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DEVELOPMENT OF A METHOD FOR PROCESSING CONCENTRATES FROM WATER DESALINATION PROCESSES TO OBTAIN ALUMINUM COAGULANTS

The process of processing concentrates and eluates formed during desalination of natural surface, artesian, and mine waters with increased mineralization by reverse osmosis and ion exchange methods has been studied. Specifically, this study examined the processes of processing sodium chloride solutions and mixtures of sodium chloride and sodium sulfate via electrodialysis, and obtaining alkaline and aluminum salt solutions, were examined.

Aluminum salts were produced using AD-31 aluminum anodes. A stainless-steel plate of grade 12H18N10T was used as the cathode. The process was conducted at current densities ranging from 1.67 to 8.33 A/dm^2 in two- and three-chamber electrolyzers using MK-40 cation-exchange membranes and MA-41 anion-exchange membranes. In all experiments, alkaline solutions were obtained in the cathode region and aluminum salt solutions in the anode region. When using a three-chamber electrolyzer, the salt solution was placed in the working chamber, separated by a cation-exchange membrane from the catholyte and an anion-exchange membrane from the anode zone. During electrolysis, alkali concentration occurred in the catholyte and aluminum salts in the anolyte. In the three-chamber electrolyzer, desalination occurred in the working chamber due to the diffusion of sodium ions through the cation-exchange membrane into the catholyte and the diffusion of anions (chlorides and sulfates) through the anion-exchange membrane into the anode area. Aluminum oxidation in the anode area resulted in the formation of Al^{3+} cations, and in the presence of chlorides, aluminum chloride was formed. Hydrolysis of aluminum chloride partially produced aluminum hydroxychlorides, predominantly forming 1/3 aluminum hydroxychloride. Before electrolysis, the anode chamber pH was adjusted to 2.5 with hydrochloric acid. During electrolysis, the pH was maintained at 2.5–3 due to electrode reactions. The salt content in the working chamber decreased to 2–20 mg-eq/dm^3. In a two-chamber electrolyzer, electrolysis produced alkali in the catholyte and aluminum chloride in the anolyte. Conversion of sodium chloride in the anolyte was limited due to poisoning of the cation-exchange membrane by aluminum ions.

Keywords: *demineralization, concentrate, reverse osmosis, ion exchange, electrolysis, electrodialysis, coagulant, aluminum chloride, membrane.*

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1. Introduction

The development of efficient water desalination technologies is currently a highly relevant issue. This is driven by the growing demand for softened or desalinated water in industrial and municipal water and heat supply systems, as well as for deeply demineralized water in the energy sector. Given the limited availability of freshwater resources, the challenge of demineralizing seawater and artesian water has become particularly pressing. Desalination of highly mineralized mine water is also considered expedient to expand the sources of potable and industrial water supply. Moreover, the desalination of industrial and mine wastewater is essential for protecting aquatic ecosystems from excessive mineralization.

Outdated water treatment and wastewater purification technologies, which are unsuitable for effective demineralization, are increasingly being replaced by high-efficiency membrane technologies that offer superior water purification quality. These technologies are no longer limited to small, localized polishing units; large-capacity membrane modules are now frequently deployed for full-scale water treatment. Their high effectiveness in purifying low-mineralized water allows them to be used directly at consumption sites, utilizing local sources such as artesian and mine waters. This approach is significantly more cost-effective than transporting water over long distances and helps preserve water quality by avoiding extended transport pipelines.

The widespread implementation of desalination technologies, such as ion exchange [1–3], membrane filtration [4, 5], ceramic membranes [6], and electrodialysis [7, 8], is hindered by the lack of efficient methods for treating the resulting eluates and concentrates. Challenges arise even when discharging concentrates with a mineralization level above 1000 mg-eq/dm^3 into the sea, and discharge into freshwater rivers and lakes is strictly prohibited.

Existing methods for treating highly mineralized concentrates include solution evaporation and sludge drying [9], freeze crystallization [10, 11], reagent-based techniques [12, 13], and electrolysis for the production of active chlorine and its derivatives [14–16].

However, these methods have significant drawbacks. Evaporation, freeze crystallization, and sludge drying are highly energy-intensive. Additionally, mineral salt sludge can only be disposed of in specially equipped landfills, which substantially increases disposal costs. Reagent-based processing is effective only for sulfate-rich concentrates and requires the use of expensive aluminum hydroxy-sulfates and hydroxy-chlorides. Electrolytic treatment of sodium chloride solutions to produce active chlorine and related oxidants is only feasible with expensive inert anodes (platinum, gold, or ruthenium oxide-coated titanium) and requires a NaCl concentration above 100 g/dm^3. This makes it unsuitable for processing reverse osmosis brine, which typically has a mineralization level between 4–20 g/dm^3, and in some cases up to 40–45 g/dm^3.

A promising alternative is the electrochemical decomposition of sodium chloride solutions using aluminum anodes to produce caustic alkali and aluminum chloride. This method offers several advantages over existing technologies, as it enables the use of readily available aluminum anodes and allows for the processing of sodium chloride solutions with concentrations ranging from 1 to 150 g/dm^3, resulting in the production of valuable reagents such as aluminum chloride and caustic alkali. Aluminum chloride and its partially hydrolyzed forms are highly effective coagulants [17], while alkali is a widely used reagent. This approach has not previously been applied to the processing of sodium chloride, the main component of reverse osmosis brine. Furthermore, the electrodialysis of such solutions in two- and three-chamber electrolyzers with aluminum anodes remains largely unexplored. As a result, studying the electrodialysis of sodium chloride solutions using aluminum anodes is of considerable scientific and practical interest.

The aim of this study is to develop a method for processing desalination brine concentrates via electrodialysis to produce aluminum coagulants and caustic alkali.

