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Mykola Gomelya, Yana Kryzhanovska, Tetyana Shabliy, Iryna Makarenko, Olena Hlushko, Alina Ostapenko

EVALUATION OF THE EFFICIENCY OF OXIDIZED CHLORINE COMPOUNDS SYNTHESIS BY ELECTRODIALYSIS FROM MEMBRANE DESALINATION CONCENTRATES

National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv, Ukraine

This study investigates the processing of reverse osmosis desalination concentrates containing sodium chloride, calcium bicarbonate, and magnesium bicarbonate. Water desalination was carried out using a Filmtec TW 30-1812-50 reverse osmosis membrane cassette in two stages. When desalinating water with a permeate recovery rate of 66% at the first stage, the membrane's selectivity for chlorides ranged from 74% to 95%. In the second stage, the obtained concentrate ($[Cl^-]$=110 mg-eq/dm^3) was further desalinated using the same membrane. At a permeate recovery rate of 74%, the membrane's selectivity reached 70%. The two-stage filtration process reduced the concentrate volume from 34% to 8.2% of the initial water volume. During the electrolysis of model solutions of reverse osmosis desalination concentrates, a two-chamber electrolyzer with an MA-41 anion-exchange membrane was used. A sodium chloride solution was placed in the anode chamber, while the cathode chamber was filled with an alkaline solution with a concentration of 200 mg-eq/dm^3. Electrolysis processes were conducted at a current density ranging from 0.83 to 16.7 A/dm^2, using solutions with chloride concentrations between 59 and 480 mg-eq/dm^3. It was found that the intensity of chloride oxidation increased with higher anode current density and higher chloride concentration in the solution. A decrease in the current efficiency of oxidized chlorine compounds was observed as chloride concentration in the solution decreased. The concentration of oxidized compounds in the anolyte of an open electrolyzer did not exceed 180 mg-eq/dm^3 due to significant losses of Cl_2 and ClO_2 caused by degassing.

Keywords: membrane, reverse osmosis, electrodialysis, active chlorine, catholyte, anolyte, anode current density, current efficiency.

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Introduction

The problem of desalination of natural and wastewater remains one of the most challenging issues in water treatment technology. Despite significant progress in this field, the pollution level in natural water bodies continues to rise. The issue of increasing water mineralization is particularly pressing because existing wastewater treatment technologies are largely unsuitable for water desalination. On the other hand, advanced baromembrane [1], electrodialysis [2], ion exchange [3], and thermal [4] desalination systems address water desalination locally but do not provide a comprehensive solution to the problem. This is primarily because any desalination method inevitably generates concentrated saline waste. These byproducts are often discharged into the environment, significantly deteriorating the quality of natural water resources.

Currently, the most widely used water desalination technology is reverse osmosis, as its application virtually eliminates the need for chemical reagents and significantly reduces the amount of salts discharged into surface water bodies. This method is highly efficient due to the high selectivity of membranes. However, to prevent water pollution, it is essential to develop solutions for processing the concentrates generated during baromembrane water purification.

The treatment of baromembrane desalination concentrates that contain only sulfates, bicarbonates, and hardness ions can be reduced to chemical precipitation of sulfates and hardness ions in the form of calcium carbonate, magnesium hydroxide, and calcium hydroxoaluminosulfate [5]. However, in the presence of chlorides this method cannot be used for demineralization, as chlorides remain in the water and are not removed.

During the electrolysis of solutions containing chlorides and sulfates, sulfuric acid and active chlorine can be produced [6]. However, the resulting sulfuric acid contains impurities of hydrochloric acid and active chlorine. Additionally, capturing and processing active chlorine is a complex process. When a solution contains only chloride anions, carbonates, and bicarbonates, electrodialysis can be used to produce either alkali and hydrochloric acid or sodium hypochlorite [7]. Therefore, an efficient approach involves reverse osmosis desalination preceded by ion-exchange separation of chlorides and sulfates, or chlorides, sulfates, and nitrates [8].

Membrane technologies are widely applied for chloride removal from water, with removal efficiencies ranging from 82% to 96% [9]. This variation is primarily due to differences in water characteristics and membrane properties.

Using nanofiltration or reverse osmosis membranes can achieve a high degree of chloride-ion removal [10]. However, a significant challenge in seawater desalination via reverse osmosis is the high filtration resistance, which results in increased energy consumption and reduced transmembrane flow rates.

Another approach to reducing high-energy consumption in reverse osmosis desalination is its combination with electrodialysis [11]. Electrodialysis is also widely used for chloride removal from water, providing a comprehensive desalination effect that reduces not only chloride and sulfate levels but also water hardness [12]. Under optimal conditions, wastewater desalination efficiency reaches 92%, with sulfate removal at 98% and chloride removal at 80%.

If wastewater contains chlorides, electrochemical treatment can convert them into sodium hypochlorite, active chlorine, or other oxidized chlorine compounds, which are widely used as disinfectants [13]. During electrolysis, chloride conversion efficiency can reach 85%.

This study aims to evaluate the efficiency of electrochemical processing of reverse osmosis desalination concentrates containing chlorides to produce oxidized chlorine compounds.

To achieve the goal, the following tasks were set:

1. Investigation of the desalination processes of chloride-containing water using the reverse osmosis method, determining the composition of concentrates depending on water characteristics and process parameters.

2. Determination of the efficiency of anodic oxidation of chlorides in two-chamber electrolyzers based on anode current density and concentrate characteristics.

Materials and methods

Water desalination processes

The water desalination processes were conducted using a low-pressure reverse osmosis (RO) membrane cassette, Filmtec TW30-1812-50. A solution was used as the medium (the concentration of chlorides $[Cl^-]=1030$ mg/dm^3; hardness H=0.15 mg-eq/dm^3; alkalinity A=0.28 mg-eq/dm^3).

The RO desalination process was studied in the following way. The initial volume of the solution was 10 dm^3. Water was supplied to the filter using a pump with the RO membrane. Permeate was collected in a separate container. The permeate sample volume was 1 dm^3. The concentrate was returned to the container with the initial solution. After filtration through the RO filter at a permeate recovery rate of 66%, permeate samples were obtained with a chloride content of 1.40–20.2 mg-eq/dm^3 and concentrate samples with a chloride content of 102–120 mg-eq/dm^3. Then, the concentrate obtained in the first stage of desalination was used in a repeated desalination process at a permeate recovery rate of 74%. Permeate samples were obtained with a chloride content of 15.18–85.0 mg-eq/dm^3 and concentrate samples with a chloride content of 450–500 mg-eq/dm^3. The pressure in the system was regulated using a concentrate discharge valve. A stopwatch was used to record the time required to collect each permeate sample.

