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Recovery of H_2SO_4 and NaOH from Na_2SO_4 by electrodialysis with heterogeneous bipolar membrane

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ABSTRACT

Electrodialysis (ED) with heterogeneous bipolar membranes (BPMs) was studied experimentally on a laboratory scale in order to examine the recovery of the sodium sulfate solution into sulfuric acid and sodium hydroxide. The capacity of the system was evaluated in terms of its dependence on membrane configuration, product concentration, temperature, and circulation flow rate. A preliminary economic evaluation of ED with a heterogeneous BPM in a uranium ore mining wastewater treatment plant was also carried out. This process is primarily used in cases where the purity of the sulfuric acid and sodium hydroxide recycled does not play a significant role and the high costs of the homogeneous BPMs negatively affect the economy.

Keywords: Electrodialysis; Bipolar membrane; Heterogeneous membrane; Sulfuric acid; Sodium hydroxide; Recovery

1. Introduction

Sodium sulfate is the second most common naturally occurring saline salt. Vast quantities of sodium sulfate are used in powdered detergents as filler, partially replacing phosphates due to their lower impact on environment. In the textile industry, sodium sulfate is used for dyeing of wool and cotton as a leveling agent. Indeed, when used this way it reduces negative charges on the fibers, thus allowing the dyes to penetrate equally. Sodium sulfate is an important component when it comes to the manufacturing of wood pulp, which is widely used to make paper products. It is also used in glass production, and has a variety of other applications [1].

Sulfate wastewater does not pose a direct threat to the environment, as sulfate is a chemically inert, nonvolatile, and nontoxic compound [2]. However, in many countries, there are restrictions on the amount of sulfate which can be discharged into a sewer, as large amounts will result in the formation of sulfate–aluminum complexes which swell and crack concrete

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made from certain types of cement. Aside from this, biological treatment of sulfate-rich wastewater is rather unpopular because of the production of H_2S under anaerobic conditions. Generally speaking, high sulfate concentrations in wastewater can cause an imbalance in the natural sulfur cycle [3].

In addition to the processes mentioned above, the processing of uranium ore is another source of sulfate wastewater [4]. This technology generally consists of crushing and grinding the extracted ores, followed by a leaching circuit combined with chemical processing. Uranium is then removed from leach liquor and concentrated using solvent extraction or ion exchange techniques before being precipitated to form "yellowcake" [5]. The first step in the uranium leaching operation is the oxidation of uranium constituents. The second step involves the stabilization of the uraniferous ions in a solution containing stable, soluble complexes with sulfate (SO_4^{2-}) or carbonate (CO_3^{2-}). Sulfuric acid is added as the source for sulfate ions in acid leaching. Sodium bicarbonate, sodium carbonate, or carbon dioxide are added to alkaline leach circuits to provide a carbonate source. In a typical acid leaching operation, 20–60 kg of sulfuric acid are added per metric ton of ore in order to keep the pH between 0.5 and 2.0 [5]. A large amount of sodium sulfate wastewater is also produced during the chemical beneficiation of uranium ore. This is mainly due to the fact that uranium ore contain pyrites are oxidized to sulfates. The mineralized wastewater is commonly pumped into a waste retention system and extra wastewater from the system is treated by filtration, electrodialysis (ED), reverse osmosis, and/or evaporation followed by crystallization of sodium sulfate [6,7]. Under normal operating procedures, solutions are recycled to the greatest extent, which are possible to conserve water, chemicals, and uranium. The combination of these techniques also makes it possible to produce crystalline sodium sulfate, which can be used in many other applications.

The combination of conventional ED and water splitting by bipolar membrane (BPM) presents a new ecological method used for the recovery of acids and hydroxides from corresponding salts [1]. By using electrodialysis with bipolar membrane (EDBM) process, sulfuric acid and sodium hydroxide can be obtained from extra sulfate wastewater and, consequently, reused in the technology employed during uranium leaching. The efficiency of the reuse of sulfuric acid and sodium hydroxide is dependent on their intended reuse location in the leaching technology with various input concentration requirements.

