Electromembrane Processes in Mine Water Treatment

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Abstract Electrodialysis and bipolar electrodialysis were used in two case studies with uranium mine waste water:
1. Electrodialysis increases Na2SO4 concentration before evaporator
2. Bipolar electrodialysis produces 1.5 % H2SO4 and 4 % NaOH for local reuse
New pilot and industrial units were designed and constructed with 1 m2 and 33.3 m2 of membrane surface, respectively. While the pilot module was operated for 11 months since March 2016, the industrial module has been in operation since March 2017. With the electricity consumption was 2.0 kW per kg of recycled Na2SO4, the operating cost now approximates the value of recycled chemicals.

Key words bipolar electrodialysis, uranium mine water, sodium sulphate

Introduction

ED has proved to be a good and economical choice for the treatment of waste waters polluted by inorganic salts. It has been successfully applied for recirculation of valuable products from waste waters containing quite pure salts, such as electroplating baths or fertilizers, as well as for recycling of industrial water, e.g. pulping process, acid pickling, or cooling tower blowdown (Koltuniewicz 2008). EDBM uses a unique type of ion exchange membrane by which acids and hydroxides can be produced from their respective salts (Strathmann 2004).

Application in mining industry, such as tailing pond overbalance, landfill leachate, or mine water treatment present further opportunities for the application of electromembrane processes. Large amounts of water containing high salt concentration are often treated by evaporator (EV) and crystallization, and the produced crystalline solids are marketed. Application of ED for salt concentration is a feasible way of decreasing the large operation costs for EV, given its significant power consumption. Moreover, EDBM presents an option how to recycle and reuse the original chemicals, leading not only to decreasing the cost of their purchase, but also lowering the final waste water volume.

Theory

In a direct current electric field bipolar membranes (BPM) allow for splitting of water molecules. In order to form an acid or a base, also monopolar anion exchange (AEM) and cation exchange (CEM) membranes are employed, carrying out a separation of cations and anions from the feed solution in a traditional ED process.

A cell system (fig 1) consists of AEM, BPM and CEM membranes as a repeating unit. The feed solution flows between the CEM and AEM. Water will dissociate in BPM to form equivalent amounts of H^+ and OH^- ions. The H^+ ions permeate through the cation-exchange side of the BPM and form H2SO4 with the sulphate ions provided by the sodium sulphate solution from the adjacent cell. The OH^- ions permeate the anion-exchange side of the BPM and form NaOH with the sodium ions permeating into the cell from the salt solution through adjacent CEM. The final result is the production of NaOH and H2SO4 at a significantly lower cost than by other methods

This three-circuit arrangement was found to be the most suitable for this particular application (Kroupa 2015). Other arrangements were tested as well, but none proved to be significantly better in overall performance to warrant its use. In these tests, the maximum achievable concentration was about 5 % wt. for both products. Above these concentrations, product purity and electric current efficiency would drop significantly, due to excessive water dissociation and transport of undesired ions.

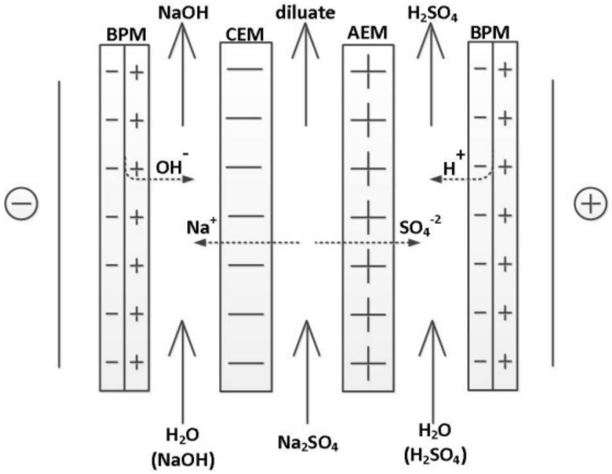

Figure 1 *Principle of EDBM in a three circuit arrangement (Kroll 1997).*

Case study 1 – Tailing pond of uranium mill, 65 m3/h, Czech Republic, 2007

Water coming from a tailing pond of uranium production is cleaned by a combined membrane technology based on ED and RO with proper pre-treatment. The final technology was designed based on 6200 hours of pilot testing.