The concentration of chlorides, hardness, and alkalinity was determined [14].

The membrane selectivity for the solution components was calculated using the following formula:

$$R=\frac{C_0-C_P}{C_0}\cdot 100\%, \quad (1)$$

where C_0 and C_p are the concentration in the initial solution and permeate, mg/dm^3, respectively.

For each subsequent sample after the first one, the increase in component concentration (C_0) due to its accumulation in the concentrate was considered.

The membrane performance (transmembrane flux rate) was determined using the following formula:

$$J = \frac{\Delta V}{S \cdot \Delta t}, \qquad (2)$$

where ΔV is the volume of permeate that passed through the membrane, dm^3; S is the membrane surface area, m^2 (here S=0.2 m^2); and Δt is the sampling time, h.

Preparation of the oxidized chlorine compounds in chloride solutions

The processes of preparing the oxidized chlorine compounds in chloride solutions were conducted in a two-chamber electrolyzer with an MA-41 anion-exchange membrane.

A plate made of alloyed steel 12X18H10T (an analogue of AISI 321) was used as the cathode, while a titanium plate coated with ruthenium oxide was used as the anode. The electrode area was $S_-=S_a=12$ cm^2. Electrolysis was carried out at an anodic current density ranging from 0.83 to 16.67 A/dm^2.

Model solutions from baromembrane water desalination with chloride concentrations ranging from 59 mg-eq/dm^3 to 480 mg-eq/dm^3 were used for electrolysis.

To determine the effect of hardness ions on the electrolysis process, a mixture of sodium chloride and calcium chloride solutions ($[Cl^-]=436$ mg-eq/dm^3) was used in Na:Ca ratios of 70:30, 50:50, or 30:70.

In the anode chamber, the working solution contained sodium chloride, while the cathode chamber was filled with a 0.2 N NaOH solution. During electrolysis, alkalinity in the cathode zone, as well as chloride content and active chlorine concentration in the anode zone, was monitored at regular time intervals.

The current efficiency was calculated as the ratio of the actual amount of substance transferred during electrolysis to the theoretical amount of substance determined according to the Faraday's law:

$$B = \frac{q_P}{q_t} \cdot 100\% = \frac{m_P}{m_t} \cdot 100\%, \qquad (3)$$

where q_P is the actual amount of electricity consumed for the transfer of one gram-equivalent of the substance; q_t is the theoretically calculated amount of electricity required for the transfer of one gram-equivalent of the substance; m_p is the actual amount of transferred substance (g-eq); and m_t is the theoretically determined amount of transferred substance (g-eq).

The actual amount of transferred substance was calculated based on the difference in concentration and the solution volume.

The theoretical amount of transferred substance (g-eq) was determined using the formula:

$$m_t = K_E It, \qquad (4)$$

where K_E is the electrochemical equivalent (0.03731 g-eq/(A·h)); I is the current strength, A; and t is the electrolysis duration, h.

The efficiency of water purification from chlorides was calculated using the following formula:

$$E = \frac{C_0 - C}{C_0} \cdot 100\%, \qquad (5)$$

where C_0 is the initial concentration of the solution, mg/dm^3; and C is the concentration of the solution at time t, mg/dm^3.

Results and discussion

To study the processes of electrolytic processing of chlorine-containing concentrates, water purified from sulfates by ion exchange was desalinated using a RO system. The desalination results are presented in Tables 1 and 2.

When using the Filmtec TW-30-1812-50 RO membrane to filter a solution (Table 1) with a chloride concentration of 1000 mg/dm^3 at a 66% concentrate recovery rate, the chloride concentration reaches 4000 mg/dm^3. The membrane's selectivity for chlorides decreases from 95.17% to 74.50%, while the chloride content in the permeate does not exceed 20 mg/dm^3.

When filtering the obtained concentrate using the same membrane at a 74% permeate recovery rate, the membrane's selectivity decreases from 86% to 70%, and the chloride concentration in the concentrate increases to 16.5 g/dm^3 (Table 2).

The chloride concentration in the permeate averaged over 7.4 dm^3 of collected filtrate, reaches 1205 mg/dm^3. It is evident that this permeate should be returned to the previous filtration stage, as its chloride content is close to that of the water used in the first stage of baromembrane desalination.

Thus, when treating water according to the scheme shown in Fig. 1, the volume of concentrate can be reduced from 34% of the initial water volume during single-stage filtration to 8.2% by re-filtering the concentrate using a RO filter.

It should be noted that the Filmtec TW-30-1812-50 membrane belongs to low-pressure RO membranes and ensures effective water desalination at pressures up to 1 MPa (in this case, P=0.4 MPa) with high membrane productivity. At the same time, during concentrate filtration, a certain decrease in membrane selectivity was observed without a significant reduction in its productivity. Therefore, in general, the application of this scheme allows for a significant reduction in concentrate volume while increasing the chloride concentration in it from 4 to 16–17 g/dm^3 with a slight increase in energy consumption.

Based on these results, in the further development of electrochemical oxidation processes of chlorides, their solutions were close in chloride concentration to the concentrates of baromembrane water desalination.

In further studies, two-chamber electrolyzers with an MA-41 anion-exchange membrane were used. In this case, the cathode is protected from calcium or magnesium hydroxide deposits, allowing electrolysis of chloride-containing solutions regardless of the content of hardness cations. The results of determining the effect of anodic current density on the efficiency of electrolysis of solutions with a chloride concentration of 60 mg-eq/dm^3 are presented in Fig. 2.

As seen in Fig. 2, the intensity of chloride oxidation increases with the rise in anodic current density. For example, when increasing the anodic current density from 0.83 A/dm^2 to 8.33 A/dm^2, the time required reaching an active chlorine concentration of 60 mg-eq/dm^3 decreases from 1 hour 30 minutes (90 minutes) to 10 minutes. At the same time, the active chlorine concentration in the anode chamber reaches 80–86 mg-eq/dm^3 at an anodic current density of 0.83–1.6 A/dm^2.