The BPM is composed of three parts, namely a cation-exchange layer, an anion-exchange layer, and a hydrophilic interface at their junction. Due to this combination of ion exchange layers, the BPM allows for the dissociation of water in the presence of an electrical field. Generated hydrogen and hydroxyl ions make it possible to obtain acid and base from the salt. The process design is closely related to that of the conventional ED using the sheet flow stack concept. However, because of the significantly higher voltage drop across a cell unit, only up to several dozen repeating cell units are placed between two electrodes in a stack [8]. The requirements for a BPM in practical applications are good water diffusivity to provide water from the external solutions to the interface, low electrical resistance at high current density, high water dissociation rate, low co-ion transport rate, high ion-selectivity, and good chemical and thermal stability in strong acids and alkalis [9]. 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 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 [10]. This allows them to 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 setup with heterogeneous membranes allowing for gentle operating conditions which reduce membrane fouling and increase useful membrane life.

Since the emergence of BPMs are readily available as commercial products, a large number of applications have been studied on a laboratory or pilot plant scale [11–13]. However, large-scale industrial plants remain relatively rare [10]. 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.

In this contribution, the EDBM process with heterogeneous membrane produced by MemBrain (Czech Republic) was studied experimentally on a laboratory scale in order to examine the recovery of the sodium sulfate solution into sulfuric acid and sodium hydroxide. Initial analysis of EDBM application in the uranium ore mining wastewater treatment plant was also carried out to identify potential process integration advantages and problems.

2. Materials and methods

2.1. Membranes and wastewaters

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 12-01-P (MemBrain, Czech Republic). Experiments were performed using either model wastewater containing sodium sulfate at a concentration of 35 g/l or the sulfate wastewater supplied by GEAM–Dolní Rožínka (Czech Republic). The model sulfate solutions were prepared from analytical reagent grade powder received from Sigma-Aldrich Chemicals and deionised water. The composition of the process, wastewater, is provided in Table 1.

2.2. Experimental procedure and analytical methods

The laboratory scale unit of type P EDR-Z/10-0.8 from MemBrain (Czech Republic) with two different configurations of EDBM stack was used for laboratory experiments. The effective transfer area of each membrane was 0.0064 m^2. The individual compartments were separated by 0.8 mm thick polyethylene spacers. Five pairs of ion exchange membranes and spacers were arranged between a platinum-coated titanium anode and a cathode which were connected to a DC voltage source (Statron 2229, Germany). The sodium sulfate solution (3.5 wt%) was used as the electrolyte rinsing solution for both electrode compartments. The unit was equipped with instruments for monitoring flow rates, temperature, conductivity, pH, and voltage.

The configurations investigated are depicted in Fig. 1. The two compartment configuration, which is shown in Fig. 1(a), consists of CEM and BPM. The sodium sulfate solution was fed to the acid/salt chamber between CEM and the anion side of BPM. Fig. 1(b) shows the three compartment configuration which consists of BPM, CEM, and AEM. The sodium sulfate solution was fed to the salt chamber between CEM and AEM.

