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INCREASING THE YIELD OF ACTIVE CHLORINE FROM CHLORINE CONCENTRATES BY IMPROVING ELECTRODIALYSIS PROCESSES

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This study investigates processes related to processing sodium chloride solutions at a concentration of 3.5–120 g/dm^3 by electrodialysis to solve the task of utilizing chlorine-containing concentrates of membrane water desalination to obtain active chlorine.

When electrolyzing the solutions, open and sealed two-chamber electrolyzers with an anion exchange membrane MA-41 were used. Solutions with NaCl were placed in the anode chamber, and the cathode chamber was filled with NaOH solutions (200–1000 mg-equiv./dm^3).

The electrolysis processes were carried out at an anode current density of 1.67–12.5 A/dm^2. With an increase in the anode current density and chloride concentration in the solution, the intensity of chloride oxidation increases. During the anodic oxidation of chlorides, hypochlorites and chlorides are formed along with the formation of chlorine in the presence of hydroxides. This confirms the ratio of the amounts of active chlorine and oxidized chlorides.

Prolonging the electrolysis time in an open electrolyzer does not contribute to an increase in the concentrations of oxidized chlorine in the anolyte because of its significant degassing. At low initial chloride concentrations (60 mg-equiv./dm^3) and at low anodic current density ($J = 0.83$ A/dm^2, 1.67 A/dm^2), the yield of sodium hypochlorite reached 100.0–87.0%, respectively. At a current density of 4.17 A/dm^2 and the same NaCl concentration, the yield of sodium hypochlorite decreased to 51.2%. The concentration of active chlorine in the solutions did not exceed 80–90 mg-equiv./dm^3.

When using a sealed two-chamber electrolyzer, the bulk of the active chlorine was concentrated in the anolyte. To capture active chlorine vapors, gases from the anode zone were passed through a NaOH solution in the absorber. The concentrations of active chlorine in the anolytes reached 1240–1920 mg-equiv./dm^3. The degree of degassing of active chlorine did not exceed 11–17%

Keywords: reverse osmosis, electrodialysis water purification, active chlorine, anodic current density

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1. Introduction

Freshwater scarcity is a serious problem in many regions of the world. The situation is significantly worsening and will worsen because of population growth, urbanization, adverse climate change, etc. At the same time, a significant deterioration in the quality of surface water is observed in almost all parts of the world. 750 million people on Earth do not have access to drinking water. According to UN estimates, about 1,500 km^3 of wastewater is discharged into surface water bodies annually. In developing countries, more than 80% of wastewater is discharged without treatment. In general, industry annually discharges 300–400 million tons of heavy metals, solvents, toxic sludge, and other waste into water bodies [1].

In Europe, water-related issues are not so acute. Irreversible water consumption there reaches 13%. However, the problem is that water resources, like the population, are distributed unevenly, which is the reason for the formation of regions with serious water shortages. These include Cyprus, Bulgaria, Italy, Spain, the countries of the former Yugoslavia, Macedonia, Malta. Ukraine also has significant problems with water supply. Almost all surface sources of Ukraine have been intensively polluted over the past 20 years.

The quality of wastewater is much worse than the maximum permissible concentrations specified by the standards. The main pollutants of water bodies are industrial enterprises in the energy, metallurgy, coal industry, housing and communal facilities, and agriculture.

In general, the problem of limiting the reserves of fresh water resources in the world is becoming increasingly acute. By 2030, the need for fresh water will exceed the level of sustainable water consumption by 40% [2]. The water crisis can be overcome by obtaining water from alternative sources, which include mineralized artesian and groundwater, mine water, sea water, and mineralized lakes. One of the most promising technologies for obtaining fresh water is reverse osmosis. However, the implementation of this technology is impossible without an effective solution to the problem of processing concentrates. It is especially relevant for desalination of water at a considerable distance from water bodies. To obtain desalinated water by reverse osmosis, a combination of osmosis with secondary purification processes of the concentrate – thermal distillation or membrane distillation – is necessary. This makes the energy balance of the desalination system as a whole unprofitable.

Today, there is no real alternative to those energy-intensive areas of processing concentrates that involve the separation of water and mineral sediments. Therefore, current research is aimed at devising energy-saving, cost-effective technologies for processing concentrates of reverse osmosis water desalination. The issue of processing concentrates contaminated with chlorides is especially acute. Processing chlorine-containing concentrates into sodium hypochlorite solutions could make it possible to significantly expand the use of membrane reverse osmosis technologies.

2. Literature review and problem statement

The main challenge in the purification of mine and mineralized artesian waters by reverse osmosis or nanofiltration is the utilization of concentrates, which significantly limits the use of baromembrane processes in water purification. In work [3], the task of processing concentrates formed during the desalination of mine waters by nanofiltration was solved by precipitating sulfates and hardness ions in the form of calcium sulfohydroxoaluminate during water liming. Precipitation was carried out in the presence of sodium hydroxoaluminate or using aluminum hydroxochlorides of different basicity [4]. This technique makes it possible to remove sulfates from water without significant contamination with chlorides. However, mine waters are often contaminated not only with sulfates but also with chlorides in significant concentrations [5]. It is difficult to remove chlorides from water using reagent methods. Therefore, sorption methods [6] and ion exchange [7] are often used to purify mineralized waters from chlorides. Sorption is an inefficient process for the removal of chlorides and sulfates. The disadvantage of ion exchange [7, 8] is the formation of significant volumes of acidic and alkaline regeneration solutions with high mineralization. The volumes of eluates when using ion exchange are several times larger than the volumes of concentrates formed when using membrane processes.

The evaporation processes described in [9] are used for the complete separation of dissolved substances. The disadvantages of these methods are also significant energy consumption and insufficient productivity of the processes. At the same time, the disposal of chloride and sulfate salts obtained by these methods in solid form remains an unsolved problem. They are prohibited from being placed at municipal waste landfills while specially equipped landfills are expensive.

Membrane processes for water desalination are more effective. The most widely used baromembrane methods are reverse osmosis [10] and nanofiltration [11]. They can provide fairly significant productivity of the water desalination process. Reverse osmosis [10] is characterized by high efficiency of water demineralization. It is suitable for obtaining drinking and energy water from sources with high water mineralization, including sea water. Nanofiltration [11] is characterized by high productivity and efficiency in removing doubly charged ions, but has low selectivity in removing singly charged ions, in particular chlorides. The disadvantage of these water desalination processes is the high requirements for the quality of preliminary mechanical water purification. However, the main disadvantage is the limitation of the mineralization of the source water and the practical absence of available technologies for processing saline liquid waste – concentrates. Electrodialysis [12], as a water desalination process, is characterized by low productivity. It is suitable for desalination of low-mineralized waters [13] and is accompanied by the formation of saline concentrates, which are difficult to process.

One of the promising areas of processing concentrated chloride solutions is electrodialysis, which ensures their oxidation to active chlorine, or other compounds with higher oxidation states [14, 15]. In addition to processing liquid chloride-containing waste, the positive side of electrodialysis is that the products obtained can be used for water disinfection [15]. However, the use of conventional technologies for obtaining active chlorine is impossible because of the significant difference in the concentrations of sodium chloride in baromembrane concentrates and solutions used in the processes of active chlorine production. In the latter case, the concentration of sodium chloride reaches 100 g/dm^3 and often has significantly higher values. The content of sodium chloride in reverse osmosis desalination concentrates reaches 4–30 g/dm^3. At such concentrations of sodium chloride when using electrolysis, the output of active chlorine by current is significantly lower than that obtained at high salt concentrations [16]. In addition, when processing membrane desalination concentrates, there is a problem not only of processing NaCl solutions but also of desalinizing these solutions to obtain fresh water. This is possible when using electrodialysis in electrolyzers with ion-exchange membranes [17]. The use of this method makes it possible to process sodium sulfate solutions [18] to obtain alkali and sulfuric acid. This technique makes it possible to process sodium chloride solutions to obtain alkali and hydrochloric acid [19, 20]. However, when using four-chamber electrolyzers, the current yield of the process products is low while energy consumption is high. It is impractical to obtain perchloric acid for this purpose. The use of ion-exchange membranes increases the efficiency of obtaining sulfuric acid from solutions containing sulfates. At the same time, the processes of obtaining active chlorine from chlorine-containing solutions by electrodialysis are promising; however, the electrolysis of chlorine-containing solutions using ion-exchange membranes has not been studied in detail, which indicates the feasibility of research into this area.

3. The aim and objectives of the study

The aim of our work was to determine the regularities of the processes of synthesis of active chlorine and sodium hypochlorite by electrodialysis from sodium chloride solutions at different anodic current densities in open and sealed two-chamber electrolyzers. This will make it possible to design processes for effective processing of concentrates formed during the desalination of natural and mine waters with the production of usable products. Solving the task of processing concentrates could significantly expand the scope of application of reverse osmosis in water desalination technologies.

To achieve this aim, the following objectives were accomplished:

– to assess the efficiency of chloride oxidation by electrodialysis depending on its concentration and on the anodic current density;

– to determine the efficiency of using a two-chamber sealed electrolyzer for the production of active chlorine from concentrates.

4. The study materials and methods

The object of our study was the processes of processing sodium chloride solutions with a concentration of 3.5–120 g/dm^3 by electrodialysis to obtain active chlorine and sodium hypochlorite.

The hypothesis of the study assumed that the use of ion-exchange membranes could ensure an increase in the current output of active chlorine and an increase in the degree of chloride conversion.

Assumptions adopted: the use of an alkali solution in the cathode chamber of a two-chamber electrolyzer should enable the diffusion of hydroxide anions into the anode chamber and the effective binding of active chlorine with the formation of hypochlorite and chloride anions with the gradual conversion of chlorides into hypochlorite anions.

Simplifications accepted: the diffusion transfer of water with hydroxide anions from the cathode to the anode region is determined by the change in the volumes of the catholyte and anolyte. Hydrogen is released quantitatively in accordance with the cathodic reaction. At neutral values of the reaction medium at the anode, the process of chloride oxidation prevails.

When conducting studies on the electrochemical processing of NaCl solutions, two-chamber open and closed electrolyzers were used.

Electrolysis in an open two-chamber electrolyzer was carried out using sodium chloride solutions with chloride concentrations from 60 mg-equiv./dm^3 to 1725 mg-equiv./dm^3. In this case, an anion exchange membrane MA-41 was used. The cathode was made of alloyed steel 12X18H10T, the anode was made of a titanium plate coated with ruthenium oxide. The area of the electrodes $S_a = S_k = 12$ cm^2. The current strength varied in the range from 0.2 A to 1.5 A. The anodic current density (j) was 1.67–12.5 A/dm^2. The chloride content in the solution was determined by the Mohr method; the hardness and alkalinity of the solution were determined by standard methodologies; and the concentration of active chlorine in the solution was determined by the iodometry method [21].

