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DETERMINING BASIC TECHNOLOGICAL PARAMETERS FOR THE PROCESS OF ELECTROCHEMICAL EXTRACTION OF COPPER FROM ACID SULFATE CONCENTRATED TECHNOLOGICAL SOLUTIONS

Mykola Yatskov
PhD, Senior Researcher, Professor*
Natalia Korchyk
PhD, Associate Professor*
Nadia Budenkova
PhD, Associate Professor*
Oksana Mysina
Corresponding author
Senior Lecturer*
E-mail: o.i.mysina@nuwm.edu.ua
Serhii Kovalchuk
PhD, Associate Professor
Department of Ecology
Separate Structural Unit "Rivne Technical Vocational College of the National University of Political Science and Technology"
Vyshivanka str., 35, Rivne, Ukraine, 33027
*Department of Chemistry and Physics
National University of Water and Environmental Engineering
Soborna str., 11, Rivne, Ukraine, 33028

This study investigates concentrated model solutions, acid sulfate spent technological solutions (STSs) from surface preparation and coating operations by a number of enterprises, in order to devise unified technologies and to design relevant equipment.

To substantiate the basic parameters for an electrolysis system within the framework of the system approach (Quality Function Deployment), it is shown that regardless of the concept and mechanism of electrochemical transformations, one of the main elements is redox reactions that occur both at the electrode-solution interface and in the solution volume.

This paper reports experimental studies on electrochemical cathodic extraction of copper from acid sulfate concentrated technological solutions under conditions of non-stationary composition and changes in the properties of STSs. The basic technological parameters of the electrolysis process have been defined; a cathodic extraction installation of metal (copper) has been designed.

To adapt the installation to changes in technological parameters and to avoid the formation of by-products together with the main product (copper), installation and dismantling of cathodes and diaphragms are implied. To eliminate secondary contamination of STS, it is proposed to abandon the use of reagents in local cycles at all stages of STS purification in favor of electrochemical technology.

The kinetic data reported here (current density, current consumption/1 mol, deposition rate) make it possible to define the basic principles of control and regulation of the electrolysis process. The pH and Eh values make it possible to adjust the type of precipitate (foil, precipitate containing foreign substances), as well as 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

Keywords: cathodic extraction, spent technological solutions, technological parameters, diaphragm and diaphragm-free electrolysis

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1. Introduction

Electroplating production is a source of environmental pollution by metal ions that have toxic, carcinogenic effects and are supplied in the form of liquid waste. The latter include weakly concentrated, from washing operations, and concentrated, from etching and coating operations. According to the concept of a cyclical economy in the field of effective and sustainable wastewater treatment technologies [1], it includes physical, chemical, physicochemical, or electrochemical methods. Concentrated waste in the form of spent technological solutions (STSs) from electroplating production can be considered a valuable resource for the extraction of metals, acids, alkalis, salts, chlorine, etc.

The processes that occur in water systems, including STSs from electroplating production, under the influence of electric current (electrochemical processes) are theoretically substantiated in [2, 3]. The use of electrochemical processes (ECPs) is promising in technologies for the complex processing of STSs with the aim of returning them to the technological process (regeneration). This also allows them to be used as chemical reagents for the extraction of metals and other components in a form suitable for further disposal [2].

STSs are the main source of contamination of liquid metal waste (their salts) with a total mass of up to 70% of the total mass of contamination, although by volume they make up only up to 6%. We consider it most promising to process STSs in combined systems, namely in local periodic systems operating to extract the bulk of polluting components for the purpose of regeneration and utilization. Further purification can be carried out in centralized continuous systems together with wastewater from washing operations. These technologies make it possible to utilize copper cathode deposits with the subsequent manufacture of electrocatalysts for reactions [4].

At the same time, metallurgical companies solve a number of economic issues by recovering metals from industrial waste [5]. The formation of deposits in metallic form is more dangerous from the point of view of the ecological state of the environment. The organization of the technological process in local cycles involves the division of STSs by chemical composition and concentration. Based on the basic principles of the theory of concentrated electrolyte solutions, it can be argued that an increase in the concentration of components leads to increased interaction between them (water-water; water-ion; ion-ion). This leads to the fact that individual components acquire new properties, new chemical compounds are formed, etc. All this affects the justification and choice of technological and design solutions and their results of implementation in the production process.

Thus, investigating cathodic extraction of metals, in particular copper from STSs from individual operations, of different composition and concentrations is an urgent task. This should enable the prediction of design solutions for the implementation of electrochemical technologies for STS processing.

2. Literature review and problem statement

Electrochemical processes have found the greatest practical application in technologies for treating wastewater from galvanic production: electrocoagulation [5] and electrodeionization [6]. In [5], an electrocoagulation technology for solutions with a concentration of 0.00132 mol/l (86 mg/l) is proposed. The results of [5] allow for effective purification from copper ions with the formation of copper sludge together with aluminum hydroxide and organic impurities. The disadvantage of [5] is the complexity and limitations of the disposal of the formed sludge. When using this technology [5], issues related to the use of the method and modes of electrolysis for acid sulfate waste technological solutions with a copper ion concentration from 0.02 mol/l to 0.9 mol/l, which corresponds to the concentrations of STS, remain unresolved.

Paper [6] reports data from studying deionization processes for the extraction of heavy metal ions. The advantages of this method in combination with reverse osmosis are a deep reduction in copper concentration to 10^{-2}–10^{-4} mg/l from weakly mineralized (weakly concentrated) solutions. The proposed technology refers to separation processes and does not provide conversion of toxic copper ions into low-toxic or non-toxic forms. In addition, these technologies cannot be used in technologies for extracting copper from concentrated solutions.

In [7], data are given on the combination of electrocoagulation methods with electroreduction of copper ions from galvanic effluents. The advantage is the extraction of copper ions with conversion into a non-toxic form. However, the application of this method is limited to a copper ion concentration of 92 mg/l (0.0014 mol/l), so it cannot be used for concentrated spent technological solutions from galvanic production.

The authors of work [8] note that electrochemical treatment in a diaphragm electrolyzer of concentrated STS, including copper ions, allows one to obtain acidic and alkaline reagents for their further use in technologies for the treatment of other categories of wastewater. This makes it possible, on the one hand, to significantly reduce the consumption of chemical reagents, and on the other hand, to ensure their effective neutralization. Simultaneous treatment in the anode chamber, for example, of alkaline spent electrolytes allows for their neutralization without the use of chemical reagents. In this case, the process is controlled by pH and Eh. However, the issue of reducing the overall degree of mineralization is not resolved, which limits its use in closed water management systems in electroplating production.

It should be noted that for concentrated water systems used for technological operations in electroplating production under stationary conditions, the laws considered by theoretical electrochemistry can be used to study the processes [9]. However, these data cannot be fully applied to production processes for the purification of concentrated STSs with a constant change in concentration. After all, they do not assume a change in their composition and properties during the electrolysis process, namely a change in concentration in a wide range associated with neutralization, utilization, and regeneration.