Table 1

Changes in chloride concentration, hardness ions, alkalinity, and pH in permeate (I) and concentrate (II), as well as membrane productivity (J) and selectivity (R) of the Filmtec TW-30-1812-50 membrane for chlorides and hardness ions, with increasing permeate recovery rate (Z) during the filtration of a model solution ([Cl]=1029.5 mg/dm^3, hardness (H)=0.15 mg-eq/dm^3, alkalinity (A)=0.28 mg-eq/dm^3, pH=7.15, P=4 atm)

Z, %	[Cl], mg-eq/dm^3		H, mg-eq/dm^3		A, mg-eq/dm^3		pH		J, dm^3/(m^2·h)	R, %	
	I	II	I	II	I	II	I	II		Cl$^-$	H
10	1.4	28.0	0.00	0.35	0.09	0.55	7.55	7.56	12.50	95.17	100.00
20	1.5	36.0	0.00	0.40	0.15	0.55	7.10	7.66	11.54	94.65	100.00
30	2.4	37.0	0.00	0.50	0.17	0.90	6.98	7.77	10.34	93.33	100.00
40	3.8	46.0	0.00	0.60	0.18	1.30	7.25	7.96	8.82	89.64	100.00
50	4.4	64.0	0.01	1.00	0.19	1.50	7.22	8.12	7.32	90.43	98.33
60	7.6	80.0	0.02	1.20	0.20	1.60	7.24	8.32	3.70	88.13	98.00
66	20.2	115.0	0.08	1.60	0.21	1.80	7.80	8.45	1.78	74.75	93.33

Table 2

Changes in chloride concentration, hardness ions, alkalinity, and pH in permeate (I) and concentrate (II), as well as membrane productivity (J) and selectivity (R) of the Filmtec TW-30-1812-50 membrane for chlorides and hardness ions, with increasing permeate recovery rate (Z) during the filtration of a model solution ([Cl]=3900 mg/dm^3, hardness (H)=1.60 mg-eq/dm^3, alkalinity (A)=1.63 mg-eq/dm^3, pH=8.32, P=4 atm)

Z, %	[Cl], mg-eq/dm^3		H, mg-eq/dm^3		A, mg-eq/dm^3		pH		J, dm^3/(m^2·h)	R, %	
	I	II	I	II	I	II	I	II		Cl$^-$	H
10	18.1	111.0	0.02	2.40	0.13	2.60	7.06	8.42	13.64	86.68	86.67
20	17.5	114.0	0.02	2.60	0.11	2.70	7.06	8.52	11.54	84.24	99.17
30	15.2	126.9	0.03	2.60	0.12	2.90	7.07	8.52	10.71	83.43	98.85
40	22.3	144.0	0.04	2.70	0.16	3.00	7.09	8.62	10.00	82.48	98.46
50	25.5	178.0	0.06	3.00	0.17	3.50	7.20	8.82	8.57	82.30	97.78
60	46.0	236.0	0.08	3.40	0.21	3.70	7.30	8.91	7.89	74.16	97.33
70	72.9	340.0	0.11	4.30	0.27	4.50	7.50	8.92	5.66	69.07	96.76
74	84.9	465.0	0.13	5.60	0.38	5.50	7.70	8.93	7.06	75.00	96.98

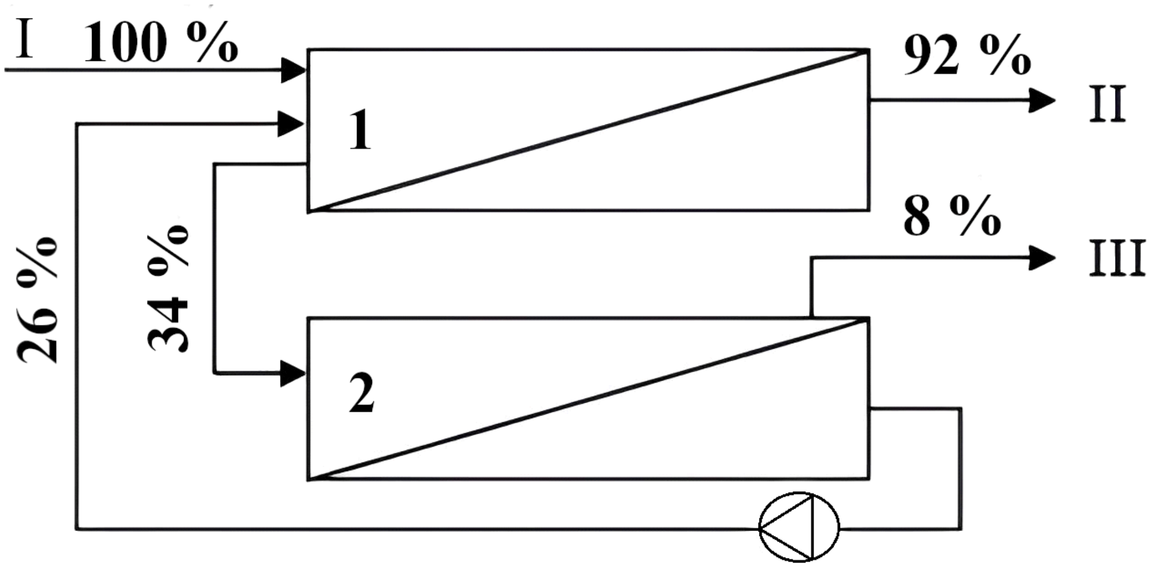

Fig. 1. Water desalination scheme using a RO filter (1) with concentrate refinement on a RO filter (2):
I – approach of water; II – removal of permeate; III – concentrate for processing