The cathode chamber was filled with a 0.2N alkali solution; the anode region was filled with a working solution of sodium chloride. At a given current strength, the electrolysis process was carried out for 2–8 hours, periodically monitoring the alkalinity in the catholyte, the content of chlorides, and active chlorine in the anolyte. The current yield (V, %) was determined from formula (1) as the ratio of the amount of substance obtained or transferred to the theoretically possible amount (according to Faraday's law)

$$B = \frac{q_R}{q_T} \cdot 100 = \frac{m_F}{m_T} \cdot 100, \tag{1}$$

where q_R is the amount of electricity for the actually transferred, or oxidized or reduced substance;

q_T is the theoretically calculated amount of electricity;

m_F is the amount of actually transferred (oxidized, reduced) substance, g-equiv.;

m_T is the theoretically possible amount of transferred (oxidized, reduced) substance, g-equiv.

The actual amount of transferred, oxidized, or reduced substance was determined from formula (2); the theoretically possible amount of transferred, oxidized, or reduced substance (g-equiv.) was determined from formula (3)

$$m_F = \left(C_0 - C_i\right) \cdot V_i, \tag{2}$$

where C_0 – initial concentration of the component in water, mg-equiv./dm^3;

C_i – residual concentration of the component in a given period of time in purified water, mg-equiv./dm^3;

V_i – volume of the purified water sample $V_p = 0.1$ dm^3

$$m_T = K_E \cdot I \cdot t, \tag{3}$$

where K_E is the electrochemical equivalent ($K_E =$ $= 0.03731$ g-equiv./(A·h));

I is the current strength, A;

t is time, h.

The efficiency of water purification from chlorides (E, %) (degree of chloride conversion) was calculated from formula (4)

$$E = \frac{\left(C_0 - C_i\right)}{C_0} \cdot 100. \tag{4}$$

Electrolysis in two-chamber sealed electrolyzers was also carried out using an anion exchange membrane MA-41 (Fig. 1).

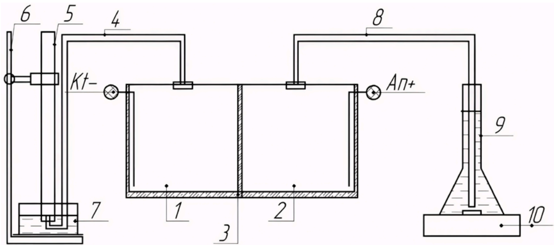

Fig. 1. Two-chamber sealed electrolyzer with anion exchange membrane MA-41

When using an anion exchange membrane in a two-chamber closed electrolyzer, the anode chamber was filled with a working solution, the cathode chamber with a 1N alkali solution. The concentration of sodium chloride varied from 30 g/dm^3 to 120 g/dm^3.

Active chlorine released from the anode chamber was absorbed by a 50% NaOH solution, which was in a volumetric flask ($V = 100$ cm^3).

During electrolysis, the alkalinity in the catholyte, pH, chloride content, active chlorine in the anolyte, and the concentration of active chlorine in the absorbate were monitored. A 50% alkali solution at a volume of 100 cm^3 was used as the absorbate.

To maintain a constant temperature, the electrolyzer was placed in a thermostat. The temperature was maintained at 25°C.

The efficiency of chloride removal from the solution was calculated using formula (4), and the output of active chlorine per current was determined using formula (1).

5. Results of research on electrochemical oxidation of chlorides in sodium chloride solutions

5. 1. Assessing the efficiency of chloride oxidation by electrodialysis depending on its concentration and anodic current density

When using a two-chamber open electrolyzer with an anion exchange membrane MA-41 during electrolysis of sodium chloride solutions with a concentration of 3.680 g/dm^3 in NaCl, the process was carried out at anodic current density, A/dm^2: 0.83, 1.67, 4.17, and 8.33.

In this case, hydrogen was reduced at the cathode and hydroxide anions were formed, which in an equivalent amount to the active chlorine formed at the anode passed through the anion exchange membrane into the anolyte. Active chlorine was formed at the anode because of the oxidation of chlorides. The charge of sodium cations, which were counterions to chlorides, was compensated by hydroxide anions that passed from the catholyte to the anolyte through the membrane. An alkali was formed in the anolyte, which, when interacting with active chlorine, formed sodium hypochlorite and sodium chloride.

The results from the electrolysis of a sodium chloride solution with a concentration of 61 mg-equiv./dm^3 (~3680 mg/dm^3) at an anodic current density of 0.83–8.3 A/dm^2 are shown in Fig. 2–5.

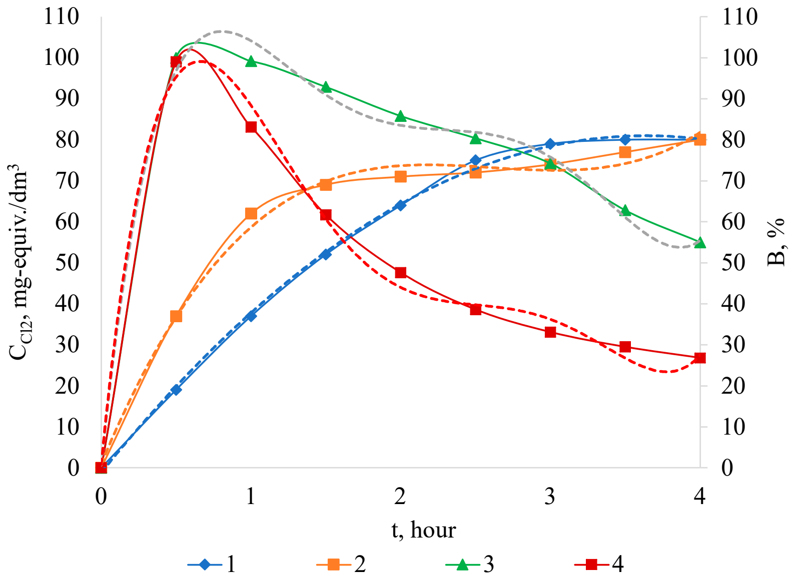

Fig. 2. Dependence of the concentration of active chlorine in the anolyte, its current output on the time of electrolysis of the NaCl solution (C_{NaCl} = 61 mg-equiv./dm^3) in the anolyte of a two-chamber electrolyzer (MA-41 membrane) at a catholyte alkalinity of 200 mg-equiv./dm^3 at different anode current densities: 1 – concentration of active chlorine in the anolyte (j = 0.83 A/dm^2), C_{Cl_2}, mg-equiv./dm^3; 2 – concentration of active chlorine in the anolyte (j = 1.67 A/dm^2), C_{Cl_2},mg-equiv./dm^3; 3 – current output of active chlorine (j = 0.83 A/dm^2), V, %; 4 – current output of active chlorine (j = 1.67 A/dm^2), V, %; —◆— – $y = 4.4242x^3 - 34.628x^2 + 87.935x + 0.9394$, $R^2 = 0.9934$; —■— – $y = -6.2078x^2 + 45.165x - 1.1515$, $R^2 = 0.9988$; —▲— – $y = 4.2738x^5 - 49.508x^4 + 213.03x^3 - 418.7x^2 + 354.36x ++ 0.6839$, $R^2 = 0.9934$; —■— – $y = 4.7569x^5 - 56.157x^4 + + 246.11x^3 - 482.57x^2 + 375.44x + 0.8336$, $R^2 = 0.9898$

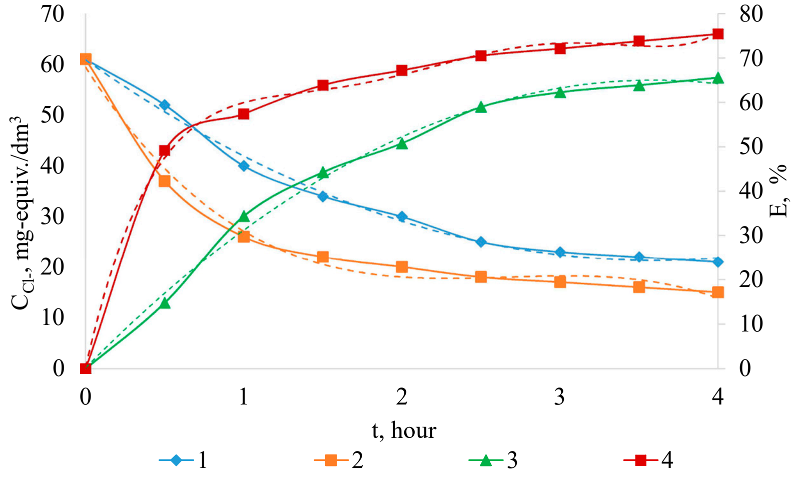

Fig. 3. Change in the concentration of chlorides in the anolyte of a two-chamber electrolyzer during electrolysis of a sodium chloride solution (C_{NaCl} = 61 mg-equiv./dm^3) (catholyte – alkali solution with a concentration of 200 mg-equiv./dm^3), the degree of chloride conversion with electrolysis time at different anodic current densities: 1 – concentration of chlorides in the anolyte (j = 0.83 A/dm^2), C_{Cl-}, mg-equiv./dm^3; 2 – concentration of chlorides in the anolyte (j = 1.67 A/dm^2), C_{Cl-}, mg-equiv./dm^3; 3 – degree of chloride conversion (j = 0.83 A/dm^2), E, %; 4 – degree of chloride conversion (j = 1.67 A/dm^2), E, %; —◆— – $y = 3.0606x^2 - 22.009x + 60.897$, $R^2 = 0.9948$; —■— – $y = -2.3165x^3 + 18.553x^2 - 48.546x + 59.434$, $R^2 = 0.988$; —▲— – $y = -5.013x^2 + 36.059x + 0.1897$, $R^2 = 0.9948$; —■— – $y = 1.5303x^5 - 17.786x^4 + 77.476x^3 - 157.54x^2 + + 155.93x + 0.3592$, $R^2 = 0.996$

