

INTEGRATION OF ELECTRODIALYSIS WITH BIPOLAR MEMBRANE INTO TECHNOLOGY OF TREATMENT OF EXTRA WASTEWATER CONTAINING SODIUM SULFATE

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Abstract

Sodium sulfate is a common waste material which can be produced in many chemical processes. Typical source of sodium sulfate wastewater is the process of beneficiation of uranium ore. At present, the sodium sulfate wastewater generated in this process is dominantly treated by combination of evaporation and crystallization eventually with integrated membrane processes such as electrodialysis and reverse osmosis. However electrodialysis with bipolar membrane is a modern alternative which is capable to improve the efficiency and environmental sustainability of the process. The process allows to recovery sodium hydroxide and sulfuric acid from corresponding waste salt. This work is focused on analyzing the possibility of reusing the products of electrodialysis with bipolar membrane back into the technology of beneficiation of uranium ore. It was found that the efficiency of the process is dependent on considered reuse location in the leaching technology with different requirements for their initial concentration and purity. Further research should be focused mainly on increasing the purity and maximum concentration produced sulfuric acid and sodium hydroxide.

Key words

Electrodialysis, Bipolar membrane, Sulfuric acid, Sodium sulfate, Sodium hydroxide.

1 Introduction

Electrodialysis with bipolar membranes (EDBPM) is a relatively new electromembrane process which may find application in many industrial fields. With this process it is possible for example to adjust the pH without direct addition of acid or base to the system. Another application of EDBPM is technology of water deionization. As an interesting application appears also the recovery acids and bases from corresponding waste inorganic or organic salts. (Strathmann 2004)

The sodium sulfate is a common inorganic salt which is to be found in many industrial technologies. The sodium sulfate can be used as feedstock in a glass, paper and textile industry, but very often the sodium sulfate can be undesirable product from many technologies (Garrett 2001). Most commonly sodium sulfate is produced as a side product of the neutralization reaction between sulfuric

acid and sodium hydroxide (or sodium carbonate) at a certain stage of production technology. Waste water containing sodium sulfate usually does not represent a direct danger to the environment because it is chemically inert, non-volatile and non-toxic compound. (Shin et al. 1995) However, in many countries, including the Czech Republic, there are standards that specify the maximum possible concentration because large amounts of sulfate in water will result in the formation of sulfate-aluminate complexes which swell and crack concrete made from certain types of cement. Also biological treatment of sulfate-rich wastewater is rather unpopular because of the production of H_2S under anaerobic conditions. Therefore, waste sulfate solutions can not be arbitrarily discharged into water streams and it is often necessary ecological recycling or disposal. (Kroupa, Kinčl, Cakl 2014)

The process which generates a large amount of wastewater containing sodium sulfate is a technology of alkaline leaching of uranium ore. In the Czech Republic, this technology is used in o.z. GEAM DIAMO s.p. Dolní Rožínka (GEAM). Nowadays the produced sodium sulfate together with other undesired products of alkaline leaching is stored in a tailing pond. The water contained in this pond is characterized by high salinity, wherein the largest component of which being sodium sulfate. Any waste water from tailing ponds is currently collected and together with other overbalanced water treated by electrodialysis (ED) in combination with evaporation and crystallization. The resulting product of this cleaning technology is pure water and sodium sulfate, which can be used for example in the glass industry. (Jež 2008)

The possible upgrade of a typical uranium ore mining wastewater treatment plant using EDBPM was suggested and consequently studied in laboratory scale in our previous contributions (i.e. Kroupa, Kinčl, Cakl 2014). A preliminary investigation showed that the EDBM process for NaOH and H_2SO_4 production from uranium production wastewater is profitable. It was concluded that the process should 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 bipolar membranes affect the economy of the process. Following these results, this work is focused on detailed analysis of specific parts of the source leaching technology from the perspective of the possible use of products from EDBPM of waste water containing sulfate salts.

2 Principle of electrodialysis with bipolar membrane

Bipolar membranes (BPM) are special type of ion exchange membranes (IEM). The structure of BPM which is shown in fig. 1 consists of three parts, the anion and cation-exchange layers that are separated by interface layer. With this arrangement it is not possible to transport ions from one BPM side to the other, as it is in the case with conventional ion exchange membranes. Nevertheless, these membranes are used in a number of electrodialysis processes, due to its ability to dissociate the water in the presence of an electrical field. As described in literature (Krol 1997), the water dissociation in BPM is accelerated up to 50 million times compared to the rate of water dissociation in standard aqueous solutions. This acceleration is influenced by strong electric field across the transition region.

