ХІМІЧНІ ТЕХНОЛОГІЇ

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BACKGROUND TECHNOLOGY FOR PURIFICATION OF POLLUTED AQUATIC ENVIRONMENT AND REGENERATION OF CONCENTRATED WASTE NITRATE-CHLORIDE-SULFATE INDUSTRIAL SOLUTIONS

Background. Recently, the problem of recycling and regeneration of concentrated waste technological solutions containing non-ferrous metal ions, in particular copper, has become acute. The particular complexity of processing such type of solutions is caused by the presence of nitrates and chlorides in their composition, causing their chemical aggressiveness. There is a great number of works devoted to electrodeposition of copper from nitrate-containing solu-tions. However, the background technology for the regeneration of nitrate-containing solutions by electrowinning method is poorly developed.

Objective. The aim of the investigation is to develop background technology for the purification of contaminated aquatic environment and to study the process of regeneration of concentrated nitrate-containing solutions by the method of copper electrowinning with establishing the influence of the cathodic current density and solution composition on the efficiency of copper extraction and the quality of cathode deposits.

Methods. The effect of the solution composition on the polarization and limiting current density of copper deposition was determined by voltammetry. The influence of current density and inter-electrode distance on the cathodic copper current efficiency and the quality of the cathode sediments were determined on the basis of gravimetric studies. The quantitative and qualitative composition of copper cathode deposits was investigated by X-ray fluorescence analysis.

Results. The possibility of compact copper obtaining in the solution with copper content of 2 M at the current densities of $15-25$ A/dm^2 with the current efficiency of about 100% was shown. It was established that for current densities less than 10 A/dm^2 the copper current efficiency exceeds 100%, which is due to the precipitation of basic copper salts in the cathode layer. On the basis of current-voltage measurements it was established that the electrodeposition of copper from the investigated nitrate-chloride-sulfate solutions occurs with diffusion limitations.

Conclusions. As a result of the conducted research the main technological parameters of the copper electrowinning process from concentrated nitrate-sulfate-chloride solutions are established. The obtained data are not indispensable for solving the important environmental problems of removing the concentrated metal-containing industrial waste. Further investigations will focus on optimization of the current mode of copper electrowinning process and development of semi-industrial plant for copper electrowinning from nitrate-contain solutions.

Keywords: background technology; nitrate-sulfate-chloride solution; copper electrowinning; compact copper; current efficiency.

Introduction

Industrial galvanic effluents and waste solutions contain heavy metal ions and other aggressive components that are environmentally hazardous. The problem of recycling concentrated nitrate-contain solutions used for etching and clarifying the particles from copper and its alloys is particularly acute. The concentration of copper ions in such solutions can be up to several moles per liter. The extraction of copper and the regeneration of such solutions by the electrowinning are hampered by the high content of chlorides and nitrates, which makes it impossible to use sufficiently accessible lead anodes due to their chemical destruction in a highly aggressive solution.

The presence of nitrate ions due to their cathodic electroreduction can significantly reduce the current efficiency of copper [1].

There are many proceedings dealing with copper electrodeposition from nitrate solutions [1−7]. But the process of copper electrowinning from such solutions is poorly observed [8, 9]. In addition, it is well known that the presence of chloride ions in nitrate solutions can, on the one hand, increase the current efficiency of copper, on the other hand, significantly impair the quality of cathode deposits [7]. In concentrated chloride solutions, chemical dissolution of copper is generally possible when a slight cathodic polarization is applied [10, 11].

Problem statement

Of particular scientific interest is the study of the possibility of copper electrowinning from nitrate-sulfate-chloride solutions and the effect of gas evolution on the anode on the cathodic deposition of copper in the duration of electrowinning process. As a result, the determination of optimal process parameters for copper electrowinning from nitrate-containing solutions will give the solution of the problems associated with the utilization of highly toxic industrial waste and copper recovery.

Research methodology

The study was subjected to an industrial waste solution for clarifying copper parts with the following ionic composition, mol/l: Cu^{2+} — 2; SO_4^{2-} — 1.57; Cl^- — 3.5; NO_3^- — 1.36; pH ≤ 1. The content of copper ions was determined by complexonometric titration with trilon-B in an alkaline medium in the presence of a murexide indicator, according to the standard method. Chloride content was determined by potentiometric titration using a 0.05 M standard solution of $AgNO_3$. The sulfate content was determined by gravimetric method by precipitation of sulfate ions in the form of lead sulfate. For preparation of solutions, reagents of h.ch. and h.d., Khimlaborreactive were used.