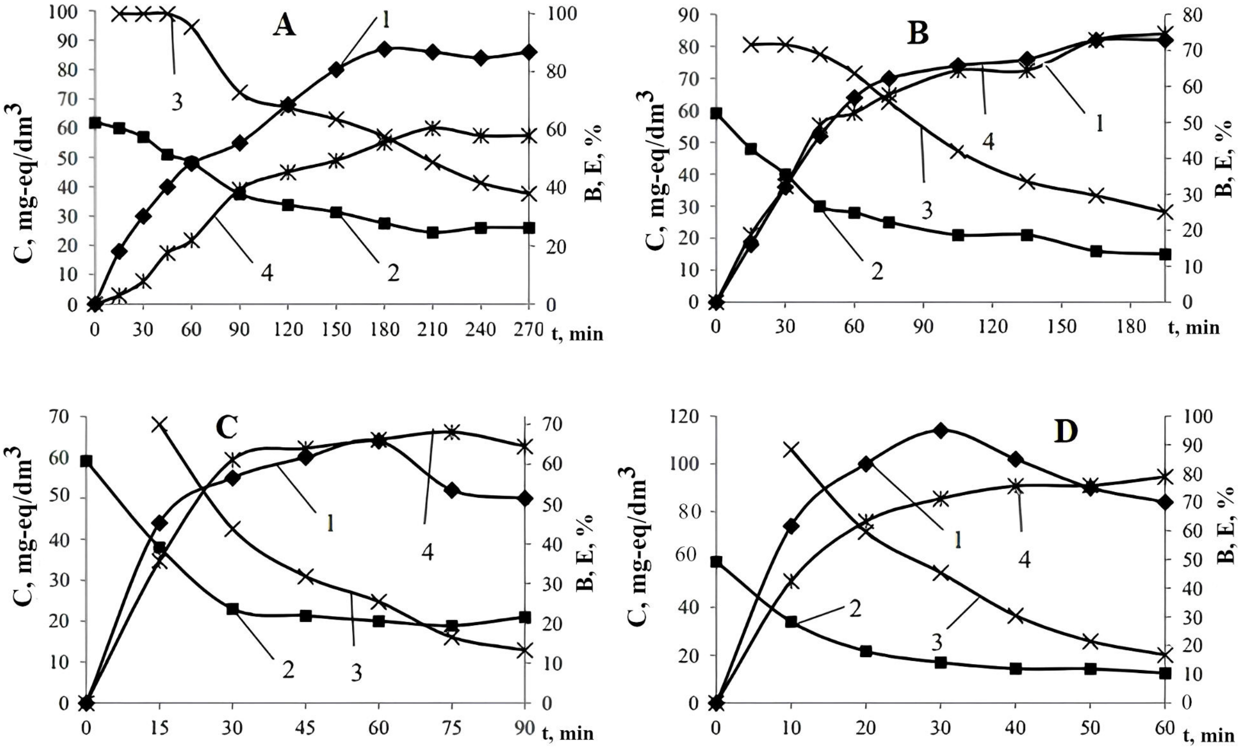

Fig. 2. Dependence of active chlorine concentration (1) and chlorides (2), current efficiency of active chlorine (3), and water purification efficiency from chlorides (4) in the anode chamber of a two-chamber electrolyzer with an MA-41 anion-exchange membrane on electrolysis time at an initial chloride concentration in the anode chamber $[Cl^-]=59.1$ mg-eq/dm^3, with alkalinity in the cathode chamber of 200 mg-eq/dm^3. Anodic current density, A/dm^2: 0.83 (A); 1.67 (B); 4.17 (C); and 8.33 (D)

At a current density of 4.17 A/dm², the maximum active chlorine concentration in the anolyte decreases to 64 mg-eq/dm³, while at an anodic current density of 8.33 A/dm², the active chlorine content increases to 114 mg-eq/dm³, which is almost twice the initial chloride concentration. The residual chloride concentration in this case decreases from 59.1 to 17.1 mg-eq/dm³. That is, only 42.1 mg-eq/dm³ of chlorides transition to the oxidized state. It is evident that, in this case, the chloride oxidation process does not stop at the Cl_2 formation stage. The formation of hypochlorite and other oxidized chlorine compounds likely occurs according to the reactions:

$$2Cl^- - 2e^- \rightarrow Cl_2; \qquad (6)$$

$$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O; \qquad (7)$$

$$ClO^- + Cl_2 + 2OH^- \rightarrow ClO_2^- + 2Cl^- + H_2O; \qquad (8)$$

$$ClO_2^- + Cl_2 + 2OH^- \rightarrow ClO_3^- + 2Cl^- + H_2O. \qquad (9)$$

It should be noted that, along with the oxidation reaction of chloride to active chlorine, diffusion of hydroxide anions from the cathode area, where they are formed during water reduction with hydrogen formation (reaction (10)), occurs through the anion-exchange membrane in an equivalent amount to the oxidized chlorides.

$$2H_2O - 2e^- \rightarrow H_2 + 2OH^- \qquad (10)$$

At the cathode, the reduction of water with the formation of hydrogen and hydroxide anions occurs in an equivalent amount to the oxidized chlorides. Under these conditions, the diffusion of hydroxide anions through the anion-exchange membrane ensures the maintenance of a stable pH level in the anode chamber. Otherwise, acidification of the solution would occur due to the interaction of active chlorine with water according to reaction (11):

$$H_2O + Cl_2 \leftrightarrow HCl + HClO \qquad (11)$$

The main issue arising in this process is the loss of active chlorine. As seen in Fig. 2D, after reaching a concentration of 114 mg-eq/dm³ in the anolyte, its concentration decreases to 84 mg-eq/dm³, while the total content of unoxidized chlorides decreases to 12 mg-eq/dm³. This phenomenon can only be explained by chlorine loss due to degassing in the form of Cl_2 and ClO_2. The formation of Cl_2 occurs according to reaction (6), while the formation of ClO_2 is possible according to reaction (12):

$$Cl_2 + 2ClO_2^- \rightarrow 2Cl^- + 2ClO_2\uparrow \qquad (12)$$

Similar results were obtained during the electrolysis of the concentrate from RO water desalination (Fig. 3), where the chloride concentration reached 4 g/dm³ (111.4 mg-eq/dm³).

The highest concentration of oxidized chlorine compounds was achieved during electrolysis at the lowest applied current density, 1.67 A/dm². After 1 hour, the concentration of oxidized chlorine compounds in terms of active chlorine reached 188 mg-eq/dm³, with approximately 50 mg-eq of chlorides oxidized. This further confirms that the solution contains a mixture of oxidized chlorine compounds, the formation of which is described by equations (6)–(12).