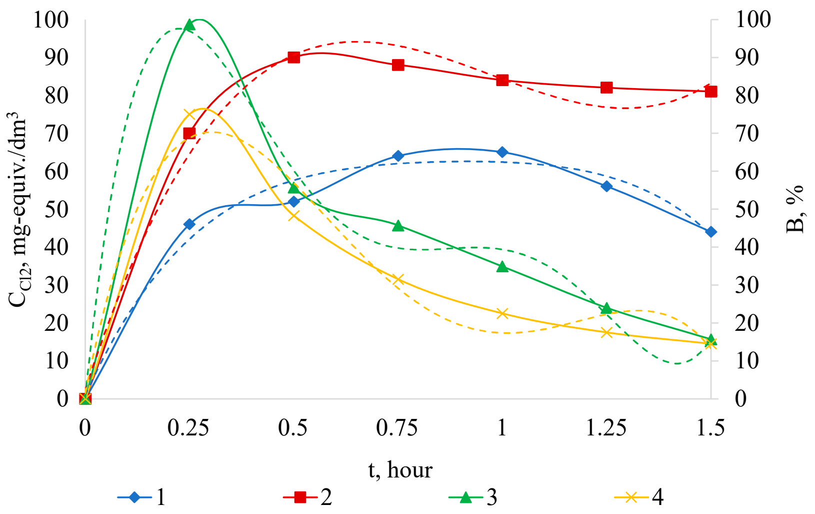

Fig. 4. Change in the concentration of active chlorine in the anolyte of a two-chamber electrolyzer (MA-41 membrane), its current output, depending on the time of electrolysis of a NaCl solution with a concentration of 61 mg-equiv./dm^3 (catholyte – NaOH solution with a concentration of 200 mg-equiv./dm^3) at different anodic current densities: 1 – concentration of active chlorine in the anolyte (j = 4.17 A/dm^2), C_{Cl_2}, mg-equiv./dm^3; 2 – concentration of active chlorine in the anolyte (j = 8.33 A/dm^2), C_{Cl_2}, mg-equiv./dm^3; 3 – current output of active chlorine (j = 4.17 A/dm^2), V, %; 4 – current output of active chlorine (j = 8.33 A/dm^2), V, %; —◆— – $y = -78.545x^4 + 272.97x^3 - 375.82x^2 + 242.87x + 0.9221$, $R^2 = 0.9775$; —■— – $y = 133.33x^3 - 389.33x^2 + 337.95x + 2.3333$, $R^2 = 0.9848$; —▲— – $y = 898.13x^5 - 3801.5x^4 + 5895.2x^3 - 4035.5x^2 + 1082.8x + 0.2982$, $R^2 = 0.9867$; —×— – $y = -333.77x^4 + 1175.2x^3 - 1368.7x^2 + 543.14x + 1.4924$, $R^2 = 0.9538$

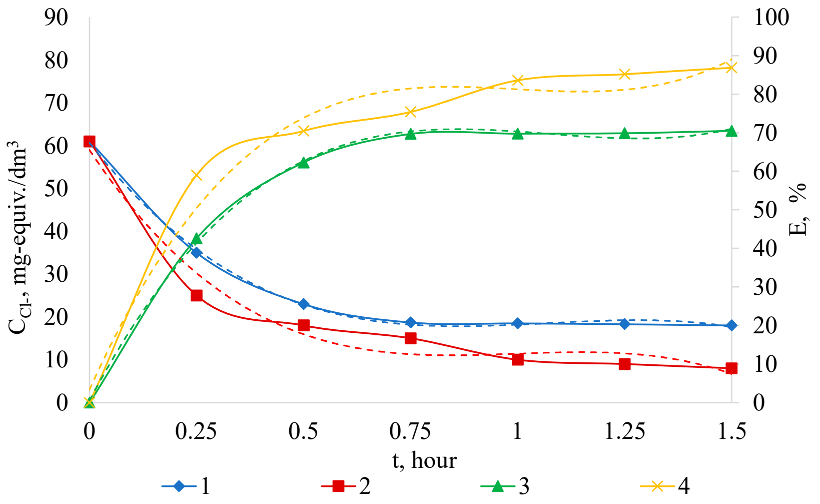

Fig. 5. Dependence of the concentration of chlorides in the anolyte of a two-chamber electrolyzer (MA-41 membrane), the degree of their conversion, on the electrolysis time, anolyte is a NaCl solution with a concentration of 61 mg-equiv./dm^3, catholyte is a NaOH solution with a concentration of 200 mg-equiv./dm^3 at different anodic current densities: 1 – concentration of chlorides in the anolyte (j = 4.17 A/dm^2), C_{Cl^-}, mg-equiv./dm^3; 2 – concentration of chlorides in the anolyte (j = 8.33 A/dm^2), C_{Cl^-}, mg-equiv./dm^3; 3 – degree of chloride conversion (j = 4.17 A/dm^2), E, %; 4 – degree of chloride conversion (j = 8.33 A/dm^2), E, %; —◆— – $y = -38.756x^3 + 124.48x^2 - 128.2x + 60.664$, $R^2 = 0.9986$; —■— – $y = -51.556x^3 + 154.29x^2 - 150.3x + 58.976$, $R^2 = 0.9716$; —▲— – $y = 63.467x^3 - 204.25x^2 + 210.59x + 0.5048$, $R^2 = 0.9989$; —×— – $y = 84.622x^3 - 253.14x^2 + 246.49x + 3.3095$, $R^2 = 0.9718$

Fig. 2 demonstrates that at an anode current density of 0.83 A/dm^2 and 1.67 A/dm^2, the concentration of active chlorine in the anolyte reaches 80–82 mg-equiv./dm^3 in 4 hours. At the same time, during the first two hours, the concentration of active chlorine increases faster at an anode current density of 0.83 A/dm^2.During the first two hours, the current output at a given anode current density decreases from 100% to 85.8%. At an anode current density of 1.67 A/dm^2, the current output in two hours decreases from 99 to 47.6%. After 4 hours, the current output at an anode current density of 0.83 A/dm^2 drops to 55%, and at an anode current density of 1.67 A/dm^2 to 26.8%. This is primarily because of the decrease in the concentration of chlorides in the anolyte during the electrolysis process. In the first case (Fig. 3), the chloride concentration decreases to 21 mg-equiv./dm^3, in the second case – to 15 mg-mg-equiv./dm^3.

The degree of chloride conversion in the first case reaches 65.6%, in the second – 75.4%. At the same time, in the first case, when converting 40 mg-equiv./dm^3 of chlorides, 80 mg-equiv./dm^3 of active chlorine was obtained.

When the anodic current density (j) increases to 4.17 and 8.33 A/dm^2 (Fig. 4), the intensity of chloride oxidation increases. With the same chloride concentration at j = 4.17 A/dm^2 during the first 25 minutes of electrolysis, the content of active chlorine in the anolyte reached 46 mg-equiv./dm^3, and at j = 8.33 the indicator was equal to 70 mg-equiv./dm^3. At the same time, in the first case, the chloride concentration decreased by 26 mg-equiv./dm^3, and in the second by 36 mg-equiv./dm^3. During further electrolysis, the concentration of oxidized chlorine compounds in the case of j = 4.17 A/dm^2 increased within an hour to 65 mg-equiv./dm^3 and then decreased to 44 mg-equiv./dm^3 over the next 30 minutes. At an anode current density of 8.33 A/dm^2, the active chlorine content reached 90 mg-equiv./dm^3 in 0.5 hours, with a further decrease to 81 mg-equiv./dm^3 in 1.5 hours of electrolysis.

At the same time, the chloride content in the anolyte constantly decreased and the degree of conversion at j = 4.17 A/dm^2 in 1.5 hours reached 70.5%, and at j = 8.33 A/dm^2 – 86.9% (Fig. 5). The current yield of active chlorine in both cases decreased from 98.7% to 15.7% at j = 4.17 A/dm^2 and from 75.0% to 14.5% at j = 8.33 A/dm^2 in 1.5 hours. This cannot be explained only by the decrease in the yield of active chlorine because of energy losses and electrolysis of water with the formation of hydrogen and oxygen. It is obvious that when using an open electrolyzer, a significant part of the electrolysis products was lost because of degassing of Cl_2.

At a chloride concentration in the anolyte of 450 mg-equiv./dm^3 (26.3 g/dm^3) at an anode current density of 1.67 A/dm^2, after 9 hours of electrodialysis, the concentration of active chlorine in the anolyte was achieved at the level of 170 mg-equiv./dm^3, and at j = 4.17 A/dm^2– 280 mg-equiv./dm^3 (Fig. 6). At the same time, in the first case, the current yield of active chlorine decreased from 92.2% to 25.3%, in the second – from 87.1% to 16.7%.

In this case, the degree of chloride conversion in the first case reached 48.9%, in the second case 82.2% (Fig. 7). In both cases, the total amount of oxidized chlorides for 9 hours of electrolysis was close to the amount of active chlorine obtained. The chloride concentration in the first case decreased by 220 mg-equiv./dm^3, in the second – by 290 mg-equiv./dm^3, which corresponds to the increase in the concentrations of active chlorine in the anolytes in the first and second cases, respectively (Fig. 6, 7). At the same time, because of the interaction of active chlorine with alkali formed during the diffusion of hydroxide anions from the cathode region, it was combined with the formation of hypochlorite and sodium chloride.

At an anode current density of 8.33 A/dm^2, an increase in the degree of chloride conversion was observed over a certain time in comparison with experiments at j = 1.67 A/dm^2 and j = 4.17 A/dm^2. Thus, in 3 hours the degree of conversion reached 63%, which is due to an increase in the rate of chloride oxidation with an increase in the anode current density (Fig. 7). However, because of significant losses of active chlorine, which is associated with the evaporation of Cl_2, the concentration of sodium hypochlorite was low – only 120 mg-equiv./dm^3 of active chlorine (Fig. 8). It is obvious that in this case the evaporation of the formed active chlorine proceeded faster than its interaction with alkali. At the same time, the excess hydroxide anions were oxidized to form oxygen and protons, which reduced the rate of alkalization of the anolyte.