High concentrations of metal salts (more than 1 mol/l) necessitate devising and improving technologies for processing concentrated STSs (regeneration, utilization, neutralization). Thus, in [10], the technologies described are distinguished by high environmental parameters and low consumption of commercial chemical reagents. However, when using such technologies, the issues of waste processing, including copper reagent sludges, remain unresolved.

The studies reported by the authors of [11] show the need to separate STSs by chemical composition and technological scheme of processing. Subsequently, this enables their utilization, including processing into a commercial reagent. At the same time, processed sludges have properties related to the conditions of their further utilization in the form of products or semi-products of certain industries. In the case of their burial at special landfills, the processing products are compounds-analogs of natural materials, which ensures their physicochemical stability and environmental safety [12].

Modern theoretical electrochemistry [13] justifies the cathodic extraction of metals from aqueous solutions and their compounds. Most often, these processes are carried out from solutions of simple and complex salts: sulfates, chlorides, nitrates, ammonia, etc. It is noted that copper belongs to the group of metals with a relatively low overvoltage with the formation of thin layers of deposits on the cathode at the electrode-solution interface. These processes are the basis of hydrometallurgical extraction of metals and cannot be fully applied to the processing of concentrated STSs for the purpose of utilization and regeneration.

A feature of the cathodic extraction of copper from STS is the need to take into account the transformations due to the electric field and the products of electrode reactions not only at the electrode-solution interface but also in the solution volume. According to the classical theory of electrochemistry [13], the cathodic process is always accompanied by a rearrangement of particles, which includes hydration-dehydration processes. It is noted [9]: the deeper these changes, the greater the overvoltage (activation polarization) should be. According to the data reported in [10], in STS at concentrations close to the limit of complete hydration, the copper ion Cu^{2+}, which belongs to the d-elements, has a high tendency to chemical hydration, as a result of which it partially loses its charge and is present in the solution in the form of the ion $[CuOH]^+$. However, the authors do not consider these hydration phenomena in electrolysis systems.

According to modern concepts of cathodic processes given in [14], they include not only the electrochemical stage but also the chemical stage (which can precede, follow, or occur almost simultaneously with the electrochemical stage). In this case, the charge transfer across the electrode-solution phase interface is accompanied by the formation of intermediates – ions of lower valence (electrochemical stage) [14]. The chemical stage includes the transformation of intermediates by disproportionation reactions (DPR) or their formation by reporportionation reactions (RPR). The high-speed DPR and RPR reactions in the bulk and near-electrode layer lead to uncertainty about the mechanism of the electrode process.

In [15], it is stated that DPR and RPR reactions are currently classified as redox (Ox-Red) and acid-base processes that include electrolysis. But the authors do not consider the change in acid-base and redox parameters in the solution volume under the influence of electrode reaction products. An option for overcoming the difficulties may be to study the change in these parameters.

Thus, in work [16], the main trends of electroreduction of metals from waste electrical and electronic equipment are considered, taking into account the nature of the aqueous medium in the solution volume in terms of pH. The disadvantage of this work is the lack of data on the Eh indicator, which, together with pH, is recommended for processes, including electrolysis, that proceed according to an uncertain mechanism.

In [8], the pH and Eh of the medium are considered as the main variable parameters for concentrated aqueous systems of uncertain composition. These parameters determine the acid-base and redox equilibrium and the direction of processes both in the solution volume and at the electrode-solution interface.

It should be noted that the process of cathodic metal extraction (including copper) in wastewater treatment technologies has limited use due to the instability of the electrolysis process and low speed. Intensification of the process and ensuring controlled conditions for metal extraction at the cathode is carried out by electrodeposition under the action of transient and magnetic fields [17, 18], special design and materials of cathodes [16]. However, the above works do not provide changes in the main technological parameters of electrolysis depending on the metal concentration and the possible influence of organic substances on the copper extraction process.

It is known that ammonium persulfate solution $(NH_4)_2S_2O_8$ has long been and very successfully used as a copper etching solution. In work [19], a technique of electrochemical regeneration of STS by cathodic copper extraction, which includes photocatalytic enhancement of the process, is described. The method is effective only for acidic and neutral electrolytes of the etching solution. The process is effective for the extraction of copper from real electroplating wastewater with a copper recovery efficiency of more than 80%. This technique is not suitable for the regeneration of alkaline persulfate etching solutions because ammonium persulfate solutions are stable only in an acidic environment. The disadvantage of this method is significant time consumption and high energy consumption.

In the technology of wastewater treatment of printed circuit board production from organic impurities, the processes of reduction of copper cations contained in the solution to metal, as well as partial reduction of organic components, occur at the cathode [20]. The reduced form of organics forms poorly soluble complexes with copper that precipitate. This achieves a higher purification coefficient from organic components and copper. Analysis of works on the electrochemical extraction of metal ions reveals the absence of a universal electrochemical mechanism. Therefore, there was a need to conduct studies on the influence of impurities of organic origin on the cathodic processes of copper extraction from acid sulfate STSs.

Thus, cathodic copper removal from STSs is practically implemented in technologies for processing coating electrolytes for the purpose of removal in a form that is easily recyclable and in surface preparation processes for the purpose of regeneration. The regeneration process includes the removal of etched copper and the restoration of the solution's ability to etch by oxidation processes at the anode or by products of anodic reactions. In the practical implementation of these processes, their instability, high values of current density at the electrodes, and the formation of uncontrolled side processes are noted. Due to the uncertainty of the mechanism of cathodic processes, it is considered possible to predict the results of technical solutions for cathodic copper removal from STS by pH and Eh indicators. At the same time, pH and Eh regulation can be ensured by chemical components in the solution volume or by the action of electrode reaction products.

Analysis of global research has shown that their main volume has recently been associated with the extraction of copper from low-concentration solutions (from 0.00132 mol/l to 0.0014 mol/l). Therefore, these technologies cannot be applied to concentrated STSs (from 0.02 mol/l to 0.9 mol/l). In addition, the processing of STS from individual operations involves taking into account their specific properties (chemical composition, concentration of individual components and their emergence) depending on their technological purpose under the conditions of galvanic production. A significant body of world scientific literature is related to the processes of electrocoagulation and deionization. These technologies involve electrochemical generation of reagents, which limits the utilization of the formed sludge (electrocoagulation) and they cannot be applied in technologies for the extraction of copper from concentrated solutions (STSs). The issue of reducing the overall degree of mineralization is also not resolved. It should be noted that the basic principles of electrochemistry do not provide for changes in the composition and properties of solutions during electrolysis, namely changes in concentration over a wide range associated with neutralization, utilization, and regeneration.