With an increase in current density to 8.33 A/dm² (Fig. 3C), the maximum concentration of oxidized chlorine compounds reached only 106 mg-eq/dm³. This concentration of active chlorine was achieved in 30 minutes, whereas at a current density of 1.67 A/dm², the maximum concentration of active chlorine was reached in one and a half hours. It should be noted that with an increase in current density, the rate of chloride oxidation increases, which is entirely logical. At the same time, the degree of chloride removal at a current density of 1.67 A/dm² after two hours of electrolysis reaches 51.5%, while at a current density of 4.17 A/dm², it reaches 74.9%, with a simultaneous decrease in chloride content from 111.4 mg-eq/dm³ to 28 mg-eq/dm³.

The decrease in the maximum concentration of oxidized chlorine compounds in the anolyte with increasing anodic current density is explained by an increase in the degassing rate of the solution, leading to the removal of active chlorine (Cl_2) and chlorine dioxide (ClO_2), which are formed according to reactions (6) and (12), respectively. It is precisely the loss of chlorine in the form of Cl_2 and ClO_2 gases that explains the sharp decrease in the yield of oxidized chlorine compounds in terms of active chlorine over the electrolysis time. If at a current density of 1.67 A/dm², during the first hour, the ratio of active chlorine to oxidized chlorides decreased from 8.21:1 to 5.01:1, then in the next half hour, it dropped to 3.76:1 and further decreased over two hours to 2:1, and after 2.5 hours to 1.4:1. This indicates that at the initial stage of electrolysis, a relatively significant amount of hypochlorites, chlorites, and chlorates with a high oxidation state of chlorine was formed in the solution. Subsequently, the relative amount of oxidized chlorine compounds in the solution decreased due to the release of gaseous Cl_2 and ClO_2. With an increase in current density, this trend intensified due to the acceleration of chlorine oxidation processes. Thus, at a current density of 4.17 A/dm^2, the ratio of active chlorine to the initial amount of chlorides decreased from 4.2:1 to 1.24:1, and at a current density of 8.33 A/dm^2, from 2.7:1 to 1:1.

The relative loss of chlorine in the form of Cl_2 and ClO_2 can be judged by the change in the pH of the medium in the anolyte. According to reactions (7), (8), and (9), hydroxide anions bind when interacting with active chlorine to form ClO^-, ClO_2^-, and ClO_3^- ions, respectively. At the same time, the amount of hydroxides transferred during diffusion through the anion-exchange membrane is equivalent to the amount of active chlorine formed. In cases where active chlorine is released from the solution in the form of gas or binds according to reaction 6 with the formation of chlorine dioxide, hydroxide anions accumulate in the anolyte, leading to an increase in the pH of the medium. At low current densities (Fig. 3), the pH increases from 7.0 to 8.49–8.94. At a current density of 8.33 A/dm^2 and with significant chlorine losses due to degassing, the pH increases to 11.59 in 1.3 hours.

It is known that the current efficiency of oxidized chlorine compounds in the electrolysis process increases with increasing chloride concentration in the solution [15]. Therefore, we studied the processes of chloride oxidation in a two-chamber electrolyzer at chloride concentrations of 16 g/dm^3. These chloride concentrations were achieved as a result of filtering primary concentrates through a RO filter using low-pressure membranes (Table 2). Electrolysis was conducted in a two-chamber electrolyzer, varying the anodic current density from 1.67 A/dm^2 to 16.67 A/dm^2 (Fig. 4).

As seen in Fig. 4, increasing the chloride concentration in the anolyte allowed for higher concentrations of active chlorine in the solution as a result of electrolysis. At a current density of 1.67 A/dm^2, a gradual increase in active chlorine concentration in the anolyte up to 188 mg-eq/dm^3 was observed over 9 hours. The ratio of active chlorine to the initial amount of chlorides reached 3.56:1 in the first hour of electrolysis, decreasing to 1.5:1 after