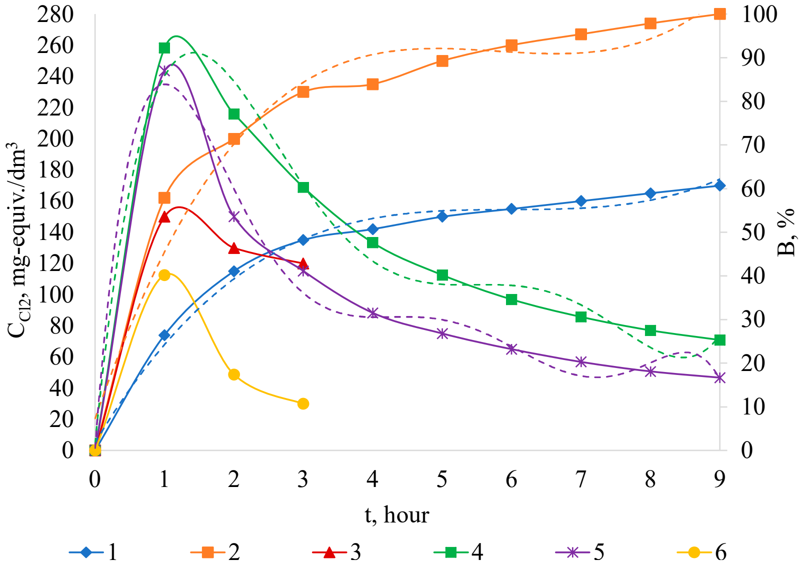

Fig. 6. Dependence of the concentration of oxidized chlorine compounds, their current yield, on the time of electrolysis of NaCl solution in the anode chamber (C_{NaCl} = 450 mg-equiv./dm^3) of a two-chamber electrolyzer at a catholyte alkalinity of 200 mg-equiv./dm^3 and at different anode current densities: 1 – concentration of oxidized chlorine compounds (j = 1.67 A/dm^2), C_{Cl_2}, mg-equiv./dm^3; 2 – concentration of oxidized chlorine compounds (j = 4.17 A/dm^2), C_{Cl_2}, mg-equiv./dm^3; 3 – concentration of oxidized chlorine compounds (j = 8.33 A/dm^2), C_{Cl_2}, mg-equiv./dm^3; 4 – current yield of oxidized chlorine compounds (j = 1.67 A/dm^2), V, %; 5 – yield of oxidized chlorine compounds by current (j = 4.17 A/dm^2), V, %; 6 – yield of oxidized chlorine compounds by current (j = 8.33 A/dm^2), V, %; —◆— – $y = 0.6944x^3 - 12.462x^2 + 74.707x + 4.9636$, $R^2 = 0.9918$; —■— – $y = 1.3087x^3 - 22.686x^2 + 128.19x + 20.485$, $R^2 = 0.9611$; —▲— – $y = 30x^3 - 175x^2 + 295x - 1E-11$, $R^2 = 1$; —■— – $y = 0.0877x^5 - 2.2854x^4 + 21.985x^3 - 93.959x^2 + 158.34x + 1.6182$, $R^2 = 0.976$; —✳— – $y = 13.183x^3 - 71.05x^2 + 98.067x - 1E-12$, $R^2 = 1$; —●— – $y = -0.0311x^6 + 0.9426x^5 - 11.113x^4 + 63.792x^3 - 180.4x^2 + 210.15x + 0.561$, $R^2 = 0.9807$

With a further increase in the chloride concentration from 875 to 1725 mg-equiv./dm^3 (from 51.2 g/dm^3 to 100.9 g/dm^3) at an anode current density of 4.17 A/dm^2, a slight increase in the concentration of active chlorine in the anolyte was noted. Over 5 hours of electrolysis, the concentration of active chlorine increased from 300 mg-equiv./dm^3 to 340 mg-equiv./dm^3 (Fig. 8).

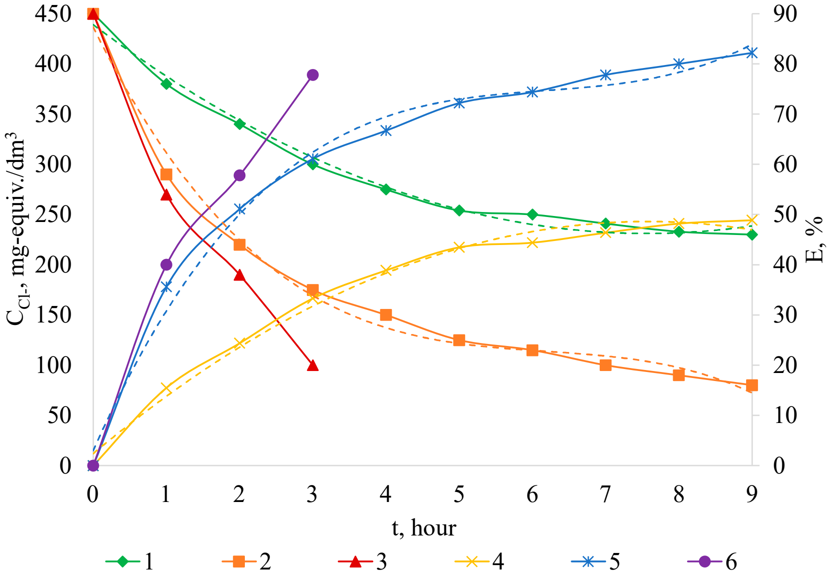

Fig. 7. Change in chloride concentration, degree of chloride conversion in the anode chamber of a two-chamber electrolyzer (C_{NaCl} = 450 mg-equiv./dm^3) at catholyte alkalinity of 200 mg-equiv./dm^3 and at different anodic current densities: 1 – chloride concentration (j = 1.67 A/dm^2), C_{Cl-}, mg-equiv./dm^3; 2 – chloride concentration (j = 4.17 A/dm^2), C_{Cl-}, mg-equiv./dm^3; 3 – chloride concentration (j = 8.33 A/dm^2), C_{Cl-}, mg-equiv./dm^3; 4 – degree of chloride conversion (j = 1.67 A/dm^2), E, %; 5 – degree of chloride conversion (j = 4.17 A/dm^2), E, %; 6 – degree of chloride conversion (j = 8.33 A/dm^2), E, %; —◆— – $y = 3.6326x^2 - 54.966x + 439.12$, $R^2 = 0.9897$; —■— – $y = -1.2385x^3 + 22.972x^2 - 146.91x + 436.68$, $R^2 = 0.991$; —▲— – $y = 22.5x^2 - 180.5x + 444.5$, $R^2 = 0.9909$; —×— – $y = -0.8057x^2 + 12.202x + 2.4027$, $R^2 = 0.9897$; —✳— – $y = 0.2754x^3 - 5.1072x^2 + 32.647x + 2.9733$, $R^2 = 0.991$; —●— – $y = -5x^2 + 40.12x + 1.22$, $R^2 = 0.9909$

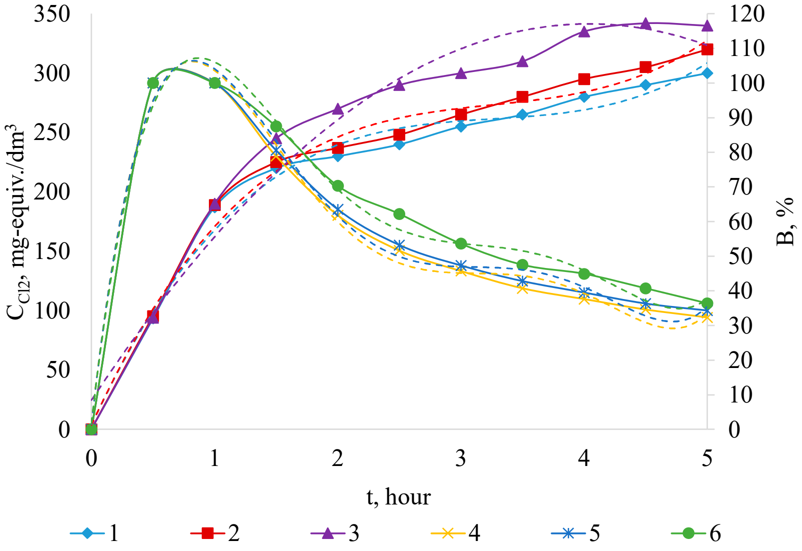

Fig. 8. Dependence of the concentration of active chlorine and its current yield on the time of electrolysis of sodium chloride solutions in the anode chamber of a two-chamber electrolyzer at a catholyte alkalinity of 200 mg-equiv./dm^3, anode current density of 4.17 A/dm^2 and at different concentrations of sodium chloride: 1 – concentration of active chlorine (C_{NaCl} = 875 mg-equiv./dm^3), C_{Cl_2}, mg-equiv./dm^3; 2 – concentration of active chlorine (C_{NaCl} = 1425 mg-equiv./dm^3), C_{Cl_2}, mg-equiv./dm^3; 3 – concentration of active chlorine (C_{NaCl} = 1725 mg-equiv./dm^3), C_{Cl_2}, mg-equiv./dm^3; 4 – current yield of active chlorine (C_{NaCl} = 875 mg-equiv./dm^3), V, %; 5 – active chlorine output by current (C_{NaCl} = 1425 mg-equiv./dm^3), V, %; 6 – active chlorine output by current (C_{NaCl} = 1725 mg-equiv./dm^3), V, %; —◆— – $y = 6.8202x^3 - 66.733x^2 + 224.18x + 3.5972$, $R^2 = 0.9878$; —■— – $y = 6.7643x^3 - 66.164x^2 + 226.52x + 3.6811$, $R^2 = 0.9897$; —▲— – $y = -19.436x^2 + 156.94x + 24.615$, $R^2 = 0.9692$; —×— – $y = 1.7154x^5 - 25.262x^4 + 137.8x^3 - 335.17x^2 + 323.01x + 1.5212$, $R^2 = 0.9892$; —✳— – $y = 1.6903x^5 - 24.904x^4 + 135.99x^3 - 331.51x^2 + 321.29x + 1.5287$, $R^2 = 0.9895$; —●— – $y = 1.5041x^5 - 22.351x^4 + 123.52x^3 - 307.16x^2 + 308.68x + 1.8393$, $R^2 = 0.9848$

At the same time, the current yield decreased from 100% in the first two hours to 32–36% in the 5th hour of electrolysis. This is due to the loss of active chlorine because of degassing. The residual chloride concentrations in the anode solutions were quite high. The degree of chloride conversion decreased from 66.9% to 40.7% and 33.3% as the sodium chloride concentration in the starting solutions increased from 875 mg-equiv./dm^3 to 1425 mg-equiv./dm^3 and 1725 mg-equiv./dm^3 (Fig. 9).

At the same anode current density, similar amounts of chlorides in different solutions were oxidized in the same time intervals. This is due to the fact that the chloride concentrations in all solutions were quite high.

Confirmation of the fact of degassing of active chlorine is the change in the reaction of the anolyte medium during electrolysis. The results of the change in the reaction of the medium are given in Table 1. At all three values of the initial chloride concentrations, an increase in the pH of the medium with the time of electrolysis was noted.

It is obvious that in the case of the formation of active chlorine (5), part of the hydroxide anions entering the anolyte through the anion exchange membrane from the cathode region reacts with chlorine to form hypochlorite and sodium chloride (6):

$$2Cl^- - 2e = Cl_2, \tag{5}$$

$$Cl_2 + 2NaOH = NaClO + NaCl + H_2O. \tag{6}$$

The amount of hydroxide anions that pass into the anolyte is equivalent to the amount of oxidized chlorides or active chlorine. During partial degassing of Cl_2, some of the hydroxide anions do not react according to reaction (6) but accumulate in the solution. However, the alkalinity of the solution is not always equivalent to the amount of active chlorine released during degassing because hydroxide anions can also be oxidized at the anode (7)

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-. \tag{7}$$

Table 1

Change in the reaction of the anolyte medium of a two-chamber open electrolyzer depending on electrolysis time at an anode current density of 4.17 A/dm^2, initial catholyte alkalinity of 200 mg-equiv./dm^3 for different values of the initial concentration of sodium chloride in the anolyte

t, h	pH		
	C_{NaCl}, mg-equiv./dm^3		
	875	1425	1725
0	7.10	7.10	7.10
1	7.48	7.9	8.00
2	7.87	8.75	8.94
3	8.25	9.56	9.86
4	8.64	10.40	10.80
5	9.02	11.20	11.70

It is reaction (7) that slows down the alkalization of the solution during chlorine degassing. At the same time, the higher the concentration of chlorides, the slower the reaction (7) and the higher the alkalinity and pH values of the solution. This is illustrated in Table 1. At an initial concentration of sodium chloride solution of 875 mg-equiv./dm^3, the pH of the solution after 5 hours of electrolysis is 9.02. At an initial concentration of sodium chloride solution of 1425 mg-equiv./dm^3, the pH is 11.2. And at an initial concentration of sodium chloride solution of 1725 mg-mg-equiv./dm^3, pH reaches 11.7.