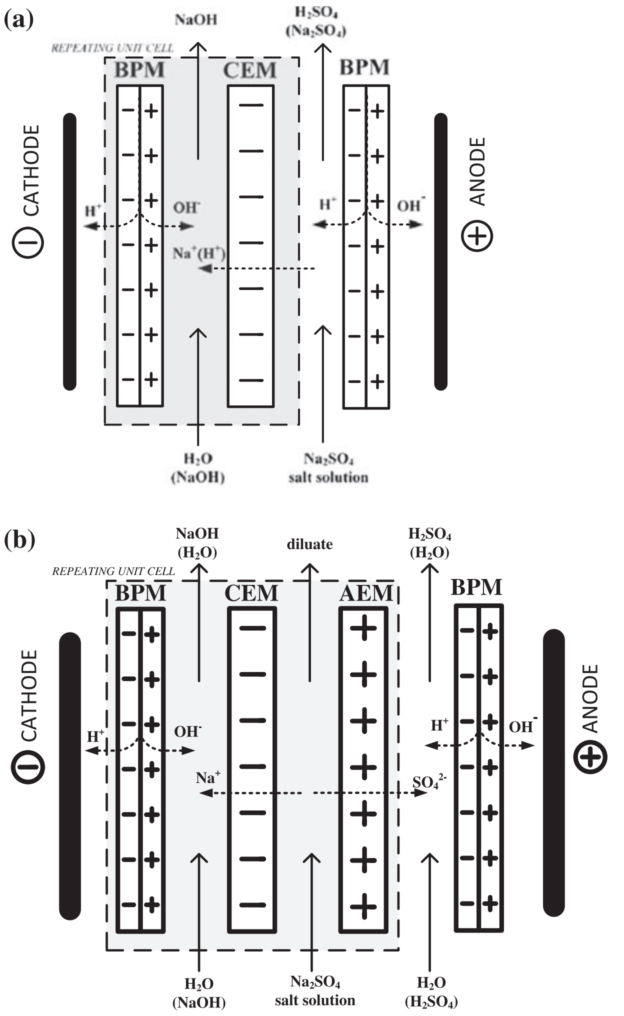

Fig. 1. Schematic representation of ED with BPM (a) two-compartment and (b) three-compartment setup. (BPM—bipolar membrane, AEM—anion-exchange membrane, CEM—cation-exchange membrane.)

All experiments were carried out in feed and bleed mode as shown in Fig. 2. Electrode rinse solution, feed salt, and both acid and hydroxide solutions with known initial concentration were introduced into transparent scaled recirculation reservoirs. Solutions were circulated through the EDBM stack using magnetic pumps (Pan World NH-30PX-D, Japan). Demi water was added continuously to acid and base streams in order to maintain a constant concentration during the experiment. The decrease in sodium sulfate concentration in the feed stream was balanced by additions of sodium sulfate from concentrated (75 g/l) stock solution. Conductivity measurements were

Table 1
Basic components contained in wastewater from GEAM-Dolní Rožínka

Constituent	Value	Unit
pH	3.54	(–)
NO_3^-	742	mg/l
$NH_3 + NH_4^+$	878	mg/l
SO_4^{2-}	23.500	mg/l
Ca^{2+}	3.10	mg/l
Mg^{2+}	3.20	mg/l
Na^+	20 800	mg/l

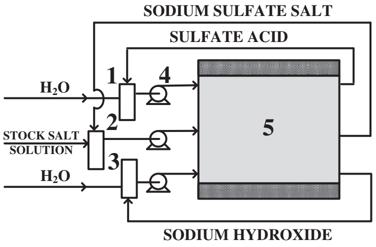

Fig. 2. Schematic diagram of the feed and bleed EBDM experimental setup (1: sulfuric acid reservoir, 2: sodium sulfate reservoir, 3: sodium hydroxide reservoir, 4: magnetic centrifugal pumps, and 5: membrane ED module).

applied in order to evaluate instantaneous concentrations of the process streams. Practically, all experiments, operation close to steady state were achieved. At the end of the experimental run, all solutions in each compartment were drained and weighed. In addition to this, the final composition of all streams was determined. Sulfuric acids solutions with different concentrations ranging from 34 to 44 g/l sodium hydroxide and 36 to 45 g/l as well as a feed sodium sulfate solution of 35 g/l were used.

Sulfuric acid and sodium hydroxide were titrated classically with a titrator (TitroLine Alpha TZ 2825, Germany). The total concentration of sulfate ions was determined either using the photometrical method with a standard test kit (WTW 14548 Sulfate) or via titration with dithiazone as an indicator and with $Pb(NO_3)_2$ as a titrant. The instantaneous concentrations of process streams were indirectly verified through the measurement of their electrical conductivity and pH with a pH/conductivity meter (WTW 432i, Germany).

3. Results and discussion

3.1. *Effect of cell configuration on concentration and purity of acid and hydroxide produced*

An important parameter in EDBM is the maximum achievable concentration of produced acid and hydroxide. The result depends primarily on the performance of the individual membranes in the stack. In addition to the limitations of BPM, the selection of AEM for a given application is the most important. This is due to their inferior permselectivity and chemical stability in comparison with CEM [14]. The objective of the preliminary experiments was to find the most effective configuration which can be operated with salt concentrations close to the real wastewater and generate relatively pure high concentrated sulfuric acid and sodium hydroxide. A two-compartment cell arrangement and the standard three-compartment cell configurations were tested under the same experimental conditions.

Fig. 3 shows acid and hydroxide concentrations vs. time in both tested configurations. The trend of concentration curves is asymptotic to values corresponding to the highest concentration reached at these conditions. The final concentrations for two-compartment configuration were achieved faster, although for both products lower values of final concentration were obtained. In both configurations, higher concentration was achieved for hydroxide than for acid.

