

У роботі представлені результати експериментальних досліджень переробки висококонцентрованих металовмісних відходів (ВКМВ) гальванічного виробництва із отриманням осаду заданого хімічного складу та заданими фізико-хімічними властивостями, що містять йони купруму. При дослідженні купрум-ферумних шламів, отриманих співосадженням купрум- і ферумвмісних відпрацьованих технологічних розчинів (ВТР), властивості отриманого осаду були такими: вологість – 89,7 %, густина – 1,17 кг/дм<sup>3</sup>, питомий опір осаду – 15–16·10<sup>11</sup> м<sup>2</sup>/кг. Такий осад легко фільтрується, що дозволяє зменшити витрату реагентів, підвищити ефективність очистки та отримати готовий до транспортування осад. Тому для легшого розділення та виключення операції кондиціювання доцільним є отримання купрумвмісних осадів (шламів) уже з вмістом феруму. Для переробки із подальшою утилізацією купрумвмісних ВКМВ розроблена технологічна схема, що включає: переведення купрум-ферумвмісного осаду у розчин додаванням сірчаної кислоти; осадження йонів феруму 25 % розчином аміаку; відділення фільтруванням отриманого осаду гідроксиду феруму (III) із направленням на утилізацію; отриманий купрумвмісний фільтрат направляють на електрохімічне вилучення купруму у формі металічного осаду або на утилізацію реагентним способом. При обробці в діафрагменному електролізері купрумвмісних ВКМВ з метою вилучення купруму у формі металічного осаду встановлено, що із збільшенням вихідної концентрації металу зменшується витрата струму, завдяки чому при концентрації йонів купруму >0,1 моль/дм<sup>3</sup> можливо забезпечити ступінь перетворення  $\alpha=0,9$  із виходом за струмом >80 %. Для реагентного осадження купруму оптимальним є використання в якості реагентів суміші КОН і К<sub>2</sub>СО<sub>3</sub>, при рН=9,5–10, для отримання осаду гідроксокарбонату. Отримані у такі способи осади придатні для подальшої утилізації шляхом переробки або є сировиною при отриманні готової до використання продукції, що може бути завершальною стадією гальванічного виробництва

**Ключові слова:** висококонцентровані металовмісні відходи (ВКМВ), відпрацьовані технологічні розчини (ВТР), гальванічне виробництво, металопокриття, мідь та її сполуки

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# DEVELOPING A TECHNOLOGY FOR PROCESSING CUPRUM CONTAINING WASTES FROM GALVANIC PRODUCTION AIMED AT THEIR FURTHER USE

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## 1. Introduction

Galvanic production is one of the most dangerous sources of environmental pollution due to formation of large volumes of wastewater (WW) and waste technological solutions (WTS), which belong to the category of concentrated water systems. They include a large variety of metal ions (Al<sup>3+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>) and Cu<sup>2+</sup> ions prevail among them. The wastewater of galvanic industries is often not purified completely before discharging to the city sewage network or nearby rivers or water bodies. They contaminate drainage water and soil at the disposal site of their sludges [1].

The most common method of purification of wastewater of galvanic industries from heavy metal ions is a reagent method. The main component in the reagent method is lime suspension. Impurities of wastewater and WTS transform into insoluble hydroxocompounds of metals under the influence of chemical reagents. There is accumulation of a large amount of galvanic sludge (precipitates) as the result. Sludges (precipitates) of the galvanic industries is a highly con-

centrated metal-containing waste generated in purification of wastewater and spent technological solutions usually with the use of chemical reagents with subsequent separation during settling and flotation [2].