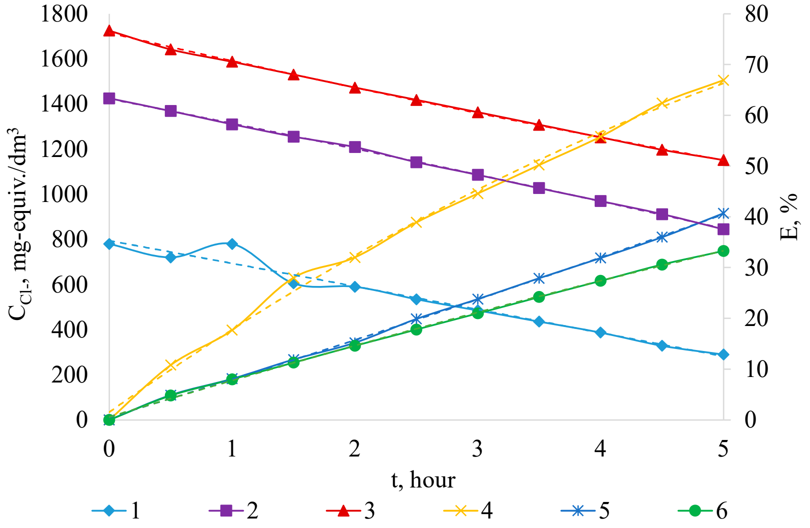

Fig. 9. Change in chloride concentration and degree of its conversion depending on time of electrolysis of sodium chloride solution in the anode chamber of a two-chamber electrolyzer at catholyte alkalinity of 200 mg-equiv./dm^3, current density of 4.17 A/dm^2 and at different sodium chloride concentrations: 1 — chloride concentration (C_{NaCl} = 875 mg-equiv./dm^3), C_{Cl^-}, mg-equiv./dm^3; 2 — chloride concentration (C_{NaCl} = 1425 mg-equiv./dm^3), C_{Cl^-}, mg-equiv./dm^3; 3 — chloride concentration (C_{NaCl} = 1725 mg-equiv./dm^3), C_{Cl^-}, mg-equiv./dm^3; 4 — degree of chloride conversion (C_{NaCl} = 875 mg-equiv./dm^3), *E*, %; 5 — degree of chloride conversion (C_{NaCl}= 1425 mg-equiv./dm^3), *E*, %; 6 — degree of chloride conversion (C_{NaCl} = 1725 mg-equiv./dm^3), *E*, %; —◆— — $y = -0.4382x^2 - 100.28x + 794.27$, $R^2 = 0.967$; —■— — $y = -1.4499x^2 - 107.79x + 1423.1$, $R^2 = 0.9997$; —▲— — $y = 2.8112x^2 - 126.95x + 1715.1$, $R^2 = 0.9993$; —×— — $y = -0.8304x^2 + 17.101x + 1.539$, $R^2 = 0.997$; —✳— — $y = 0.1263x^2 + 7.3665x + 0.5056$, $R^2 = 0.9993$; —●— — $y = -0.1627x^2 + 7.3608x + 0.5671$, $R^2 = 0.9993$

5. 2. Determining the efficiency of using a two-chamber sealed electrolyzer for obtaining active chlorine from concentrates

In the case of using a sealed electrolyzer (Fig. 10), the gases are discharged from the anode region into the absorber – a volumetric flask with a volume of 0.1 dm^3, filled with a 50% NaOH solution. The content of active chlorine in the anolyte and absorbate was determined by iodometry [21], the residual concentration of chlorides in the anolyte was determined by the Mohr method [21].

Fig. 10 demonstrates that when using a sealed electrolyzer in the anode region of the electrolyzer, it was possible to achieve quite high concentrations of active chlorine. The initial conditions were as follows: the initial concentration of chlorides in the anolyte was 600 mg-equiv./dm^3 (35.1 g/dm^3 NaCl), the anode current density was 4.17 A/dm^2 and 8.33 A/dm^2.

In the first case, the concentration of active chlorine in the anolyte was achieved at the level of 480 mg-equiv./dm^3, in the second – 690 mg-equiv./dm^3. It is obvious that in comparison with the open electrolyzer, the chlorine losses because of degassing in this case are significantly lower than in all experiments using the open electrolyzer. A significant part of the active chlorine in this case was also removed from the electrolyzer because of degassing but the bulk of it was captured in the absorber by an alkali solution. At a current density of 4.17 A/dm^2 in the absorber, the concentration of active chlorine reached 120 mg-equiv./dm^3, at a current density of 8.33 A/dm^2 it was at the level of 150 mg-equiv./dm^3.

The output of active chlorine by current, taking into account its concentrations in the anode chamber and the absorber at the beginning of the process, reached 94.5% at a current density of 4.17 A/dm^2 and 90.3% at a current density of 8.33 A/dm^2. And at the 5th hour of electrolysis, this indicator decreased to 65.2% in the first case and to 45.1% in the second case. It is likely that the main reason for this was a decrease in the concentration of chlorides in the anode chamber, which contributed to the acceleration of the electrolysis reaction of water with the formation of oxygen and hydrogen. This is confirmed by the results of monitoring the concentration of chlorides in the anolyte during the electrolysis process. At a current density of 4.17 A/dm^2, the chloride content in the anolyte decreased to 300 mg-equiv./dm^3, at a current density of 8.33 A/dm^2, its concentration decreased to 180 mg-equiv./dm^3 (Fig. 11). The degree of chloride removal reached 50% in the first case and 70% in the second case.

When electrolyzing a NaCl solution with a concentration of 117 g/dm^3 (2000 mg-equiv./dm^3) in the anode chamber of a two-chamber electrolyzer at a current density of 8.33 A/dm^2, the concentration of active chlorine in the anode chamber reached 1240 mg-equiv./dm^3. And at a current density of 12.5 A/dm^2, the concentration of active chlorine in the anode chamber was 1920 mg-equiv./dm^3 (Fig. 12). This is about 5.3% and 7.5%, respectively, of sodium hypochlorite. At the same time, in the first case, the concentration of active chlorine in the absorber reached 180 mg-equiv./dm^3, in the second – 240 mg-equiv./dm^3. At such high concentrations of NaCl solutions (~117 g/dm^3), the current yield reached 96.3% at a current density of 8.33 A/dm^2 and decreased to 83.0% at the 5th hour. For a current density of 12.5 A/dm^2, these figures reached 90.5–77.8%, respectively.

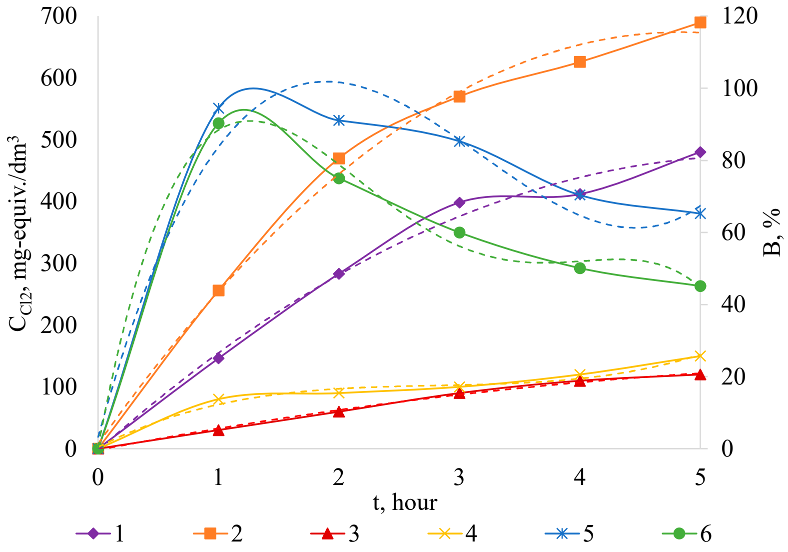

Fig. 10. Dependence of the concentration of active chlorine in the anolyte and absorbate, the current output of oxidized chlorine compounds on the time of electrolysis of a sodium chloride solution (C_{NaCl} = 600 mg-equiv./dm^3) in a two-chamber closed electrolyzer (MA-41 membrane), catholyte 1H NaOH, at different current densities: 1 – concentration of active chlorine in the anolyte (j = 4.17 A/dm^2), C_{Cl_2}, mg-equiv./dm^3; 2 – concentration of active chlorine in the anolyte (j = 8.33 A/dm^2), C_{Cl_2}, mg-equiv./dm^3; 3 – concentration of active chlorine in the absorbate (j = 4.17 A/dm^2), C_{Cl_2}, mg-equiv./dm^3; 4 – concentration of active chlorine in the absorbate (j = 8.33 A/dm^2), C_{Cl_2}, mg-equiv./dm^3; 5 – current yield of oxidized chlorine compounds (j = 4.17 A/dm^2), V, %; 6 – current yield of oxidized chlorine compounds (j = 8.33 A/dm^2), V, %; —◆— – $y = -15.775x^2 + 173.52x - 2.6214$, $R^2 = 0.9916$; —■— – $y = -28.429x^2 + 275.29x + 7.7143$, $R^2 = 0.9947$; —▲— – $y = -2.5x^2 + 37.357x - 2.1429$, $R^2 = 0.9966$; —×— – $y = 3.9815x^3 - 33.611x^2 + 98.439x + 2.6984$, $R^2 = 0.9856$; —✳— – $y = 4.7954x^3 - 45.688x^2 + 121.4x + 3.246$, $R^2 = 0.9555$; —●— – $y = -2.2104x^4 + 27.353x^3 - 115.38x^2 + 178.25x + 0.3813$, $R^2 = 0.9924$

