APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

Analysis of Preparation Conditions of H$_2$SO$_4$ and NaOH from Sodium Sulfate Solutions by Electrodialysis

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Abstract—Preparation of sulfuric acid and sodium hydroxide from solutions containing sodium sulfate was studied by the electrodialysis method in a three-chamber (?three-compartment) electrodialyzer equipped with two membranes, an anion-exchange membrane AESD-2a and a cation-exchange membrane Nafion 427.

Manufacture of some fatty acids [1, 2], synthetic fibers, and inorganic and organic compounds [3] and integrated processing of worked-out lead batteries [4] yield spent solutions containing sodium sulfate, which are considered nontoxic and are discharged as wastewater. In most cases, sodium sulfate is formed in spent solutions when sulfuric acid and sodium hydroxide are used as technological solutions. Hence follows that it would be possible to solve the ecological problems associated with the formation and discharge of spent solutions containing sodium sulfate if there existed an effective and cost-efficient method for their processing to obtain sulfuric acid and sodium hydroxide. This would enable development of integrated (conjugated) closed cycles. H$_2$SO$_4$ and NaOH of purity and concentration sufficient for recycling can be obtained at a plant using sulfuric acid and sodium hydroxide, with sodium sulfate solutions formed along with the target product [5, 6].

The possible technologies based on this principle of processing of spent solutions containing sodium sulfate were described in [4]. It was suggested to use for this purpose electrodialysis in a three-chamber apparatus (electrodialyzer) with two, anion-exchange and cation-exchange, membranes.

The aim of this study was to determine how the current density in the range 2.5–10.0 A dm^{-3}, initial concentration of sodium sulfate (50 and 100 g dm^{-2}), and dialyzate composition affect the current efficiency by sulfuric acid and sodium hydroxide and the direction of transfer and amount of water transferred across the membranes in the course of electrodialysis.

EXPERIMENTAL

The electrodialyzer is shown schematically in Fig. 1. It comprises clamping plates *1, 9*, anode chamber *2*, anode *3* made of perforated lead sheet, anion-exchange membrane *4*, central chamber *5*, cation-exchange membrane *6*, cathode *7* made of perforated nickel sheet, and cathode chamber *8*. The separate elements are connected via 2-mm-thick rubber sealing gaskets. The whole set is assembled into a rigid stack by means of steel coupling bolts. The working size of each membrane and electrode is 5 × 20 cm.

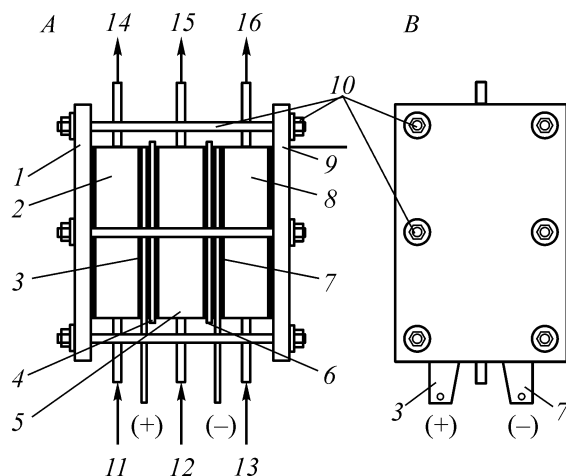**Fig. 1.** Schematic of the electrodialyzer unit. (*A*) Front view and (*B*) side view. (*10*) Coupling bolts, (*11*) inlet for water (dilute H$_2$SO$_4$), (*12*) inlet for Na$_2$SO$_4$ solution, (*13*) inlet for water (dilute NaOH), (*14*) outlet for H$_2$SO$_4$ solution and oxygen, (*15*) outlet for dialyzate, and (*16*) outlet for NaOH solution and hydrogen. The rubber separators are colored black.

The AESD-2a membrane manufactured by GALENA pharmaceutical plant (Wroclaw) is a single-layer anion-exchange membrane used without a reinforcing grid at temperatures of up to 45°C [7]. The membrane is fabricated from polyethylene modified with a copolymer of styrene and divinylbenzene, functionalized with $-NH(CH_3)$ groups, and has thickness of 170 μm. The formal selectivity of the membrane is 0.93, and the swelling capacity, 22–24%.

The Nafion 427 membrane manufactured by E.I. Du Pont de Nemours & Co (USA) is a single-layer cation-exchange membrane composed of a perforated mass with $-SO_3H$ functional groups. The membrane has a thickness of 127 μm, mass equivalent ME = 1200, and a reinforcing Teflon fabric of T-12 brand. Nafion 427 membranes are intended for regeneration of technological media, including acids and alkalis [8].

