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DETERMINING BASIC TECHNOLOGICAL PARAMETERS FOR THE PROCESS OF ELECTROCHEMICAL REGENERATION OF HYDROCHLORIDE-ACID CONCENTRATED PROCESS SOLUTIONS

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This work investigates model chloride solutions, copper-containing chloride acid (peroxide and ammonia) spent technological solutions for etching printed circuit boards, in order to design unified technologies and equipment.

This paper reports results of research on determining basic technological parameters for electrochemical regeneration that provide energetically favorable conditions for the process. It was established that when maintaining Eh in the cathode chamber from 400 mV to 450 mV, the specific current consumption for the regeneration process (38–40% copper extraction degree) is from $46 \cdot 10^3$ C/mol to $48 \cdot 10^3$ C/mol (current consumption from $15 \cdot 10^3$ C/l to $36 \cdot 10^3$ C/l), which is 4 times less compared to electrolysis without Eh correction.

The study has made it possible to carry out regeneration in a diaphragm electrolyzer under energy-efficient conditions and increase the maximum degree of copper extraction from 43% to 98% by adjusting Eh. In this case, the specific current consumption is 4 times lower than that without adjusting Eh.

Maintaining Eh in the cathode chamber at about 450 mV allows for more complete extraction of copper. Adjustment of the composition and redox properties of the regenerated solutions is carried out by mixing in a certain ratio of SPS with catholyte and anolyte. It is recommended to send the mixture of catholyte and anolyte after electrolysis to a centralized wastewater treatment system.

Experimental and industrial studies of the basic elements in the schemes of electrochemical regeneration in a diaphragm electrolyzer given in this work have been carried out. These schemes are supplemented with additional elements for pre-treatment: an intermediate tank, a diaphragm-free electrolyzer (for adjusting Eh); and a chamber adjacent to the anode (for adjusting the composition of the solution after regeneration)

Keywords: electrochemical regeneration, copper-containing hydrochloric acid etching solutions, technological, redox parameters

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1. Introduction

Based on the acquisition, generalization, and systematization of information provided from a number of electroplating and printed circuit board industries, it has been shown that spent process solutions (SPSs) from etching constitute 85% of the total volume of acidic metal-containing wastewater. They are among the most aggressive liquid wastes with a concentration of chemical components from 100 g/l to 300 g/l and a discharge frequency of up to 260 times per year [1]. Such liquid wastes are recommended to be subjected to regeneration or disposal. In the case of neutralization, it is necessary to provide separate special blocks-modules for this purpose [2]. This could ensure the integrated use of resources (chemical reagents, water, etc.), using secondary raw materials, devising closed production cycles for wastewater and waste gas treatment, neutralization, and processing of concentrated wastes [3].

The most advanced option is to include an element that enables electrochemical regeneration of SPSs in the basic system of the acidic [4] and alkaline [5] etching section. Electrochemical processes are capable of designing a multifunctional technology and unified equipment for the transformation and separation of multicomponent systems [6, 7]. These processes are based on redox transformations, as a result of which phase-dispersive, structural transformations occur in a non-equilibrium heterogeneous system [8]. Electrochemical technologies for the regeneration of etching solutions allow for a comprehensive effect on all components of SPS aqueous system and solve its basic tasks: the extraction of the metal being etched and an increase in its oxidizing ability [9, 10].

However, electrochemical technologies have not become common because of their parametric instability and high energy consumption. Thus, there is a need to continue research into electrochemical technologies in order to improve methods of regeneration (neutralization) and equipment in order to devise a stable technological regime that would ensure a reduction in energy consumption and the formation of toxic waste. Therefore, it is a relevant task to determine energetically advantageous technological parameters in the process of electrochemical regeneration of concentrated hydrochloric acid technological solutions.

2. Literature review and problem statement

Chloride SPSs from etching operations (printed circuit board production) belong to a separate group of wastewater in terms of copper concentration (100–150 g/l) and discharge frequency (up to 260 times per year). For such wastewater, special treatment is most appropriate, which involves returning the etching solution or part of the reagents to the technological process. The choice of an appropriate processing technique for the purpose of neutralizing chloride SPSs from copper etching depends on their quantity and chemical composition. In small quantities, solutions from etching operations are mixed with wastewater from washing operations (which make up 85% of the total volume of wastewater) and neutralized together using lime with subsequent clarification processes (settlement, filtration). With significant amounts of washing water and a small amount of hydrochloric acid SPSs from copper etching, it is recommended to use lime neutralization of SPS together with the sludge formed during the purification of washing water. The disadvantage of this technology is that a large number of chemical reagents are lost, which after treatment are subject to transportation to special landfills for solid toxic waste. It should be noted that despite the small volume of SPSs in relation to the total flow of wastewater, up to 90% of all contaminants, including copper, enter with them [11].

It is known that electrochemical technologies allow for the purposeful regulation of the physicochemical properties of wastewater in order to transform the components of the aqueous solution. Under the influence of an electric field (at the electrode-solution interface), the extraction of the metal being etched (copper) is ensured. The products of electrode reactions, similar to commercial chemical reagents, significantly affect the physicochemical properties in the bulk solution, including Eh, which characterizes the oxidizing ability of the components [12]. However, it is believed that the use of electrolysis is limited by the instability of the process and high residual concentrations of metal and salts.

Transformations at the electrode-solution interface are theoretically substantiated in [13]. In [14], practical data on the basic technological parameters (current consumption, current density, deposition rate, change in pH, Eh of the solution) for sulfate-acid SPSs from surface preparation and coating operations are given. The pH and Eh values can be used to regulate the type of precipitate (foil, precipitate containing foreign substances), as well as to determine the purpose of the technological process (regeneration, disposal). It is recommended to use diaphragm-free electrolysis in local regeneration cycles, and diaphragm electrolysis in local disposal cycles. The disadvantage of the cited work is that electrode processes associated with the formation of the gas phase (O_2, Cl_2, NH_3 etc.) and its influence on the nature of the course of electrochemical processes are not considered. At the same time, technical solutions do not solve the task to dispose of such gases.

There is also a known technique of electrochemical regeneration of chloride SPS by passing it through the cathode chamber of a diaphragm electrolyzer, where excess copper is removed at the cathode, and then through the anode chamber, where polyvalent metal ions (copper) are oxidized. In this process, the redox potential in the anode chamber reaches +0.48...+0.55 V [15]. The disadvantage of the process is its high energy consumption (the solution temperature during the process reaches 50°C). The increase in the energy consumption of the process can be explained by the fact that the process occurs through the stage of formation of monovalent copper ions.

In [16], one of the solutions to the task to intensify the process of reduction of hydrochloric acid SPS from etching is proposed. Reduction of the copper-chloride etching solution is carried out by deposition of metallic copper in a closed cathode chamber when the anolyte redox potential is reached from +1.1 V to +1.2 V. Chlorine gas, which is released in the anode chamber, is sent to the solution before feeding it to the anode chamber. In this case, it is assumed to process only a part of the solution up to 30% of the total volume to the maximum value of Eh, which after electrolysis is mixed with the remaining part and sent to the etching process. This technology cannot be implemented for hydrochloric acid SPSs from etching, which include the ammonia compound NH_4Cl. During electrolysis, the copper complex is first reduced to the intermediate ammonia of copper(I), then the copper(I) ion is finally reduced to the pure metal, which is deposited on the electrode. The stages of the process are accompanied by the release of ammonia and its transformation into ammonium cation. This may be the reason for the manifestation of redox buffering and an increase in energy consumption for redox processes in the electrolysis system, which are necessary to restore the properties of solutions during the regeneration process.

Redox transformations (including redox buffering phenomena) associated with a change in Eh have a complex nature, combined not only with the electrode processes of electrolysis gas formation but also with their interaction with the components of the solution. All this leads to the formation of a new heterogeneous structural unit and to changes in the water system as a whole.

It is noted in [17, 18] that when an electric field acts on a water system, its electrical conductivity and electrical permeability increase, which is associated with a change in the structure of the water system, the basic element of which are clusters, individual water molecules. During their interaction, OH^* radicals and H_3O^+ ($H_5O_2^+$), ions can be formed, which lead to the formation of hydrogen peroxide H_2O_2, atomic hydrogen, and new clusters [18]. In addition, the authors of [19] consider interphase phenomena occurring at the gas-liquid interface, which can be accompanied by the generation of radicals in the aqueous environment and are capable of carrying out various redox transformations. However, the studies relate to low-concentration water systems (distilled water, natural water) and do not consider technological solutions with high concentrations of components of organic and inorganic origin [20].

Due to the fact that the redox heterogeneous electrolysis system is characterized by a non-equilibrium state, there is a need to experimentally determine parameters for controlling the state of copper-containing chloride acid SPSs and technological parameters of regeneration. For the further creation of a more stable regime of electrochemical regeneration, it is necessary to ensure the disposal of gases and the process under more energy-efficient conditions. All this gives grounds to assert that there is a need to improve the electrochemical regeneration process under the conditions of control and regulation of the redox parameters of the state of spent process solutions.