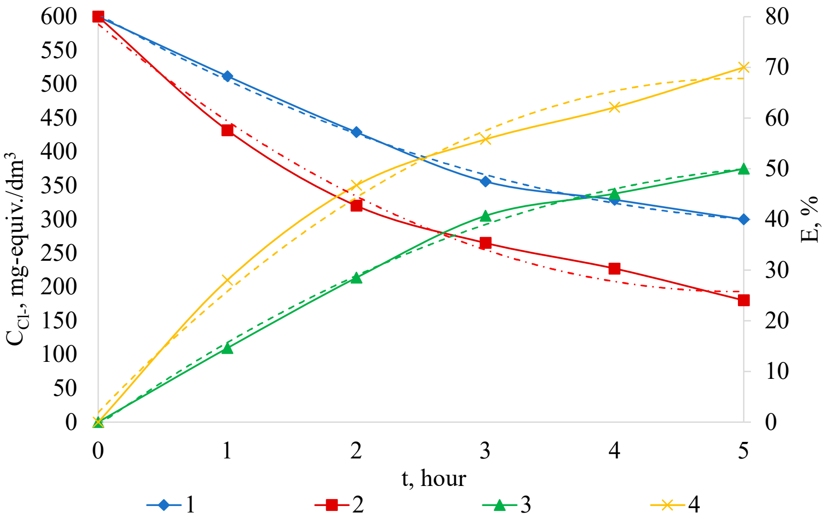

Fig. 11. Dependence of the concentration of chlorides in the anolyte, the degree of their conversion on the time of electrolysis of a sodium chloride solution (C_{NaCl} = 600 mg-equiv./dm^3) in a two-chamber electrolyzer (membrane MA-41), catholyte – 1N NaOH, at different current densities: 1 – concentration of chlorides in the anolyte (j = 4.17 A/dm^2), C_{Cl-}, mg-equiv./dm^3; 2 – concentration of chlorides in the anolyte (j = 8.33 A/dm^2), C_{Cl-}, mg-equiv./dm^3; 3 – degree of chloride conversion (j = 4.17 A/dm^2), E, %; 4 – degree of chloride conversion (j = 8.33 A/dm^2), E, %; ◆ – $y = 9.2679x^2 - 106.97x + 603.46$, $R^2 = 0.9973$; ■ – $y = 16.089x^2 - 159.59x + 588.82$, $R^2 = 0.9905$; ▲ – $y = -1.5446x^2 + 17.829x - 0.5964$, $R^2 = 0.9971$; × – $y = -2.6804x^2 + 26.585x + 1.875$, $R^2 = 0.9903$

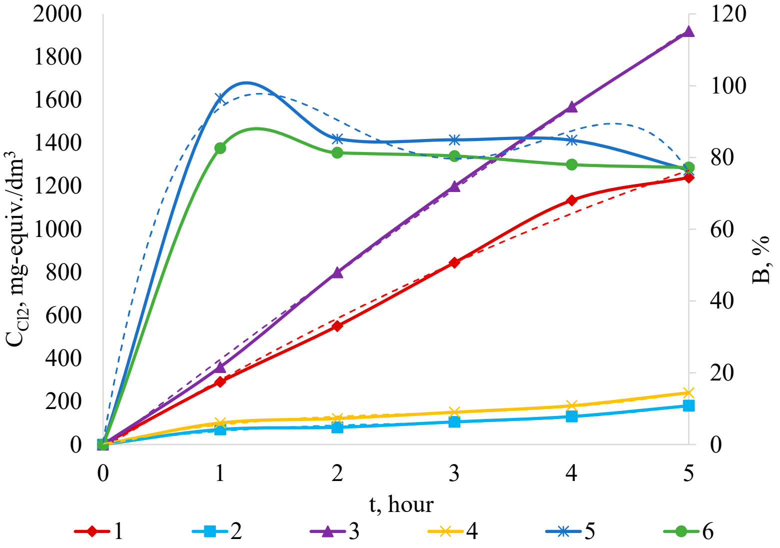

Fig. 12. Dependence of the concentration of active chlorine in the anolyte and absorber, the current output of active chlorine compounds on the time of electrolysis of a sodium chloride solution (C_{NaCl} = 2000 mg-equiv./dm^3) in a two-chamber electrolyzer (MA-41 membrane), catholyte – 1N NaOH, at different current densities: 1 – concentration of active chlorine in the anolyte (j = 8.33 A/dm^2, pH = 7.0–7.5), C_{Cl_2}, mg-equiv./dm^3; 2 – concentration of active chlorine in the absorber (j = 8.33 A/dm^2, pH = 7.0–7.5), C_{Cl_2}, mg-equiv./dm^3; 3 – concentration of active chlorine in the anolyte (j = 12.5 A/dm^2, pH = 6.5–7.0), C_{Cl_2}, mg-equiv./dm^3; 4 – concentration of active chlorine in the absorber (j = 12.5 A/dm^2, pH = 6.5–7.0), C_{Cl_2}, mg-equiv./dm^3; 5 – current yield of active chlorine compounds (j = 8.33 A/dm^2, pH = 7.0–7.5), V, %; 6 – current yield of active chlorine compounds (j = 12.5 A/dm^2, pH = 6.5–7.0), V, %; ◆ – $y = -14.357x^2 + 329.7x - 16.143$, $R^2 = 0.9945$; ■ – $y = 3.5185x^3 - 27.103x^2 + 83.347x + 2.3016$, $R^2 = 0.9915$; ▲ – $y = -5.8929x^2 + 418.89x - 18.214$, $R^2 = 0.9993$; × – $y = 4.8148x^3 - 38.968x^2 + 122.25x + 2.6984$, $R^2 = 0.9937$; ✳ – $y = -2.65x^4 + 30.811x^3 - 122.28x^2 + 187.48x + 0.5238$, $R^2 = 0.989$; ● – $y = -1.6917x^4 + 20.822x^3 - 88.775x^2 + 150.07x + 0.3619$, $R^2 = 0.9938$

This is due to high residual chloride concentrations during the electrolysis process for 5 hours (Fig. 13).

Fig. 13 demonstrates that the chloride concentration decreased in 5 hours at a current density of 8.33 A/dm^2 to 1290 mg-equiv./dm^3, and at a current density of 12.5 A/dm^2 to 920 mg-equiv./dm^3.

This provided a chloride conversion rate of 34.3% in the first case and 54.0% in the second case.

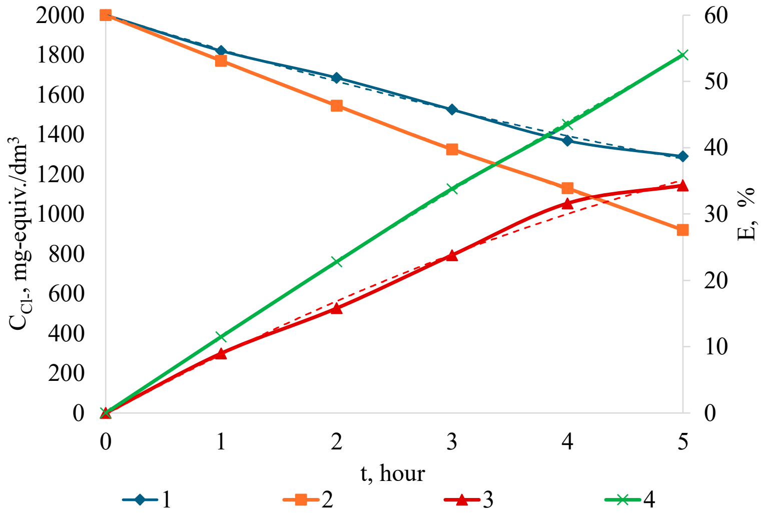

Fig. 13. Dependence of the concentration of chlorides in the anolyte, the degree of their conversion on the time of electrolysis of a sodium chloride solution (C_{NaCl} = 2000 mg-equiv./dm^3) in a two-chamber electrolyzer (membrane MA-41), catholyte – 1N NaOH, at different current densities: 1 – concentration of chlorides in the anolyte (j = 8.33 A/dm^2), C_{Cl^-}, mg-equiv./dm^3; 2 – concentration of chlorides in the anolyte (j = 12.5 A/dm^2), C_{Cl^-}, mg-equiv./dm^3; 3 – degree of chloride conversion (j = 8.33 A/dm^2), E, %; 4 – degree of chloride conversion (j = 12.5 A/dm^2), E, %; –◆– – $y = 7.5357x^2 - 182.42x + 2001.6$, $R^2 = 0.9969$; –■– – $y = 3.9286x^2 - 235.07x + 2000$, $R^2 = 0.9999$; –▲– – $y = -0.4911x^2 + 9.5211x - 0.2179$, $R^2 = 0.995$; –×– – $y = -0.2036x^2 + 11.789x - 0.0071$, $R^2 = 0.9999$

In general, when using a sealed electrolyzer, there were no significant losses of active chlorine due to degassing. This is confirmed by the results of monitoring the reaction of the medium in the anolytes in the experiments conducted in closed electrolyzers (Table 2).

Table 2

Dependence of the reaction of the anolyte medium in a two-chamber closed electrolyzer on the electrolysis time at chloride concentrations of 600 mg-equiv./dm^3 and 2000 mg-equiv./dm^3 at anodic current density, A/dm^2: 4.17, 8.33, and 12.5

t, h	pH			
	C_{NaCl}, mg-equiv./dm^3			
	600		2000	
	j, A/dm^2		j, A/dm^2	
	4.17	8.33	8.33	12.50
0	7.00	7.00	6.50	6.50
1	7.10	7.08	6.60	6.69
2	7.15	7.12	6.74	6.85
3	7.17	7.18	6.87	7.12
4	7.16	7.25	7.00	7.30
5	7.20	7.70	7.10	7.50

In all cases, the reaction of the medium in the anolytes changed little. The slight increase in pH is due to the degassing of a small amount of active chlorine from the anolyte trapped in the absorber.

6. Results of investigating the processing of sodium chloride solutions by electrodialysis: discussion

The processing of membrane and ion-exchange water desalination concentrates is a complex problem. The most well-known evaporation processes [9] are too energy-intensive and costly and do not solve the problem of recycling these wastes. In Ukraine, the production of active chlorine, sodium hypochlorite, and sodium chlorite is very limited. And this creates problems in water disinfection. Therefore, the processing of sodium chloride solutions to obtain active chlorine is a rather promising direction [18]. When using electrodialysis, it is possible to successfully solve the task of processing NaCl solutions [17] and ensuring effective water disinfection with its reagents [22, 23].

Technologies for obtaining active chlorine, sodium hypochlorite, and sodium chlorate and chlorite are well studied. However, they are focused on the use of concentrated sodium chloride solutions (CNaCl > 100 g/dm^3). Concentrates from water desalination processes contain sodium chloride in concentrations from 3 g/dm^3 to 30 g/dm^3. When using them in conventional processes for obtaining active chlorine, it is impossible to obtain high-quality products. In this case, the output of oxidized chlorine compounds will be low [17].

At existing production facilities, the concentration of working NaCl solutions is adjusted by diluting dry salt. When processing NaCl solutions formed during desalination of brackish waters, the task is to process them for effective utilization. Therefore, our studies are aimed at determining the parameters of the processes for manufacturing active chlorine, sodium hypochlorite, or other products suitable for water disinfection from existing solutions – waste water desalination, oxidants for other technological processes.