To address the scientific challenge of creating an efficient method for salt solution processing, the following tasks were set:

- to evaluate the efficiency of electrodialytic processing of sodium chloride solutions in a two-chamber electrolyzer using a cation-exchange membrane and an aluminum anode to obtain caustic alkali and aluminum chloride;
- to study the electrochemical desalination of sodium chloride solutions in a three-chamber electrolyzer with an aluminum anode for the same purposes;
- to determine how electrolysis efficiency depends on NaCl concentration, anodic current density, and electrolysis duration;
- to investigate the electrochemical desalination of mixed sodium chloride and sodium sulfate solutions in a three-chamber electrolyzer with an aluminum anode;
- to assess the effect of salt concentration in the working chamber on the current efficiency of caustic alkali production and the resulting mixture of aluminum chloride and aluminum sulfate.

2. Materials and Methods

The object of this study was the recycling of concentrates and eluates generated during the desalination of natural surface, artesian, and mine waters with elevated mineralization using reverse osmosis and ion exchange methods.

Research on the electrodialytic decomposition of salts in aqueous solutions was carried out using two- and three-chamber electrolyzers (Fig. 1, 2), with each experiment repeated three times ($n=3$).

Electrolysis of a sodium chloride solution with a concentration of 1900 mg-eq/dm^3 was conducted in a two-chamber electrolyzer with an MK-40 membrane at a current density of 8.33 A/dm^2. The sodium chloride solution was placed in the anode chamber, while the cathode chamber contained an alkaline solution with a concentration of 63 mg-eq/dm^3. During electrolysis, the following parameters were monitored: time, voltage, current, alkalinity in the cathode chamber, and aluminum ion concentration in the anode chamber. The process continued until the current dropped from 1 A to 0.2 A. As a result, an alkaline solution was obtained in the catholyte, and aluminum chloride formed in the anolyte.

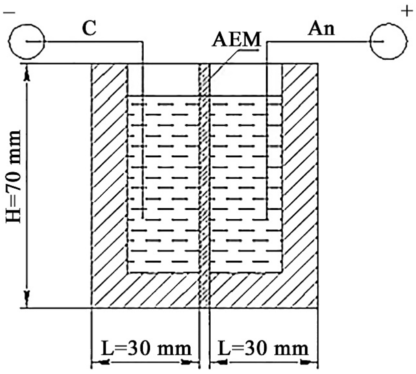

Fig. 1. Two-chamber open electrolyzer

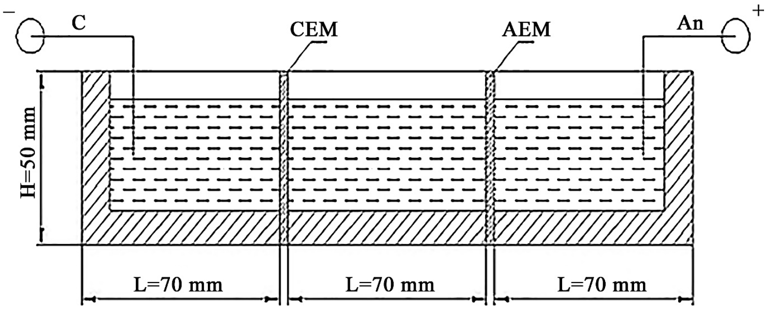

Fig. 2. Three-chamber open electrolyzer

Electrolysis of sodium chloride solutions and mixtures of sodium chloride and sodium sulfate was performed in a three-chamber electrolyzer using MK-40 cation-exchange and MA-41 anion-exchange membranes. An AD-31 aluminum plate was used as the anode, and a 12X18H10T stainless steel plate served as the cathode. The process was carried out at a current density of 4.14–8.33 A/dm^2. The cathode chamber was filled with a diluted alkaline solution ($[NaOH]=$ $=50–80$ mg-eq/dm^3), and the anode chamber was filled with an acidified sodium chloride solution ($[NaCl]=10$ mg-eq/dm^3, $K=8.8$ mg-eq/dm^3). The working chamber was filled either with a sodium chloride solution ($[NaCl]=10.0–111.2$ g/dm^3) or with a mixture of sodium chloride and sodium sulfate ($[NaCl]=25.4$ g/dm^3, $[Na_2SO_4]=44.42$ g/dm^3). The following parameters were monitored during electrolysis: time, current, voltage, catholyte alkalinity, alkalinity and chloride/sulfate concentrations in the working chamber, and chloride, aluminum, and sulfate concentrations in the anode chamber.

All data were obtained from three parallel experiments. To maintain a stable temperature of 25–30°C during the process, the electrolyzers were placed in a 25°C water bath.

The degree of conversion of sodium chloride and sodium sulfate was calculated using the following formula

$$D=\frac{C_{init}-C_{res}}{C_{init}}\cdot 100\%, \tag{1}$$

where C_{init} is the initial concentration of chlorides or chlorides and sulfates in the working chamber solution, mg-eq/dm^3; C_{res} denotes the residual concentration of chlorides or a mixture of sulfates and chlorides in the working solution of a three-chamber electrolyzer.

For a two-chamber electrolyzer, the conversion degree of sodium chloride was calculated based on the reduction in sodium ion concentration in the anolyte. In this case, C_{init} is the initial concentration of sodium ions in the anolyte, C_{res} is the residual concentration of sodium ions in the anolyte. The initial sodium ion concentration is given as C_{init} = [NaCl], mg-eq/dm^3

$$C_{res} = C_{init} - \Delta Alk, \tag{2}$$

where ΔAlk is the change in alkalinity of the catholyte over time, mg-eq/dm^3

$$\Delta Alk = Alk - Alk_{init}, \tag{3}$$

where Alk is the alkalinity of the catholyte at a given time during electrolysis, mg-eq/dm^3; Alk_{init} is the initial alkalinity of the catholyte, mg-eq/dm^3.

