

Processing of sodium sulphate solutions using the EED method: from a batch toward a continuous process

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In a batch electro-electrodialysis (EED), sodium sulphate solution with an initial concentration of 80.90 g/dm³ was converted to obtain solutions of sodium hydroxide (13.96%) and sulphuric acid (10.15%) and a dialysate (3.23 g/dm³ of sulphate ions). Changes in the EED process' performance (temperature, cell voltage, concentrations, energy consumption) with an increasing conversion degree of salt are presented. Based on the presented results of the batch experiment, conditions necessary to run the process continuously are discussed. A single pass method is inapplicable due to excessive heating of the electro-electrodialyser. A cascade method enables interstage cooling of the solutions, providing temperatures suitable for ion-exchange membranes to work. Increasing the number of stages in the cascade reduces both the number of electro-electrodialysers and specific electric energy consumption, providing the same production capacity. However, this increases the investment cost.

Keywords: electro-electrodialysis, waste processing, process conditions.

INTRODUCTION

The electro-electrodialysis method (EED process) enables the processing of sodium and potassium salts of some oxo-acids into their originating acids and bases. In the opinion of many authors, the main industrial application of this method would be the processing of sodium sulphate solutions, generated as a by-product of some chemical synthesis processes, into sulphuric acid and sodium hydroxide. It is believed that an advantageous way of utilising the EED process would be the concept of integrated systems, where the acid and hydroxide obtained could be used in the synthesis process in which a waste solution of Na₂SO₄ is formed. One of the systems where the use of such an arrangement is suggested is that of the regeneration of the “sulphated” active mass of lead-acid batteries¹.

Publications concerning the processing of sodium sulphate solutions using the EED method present the results of research conducted on a batch system (e.g.²), or describe some selected aspects of the process, e.g. the transport across membranes^{3–5}, illustrated by results obtained under steady-state conditions. However, the aim of industrial electrochemical processes is to achieve conditions suitable for continuous operation of a plant, where the obtained product solutions have a stable composition, which facilitates further processing thereof. It was pointed out⁶ that processing of waste solutions in a continuous manner often requires passing the solution through a cascade of apparatus. The effect of process parameters on EED processing of waste sodium sulphate solutions was discussed in detail in our previous papers^{2,7}. This article presents discussion of factors that must be taken into account when making the transition from research conducted on a batch system to the development of a continuous process: heat transfer, operation mode (cascade or single pass), number of stages in a cascade. These considerations are discussed based on conditions and results of processing a batch of solution with an initial concentration of 80.90 g Na₂SO₄/dm³ (7.57%). The selected requirements are: the concentration of the

SO₄²⁻ ions in the solution obtained after EED should be lower than 3.5 g/dm³ to assure a high salt conversion degree, while the concentration of the sulphuric acid produced should be 10%.

EXPERIMENTAL

The experimental setup is shown in Figure 1. The process was run in an electro-electrodialyser **1** with a dilution chamber **5** separated from an anode chamber **3** by Ultrex AMI 7001S (Membranes International Inc., USA) anion-exchange membrane **4** and from a cathode chamber **7** by Nafion N-423 (E.I. Du Pont de Nemours and Co., USA) cation-exchange membrane **6**. The anode **2** was made of perforated titanium sheet with a layer of platinum 10 μm thick, the cathode **8** was made of stainless steel. The effective surface area of each electrode and of each membrane was equal to 600 cm². Constant current density of 750 A/m² (I = 45 A) was supplied to the electrodes (from a rectifier not shown in the figure). Such a high value was to increase the rate of salt conversion to products and reduce both the membrane area and stack number required without overheating the solution⁷. The setup included pumps **9**, rotameters **10** and circulation tanks for: anolyte **11**, Na₂SO₄ solution **12** and catholyte **13** with a capacity of V = 10 dm³ each.

The process was conducted in batch recirculation mode. Circulation of solutions through chambers **3**, **5** and **7** and respective circulating tanks **11**, **12** and **13** with a flow rate of 100 dm³/h ensured the dissipation of Joule heat and a mixing and discharge of gases: oxygen from the anode chamber **3**, and hydrogen from the cathode chamber **7**.