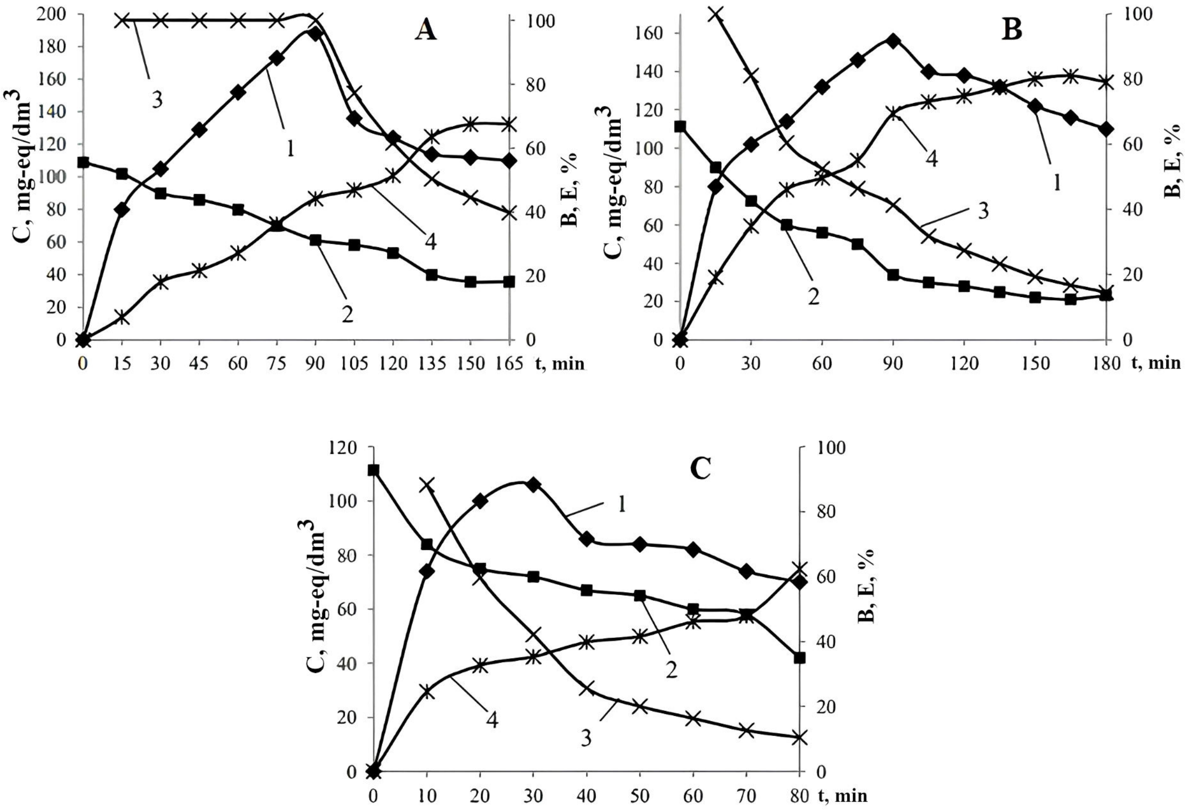

Fig. 3. Dependence of active chlorine concentration (1) and chlorides (2), current efficiency of active chlorine (3), and solution purification efficiency from chlorides (4) in the anode chamber of a two-chamber electrolyzer with an MA-41 anion-exchange membrane on electrolysis time of the RO concentrate placed in the anode chamber, with alkalinity in the cathode chamber of 200 mg-eq/dm^3, and an initial chloride concentration in the anolyte of 111 mg-eq/dm^3 (4 g/dm^3). Anodic current density, A/dm^2: 1.67 (A); 4.17 (B); and 8.33 (C)

2–3 hours, then to 1.24:1, and finally stabilizing in the range of (0.84–1):1. This indicates that the formation of chlorine compounds with oxidation states +3 and +5 occurs relatively intensively only at the beginning of the process, when chloride concentrations are still relatively high. As the process continues, oxidation primarily leads to the formation of Cl_2 and ClO^-.

Given the slight increase in pH (from 7.0 to 8.0), it can be inferred that chlorine losses due to degassing are minimal.

However, considering that an increase in pH at the anode also accelerates the competing oxygen oxidation reaction (reaction (13)), pH changes alone make it difficult to assess chlorine losses in the form of Cl_2 and ClO_2.

During oxygen oxidation, acidification of the medium occurs:

$$2H_2O-4e^-\rightarrow O_2+4H^+ \tag{13}$$

Reaction (13) may be responsible for the significant decrease in the current efficiency of active chlorine. At a current density of 4.17 A/dm^2, the active chlorine content in the anolyte reached 274 mg-eq/dm^3, with a residual chloride concentration of 180 mg-eq/dm^3. In this case, the ratio of active chlorine to the initial amount of chlorides is 0.95:1. The residual pH of the medium is 9.01. Evidently, in this case, the chlorine oxidation processes stop at the formation of Cl_2 and ClO^-. At the same time, partial loss of Cl_2 occurs due to its degassing. At a current density of 8.33 A/dm^2 and 16.67 A/dm^2, the intensity of chlorine degassing increases as the contribution of oxygen oxidation processes (reaction (13)) in the anode increases. All this leads to significant losses of active chlorine. Thus, the ratio of active chlorine to chlorides after 1–2 hours is only 0.2:1. That is, no more than 1/5 of the chlorides remain in solution after oxidation. The main reason for this is the decrease in the pH of the medium at high current densities due to reaction 8. The pH of the medium at a current density of 8.33 A/dm^2 reaches 8.21, while at a current density of 16.67 A/dm^2, the pH is 8.01. If we consider that at least 1/5 of the oxidized chlorides, amounting to 210 mg-eq/dm^3, were lost due to degassing, the expected pH increase should be around 0.69, meaning from 7.00 to 7.69.

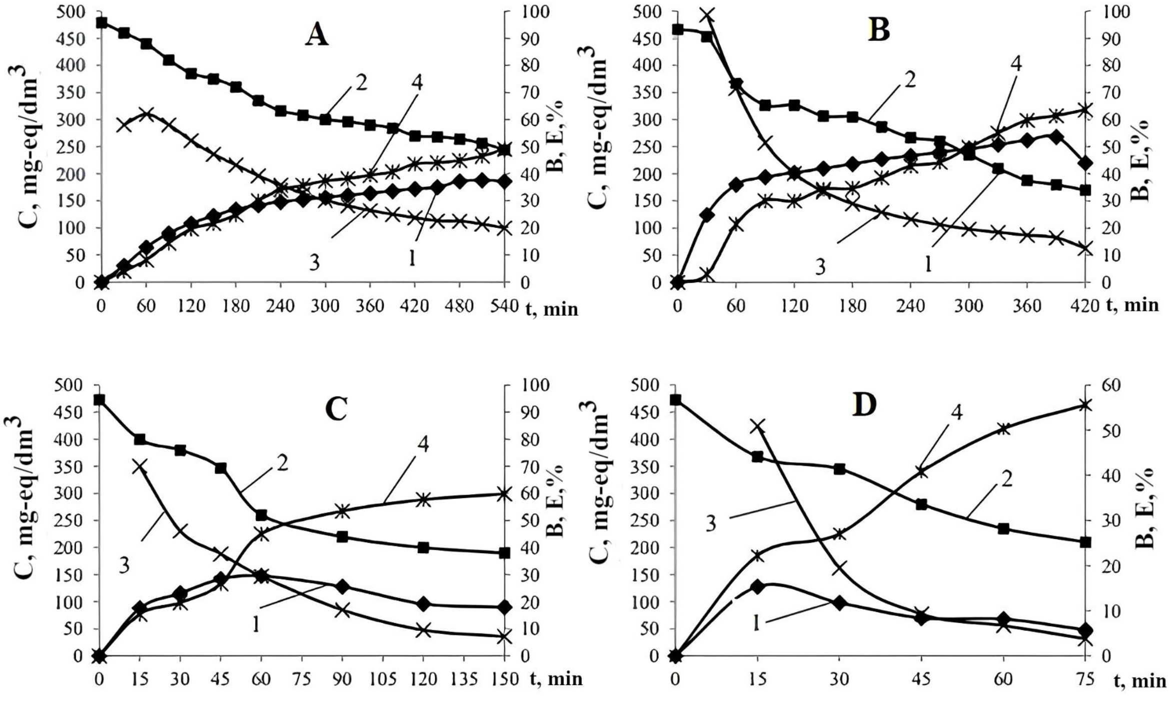

Fig. 4. Dependence of active chlorine concentration (1) and chlorides (2), current efficiency of active chlorine (3), and solution purification efficiency from chlorides (4) in the anode chamber of a two-chamber electrolyzer with an MA-41 anion-exchange membrane on the electrolysis time of the concentrate after RO ([Cl^-]=480 mg-eq/dm^3), which is placed in the anode chamber, with alkalinity in the cathode chamber of 200 mg-eq/dm^3. Anodic current density, A/dm^2: 1.67 (A); 4.17 (B); 8.33 (C); 16.67 (D); pH: pH_initial=7.00, pH_final=8.00 (A); pH_initial=7.02, pH_final=9.01 (B); pH_initial=7.10, pH_final=8.21 (C); pH_initial=7.05, pH_final=8.01 (D)

In reality, in this case, the pH increases from 7.00 to 8.01. This may be due to a larger volume of lost chlorine or over-equivalent diffusion of hydroxides through the anion-exchange membrane due to the high alkali concentration in the cathodic region.