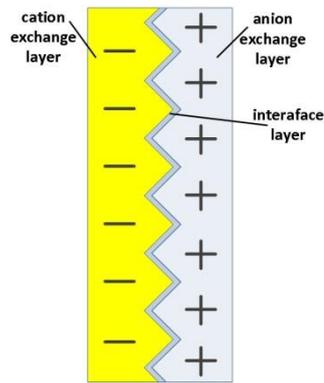


Figure 1.: Structure of bipolar membrane

The principle of electrodialysis with bipolar membrane is shown in fig.2. A cell system consists of an anion (AEM), a bipolar (BPM) and a cation (CEM) exchange membrane as a repeating unit. The Na_2SO_4 solution flows between the CEM and AEM. When a direct current is applied, water will dissociate in BPM to form equivalent amounts of amounts of H^+ and OH^- ions. The H^+ ions permeate through the cation-exchange side of the BPM and form H_2SO_4 with the sulfate ions provided by the Na_2SO_4 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 H_2SO_4 at a significantly lower cost than by other methods. □

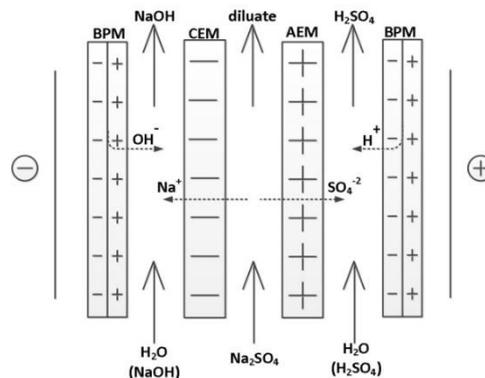


Figure 2.: Principle of electrodialysis with bipolar membrane

3 Technology of beneficiation of uranium ore and treatment of waste water

Fig. 3 shows the simplified diagram of the entire process of chemical beneficiation of uranium ore in company GEAM. The technology is based on alkaline leaching process. The production process after finishing crushing and grinding is divided into three technology circuits:

- transfer of uranium from the ore into the solution by leaching,
- separation of uranium from solution by selective ion exchange resins,
- precipitation of uranium as ammonium diuranate $(\text{NH}_4)_2\text{U}_2\text{O}_7$ (yellowcake). (Jež 2008)

The final product is a concentrate of uranium in the form of yellowcake which requires significant further processing to produce fuel-grade feed.

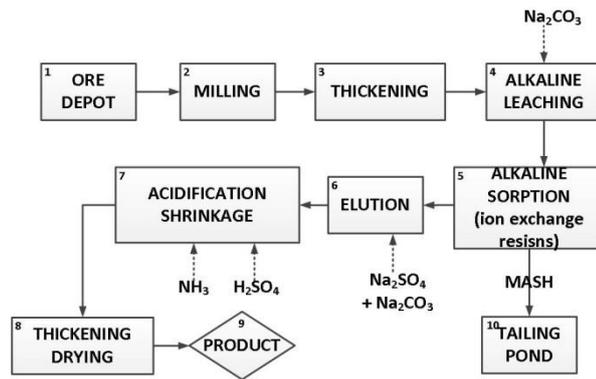


Figure 3.: Simplified diagram of the entire process of chemical beneficiation of uranium ore

The by-product of chemical beneficiation process is the leached mash which is landfilled at the tailing pond. The composition of waste water in the pond is very diverse, but the main component is sodium sulfate. The pond is operated in the strict environmental regime. It means that drainage water from the pond is fed back into the pond using powerful pumps and prior to discharge to watercourse all the water is treated to be free of contaminants. However, some water can also be used back in the source technology. Fig. 4 shows diagram of technology which is used for the treatment of overbalanced waste water from tailing pond. Technology is based on evaporation in the evaporating station, followed by crystallization unit. The resulting products are pure water which is discharged into watercourse, and the crystalline sodium sulfate. To increase proces operating efficiency membrane separation processes (electrodialysis and/or reverse osmosis) or ion exchange resins are also used. Membrane processes are used mainly to increase the concentration of salts in water prior to the evaporation and crystallization. The permeate and/or diluate leaving membrane equipment with a minimum salt concentration is discharged together with water from the evaporating station into watercourse. Ion exchange resins are used for treatment of rainwater contaminated by radionuclides from operation of chemical treatment plant. (Jež 2008) Annually, it is necessary to process about 430,000 cubic meters of overbalanced water, which contains approximately 6300 tons of sodium sulfate.