Copper electrowinning was carried out in a two-electrode rectangular plexiglas cell with a volume of 0.5 dm^3. As a cathode was used a AISI 304 stainless steel plate with an area of 0.12 dm^2, and as the anodes were used titanium plates coated with ruthenium and titanium oxides layer (ORTA) with an area of 0.48 dm^2. The interelectrode distance was 11 and 22 mm. The cathode current efficiency of copper (*CE*) was determined by gravimetric method using analytical weights of VLR-200, at least two parallel experiments were performed at each value.

The polarization measurements were carried out with the potentiostat PI-51.1 in a standard three-electrode cell with separated by glass diaphragm anode compartment. As a cathode (working electrode) was used a copper core (grade M0) pressed into teflon; the cathode working area was of 0.5 cm^2. A graphite core served as the auxiliary electrode (anode). Before the volt-ampere measurements, the surface of the cathode was mechanically cleaned with 1000 grit sandpaper. Afterwards, cathode was degreased with Viennese lime and washed. Potential values are indicated on the scale of a saturated silver-chloride electrode (Ag/AgCl), which
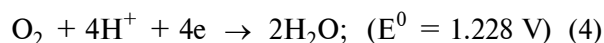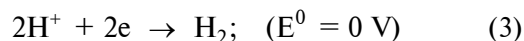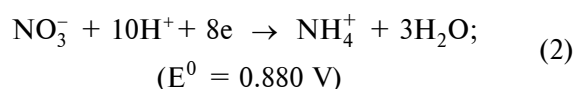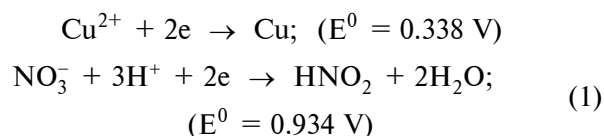
was used as the reference electrode. The current-voltage curves were recorded on a PDA-1 two-coordinate recorder. The potential scanning rate wearied within 2−20 mV/s [12].

The composition of the cathode deposits was determined using a metal-free express X-ray fluorescence analyzer EXPERT 3L in Center for Electron Microscopy of Igor Sikorsky KPI.
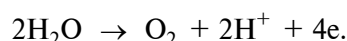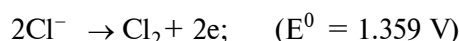
Results and discussion

Effect of current density on the cathodic copper electrodeposition process. During the electrowinning of copper from the observed solution, the following reactions can occur,

on the cathode:

$$Cu^{2+} + 2e \rightarrow Cu; \quad (E^0 = 0.338 \text{ V})$$

$$NO_3^- + 3H^+ + 2e \rightarrow HNO_2 + 2H_2O; \\ (E^0 = 0.934 \text{ V}) \tag{1}$$

$$NO_3^- + 10H^+ + 8e \rightarrow NH_4^+ + 3H_2O; \\ (E^0 = 0.880 \text{ V}) \tag{2}$$

$$2H^+ + 2e \rightarrow H_2; \quad (E^0 = 0 \text{ V}) \tag{3}$$

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O; \quad (E^0 = 1.228 \text{ V}) \tag{4}$$

on the anode:

$$2Cl^- \rightarrow Cl_2 + 2e; \quad (E^0 = 1.359 \text{ V})$$

$$2H_2O \rightarrow O_2 + 2H^+ + 4e.$$

During the experiments, it was found that the copper current efficiency (*CE*) and the quality of the cathode deposits are significantly influenced by values of the cathodic current density (*i*) and interelectrode distance (Figs. 1, 2).

At the current density of 1 A/dm^2 (Fig. 2), the precipitation on a cathode of white crystalline salts with a green tint occurred. Such precipitates were partially peeled off during electrolysis.

The obtained dependencies of the *CE–i* (Fig. 2) are of extreme nature, whereby at 1 A/dm^2 the current efficiency varies within 50−80%. This, on the one hand, may be related to the predominant occurrence of adverse cathodic reactions (1)−(4). On the other hand, it may be due to the detachment of saline precipitates.