The results confirm that two-compartment cell arrangement is appropriate for converting sodium sulfate into a mixed acid/salt stream and a relatively pure, but low, concentrated sodium hydroxide product. As can be seen in Fig. 1(a) in the two-compartment cation cell, both Na^+ and H^+ ions can be transported through the cation membrane. However, only transport of Na^+ ions results in the formation of sodium hydroxide; H^+ ions which migrate through CEM recombine with OH^- in the base chamber and reduce the current utilization.

In the three-compartment configuration (Fig. 3), the acid as well as hydroxide were obtained with more than two times higher concentration compared to the two-compartment system. The results indicate that the maximum concentrations are primarily determined by the properties of the AEM which has limited retention for protons due to the tunneling mechanism of the proton transport. Similarly, but to a lesser extent, the hydroxide ions at higher concentration can permeate through the CEM. The net result is that H^+ and OH^- ions generated in the BPM neutralize each other in the feed compartment. Thus,

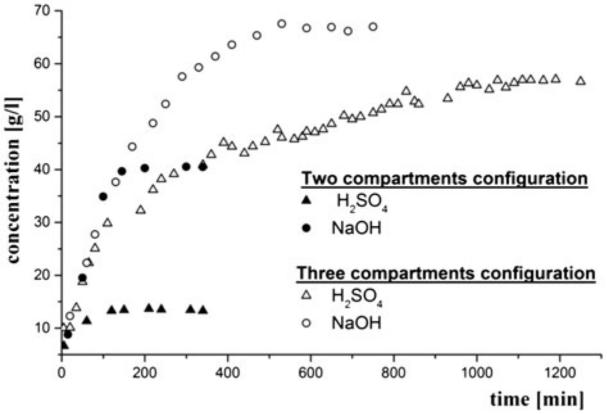

Fig. 3. Effect of cell configuration on produced acid and base concentration (i = 300 A/m^2, T = 24.5°C, and u = 5.2 × 10^{-2} m/s).

at high acid and base concentrations, the current utilization can reach uneconomically low values (see also Fig. 5).

The sodium and sulfate ions in the acid and hydroxide streams form impurities in the products. The experimental results for the three compartment EDBM cell showed that the purity of produced acid ranged between 71.9 and 83.3%, and that the purity of produced hydroxide was higher and varied between 97.0 and 98.3% for the same model feed solutions tested. The main explanation for these patterns relates to the undesired transport of Na^+ and SO_4^{2-} ions through the BPM at high concentrations due to the incomplete permselectivities of the BPM's ion exchange layers [15]. The flux of sulfate anions into the hydroxide stream was lower than the flux of smaller sodium cations into the acid.

3.2. *Effect of process parameters on specific energy consumption*

The energy efficiency of the EDBM stack can be determined in terms of specific energy consumption *E*, which describes the energy needed for the recovery of unit mass of sodium sulfate from the feed solution. In addition to energy consumed by the water splitting operation, there are also ohmic resistances which must be overcome. These resistances are associated with the transport of ions in the acid, salt, and hydroxide solutions and through the cation, anion, and BPMs. For the voltage drop U across the EDBM stack and the time averaged electrical current I, the total specific energy consumption can be expressed as [16]:

$$E = \frac{U \cdot I \cdot t}{m_s} \qquad (1)$$

where m_s represents the total mass of sodium sulfate salt which was removed from the feed compartment during the operational time t.

In order to investigate the effect of temperature, the experiments were performed in the three compartment cell at three different temperatures (17, 25, and 31℃).

As can be seen from Fig. 4(a), the lowest power consumption (1.3 kWh/kg Na_2SO_4) was obtained for the highest temperature in comparison with significantly higher power consumption (3 kWh/kg Na_2SO_4) at the lowest temperature. This indicated that the mobility of ions, which increases with temperature probably, has a dominant effect on the decrease in the membrane's stack resistance.