The advantage of the two-chamber electrolyzer with an anion-exchange membrane is its effective operation in the presence of hardness ions. The effect of hardness ions on the efficiency of electrochemical oxidation of chlorides can be assessed based on the results presented in Fig. 5.

As seen in Fig. 5, the chloride concentration in this case was at 15 g/dm^3, which corresponds to its content in the concentrate after two-stage filtration. Judging by the active chlorine concentrations in these solutions, at NaCl to $CaCl_2$ equivalent ratios of 70:30 and 50:50, the electrolysis results are similar to those obtained using a pure NaCl solution. Thus, at these ratios, calcium ions do not affect the chloride oxidation processes. However, at a NaCl:$CaCl_2$ ratio of 30:70, the efficiency of chloride oxidation increases. The current efficiency of active chlorine during the experiment did not drop below 34%, whereas in a pure NaCl solution, this indicator decreased from 58% to 20%.

Additionally, over 8 hours, the active chlorine concentration in the solution increased to 280 mg-eq/dm^3, with a chloride removal rate of 75%. In a pure sodium chloride solution, under the same conditions and at 1.67 A/dm^2, the active chlorine concentration in the anolyte did not exceed 188 mg-eq/dm^3, with a chloride removal rate of 45%.

Thus, the presence of calcium ions not only does not reduce the efficiency of electrochemical chloride oxidation but actually enhances it, possibly due to the higher stability of calcium hypochlorites, chlorites, and chlorates compared to their sodium counterparts.

The decomposition and degassing ability of oxidized chlorine compounds can be assessed based on the decrease in active chlorine concentration over storage time.

At a solution pH of 7.81, approximately 30% of oxidized chlorine compounds (in terms of active chlorine) decompose over 30 days. At pH 11.10, the decomposition process is somewhat slower, with the decomposition degree reaching 20% over the same period. The intensity of active chlorine degassing decreases as its concentration in the solution decreases. At an active chlorine concentration of

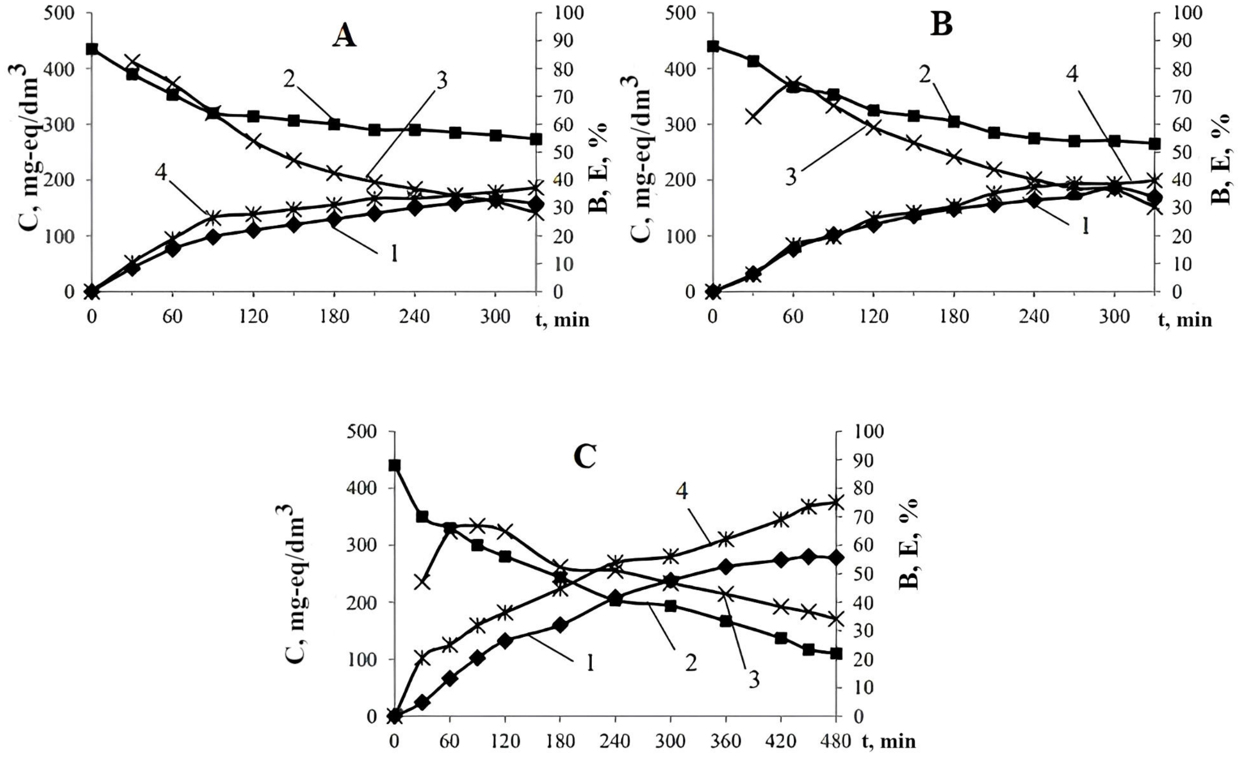

Fig. 5. Dependence of active chlorine concentration (1) and chlorides (2), current efficiency of active chlorine (3), and water purification efficiency from chlorides (4) in the anode chamber of a two-chamber electrolyzer with an MA-41 anion-exchange membrane on electrolysis time at a chloride concentration of [Cl^-]=440 mg-eq/dm^3, alkalinity in the cathode chamber of 200 mg-eq/dm^3, an anodic current density of 1.67 A/dm^2. NaCl:$CaCl_2$: 70:30 (A); 50:50 (B); and 30:70 (C)

58 mg-eq/dm^3, after 5 days, 7.54 mg-eq/dm^3 was lost at pH 7.81 (1.5 mg-eq/dm^3 per day), while over the next 25 days, 9.9 mg-eq/dm^3 was lost (0.4 mg-eq/dm^3 per day). At pH 11.10, the active chlorine losses over 5 days were 7.0 mg-eq/dm^3 (1.4 mg-eq/dm^3 per day), and over 25 days, the losses amounted to 4.6 mg-eq/dm^3 (0.2 mg-eq/dm^3 per day). These parameters of the oxidized chlorine compound formation process from chlorides should be considered when processing chlorine-containing concentrates from RO water desalination.