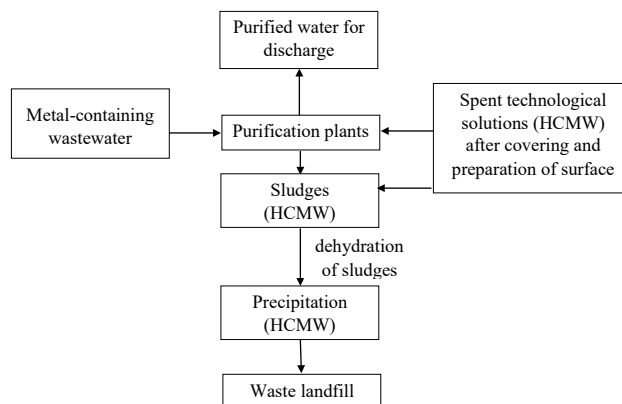


Fig. 1. Highly concentrated metal-containing waste from galvanic production

Galvanic metal-containing HCMW (sludges) are complex and instable in the composition [3, 4]. Therefore, in practice, as a rule, these sludges are not processed for disposal, but simply discharged into refuse dumps and landfills. Heavy metal compounds constantly change their chemical composition under the influence of external physical-and-chemical factors in the sludges on landfills. The constant change in the chemical composition of sludges significantly complicates and makes unprofitable their further processing. It also leads to the gradual transition of heavy metals into soluble forms. Soluble forms of metals gradually penetrate soils and drainage waters and pollute the environment. It is violation of the requirements of EU 96/61/EC Directive. According to the Directive, if it is impossible to recycle products, recycling products must be compounds analogous to natural materials (minerals), which ensures their physical-and-chemical stability for further disposal.

The volume of sludges makes up 3–5 % of the wastewater volume on average. The content of metals in sludges depends on their moisture content. The content of metal hydroxides is less than 1 % in liquid galvanic metal-containing sludges with the moisture content of 95–99 %. Pasty-shaped galvanic precipitates with the moisture content of 70–95 % formed after dehydration of sludges on vacuum filters, centrifuges and dehydrated on press filters to a moisture content of 50–70 %, contain up to 15 % of hydroxides of nonferrous metals and up to 65 % of ferrum hydroxides. The density of the precipitates is 1.16–1.24 g/cm<sup>3</sup> (at moisture content of 60–85 %), with pH=3.2–7.9 [4].

## 2. Literature review and problem statement

Indicators of non-ferrous metals content (Table 1) [5] evidence possibility of processing with extraction of metals or their compounds from HCMW for production of certain types of products.

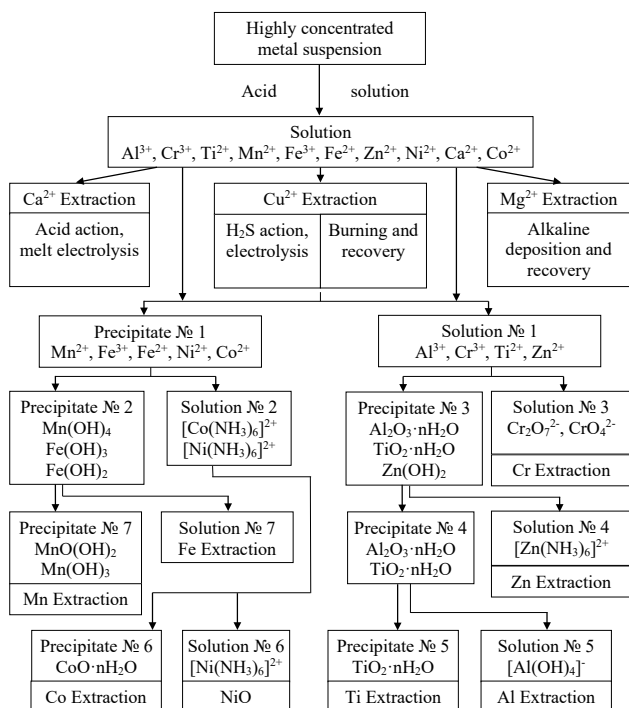


Fig. 2. Scheme of processing of highly concentrated metal-containing waste with ion extraction by systematic analysis

Authors of paper [5] presented the results of studies of the possibility of selective extraction of metals from a mixture of precipitates deposited or landfilled according to the schemes presented in Fig. 2. They showed that the method made it possible to remove the metals from galvanic sludges almost completely as compounds of individual metals. However, the method included a large number of steps, treatment schemes, stages of extraction, reagents, constant changes in pH and other parameters, application of expensive equipment, which makes the studies impractical.

Authors of work [6] presented a method for extraction of copper and zinc from corresponding sludges by burning with a sulfur-containing promoter (sulfur or pyrite) at the temperature of 500 °C for 1.5 h followed by leaching with sodium thiosulfate. However, the issue of disposal of the obtained residues of sludge after leaching, which still contained more than 37 % of copper compounds and 27 % of the original zinc, remained unresolved. Therefore, the studies are inexpedient.