The installation is shown schematically in Fig. 2. It comprises three reservoirs preliminarily filled with an anolyte, a Na_2SO_4-containing solution, and a catholyte. The anolyte (H_2SO_4 solution of initial concentration 16 g dm^{-3}) is delivered from a reservoir *1* by a dosing pump *2* and passes through an anode chamber *3* into a sulfuric acid collector *4*. The catholyte (NaOH solution of initial concentration 12 g dm^{-3}) from a reservoir *5* is delivered by a dosing pump *6* and passes through a cathode chamber *7* into a collector *8*. The sodium sulfate solution from a reservoir *9* is delivered by a dosing pump *10* into a central chamber *11* and then into a dialyzate collector *12*. Gaseous products of electrodialysis (oxygen and hydrogen) are released into the atmosphere.

The volume of the solutions obtained (anolyte, catholyte, and dialyzate) was measured at certain intervals of time. The concentration of sulfuric acid was measured in the anolyte, and that of sodium hydroxide, in the catholyte. A selective determination of SO_4^{2-} ions in the catholyte gave a negative result. SO_4^{2-} ions and an excess amount of free acid or hydroxide were found in the dialyzate. These data were used to calculate the concentrations of Na_2SO_4 and H_2SO_4. The results obtained were used, together with the data furnished by direct determination of the products concentration and dialyzate composition, to calculate the current efficiency by sulfuric acid and sodium hydroxide, as well as the amount of water transferred across both the ion-exchange membranes.

The results obtained were mathematically processed using the procedure suggested by Kafarov [9]. For this purpose, equations describing the dependences of the current efficiency on the process parameters
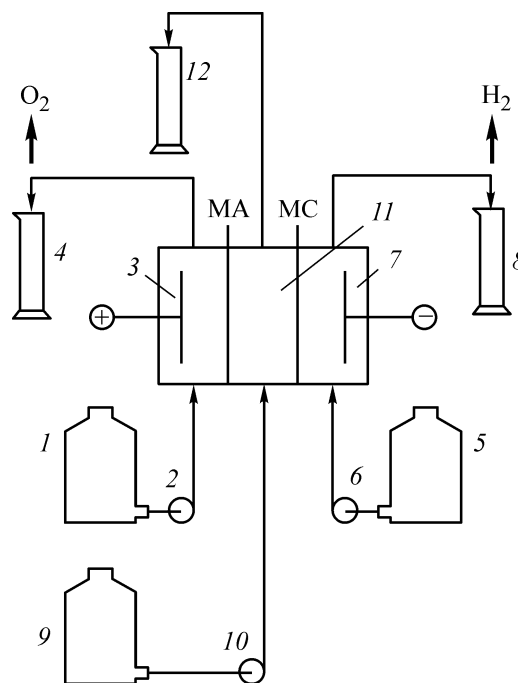

Fig. 2. Schematic of the installation for electrodialysis. Membrane: MA, of anion-exchange, and MC, of cation-exchange types.

were set up in the form of second-degree polynomials including all combinations of the process parameters (as independent variables). Statgraph software was used to calculate the numerical coefficients of individual terms and to analyze their significance. Using terms with a significance level higher than 0.05, we derived functions with only significant terms, which makes it possible to determine the influence exerted by separate parameters on the current efficiency. As two products (sulfuric acid and sodium hydroxide) are formed in the course of electrodialysis, the equations for sulfuric acid for sodium hydroxide were set up and processed independently

$$CE_{H_2SO_4} = f(K_1, j_m, c_{H_2SO_4}), \qquad (1)$$

$$CE_{NaOH} = f(K_2, j_m, c_{NaOH}), \qquad (2)$$

where $CE_{H_2SO_4}$ and CE_{NaOH} are the current efficiencies by sulfuric acid and sodium hydroxide, respectively (%); K_1 and K_2, constants (free terms reflecting the influence of the membrane characteristics); j_m, current density recalculated to the geometric area of the membrane (A dm^{-2}); and $c_{H_2SO_4}$ and c_{NaOH}, concentrations of H_2SO_4 and NaOH in the solutions flowing out of the respective chamber of the electrodialyzer (g dm^{-3}).