In general, the course of *CE–i* dependences in the range of current densities up to 10 A/dm^2 —
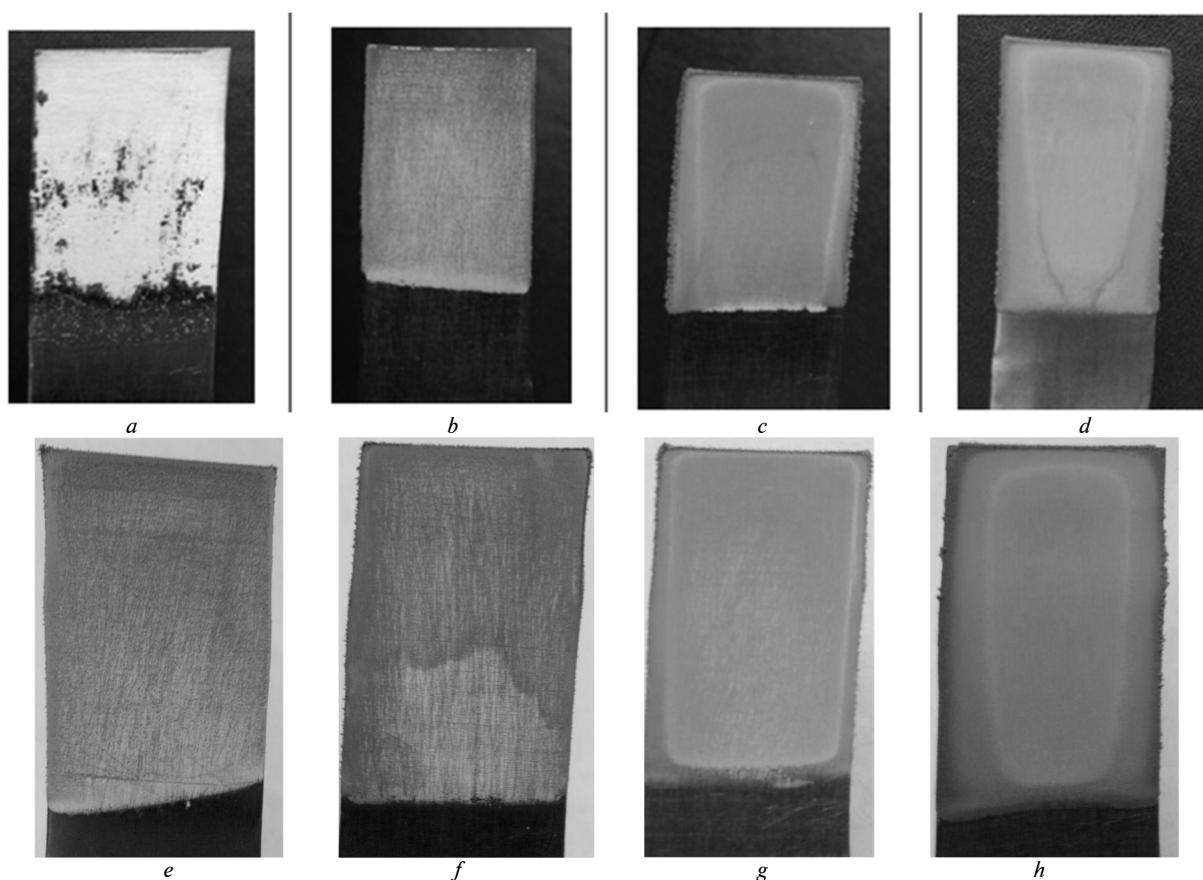
Fig. 1. The effect of current density on the appearance of copper cathode deposits. Interelectrode distance, mm: *a–d* – 11; *e–h* – 22. Cathodic current density, A/dm^2: *a* – 1; *b, e* – 5; *f* – 10; *g* – 15; *c* – 20; *d, h* – 25. Average deposit thickness – 10 μm
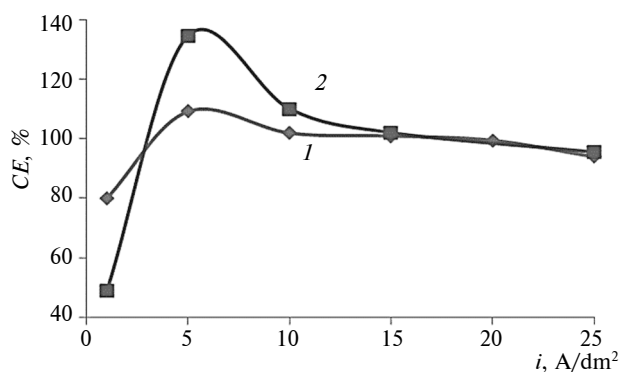