Samples of the anolyte and of the catholyte were taken (20 cm³ each) at intervals of Δτ = 1 h and, upon cooling to 22°C, their electrical conductivity was measured. The concentrations of H₂SO₄ in the anolyte and of NaOH in the catholyte were determined based on conductivity vs. concentration curves plotted beforehand. After the conductivity measurement, samples were poured back into the solution from which they were taken. The volumes of the solutions were measured prior to the EED process and upon completing it and cooling; a linear change of the

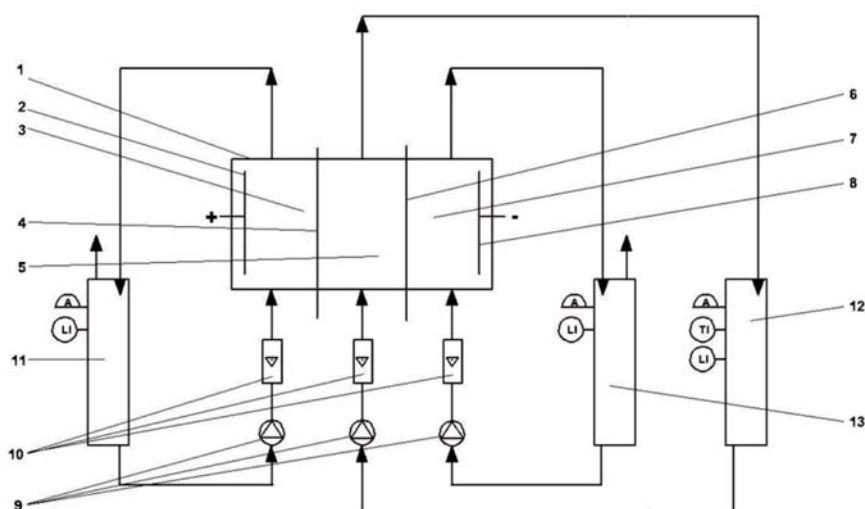


Figure 1. Diagram of experimental setup 1 – electro-electrodialyser, 2 – anode, 3 – anode chamber, 4 – anion exchange membrane, 5 – dilution chamber, 6 – cation exchange membrane, 7 – cathode chamber, 8 – cathode, 9 – pumps, 10 – rotameters, 11 – circulation tank for anolyte, 12 – circulation tank for dialysate, 13 – circulation tank for catholyte

volume of catholyte and dialysate solutions was assumed. The volume of the anolyte after the process was identical to the starting volume and it was assumed that it remained constant throughout the process.

The current efficiencies were calculated according to equation:

$$CE = 100 \frac{C_0 V_0 - C_\tau V_\tau}{k I \tau} \quad (1)$$

where: I – current (A); k – electrochemical equivalent (g/Ah), C and V are the compound concentration (g/dm³) and volume (dm³) at the start and time τ (h), respectively.

Furthermore, upon completing the EED process, the concentrations of NaOH in the catholyte, of H₂SO₄ in the anolyte and dialysate and of SO₄²⁻ in the dialysate were determined and, based on the results, the concentration of Na₂SO₄ in the dialysate was calculated. The composition of the dialysate was calculated based on the weight loss

of SO₄²⁻ (due to transfer to the anolyte), of Na⁺ (to the catholyte) and on volume.

RESULTS AND DISCUSSION

The results of measurements, determinations and calculations are shown in Table 1.

The values marked as “differential” indicate current efficiencies or specific electric energy consumption calculated for particular intervals $\Delta\tau = 1$ h, for instance: from hour 1 to hour 2, and so on. The relationships between changes of cell voltage, concentrations and current efficiencies and the conversion of sodium sulphate (and electric charge) were previously discussed in detail^{2,7}; herein, they form the basis for designing a continuous process.

Applicability of a single pass system. Some electromembrane processes, e.g. membrane electrolysis of sodium and potassium chloride solutions, as well as some industrial applications of electro dialysis, are performed through a single