3. The aim and objectives of the study

The purpose of our research is to substantiate the use of electrochemical regeneration of copper-containing chloride acid SPSs from etching operations as an element in a combined system at treatment facilities. This will make it possible to ensure the disposal of electrolytic gases in order to adjust the redox properties of SPSs for their subsequent regeneration under energy-efficient conditions.

To achieve this goal, the following tasks were set:

– to substantiate basic parameters for the redox state of copper-containing chloride acid SPSs under the action of electric current;

– to define basic parameters for the redox state of copper-containing chloride acid peroxide SPSs and technological parameters for electrochemical regeneration under more energy-efficient conditions;

– to determine basic parameters for the redox state of copper-containing ammonium chloride SPSs and technological parameters for electrochemical regeneration under more energy-efficient conditions;

– to devise functional schemes for the regeneration of copper-containing chloride-acid SPSs based on the results of research into their individual elements under experimental and industrial conditions.

4. The study materials and methods

The object of our study is model chloride solutions, copper-containing hydrochloric acid (peroxide and ammonia) spent process solutions for etching printed circuit boards, in order to design unified technologies and equipment. Hydrochloric acid solutions contain copper ions with a concentration of 1.25 mol/l to 0.01 mol/l, and the model solutions are 0.5M NaCl solutions.

The principal hypothesis assumes that due to the uncertainty of the mechanism of cathodic processes, it is considered possible to predict the results of technical solutions that ensure the regeneration process under energetically favorable conditions according to pH and Eh indicators. At the same time, pH and Eh can be regulated by chemical transformation under the influence of electrode reaction products, including in the gaseous state. The non-equilibrium state of aqueous systems containing an electrolytic gas phase cannot be justified theoretically and requires experimental research. Changing the redox balance of an aqueous system can be accomplished by selecting an appropriate electrochemical process.

The following assumptions were adopted:

1) when interpreting experimental data and devising technical solutions based on kinetic data, it is possible to adhere to the mechanism of electrode processes, in which chemical reactions of intermediates of the electrochemical stage take part;

2) the state of the redox system can be characterized by values of the following indicators: pH, Eh, and the activity of free electrons $\rho_{\bar{e}}$ [3];

3) electron transfer in redox processes is accompanied by proton transfer, which causes a significant relationship between Eh and pH.

The following simplifications were accepted:

1) concentrated solutions included SPS with a concentration from 1.25 mol/l to 0.01 mol/l;

2) we do not take into account the hydrodynamic conditions of the process.

The acid-base and redox properties of copper-containing SPSs were studied by potentiometric titration for the purpose of purification, regeneration, and disposal. The technological parameters of the process were set in a diaphragm (diaphragm-free) electrolyzer with a graphite anode and cathodes made of stainless steel, titanium, and copper of a rectangular shape measuring 315 mm by 255 mm (Fig. 1). Potentiometric titration was carried out under laboratory conditions on the potentiometer EV 74, and under industrial-research conditions using the portable pH meter pH 602 (Ukraine). Based on the results from the determined pH and Eh values, the free electron activity was calculated with the construction of a redox buffering curve according to the data given in [3].

Quantitative studies on the content of Cu^{2+} ions were carried out in a laboratory setting by the method of extraction-photometric determination with lead diethyldithiocarbamate in surface and wastewater [21]. The concentration of Cu^{2+} ions in g/l was determined according to the calibration plot. To construct it, a series of reference solutions was prepared according to the specified concentrations of model solutions. Measurements were repeated five times for each solution and, using the calibration plot, the content of Cu^{2+} ions in the studied solution was determined. Statistical processing of the research results was carried out according to known methodologies, namely, the average values of the sample (the number of values in the sample was 5), dispersions, coefficients of approximation reliability (R^2), confidence intervals, and measurement errors were calculated. The least squares method was used to find the measurement error ($\Delta = \pm(0.005{-}0.012)$) in the concentration range (0.01–0.08 mg/l). The mathematical processing of the potentiometric titration results is given in the form of kinetic (differential) curves of the redox state. All studies were conducted at a certified laboratory.

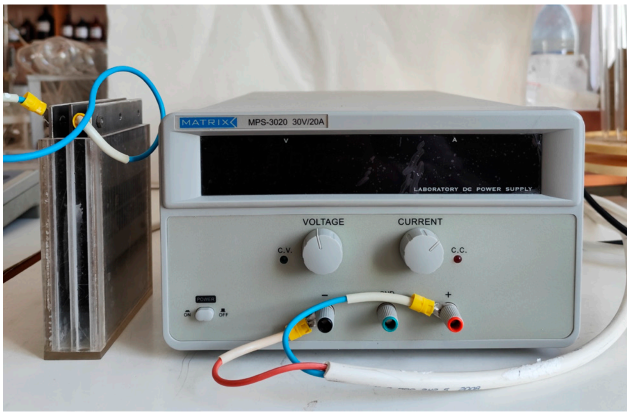


Fig. 1. Photograph of the electrolyzer

5. Results of investigating the electrochemical regeneration of copper-containing chloride acid etching solutions

5. 1. Results of substantiating basic parameters for the redox state of copper-containing chloride acid etching solutions

Our work considers model chloride solutions (0.5M NaCl solution), copper-containing chloride peroxide and copper-containing chloride ammonia SPSs from etching of printed circuit boards (Table 1).

Thus, our work considers SPSs that are concentrated aqueous solutions of electrolytes [1].

We investigate basic parameters for redox systems in the following aqueous systems with the corresponding initial values:

– 0.5 M NaCl model solution (Eh = 182 mV, $\rho_{\bar{e}} = 3$ V, pH = 5.76);

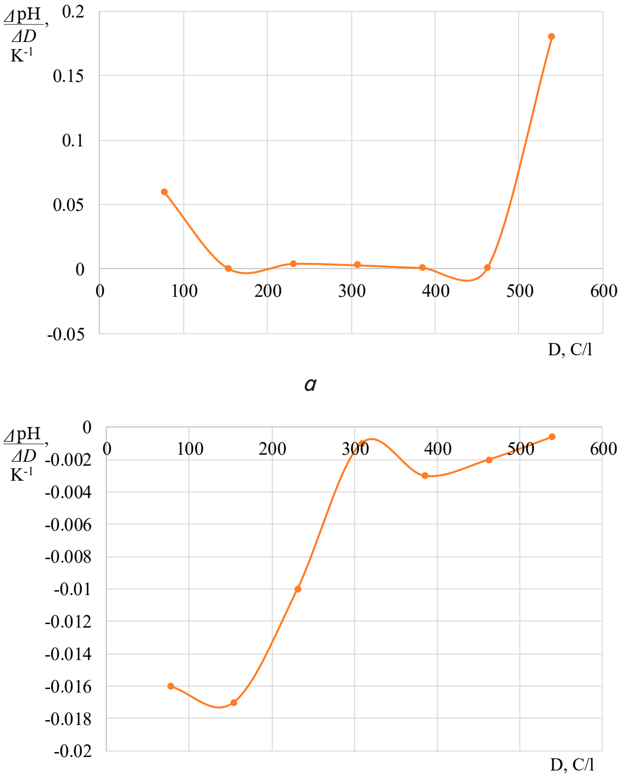
– copper-containing chloride-acid peroxide SPSs (Eh = 400 mV, $\rho_{\bar{e}} = 8.4$ V, pH = 2.1);

– copper-containing chloride-acid ammonia SPSs (Eh = 645 mV, $\rho_{\bar{e}} = 0.645$ V, pH = 2.8).

Fig. 2, 3 show kinetic curves of the redox state of model solutions in the process of electrolysis according to the pH, Eh indicators. For model solutions, the absence of extreme values on the curves in the differential form according to the pH indicator is noted. On the differential curves based on the Eh indicator (Fig. 3), the presence of extreme values (Eh) is noted, which corresponds to the range of minimum current consumption per unit change in Eh, that is, more energetically favorable conditions for the process.

Fig. 4 shows kinetic curves of the redox state of model solutions during electrolysis based on the $\rho_{\bar{e}}$ indicator.