Thus, given an uncertain mechanism behind cathodic metal (copper) extraction [4, 14], in order to regulate technological parameters (metal extraction rate, electric current consumption, current density), it is necessary to conduct experimental studies and determine the efficiency of its use in accordance with the technological operations of the galvanic enterprise. All this gives grounds to assert that there is a need to improve the process in the electrolyzer and improve the organization of the technological process under the conditions for their control and regulation.

3. The aim and objectives of the study

The purpose of our research is to substantiate the use of electrolysis as an element in a combined system of treatment facilities in technologies for the utilization and regeneration of copper-containing STSs from surface preparation and coating operations. This will make it possible to carry out processes under the conditions for their control and regulation.

To achieve this goal, the following tasks were set:

– to substantiate the most important characteristics (parameters) of a complex electrolysis system for cathodic extraction of copper from STS of galvanic production using the QFD (Quality Function Deployment) methodology;

– to determine the change in the main technological parameters of cathodic extraction of copper from acid sulfate STSs from coating operations at different current densities in the electrolysis process by the indicators of current consumption per 1 mol, speed, and extraction effect;

– to determine the change in the technological parameters of cathodic extraction of copper from acid sulfate STSs from surface preparation operations by the indicators of pH and Eh;

– to determine the influence of impurities of organic origin on the cathodic processes of copper extraction from acid sulfate STSs;

– to investigate under industrial conditions the cathodic extraction of copper from acid sulfate STSs using a specially designed CME (cathodic metal extraction) installation in order to improve the process in the electrolyzer and improve the organization of the technological process under the conditions of their control and regulation.

4. The study materials and methods

The object of our study is model solutions, sulfate acid STSs from surface preparation and coating operations (matte, bright) by a number of enterprises. Model solutions, which were prepared for the preliminary study, contain copper ions with a concentration of 0.02 mol/l to 0.9 mol/l. These model solutions are analogs of technological highly concentrated solutions and wastewater from the etching area.

The hypothesis of the study assumed that because of the uncertainty about the mechanism behind cathodic processes it would be possible to predict results regarding the technological and design solutions for cathodic copper extraction from pH and Eh indicators. At the same time, pH and Eh could be regulated by chemical components in the solution volume or by the action of electrode reaction products.

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 transformation of intermediates of the electrochemical stage take part.

2. Regardless of the current density, there are reasons to believe that changes in the activation energy of cathodic processes play a special role in polarization effects.

3. STSs, in terms of the content of the main components, belong to concentrated electrolyte solutions, which are characterized by emergence.

The following simplifications were accepted:

1. The change in activation energy of cathodic processes was considered from the point of view of hydration⇄dehydration processes.

2. Concentrated solutions included STSs with a concentration from 0.02 mol/l to 0.9 mol/l.

The basic components in the technology of cathodic copper extraction from STSs from electroplating production were justified within the framework of a system analysis using the QFD (Quality Function Deployment) methodology [21] from acidic copper-containing STSs from coating and surface preparation operations.

The acid-base and redox properties of copper-containing STSs and the technological parameters of their processing for the purpose of purification, regeneration, and utilization were studied by potentiometric titration methods and in a diaphragm (diaphragm-free) electrolyzer with a graphite anode and cathodes made of stainless steel, titanium, and copper of rectangular shape, measuring 315 mm by 255 mm (Fig. 1).

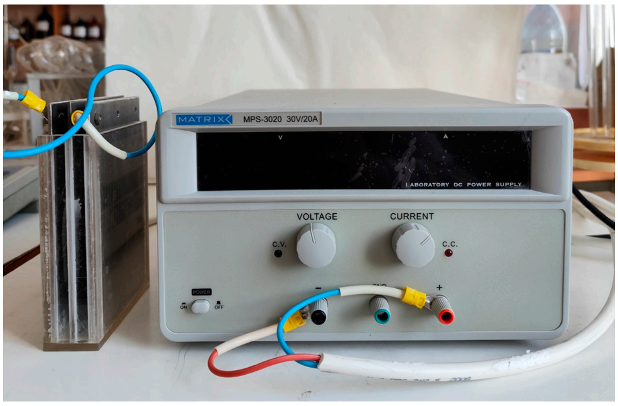

Fig. 1. Photograph of the electrolyzer

Potentiometric titration was carried out under laboratory conditions on a potentiometer EV 74 brand and under industrial-research conditions using a portable pH meter pH 602 (Ukraine). Quantitative studies on the content of Cu^{2+} ions were carried out under laboratory conditions by the method of photometric determination. The method is based on the formation of an ammonia complex of copper, which has an intense blue-violet color [22]. The concentration of Cu^{2+} ions in g/l was found according to the calibration plot. To construct the calibration plot, a series of reference solutions were 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 found. Statistical processing of the research results was carried out according to known methodologies, namely, the average values of the sample (number of values in the sample is 5), variance, standard deviations, 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). All studies were conducted in a certified laboratory.

5. Results of investigating cathodic copper extraction from spent technological solutions of galvanic production

5. 1. Results of substantiating the basic parameters for an electrolysis system

Acid copper-containing STSs from surface preparation and coating operations are characterized by a total mass of soluble substances of 118–257 g/l. To determine the main tasks of electrochemical technologies, it is necessary to take into account the volumes and multiplicity of STS discharges. Thus, according to a number of enterprises, up to 800 kg of copper per year is received from copper sulfate plating operations, and up to 36,000 kg per year from copper sulfate etching solutions. Thus, for copper-containing acid sulfate STSs from coating operations, electrochemical technologies for extracting copper in a form that is subject to further utilization (processing) into a finished product are recommended. For copper-containing STS from etching operations – electrochemical technologies, which include solution regeneration (return to the main technological process) by cathodic extraction of copper (which is subject to further utilization) and oxidation of the solution as a result of anodic reactions.