The current efficiency (CE, %) was determined using the following formula, which is based on Faraday's law as the ratio of the actual amount of transferred or generated substance to its theoretical value

$$CE = \frac{m_{act}}{m_t} \cdot 100\%, \tag{4}$$

where m_{act} is the actual amount of transferred or produced substance, in gram-equivalents (g-eq); m_t is the theoretically possible amount of the substance, in gram-equivalents (g-eq).

The actual amount of transferred substance was calculated from the change in concentration and the solution volume

$$m_{act} = \left(C_{init} - C_{res}\right) \cdot V_s, \tag{5}$$

where V_s is the volume of the solution, dm^3.

The theoretical amount of the substance that could be transferred or produced was calculated as

$$m_t = K_F \cdot I \cdot t, \tag{6}$$

where K_F is the electrochemical equivalent (0.03731 $\frac{\text{g-eq}}{(\text{A}\cdot\text{h})}$); I is the current strength, in amperes (A); t is the duration of electrolysis, in hours (h).

The experimental data were processed mathematically according to the method presented in [18].

3. Results and Discussion

3.1. Research results

At the initial stage of the study, electrolysis of a sodium chloride solution was performed in a two-chamber electrolyzer equipped with an MK-40 cation-exchange membrane, a cathode made of alloyed steel, and an aluminum anode. The two-chamber design has an advantage over the three-chamber configuration due to better electrical conductivity and lower energy consumption for heating. Additionally, the MK-40 membrane has significantly higher conductivity for monovalent sodium cations than for trivalent aluminum ions. The results are presented in Fig. 3, 4.

As shown in Fig. 3, the electrolysis process demonstrated good efficiency. However, the current efficiencies for both alkali and aluminum remained in the 50–80% range only during the first two hours. After that, the values dropped to 30–8%, and by the ninth hour, the current (Fig. 4) had fallen to 0.2 A, effectively stopping the process. This was attributed to cation-exchange membrane fouling by aluminum ions, which blocked the gel layer and reduced membrane conductivity.

Overall, an aluminum chloride current efficiency of 60% was achieved. The resulting $AlCl_3$ concentration reached 54 g/dm^3 (5.4%), which is insufficient for coagulant use. Commercial aluminum hydroxychloride coagulants typically contain up to 16% Al_2O_3.

Next, the electrolysis process was conducted in a three-chamber electrolyzer. The cathode compartment was filled with a dilute alkali solution (Alk=50–80 mg-eq/dm^3), and the anolyte contained a weakly acidified NaCl solution (pH 2.5–2.8). A small amount of alkali and salt was added at the start to ensure conductivity. Acidic conditions in the anolyte were maintained to prevent hydrolysis of aluminum chloride and passivation of the aluminum anode. The initial sodium chloride concentration was 10 g/dm^3, simulating reverse osmosis brine conditions (Fig. 5).

Due to the rapid depletion of NaCl in the working chamber, the solution was replaced every 3 hours. After 9 hours, the catholyte alkalinity reached 644 mg-eq/dm^3, and the aluminum chloride concentration in the anolyte was 630 mg-eq/dm^3. Current efficiencies were: alkali – 62–66%, chloride transfer – 67–68%, and aluminum chloride current efficiency – 66–69% (Fig. 6). The overall NaCl conversion reached 97%.

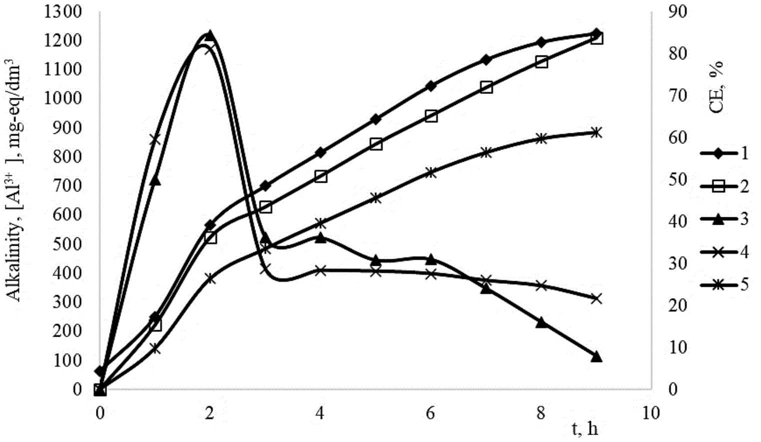

Fig. 3. Changes in solution characteristics in the catholyte and anolyte, and process parameters over time during electrolysis of a sodium chloride solution (concentration 111.2 g/dm^3) in a two-chamber electrolyzer (MK-40 membrane), current 1 A (j=8.33 A/dm^2): 1 – alkalinity in the catholyte; 2 – aluminum ion concentration in the anolyte; 3 – current efficiency for alkali; 4 – current efficiency for aluminum; 5 – NaCl conversion rate

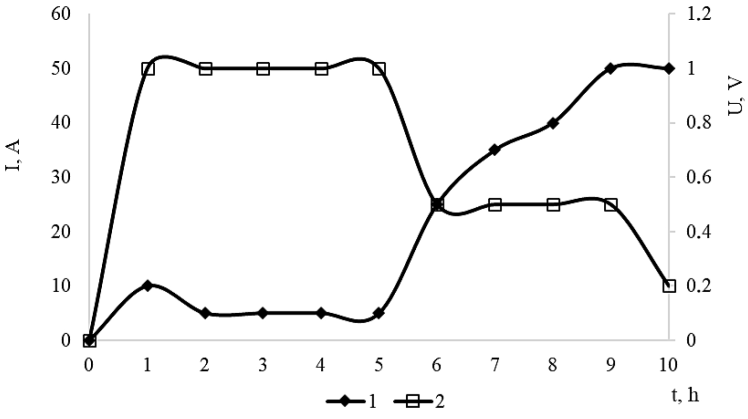

Fig. 4. Changes in voltage and current over time during electrolysis of a NaCl solution ([NaCl] = 111.2 g/dm^3) in the anolyte and alkali production in the catholyte (Alk_{init}=65 mg-eq/dm^3): 1 – voltage; 2 – current