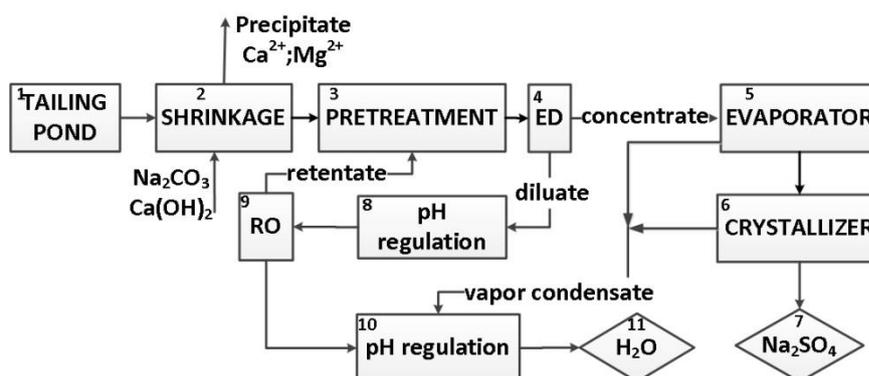


Figure 4.: Scheme of water treatment plant in GEAM

4 Possibility of reuse acquired sulfuric acid and sodium hydroxide

Throughout the GEAMs technology there are several specific parts that utilize sulfuric acid and sodium hydroxide of different concentrations and purity requirements. The following text attempts to describe these parts.

4.1 Sulfuric acid

4.1.1 Decomposition of uranyl tricarbonate

Sulfuric acid (98%) is standardly used for decomposition of uranyl tricarbonate contained in the elution solution. In fig 3, this technological step is numbered 7. Used concentration of sulfuric acid is as high as possible, because dilute solutions brings into the system excess of water, which causes water imbalance in the system. The minimum concentration of sulfuric acid useable for this process is estimated at 30% . Sulfuric acid used should be pure without molybdenum and fluorides impurities.

4.1.2 Pretreatment of technological water for electro dialysis

Because of the precipitation, the pH of process water entering the step 3 (in fig. 4) is very high (in alkali region). The feed with this pH is not suitable for subsequent electro dialysis. For this reason it is necessary to adjust the pH by adding sulfuric acid of technical quality. Again, in this step it is preferred to use higher acid concentration in order to reduce the water volume processed (see 4.1.1)

4.1.3 Regeneration of cation exchange resins

Cation exchange resins are used in the technology in several places, for example, for alkaline sorption and elution of uranium in steps 3 and 5 (in fig 3), or during the ion-exchange sorption of heavy metals in water pretreatment in step number 3 (in fig. 4). The regeneration of ion exchangers is carried out using 10% sulfuric acid of higher purity.

4.1.4 Ammonia absorption

Ammonia is used for precipitation of solution containing decomposed uranyl tricarbonate in step number 7 (in fig 3). Free ammonia from this technological stage has to be removed from the gaseous phase by absorption. For these purposes, absorbers are used with the working solution of diluted sulfuric acid with pH within the range 2.5 – 3. The quality of sulfuric acid used in this application is not significant.

4.2 Sodium hydroxide

4.2.1 Precipitation of calcium and magnesium from waste water treated

At present the precipitation of calcium and magnesium from water treated is performed with lime milk and soda ash (fig 4, step 2). The calcium is precipitated as calcium carbonate and magnesium is precipitated as magnesium hydroxide. The optimal pH value for precipitation is about 11.8. This pH value can be achieved not only using the above mentioned mixture, but also by the addition of sodium

hydroxide. Furthermore, the use of sodium hydroxide reduces the total quantity of soda required, because into the system there is not introduced additional calcium in the lime milk. The sodium hydroxide used need not meet any stricter requirements for purity and concentration limit.

4.2.1 Regeneration of cation exchange resins

Cation exchange columns used for the sorption of heavy metals in the pretreatment of water (step 3 in fig. 4) are operated in the H^+ and Na^+ cycle. Due to this fact some amount of 10% sodium hydroxide is also needed in this technology. The purity of sodium hydroxide used should be as high as possible to prevent the sorption of impurities. Alternatively, when using the impure hydroxide the two-stage regeneration could be also used.

4.2.2 Production of sodium ash

Carbon dioxide is created during the decomposition of uranyl tricarbonate (fig. 3, step 7), which could be used in combination with sodium hydroxide obtained to prepare soda solution. This component should be used in the technology of chemical treatment of uranium ore to alkali leaching, as shown in step 4 (fig. 3). In this case the purity of hydroxide does not matter much, because leaching stream contains large amounts of pollutants. Another potential use of soda solution is in the regeneration of anion exchange resins where the solution purity is conversely important and sodium hydroxide should therefore have a low concentration of sulfates and molybdenum. Production of soda is not a part of the existing technology, so it is only a hypothetical use for which first it is necessary to process the broader technical - economic considerations.