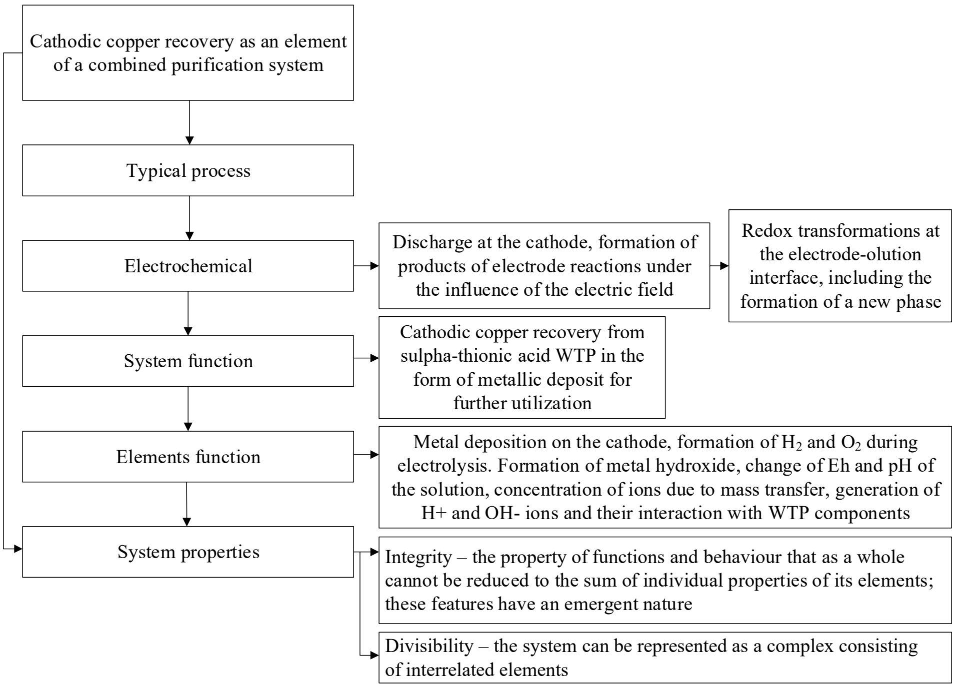

Fig. 2. Cathodic extraction of copper from spent technological solutions of electroplating production using the Quality Function Deployment method

Based on the characteristics of copper-containing STSs from galvanic production, they can be attributed to aqueous electrolyte solutions with a concentration of components corresponding to or near the full hydration limit (FHL).

For the general characteristics of the cathodic extraction of copper from acid sulfate copper-containing STSs from coating and etching operations, in our work, within the framework of a systems approach, the expert method QFD (Quality Function Deployment) [21] is applied to determine the most important characteristics (parameters) and tasks of each subsystem of a complex electrolysis system for the cathodic extraction of copper from STSs from galvanic production (Fig. 2).

As a result of applying the QFD methodology, in addition to establishing the basic requirements for technological operations, the requirements for each stage of the production process are considered. Regardless of the concept and mechanism behind ECP, there is a need to consider chemical transformations (redox, chemical precipitation) that accompany or precede the electrochemical stage. Such transformations include the phenomena of hydration and interaction between the products of electrode reactions in the volume and at the phase interface (electrode–solution). The presence of a chemical component in the cathodic process (copper discharge) significantly complicates the discussion of research results. However, it should be noted that the main factor of the chemical or electrochemical stage is electron transfer to the boundary of PES or the volume of STS, i.e., redox transformations, the direction of which is determined by the pH and Eh parameters.

To substantiate the basic parameters of the electrolysis system within the framework of the system approach (Quality Function Deployment), it is shown that regardless of the concept and mechanism behind electrochemical transformations, one of the main elements is the redox reactions that occur both at the electrode-solution interface and in the solution volume.

Thus, in addition to the basic technological parameters of electrolysis (current consumption, current density, etc.), Eh and pH can be used as control and regulation parameters for copper-containing acid sulfate STSs from coating and etching operations, respectively.

5. 2. Results of investigating changes in the basic technological parameters of cathodic copper extraction from acid sulfate solutions

The acid sulfate STS of copper from coating operations related to unsaturated electrolyte solutions (the maximum total number of moles does not exceed 2) is considered. For this category of STS, it can be assumed that one of the important factors that will influence the process of cathodic copper extraction is a high degree of hydration and partial formation of covalent bonds with water with the formation of the $[CuOH]^+$ ion. This process causes concentration and activation polarization.

Fig. 3 and Tables 1–3 give data on the results of investigating cathodic copper extraction from model solutions with a copper concentration of ≈6 g/l and sulfuric acid ≈1 g/l at different values of current density at the cathode (from 50 A/m^2 to 200 A/m^2).

The dependences are fitted to function

$$y = A + B_1x^1 + B_2x^2. \tag{1}$$

Near the value of the current flow in the interval from 16,000 C/l to 19,000 C/l, an inflection point of the curves is observed; therefore, the approximation was carried out by two segments: *a* – for the curve at a current density of 50 A/m^2; *b* and *c* – for the curve at a current density of 200 A/m^2; *d*, *e* – for the curve at a current density of 150 A/m^2. Parameters of approximation for the curve segments:

a) $A = 5.96726$; $B_1 = -3.39286E-5$; $B_2 = -1.86012E-8$;
b) $A = 6$; $B_1 = 3.03841E-5$; $B_2 = -1.47711E-8$;
c) $A = 5.7325$; $B_1 = -2.37907E-4$; $B_2 = 2.76957E-9$;
d) $A = 6$; $B_1 = -1.18045E-4$; $B_2 = 8.29311E-10$;
e) $A = 16.30981$; $B_1 = -9.00624E-4$; $B_2 = 1.30073E-8$.

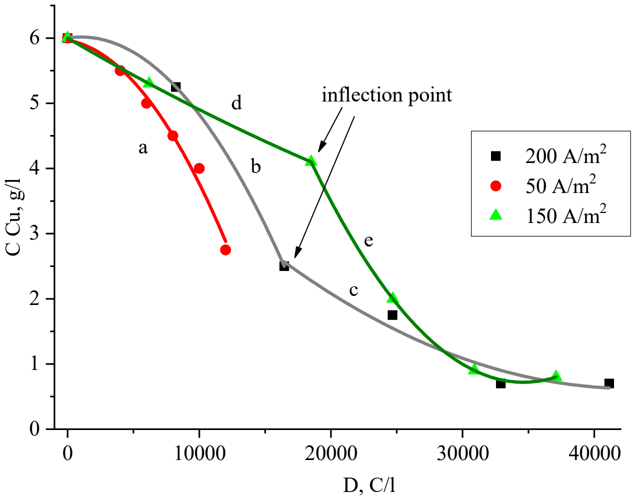

Fig. 3. Results of investigating changes in copper concentration depending on current flow at different values of current density

Table 1

Results of calculating current consumption per 1 mol of copper cathodically removed from an acid sulfate model solution at a current density of 200 A/m^2

Initial copper concentration, mol/l	ΔD, C/l	ΔC, mol/l	Time, τ, s	$\frac{\Delta D}{\Delta C}$, C/mol
0.09	8228	0.012	3600	$0.7 \cdot 10^6$
0.08	8228	0.042	7200	$0.7 \cdot 10^6$
0.04	8228	0.012	10800	$0.7 \cdot 10^6$
0.03	8228	0.016	14400	$0.5 \cdot 10^6$
0.01	8228	0.02	18300	$0.4 \cdot 10^6$

Table 2

Results of calculating current consumption per 1 mol of copper cathodically removed from an acid sulfate model solution at a current density of 150 A/m^2

Initial copper concentration, mol/l	ΔD, C/l	ΔC, mol/l	Time, τ, s	$\frac{\Delta D}{\Delta C}$, C/mol
0.09	6200	0.01	3600	$0.62 \cdot 10^6$
0.08	6200	0.01	7200	$0.62 \cdot 10^6$
0.064	6200	0.034	10800	$0.38 \cdot 10^6$
0.03	6200	0.016	14400	$0.18 \cdot 10^6$
0.014	6200	0.0015	18000	$4.1 \cdot 10^6$