Table 1. Changes in performance indicators during an EED process

Parameter	Unit	EED process duration, hours							
		0	1	2	3	4	5	6	7
Electric charge	A·h	0	45	90	135	180	225	270	315
Temperature	°C	22	45.8	49	49.9	51.6	51.9	53.5	61.8
Cell voltage	V	6.75	6.23	6.27	6.33	6.51	6.86	7.8	16.1
Catholyte (NaOH)									
Volume	cm ³	6000	–	–	–	–	–	–	7150
Concentration	g/dm ³	149.5	153.39	156.92	159.91	162.23	164.22	164.14	161.26
Concentration	%	13.05	13.33	13.64	13.9	13.98	14.15	14.14	13.96
Differential current efficiency	%	–	73.56	72.17	68.73	63.56	61.35	40.72	13.14
Mean current efficiency	%	–	73.56	72.86	71.49	69.51	67.87	63.35	56.18
Anolyte (H₂SO₄)									
Volume	cm ³	6000	–	–	–	–	–	–	6000
Concentration	g/dm ³	54.11	63.18	71.57	79.52	87.38	94.78	101.82	108.49
Concentration	%	5.24	6.07	6.82	7.61	8.29	8.94	9.56	10.15
Differential current efficiency	%	–	63.75	61.2	57.96	57.32	54.04	51.3	48.67
Mean current efficiency	%	–	63.75	62.48	60.97	60.06	58.85	57.59	56.17
Dialysate									
Volume	cm ³	6000	5790	5580	5360	5140	4920	4700	4470
Concentration of SO ₄ ²⁻ ions	g/dm ³	54.69	48.08	41.05	34.02	26.49	18.82	11.07	3.23
Concentration of H ₂ SO ₄	g/dm ³	0	1.67	3.35	5.14	6.37	7.87	6.56	0.73
Concentration of Na ₂ SO ₄	g/dm ³	80.9	68.69	55.86	42.87	29.96	16.43	6.87	3.72
Charge load of SO ₄ ²⁻	%init.	100	84.83	69.8	55.57	41.49	28.22	15.86	4.41
Differential specific energy consumption	kW·h/kg Na ₂ SO ₄	–	3.84	3.88	4.12	4.29	4.79	5.74	12.49
Mean specific energy consumption	kW·h/kg Na ₂ SO ₄	–	3.84	3.87	3.96	4.03	4.16	4.38	5.28

pass of solutions through the cell. In this mode (“single pass”), the flow rates of the solutions are set so that the residence time in the cells at a particular electric current ensures the assumed conversion degree. It is considered to be advantageous, as it does not require the use of elaborate apparatus. Limitations in its use arise, among others, from the need to maintain temperatures at which the ion exchange membranes can function. Under applied electric current, due to the compact structure of the electro-dialyser, most of the Joule heat resulting from the electric resistance of solutions and membranes is carried out by the flowing solutions. Perfluorinated cation-exchange membranes (e.g. Nafion) may be used at temperatures up to the boiling point of solutions ($\geq 100^\circ\text{C}$), whereas anion-exchange membranes can, according to the manufacturers’ recommendations, be permanently used at temperatures below 60°C ⁸, some even below 40°C .

The amount of Joule heat emitted in a unit of time can be calculated when the cell voltage, decomposition voltage and current density are known. The decomposition voltage of water under standard conditions is $2.057\text{ V} = \text{ca. } 2\text{ V}$:



Every additional 1 V causes, during a period of one hour, the emission of the following quantity of heat: $Q = 1\text{ V} \cdot 45\text{ A} \cdot 1\text{ h} = 45\text{ W} \cdot \text{h}$, equal to 162 kJ.

When it is assumed, as indicated in Table 1, that during a continuous process at $I = 45\text{ A}$, the flow rate of each of the inflowing solutions is $\tilde{V} = \frac{6\text{ dm}^3}{7\text{ h}} = 0.857\text{ dm}^3/\text{h}$,

the heat capacity is independent from temperature and the data listed in Table 2 are taken and heat losses to the surroundings disregarded, it may be calculated that the emission of the calculated amount of heat causes an approximate increase of the temperature of solutions by 18.5°C :

$$\Delta t = \frac{Q}{\tilde{V} \cdot c_w} = \frac{162}{2.517 \cdot 3.48} = 18.5 \quad (4)$$

where: Q – heat (kJ); \tilde{V} – flow rate (dm^3/h), c_w – heat capacity ($\text{kJ}/(\text{dm}^3 \cdot \text{K})$).