Fig. 2. Current efficiency (*CE*) vs current density dependences; interelectrode distances, mm: *1* – 11; *2* – 22

is similar to that, which was obtained in concentrated chloride electrolytes [11]. According to the same work, at the current densities of 0.5−1 A/dm^2 in the chloride electrolyte *CE* is also much less than 100% due to the corrosion of the copper cathode under the low cathode polarization. At a low concentration of free chlorides in solution, this process proceeds with the formation of insoluble copper mono chloride by the reaction:

$$Cu + Cu^{2+} + 2Cl^- \rightarrow 2CuCl. \qquad (5)$$
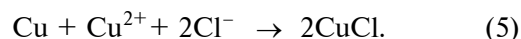
Similar processes can occur in the investigated nitrate-chloride-sulfate electrolyte, because the concentration of chloride ions is less than the concentration of copper ions.

The pH of near-cathode layer can increase due to adverse processes (1)−(4). This in turn can lead to formation of insoluble basic copper salts which in general terms can be represented as: $Cu_x(OH)_yA_z$, where A − anion Cl^-, SO_4^{2-}, NO_3^-. Usually such salts have a greenish tint.

X-ray fluorescence analysis of the separated saline precipitate sample showed the following content, in wt.%: Cu − 49.2; Cl − 50.3; S − 0.3. The pure substance CuCl must contain 64 wt.% Cu and 36 wt.% Cl. Accordingly, this confirms the assumption that not only CuCl, but also the basic copper salts, can be formed during electrowinning at a current density of 1 A/dm^2.

At a current density of 5 A/dm^2, the current is redistributed in favor of the predominant copper deposition process. The cathodic potential shifts toward more negative values, which partially eliminates the copper corrosion process and the formation of CuCl. The acidity of the near-cathode layer increases due to the intensification of gas evolution and mixing. The intensity of this process is also depends on the interelectrode distance (Fig. 2). This partially eliminates the process of salt-like sediments precipitation. As the result CE exceeds 100% (Fig. 1, b, e; Fig. 2).

Further increase in current density up to 10—25 A/dm^2 due to even greater intensification of mixing completely eliminates precipitation of salt-like sediments. In addition, the values of the cathode potential make it thermodynamically impossible for copper cathode corrosion by reaction (5). At such current densities, CE is almost 100%, and compact fine crystalline cathode copper deposits are formed (Fig. 1, c, d, h, g).

Polarization measurements. The potentialdynamic polarisation measurements were performed to determine the effect of changing the solution composition on the copper electrodeposition process (Figs. 3, 4).

From the potentiodynamic curves (Fig. 3, a, b) it can be seen that in the range of small polarizations the first wave with a limiting current of ~1 A/dm^2 is observed. This limiting current may correspond to the reduction process of Cu^{2+} to Cu$^+$. The second wave corresponds to the process of direct electrodeposition of copper. After the limiting current, the next wave which corresponds to the process of hydrogen evolution is observed. After obtaining the polarization curves in solutions with copper contain of 2 and 1.3 M (the original solution and depleted by 33%, respectively), large crystalline copper sponge was observed on the working electrode (cathode).

As can be seen from Fig. 4, in the solution depleted by copper up to 0.26 M, the value of the limiting current decreased slightly compared to the solution containing 1.3 M copper. According to [1], this is due to the intensification of the nitrate ions electroreduction process in a solution with increased content of HNO$_3$. After polarization measurements, the formation of white-green sediments (apparently CuCl and basic salts) parallel with the copper deposition on cathode was observed. This can explain the course of the curve 3 (Fig. 4), and may indicate partial passivation of the cathode.