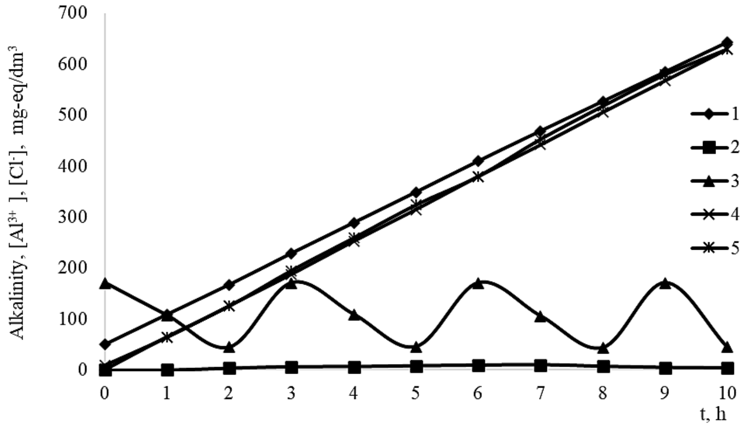

Fig. 5. Changes in alkalinity, chloride concentration, and aluminum concentration during electrolysis of a NaCl solution ($[NaCl]=10$ g/dm^3) in a three-chamber electrolyzer (MK-40 and MA-41 membranes) with an AD-31 aluminum anode; analyte acidity 8.8 mg-eq/dm^3 (pH 3.1); ($S_a=S_k=12$ cm^2; $I=0.5$ A; $j=4.17$ A/dm^2): 1 – catholyte alkalinity; 2 – working chamber alkalinity; 3 – chloride concentration in the working chamber; 4 – chloride concentration in the anolyte; 5 – aluminum concentration in the anolyte

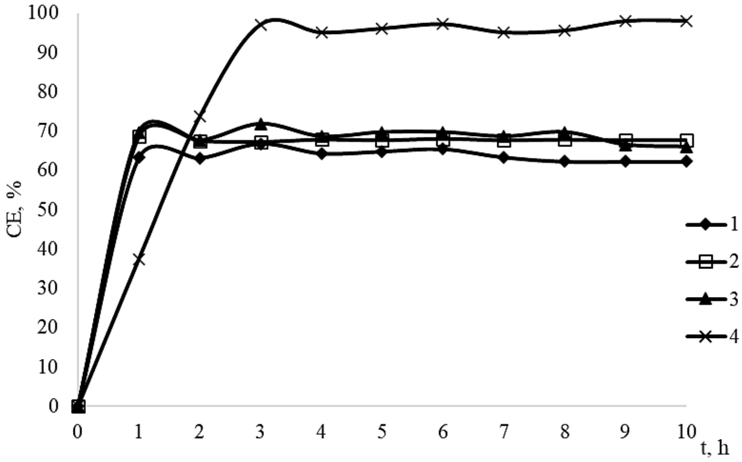

Fig. 6. Process parameter changes over time in a three-chamber electrolyzer (MK-40 and MA-41 membranes) with an AD-31 aluminum anode; analyte acidity 8.8 mg-eq/dm^3 (pH 3.1); ($S_a=S_k=12$ cm^2; $I=0.5$ A; $j=4.17$ A/dm^2): 1 – current efficiency for alkali; 2 – current efficiency for chloride transfer; 3 – current efficiency for aluminum dissolution; 4 – NaCl conversion rate

To shorten experiment time, and based on previous studies [19], subsequent tests used an initial NaCl concentration of 100 g/dm^3. Electrolysis was conducted in a three-chamber electrolyzer with $[NaCl]=1700$ mg-eq/dm^3, $I=0.5$ A, $j=4.17$ A/dm^2, using an aluminum anode (Fig. 7, 8). The working solution was replaced as NaCl was depleted. Aluminum concentration in the anolyte exceeded that of chloride during the first 12 hours.

As shown by curve 5 in Fig. 7, aluminum ion concentration in the anolyte exceeded that of chloride during the first 12 hours. This indicates significant chemical dissolution of aluminum. The anode underwent electrochemical oxidation, while hydrogen reduction occurred at the cathode. In acidic media (pH 2–3), aluminum dissolution was enhanced without passivation, increasing current efficiencies.

Current efficiency for Al^{3+} exceeded 100% due to simultaneous chemical dissolution

$$2Al+6H_2O=2Al_3^{+}+6OH^{-}+3H_2\uparrow. \qquad (7)$$

Alkalinity increased slowly during the first 11 hours, likely due to acidification from water oxidation:

$$2H_2O-4e=O_2+4H^{+}. \qquad (8)$$

$$OH^{-}+H^{+}=H_2O. \qquad (9)$$

By hour 12, aluminum reached 3111 mg-eq/dm^3 and chloride 2355 mg-eq/dm^3, indicating formation of $Al(OH)Cl_2$ (~756 mg-eq/dm^3).

As NaCl concentration dropped, OH^- diffusion into the anolyte increased, raising its alkalinity and initiating hydrolysis:

$$Al(OH)Cl_2+2OH^{-}=Al(OH)_3+2Cl^{-}, \qquad (10)$$

$$AlCl_3+3OH=Al(OH)_3+3Cl^{-}. \qquad (11)$$

Hydrolysis also occurred via water and acidification:

$$Al(OH)Cl_2+2H_2O=Al(OH)_3+2HCl, \qquad (12)$$

$$AlCl_3+3H_2O=Al(OH)_3+3HCl. \qquad (13)$$

Amorphous aluminum hydroxide formed, while electrolysis continued to increase aluminum concentration.