Assuming that the temperature inside the electro-electrodialyser must not exceed 60°C , and that the temperature of the feed solutions is 23°C at the most, and that the (measured under process conditions) voltage drop across the membranes is only ca. 1 V ($0.48 + 0.53\text{ V}$), a single pass system could be used in the process in question provided that the total voltage drop across the solutions does not exceed 1 V (in such case the temperature of solutions would increase to 37°C). The fulfilment of that condition under the assumed salt conversion degree seems unattainable because dilute solutions of sodium sulphate have low electrical conductivity. This is indicated by the values of cell voltage given in Table 1.

Determination of cascade process conditions. The considerations presented provide a compelling argument for adopting a method of processing the Na_2SO_4 solution in a multi-stage (cascade) system, where interstage cooling of the solutions is possible (Fig. 2).

The cascade process may take on the form of a flow-through system (Fig. 2A) or of a flow-through/circulation

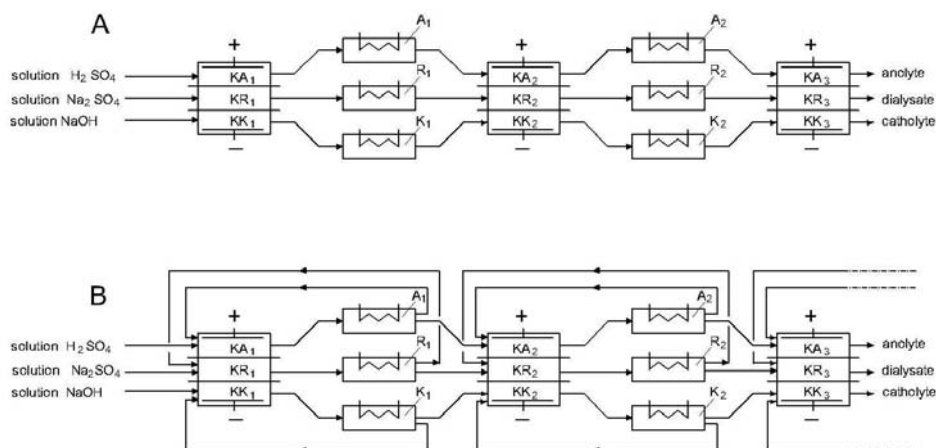


Figure 2. Simplified diagrams of the processing of sodium sulphate solutions using the EED method in a continuous process A – flow-through system, B – circulation and flow-through system KA₁, KA₂,...KA_n – anode chambers of electro-electrodialysers of stage 1,2,...n KR₁, KR₂,...KR_n – dilution chambers of electro-electrodialysers of stage 1,2,...n KK₁, KK₂,...KK_n – cathode chambers of electro-electrodialysers of stage 1,2,...n A₁, A₂,...A_n – anolyte coolers of stage 1, 2, ...n R₁, R₂,...R_n – Na_2SO_4 solution coolers of stage 1,2,...n K₁, K₂,...K_n – catholyte coolers of stage 1, 2, ...n

Table 2. Data for calculating increase of solution temperature

Solution	Inlet		Outlet	
	Flow rate, [dm^3/h]	Heat capacity**, $\text{kJ}/(\text{dm}^3 \cdot \text{K})$	Flow rate, [dm^3/h]	Heat capacity**, $\text{kJ}/(\text{dm}^3 \cdot \text{K})$
Catholyte	0.857	3.33	1.021	3.31
Dialysate	0.857	3.69	0.639	4.16
Anolyte	0.857	3.73	0.857	3.30
Total	2.571	3.58	2.517	3.48 [†]

[†]weighted mean

**heat capacity was interpolated based on data from⁹

system (Fig. 2B) – circulation enables higher flow rates and more efficient dissipation of heat. In a flow-through system the smallest unit consists of two EED stages and one stage of cooling in between (each EED stage corresponds to the single pass system described above), in the flow-through/circulation system the smallest unit consists of one EED stage and one cooling stage. Depending on the size of the plant, every EED stage may consist of one, of several or of dozens of electro-electrodialysers in a parallel arrangement. The plant may have all electro-electrodialysers supplied with direct current in a series (one power source), or each stage may have a separate power supply or other power supply combinations may be applied.

In both systems shown in Figure 2 the conversion of the solutions increases gradually as they flow through subsequent stages, and in the case of seven EED stages the process performance indicators would change as shown in Table 1 – each stage corresponding to each one-hour period indicated. The splitting of a plant into stages must not be done in an indiscriminate way because the number of stages affects EED performance and has an impact on capital expense. These issues are discussed using the data given in Table 1.