The activity of free electrons $\rho_{\bar{e}}$ was used to determine the redox potential of the system and the buffering phenomenon in relation to redox processes. In Fig. 4, the buffering phenomenon corresponds to the current consumption interval *D* from 230 C/l to 385 C/l.



a

b

Fig. 2. Kinetic curves of the redox state of model solutions during electrolysis according to pH: *a* — cathode chamber; *b* — anode chamber

Table 1

Characteristics of SPSs from printed circuit boards in terms of the concept of molecular concentration of components [G. Hertz]

No.	Solution	Masses of components, g/l	Molar concentrations of components, mol/l	pH/Eh
1	Copper-containing (chloride-acid peroxide)	$m(Cu^{2+}) = 80 - 5.12$	$C_{Cu^{2+}} = 1.25 - 0.08$	0.1/(from +500 mV to +1100 mV)
		$m(Cl^{-}) = 77 - 4.92$	$C_{Cl^{-}} = 2.17 - 0.14$	
2	Copper-containing (chloride-acid ammonia)	$m(Cu^{2+}) = 35 - 0.64$	$C_{Cu^{2+}} = 0.55 - 0.01$	0.24/(from –115 mV to +800 mV)
		$m(Cl^{-}) = 34 - 0.62$	$C_{Cl^{-}} = 0.96 - 0.02$	
		$m(NH_4^{+}) = 40 - 0.36$	$C_{NH_4^{+}} = 2.2 - 0.02$	

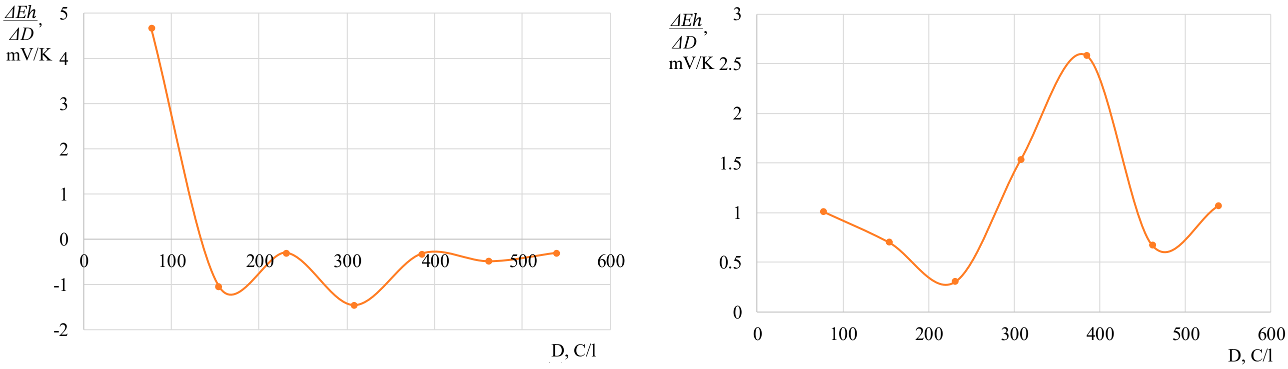
The following stages of research are related to SPS (etching areas of printed circuit boards), which are related to copper-containing chloride-acid peroxide (Table 1) with the following initial parameters: Eh = 400 mV, $\rho_{\bar{e}} = 8.4$ V, pH = 2.1.

Fig. 5, 6 show kinetic curves of the change in the redox state during electrolysis based on indicators Eh and $\rho_{\bar{e}}$.

Based on our studies, illustrated by the kinetic curves of the redox state of copper-containing chloride-acid peroxide SPSs (Fig. 5, 6, *a*), it was established that the buffering effect determined at a current flow of 35,5 · 10^3 C/l corresponds to Eh = 300 mV and the activity of hydrated electrons $\rho_{\bar{e}} = 5$ V. In the anode chamber (Fig. 5, 6, *b*), gaseous chlorine stably exhibits oxidizing properties and Eh rapidly acquires a maximum value Eh = 1100–1200 mV, which corresponds to a current flow D = 10103 C/l.

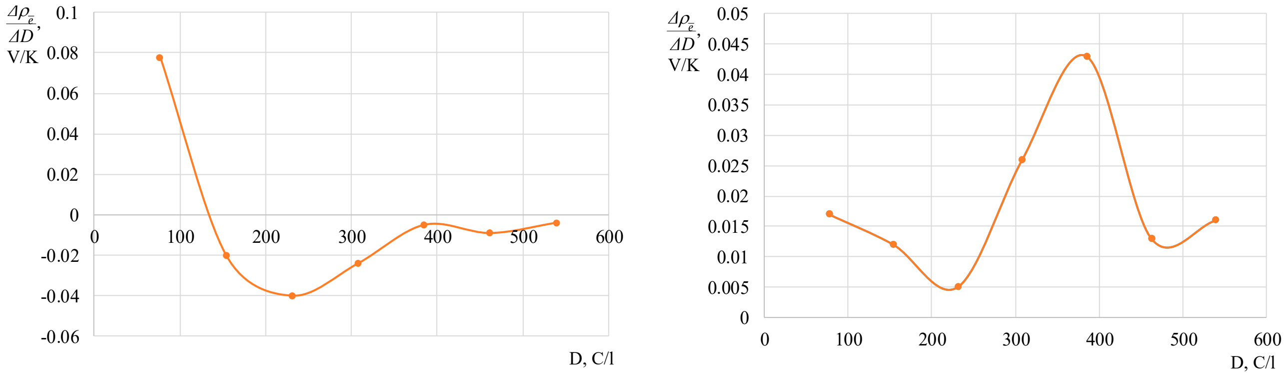
Fig. 7, 8 show results of investigating copper extraction from SPSs (etching areas of printed circuit boards), which belong to copper-containing chloride-acid ammonia (Table 1). Studies have shown (Fig. 7, 8) that in the cathode and anode chambers, the phenomenon of redox buffering is observed both in terms of the Eh indicator and in terms of $\rho_{\bar{e}}$, corresponding to the current flow of 5236 C/l at Eh = 385 mV and $\rho_{\bar{e}} = 15.7$. Thus, there is a need to adjust the Eh value in this Eh interval in order to create energetically favorable conditions for cathodic metal extraction.

Based on our calculations and analysis of basic indicators of the redox state (pH, Eh, $\rho_{\bar{e}}$) at different values of current flow (D), the possibility for determining the technological parameters of electrochemical regeneration under energetically favorable conditions of the process has been established.



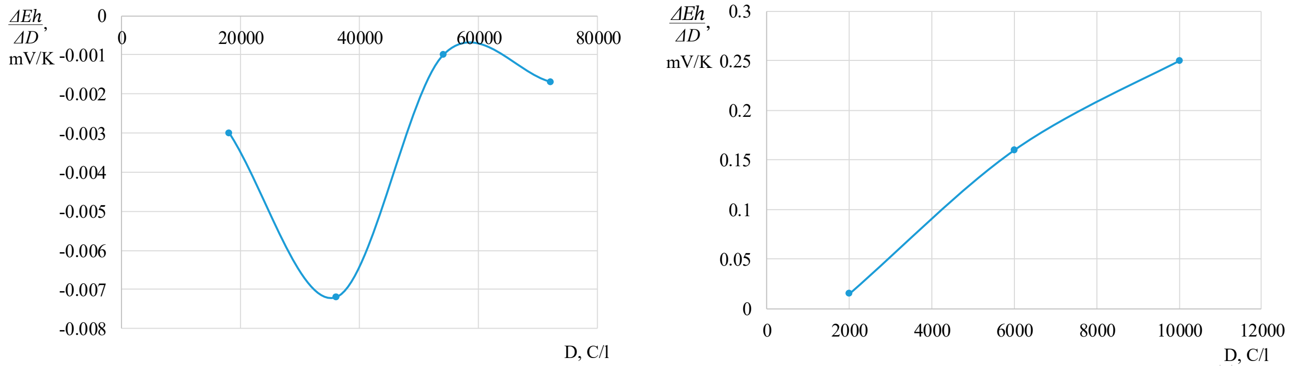
a *b*

Fig. 3. Kinetic curves of the redox state of model solutions during electrolysis according to the Eh indicator: *a* — cathode chamber; *b* — anode chamber



a *b*

Fig. 4. Kinetic curves of the redox state of model solutions during electrolysis based on the $\rho_{\bar{e}}$ indicator: *a* — cathode chamber; *b* — anode chamber



a *b*

Fig. 5. Kinetic curves of the redox state of copper-containing chloride-acid peroxide spent process solutions in the process of electrochemical regeneration based on the Eh indicator: *a* — cathode chamber; *b* — anode chamber