Pilot testing

To obtain reliable data for scale up, a complete pilot technology was installed on site, including chemical pre-treatment, ED and RO (Černín 2007). Three sources were fed into the technology: sludge bed water, drainage water and their 2:1 mixture. Process data were logged three times a day, including the analysis of sulphates and total organic carbon.

Pre-treatment process had to be enchased as AEMs were losing their long term electric properties. Sulphonated polystyrene structures were found to be the major pollutant, causing membrane fouling and consequent membrane poisoning. Concentration of these compounds was decreased by oxidation and adsorption on active carbon.

Industrial technology

Industrial technology (fig 2) consist of precipitation of calcium and magnesium by lime and soda ash, sedimentation, sand filtration, sorption of heavy metals and uranium in ion exchange columns, oxidation, sorption of oxidation products on active carbon and acidification by sulphuric acid. 65 m^3/h of pretreated water with total dissolved solids (TDS) 35 g/L is partially desalted by ED to 12 g/L. ED diluate is further desalted by RO reaching TDS of 0.18 g/L and discharged into the local river, while meeting the effluent restrictions. RO retentate is mixed with the ED feed. The final step of current technology is the concentration of ED concentrate having TDS of about 110 g/L by EV, preceding the sodium sulphate crystallization.

Figure 2 *ED (left) and RO (right) in the GEAM plant (Toman 2009).*

Technological parameters of the installed technology were compared with the previous technology based on EV only (tab 1). Electric energy consumption is about the same for the combined process as for EV alone due to large consumption of EV caused by circulation pumps. Large heat consumption of EV is reduced by 37% because of increase of EV feed concentration by upstream ED + RO. Water recovery was slightly increased too. The only drawback of membrane processes is their chemical consumption, but comparison to the huge saving on heat, the costs of common chemicals are almost negligible.

Table 1 *Technological comparison of EV and the combined process (Toman 2009).*

Parameter	EV	ED + RO + EV
El. energy consumption (kWh/m^3)	26.02	25.22
Heat consumption (GJ/m^3)	0.62	0.39
Clean water recovery (%)	77	80
H_2SO_4 consumption (kg/m^3)	0.663	2.51
NaOH consumption (kg/m^3)	0	0.2

The latest technology, based on modern ED modules EDR-II/200-0.8 (MEGA a.s., Czech republic), has been in operation since 2007 without any difficulties. ED and RO membranes are cleaned chemically three times per year. Less than 1% of ED membranes were replaced so far. The first RO membranes lasted in the technology for 6 years. The customer now treats up to 440,000.0 m^3/year of waste water.

Case study 2 – Application of EDBM for recycling of sulphuric acid and sodium hydroxide, Czech Republic, 2016 -- now

As the market demand for crystalline sodium sulphate is low, new technologies are being investigated. EDBM was chosen as both products can be reused on site. About 7 % of total sodium sulphate contained in the waste water is processed (fig 3).

Development of EDBM components

Bipolar membranes

Easier production is the major developmental step in the third version of heterogeneous membrane Ralex® BM-3.0. Previous heterogeneous BPM Ralex® was hot-pressed to form necessary internal microstructure (Neděla 2015). Ralex® BM-3.0 is produced by simple co-extrusion of two layers and its capacity, energy consumption, selectivity, chemical and mechanical stability remains the same as for hot-pressed BPM.

