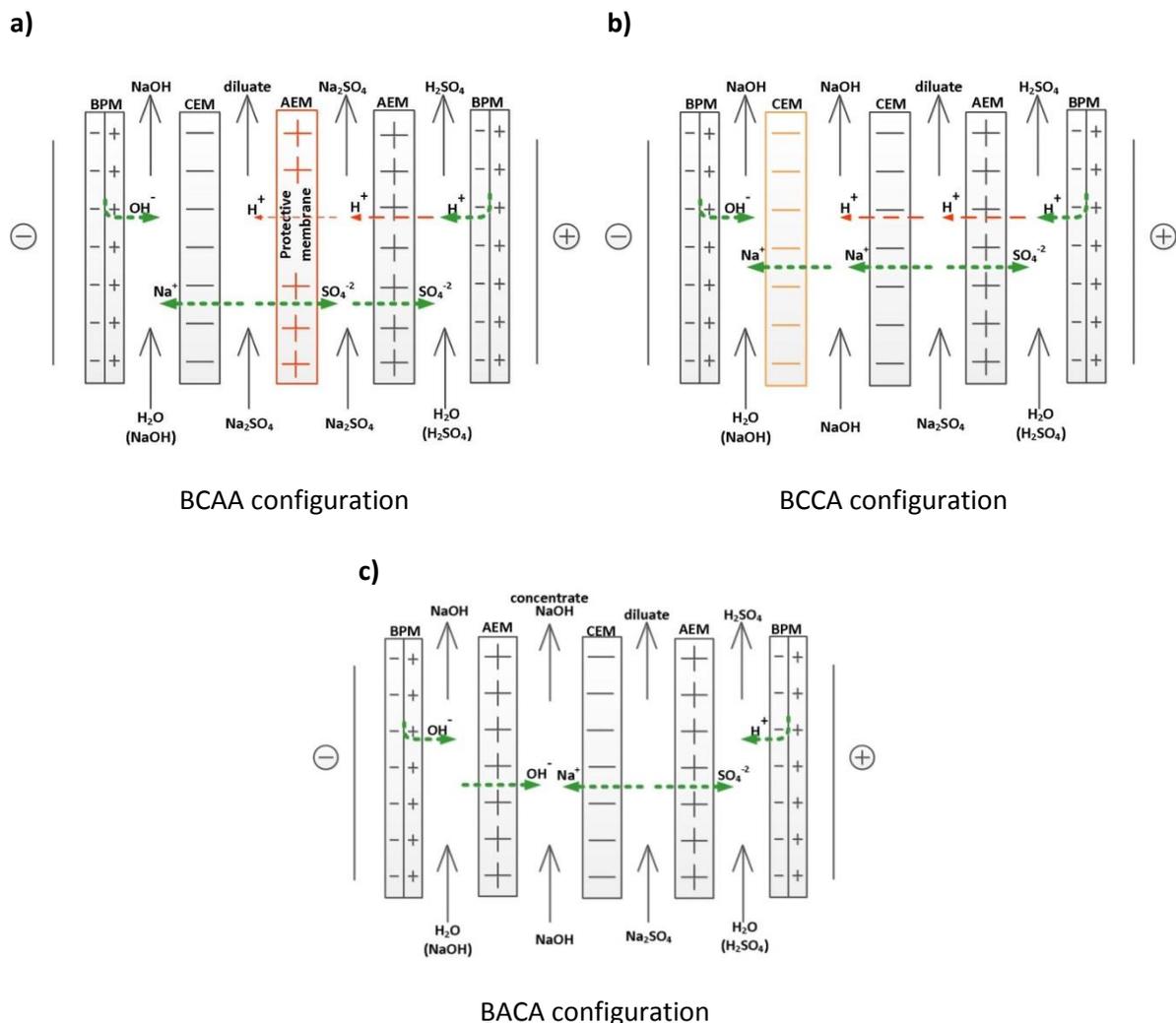


Fig. 2: Four compartment configuration of bipolar membrane electrodesialysis stack (AEM – anion exchange membrane, CEM – cation exchange membrane, BPM - bipolar membrane)

For implementation of classical electrodesialysis monopolar membrane configuration shown in Fig. 3 was used. Between the electrodes cation and anion exchange membranes were alternately placed, making a so called diluate and concentrate circuits. Into the diluate circuit solution to be treated was fed. Due to the electrical field ions started to migrate through membranes to the adjacent chambers in dependence on its charge and the type of ion exchange membrane. This migration caused that concentration in feed stream chambers decreased (diluate stream) and concentration in the neighboring chambers increased (concentrate stream).