Fig. 4(b) illustrates the influence of the process stream hydrodynamics on the specific energy consumption. The results showed that the energy

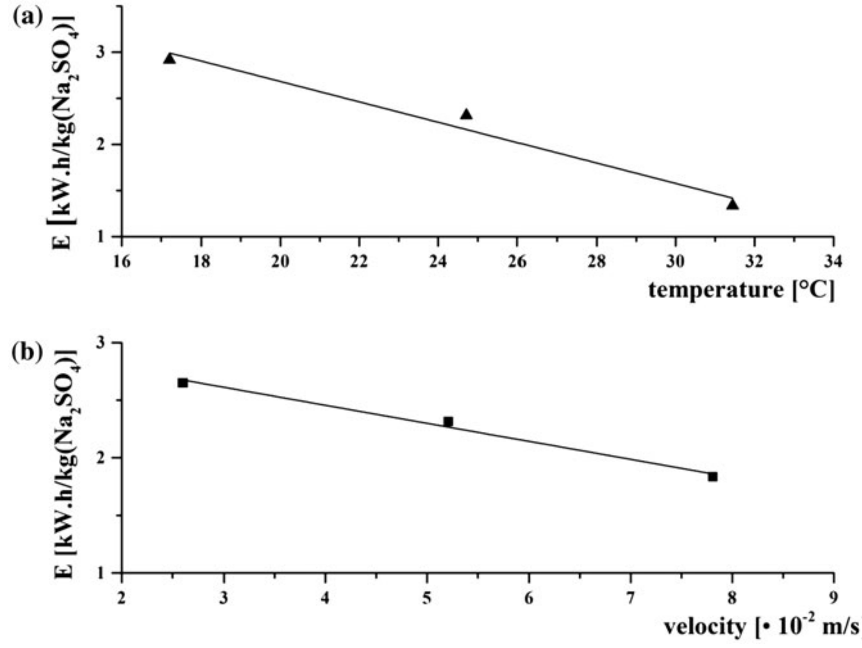

Fig. 4. Effect of EDBM operation conditions on specific energy consumption (a) (i = 300 A/m^2, and u = 5.2 × 10^{-2} m/s, $c_{H_2SO_4}$ = 37 g/l, c_{NaOH} = 40 g/l) and (b) (i = 300 A/m^2, T = 25℃, $c_{H_2SO_4}$= 36.1 g/l, c_{NaOH} = 40.1 g/l).

consumption decreased with an increase in circulation velocity. This can be explained by the fact that the faster flow creates the dynamic forces and turbulence which prevents concentration polarization formation in the stack [17]. It should also be noted that the power consumption detailed in Eq. (1) does not include the energy required to pump the circulating solutions through the cell. In EDBM, the energy consumption due to the pumping of the solutions through the stack can often be neglected. Nevertheless, in certain cases, the energy requirements for circulating the solution through the cell may become a significant portion of the total energy consumption. The pressure drop in the various cells is then determined by the stream flow velocities and the cell design.

Fig. 5 shows the effect of acid and hydroxide concentration on energy consumption. Results revealed that energy consumption increased with rising concentration of acid across the entire range of concentrations measured. However, the dependence of the specific energy consumption on the hydroxide concentration had the opposite trend for low and high concentrated acid solutions. This was due to the fact that it is more energy efficient when it comes to the simultaneous production of high concentrated hydroxide and low concentrated acid.

3.3. Integration of EDBM into uranium ore wastewater treatment technology

The possible upgrade of a typical uranium ore mining wastewater treatment plant is shown in Fig. 6 (based on the system used in GEAM Dolní Rožínka, Czech Republic). The volume of treated wastewater is approximately 450,000 m^3/year.

Fig. 7 shows the average consumption of sulfuric acid and sodium hydroxide to treat 1 m^3 of wastewater by the processes of evaporation and membrane alone or by a combination of both processes in the present wastewater treatment plant.

It can be seen that for the most advanced process, i.e. the combination of evaporation and standard membrane separation, the average annual sulfuric acid consumption is approximately 1.125 t and sodium hydroxide consumption is around 110 t/year. This means that both products of EDBM have high potential for reuse in the current water treatment process. Thus, a process is proposed which uses the concentrate from ED containing Na_2SO_4 (see Table 1) for conversion to acid and hydroxide via the three compartment EDBM cell. Here, the dashed arrows illustrate some options, where the sulfuric acid and sodium hydroxide can be reintroduced to the process. An acid stream can be directed to the