The issue of implementation of utilization methods [5, 6] is that the sludges obtained by the reagent purification of wastewater and spent technological solutions do not meet the necessary requirements in terms of physical-and-chemical properties of the precipitate. They are complex and instable in the chemical composition. Therefore, it is not possible to process these HCMW in the form of sludges with extraction of metal ions effectively due to the need for constant adaptation of technological solutions to the specific physical-and-chemical properties of individual batches of sludges (precipitates). The consequence is significant technological complexity or excessively significant financial costs for implementation of the mentioned methods.

Despite the more advanced methods of reagent treatment, we have not much data on physical-and-chemical properties of precipitates and their dependence on technological parameters of wastewater treatment processes and spent technological solutions. As a rule, technological data is enough to ensure completeness of precipitation in practice. However, technological data does not ensure stability of a chemical composition and certainty of physical-and-chemical properties of the obtained sludge (precipitate). Therefore, researchers and technologists in the industry cannot carry out the process of chemical precipitation as a stage of reagent purification (neutralization), which would include obtaining of a sludge in the form of precipitates with specified technological and consumer properties. The properties are necessary for their further utilization in the form of raw materials for heavy industry or in the form of by-products in the national economy [7].

The chemical composition of the precipitates formed during reagent purification of wastewater of galvanic production depends largely on the metal ion/reagent ratio [8]. However, at present, as a rule, purification of wastewater and spent technological solutions occurs without respect to the stoichiometric norm of reagent consumption using its significant excess or deficiency. As a result, the precipitate often consists not only of insoluble metal hydroxide and an acid residue, but also of a complex basic or mixed salt. It is difficult to forecast or analyze the true composition of the resulting precipitate in this case.

Therefore, it is necessary to put possibility of sludges processing in the technology of their production, that is in the technology of purification of wastewater and spent technological solutions at the level of an individual enterprise, in order to solve the problem of sludge processing.

Authors of paper [9] applied such approach partly. It implied creation of a combined wastewater treatment system for galvanic industries, including etching operations, to improve wastewater treatment technologies. The base of the improvement is the inclusion of separation of wastewater by physical-and-chemical properties, which made it possible to provide for further separation of sludges formed of the total wastewater flow by parameters.

However, ensuring a possibility of separation of sludges is only a prerequisite for further obtaining of precipitates of a certain chemical composition with specified physical-and-chemical properties. In addition, the sludges should have the optimal properties in terms of conditions of further disposal through processing or they should be by-products for use in the industry or economy. Obtaining of such precipitates requires studies to determine optimal technological parameters and necessary conditions for precipitation with further improvement of technologies for neutralization of liquid highly concentrated metal-containing waste of galvanic production.

### 3. The aim and objectives of the study

The objective of the study is to develop a technology for obtaining highly concentrated copper containing waste from galvanic industries in the form of precipitates of the predefined constant chemical composition and properties, which ensure a possibility of their further utilization and processing.

We set the following tasks to achieve the objective:

- experimental studies of determination of parameters for obtaining of conditioning precipitates for easier separation and elimination of the conditioning operation to obtain a precipitate, which is ready for transportation and subsequent disposal;
- experimental studies to obtain the technology of neutralization of WTS with obtaining of a precipitate, which is ready for further utilization by processing;
- experimental studies to determine parameters necessary for utilization of cuprum-containing highly concentrated waste by the electrochemical method with obtaining of a product for further use;
- experimental studies to determine deposition parameters for obtaining of precipitates with preliminary specified composition and defined physical-and-chemical properties, which are suitable for further utilization by processing or obtaining of a precipitate in the form of a product, which is ready for further use in the industry;
- determination of possibility of safe utilization of the residue filtrate obtained after separation of a metal-containing precipitate at neutralization of cuprum-containing spent technological solutions by reagent and electrochemical methods.

### 4. Materials and methods to study WTS regeneration and purification

The studies were carried out within the framework of “Physical-and-chemical methods of water systems puri-

fication” (state registration number 0112U005999 dated 03.02.2016) scientific research in the Department of Chemistry and Physics at the National University of Water Management.