Table 1. Parameters and efficiency of electrodialysis (initial solution contains 50 g dm^{-3} Na$_2$SO$_4$)

j_m, A dm^{-2}	Dialyzate,* g dm^{-3}	Catholyte			Anolyte		
		c_{NaOH}, g dm^{-3}	CE,** %	Water transport, mole H$_2$O/mole NaOH	$c_{H_2SO_4}$, g dm^{-3}	CE,*** %	Water transport, mole H$_2$O/mole H$_2$SO$_4$
2.5		14.95	78.43		19.22	71.26	
2.5		17.81	78.56		22.72	71.24	
2.5		20.64	78.80		26.28	71.31	
2.5		23.45	78.94		29.98	71.60	
2.5	$\frac{21.56}{1.15}$	26.22	79.12		33.64	71.52	
2.5		28.98	79.01	+4.39	37.43	71.41	−12.31
5.0		18.15	80.94		22.82	71.96	
5.0		24.06	81.12		30.20	72.09	
5.0		29.85	81.28		38.03	72.16	
5.0		34.53	81.28		46.35	72.16	
5.0	$\frac{5.92}{5.29}$	41.41	81.28		56.13	72.16	
5.0		46.57	81.28	+4.22	66.40	72.02	−15.42
7.5		21.28	82.48		25.94	71.96	
7.5		28.77	82.36		37.34	72.16	
7.5		36.17	82.30		49.89	72.30	
7.5		43.63	82.24		63.74	72.11	
7.5	$\frac{6.93}{4.43}$	51.27	81.98		79.12	72.02	
7.5		59.25	81.90	+3.83	96.32	71.92	−19.56
10.0		23.73	80.10		31.93	70.86	
10.0		35.41	79.96		47.66	70.78	
10.0		47.02	79.58		63.36	70.64	
10.0		58.55	79.32		80.00	70.64	
10.0	$\frac{6.86}{4.02}$	70.07	79.06		97.58	70.49	
10.0		81.56	78.91	+4.15	117.14	70.40	−17.68

* Numerator, Na$_2$SO$_4$ concentration; denominator, H$_2$SO$_4$ concentration.

** $CE_{NaOH} = 72.81 + 2.57j_m + 0.42c_{NaOH} - 0.17j_m^2 - 0.0067j_m c_{NaOH}$, $R^2 = 95.09\%$. (3)

*** $CE_{H_2SO_4} = 69.29 + 0.94j_m + 0.011c_{H_2SO_4} - 0.08j_m^2 - 0.00011c_{H_2SO_4}^2$, $R^2 = 95.32\%$. (4)

The data obtained for the initial Na$_2$SO$_4$ concentrations c_0 of 50 and 100 g dm^{-3} are listed in Tables 1 and 2. The sign (+) stands for water transfer from the central chamber into the electrode chamber, and the sign (−), for water transfer from the electrode chamber into the central chamber.

It follows from the data in Table 2 that the current efficiency by sodium hydroxide increases from 78 to 85% as the current density is raised from 2.5 to 10.0 A dm^{-2}. Simultaneously, the current efficiency by sulfuric acid increases from approximately 72.3 to 74%. The increase in the current efficiency can be explained as follows. The product yield is determined by competition of two processes. These are, first, an increase in the amount of the product as a result of electrodialysis and transfer of Na$^+$ and SO$_4^{2-}$ ions under the action of electric current, and, second, loss of the product via exchange with the membrane, which results from the fact that the true selectivity of the

membrane is always lower than inity (frequently, even lower than the formal selectivity given in the data sheet). The ion transfer in an electric field, e.g., across a membrane, is associated with the transport of an electric current and depends on its density. At the same time, the effects of exchange of solution components via diffusion and osmosis mainly depend on the solution composition and time of exchange. Hence follows that the higher the current density, the faster the accumulation of the product obtained and, thereby, the smaller the amount of loss.

With some simplification, the current density can be considered a factor determining the processing rate of the substrate (Na$^+$ and SO$_4^{2-}$ ions) fed into the central chamber. The throughput of this processing depends on the content of the substrate in the dialyzate.

Comparison of the data in Tables 1 and 2 shows that the current efficiencies by both the products are