If circulation between the chambers of the electro-electrodialysers and the circulation coolers is intense, concentrations of the media tend to equalise, that is to attain a condition of a perfectly mixed reactor. If a plant is in the form of one stage (EED + circulation coolers), then in an KR1 + R1 arrangement the final concentration of SO_4^{2-} must agree with the assumed conversion degree, which corresponds to concentration $< 3.5 \text{ g/dm}^3$. Therefore the EED process takes place under conditions which in Table 1 correspond to $\Delta\tau = 7 \text{ h}$, $Q = 315 \text{ A} \cdot \text{h}$. The cell voltage is ca. 16.1 V, current efficiency of sulphuric acid is 48.67%, and specific electric energy consumption is $12.49 \text{ kW} \cdot \text{h/kg Na}_2\text{SO}_4$.

If a plant is split into two stages, then it must be provided with two cooling stages, which increases the capital expense. But on the other hand the current efficiency of H_2SO_4 attained in the first stage (ca. 60.97%) is higher than in the second stage (ca. 48.67%) and the plant maintains the same production capacity with a lower number of electro-electrodialysers: if that number in the previously described single-stage system is, for instance, 100, then in a two-stage system it would be 92, and the specific electric energy consumption is $7.56 \text{ kW} \cdot \text{h/kg Na}_2\text{SO}_4$.

If the plant is split into three identical stages, then it must be provided with three stages of circulation cooling, and the number of electro-electrodialysers providing the same production capacity is 90, and the specific electric energy consumption is $6.49 \text{ kW} \cdot \text{h/kg Na}_2\text{SO}_4$ (see Fig. 3).

Further increase of the number of stages entails reduction of the beneficial effects (Fig. 3). With seven stages, the required number of electro-electrodialysers drops to 87, and the specific electric energy consumption is $5.28 \text{ kW} \cdot \text{h/kg Na}_2\text{SO}_4$.

CONCLUSIONS

The results of a batch recirculation EED process in which a high salt conversion degree was obtained allows for analysis of the factors affecting the design of a continuous process for obtaining the same results (concentration of products and salt conversion degree). Use of selected ion-exchange membranes limits process

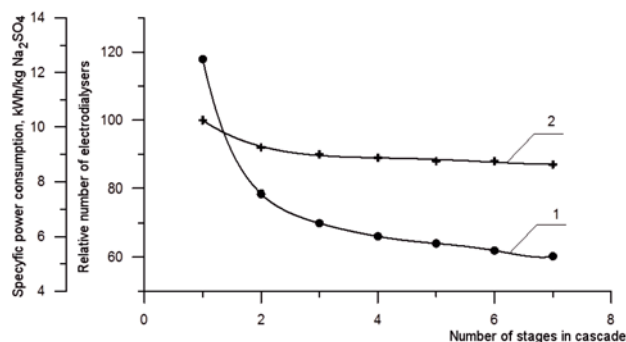


Figure 3. The relationship between specific electric power consumption (1) and relative number of electro-electrodialysers in a plant (2) and the number of stages in a series/circulation system. (Assumption adopted: 100 apparatus in one stage)

temperature to below 60°C . This excludes a single pass of solutions through the electro-electrodialyser under an assumed constant current density, allowing for a multi-stage system with interstage cooling of the solutions. Increasing the number of stages in the cascade has a positive effect on specific electric energy consumption. However, the number of stages utilized should always be determined on the basis of an economic analysis which takes into account capital expense as well as operating cost (cost of electric energy used by EED and pump drives, etc.). Two extreme cases may be considered.

1) If a high conversion degree of sodium sulphate is required (low concentration of sodium sulphate in the dialysate), splitting the plant into a higher number of stages, e.g. $4 \div 7$, may prove advantageous. This may entail a certain increase in capital expense, but poorer performance (low current efficiency, high energy consumption) is observed only in the last stage or two of the plant.

2) If the required final concentration of the SO_4^{2-} ions in dialysate is relatively high, then the EED process can operate under conditions ensuring better performance. Operating a plant under conditions of low concentrations, high voltages and low efficiency can be avoided by, for instance, concentrating the partly reacted dialysate¹⁰ before recycling it for EED processing. In such a case the number of stages may be considerably reduced (to $2 \div 3$).

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