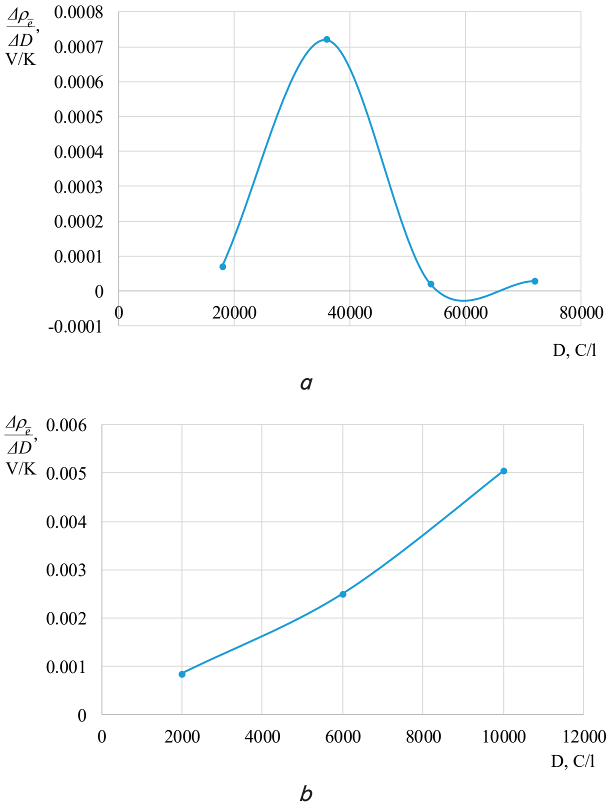


Fig. 6. Kinetic curves of the redox state of copper-containing chloride-acid peroxide spent process solutions in the process of electrochemical regeneration based on the $\rho_{\bar{e}}$ indicator: *a* — cathode chamber; *b* — anode chamber

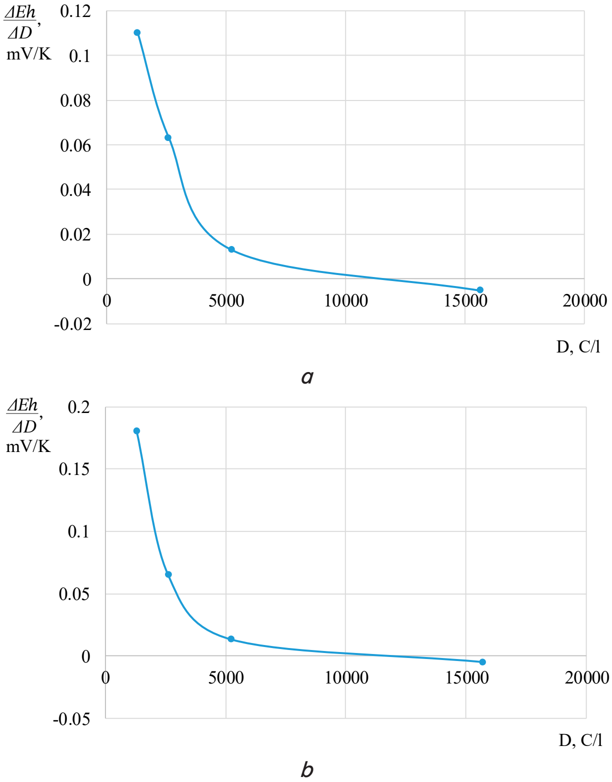


Fig. 7. Kinetic curves of the redox state of copper-containing chloride-acid ammonia spent process solutions in the process of electrochemical regeneration based on th Eh indicator: *a* — cathode chamber; *b* — anode chamber

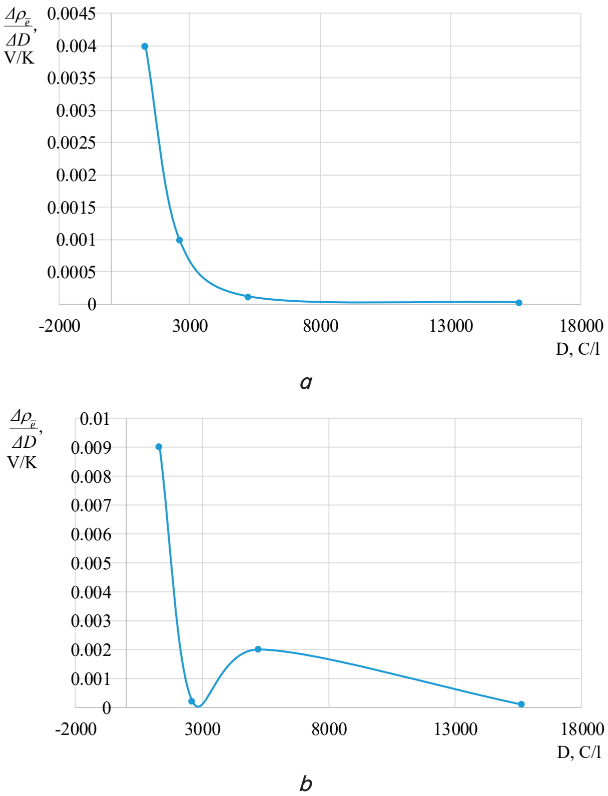


Fig. 8. Kinetic curves of the redox state of copper-containing chloride-acid ammonia spent process solutions in the process of electrochemical regeneration based on the $\rho_{\bar{e}}$ indicator: *a* — cathode chamber; *b* — anode chamber

5. 2. Results of investigating basic technological parameters of electrochemical regeneration of copper-containing chloride-acid peroxide solutions

At the next stage, industrial chloride-acid peroxide SPSs of copper from etching operations were investigated. Chloride-acid peroxide SPSs are formed according to the following chemical reactions:

$$Cu^0 + CuCl_2 \rightarrow 2CuCl, \tag{1}$$

$$2CuCl + 2HCl + H_2O_2 \rightarrow 2CuCl_2 + 2H_2O. \tag{2}$$

Such SPS are characterized by a low pH value, namely from pH = 1.2 to pH = –0.25 with a high oxidizing environment within Eh from 620 mV to 320 mV.

According to the data shown in Fig. 9, in the processes of cathodic extraction of copper in a diaphragm electrolyzer (cathode chamber) in the concentration range from 1.15 mol/l to 0.63 mol/l, the specific current consumption *D* is from $180 \cdot 10^3$ C/mol to $180 \cdot 10^3$ C/mol. The degree of extraction (within the concentration range of 1.15–0.63 mol/l) is 45%.

The dependences are approximated by function $y = y_0 + A_1 \exp(-x / t_1)$. Curve approximation parameters are as follows:

– in the cathode chamber: $y_0 = 77.94668$; $A_1 = -1.94561$; $t_1 = -74438.63228$;

– in a mixture of cathode and anode chambers: $y_0 = -8.62172$; $A_1 = 77.9485$; $t_1 = 50086.09301$.

Based on the statistical evaluation of the approximation functions, the approximation reliability coefficient R^2 was derived, which for the cathode chamber is 0.9288, for the mixture of cathode and anode chambers – 0.959. The resulting equations explain more than 92–95% of variance in the experimental data. The average relative approximation error for the cathode chamber is 4.79%, and for the working zone of the mixture of cathode and anode chambers – 11.84%. The confidence intervals in combination with the error values correspond to the statistical reliability of our findings.

As a result of the studies, it was found that in the electrolysis process, the concentration of Cu^+ in relation to the total concentration increases from 4.4% to 33% at a current flow rate up to the values of $D = 36 \cdot 103$ C/l (Table 2).

Table 2

Results of investigating cathodic copper extraction without correction for Eh values

$C(Cu^{2+})$, mol/l	$C(Cu^{+})$, mol/l	Eh, mV	Specific current consumption *D*, C/mol	Current consumption *D*, C/l
1.01	0.047	450	–	$18 \cdot 10^3$
0.98	0.078	300	$600 \cdot 10^3$	$36 \cdot 10^3$
0.86	0.125	280	$150 \cdot 10^3$	$54 \cdot 10^3$
0.63	0.31	250	$78 \cdot 10^3$	$72 \cdot 10^3$

In order to reduce Cu^+ concentration and decrease current consumption by regulating the redox properties of the catholyte, anolyte was used as a chemical reagent. For this purpose, SPSs were pre-treated in the anode chamber of a diaphragm electrolyzer until we achieved pH = 0.4; Eh = 1200 mV ($D = 10 \cdot 10^3$ C/l); $\rho_{\bar{e}} = 20.16$ V.

The results of our study of cathodic copper extraction after adjusting the catholyte for Eh values are given in Table 3.

As studies have shown, after adjusting the redox properties of the catholyte by the value of Eh, the concentration of Cu^+ decreases approximately by 10 times (Tables 2, 3), so the process takes place under more energetically favorable conditions.

Table 3

Results of studies on cathodic copper extraction after correction for Eh values

C (copper), mol/l	pH	Eh, mV (catholyte)	Specific current consumption D, C/mol	Current consumption D, C/l	$C(Cu^{+})$, mol/l (mixture of catholyte and anolyte)
1.02	2.7	450	$48 \cdot 10^3$	$15 \cdot 10^3$	0.016
0.63	2.7	450	$46 \cdot 10^3$	$36 \cdot 10^3$	0.0078
0.08	2.7	400	$375 \cdot 10^3$	$75 \cdot 10^3$	0.0078

According to the research data (Table 3), when maintaining Eh in the cathode chamber from 400 mV to 450 mV, the concentration of total copper (a mixture of catholyte and anolyte) decreases from 1.02 mol/l to 0.08 mol/l. At the same time, the specific current consumption for the regeneration process (which corresponds to a degree of extraction of 38–40%) is from $46 \cdot 10^3$ C/mol to $48 \cdot 10^3$ C/mol (current consumption from $15 \cdot 10^3$ C/l to $36 \cdot 10^3$ C/l), which is 4 times less compared to electrolysis without Eh adjustment. The following redox parameters correspond to the regeneration process: pH = 1–1.7, Eh = 800 mV, $\rho_{\bar{e}} = 13.44$ V.