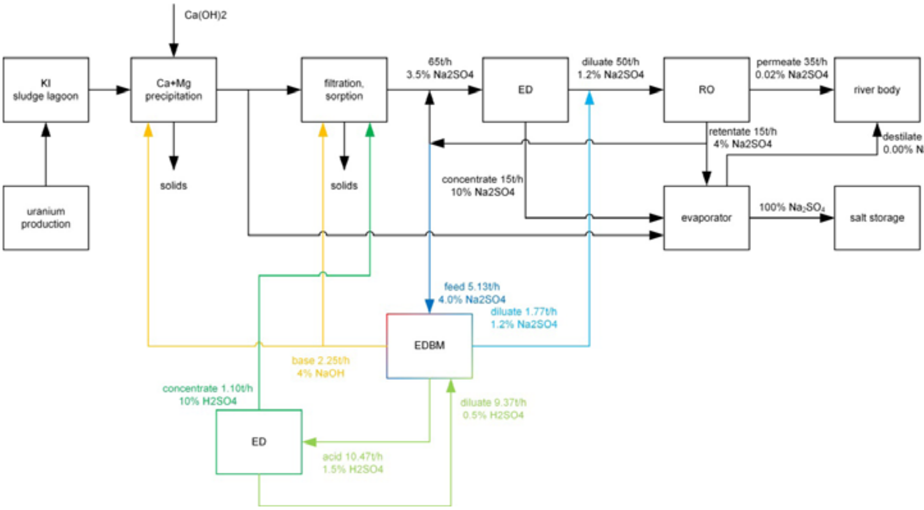

***Figure 3** Current (black) and future (colour) technology in the uranium mine waste water treatment facility.*

EDBM modules

Three sizes of EDBM modules were developed (fig 4):

- *Laboratory module* EDBM-Z with active membrane surface of 0.032 m^2, best suited for laboratory testing of new BPM samples and preliminary estimate of process parameters.

- *Pilot module* EDBM-Y with active membrane surface of 1 m^2, allowing for optimization according to product quality and costs.
- *Industrial scale module* EDBM-II with active membrane surface of 33.3 m^2.

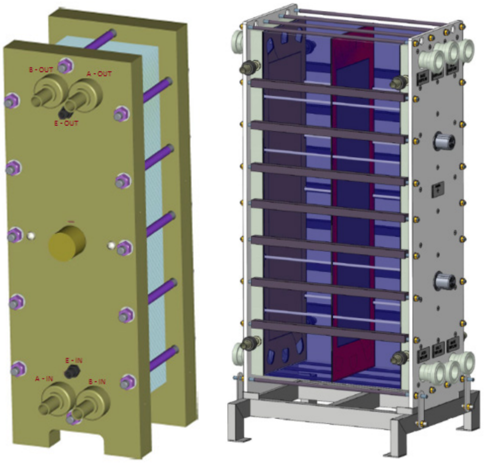

Figure 4 *Pilot module (left) and industrial scale module (right).*

To evaluate the module and membrane performance, a set of standardized laboratory and pilot test based on sodium sulphates were established. All modules fit their limits of external leakage (lower than 0.3 $L/m^2/h$), internal leakage (lower than 0.024 $L/m^2/h$), capacity (salt transport intensity higher than 0.4 $kg/m^2/h$), energy consumption (current efficiency higher than 60 %, energy consumption lower than 2 kW.h/kg of transported salts) and product purity (higher than 85 % for both acid and base).

EDBM units

Two new units to run EDBM modules were developed:

- *Pilot unit* P1 EDBM-Y was developed for long term pilot testing, operating EDBM-Y module in batch, feed-and-bleed or one-pass mode. Automatic logging of process parameters is included, allowing for the evaluation of optimum flowrate, voltage and product concentration, and their effect on capacity, energy consumption or current efficiency.
- *Industrial unit* B15 EDBM-II based on an existing ED unit was developed for long term industrial scale testing.

Laboratory scale tests

A three-circuit EDBM module proved to be the most effective as addition of protective compartments had no positive effect on process performance, and reduction to two compartments was not suitable due to lower product concentration and purity. Optimum voltage was found to be 3 V/cell in order to achieve industrially acceptable salt transport intensity of about 0.4 $kg/m^2/h$.

The largest possible flowrate is favourable for EDBM operation, given that (i) the pump energy consumption is by an order of magnitude lower than that of ion transport, and (ii) the boundary layer, where slow diffusion prevails, is less developed at increased flowrates. Flowrate is only limited by the pressure drop of industrial EDBM module and should be kept below 0.5 bar, typically occurring at linear velocities of around 0.07 m/s.