At hour 17, $[Al^{3+}]=3350$ mg-eq/dm^3, $[Cl^-]=3236$ mg-eq/dm^3, resulting in a stable $AlCl_3$ solution containing minor amounts of aluminum hydroxychloride. Alkali reached 1500 mg-eq/dm^3 at hour 8 and 1450 mg-eq/dm^3 at hour 17. NaCl dropped from 1700 to 75 mg-eq/dm^3 at hour 8 (95% conversion), and to 8 mg-eq/dm^3 by hour 17 (99.5%, Fig. 8).

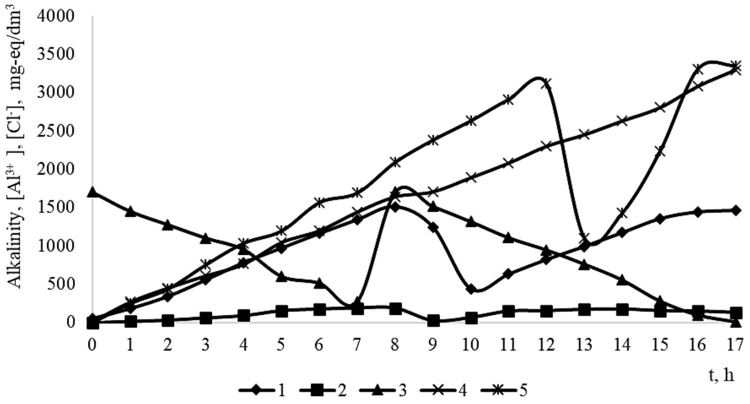

Fig. 7. Changes in solution parameters during electrolysis of NaCl ($[NaCl]=100$ g/dm^3) in a three-chamber electrolyzer with aluminum anode ($I=0.5$ A; $j=4.17$ A/dm^2): 1 – catholyte alkalinity; 2 – working chamber alkalinity; 3 – chloride in working chamber; 4 – chloride in anolyte; 5 – aluminum in anolyte

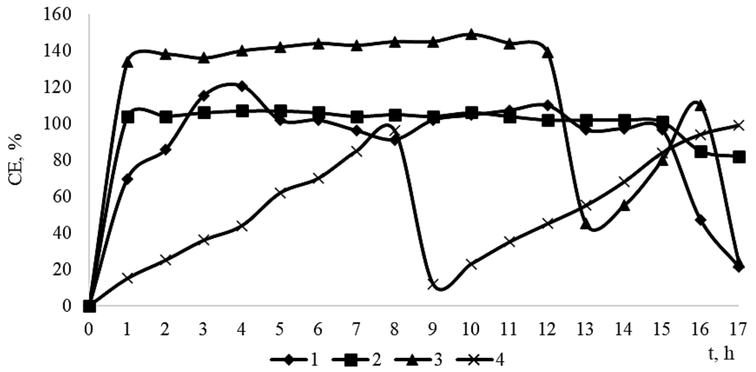

Fig. 8. Process parameters during electrolysis of NaCl ([NaCl] = 100 g/dm^3) in a three-chamber electrolyzer with aluminum anode (I = 0.5 A; j = 4.17 A/dm^2): 1 – alkali current efficiency; 2 – chloride transfer; 3 – aluminum dissolution; 4 – NaCl conversion

Fig. 8 confirms current efficiencies for alkali and chloride near or above 100%. Aluminum dissolution efficiency peaked at 140% due to chemical contributions.

Similar results were obtained with a more concentrated solution ([NaCl] = 1900 mg-eq/dm^3), j = 8.33 A/dm^2 (I = 1 A), as shown in Fig. 9, 10.

The process proceeded with greater intensity compared to electrolysis at a current density of 4.17 A/dm^2. A 99.9% conversion of sodium chloride was achieved within 5 hours. An aluminum chloride solution was obtained in the anode compartment at a concentration of 1956 mg-eq/dm^3, and an alkaline solution in the cathode compartment with a concentration of 1960 mg-eq/dm^3. It should be noted that the current efficiencies of the main processes in this case were lower than those observed at an anode current density of 4.17 A/dm^2. This is due to the fact that, with increasing anode current density, the contribution of the chemical dissolution of aluminum decreases.

It is known that mineralized waters often contain not only chlorides but also sulfates. There are known methods of sulfate removal from water with reagent recovery [20]. These methods allow for the separation of chlorides and sulfates. However, sulfate precipitation is incomplete, and the precipitation process itself involves the use of expensive reagents, while the presence of sulfates practically does not affect the effectiveness of aluminum coagulants. On the other hand, electrochemical methods are quite often used for the treatment of sodium sulfate-containing liquid waste. Therefore, it is reasonable to process mixtures of sodium chloride and sodium sulfate solutions via electrolysis to obtain mixed aluminum chloride-sulfate salts, which are also effective coagulants.

The results of electrolysis of a mixed sodium chloride and sodium sulfate solution are presented in Fig. 11, 12.

As shown in Fig. 11, within 5 hours, the concentration of chlorides in the working chamber decreased from 435 to 5 mg-eq/dm^3, and sulfates from 625 to 20 mg-eq/dm^3. The extraction degree for chlorides during this time reached 98.8%, and for sulfates, 96.8% (Fig. 12). This is due to the fact that, because of the high hydration of sulfates, the anion-exchange membrane has an electrical conductivity for them close to that for chlorides. During this time, the alkalinity of the catholyte reached 1000 mg-eq/dm^3, and the aluminum ion concentration was around 1030 mg-eq/dm^3 (Fig. 11). The pH of the anolyte environment was between 2.7 and 3.0.