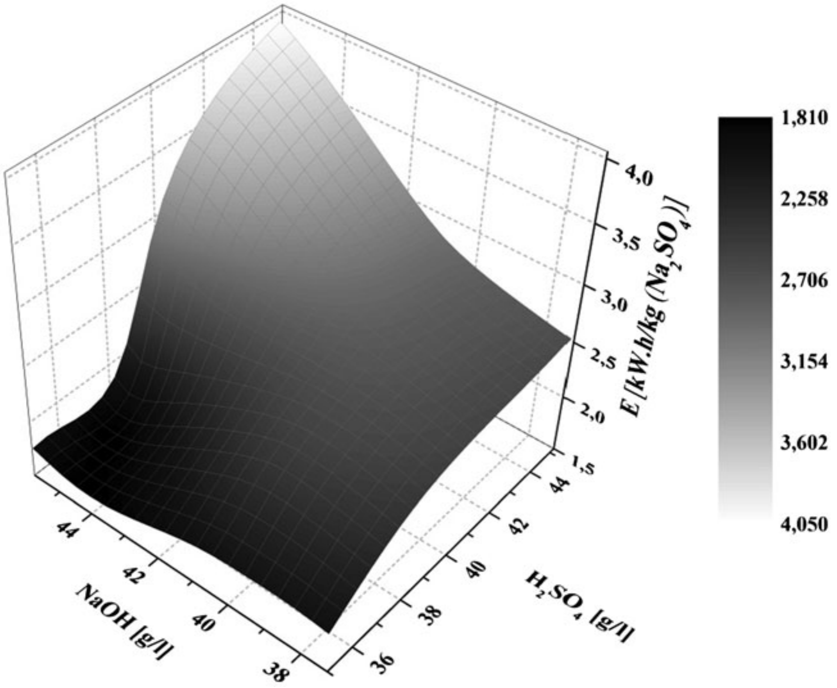

Fig. 5. Effect of acid and base concentration on specific energy consumption E ($i = 300$ A/m^2, $u = 5.2 \times 10^{-2}$ m/s, and $T = 25$°C).

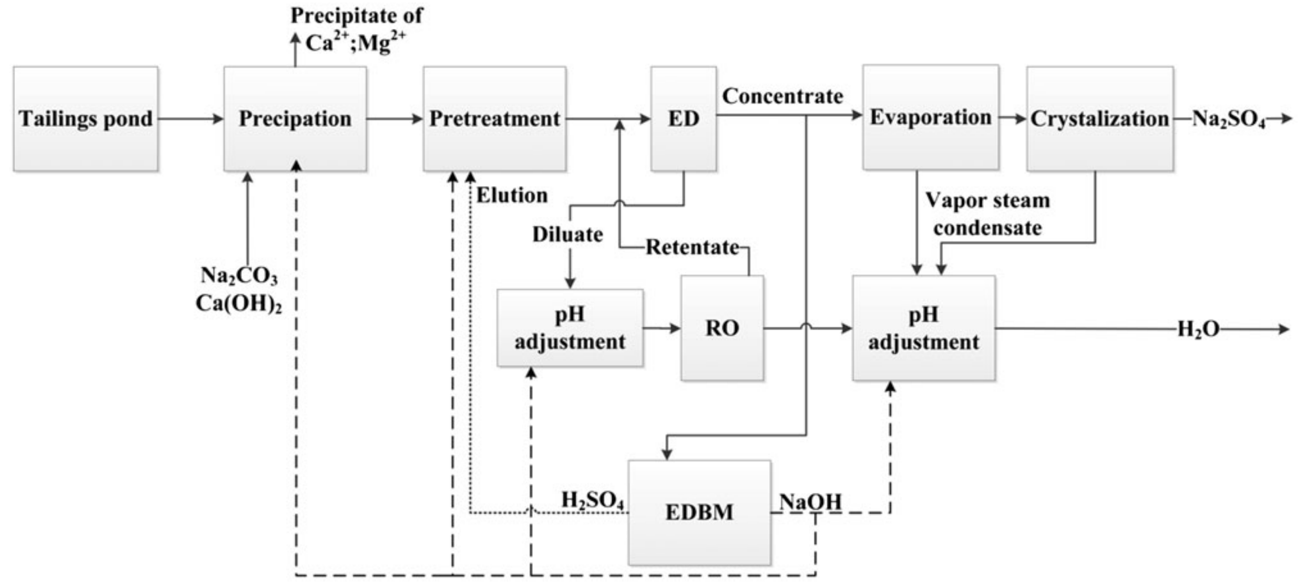

Fig. 6. Flow sheet of uranium ore mining wastewater treatment plant equipped with EDBM (ED—electrodialysis, RO—reverse osmosis, EDBM—electrodialysis with BPM).