5. 3. Results of investigating basic parameters of electrochemical regeneration of copper-containing chloride-acid ammonia solutions

The following stage is related to determining the change in the concentration of copper from chloride-acid ammonia SPSs in the cathode and anode chambers of the diaphragm electrolyzer. Cathodic extraction of copper from such solutions occurs with the release of ammonia according to the following chemical model:

$$\left[Cu\left(NH_3\right)_4\right]^{2+} + \bar{e} \rightarrow \left[Cu\left(NH_3\right)_2\right]^{+} + 2NH_3, \qquad (3)$$

$$\left[Cu\left(NH_3\right)_2\right]^{+} + \bar{e} \rightarrow Cu^0 + 2NH_3. \qquad (4)$$

Based on data shown in Fig. 10, the processes of cathodic extraction of copper in a diaphragm electrolyzer (cathode chamber) in the concentration range from 0.55 mol/l to 0.37 mol/l at a current flow rate *D* from $2.608 \cdot 10^3$ C/l to $36.540 \cdot 10^3$ C/l, the degree of extraction is from 10% to 32%. At the same time, the calculated specific current flow rate is from $208 \cdot 10^3$ C/mol to $7000 \cdot 10^3$ C/mol, respectively. This is 10 times more compared to peroxide hydrochloric acid solutions. The process of cathodic extraction of copper does not occur further under these conditions. The end of the process corresponds to the following redox parameters: pH = 1, Eh = +370 mV, $\rho_{\bar{e}} = 6.21$ V.

The dependences are approximated by function $y = y_0 + A_1 \exp(-x / t_1)$. The parameters of curve approximation are as follows:

– in the cathode chamber: $y_0 = 22.38542$; $A_1 = 11.79781$; $t_1 = 8881.10475$;

– in the anode chamber: $y_0 = 21.10042$; $A_1 = 14.66148$; $t_1 = 14648.70675$.

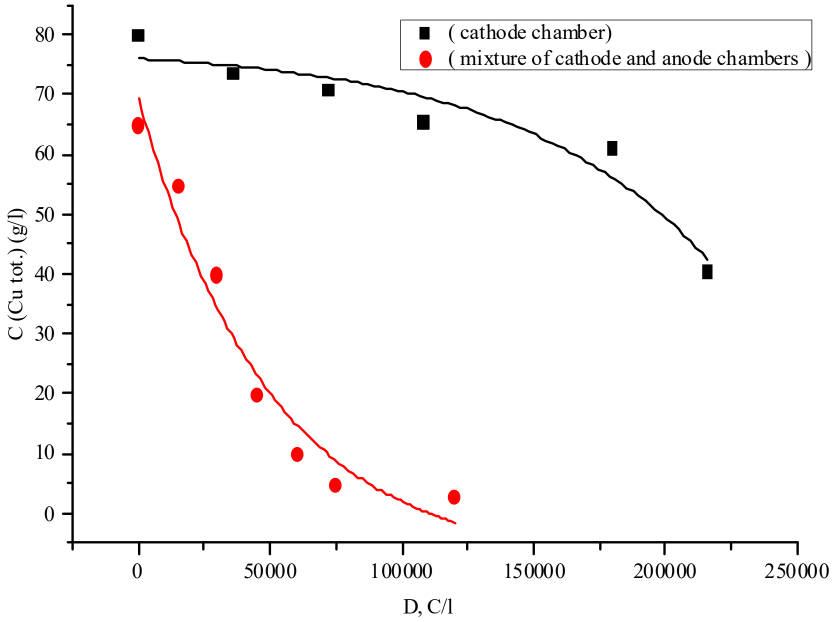


Fig. 9. Change in copper concentration from chloride-acid peroxide spent process solutions (current density i = 200 A/m^2) depending on current consumption

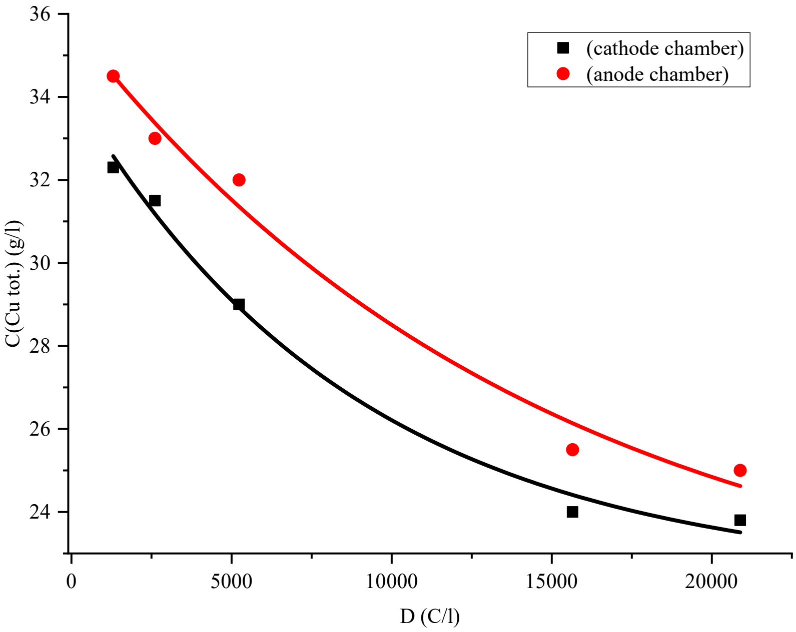


Fig. 10. Change in copper concentration from chloride-acid ammonia spent process solutions without Eh regulation (current density $i = 200$ A/m^2) as a function of current flow

Based on the statistical evaluation of the approximation functions, the approximation reliability coefficient R^2 was derived, which for the cathode chamber is 0.9895, and for the anode chamber – 0.9831, which indicates the reliability of the approximation. The resulting equations explain more than 98% of variance in the experimental data. The average relative approximation error for the cathode chamber is 1.23%, and for the anode – 1.56%. Confidence intervals in combination with low error values correspond to the statistical reliability of our results.

To adjust Eh, the chloride-acid ammonia solution was pre-treated in the cathode chamber of the electrolyzer at a current density of $i = 500$ A/m^2. The results of investigating the change in Eh in the cathode chamber at $i = 500$ A/m^2 are given in Table 4.

According to the results of our study, the following technological parameters for pre-treatment are recommended: $D = 12000$ C/l, which corresponds to Eh = –40 mV (copper extraction rate is 20%).

Fig. 11 shows results of investigating the changes in copper concentration from chloride-acid ammonia SPSs after preliminary correction of the Eh value $\left(\rho_{\bar{e}}\right)$. The data demonstrate that at current flows in the range of values $36 \cdot 10^3$–$72 \cdot 10^3$ C/l, the degree of copper extraction is 43–98%. At the same time, the average specific current flow rate is from $120 \cdot 10^3$ C/mol to $4000 \cdot 10^3$ C/mol.

The dependences are approximated by function $y = y_0 + A_1 \exp(-x/t_1)$. Curve approximation parameters are as follows:

– in the cathode chamber: $y_0 = 0.02289$; $A_1 = 52.38389$; $t_1 = 28791.75792$;

– in the anode chamber: $y_0 = -1.16988$; $A_1 = 50.44061$; $t_1 = 48913.36656$.