We applied the systematic results of studies of model solutions and spent technological solutions and sludges obtained in the processing of copper waste of galvanic production:

- spent technological solutions of coppering operations;
- cuprum and ferrum containing WTS of etching operations;
- sludges obtained at purification of wastewater of galvanic production.

WTS and sludges were collected at the enterprises of Public Joint Stock Company “ZAVOD “LTAVA” (Poltava, Ukraine and MOTOR SICH JSC (Zaporizhzhia, Ukraine). We divided WTS and sludges of separate operations in flows, which contained cuprum and ferrum ions with a concentration of 5 to 25 g/dm<sup>3</sup>.

The acid-base and oxygen-recovering properties of WTS, Surface water were studied by the methods of potentiometric titration and chemical deposition. We carried out the experiments in a batch reactor with intensive mixing of reactants.

The experimental studies were performed in measuring cups and at the experimental-laboratory plant (Fig. 3) under static and dynamic conditions in the laboratory. The experimental-laboratory unit was able to purify 5 dm<sup>3</sup> of processed wastewater (model, industrial) with possibility of heating of solutions and regulation of the speed of reagents dosing. We mixed reactants with an electric mixer with speed control.

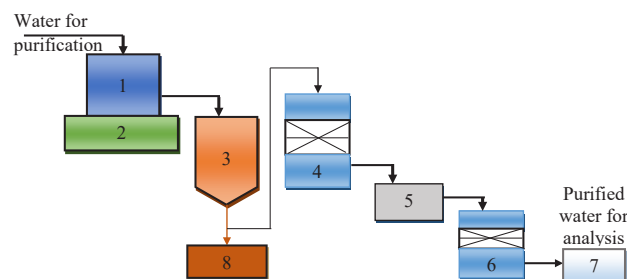


Fig. 3. Scheme of the experimental-laboratory plant: 1 – averager – a chemical reactor, 2 – an electric mixer, 3 – a precipitation tank, 4 – a filter with foam polystyrene loading, 5 – an intermediate capacity, 6 – a filter with ion exchange resin loading, 7 – a purified water storage, 8 – a precipitate storage

Table 1

Main composition of sediments coming to one of the regional specialized landfills (Central Ukraine)

| Content of components, g/kg |           |           |         |          |           |           |         |        |
|-----------------------------|-----------|-----------|---------|----------|-----------|-----------|---------|--------|
| Cd                          | Mn        | Cu        | Ni      | Pb       | Cr        | Zn        | Ca      | Al     |
| 15–213                      | 122–1,060 | 218–2,056 | 179–436 | 14–1,463 | 276–2,411 | 365–3,552 | 600–200 | 28–356 |

Filtration was carried out through a tissue filter – a “Belting” type cloth with a use of a Buchner funnel and a laboratory NUTCH-filter.

We performed quantitative analyzes on the content of metal ions according to the general measurement methods given in Table 2.

Methods for measurement of concentrations of substances

| No. | Parameter                                     | Measurement methodology  |
|-----|---|--|
| 1   | NH <sub>4</sub> <sup>+</sup> ammonium content | KND 211.1.4.030-95. Methodology of photometric determination of ammonium ions with Nessler reagent in wastewater                                 |
| 2   | Solid residue                                 | KND 211.1.4.042-95. Methodology of gravimetric determination of dry residue (solutes)  |
| 3   | Determination of suspended solids content     | KND 211.1.4.039-95. Methodology of gravimetric determination of suspended substances in natural and wastewaters                                  |
| 4   | pH Hydrogen index                             | MVV 081/12-0317-06. Methodology of measurements of hydrogen index (pH) by the electrometric method   |
| 5   | Eh Oxygen-recovering potential                | MVV 081/12-03311-06. Methodology of temperature measurements (thermocouple measurements)   |
| 6   | Temperature                                   | KND 211.1.4.037-95. Methodology of mercury-metric determination of chlorides in natural and wastewaters  |
| 7   | Cl <sup>-</sup> chloride content              | KND 211.1.4.035-95. Methodology of extraction-photometric determination of copper with diethyldithiocarbamate of lead in surface and wastewaters |
| 8   | Cu <sup>2+</sup> cuprum content               | MVV № 081/12-0175-05. Methodology of measurements of mass concentration of iron (II, III) by photocolorimetric method with rhodanide             |
| 9   | Fe <sup>2+</sup> ferrum content               | KND 211.1.4.026-95. Methodology of turbidimetric determination of sulfate ions in purified wastewater  |
| 10  | SO <sub>4</sub> <sup>2-</sup> sulfate content |  |