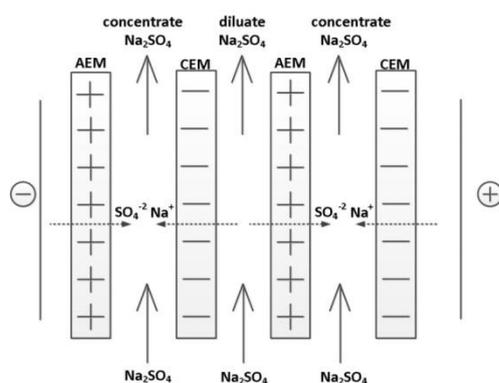


Fig. 3: Standard electrodesialysis with two compartment stack configuration (AEM – anion exchange membrane, CEM – cation exchange membrane)

The experiments were carried out in both batch and feed and bleed modes. The feed circuits were operated in the feed and bleed mode so that the concentration was kept to be constant during the experiment. Acid as well as base product circuits were operated in batch mode. At the beginning of each experiment circuits were filled with demi water and during the experiment concentrations of products were increased. Possible ancillary circuits in four-chambered arrangements were filled with aqueous solutions of the substances shown in Fig. 2. During the experiments operating parameters such as circulation velocity, temperature and current density were kept constant. Conductivity values and pH were also monitored.

Feed and products samples were collected and analyzed at regular time intervals. The volume of samples ranged from 5-15 ml. The concentrations of formed sulfuric acid and sodium hydroxide in the process streams were determined by conventional acid-base titration using a standard solution of 0.1M NaOH or 0.1M HCl. The automatic titrator TitroLine Alpha and TitroLine Alpha Plus (Schott, Germany) were used for these analyses. The total concentration of sulfate ions was determined by turbidimetry measurements of barium sulfate precipitates. Immediate concentrations in various process streams were also checked indirectly by measuring the electrical conductivity and the pH at a constant temperature using pH/Conductivity meter (432i WTW, Germany).

Results and discussion

The experimental results are summarized in graphs of time–concentration dependence which are shown in Figs 4 and 5.

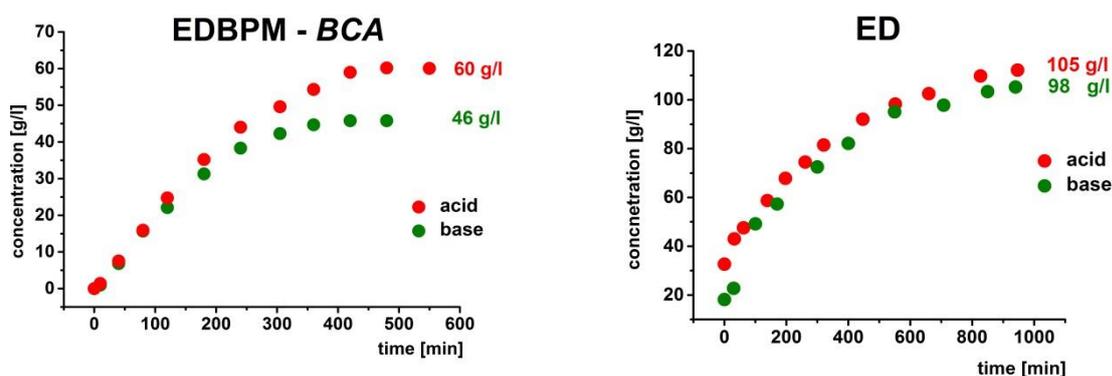


Fig. 4: Time – concentration dependences of produced sulfuric acid and sodium hydroxide in batch operation modes. Here BCA is the three compartment configuration with feed solution sodium sulfate (concentration $c = 35\text{g/l}$) and ED is standard electrodialysis with feed solution sulfuric acid (or sodium hydroxide), concentration $c = 25\text{g/l}$.

It can be seen from Fig. 4 that electrodialysis with the use of heterogeneous bipolar membrane in the three-chamber arrangement (EDBPM-BCA) gives the sulfuric acid at a maximum concentration of 60 g/l and sodium hydroxide at maximum concentration of 46 g/l. If the acid produced was subsequently subjected to classical electrodialysis (ED), the concentration of acid was increased up to twice the maximum concentration attainable in conventional three-chamber EDBPM (see also Fig. 4). Experimentally measured maximum concentration that is close to 100 g/l already meets the requirements on the concentration of agent appropriate for the regeneration of ion-exchange columns in the source technology. Other possible uses of these concentrated products are described and discussed in our previous paper (Kroupa et al., 2014). However it is necessary to mention, that this procedure brings extra operating costs related to the subsequent ED process. In addition, economy technology can also be strongly affected by high capital investment necessary to build additional ED unit.

Therefore, the experimental study was also focused on the four-chamber arrangements of EDBPM, which, owing to different number and arrangement of membranes in the stack, could produce acid and hydroxide of higher concentration and purity. Especially the investment costs of the technology could be significantly lower. In this work we have tested three modifications of the four chambers set up. The first two, i.e. BCAA and BCAA had introduced into the stack structure additional monopolar membrane

to create "protecting" barrier to unwanted transports, in particular of H^+ ions. The third test BACA variant was created as a combination of the three-compartment EDBPM and conventional ED. Comparison of the studied variants with regard to the maximum attainable concentration of both products is shown in Fig. 5. It is evident that the studied arrangements have a negligible effect on the maximum achievable concentration of the acid. However, more interesting trends can be observed in terms of maximum achievable concentration of NaOH.