4.2.3 Precipitation of U – concentrate

Another potential application of sodium hydroxide is the precipitation of U-concentrate. At present the precipitation is based on precipitation with ammonia when product is ammonium diuranate. The sodium hydroxide can fully replace ammonia, but purity of sodium hydroxide has to be high to avoid contamination of the final product.

4.3 Preliminary balance of expected consumption of chemicals

Table 1 shows the average consumption of sodium hydroxide and sulfuric acid in the current technology.

It is evident that in the current technology is the average daily consumption of acid approximately three times greater than the consumption of hydroxide. The estimated annual consumption during normal operation technology 11 months/year would be approximately 3200 tons of sulfuric acid and 990 t NaOH. The annual amount of sodium sulfate produced is about 6 300t/year. From this amount it is theoretically possible, in full decomposition of sodium sulfate by stoichiometry of 1: 0.56 for sodium hydroxide and 1: 0.69 for the sulfuric acid, to produce up to 4350 tons/year of sulfuric acid and 3550 tons/year of sodium hydroxide. These products could meet all current requirements of the whole technological process in GEAM. Important fact is that presented balance is done for pure, concentrated components. Due to this fact the balance is only illustrative.

Table 1 Average daily consumption of sodium hydroxide and sulfuric acid

ACID 98%		HYDROXIDE 100%	
	kg/day		kg/day
Decomposition of uranyl tricarbonate	3665	Production of sodium ash	?
Pretreatment of technological water for ED	2000	Precipitation of Ca ²⁺ and Mg ²⁺	2160
Regeneration of catex exchange resins	818	Regeneration of catex exchange resins	818
Ammonia absorption	3150	Precipitation of U-concentrate	900
TOTAL	9633	TOTAL	3878

5 Limitation of EDBPM

The basic operation characteristic of EDBPM are in more details described in our previous paper (Kroupa, Kinčl, Cakl 2014). A laboratory test unit P EDR-Z / 10-0.8 (MemBrain, Czech Republic) equipped with heterogeneous membranes Ralex (MemBrain, Czech Republic) in a three-chamber arrangement was used. The experiments were carried out with model as well with real waste water provided by GEAM. The composition of real waste water is given in table 2.

Table 2 The composition of wastw water from GEAM

COMPONENT	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

The experiments were focused especially on the study of effects of voltage, current density, flow rate and temperature of individual process streams on energy consumption and maximum achievable concentration of acid and base. It was found that in the three compartments configuration operated with current density $i = 300 \text{ A/m}^2$ the maximum achievable concentration was 5.5% for sulfuric acid and 6.5% for sodium hydroxide. The products purity was in the range 71.9 – 83.3% for acid and in the range 97.0 - 98.3% for sodium hydroxide. The dominant pollutants were sodium ions in the case of acid, whereas for hydroxide these were sulfate ions. Furthermore, it appears that the key element determining the purity of the products is bipolar membrane, whereas the maximum achievable concentration is determined by the selectivity and performance of the monopolar membranes. Comparisons of the products obtained with the limits and requirements discussed in Chapter 4 are summarized in table 3.

Table 3 Purity and concentration limits

PROCESS	PURITY		CONCENTRATION	
			ACID	
DECOMPOSITION OF URANYL TRICARBONATE	without Mo ^{x+} F ⁻	YES	min 30%	NO
APRETREATMENT OF TECHNOLOG. WATER FOR ELECTRODIALYSIS	technical quality	YES	concentrated solution	NO
REGENERATION OF CATION EXCHANGE RESISN	pure	NO	10%	NO
AMMONIA ABSORPTION	negligible	YES	pH< 2,5	YES

PROCESS	PURITY		CONCENTRATION	
			HYDROXIDE	
PRODUCTION OF SODIUM ASH	?	-	?	-
PRECIPITATION OF Ca ²⁺ and Mg ²⁺	negligible	YES	negligible	YES
REGENERATION OF CATION EXCHANGE RESISN	pure	YES	10%	NO
PRECIPITATION OF U-CONCENTRATE	pure	YES	-	-

It is evident that the maximum achievable concentration of the products as well as their purity are critical parameters for the use of the process considered. Both of these parameters will be subject to further research.

6 Conclusion

In the technology of chemical treatment of uranium ore were identified several sub processes in which it would be possible to re-use sulfuric acid and sodium hydroxide, which can be obtained from the sulfate waste water using electrodialysis with bipolar membranes. Consequently each sub process was described and specified by its concentration and purity limits. Also preliminary mass balance of the sub-processes was carried. It appears that the processes being studied are an interesting alternative, which leads to savings in raw materials and consequently to reduction of the overall environmental impact source technology. Further research should be focused on increasing the purity and maximum concentrations of acid and hydroxide produced.

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