4.0 % wt. hydroxide and 1.5 % wt. acid were found to be optimum product concentrations, while providing acceptable purity and current efficiency. The base can be reused at site directly; the acid requires further concentration on existing ED technology to reach to 10 % wt.

Pilot tests

During 11 months of pilot testing the unit has been in stable operation, producing the required product concentrations and approaching purities of 80 %. Compared to the laboratory tests, the pilot unit was operated at lower current densities of about 350 A/m^2 with current efficiency of about 62 %. Energy consumption of 2.0 kWh/kg of transported sodium sulphate could not be compared to previous studies as the operating conditions differed considerably.

Industrial scale tests

Industrial production started in March 2017 on the newly developed B15 unit with one EDBM-II module. As the data cover less than one month of operation it is still early to publish any results. However, before the end of 2017 a feasibility study based on industrial scale data will be completed.

Operation costs

In the projected application of EDBM into existing technology (fig 3), the feed is 5.13 t/h of RO retentate with 4.0 % sodium sulphate. EDBM products are 1.77 t/h diluate with 1.2 % sodium sulphate, which is used as RO feed, 2.25 t/h of 4.0 % NaOH, which is used directly on site, and 10.47 t/h of 1.5 % H_2SO_4, which is concentrated in existing ED to 1.10 t/h of 10 % H_2SO_4, while 9.37 t/h ED diluate with 0.5 % H_2SO_4 is recycled back to EDBM for acid solution make-up. Exiting ED capacity should remain approximately constant. Time needed for H_2SO_4 concentration should be freed by decreasing salt amount for desalination by feeding a part of 4 % sodium sulphate solution into EDBM.

The estimate of operation costs (tab 2) is based on 11 month of pilot testing, given the electric energy price (0.064 €/kWh) and 300 workdays in a year. Electrical energy is 88 % of total operation costs, remaining 12 % are spare parts, such as membranes, spacers, and electrodes.

Current price of produced acids and bases is 317,034 €/year at given chemical prices (210 €/t 50 % NaOH and 55 €/t 94 % H_2SO_4). That is much more than operation costs of 223,358 €/year, operating profit is 119,410 €/year only by reduced chemicals purchase. EDBM technology brings more flexibility to the water treatment on site. Large EV with large operation expenses does not have to run permanently and crystalline sodium sulphate is not produced when capacity demand is low such as during a low rainfall winter period.

Table 2 *Operation costs of EDBM.*

	Operation cost (€/year)	**Operation cost (%)**
Electric energy	195,970	88
Chemicals	62	0
Spare parts	27,326	12
Total operation costs	223,358	100

Conclusions

Combination of desalination and concentration technologies proved to be the most competitive when compared to using each technology separately. Combined technology of ED, RO and thermal concentration (EV, crystallizer) decreases both investment and operation costs of waste water treatment and brings us closer to zero liquid discharge. In this combination:

- Thermal step is used for production of solid salts and reduction of salt discharge into water bodies.
- ED is used for decreasing both investment and operating costs of the thermal step. Concentration of the EV feed up to 18 % wt. brings significant heat consumption savings. Total costs are lower with membrane processes despite the need of larger chemical and mechanical pre-treatment.
- RO is used for meeting strict water discharge limits while RO retentate is pumped back into ED without any additional costs.
- Long membrane lifetime of both RO and ED is achievable with proper pre-treatment.

New heterogeneous BM-3.0 used in new laboratory and pilot scale modules was used for production of sulphuric acid and sodium hydroxide from sodium sulphate, with salt transport intensity 0.45 $kg/m^2/h$, 62 % current efficiency and energy consumption 2.0 kWh per kg of transported salt. Application of EDBM technology on DIAMO s.p., division GEAM is economically feasible because of the eliminated costs for the recycled chemicals. EDBM brings also higher flexibility for changing capacity needs in case an unusual weather change occurs.

Acknowledgements

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