Table 3

Results of calculating current consumption per 1 mol of copper cathodically removed from an acid sulfate model solution at a current density of 50 A/m^2

Initial copper concentration, mol/l	ΔD, C/l	ΔC, mol/l	Time, τ, s	$\frac{\Delta D}{\Delta C}$, C/mol
0.085	2000	0,001	7200	$2 \cdot 10^6$
0.084	2000	0,001	10800	$2 \cdot 10^6$
0.069	2000	0,015	14400	$0,13 \cdot 10^6$
0.042	2000	0,027	21600	$0,15 \cdot 10^6$

Table 1 (i = 200 A/m^2) and Fig. 3 demonstrate that within the concentration range of 0.095 – 0.01 mol/l, the current consumption per 1 mol of copper is $0.7 \cdot 10^6$–$0.4 \cdot 10^6$ C/mol; the copper extraction rate is from $6 \cdot 10^{-6}$ mol/s to $3.2 \cdot 10^{-6}$ mol/s, respectively. At a total current consumption $D = 33 \cdot 10^3$ C/l, the total degree of copper extraction is 77%. This is the maximum degree of extraction. At a current flow in the range from $D = 16.5 \cdot 10^3$ C/l (inflection point) to $D = 25 \cdot 10^3$ C/l, which corresponds to the final degree of extraction (from 58% to 70% of the total flow), the value of the current flow per 1 mol of copper extracted will be 30% lower compared to the beginning of the process. In this case, the speed decreases by 46%, respectively. The average value of current flow per 1 mol of copper extracted is $0.6 \cdot 10^6$ C/mol.

Table 2 (i = 150 A/m^2) and Fig. 3 demonstrate that within the concentration range of 0.09–0.014 mol/l, the current consumption per 1 mol of copper is $0.62 \cdot 10^6$–$4.1 \cdot 10^6$ C/mol; the copper extraction rate is from $9.4 \cdot 10^{-6}$ mol/s to $2.7 \cdot 10^{-6}$ mol/s, respectively. At a total current consumption $D = 18.5 \cdot 10^3$ C/l, the total degree of copper extraction is 67%. At a current consumption in the range from $D = 12.3 \cdot 10^3$ C/l to $D = 18.5 \cdot 10^3$ C/l (inflection point), the current consumption per 1 mol of extracted copper decreases compared to the beginning of the process. At a current consumption of more than $18.5 \cdot 10^3$ C/l, the process speed decreases by 2.1 times (the current consumption per 1 mol increases by 22 times). The average current consumption per 1 mol of copper extracted is $1.18 \cdot 10^6$ C/mol.

Table 3 (i = 50 A/m^2) and Fig. 3 demonstrate that within the concentration range of 0.1–0.042 mol/l, the current consumption per 1 mol of copper is $2 \cdot 10^6$–$0.13 \cdot 10^6$ C/mol; the copper extraction rate is from $3 \cdot 10^{-6}$ mol/s to $8 \cdot 10^{-6}$ mol/s, respectively. At a total current consumption $D = 12 \cdot 10^3$ C/l, the total extraction degree is 60%. At a current consumption $D = 6 \cdot 10^3$ C/l (50% of the total consumption), the value of the current consumption per 1 mol of copper extracted will be 35% lower compared to the beginning of the process. At the same time, the rate increases by 33%, respectively. At the final stage of the process, the extraction rate increases by 2.6 times. The average value of the current consumption per 1 mol of copper extracted is $1.07 \cdot 10^6$ C/mol.

Thus, the difference in the basic technological parameters with the same composition of solutions and different values of current density has been established, namely: the total degree of extraction at $i = 200$ A/m^2 is 77%, at $i = 50$ A/m^2 – 60%. The average value of current consumption per 1 mol of copper extracted at $i = 200$ A/m^2 is $0.6 \cdot 10^6$ C/mol, at $i = 50$ A/m^2 – $0.7 \cdot 10^6$ C/mol. The average value of the copper extraction rate at $i = 200$ A/m^2 is $5 \cdot 10^{-6}$ mol/s, at $i = 50$ A/m^2 – $4.5 \cdot 10^{-6}$ mol/s.

5. 3. Results of investigating changes in pH and Eh during the cathodic extraction of copper from technological solutions

Table 4 gives the results of investigating changes in Eh and pH values depending on the concentration of copper during the electrolysis of acid sulfate STSs.

As the results of our research showed, in the process of cathodic copper extraction in a diaphragm-free electrolyzer, the pH changes in the range of values from 1.15 to 0.15, and Eh from 500 mV to 1100 mV, which corresponds to the end of the process. When carrying out the process in a diaphragm electrolyzer, it was found that in the cathode chamber the pH changes in the range of values from 1.15 to 0.85, and Eh from +500 mV to –100 mV, which corresponds to the end of the process. At the same time, in the anode chamber the pH changes in the range of values from 1.15 to 0.2, and Eh from +500 mV to +620 mV, which corresponds to the end of the process. At pH > 0.65, the formation of a precipitate in the form of a foil is observed, which is firmly grafted to the cathode surface, while Eh is no more than +500 – +700 mV. At lower pH values and higher Eh values, a precipitate is formed with the inclusion of foreign substances, which slides off the electrode surface.

Table 4

Results of investigating changes in pH and Eh depending on copper concentration in the process of electrolysis of acid sulfate STSs from etching operations

Cathode chamber			Anode chamber			Diaphragm-free electrolysis		
pH	Eh, mV	C(Cu^{2+}), mol/l	pH	Eh, mV	C(Cu^{2+}), mol/l	pH	Eh, mV	C(Cu^{2+}), mol/l
0.85	–95	0.0018	0.2	+625	0.0042	–	–	–
0.8	+50	0.005	0.25	+615	0.078	0.15	+1115	0.042
0.75	+115	0.012	0.25	+615	0.1	0.35	+1115	0.073
0.85	+170	0.025	0.3	+845	0.15	0.4	+1115	0.13
0.95	+175	0.125	0.45	+715	0.23	0.65	+1105	0.24
1.15	+490	0.38	1.15	+490	0.38	1.15	+490	0.37

Thus, the pH and Eh values can be used to predict the type of precipitate (foil, precipitate containing foreign substances), as well as determine the purpose of the technological process (regeneration, utilization).

5. 4. Results of investigating the influence of impurities of organic origin on the cathodic extraction of copper from technological solutions

To obtain bright deposits on the cathode, thiourea, sulfanol, naphthalene, disulfonic acid, polyacrylamide are added to the electrolyte. STSs contain condensation products of monosaccharides or polysaccharides, amine derivatives, etc.

Fig. 4 shows data on the change in copper concentration depending on current consumption from matte and bright copper plating operations.