Table 2. Parameters and efficiency of electrodialysis (initial solution contains 100 g dm^{-3} Na$_2$SO$_4$)

j_m, A dm^{-2}	Dialyzate,[*] g dm^{-3}	Catholyte			Anolyte		
		c_{NaOH}, g dm^{-3}	CE,[**] %	Water transport, mole H$_2$O/mole NaOH	$c_{H_2SO_4}$, g dm^{-3}	CE,[***] %	Water transport, mole H$_2$O/mole H$_2$SO$_4$
2.5		16.83	78.02		21.64	72.28	
2.5		21.28	77.96		27.67	72.32	
2.5		25.56	78.02		33.92	72.32	
2.5		29.70	77.96		40.39	72.30	
2.5	$\dfrac{81.02}{2.28}$	33.71	78.04		47.12	72.32	
2.5		37.64	78.04	+5.72	54.14	72.36	–13.76
5.0		22.28	82.59		27.28	73.12	
5.0		32.40	83.10		40.42	73.07	
5.0		42.29	83.23		55.05	73.07	
5.0		52.02	83.20		71.33	73.07	
5.0	$\dfrac{87.44}{1.56}$	61.62	83.15		89.69	72.81	
5.0		71.14	83.05	+3.75	110.49	72.98	–19.28
7.5		27.83	84.24		32.83	73.35	
7.5		43.30	84.16		53.22	73.35	
7.5		58.52	84.06		76.93	73.82	
7.5		73.26	84.10		104.85	73.66	
7.5	$\dfrac{54.20}{3.68}$	87.94	84.06		138.10	73.24	
7.5		101.90	84.06	+3.54	179.72	73.18	–21.28
10.0		32.62	85.18		38.49	74.18	
10.0		53.11	85.10		64.85	74.06	
10.0		73.56	85.10		95.23	73.92	
10.0		94.01	85.04		127.56	73.82	
10.0	$\dfrac{46.12}{3.89}$	114.45	84.96		164.58	73.66	
10.0		134.92	84.96	+3.92	206.34	73.66	–22.94

[*] Numerator, Na$_2$SO$_4$ concentration; denominator, H$_2$SO$_4$ concentration.

[**] $CE_{NaOH} = 71.88 + 2.95j_m + 0.00086c_{NaOH} - 0.16j_m^2$, $R^2 = 96.88\%$. (5)

[***] $CE_{H_2SO_4} = 71.53 + 0.35j_m + 0.000012c_{H_2SO_4} - 0.0096j_m^2$, $R^2 = 95.40\%$. (6)

lower at a lower initial concentration of Na$_2$SO$_4$ and a lower concentration of the dialyzate. The difference is the larger, the higher the current density. The current efficiency by H$_2$SO$_4$ and NaOH at the initial Na$_2$SO$_4$ concentration of 50 g dm^{-3} is determined by the transfer of Na$^+$ and SO$_4^{2-}$ ions. This is indicated by the fact that the current efficiency decreases as the current density increases from 7.5 to 10.0 A dm^{-2} (Table 1). This behavior is observed at $c_0 = 100$ g dm^{-3} Na$_2$SO$_4$ (Table 2).

The concentrations of sodium sulfate in the solution fed into the central chamber of the dialyzer, which are used in the study, are comparable with the concentrations in spent solutions and have comparatively low values: the Na$_2$SO$_4$ concentration of 100 g dm^{-3} corresponds to a concentration of about

0.7 mol dm^{-3}, and 50 g dm^{-3}, to 0.35 mol dm^{-3}. In the central chamber, the concentration decreases to the value found for the dialyzate. As the rate of the solution flow through the central chamber was 1–2 cm min^{-1}, it may be suggested that a concentration gradient is formed: the highest concentration of the solution is observed in the bottom part and the lowest, in the top part (on the feed side).

The current efficiencies by sodium hydroxide and sulfuric acid are different, with that by sodium hydroxide higher in all cases. Accordingly, the dialyzate outflowing from the central chamber contains, in addition to sodium sulfate, also sulfuric acid, whose concentration depends on the transport number and on the solution flow rate. Generalization of this fact shows that, if the current efficiencies by the products
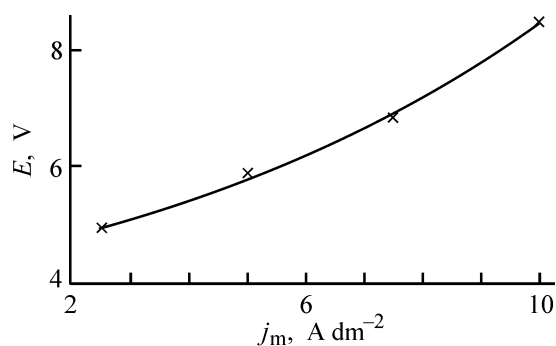
Fig. 3. Electrodialyzer voltage E vs. the current density on the membrane j_m. Initial solution contains 50 g dm^{-3} Na$_2$SO$_4$.

obtained in the electrode chambers of the electrodialyzer are different (which is primarily determined by the characteristics of the membranes used), then the product with a lower current efficiency will be also present in the dialyzate.