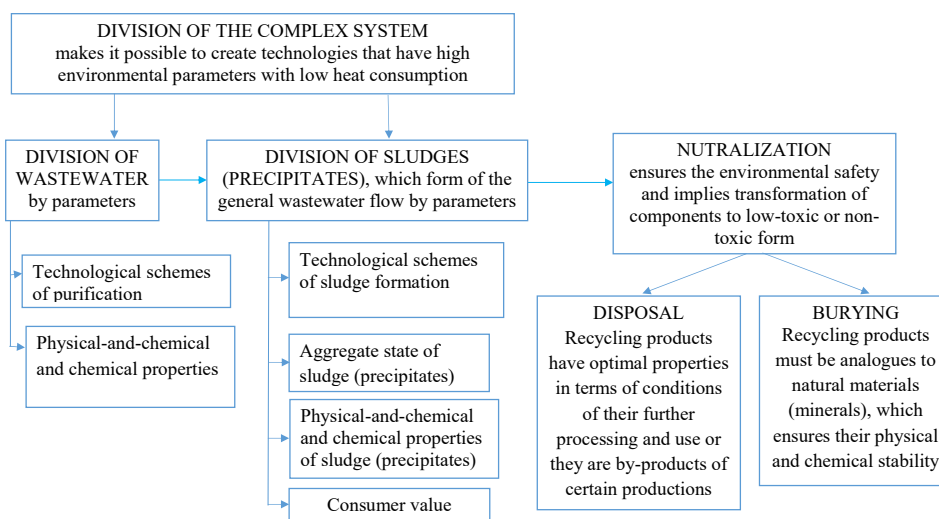


Fig. 4. General concept of creating the systems for processing metal-containing waste

We performed potentiometric titration at EV-74 potentiometer (Belarus) (under laboratory conditions) and using pH 602 portable pH meter (Ukraine) under industrial conditions. Potentiometric determinations were carried out according to a standard method of titration of WTS solutions with a standard alkali solution according to MVV No. 081/12-0317-06.

Table 1 gives a typical composition of precipitates coming to a specialized regional landfill from many enterprises of galvanic production [5]. Such indicators evidence that there is practical interest in possibility of extraction of metals and their compounds from HCMW (highly-concentrated metal-containing waste) for production of certain types of products.

The developed concept of creation of systems for processing of metal-containing waste (Fig. 4) reflects principles of control of physical-and-chemical properties of a precipitated. We performed further studies according to it.

Division of wastewater into separate flows by parameters of technological operations and physical-and-chemical properties is necessary for creation of technologies of utilization of spent technological solutions and wastewater of galvanic

production. Recycling involves not only disposal of WTS and wastewater, but also utilization of processing products in the form, which is suitable for further use or disposal in physical-and-chemical stable form to meet the requirements of EU 96/61/EC Directive.

## 5. Results of studies of the development of technology for processing of cuprum-containing waste of galvanic production with its further use

### 5.1. Results of studies of the technology of obtaining of conditioning precipitates (sludges), which are ready for further transportation and utilization

We considered the precipitate formed during purification of alkaline cuprum-etching solutions of cuprum in our studies. The material balance of the process was derived based on the analytical control over the main components. Table 3 presents them.

Based on the material balances given in Tables 3 and 4, it was established that the WTS of etching operations belongs to concentrated water systems, the resulting precipitations

(sludges) – to highly concentrated ones, the filtrate and clarified liquid – to low concentrated water systems (Fig. 5).

According to the concentration of components, one can consider that such sludges as HCMW include a modified structure of water with zones of existence of elements of aqueous and crystalline hydrate forms:

1) In the study of cuprum-ammonia sludges obtained by the method of processing of cuprum-containing technological suspensions,  $v_{\text{HOH}}/v_{\text{el}} > 10$ , which indicates presence of compounds of cuprum in the form of aqueous elements (chemically and physically hydrated). The highest capacity for hydration of cuprum ions in the system explains difficulties in its dehydration. The parameters of the resulting precipitation resulting from dehydration of the sludge are as follows: thickness of precipitation – 2 mm, humidity – 92 %, density – 1.09 kg/dm<sup>3</sup>, specific resistance – 45–65·10<sup>11</sup> m<sup>2</sup>/kg. Thus, the sludge obtained in the processing of copper-ammonia WTS belongs to the class of poor-filtrated by its properties.