One of the limitations to the maximum attainable hydroxide concentration lies in high permeability of AEM part of EDBPM to H^+ ions. These cations are very small and in view of their high mobility are able to pass easily through the membrane. Therefore, the AEM membranes in stack were doubled (BAAC arrangement) in order to increase the "resistance" to H^+ ions penetrating into the base circuit. As it can be seen from Fig. 5, the doubling of AEM had a positive, but not very pronounced effect on the increase of the maximum achievable concentration of hydroxide. The value of 50 g/l was reached.

BACC configuration was also aimed to limit the transport of H^+ ions into the hydroxide circuit through a chemical reaction between the penetrating H^+ ions and neutralizing OH^- ions. This was achieved by doubling the CEM and filling the space between the membranes with circulating sodium hydroxide, which was used as neutralizing agent. In this arrangement the maximum hydroxide concentration was increased to the value of 58 g/l. Unfortunately, even this increase is not sufficient to improve the usability of sodium hydroxide in the source GEAM technology. Finally, a great limitation of this set up constitutes the protection circuit of sodium hydroxide alone, in which gradual decline of hydroxide concentration was observed during the process. This would in practice mean that part of the produced hydroxide is used in the protective circuit thereby reducing the overall efficiency of the process.

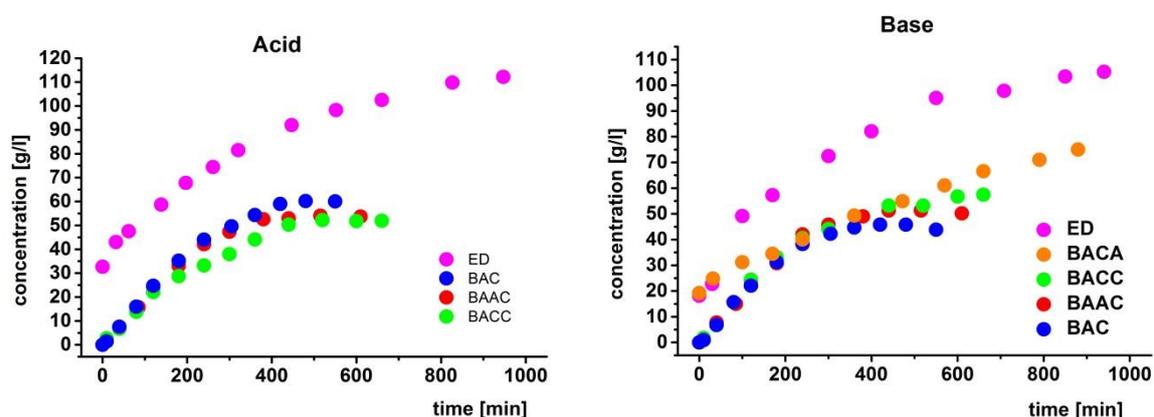


Fig. 5: Time – concentration graphs of produced sulfuric acid and sodium hydroxide in batch mode, BCA – three compartment configuration, feed solution sodium sulfate, concentration $c = 35\text{g/l}$. ED – standard electro dialysis, feed solution sulfuric acid (sodium hydroxide), concentration $c = 25\text{g/l}$. BACA, BACC, BAAC – four compartment configuration, feed solution sodium sulfate, concentration $c = 35\text{g/l}$.

Last configuration measured (BACA) was a combination of classic ED and EDBPM when additional AEM was inserted between BPM and CEM in a standard three-compartment set up. It created "pseudo" concentrate circuit, which is known from ED. It is necessary to mention that this configuration is applicable only to increase the sodium hydroxide concentration. The results show that in this case the highest concentration of hydroxide was achieved. Although during the experiment the concentration was not fully stabilized, it can be estimated that the maximum achievable concentration is probably in the range of 75 - 80 g/l.

Conclusions

In this work, we have investigated experimentally four methods potentially suitable for increasing the maximum achievable concentration of sulfuric acid and sodium hydroxide which are the products of decomposition of sodium sulfate through EDBPM. It was a standard electro dialysis of both acid and hydroxide obtained in the three compartments EDBPM and different configurations of the four-

compartments EDBPM set up. Four-compartment EDBPM arrangements had entirely negligible effect on the maximum achievable concentration of the acid. In contrast, the hydroxide concentration could be increased up to 80 g/l. When there is a request to increase the concentration of acid and hydroxide to a value of at least 100 g/l it is necessary to use classical electro dialysis for products obtained by EDBPM in the three compartment configuration.

Acknowledgment

This work was supported by project TAČR TH01031077 and University of Pardubice, project SGSFChT2015006.

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