Table 4

Results of investigating changes in Eh in the cathode chamber of chloride-acid ammonia SPSs (current density $i = 500$ A/m^2)

Indicator	Value							
Eh, mV	+300	+150	+90	–40	–50	–60	–80	–90
D, C/l	1304	6000	8000	12000	16000	20000	30000	48000

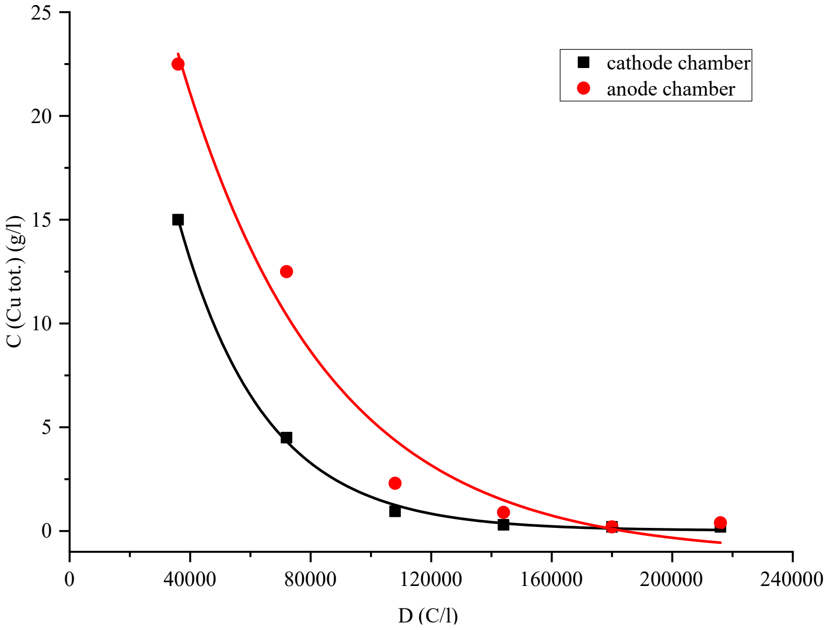


Fig. 11. Change in copper concentration from chloride-acid ammonia spent process solutions with Eh adjustment (current density $i = 200$ A/m^2) depending on current consumption

Based on the statistical evaluation of the approximation functions, the approximation reliability coefficient R^2 was derived, which for the cathode chamber is 0.9985, and for the anode chamber – 0.9835, which indicates the reliability of the approximation. The resulting equations explain more than 98% of variance in the experimental data. The confidence intervals correspond to the statistical reliability of our results.

For SPSs without Eh correction at a current flow rate of $36 \cdot 10^3$ C/l, the degree of copper extraction will be lower (32%) compared to Eh correction (43%). In this case, the specific current flow rate without Eh correction is $7000 \cdot 10^3$ C/mol, and with Eh correction – $120 \cdot 10^3$ C/mol. Taking into account the current flow rate for Eh correction (Table 4), the specific current flow rate will be 4.3 times lower compared to without Eh correction, that is, the process occurs under more energetically favorable conditions. The following redox parameters correspond to the end of the process: pH ≤ 2, Eh = +880 mV, $\rho_{\bar{e}} = 17.78$ V.

5. 4. Designing functional schemes for the regeneration of hydrochloric acid spent process solutions

Fig. 12, 13 show functional schemes for the regeneration of hydrochloric acid SPSs using a cathodic metal extraction (CME) unit [14]. Basic elements of the functional regeneration schemes were studied under experimental and industrial conditions.

The basic elements in Fig. 12, 13 are diaphragm and diaphragm-free electrolyzers, arranged with an adjacent additional capacity. The process was carried out at a current density of 500–700 A/m^2.

According to the functional scheme, regeneration includes the extraction of copper at the cathode; restoration of properties for etching through the products of anodic reactions in a diaphragm electrolyzer (with an inert diaphragm); intermediate and adjacent to the electrolyzer tanks. In this case, the cathode chamber operates under a semi-periodic mode. When Eh in the cathode chamber reaches 300 mV $\left(\rho_{\bar{e}}=5\,\text{V}\right)$, it is recommended to ensure Eh adjustment in the range of 400–450 mV by anolyte. For this purpose, the catholyte is mixed with the anolyte, which has an Eh of 1100–1200 mV (current consumption is $10 \cdot 10^3$ C/l) in the intermediate tank until Eh reaches about 450 mV, which provides energetically favorable conditions for further extraction of copper in the cathode chamber of the electrolyzer. In addition, chlorine is supplied to the intermediate tank, which is released into the above-electrode space of the anode chamber.

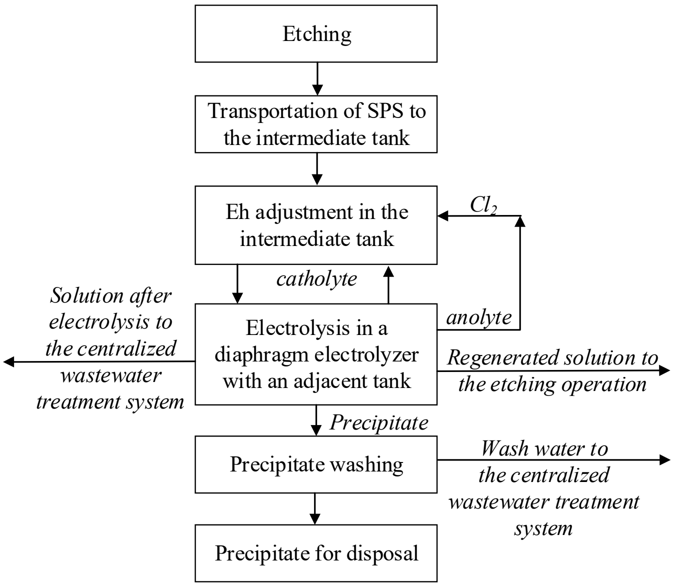


Fig. 12. Functional scheme for the regeneration of peroxide-hydrochloric acid spent process solutions

It is recommended to complete the electrochemical regeneration process while controlling the following basic parameters of the redox state of the regenerated solution (a mixture of catholyte and anolyte): pH = 2, Eh = +800 mV. This corresponds to the following technological parameters: specific current flow in the range from $46 \cdot 10^3$ C/mol to $48 \cdot 10^3$ C/mol, which corresponds to a current flow of $36 \cdot 10^3$ C/l. In the event that regeneration cannot be ensured, it is recommended to carry out the process to a deeper extraction of copper, which corresponds to a specific current flow of $375 \cdot 10^3$ C/mol (current flow of $75 \cdot 10^3$ C/l). This will ensure a copper extraction rate of 92%. For further processing, it is recommended to feed the catholyte together with the anolyte into a centralized system for further purification.

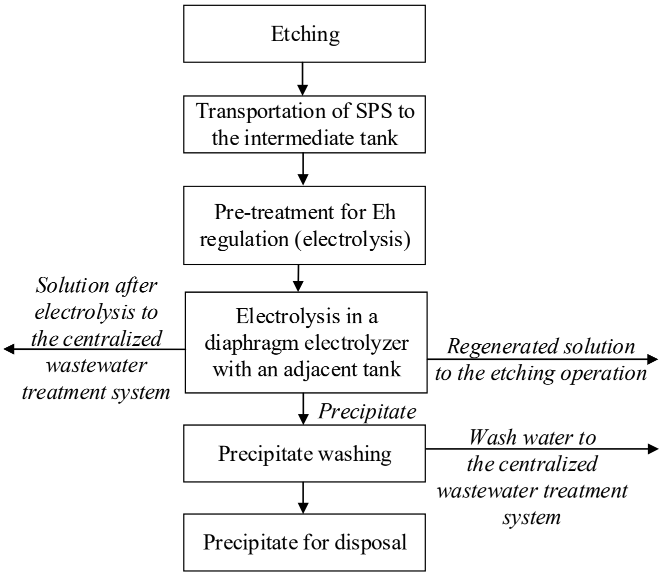


Fig. 13. Functional scheme for the regeneration of chloride-acid ammonia spent process solutions

Due to the fact that the regeneration process of chloride-acid ammonia SPSs is limited by their redox buffering, there is a need for their full pre-treatment in a diaphragm or diaphragm-free electrolyzer. To ensure energetically favorable conditions for copper extraction, the SPS is subject to preliminary electrochemical treatment with parameters that differ from the basic element (diaphragm electrolyzer) in the functional scheme shown in Fig. 13. After adjusting Eh to values close to –40 mV, the SPS is fed into a diaphragm electrolyzer with an adjacent chamber.

It is recommended to complete the electrochemical regeneration process by controlling the following basic parameters of the redox state: $\text{pH} \leq 2$, Eh = +880 mV; as well as technological parameters: current consumption $36 \cdot 10^3$ C/l (specific current consumption is $120 \cdot 10^3$ C/mol). In the case of impossibility to ensure regeneration, it is recommended to carry out the process to a deeper extraction of copper, which corresponds to a current consumption of $72 \cdot 10^3$ C/l (specific current consumption is $4000 \cdot 10^3$ C/mol). This will allow for a degree of copper extraction of 98%. For further processing, it is recommended to feed the catholyte and anolyte into a centralized system for further purification.

6. Discussion of results based on investigating the cathodic extraction of copper from hydrochloric acid spent process solutions

According to current ideas [22], one of the basic stages in the electrochemical process is a chemical stage, which proceeds at a high speed in the volume and near the electrode layer, which leads to uncertainty behind the mechanism of electrode process. This chemical stage currently refers to redox and acid-base processes. However, studies of electrochemical technologies for adjusting the redox properties of water systems, including wastewater [23], do not include a targeted reduction in redox buffering to enable energetically favorable conditions for the process. Therefore, in our work, the following indicators of the redox state have been experimentally determined: pH, Eh, free electron activity $\rho_{\bar{e}}$, in order to adjust them under conditions of their maximum redox buffering.