From Fig. 2, 3 it is seen that during the electrolysis of sodium chloride solutions (CNaCl = 61 mg-equiv./dm^3 = 3.57 g/dm^3) in the anode region of a two-chamber electrolyzer with an anion exchange membrane MA-41, sodium hypochlorite solutions can be obtained. At an anode current density of 0.83 A/dm^2, active chlorine with a concentration of 80 mg-equiv./dm^3 is obtained.

In this case, the yield of active chlorine by current decreased from 100% during the first 30 minutes to 55% in 4 hours. First of all, this is because of the decrease in the chloride content in the anolyte from 61 mg-equiv./dm^3

to 21 mg-equiv./dm^3. A total of 40 mg-equiv./dm^3 of chlorides were oxidized to hypochlorite anions. In this case, the obtained active chlorine, when interacting with hydroxide anions, which pass from the cathode chamber through the anion exchange membrane into the anolyte, turned into hypochlorite and chloride anions. It remained completely in the anolyte. The real yield of sodium hypochlorite in terms of oxidized chlorides was 100%.

At an anode current density of 1.67 A/dm^2, 46 mg-equiv./dm^3 of chlorides were oxidized. Of these, 40 mg-equiv./dm^3 of sodium hypochlorite were formed, which were determined in solution as 80 mg-equiv./dm^3 of active chlorine. The yield of sodium hypochlorite in terms of the amount of oxidized chlorides reached 87%. 13% of oxidized chlorides were lost because of degassing in the form of active chlorine. When the anodic current density increased to 4.17 A/dm^2 and 8.33 A/dm^2 (Fig. 4, 5), the yield of sodium hypochlorite from oxidized chlorides significantly decreased compared to the previous cases without a significant increase in its concentration in the solution. At a current density of 4.17 A/dm^2, 43 mg-equiv./dm^3 of chlorides were oxidized. Their concentration in the solution decreased from 61.0 mg-equiv./dm^3 to 18.0 mg-equiv./dm^3 in just 1.5 hours. This is because of the increase in the intensity of active chlorine evaporation with an increase in the rate of chloride oxidation because of an increase in the anodic current density. In this case, only 22 mg-equiv./dm^3 of sodium hypochlorite was obtained, which was determined as 44 mg-equiv./dm^3 of active chlorine. The yield of hypochlorite reached 51.2%. The loss of chlorides because of the degassing of active chlorine was 48.8%.

When the current density increased to 8.33 A/dm^3 and the intensity of chloride oxidation increased, 53 mg-equiv./dm^3 of chlorides were oxidized in 1.5 hours. At the same time, the amount of hypochlorite formed reached 40.5 mg-equiv./dm^3, and the yield of oxidized chlorides was 76.4%. Losses of active chlorine were 23.6%.

Obviously, under these conditions, a significant part of the formed active chlorine did not have time to react with hydroxide anions coming from the catholyte. The latter were partially oxidized at the anode with the formation of oxygen. The process of degassing active chlorine was visible from the change in its concentration in the anolyte over time. After 0.25 hours, the Cl_2 concentration reached 70 mg-equiv./dm^3, after half an hour – 90 mg-equiv./dm^3, and after 1.5 hours it decreased to 81 mg-equiv./dm^3. Obviously, the loss of active chlorine occurred from the first minutes of the experiment. Therefore, the current yield of active chlorine at a current density of 4.17 A/dm^2 decreased from 98.7% to 15.7% in 1.5 hours, and at a current density of 8.33 A/dm^2 it decreased from 75.0% to 14.5%. The degree of chloride conversion increases with increasing anodic current density.

The loss of active chlorine formed as a result of electrodialysis can be explained by the significant dependence of the yield of active chlorine and sodium hypochlorite on its stability at a temperature of 25°C. In addition, the increase in the rate of chlorine degassing with increasing its concentration in the solution is also significant. Therefore, a high yield of active chlorine in an open electrolyzer can be achieved only at low values of the anode current density, and therefore a low rate of generation of active chlorine and its low concentration. With increasing anode current density, the rate of generation of active chlorine increases. However, with low stability of sodium hypochlorite, active chlorine slowly converts to hypochlorite, which contributes to its degassing from the anolyte in an open electrolyzer.

The main disadvantage of the processes under these conditions is the low intensity of chloride oxidation and the insignificant concentration of the sodium hypochlorite solution at low values of the anodic current density. In addition, significant losses of active chlorine are observed because of degassing when the values of the anodic current density are increased. Thus, these two disadvantages do not make it possible to obtain concentrated solutions in terms of active chlorine.

One of the approaches to increasing the efficiency of the synthesis of sodium hypochlorite is to increase the concentration of NaCl in the initial solutions. The concentration of sodium chloride can be increased by electrodialysis [17] during the desalination of dilute solutions and obtaining an alkali solution and a concentrated NaCl solution. Therefore, the processes of obtaining sodium hypochlorite solutions in two-chamber electrolyzers with an increase in the concentration of NaCl in the initial solutions were investigated.

From the data shown in Fig. 6, it is seen that at a sodium chloride concentration of 450 mg-equiv./dm^3 (26.3 g/dm^3) the concentration of active chlorine in the anolyte increased, compared to previous experiments. At an anode current density of 1.67 A/dm^2, the concentration of active chlorine in the anolyte during the electrolysis of NaCl solution for 9 hours reached 170 mg-equiv./dm^3, and at a current density of 4.17 A/dm^2 the concentration of active chlorine was 280 mg-equiv./dm^3. At these values of the anode current density, the degree of chloride conversion reached 48.9% and 62.2%, respectively, and the residual chloride concentrations were 230 mg-equiv./dm^3 and 160 mg-equiv./dm^3, respectively (Fig. 7).

When the anode current density was increased to 8.33 A/dm^2, no significant increase in the concentration of active chlorine in the anolyte was observed (Fig. 6). This is because of the rapid formation of active chlorine and its losses during degassing. At a degree of chloride oxidation of 77.8%, the concentration of active chlorine in the anolyte was at the level of 120 mg-equiv./dm^3 after 3 hours.

Chlorine losses during degassing at a given chloride concentration decrease when the anode current density decreases to 4.17 A/dm^3. Under these conditions, the sodium hypochlorite concentration in the anolyte reached 140 mg-equiv./dm^3 (280 mg-equiv./dm^3 in terms of active chlorine). In total, 290 mg-equiv./dm^3 of chlorides were oxidized in this case, of which 140 mg-equiv./dm^3 of chlorides were converted to sodium hypochlorite, the yield of sodium hypochlorite was 48.3%. Active chlorine losses during degassing were 130 mg-equiv./dm^3 (51.7%).

At a current density of 1.67 A/dm^2, 220 mg-equiv./dm^3 of chlorides were oxidized. The NaClO yield was 38.6%, and the active chlorine losses were 135 mg-equiv./dm^3 (61.4%).

At an anode current density of 8.33 A/dm^2, the sodium hypochlorite yield from oxidized chlorides was only 17.14%, and the active chlorine losses during degassing reached 82.8%. Obviously, the best option in this case at a chloride concentration of 450 mg-equiv./dm^3 is to use an anode current density of 4.17 A/dm^2. Although even in this case, the active chlorine losses were significant.

With a further increase in the sodium chloride concentration in the anolyte of the two-chamber electrolyzer at the same anode current density of 4.17 A/dm^2, it was not possible to significantly increase the concentration of sodium hypochlorite (active chlorine) in the working solution (Fig. 8). When the chloride concentration in the anolyte increased to 875 mg-equiv./dm^3, 1425 mg-equiv./dm^3 and 1725 mg-equiv./dm^3, the concentration of active chlorine increased to 300 mg-equiv./dm^3, 320 mg-equiv./dm^3 and 340 mg-equiv./dm^3, respectively. These values of active chlorine concentrations corresponded to sodium hypochlorite concentrations of 150 mg-equiv./dm^3, 160 mg-equiv./dm^3 and 170 mg-equiv./dm^3, respectively. At a chloride concentration of 450 mg-equiv./dm^3 (Fig. 7), the concentration of active chlorine increased to 280 mg-equiv./dm^3 (sodium hypochlorite concentration – 140 mg-equiv./dm^3). In relation to the amount of oxidized chlorides at their initial concentration of 875 mg-equiv./dm^3, the yield of sodium hypochlorite was 25.6%, and chlorine losses were at the level of 74.4% (Fig. 9). At a chloride concentration of 1425 mg-equiv./dm^3, the yield of sodium hypochlorite reached 27.6%, and chlorine losses were 72.4%. At a chlorine concentration of 1725 mg-equiv./dm^3, the yield of sodium hypochlorite reached 29.6%, and chlorine losses were at the level of 70.3%.

It is obvious that with an increase in the concentration of sodium chloride in the anolyte, as well as with an increase in the anodic current density, the rate of chloride oxidation increases. This causes an increase in the concentration of active chlorine and sodium hypochlorite in the solution. But because of the low thermodynamic stability of the latter, the rate of the reverse reaction increases – the decomposition of hypochlorite into chloride and active chlorine, which is removed by evaporation from the open electrolyzer. This is a significant drawback of processing sodium chloride solutions (Table 1).

When carrying out electrochemical oxidation of chlorides in a sealed two-chamber electrolyzer using an absorber to capture active chlorine, a sodium chloride solution with a concentration of 600 mg-equiv./dm^3 was used at the first stage (Fig. 10, 11). In this case, in comparison with the open electrolyzer, a significant increase in the concentration of sodium hypochlorite in the anolyte and significant amounts of captured active chlorine were noted. In this case, a large amount of oxidized chlorine is equivalent to the total amount of sodium hypochlorite in the anolyte and in the absorber. 80% of oxidized chlorides were retained in the anolyte in the form of sodium hypochlorite, approximately 20% of oxidized chlorides were fixed in the absorbate at an anode current density of 4.17 A/dm^2. At an anode current density of 8.33 A/dm^2, the concentration of active chlorine in the anolyte reached 690 mg-equiv./dm^3 (345 mg-equiv./dm^3 in terms of NaClO), which was 82% of the amount of oxidized chlorides. In the absorber, the concentration of Cl_2 reached 150 mg-equiv./dm^3 (75 mg-equiv./dm^3 in terms of NaClO), which corresponded to 17.9% of the amount of oxidized chlorine.