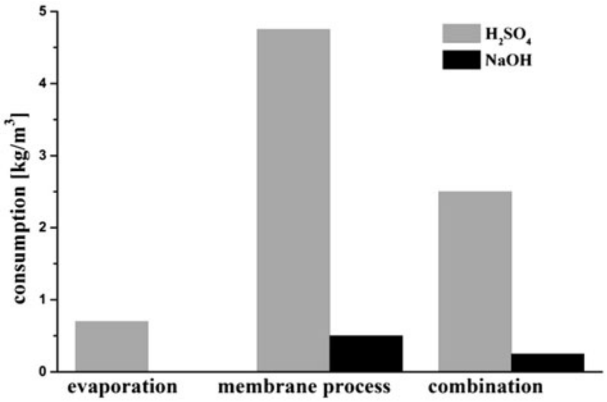

Fig. 7. Average consumption of sulfuric acid and sodium hydroxide to treat 1 m^3 of wastewater in GEAM Rožínka.

pretreatment step and a NaOH stream produced is ready for use in the precipitation, pretreatment, and pH adjustment steps. Sulfuric acid can also be used in regeneration of the ion exchange columns whereby pH sensitive Lewatite is used to remove certain heavy metals. However, in this application the acid must be relatively pure. The presence of contaminants should be kept low (50–500 ppm) in order to ensure efficient total regeneration of the columns. Nevertheless, two-stage regeneration, first with process stream outputs and, consequently, with diluted pure grade substances can also be effectively used.

Another option is the use of sodium hydroxide produced for regeneration of the Lewatite ion exchange resin in the pretreatment part of the uranium ore beneficiation process. Here, the hydroxide concentration needed is approximately 5%. This concentration is close to the maximal experimentally obtained value. Low concentrated sulfuric acid and sodium hydroxide can also be used for the treatment of reverse osmosis membrane.

3.4. Preliminary economic evaluation

The total costs in EDBM are the sum of fixed costs associated with the amortization of the plant capital costs and the plant operating costs. The energy required in an ED process is an additive of several terms: the electrical energy needed for the water dissociation in the BPM, energy to transfer the ionic components from one solution through the membranes into another solution, the energy required to pump the solutions through the EDBM unit, the energy consumption due to electrode reactions, and operating the process control devices. The last three can often be neglected in large industrial size plants. The membrane stack related investment costs dominate the total investment costs.

Obtained experimental dependences regarding EDBM capacity, specific current efficiency, DC energy consumption, AC energy consumption on temperature, flow rate, concentration of H_2SO_4 in the product,

Table 2
Unit prices used for operation costs estimation

Quantity	Unit	Value
Energy	€/kWh	0.073
Water	€/m^3	1.82
H_2SO_4 98%	€/kg	0.152
NaOH 99%	€/kg	0.304

and concentration of NaOH in the product were used to estimate optimal parameters of the EDBM process. Energy consumption scenarios included temperature control by additional heating. Optimum levels were found for the lowest temperature used (17.2°C), standard linear velocity (5 cm/s), maximal concentration of acid in the product (4.44%), and average concentration of the hydroxide in the product (4.00%). The fact that optimum performance was found at the lowest temperature means that there is no chance of heating due to high heating costs; ED must work without additional heating. Operation costs for optimal process parameters were estimated using unit prices which are provided in Table 2. The operation cost of treating 94,470 tones of Na_2SO_4 solution per year was estimated to be 390,435 €, while income from NaOH and H_2SO_4 produced was 548,662 €, making an annual profit of 158,227 € which can be used for technology repayment first and for gross profit generation afterwards. Economically, optimal parameters of technology can change according to the requirement of the product (NaOH and H_2SO_4) and depend on its placement in the technological process.

4. Conclusions

The effect of certain operating parameters, such as membrane configuration in stack, flow rate, temperature or acid, and hydroxide concentration were investigated in order to verify the feasibility of ED with heterogeneous BPM for the recovery of sodium sulfate to sulfuric acid and sodium hydroxide.

The results of this study indicate that an EDBM with a heterogeneous membrane performs best when operating in a three-compartment configuration. The permselectivity of the BPM was the key determinant of product purity, while the monopolar membrane selectivities determined the maximum attainable product concentrations. In the range of tested concentrations, the most energy efficient was the simultaneous production of high concentrated hydroxide and low concentrated acid. The increasing of acid concentration caused a rapid increase in specific energy consumption. Variations of temperature and flow rate had the opposite effect and the specific energy consumption was also decreased with increasing temperature and flow rate.