As a result, for the initial solution with copper ions content 2 M (Fig. 3), the limiting current is about 30 A/dm^2 (at a scanning rate of 2 mV/s, which

corresponds to stationary conditions). For a solution with a copper content of 1.3 M, the limiting current density is about 20 A/dm^2. The values of the minimum of limiting current density for all investigated scan rates are close (Fig. 3, a, b). Comparing the data obtained (Figs. 3, 4), it can be assumed that for a solution with a copper content of 0.26 M, the limiting current value corresponds to the minimum of curve 3 (Fig. 4), and is about 10 A/dm^2.
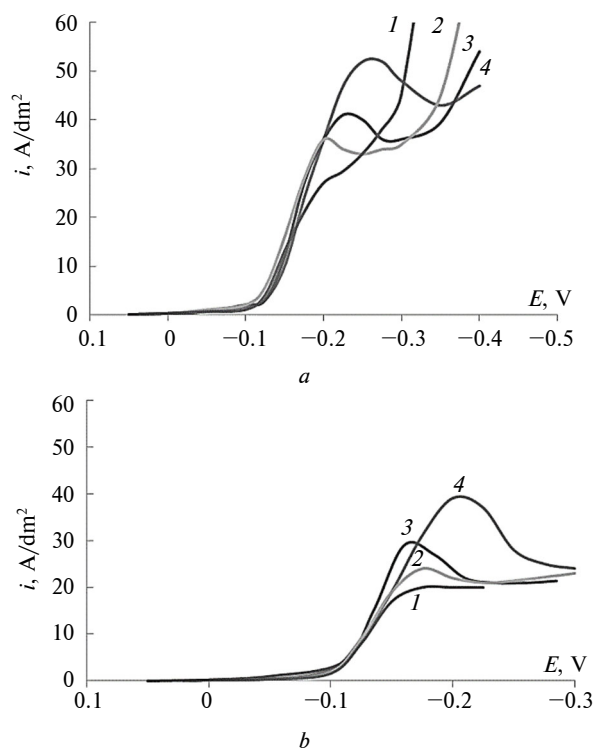

Fig. 3. Potentiodynamic polarization curves in the initial solution with a copper content of 2 M (a) and in a solution with a copper content of 1.3 M depleted by 33% (b), potential scanning rate, mV/s: 1 – 2; 2 – 5; 3 – 10; 4 – 20
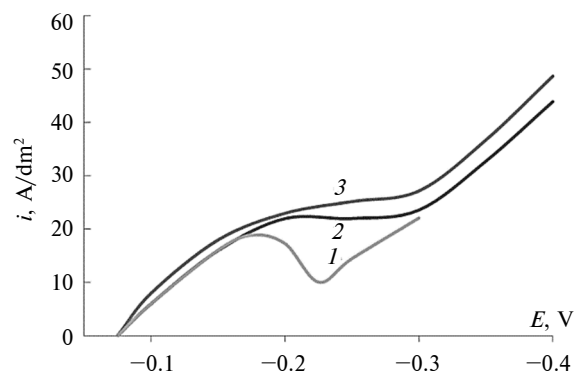

Fig. 4. Potentiodynamic polarization curves in solution with a copper content 0/26 M depleted by 87%, potential scanning rate, mV/s: 1 – 2; 2 – 10; 3 – 20

Dependences of the maximum of limiting current density (i_{Lp}) on the square root of the potential scanning rate ($\sqrt{v}$) are linear (Fig. 5).

This according to [12] indicates that the electrodeposition of copper from the investigated solutions in the concentration range of copper ions 2–1.3 M occurs with diffusion limitations. This confirms that solution mixing is a major factor in the intensification of the electrowinning process.

On the basis of determined influence of the solution composition on the limiting current density, it is possible to develop the optimal current mode of the electrowinning process [9, 13, 14]. The effect of chloride ions should also be taken into account in developing current mode. According to [7], it is not possible to obtain compact fine crystalline copper deposits of considerable thickness from nitrate solutions without special organic additives and in the presence of a large amount of chloride ions. Copper deposits of considerable thickness will be formed in the form of dendrites. However, in the process of electrodeposition, dendrites can coalesce and form a monolithic structure. This will increase the cathode true surface area and may be also a factor of the electrowinning process intensification.

Copper electrowinning with solution depletion. Taking into account the above experimental data it has been proposed to conduct copper electrowinning under the current mode, which is shown in Fig. 6, *a*. For experiments, a rectangular cell with an interelectrode distance of 22 mm was used.