Based on the study of processes occurring in the volume of the copper etching SPS under the action of electrode reaction products, the possibility for ensuring controlled conditions for copper extraction according to pH and Eh indicators has been shown [14]. In contrast to the technology reported in [14], our work considers processes occurring during the electrolysis of copper-containing chloride SPSs from etching, including under the action of reaction products. This includes the transformation of both cationic and anionic components of the solution. In this case, the electrolysis processes of chloride-acid SPSs from etching are accompanied by the formation of products in the gaseous state, largely Cl_2, which determines a significant change in the redox properties of the water system [23]. It should be noted that the high solubility of chlorine and ammonia is associated with the chemical interaction of these gases with water molecules. This allows for the effective use of these components for chemical transformations in the solution volume in order to restore its ability to etch metal and create energetically favorable conditions for cathodic metal extraction.

The formation of a heterogeneous structural unit of the aqueous system (gas-bubble) leads to a non-equilibrium state of the aqueous system. Therefore, there is a need to conduct experimental studies to determine technological parameters that correspond to more energetically favorable conditions for the electrochemical regeneration of copper-containing chloride-acid SPSs**.**

A feature of this category of solutions studied in our work is a strong acidic-oxidative environment (range of pH values from 0.3 to 1.8, Eh – from +500 mV to +600 mV). Under the action of chlorine, which is released during electrolysis at the anode, Eh rapidly increases to a maximum value of +1100–1200 mV [16] under the conditions of the absence of components that exhibit redox buffering.

In order to unify the regeneration technology, our studies were conducted to take into account that copper ions in the solution are contained in the form of complex compounds [24] and the components of SPSs and the products of their electrochemical transformation exhibit a redox buffering effect.

When interpreting experimental data on model solutions, the absence of extreme values on the curves in the differential form according to the pH indicator is noted (Fig. 2). Thus, the pH changes slightly, which corresponds to data reported by other researchers [23]. When analyzing the differential curves based on the Eh index (Fig. 3), the presence of extreme values was determined, by which it is possible to determine the energetically favorable conditions for the process. In addition, the presented differential curves based on the Eh index could be used to determine the buffer index Eh (similar to the buffer index by the pH index) and to control and regulate the electrochemical process in the current consumption range.

However, the direct use of Eh as a variable parameter is limited by the dependence on temperature, the impossibility of its use in an alkaline environment, unlike the $\rho_{\bar{e}}$. indicator. A more pronounced redox buffering interval (the indicator is the inverse of the buffer index) was determined on the differential curve based on the $\rho_{\bar{e}}$ indicator (Fig. 4).

Based on our studies conducted on model solutions, main indicators of the redox state pH, Eh, $\rho_{\bar{e}}$, were determined, which can be used to substantiate technological parameters that correspond to energetically favorable conditions for the SPS regeneration process. In this case, one indicator complements the other.

When interpreting the results, in contrast to the data given in [15], it was taken into account that not only cationic components of SPS, but also anionic components participate in electrochemical transformations. This could lead to the formation of both a strongly oxidizing and a strongly reducing environment. When analyzing the curves of the change in the redox state of copper-containing chloride-acid peroxide SPSs during electrochemical regeneration (Fig. 5, 6), a decrease in Eh and $\rho_{\bar{e}}$. is observed. This is associated with the accumulation of products of cathodic reactions, as well as intercomponent chemical interaction. Thus, hydrogen evolution at the cathode is noted, the accumulation of Cu^+ ions (Table 2) due to the disproportionation reaction $2Cu^+ \rightleftarrows Cu^0 + Cu^{2+}$ [22, 25]. This, among other things, leads to an increase in energy costs for the regeneration process.

One of the effective ways to change the direction of the electrode process is the introduction of other substances (reagents) into the solution [13]. Therefore, in order to reduce the concentration of Cu^+ and reduce the current consumption, the catholyte properties were adjusted according to the value of Eh using a chemical reagent. In this case, SPS was used as a chemical reagent, which was pre-treated in the anode chamber of the diaphragm electrolyzer (Table 3) with Eh = 1100–1200 mV. In the anode chamber (Fig. 5, 6, *b*), gaseous chlorine leads to a rapid increase in the redox potential up to the maximum value of Eh = 1100–1200 mV ($\rho_{\bar{e}}$ = 18 – 20 V). The results illustrated in Fig. 5, 6 and Tables 2, 3 data demonstrate the maximum buffering effect at the following redox parameters: Eh = 300 mV and ($\rho_{\bar{e}}$ = 5 V). Therefore, it is recommended to adjust and maintain the value of Eh (approximately 450 mV) in the cathode chamber in order to create energetically favorable conditions for cathodic copper extraction.

When analyzing the results of investigating (Table 1) copper-containing hydrochloric acid solutions, it was taken into account that copper is in ammonia complexes (equations (3), (4)).

The multi-stage nature of this process complicates its implementation, which is also associated with the values of the corresponding indicators of the redox system and the phenomenon of redox buffering.

Studies of the redox parameters of electrochemical regeneration of copper-containing chloride-acid ammonia SPSs showed (Fig. 7, 8) that in the cathode and anode chambers there is a phenomenon of redox buffering both in terms of Eh and $\rho_{\bar{e}}$ values. Therefore, there is a need to adjust the Eh values ($\rho_{\bar{e}}$) in order to create energetically favorable conditions for electrochemical regeneration.

It is known [20] that at Eh at the order of –0.01 V, hydrated electrons appear in the aqueous system, which behave like ordinary particles, penetrating into the double electric layer [22]. Therefore, it can be assumed that the process of copper ion reduction under conditions of Eh ≤ –0.01 V will occur both due to electrochemically generated electrons and due to those electrons that penetrate into the double electric layer from the depth of the solution. Therefore, there is a need to adjust the value of Eh in the cathode chamber, which will be less than –0.01 V and thus provide more energetically favorable conditions for the extraction of copper from SPSs, in which copper is in ammonia complexes.

Due to the presence of NH_4^+ ions in the anode chamber, the value of Eh = 800 mV does not reach maximum value, which is characteristic of chloride solutions. The phenomenon of buffering the redox system in relation to oxidation processes is explained by the fact that the NH_4^+ ion, when interacting with water, contributes to the formation of hydrated electrons OH^- [18], which compensates for the process of achieving the maximum value of Eh (1100–1200 mV).

Based on calculations and analysis of changes in the basic indicators of the redox state (pH, Eh, $\rho_{\bar{e}}$) at different values of current flow (*D*) in a graphical-differential form, it is possible to define technological parameters that correspond to more energetically favorable conditions for the process.

For chloride SPSs from etching, a cycle of cathodic copper extraction for further disposal and oxidation of the solution for return to the production process (regeneration cycle) is recommended. It is known that electrochemical technologies are energy-intensive [15] and, in this regard, are characterized by relatively high residual concentrations of metals. Therefore, the regeneration process does not require deep metal extraction to low concentrations but enables returning of the basic components ($CuCl_2$, HCl, and others) to the technological process [9].

Taking into account the phenomenon of redox buffering and the need to dispose of electrolysis gases, technological parameters for electrochemical regeneration of copper-containing hydrochloric acid etching solutions were determined. Our research yielded results that make it possible to reduce energy consumption, including under conditions of deeper metal extraction, and will make it possible to increase the stability of the process by adjusting and controlling the redox state of the solution.

When analyzing the results of our study from the diaphragm electrolyzer, an increase in the extraction effect and an increase in current consumption compared to sulfate solutions of the corresponding concentrations are noted [14]. This can be explained by the peculiarities of SPS composition and its redox parameters.

In order to reduce the current consumption (energy), the properties of the solution were regulated by the Eh indicator when its value in the catholyte reached 300 mV. For this purpose, an anolyte was used as a chemical reagent, which is characterized by the following indicators of the redox environment: Eh = 1100–1200 mV, $\rho_{\bar{e}} = 20.16$ V. By dosing the anolyte into the catholyte, Eh was maintained at a value close to 450 mV. That made it possible to influence the nature of the process, which is accompanied by a lower concentration of Cu^+.

The basic reaction at the anode is the formation of gaseous chlorine $2Cl^- - 2\bar{e} \rightarrow Cl_2$. When chlorine is dissolved in the anolyte, its hydrolysis occurs: $Cl_2 + H_2O \rightleftarrows H^+ + Cl^- + HOCl$. Therefore, hydrolyzed chlorine enters the SPS with the anolyte, which in an acidic environment can participate in the cathodic process $OCl^- + 2H^+ + 2\bar{e} \rightleftarrows Cl^- + H_2O$ (but current losses are insignificant [13], not more than 3.5%). In the cathode chamber, the Eh value is maintained at no more than 450 mV, as a result of which the Cu^+ concentration is significantly reduced, current consumption is reduced (Table 3), and the process takes place under more energetically favorable conditions.