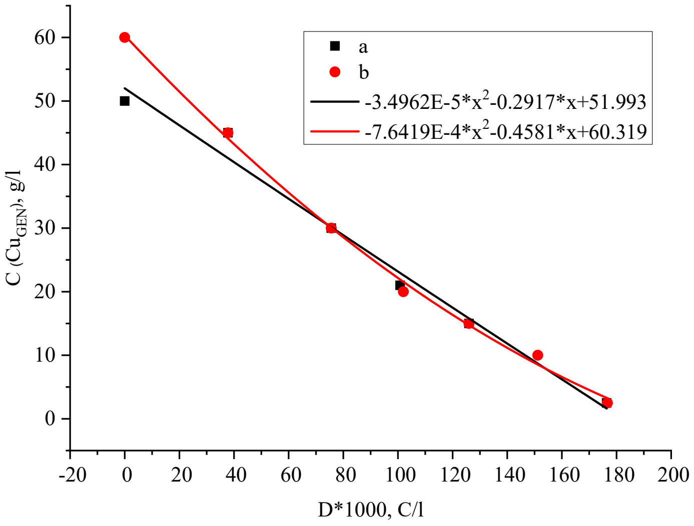

Fig. 4. Change in copper concentration from current consumption depending on matte and bright copper plating operations: *a* – matte copper plating; *b* – bright copper plating

As a result of our research, it was found that for bright copper plating (coatings containing organic impurities) at concentrations of 0.94–0.1 mol/l, the current consumption D is from $164{\cdot}10^3$ C/mol to $315{\cdot}10^3$ C/mol (average value 239.5 C/mol). At the same time, the degree of extraction (within the concentration range of 0.94–0.04 mol/l) is 97%. For matte copper plating at concentrations of 0.71–0.04 mol/l, the current consumption D is from $180{\cdot}10^3$ C/mol to $315{\cdot}10^3$ C/mol (average value 247.5 C/mol). At the same time, the degree of extraction (within the concentration range of 0.71–0.04 mol/l) is 96%.

Thus, the influence of organic impurities on the cathodic processes of copper extraction from acid sulfate STSs has been established, namely, an increase in the degree of copper extraction and a decrease in the average value of current consumption per mole.

5. 5. Results of experimental and industrial studies on the cathodic extraction of copper from acid sulfate spent technological solutions

Fig. 5 shows a functional diagram of copper extraction from acid sulfate STSs using a cathodic metal extraction unit (CMU).

Technical specifications have been compiled for the design of installations [23] with a capacity of 100 and 200 l per day (CMU-100 and CMU-200, respectively). The basis of the installation is an electrolyzer with a housing lined with polymer material. An electrode module is placed in the electrolyzer housing, the anodes are made of graphite carbon, the cathodes are made in a set: titanium, copper, galvanized steel.

Fig. 6 and Tables 5, 6 give the results from pilot-industrial studies of cathodic extraction of copper from acid sulfate STSs at various technological parameters: processing time, temperature, current strength, voltage, current consumption.

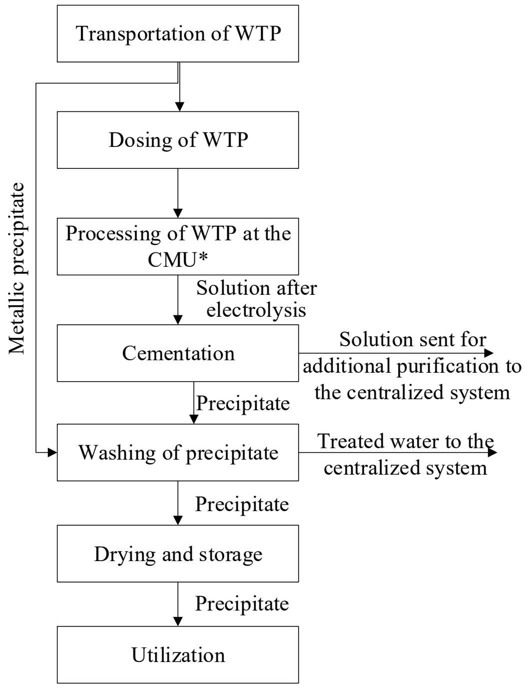

Fig. 5. Functional diagram of copper extraction from acid sulfate spent technological solutions: CMU* – cathodic metal extraction unit

The dependences are fitted to function

$$y = y_0 + A_1 \exp(-(x + x_0 / t_1)). \qquad (2)$$

Near the value of the current flow rate of 10000 C/l, an inflection point of both curves is observed; therefore, the approximation was carried out by two segments: a, b – for the curve at a current density of 500 A/m^2; c, d – for the curve at a current density of 200 A/m^2. The parameters of the segment approximation:

a) $y_0 = 7.370$; $x_0 = 79990$. $A_1 = 8.868$; $t_1 = 85438$;
b) $y_0 = -0.229$; $x_0 = 100933.8$. $A_1 = 14.430$; $t_1 = 40361$;
c) $y_0 = 7.0156$; $x_0 = 57353$. $A_1 = 8.762$; $t_1 = 35573$;
d) $y_0 = 0.8778$; $x_0 = 99062$. $A_1 = 9.51546$; $t_1 = 20717$.

Table 5

Cathodic copper extraction from acid sulfate STSs (CMU installation). Experiment No. 1

Processing time, τ_{proc}, min	Temperature, °C	Current strength I, A at a current density of 200 A/m^2	Voltage U, V
15	22	1300	2.5
30	25	1300	2.5
45	29	1300	2.5
60	33	≈1350	≈2.4

Table 6

Cathodic copper extraction from acid sulfate STSs (CMU installation). Experiment No. 2

Processing time, τ_{proc}, min	Temperature, °C	Current strength I, A at a current density of 500 A/m^2	Voltage U, V
15	37	≈1350	≈2.4
30	41	≈1350	≈2.4
45	45	≈1350	≈2.4
60	48	≈1350	≈2.3

Note: I_{start}=1400 A; U_{start}=2,2 B; t_{start}=19°C.

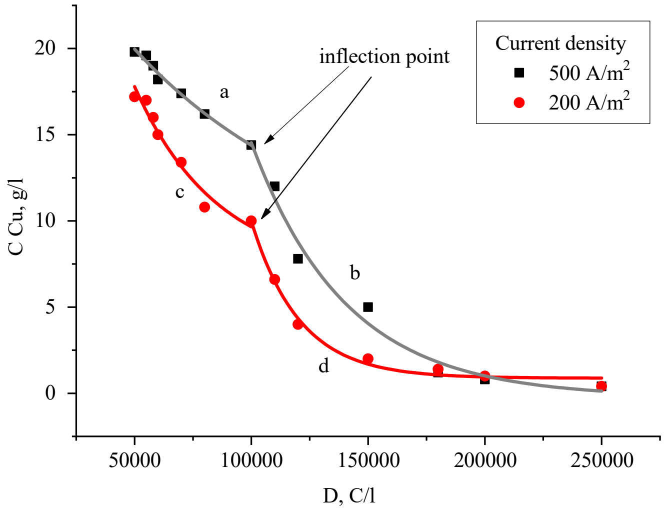

Fig. 6. Change in copper concentration depending on current consumption during cathodic copper extraction from acid sulfate spent technological solutions

Based on experimental and industrial research, it is recommended to carry out the electrolysis process at moderate current densities at the cathode, not exceeding 200 A/m^2.