As in the case of electrolysis of sodium chloride solutions, the current efficiencies of soluble aluminum, alkali, and the total diffusion of chlorides and sulfates exceeded theoretical values. This is, as with sodium chloride, due to contributions from aluminum's chemical dissolution and hydrogen evolution. Overall, the process of obtaining aluminum coagulant from a sodium chloride and sulfate mixture solution does not differ from the process involving only sodium chloride solution.

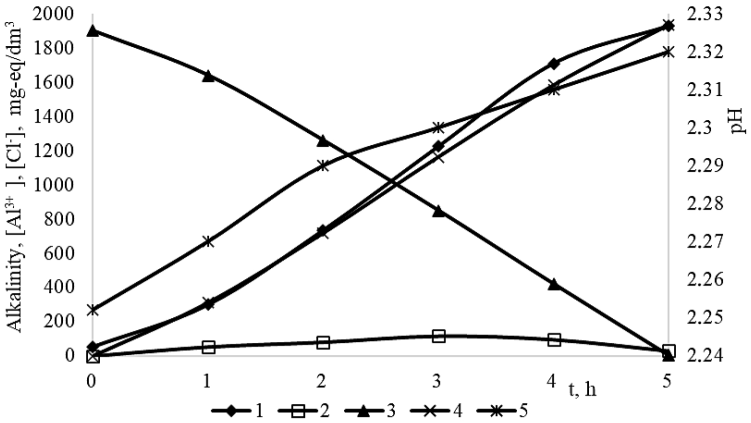

Fig. 9. Dependence of solution characteristics and process parameters on electrolysis time of sodium chloride solution ([NaCl] = 111.2 g/dm^3) in a three-chamber electrolyzer (MK-40 and MA-41 membranes) using an aluminum anode, current of 1 A (j = 8.33 A/dm^2), initial alkalinity of catholyte 54 mg-eq/dm^3, initial acidity of anolyte 9.0 mg-eq/dm^3, pH 2.522: 1 – alkalinity in the cathode compartment; 2 – alkalinity in the working chamber; 3 – chloride concentration in the working chamber; 4 – aluminum concentration in the anolyte; 5 – anolyte pH

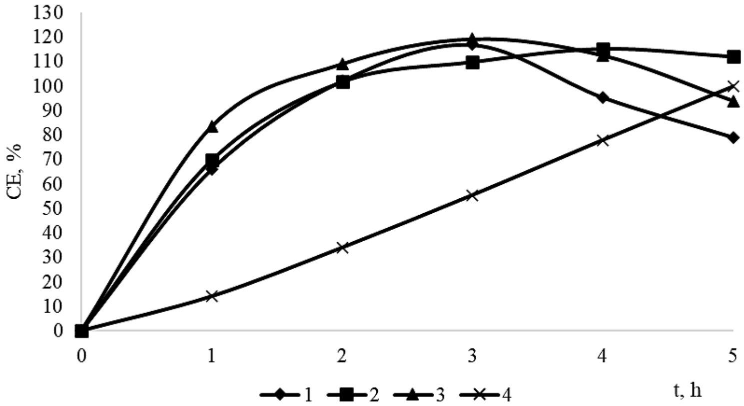

Fig. 10. Changes in process parameters with electrolysis time of sodium chloride ([NaCl] = 111.2 g/dm^3) in a three-chamber electrolyzer using an aluminum anode, current of 1 A (j = 8.33 A/dm^2), initial alkalinity of the catholyte 54 mg-eq/dm^3, initial acidity of the anolyte 9.0 mg-eq/dm^3, pH 2.522: 1 – current efficiency for alkali production; 2 – aluminum dissolution; 3 – chloride diffusion into the anode compartment; 4 – NaCl conversion degree

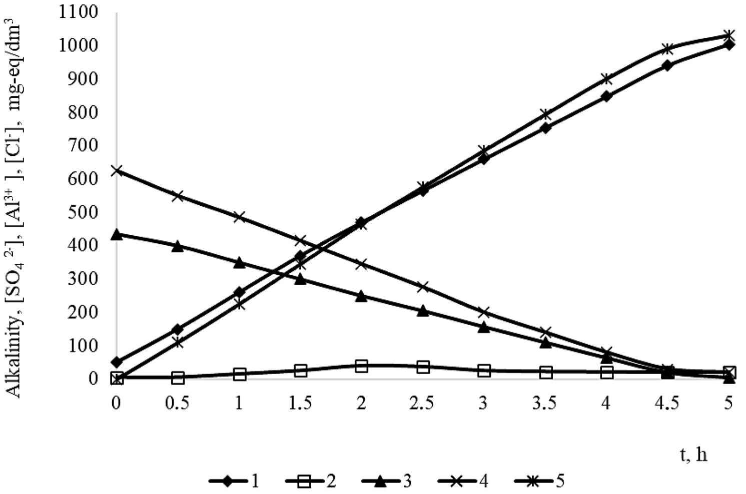

Fig. 11. Dependence of solution characteristics on electrolysis time of a sodium chloride and sulfate mixture ([NaCl] = 435 mg-eq/dm^3; [Na_2SO_4] = 625 mg-eq/dm^3) in a three-chamber electrolyzer (MK-40 and MA-41 membranes) with a current density of 1.17 A/dm^2 (I = 0.5 A), initial catholyte alkalinity 50 mg-eq/dm^3, working solution 50 mg-eq/dm^3, initial anolyte acidity 8.8 mg-eq/dm^3, pH 2.70: 1 – catholyte alkalinity; 2 – alkalinity of the working solution; 3 – chloride concentration in the working chamber; 4 – sulfate concentration in the working chamber; 5 – aluminum ion concentration in the anolyte