Deposited during 5.5 h copper had a dendritic structure, a white sledge of insoluble copper salts in a small amount was observed on the surface of the deposit (Fig.6, *b*). In general, obtained deposit is quite dense and does not completely lose its solidity after the removing from the cathode plate. The purity of the copper on dendritic fragments was 99.9 wt.%, which corresponds to the metal grade M0. When the solution was depleted from 2 to 0.26 M, the average *CE* was about 80% of the specific energy consumption of 5.02 kWh/kg. The value of the specific energy consumption is comparable to that achieved for the compact copper electrowinning process from sulfate solutions. However, the mass velocity of the electrowinning process in observed solution is 8–10 times higher. Additional increases in *CE* and a reduction in specific energy consumption are possible due to the optimization of the current mode, which was outlined in previous papers [13, 14].
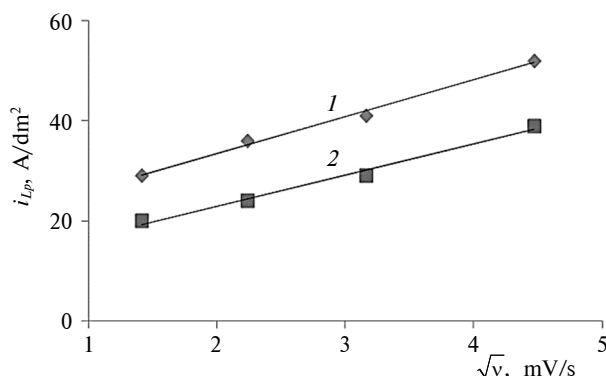

Fig. 5. Dependence of i_{Lp} on $\sqrt{v}$ in the initial solution with the copper ions content of 2 M (*1*) and in the solution with the copper ions content of 1.3 M depleted by 33% (*2*)
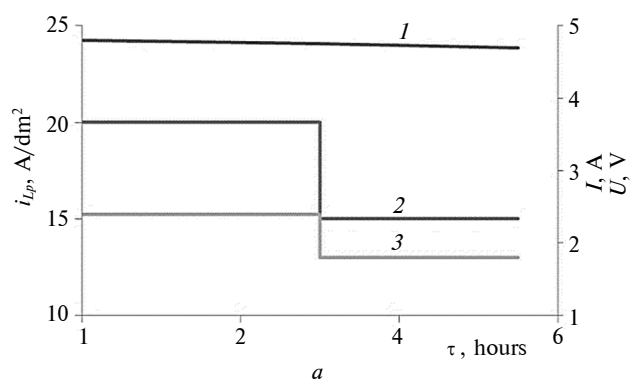

a

b

Fig. 6. Dependences of change in time (*a*) cell voltage (*1*), current density (*2*), and current (*3*) during electrowinning; electrochemically deposited copper (*b*)

Conclusions

As a result of the investigations the background technology of aqueous medium purification and the regeneration of copper from concentrated nitrate-chloride-sulfate solutions by the electrowinning method were developed.

It has been established that, in tasted solution with 2 M Cu^{2+}, at low current densities of <5 A/dm^2, salt-like deposits, apparently CuCl and basic copper salts, are deposited on the cathode. At a current density of $10-25$ A/dm^2 dense compact crystalline copper is deposited. This is predetermined to the intensification of solution mixing, which is due to an increase in the cathodic current density and a decrease in the interelectrode distance.

It has been shown that during copper electrowinning at an average current density of 17.5 A/dm^2 with the depletion of nitrate-chloride-sulfate solution from 2 to 0.26 M, the average current efficiency is about 80%, and the specific energy consumption is 5.02 kWh/kg.

Further studies will focus on optimizing the current mode of copper electrowinning process and developing a semi-industrial plant for copper electrowinning from nitrate-containing solutions.

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ТЕХНОЛОГІЧНІ ЗАСАДИ ОЧИЩЕННЯ ЗАБРУДНЕНОГО ВОДНОГО СЕРЕДОВИЩА ТА РЕГЕНЕРАЦІЯ КОНЦЕНТРОВАНИХ ВІДПРАЦЬОВАНИХ НІТРАТНО-ХЛОРИДНО-СУЛЬФАТНИХ ПРОМИСЛОВИХ РОЗЧИНІВ

Проблематика. Останнім часом гостро постає проблема утилізації та регенерації концентрованих відпрацьованих технологічних розчинів, що містять іони кольорових металів, зокрема міді. Особливу складність переробки таких розчинів спричиняє наявність у них нітратів і хлоридів, які зумовлюють їх високу агресивність. Електроосадженню міді з такого типу розчинів присвячена дуже велика кількість праць. Проте технологічні засади регенерації нітратовмісних розчинів методом електроекстракції є малорозробленими.