The multi-stage nature of the copper extraction process from ammonia complexes complicates its implementation. This is also associated with the values of the corresponding indicators of the redox system and the phenomenon of redox buffering of the water system according to the following indicators: current consumption 5236 C/l, Eh = 385 mV and $\rho_{\bar{e}} = 15.7$ V.

The process is characterized by high energy costs. Thus, the maximum extraction degree of 32% corresponds to a specific current consumption of $7000 \cdot 10^3$ C/mol, which is tens of times higher compared to other copper-containing SPSs.

In order to reduce energy costs, its preliminary treatment is recommended to adjust Eh to a value close to −40 mV, for example, by electrolysis. This would provide more energy-efficient conditions for the extraction of copper from copper-containing chloride acid SPSs from etching operations in which copper is in ammonia complexes.

The process after correction (Fig. 11) of the redox properties by indicator $Eh < 0.01\ V \left(\rho_{\bar{e}}\right)$ made it possible to carry out regeneration under energy-efficient conditions and increase the maximum degree of copper extraction to 43% (instead of 32%). At the same time, the specific current consumption will be significantly lower than without Eh correction – approximately by 4 times (taking into account the current consumption for pre-treatment). Maintaining Eh in the cathode chamber at about 450 mV allows us to ensure more complete extraction of copper in the processes of neutralization of these solutions. Thus, at a current flow rate of $180 \cdot 10^3$ C/l, the degree of extraction is 98% (specific current flow rate is $4000 \cdot 10^3$ C/mol).

As a result of our experimental-industrial and scientific studies using the cathodic metal extraction unit (Fig. 12), it was established that it is necessary to include additional elements in its structure to improve the process in the apparatus under the following conditions:

– regeneration of SPS in the diaphragm electrolyzer is supplemented by oxidation operations in an additional tank adjacent to the anode chamber;

– gaseous chlorine, released into the above-electrode space of the anode chamber, is transported through the pipeline to an adjacent tank with the anode chamber where it is partially dissolved, passing through the solution thickness;

– transportation of chlorine gas is possible when creating the necessary pressure drops;

– the discharge of the regenerated solution is carried out with a tank adjacent to the anode chamber.

The organization of the technological process improves through the following operations:

– in the structure, there is a need to ensure that the cathode chamber operates under a semi-periodic mode (when Eh reaches 300 mV in the cathode chamber ($\rho_{\bar{e}} = 5$ V), it is recommended to adjust Eh in the range of 400–450 mV with anolyte);

– in this case, the SPS solution is fed into an intermediate tank (Fig. 12), and then enters the cathode and anode chambers with the removal of the regenerated solution from a tank adjacent to the anode chamber;

– part of the anolyte at Eh from + 1100 mV to + 1200 mV at a current flow rate of $D = 10 \cdot 10^3$ C/l is fed into the intermediate tank to adjust the Eh of the catholyte;

– in the adjacent tank with the anode chamber, the composition and properties of the regenerated solution are adjusted by mixing the SPS, catholyte, anolyte, and gaseous chlorine supplied from the anode chamber.

For peroxide-chlorinated SPSs, control and regulation of redox properties according to the Eh indicator by using anolyte as a chemical reagent ensures that the process is carried out under energy-efficient conditions.

As regards unified technologies and equipment, the structure and technology of regeneration of chloride-acid ammonia SPSs has been recommended in accordance with the schemes shown in Fig. 13, which includes other additional elements compared to the scheme of regeneration of peroxide chloride-acid SPSs (Fig. 12):

– SPS regeneration in a diaphragm electrolyzer is supplemented by SPS pre-treatment operations to adjust Eh from –10 mV to –40 mV in an intermediate tank with an additional electrolyzer;

– gaseous chlorine, released into the above-electrode space of the anode chamber, is transported through a pipeline to an adjacent tank with the anode chamber of the diaphragm electrolyzer.

By ensuring energetically favorable conditions by pre-regulating Eh from –10 mV to –40 mV and carrying out the process at a moderate current density on the electrodes ($i = 500–700\ \mathrm{A/m^2}$), additional oxidation with chlorine, which is released into the above-electrode space and fed into the tank adjacent to the anode chamber of the diaphragm electrolyzer, the following is achieved:

– additional oxidation of the solution not only due to electrode reactions but also due to processes occurring in the solution volume;

– the capability to increase the degree of copper extraction within 53–97%.

In the event that it is impossible to ensure regeneration after deeper copper extraction, it is recommended to feed the catholyte and anolyte into a centralized system for further purification.

After adjusting the solutions in a tank adjacent to the electrolyzer (Fig. 12, 13), regenerated solutions (hydrochloric acid) of the following composition were obtained: Cu^{2+} – 90–100 g/l; Cu^{+} – 0.1–0.2 g/l; Eh – +0.55–(+0.65) V. At the same time, the electricity consumption for the regeneration of 1 m^3 of SPS was 1 – 1.5 kW h.

Our study on determining the cathodic extraction of copper from chloride acid SPSs is limited to application only for concentrated acidic chloride (peroxide) and acidic chloride ammonia (with a concentration of 1.25 mol/l to 0.01 mol/l).

The disadvantage of the technology is the lack of a balance technological scheme that takes into account correction of the properties of both the catholyte and the solution as a whole, to ensure energetically favorable conditions for the regeneration process. In addition, it is necessary to prepare a technical task for designing a cathodic extraction plant for regeneration.

In the future, it is advisable to prepare a technical task for design, which includes the material and energy balances of the process, and a technical task for manufacturing a cathodic extraction plant. In this case, the technical specifications for the design and construction imply ensuring maximum solubility of gases (chlorine and ammonia) and the removal of excess electrolytic gases for disposal and SPS regeneration technology.

7. Conclusions

1. We have established that for electrochemical regeneration of chloride-acid peroxide and chloride ammonia SPSs in a diaphragm electrolyzer in order to reduce current consumption, it is advisable to adjust the redox properties of the medium based on the pH and Eh indicators, which characterize the phenomena of redox buffering. It was determined that regulating the redox properties of the catholyte within the range of Eh = 300–450 mV provides energetically favorable conditions for the process. For this purpose, our work proposes using anolyte as a chemical reagent at Eh = 1100–1200 mV.

2. It has been established that during electrochemical regeneration of chloride-acid peroxide SPSs when maintaining Eh in the cathode chamber within 400–450 mV, the concentration of total copper in the mixture of catholyte and anolyte decreases from 1.02 mol/l to 0.08 mol/l. In this case, the specific current consumption is $46–48 \cdot 10^3$ C/mol, which is 4 times less than electrolysis without Eh correction, with a copper extraction rate of 38–40%. In the case of impossibility to carry out the regeneration process, the recommended current consumption is $75 \cdot 10^3$ C/l ($375 \cdot 10^3$ C/mol), which enables cathodic copper extraction at the level of 92%.

3. We have found that electrochemical regeneration of chloride-acid ammonia SPSs after correction of redox properties to the value of Eh < –0.01 V ensures the process under energy-favorable conditions. At the same time, the maximum degree of copper extraction increases to 43% (32% – without Eh adjustment) in regeneration technologies. In the event of impossibility of carrying out the regeneration process with Eh correction, a degree of copper extraction of 98% (32% – without correction Eh) is achieved. At the same time, the specific current consumption decreases by 4 times compared to the process without Eh adjustment.

4. Our experimental and industrial studies confirmed the need to include additional elements in the design of the cathodic metal extraction installation for disposal (Eh correction) of electrolysis gases in order to ensure energy-favorable conditions for the regeneration process. For practical implementation, basic elements in the technological schemes have been defined. They include pre-treatment for the purpose of electrochemical Eh adjustment of chloride-acid ammonia SPSs, Eh adjustment of catholyte by dosing anolyte in order to reduce the concentration of Cu^{+} in peroxide chloride-acid SPSs. Adjustment of the composition and redox properties of regenerated solutions is carried out by mixing SPS, catholyte, and anolyte in a technologically justified ratio. If the regeneration process cannot be carried out, it is recommended to send the mixture of catholyte and anolyte after deep extraction of copper (98%) to a centralized wastewater treatment system.

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 and the results reported in this paper.

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Data availability

The data will be provided upon reasonable request.

Use of artificial intelligence

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

Authors' contributions

Mykola Yatskov: Supervision, Project administration, Funding acquisition; **Natalia Korchyk:** Conceptualization, Methodology, Investigation, Resources, Writing – original draft, Writing – review & editing, Funding acquisition; **Nadia Budenkova:** Validation, Data Curation, Writing – original draft, Writing – review & editing, Funding acquisition; **Oksana Mysina:** Formal analysis, Data Curation, Writing – original draft, Writing – review & editing, Visualization, Funding acquisition; **Svitlana Kyryliuk:** Software, Formal analysis, Funding acquisition.

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