A preliminary economics investigation showed that the EDBM process for NaOH and H_2SO_4 production from uranium production wastewater is profitable. The process should and can be primarily used in cases where the purity of the sulfuric acid and sodium hydroxide does not play a significant role and the high costs of the homogeneous BPMs affect the economy of the process. In any case, the process offers an interesting alternative to supply H^+ or OH^- ions *in situ* and does not involve the introduction of any extra chemicals.

Acknowledgments

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Symbols

AC	—	alternating current
AEM	—	anion-exchange membrane
BPM	—	bipolar membrane
CEM	—	cation-exchange membrane
DC	—	direct current
E	—	specific energy consumption
ED	—	electrodialysis
EDBM	—	electrodialysis with bipolar membrane
i	—	current density
I	—	averaged electrical current
m_s	—	mass of salt
RO	—	reverse osmosis
t	—	time
T	—	temperature
u	—	average velocity
U	—	voltage drop across the stack

References

[1] D.E. Garrett, Sodium Sulfate Handbook of Deposits, Processing, Properties and Use, Academic Press, San Diego, CA, 2001.
[2] H.S. Shin, J.Y. Jung, B.U. Bae, B.C. Paik, Phase-separated anaerobic toxicity assays for sulfate and sulfide, Water Environ. Res. 67 (1995) 802–806.
[3] C. Namasivayam, M.V. Sureshkumar, Removal of sulfate from water and wastewater by surfactant modified coir pith, an agricultural solid 'waste' by adsorption methology, J. Environ. Eng. Manage. 17 (2007) 129–135.

[4] S. Tait, W.P. Clarke, J. Keller, D.J. Batstone, Removal of sulfate from high-strength wastewater by crystallisation, Water Res. 43 (2009) 762–772.

[5] A. Costine, A.N. Nikoloski, M. Costa, K.F. Chong, R. Hackl, Uranium extraction from a pure natural brannerite mineral by acidic ferric sulphate leaching, Miner. Eng. 53 (2013) 84–90.

[6] K. Thomas, Management of wastes from uranium mines and mills, Int. At. Energy Agency Bull. 23 (1981) 33–35.

[7] R. Mujeriego, T. Asano, The role of advanced treatment in wastewater reclamation and reuse, Water Sci. Technol. 40 (1999) 1–9.

[8] T. Franken, Bipolar membrane technology and its applications, Membr. Technol. 2000 (2000) 8–11.

[9] C. Huang, T. Xu, Electrodialysis with bipolar membranes for sustainable development, Environ. Sci. Technol. 40 (2006) 5233–5243.

[10] V. Zabolotskii, N. Sheldeshov, S. Melnikov, Heterogeneous bipolar membranes and their application in electrodialysis, Desalination 342 (2014) 183–203.

[11] C. Jiang, Y. Wang, T. Xu, An excellent method to produce morpholine by bipolar membrane electrodialysis, Sep. Purif. Technol. 115 (2013) 100–106.

[12] Y. Zhang, Y. Chen, M. Yue, W. Ji, Recovery of L-lysine from L-lysine monohydrochloride by ion substitution using ion-exchange membrane, Desalination 271 (2011) 163–168.

[13] I. Zaslavschi, H. Shemer, D. Hasson, R. Semiat, Electrochemical $CaCO_3$ scale removal with a bipolar membrane system, J. Membr. Sci. 445 (2013) 88–95.

[14] T. Sata, T. Sata, W. Yang, Studies on cation-exchange membranes having permselectivity between cations in electrodialysis, J. Membr. Sci. 206 (2002) 31–60.

[15] F.G. Wilhelm, I. Pünt, N.F.A vanderVegt, M. Wessling, H. Strathmann, Optimisation strategies for the preparation of bipolar membranes with reduced salt ion leakage in acid–base electrodialysis, J. Membr. Sci. 182 (2001) 13–28.

[16] M.A. Masigol, A. Moheb, A. Mehrabani-Zeinabad, An experimental investigation into batch electrodialysis process for removal of sodium sulfate from magnesium stearate aqueous slurry, Desalination 300 (2012) 12–18.

[17] J.J. Krol, M. Wessling, H. Strathmann, Concentration polarization with monopolar ion exchange membranes: Current–voltage curves and water dissociation, J. Membr. Sci. 162 (1999) 145–154.