When using a closed electrolyzer with a sodium chloride solution with a concentration of 2000 mg-equiv./dm^3 (Fig. 12, 13),the active chlorine content in the anolyte was 1240 mg-equiv./dm^3 at a current density of 8.33 A/dm^2 and 1920 mg-equiv./dm^3 at a current density of 12.5 A/dm^2. The current yield of active chlorine reached 96.5% during the first hour of electrolysis and decreased to 84.6% after 4 hours at a current density of 8.33 A/dm^2. When the current density was increased to 12.5 A/dm^2, the current yield in the first hour reached 82.6%, and after 4 hours it was 77.2%. It is obvious that with an increase in the anodic current density, the influence of the water electrolysis process increased somewhat. In the anolyte at a current density of 8.33 A/dm^2, the hypochlorite content was 87.3% of the amount of oxidized chlorides, and in the absorber, respectively, 12.7% of the amount of oxidized chlorides. At a current density of 12.5 A/dm^2, these parameters were 89.0% and 11.0%, respectively.

Therefore, the use of a sealed two-chamber electrolyzer significantly improves the conditions for obtaining sodium hypochlorite in the anolyte because of the effective oxidation of chlorides at the anode and the diffusion of hydroxide anions into the anolyte through the membrane from the catholyte (Table 2). In this case, the amount of active chlorine formed is equivalent to the amount of hydroxide anions formed at the cathode, which enter the anolyte through the membrane. They ensure effective binding of active chlorine with the formation of sodium hypochlorite.

The advantage of this method is that chlorides, a by-product of the interaction of active chlorine with water or alkali, are in the anolyte and can be further oxidized at the anode. This allows for almost complete oxidation of chlorides.

The use of the method is limited by the need to design sealed two-chamber electrolyzers with chemically stable anodes (titanium coated with ruthenium oxide) and an anion exchange membrane. The limitation is the need to adjust the chloride concentration in the starting electrolytes to obtain concentrated sodium hypochlorite solutions. The method can be implemented only if there are installations for packaging sodium hypochlorite solutions in containers suitable for their storage and transportation.

The disadvantage of our paper is the insufficient study of the effect of temperature on the yield of sodium hypochlorite. After all, even when using a sealed electrolyzer at 25°C, part of the active chlorine evaporated and was retained in the absorber. By lowering the process temperature in the planned future studies, it is possible to obtain sodium hypochlorite with a high yield without using an absorber. Its concentration can be adjusted by the initial concentration of sodium chloride in the anolyte.

In further studies, it is necessary to determine the effect of temperature on the conversion of chlorides, the concentration of sodium hypochlorite in the anolyte and active chlorine in the absorber depending on the anode current density and electrolysis time.

7. Conclusions

1. We have demonstrated that during the electrolysis of NaCl solutions in the anode chamber of an open two-chamber electrolyzer with an anion exchange membrane MA-41, when using an alkali solution as a catholyte, chlorides are oxidized to form sodium hypochlorite. With an increase in the anode current density, the degree of conversion (oxidation) of chlorides increases. However, a high yield of sodium hypochlorite was achieved only at a low concentration of chlorides at a low anode current density ($J = 0.83$ A/dm^2). Under these conditions, the yield of hypochlorite is close to 100%. With an increase in the anode current density to 1.67 A/dm^2 and 4.17 A/dm^2, the yield of sodium hypochlorite decreased to 87.0% and 51.2%, respectively. In general, the yield of sodium hypochlorite depends on the concentration of sodium chloride, the anode current density, and the intensity of active chlorine degassing. The yield of active chlorine and sodium hypochlorite increases with increasing NaCl concentration and with increasing anodic current density. However, with increasing active chlorine concen-

tration, the rate of its degassing in an open electrolyzer increases significantly. This causes a significant decrease in the final yield of sodium hypochlorite during electrolysis. The current yield in all cases decreases with the time of electrolysis, which is due to a decrease in the concentration of chlorides in the solution and the low thermodynamic stability of hypochlorites and significant losses of active chlorine during degassing.

2. It has been found that when using a two-chamber sealed electrolyzer with an anion exchange membrane MA-41 with an absorber, the main amount of active chlorine is concentrated in the anolyte in the form of sodium hypochlorite during the interaction of active chlorine with hydroxides. Hydroxide anions are formed at the cathode and enter the anolyte through the anion membrane. The yield and concentration of sodium hypochlorite in a sealed electrolyzer increase with the concentration of chlorides in the anolyte, with an increase in the anode current density and with the electrolysis time. This is because of a significant decrease in the degassing of active chlorine in a sealed electrolyzer. Losses of active chlorine due to degassing under these conditions, based on the amount of chlorine captured in the absorbers, were 11–17%.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

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

References

1. WHO Country Office in Ukraine annual report 2024 (2025). Copenhagen: WHO Regional Office for Europe, 116.
2. Our Mission (2021). World Economic Forum.
3. Trus, I., Gomelya, M., Tverdokhlib, M., Halysh, V., Radovenchyk, I., Benatov, D. (2022). Purification of Mine Waters Using Lime and Aluminum Hydroxochloride. Ecological Engineering & Environmental Technology, 23 (5), 169–176. https://doi.org/10.12912/27197050/152104
4. Trus, I. M., Gomelya, M. D. (2021). Desalination of mineralized waters using reagent methods. Journal of Chemistry and Technologies, 29 (3), 417–424. https://doi.org/10.15421/jchemtech.v29i3.214939
5. Pro yakist vody, pryznachenoi dlia spozhyvannia liudynoiu (1998). Dyrektyva Rady 98/83/IeS. 03.11.1998. Available at: https://online.budstandart.com/ua/catalog/doc-page.html?id_doc=60063
6. Nyangi, M. J. (2023). Simultaneous removal of chloride and hardness from groundwater by cassava peel biosorption: Optimization and sorption studies. Remediation Journal, 34 (1). https://doi.org/10.1002/rem.21770
7. Tsutano, K. (2022). Application of Monolithic Ion Exchange resins for the field of Ultrapure Water. Journal of Ion Exchange, 33 (3), 51–55. https://doi.org/10.5182/jaie.33.51
8. Koliehova, A., Trokhymenko, H., Melnychuk, S., Gomelya, M. (2019). Treatment of Wastewater Containing a Mixture of Heavy Metal Ions (Copper-Zinc, Copper-Nickel) using Ion-Exchange Methods. Journal of Ecological Engineering, 20 (11), 146–151. https://doi.org/10.12911/22998993/112746
9. Wang, Y., Yang, S. (2019). Thermodynamic analysis of an absorption-assisted multi-effect thermal desalination system with an extended operating temperature range. Desalination and Water Treatment, 155, 370–380. https://doi.org/10.5004/dwt.2019.23874
10. Safder, U., Ifaei, P., Nam, K., Rashidi, J., Yoo, C. (2018). Availability and reliability analysis of integrated reverse osmosis – forward osmosis desalination network. Desalination and Water Treatment, 109, 1–7. https://doi.org/10.5004/dwt.2018.22147
11. Vargas, C., Bórquez, R. (2020). Evaluation of the operation seawater and brackish water desalination system using two-pass nanofiltration. Desalination and Water Treatment, 204, 50–58. https://doi.org/10.5004/dwt.2020.26287
12. Bagastyo, A. Y., Sari, P. P. I., Direstiyani, L. C. (2020). Effect of chloride ions on the simultaneous electrodialysis and electrochemical oxidation of mature landfill leachate. Environmental Science and Pollution Research, 28 (45), 63646–63660. https://doi.org/10.1007/s11356-020-11519-z
13. Zhu, M., He, F., Feng, L., Chi, Y., Li, Y.-Y., Tian, B. (2024). Comparison of bipolar membrane electrodialysis, electrodialysis metathesis, and bipolar membrane electrodialysis multifunction for the conversion of waste Na2SO4: Process performance and economic analysis. Journal of Environmental Management, 370, 122513. https://doi.org/10.1016/j.jenvman.2024.122513
14. Gomelya, M., Kryzhanovska, Y., Makarenko, I., Shabliy, T., Kyrylyuk, O. (2025). Evaluation of the efficiency of the processing of sodium chloride solutions by electrodialysis in a three-chamber electrolyzer using a high-basic anionite. Proceedings of the NTUU “Igor Sikorsky KPI”. Series: Chemical Engineering, Ecology and Resource Saving, 2, 60–69. https://doi.org/10.20535/2617-9741.2.2025.333975

15. Gomelya, M., Kryzhanovska, Y., Pliatsuk, Y. (2024). Production of active chlorine and sodium hypochlorite in a closed electrolyser. Proceedings of the NTUU "Igor Sikorsky KPI". Series: Chemical Engineering, Ecology and Resource Saving, 4, 41–50. https://doi.org/10.20535/2617-9741.4.2024.319015
16. Liu, Q., Feng, T., Zhu, S., Lu, G. (2024). Simulation study of the electrothermal field in a chloride electrolysis cell with 16 electrode pairs. The Canadian Journal of Chemical Engineering, 102 (11), 3909–3921. https://doi.org/10.1002/cjce.25281
17. Gomelya, M., Kryzhanovska, Y. (2023). Concentration of sodium chloride solutions in the processing of concentrates for reverse osmotic water desalification. Proceedings of the NTUU "Igor Sikorsky KPI". Series: Chemical Engineering, Ecology and Resource Saving, 3, 85–93. https://doi.org/10.20535/2617-9741.3.2023.288253
18. Akhter, M., Habib, G., Qamar, S. U. (2018). Application of Electrodialysis in Waste Water Treatment and Impact of Fouling on Process Performance. Journal of Membrane Science & Technology, 8 (2). https://doi.org/10.4172/2155-9589.1000182
19. Martins, V. L., Ogden, M. D., Jones, M. R., Trowsdale, S. A., Hall, P. J., Jensen, H. S. (2020). Opportunities for coupled electrochemical and ion-exchange technologies to remove recalcitrant micropollutants in water. Separation and Purification Technology, 239, 116522. https://doi.org/10.1016/j.seppur.2020.116522
20. Li, F., Jia, Y., Wang, M. (2024). Recovery of low-concentration waste acid by electrodialysis: Modeling and validation. Journal of Cleaner Production, 482, 144203. https://doi.org/10.1016/j.jclepro.2024.144203
21. Gomelya, M., Kryzhanovska, Y., Shabliy, T., Makarenko, I., Hlushko, O., Vember, V. (2025). Synthesis of oxidized chlorine compounds by electrodialysis using a strongly basic anion exchange resin. Ecological Engineering & Environmental Technology, 26 (6), 98–107. https://doi.org/10.12912/27197050/204068
22. Scarazzato, T., Panossian, Z., Tenório, J. A. S., Pérez-Herranz, V., Espinosa, D. C. R. (2017). A review of cleaner production in electroplating industries using electrodialysis. Journal of Cleaner Production, 168, 1590–1602. https://doi.org/10.1016/j.jclepro.2017.03.152
23. Wang, D., Chen, X., Luo, J., Shi, P., Zhou, Q., Li, A., Pan, Y. (2024). Comparison of chlorine and chlorine dioxide disinfection in drinking water: Evaluation of disinfection byproduct formation under equal disinfection efficiency. Water Research, 260, 121932. https://doi.org/10.1016/j.watres.2024.121932