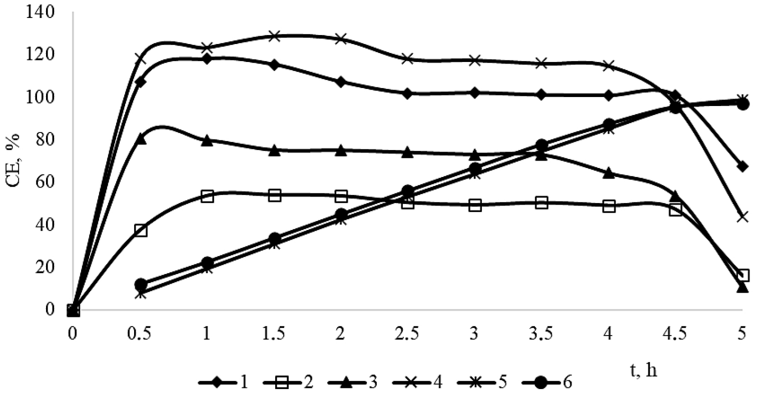

Fig. 12. Dependence of process parameters on electrolysis time of a NaCl and Na_2SO_4 solution ([NaCl] = 435 mg-eq/dm^3; [Na_2SO_4] = 625 mg-eq/dm^3) in a three-chamber electrolyzer with a current density of 1.17 A/dm^2 (I = 0.5 A), initial alkalinity of the catholyte 50 mg-eq/dm^3, working solution 50 mg-eq/dm^3, initial acidity of the anolyte 8.8 mg-eq/dm^3, pH 2.70: 1 – current efficiency for alkali production; 2 – chloride diffusion; 3 – sulfate diffusion; 4 – aluminum ion diffusion; 5 – sodium chloride conversion degree; 6 – sodium sulfate conversion degree

Based on the obtained experimental results, mathematical data processing was performed using variational statistics (Table 1).

Table 1

Results of Mathematical Data Processing by the Method of Variation Statistics

Figure No.		Investigated Parameter	Units	ΔX	E_x, %
1		2	3	4	5
Fig. 3		Alk_{cat}	mg-eq/dm^3	0.599	0.785
		$[Al^{3+}]_{an}$	mg-eq/dm^3	0.987	0.461
Fig. 4		I	A	1.012	0.399
		U	V	0.951	0.854
Fig. 5		Alk_{cat}	mg-eq/dm^3	0.603	0.549
		Alk_{work}	mg-eq/dm^3	0.177	2.523
		$[Cl^{-}]_{work}$	mg-eq/dm^3	0.469	0.651
		$[Cl^{-}]_{an}$	mg-eq/dm^3	0.893	0.979
		$[Al^{3+}]_{an}$	mg-eq/dm^3	0.994	1.101
Fig. 7	I	Alk_{cat}	mg-eq/dm^3	1.077	0.315
		Alk_{work}	mg-eq/dm^3	0.450	1.365
		$[Cl^{-}]_{work}$	mg-eq/dm^3	0.306	0.024
		$[Cl^{-}]_{an}$	mg-eq/dm^3	2.760	0.612
		$[Al^{3+}]_{an}$	mg-eq/dm^3	2.512	0.571
Fig. 7	II	Alk_{cat}	mg-eq/dm^3	0.450	0.095
		Alk_{work}	mg-eq/dm^3	0.854	1.275
		$[Cl^{-}]_{work}$	mg-eq/dm^3	0.618	0.047
		$[Cl^{-}]_{an}$	mg-eq/dm^3	0.645	0.031
		$[Al^{3+}]_{an}$	mg-eq/dm^3	0.412	0.014
Fig. 9		Alk_{cat}	mg-eq/dm^3	0.423	0.056
		Alk_{work}	mg-eq/dm^3	0.968	1.153
		$[Cl^{-}]_{work}$	mg-eq/dm^3	0.776	0.089
		$[Al^{3+}]_{an}$	mg-eq/dm^3	0.764	0.097
		pH	mg-eq/dm^3	0.153	0.021
Fig. 11		Alk_{cat}	mg-eq/dm^3	0.042	0.014
		Alk_{work}	mg-eq/dm^3	0.521	0.654
		$[Cl^{-}]_{work}$	mg-eq/dm^3	0.988	0.068
		$[SO_4^{2-}]_{work}$	mg-eq/dm^3	0.741	0.749
		$[Al^{3+}]_{an}$	mg-eq/dm^3	0.104	0.351

3.2. Discussion of the obtained results

It is known that previously studied and described methods for processing and utilizing concentrates from reverse osmosis water purification, as well as wastes from other desalination processes –

such as solution evaporation and sludge drying [9], reagent-based methods [12, 13], and electrolysis for producing active chlorine and its derivatives [14–16] – have serious drawbacks. A much simpler and more efficient method is desalination of sodium chloride or sodium sulfate solutions by electrodialysis, using readily available aluminum anodes in two- and three-chamber electrolyzers with ion-exchange membranes, resulting in the production of alkali, hydrogen, and aluminum chloride. Alkali is a valuable reagent, hydrogen is a clean fuel that does not contribute to greenhouse gas emissions, and aluminum chloride and sulfate are effective coagulants widely used in water treatment.

It is known that high-performance coagulants, such as aluminum hydroxychlorides [17], are produced from metallic aluminum in weakly acidic solutions, typically using aluminum shavings and dilute hydrochloric acid. However, in chemical aluminum dissolution, maintaining the solution's pH is difficult. At high acidity, the process proceeds too rapidly, posing an explosion risk. At low acidity, solution alkalization occurs due to aluminum dissolution, leading to aluminum chloride hydrolysis, surface passivation, and a slowdown of metal dissolution. Furthermore, the cost of reagents increases due to the use of acid. Hydrochloric acid is also a volatile, highly toxic, and aggressive reagent. Thus, obtaining aluminum chloride from water treatment waste, along with valuable by-products, is a competitive process. This also addresses the challenge of high-mineralization wastewater, which limits modern desalination processes.