Мета дослідження. Розробка технологічних засад очищення забрудненого водного середовища та дослідження процесу регенерації концентрованих нітратовмісних розчинів методом електроекстракції міді зі встановленням впливу катодної густини струму і складу розчину на ефективність вилучення міді та якість катодних осадів.

Методика реалізації. Методом вольтамперометрії встановлено вплив складу розчину на поляризацію та граничну густину струму осадження міді. На основі гравіметричних досліджень визначено вплив густини струму і міжелектродної відстані на катодний вихід за струмом міді та якість катодного осаду. Методом рентгенофлюоресцентного аналізу досліджено кількісний та якісний склад катодних осадів міді.

Результати дослідження. Показано можливість отримання компактної міді за густин струму 15–25 А/дм^2 при виході за струмом близько 100 % та вмісті міді в розчині 2 М. Встановлено, що за густин струму, менших 10 А/дм^2, вихід за струмом міді перевищує 100 %, що пов'язано з випаданням основних солей міді у прикатодному шарі. На основі вольт-амперних вимірювань

встановлено, що електроосадження міді з досліджуваних нітратно-хлоридно-сульфатних розчинів відбувається з дифузійними обмеженнями.

Висновки. У результаті проведених досліджень встановлено основні технологічні параметри процесу електроекстракції міді з концентрованих нітратно-сульфато-хлоридних розчинів. Отримані дані є необхідними для вирішення важливих екологічних проблем утилізації концентрованих металовмісних промислових відходів. Подальші дослідження будуть спрямовані на оптимізацію струмового режиму процесу електроекстракції міді та розробку напівпромислової установки для електроекстракції міді з нітратовмісних розчинів.

Ключові слова: технологічні засади; нітратно-сульфатно-хлоридний розчин; електроекстракція міді; компактна мідь; вихід за струмом.

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ТЕХНОЛОГИЧЕСКИЕ ОСНОВЫ ОЧИСТКИ ЗАГРЯЗНЕННОЙ ВОДНОЙ СРЕДЫ И РЕГЕНЕРАЦИЯ КОНЦЕНТРИРОВАННЫХ ОТРАБОТАННЫХ НИТРАТНО-ХЛОРИДНО-СУЛЬФАТНЫХ ПРОМЫШЛЕННЫХ РАСТВОРОВ

Проблематика. В последнее время остро стоит проблема утилизации и регенерации концентрированных отработанных технологических растворов, содержащих ионы цветных металлов, в частности меди. Особую сложность переработки таких растворов вызывает наличие в них нитратов и хлоридов, которые обусловливают их высокую агрессивность. Электроосаждению меди из такого типа растворов посвящено большое количество работ. Однако технологические основы регенерации нитратсодержащих растворов методом электроэкстракции малоразработаны.

Цель исследования. Разработка технологических основ очистки загрязненной водной среды и исследование процесса регенерации концентрированных нитратсодержащих растворов методом электроэкстракции меди с определением влияния катодной плотности тока и состава раствора на эффективность извлечения меди и качество катодных осадков.

Методика реализации. Методом вольтамперометрии установлено влияние состава раствора на поляризацию и предельную плотность тока осаждения меди. На основе гравиметрических исследований определено влияние плотности тока и межэлектродного расстояния на катодный выход по току меди и качество катодного осадка. Методом рентгенофлюоресцентного анализа исследован количественный и качественный состав катодных осадков меди.

Результаты исследования. Показана возможность получения компактной меди в интервале плотностей тока 15–25 А/дм^2 при выходе по току около 100 % и содержании меди в растворе 2 М. Установлено, что при плотностях тока меньше 10 А/дм^2 выход по току меди превышает 100 %, что связано с осаждением основных солей меди в прикатодном слое. На основе вольтамперных измерений установлено, что электроосаждение меди из исследуемых нитратно-хлоридно-сульфатных растворов происходит с диффузионными ограничениями.

Выводы. В результате проведенных исследований установлены основные технологические параметры процесса электроэкстракции меди из концентрированных нитратно-сульфатно-хлоридных растворов. Полученные данные являются необходимыми для решения важных экологических проблем утилизации концентрированных металлосодержащих промышленных отходов. Дальнейшие исследования будут направлены на оптимизацию токового режима процесса электроэкстракции меди и разработку полупромышленной установки для электроэкстракции меди из нитратсодержащих растворов.

Ключові слова: технологические основы; нитратно-сульфатно-хлоридный раствор; электроэкстракция меди; компактная медь; выход по току.