6. Results of investigating cathodic copper extraction from acid sulfate technological solutions from coating operations: discussion

When interpreting experimental data and devising technical solutions based on kinetic data, one can adhere to the mechanism of electrode processes, in which chemical reactions of transformation of intermediates of the electrochemical stage take part. In an acidic environment, copper is in the form of Cu^{2+} ions. In addition, in the presence of metallic copper, along with Cu^{2+}, Cu^{+} ions may be present in the solution in small quantities, which are formed as a result of the course of the disproportionation reaction $Cu+Cu^{2+} \rightarrow 2Cu^{+}$ [13].

At a current density of 50 A/m^2, current consumption at the initial moment can be 2 times higher, which is explained by the slow stage of particle transport (concentration polarization). Regardless of the current density, there is reason to believe that changes in the activation energy of cathodic processes (including hydration⇄dehydration) play a special role in polarization effects [9]. Thus, at lower concentrations in electrolyte solutions, including STS, the main part of copper ions is in the form of aqua complexes $[Cu^{2+}]\cdot mH_2O$. The increase in speed during the process can be explained by the polarizing effect of the electric field, under the action of which the part of hydrated copper ions increases with the formation of a covalent bond. In this case, the formation of complexes with a covalent bond increases the movement of bound water molecules compared to the low rate of removal of coordination water from the aqua complex. Therefore, the removal of copper from the complex ion $[CuOH]^{+}$ occurs at a higher rate [13].

Based on our studies, current consumption per 1 mol of cathodically extracted copper has been established, the rate of cathodic extraction, and it is recommended to carry out the process at a current density of 200 A/m^2 (Fig. 3). As can be seen from our experimental data (Fig. 3, Tables 1–3), in the range of current consumption from $16.5 \cdot 10^3$ C/l (inflection point) to $25 \cdot 10^3$ C/l, which corresponds to the final degree of extraction (70%), the current consumption per 1 mol of extracted copper will be 30% lower compared to the beginning of the process. At the same time, in the concentration range from 0.03 mol/l ($i = 150$ A/m^2) to 0.043 mol/l ($i = 50$ A/m^2) inclusively up to 0.04 mol/l ($i = 200$ A/m^2), there is a decrease in the current per 1 mol of copper with an increase in the degree of its extraction. There are reasons to believe that this is due to the polarization effect of the electric field and the coordination dehydration of copper ions in the specified concentration range. The inflection point determined the conditions of cathodic extraction (current consumption, current density, current consumption per 1 mol), under which this process is energetically advantageous.

Unlike known technologies for cathodic copper extraction [5, 7], the basic technological parameters (current density, current consumption/1 mol, deposition rate) under non-stationary conditions are justified on the basis of the theory of concentrated solutions. This allows us to work out the basic principles of control and regulation of the electrolysis process in order to improve the organization of the technological process and improve the process in the apparatus.

When conducting studies of acid sulfate STSs from surface treatment, it was found that the pH and Eh values change during the processes in the diaphragm and diaphragm-free electrolyzer. The solution after electrolysis in the diaphragm-free electrolyzer with pH 0.15 and Eh = 1100 mV can be recommended for return to the technological process of surface preparation (etching). Separation of reaction products using an inactive diaphragm leads to the production of solutions in the cathode chamber with pH 0.85 and Eh = –100 mV, and in the anode chamber with pH 0.2 and Eh = 620 mV (Table 4). The change in pH and Eh values is explained by the discharge of water molecules on the electrodes and the participation in the electrode processes of side impurities entering the STS during the etching process, as well as intercomponent interaction in the volume of the solution [8]. Solutions after electrolysis can be further used as chemical reagents (oxidant, reductant) in other operations. Based on the study of the processes that occur in the volume of the STS of copper etching under the influence of electrode reaction products, the possibility of ensuring controlled conditions for copper extraction according to pH and Eh indicators is shown. At the same time, the organization of the technological process in the diaphragm and diaphragm-free electrolyzer is ensured depending on the conditions of galvanic production (structure, volume of effluents and copper concentration). The use of unified equipment significantly expands the use of electrolysis in recycling and regeneration technologies, in contrast to known technologies [16–18], which have significant limitations.

In most cases, regardless of the nature and concentration of organic substances, their effect is expressed in an increase in cathodic polarization and a decrease in the electrodeposition rate, which is explained by a change in PES. If the adsorption layer of organic substance molecules goes beyond PES, then the slowest stage of the process may be the penetration of ions through a continuous adsorption film of organic matter. Thus, an additional activation or potential barrier appears at the electrode-electrolyte solution interface (an increase in activation energy is necessary). The effect on the electrochemical process for most organic substances depends on the nature and concentration of solution ions.

As a result of studies (Fig. 4) of the cathodic extraction of copper from a bright coating in comparison with a matte one, the presence of organic impurities increases the effect of copper extraction. This can be explained by the fact that organic substances are able to adsorb on the electrode surface, forming surface complexes that facilitate the transfer of an electron from the cathode to the ion being discharged [9].

Given the emergence of concentrated solutions, technological parameters of cathodic copper extraction from STS containing organic substances have been justified, taking into account its purpose in the technological process. At the same time, in most cases [16, 17], generalized data of the studied wastewater containing copper are used, which do not take into account their origin at the stages of the principal technological process.

Thus, cathodic copper removal from STSs from galvanic production should be carried out in combined systems, which includes their preliminary treatment in local cycles using electrolysis. Their further treatment should be carried out at centralized stations intended for the main volume of wastewater from washing operations. At the same time, taking into account the volumes and periodicity of discharges for acid sulfate STS coatings, a cycle with cathodic copper removal for further utilization is recommended, and for surface preparation (etching) – return to the production process (regeneration cycle).

Based on our experimental and industrial studies (Fig. 6), it was established that in the concentration range from 0.225 mol/l (inflection point) to 0.02 mol/l ($i = 500$ A/m^2) and from 0.2 mol/l (inflection point) to 0.022 mol/l ($i = 200$ A/m^2), current consumption per 1 mol of copper extracted decreases by 3 times compared to the beginning of the process. At the same time, in the indicated concentration ranges, the degree of copper extraction is from 40% to 93.9% ($i = 500$ A/m^2) and from 40% to 92% at $i = 200$ A/m^2. Experimental and industrial studies, as well as the results of laboratory research, have shown that the inflection point allows us to determine the conditions of cathodic extraction (current consumption, current density, current consumption per 1 mol), under which this process is energetically advantageous. At a current density of 500 A/m^2, the temperature of the electrodes and the solution increases significantly (Table 6), which necessitates the use of a cooling system. Therefore, it is recommended to carry out the electrolysis process at moderate current densities at the cathode, which are no more than 200 A/m^2.