Despite the simplicity of salt solution recycling methods, they are under-researched, and implementation may face issues, particularly with reducing energy consumption by increasing the current efficiency of reaction products.

An important advantage of the process is that during electrolysis of sodium chloride solutions in two- or three-chamber electrolyzers, the acidity in the anolyte self-regulates due to aluminum dissolution. If acidity increases, aluminum dissolves faster, compensating for it. If acidity drops, anodic water oxidation increases acidity. Also, alkali is generated in the catholyte. Hydrogen gas collected from the cathode can be used as a clean fuel.

However, as seen in Fig. 3, 4, when using a two-chamber electrolyzer with an MK-40 cation-exchange membrane, electrochemical aluminum dissolution is effective only in the first few hours. Then, aluminum concentration in the anolyte plateaus, and the current efficiency of alkali and aluminum chloride production drops from 50–87% to 35–10%. This is due to leading to blockage of membrane fixed charges by hydrated Al^{3+} ions, which enter the tight layer of counterions near negatively charged centers (sulfate anions). These ions, along with strongly bound water, block the anionic groups, significantly reducing the membrane's conductivity. After 9 hours of electrolysis, the current drops to 0.2 A, while the voltage rises to 50 V, effectively stopping the electrolysis. Despite certain advantages of two-chamber electrolyzers, including lower system resistance, they are not suitable for aluminum chloride production from salt solutions.

In contrast, three-chamber electrolyzers, despite their higher electrical resistance, offer several benefits. When the salt solution is placed in the middle (working) chamber, desalination occurs via sodium cation diffusion to the cathode and chloride or sulfate anion diffusion to the anode. The MK-40 cation-exchange membrane has high conductivity for sodium cations, while the MA-41 anion membrane effectively conducts chloride and sulfate anions. This is confirmed by the high desalination degrees observed in almost all experiments (Fig. 6, 8, 10, 12), where desalination reached nearly 100% regardless of the initial salt concentration.

For example, with an initial NaCl concentration of 10 g/dm^3 in the working chamber and anodic current density of 4.17 A/dm^2, the current efficiencies were: alkali – 62–66%, chloride diffusion – 67–68%, and aluminum dissolution – 66–69%. At a higher initial NaCl concentration of 100 g/dm^3, the efficiencies over 10 hours were: alkali and chloride diffusion – ~100%, and aluminum dissolution – 137–142% (Fig. 8). This is likely due to enhanced conductivity and ion transport at higher concentrations.

In both experiments, NaCl solution in the working chamber was periodically replaced when its concentration dropped to 3–5 mg-eq/dm^3. In Fig. 5, replacement occurred every 2–3 hours; in Fig. 7, after 8 hours of electrolysis.

When increasing the current density to 8.33 A/dm^2, the electrolysis rate significantly increased. After 5 hours, chloride concentration in the working chamber dropped to 2 mg-eq/dm^3, while in the anolyte it reached 1898 mg-eq/dm^3, alkali in the catholyte – 1960 mg-eq/dm^3, and aluminum ion concentration in the anode region – 1956 mg-eq/dm^3. These values are about twice as high as those at 4.17 A/dm^2. Moreover, there was no significant excess of Al^{3+} over chloride in the anolyte, suggesting that the contribution of chemical aluminum dissolution to aluminum chloride formation decreased significantly. The resulting aluminum chloride solution was stable and resistant to hydrolysis.

Fig. 11, 12 show that the electrolysis of mixed NaCl and Na_2SO_4 solutions proceeds similarly to NaCl electrolysis, producing alkali, hydrogen, and a mixture of aluminum chloride and sulfate.

The results presented explain the nuances of producing aluminum-based coagulants from concentrates and eluates, enabling manufacturers to obtain commercial products with a high active substance content.

In future work, the method for producing oxidized chlorine compounds from NaCl solutions by electrodialysis in two-chamber electrolyzers will be further improved.

4. Conclusions

It was shown that the electrolysis of sodium chloride in the anode chamber of a two-chamber electrolyzer (MK-40 membrane) at a current density of 8.33 A/dm^2 using an aluminum anode (AD-31) proceeds with a sodium chloride conversion of 60%, resulting in the formation of alkali in the cathode region at a concentration of 1100 mg-eq/dm^3 and aluminum chloride in the anolyte at a concentration of 1150 mg-eq/dm^3. Due to fouling of the cation exchange membrane by Al^{3+} ions, the electrolysis process ceased after 10 hours. The aluminum chloride current efficiency did not exceed 60%.

It was found that during the electrolysis of sodium chloride solutions placed in the working chamber of a three-chamber electrolyzer, the conversion degree of sodium chloride reaches 99.5–99.9%. The current efficiency of the aluminum dissolution process in the anode chamber of the three-chamber electrolyzer with an aluminum anode at an anodic current density of 4.17 A/dm^2 reached 140%, which is attributed to the chemical dissolution of aluminum in a mildly acidic environment. This contributes to an increase in current efficiency for both alkali and aluminum chloride production. At a current density of 8.33 A/dm^2, there is a significant increase in the intensity of sodium chloride conversion and in the formation of aluminum chloride and alkali, with current efficiencies approaching 100%. The contribution of chemical aluminum dissolution to aluminum chloride formation significantly decreased under these conditions.

It was demonstrated that the electrochemical decomposition of a mixture of aluminum chloride and aluminum sulfate salts in a three-chamber electrolyzer with an aluminum anode proceeds via a mechanism similar to that of sodium chloride electrolysis. The process shows high conversion degrees for both sodium chloride and sodium sulfate, with quantitative current efficiencies of alkali, aluminum chloride, and aluminum sulfate.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this study, including financial, personal, authorship, or other interests, which could affect the study and its results presented in this article.

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Use of artificial intelligence

The authors confirm that they did not use artificial technologies intelligence when creating the presented work.

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