The presence of sulfuric acid in the central chamber, which results from the lower selectivity of the anion-exchange membrane, may be responsible for the decrease in the current efficiency by sodium hydroxide obtained in the cathode chamber. This is because the solution contains, in addition to Na$^+$ cations, also hydroxonium ions H$_3$O$^+$ involved in the transfer across the cation-exchange membrane. The transfer of H$_3$O$^+$ ions from the central chamber to the catholyte does not yield sodium hydroxide and only promotes transport of water, thereby diluting the catholyte. Each hydroxonium ion that passes into the catholyte across the membrane interacts with a hydroxy ion to form water:

$$H_3O^+ + OH^- = 2H_2O.$$

Analysis of Eqs. (3)–(6) confirms the above observations. In these dependences, the influence of the membranes on the CE is reflected by the free term, with this effect being predominant. It may be considered that use of membranes with certain characteristics predetermines the limiting current efficiency, whereas changing the electrodialysis parameters produces a considerably weaker effect.

The numerical coefficients in the terms containing the current density j_m are positive, which confirms the character of their influence on the current efficiency. The presence of j_m terms (with considerably smaller numerical coefficients) shows that this influence is not linear. However, use of very high current densities in the process under discussion is unfeasible for economic reasons and the optimal current density

is considerably lower than its highest admissible value indicated by membrane manufacturers. Thus, the solution in the central chamber (dialyzate) should change its concentration in the course of the electrodialysis to an as low value as possible and its electrical conductivity should be low. Under the conditions described in Table 1, the process performed at a current density $j_m = 2.5$ A dm^{-2} occurred at a voltage $E = 4.9$ V, and that carried out at $j_m = 7.5$ A dm^{-2}, at 6.8 V. Hence follows that the rise in the current efficiency by a value not exceeding 4 % was determined by an increase in the voltage by more than 1.9 V, i.e., by approximately 39 % (Fig. 3). Although the dependence of the voltage E on the current density is determined by the electrodialyzer design and can be improved, it would be expected that the optimal current densities in an industrial process should be the same as those in a typical electrodialysis process, i.e., in the range from one to several amperes per square decimeter.

Varying the concentration of sulfuric acid in the anolyte and that of sodium hydroxide in the catholyte at a constant current density within the range studied has no significant effect on the current efficiency.

The purpose of application of electrodialysis is to process sodium sulfate solutions to obtain reusable sulfuric acid and sodium hydroxide. However, a dialyzate containing sodium sulfate and a minor amount of sulfuric acid or sodium hydroxide is also formed, in addition to these products. The desire to obtain in electrodialysis a dialyzate of purity conforming to, at least, the requirements to wastewater commonly leads to gross energy expenditure because of the low current efficiency and the low electrolytic conductivity of the solution in the middle chamber. This adverse effect can be diminished by making the middle chamber very narrow (about 2 mm). The problems encountered when using the dialyzate can be solved in many cases in integrated systems. Commonly, at least one of these products can contain sodium sulfate in an industrial process using sulfuric acid and sodium hydroxide. If this is, i.e., sulfuric acid (as it occurs when obtaining pure silica), then the dialyzate can be used to feed the anode chamber. In this case, all the dialyzate components remain in the closed cycle of the solutions. If, however, the resulting sulfuric acid is of high purity (as is the case in integrated processing of scrap lead batteries [3]) and a sodium hydroxide solution used for desulfation of the sulfate–oxide fraction contains sodium sulfate, then the dialyzate is fed into the cathode chamber. In systems of this kind, the electrolytic conductivity of the dialyzate may be reasonably high at a low energy

expenditure (depending on the admissible Na_2SO_4 concentration), and sodium sulfate does not penetrate into wastewater at all.

CONCLUSIONS

(1) Electrodialysis is the process that makes it possible to obtain sulfuric acid, sodium hydroxide, and a dialyzate from a spent solution containing sodium sulfate, and is especially suitable for closed integrated systems. The current efficiency by the products primarily depends on the parameters of ion-exchange membranes and, to a considerably lesser extent, on the process parameters.

(2) If the membranes used in electrodialysis have different selectivities, the dialyzate contains, in addition to the residual sodium sulfate, also the product (acid or hydroxide) obtained in an electrode chamber with a lower current efficiency.

(3) In the case when one of the electrodialysis products contains sodium sulfate, the dialyzate can be used to feed that electrode chamber in which this product is formed. This makes it possible to diminish the energy expenditure, facilitates enables closed

circulation of the solutions, and prevents penetration of sodium sulfate into wastewater.

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