As a result of our experimental and research activities using the CMU installation (Fig. 5, 6, Tables 5, 6), it was established that the process in the apparatus can be improved under the following conditions:

– the design of the electrolyzer (CMU installation) provides for the possibility of dismantling and replacing one type of cathode with another, depending on the type of STS being processed;

– the possibility of installing and dismantling a diaphragm made of chlorin fabric is provided, depending on the mode of electrolysis (diaphragm or diaphragm-free) of the installation.

Improvement of the organization of the technological process is achieved under the following conditions:

– for further purification of solutions from metal after electrolysis, the solution is supplied to cementation for contact separation of metal (copper) on the surface of iron filings;

– water from washing the installation together with powdered sediment is discharged from the lower point of the CMU installation through the sediment discharge pipeline into the sediment washing tank;

– water from the washing of the CMU unit is filtered through the tank tray and sent to a centralized system for cleaning.

In the process of processing highly concentrated STSs at the CMU unit, 90.8% of the metal mass is removed. Foil is grown on the cathodes during electrolysis with a thickness of 1–1.5 mm. The foil has weak adhesion to the cathode surface, so it is easily peeled off. The powdery precipitate (a mixture of copper and copper hydroxo compounds) is a finely dispersed powder, which must be dried after filtration. It is most effective to dry such precipitates in drying cabinets, or it is possible to dry the precipitates under natural conditions.

As a result of our experimental and industrial and scientific research efforts using CMU installations, the presence of a non-electrochemical component of the reaction was established, when the interaction of reactants occurs according to a chemical and electrochemical or exclusively chemical mechanism. The electrochemical oxidation and reduction reaction includes a wide range of processes: from the simplest ionic recharge to complex transformations in the volume of the solution under the action of reaction products. The transformation occurs in parallel according to a chemical and electrochemical mechanism. At the same time, the role of the electrochemical and chemical mechanisms at different stages may be different. Therefore, the process is non-stationary. Thus, in order to adapt the CMU installation to changes in technological parameters and avoid the formation of by-products together with the main product (copper), the installation and dismantling of cathodes is provided. In order to unify the installation for use in technologies for the utilization of STS coating and the regeneration of STS surface preparation, the installation and dismantling of the diaphragm is provided. To eliminate secondary contamination of the treated waste water, it is proposed to abandon the use of reagents in local cycles at all stages of waste water purification in favor of electrochemical technology. The latter allows for a wide range of changes in the physicochemical properties of the solution.

The study of determining the basic parameters of cathodic copper extraction from acid sulfate waste water is limited to application only to concentrated sulfate and persulfate solutions (with a concentration of 0.02 mol/l to 0.9 mol/l).

The disadvantage of this technology is the lack of electrolysis gas utilization systems. Therefore, this installation cannot be used for cathodic copper extraction from chloride waste technological solutions.

In the future, it is advisable to investigate the basic technological parameters for the process of electrochemical (cathodic) copper extraction from chloride-type waste water with the justification of the main elements of gas (chlorine) utilization in the technology of copper regeneration and utilization.

7. Conclusions

1. To substantiate the basic parameters for the electrolysis system within the framework of the system approach (Quality Function Deployment), it is shown that, regardless of the concept and mechanism behind electrochemical transformations, one of the main elements is redox reactions that occur both at the electrode-solution interface and in the solution volume. In this case, the control and regulation parameters, in addition to the basic technological parameters of electrolysis (current consumption, current density, etc.) for sulfate-containing copper-containing STSs from coating and etching operations, are Eh and pH.

2. Based on our studies of cathodic copper extraction, the difference in the basic technological parameters with the same composition of STS solutions and different values of current density was established, namely: the total extraction effect at $i = 200$ A/m^2 is 77%, at $i = 50$ A/m^2 – 60%. The average value of current consumption per 1 mol of copper extracted at $i = 200$ A/m^2 is $0.6 \cdot 10^6$ C/mol, at $i = 50$ A/m^2 – $0.7 \cdot 10^6$ C/mol. The average value of the copper extraction rate at $i = 200$ A/m^2 is $5 \cdot 10^{-6}$ mol/s, at $i = 50$ A/m^2 – $4.5 \cdot 10^{-6}$ mol/s. Based on experimental and industrial studies, it is recommended to carry out the electrolysis process at moderate current densities at the cathode, which is no more than 200 A/m^2.

3. In a diaphragm-free electrolyzer, the pH varies in the range of values from 1.15 to 0.15, and Eh from 500 mV to 1100 mV, which corresponds to the end of the process. In a diaphragm electrolyzer, the pH varies in the range of values from 1.15 to 0.85 (cathode chamber) and from 1.15 to 0.2 (anode chamber). In this case, Eh varies from +500 mV to –100 mV (cathode chamber) and from +500 to +620 mV (anode chamber), which corresponds to the end of the process. At pH > 0.65, the formation of a precipitate in the form of a foil is observed, which is firmly grafted to the cathode surface, while Eh is no more than +500–+700 mV. At lower pH values and higher Eh values, a precipitate is formed with the inclusion of foreign substances, which slides off the electrode surface.

4. As a result of our studies on the influence of organic impurities on the cathodic processes of copper extraction from acid sulfate STSs, it was found that for matte copper plating (coatings that do not contain organic impurities) at concentrations of 0.94–0.1 mol/l, current consumption *D* is from $164 \cdot 10^3$ C/mol to $315 \cdot 10^3$ C/mol (average value 239.5 C/mol). At the same time, the degree of extraction (within the concentrations of 0.94–0.04 mol/l) is 96%. For bright copper plating at concentrations of 0.71–0.04 mol/l, the current consumption *D* is from $180 \cdot 10^3$ C/mol to $315 \cdot 10^3$ C/mol. At the same time, the degree of extraction (within the concentration range of 0.71–0.04 mol/l) is 97%. The influence of organic impurities on the cathodic processes of copper extraction from acid sulfate STSs has been established, namely, an increase in the degree of copper extraction and a decrease in the average value of current consumption per mole.

5. As a result of our research conducted under experimental and industrial conditions, current consumption, current density, current consumption per 1 mol, at which this process is energetically advantageous, have been determined. To regulate the normal temperature regime, it is recommended to carry out the electrolysis process at moderate current densities at the cathode, which is no more than 200 A/m^2. Improvement of the process and unification of the equipment is achieved by installing and dismantling cathodes and diaphragm depending on what type of STS is processed and under which mode of electrolysis the installation operates. Further purification of solutions from copper occurs on the surface of iron filings, which allows electrolysis to be carried out only under energetically advantageous conditions.

Conflicts of interest

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

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Data availability

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.

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