Conclusions

It has been shown that the low-pressure reverse osmosis membrane Filmtec 30-1812-50 provides 74–95% water purification efficiency from chlorides at an initial concentration of 1000 mg/dm^3 and 70–86% at an initial chloride concentration of 4000 mg/dm^3. When using two-stage filtration, a permeate recovery rate of 82% can be achieved, with a chloride concentration in the concentrate reaching 15–17 g/dm^3.

The electrolysis processes of model solutions of reverse osmosis desalination concentrates were studied in two-chamber electrolyzers with an MA-41 anion-exchange membrane. It was found that, in addition to active chlorine, other oxidized chlorine compounds with higher oxidation states are formed during electrolysis. The intensity of the process increases with higher anode current density and increased chloride concentration in the water.

The dependencies of the concentration of oxidized chlorine compounds in anolytes during electrodialysis of chloride solutions in open two-chamber electrolyzers were determined based on the electrolysis conditions and duration. It was shown that the limitation of active chlorine concentration occurs due to its losses through the degassing of Cl_2 and ClO_2.

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ОЦІНЮВАННЯ ЕФЕКТИВНОСТІ СИНТЕЗУ ОКИСНЕНИХ СПОЛУК ХЛОРУ МЕТОДОМ ЕЛЕКТРОДІАЛІЗУ З КОНЦЕНТРАТІВ МЕМБРАННОГО ЗНЕСОЛЕННЯ

М. Гомеля, Я. Крижановська, Т. Шаблій, І. Макаренко, О. Глушко, А. Остапенко

У цьому дослідженні розглянуто перероблення концентратів зворотноосмотичного знесолення, що містять натрій хлорид, кальцій гідрокарбонат та магній гідрокарбонат. Знесолення води здійснювали у два етапи з використанням касетного зворотноосмотичного мембранного елемента Filmtec TW 30-1812-50. При знесоленні з коефіцієнтом вилучення пермеату 66% на першому етапі селективність мембрани щодо хлоридів становила від 74% до 95%. На другому етапі одержаний концентрат ([Cl^-]=110 мг-екв/дм^3) додатково знесолювали за допомогою тієї ж мембрани. При коефіцієнті вилучення пермеату 74% селективність мембрани становила 70%. Двоетапна фільтрація дозволила зменшити об’єм концентрату з 34% до 8,2 % від початкового об’єму води. Під час електролізу модельних розчинів концентратів зворотноосмотичного знесолення використовувався двокамерний електролізер з аніон-обмінною мембраною МА-41. У анодну камеру подавали розчин натрій хлориду, тоді як катодну заповнювали лужним розчином із концентрацією 200 мг-екв/дм^3. Електроліз проводили при густині струму в межах від 0,83 до 16,7 А/дм^2, використовуючи розчини з концентрацією хлоридів від 59 до 480 мг-екв/дм^3. Встановлено, що інтенсивність окиснення хлоридів зростала зі збільшенням густини струму на аноді та концентрації хлоридів у розчині. Водночас зі зменшенням концентрації хлоридів у розчині спостерігалося зниження виходу за струмом окиснених сполук хлору. Концентрація окиснених сполук в аноліті відкритого електролізера не перевищувала 180 мг-екв/дм^3 через значні втрати Cl_2 та ClO_2 внаслідок дегазації.

Ключові слова: мембрана; зворотний осмос; електродіаліз; активний хлор; католіт; аноліт; густина анодного струму; вихід за струмом.

EVALUATION OF THE EFFICIENCY OF OXIDIZED CHLORINE COMPOUNDS SYNTHESIS BY ELECTRODIALYSIS FROM MEMBRANE DESALINATION CONCENTRATES

Mykola Gomelya, Yana Kryzhanovska, Tetyana Shabliy, Iryna Makarenko, Olena Hlushko, Alina Ostapenko *

National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv, Ukraine

* **e-mail: alina-ostapenko@ukr.net**

This study investigates the processing of reverse osmosis desalination concentrates containing sodium chloride, calcium bicarbonate, and magnesium bicarbonate. Water desalination was carried out using a Filmtec TW 30-1812-50 reverse osmosis membrane cassette in two stages. When desalinating water with a permeate recovery rate of 66% at the first stage, the membrane’s selectivity for chlorides ranged from 74% to 95%. In the second stage, the obtained concentrate ([Cl^-]=110 mg-eq/dm^3) was further desalinated using the same membrane. At a permeate recovery rate of 74%, the membrane’s selectivity reached 70%. The two-stage filtration process reduced the concentrate volume from 34% to 8.2% of the initial water volume. During the electrolysis of model solutions of reverse osmosis desalination concentrates, a two-chamber electrolyzer with an MA-41 anion-exchange membrane was used. A sodium chloride solution was placed in the anode chamber, while the cathode chamber was filled with an alkaline solution with a concentration of 200 mg-eq/dm^3. Electrolysis processes were conducted at a current density ranging from 0.83 to 16.7 A/dm^2, using solutions with chloride concentrations between 59 and 480 mg-eq/dm^3. It was found that the intensity of chloride oxidation increased with higher anode current density and higher chloride concentration in the solution. A decrease in the current efficiency of oxidized chlorine compounds was observed as chloride concentration in the solution decreased. The concentration of oxidized compounds in the anolyte of an open electrolyzer did not exceed 180 mg-eq/dm^3 due to significant losses of Cl_2 and ClO_2 caused by degassing.

Keywords: membrane; reverse osmosis; electrodialysis; active chlorine; catholyte; anolyte; anode current density; current efficiency.

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