2) In the study of cuprum-ferrum sludges obtained by coprecipitation of cuprum- and ferrum-containing WTS,  $v_{\text{HOH}}/v_{\text{el}} < 10$ , which corresponds to the structure of an aqueous system – the boundary after complete hydration, where compounds of cuprum with ferrum are presented in the form of crystalline hydrates and only chemically bound water remains. We can dehydrate such a system easily to low-water crystalline hydrates, it is more easily filtered and dehydrated. The parameters of the resulting precipitate are humidity – 89.7 %, density – 1.17 kg/dm<sup>3</sup>, specific precipitation resistance – 15–16·10<sup>11</sup> m/kg. Thus, we can filter the sludge easily.

Table 4

Chemical composition of concentrated cuprum-containing WTS and products of their processing

| Type of suspension                       | Substance                            | C, g/dm <sup>3</sup> | C <sub>v</sub> , mol/dm <sup>3</sup> | $v_{\text{HOH}}/v_{\text{el}}$ |
|--|--------------------------------------|----------------------|--------------------------------------|--------------------------------|
| Output WTS (acidic)                      | CuCl <sub>2</sub>                    | 64.5                 | 1.134                                | 9.88                           |
|  | NH <sub>3</sub> (NH <sub>4</sub> OH) | 75.8                 | 2.166                                |                                |
|  | HCl                                  | 63.2                 | 1.732                                |                                |
|  | H <sub>2</sub> O                     | 895                  | 49.72                                |                                |
| Output WTS (alkaline)                    | NH <sub>4</sub> Cl                   | 32.55                | 0.62                                 | 58                             |
|  | CuNH <sub>4</sub> (OH) <sub>3</sub>  | 39.75                | 0.3                                  |                                |
|  | NH <sub>4</sub> OH                   | 1.4                  | 0.04                                 |                                |
|  | H <sub>2</sub> O                     | 1,018                | 56.6                                 |                                |
| Averaged (mixed acidic and alkaline WTS) | CuCl <sub>2</sub>                    | 90.1                 | 0.67                                 | 24.3                           |
|  | NH <sub>4</sub> Cl                   | 40.42                | 0.77                                 |                                |
|  | NH <sub>4</sub> OH                   | 25.9                 | 0.74                                 |                                |
|  | H <sub>2</sub> O                     | 953.3                | 53                                   |                                |
| Clarified liquid (after settling)        | CuCl <sub>2</sub>                    | 47.6                 | 0.3543                               | 27.23                          |
|  | NH <sub>4</sub> Cl                   | 68.8                 | 1.2914                               |                                |
|  | NH <sub>4</sub> OH                   | 10.8                 | 0.3086                               |                                |
|  | H <sub>2</sub> O                     | 957.6                | 53.2                                 |                                |
| Filtrate                                 | CuCl <sub>2</sub>                    | 29                   | 0.2158                               | 31.9                           |
|  | NH <sub>4</sub> Cl                   | 74                   | 1.3834                               |                                |
|  | HCl                                  | 1.6425               | 0.045                                |                                |
|  | H <sub>2</sub> O                     | 943.56               | 52.42                                |                                |

Table 5

Chemical composition of precipitates after processing with a reagent-precipitator

| Type of precipitations | Substance          | C, mol/dm <sup>3</sup> | $v_{\text{HOH}}/v_{\text{el}}$ | Type of hydration   |
|------------------------|--------------------|------------------------|--------------------------------|---|
| Ferrum-cuprum          | FeCl <sub>3</sub>  | 2.6                    | 4.65                           | After the limit of complete hydration (there is chemically bound water only)                      |
|                        | CuCl <sub>2</sub>  | 1.9                    |                                |   |
|                        | NaCl               | 0.7                    |                                |   |
|                        | NaOH               | 0.3                    |                                |   |
|                        | H <sub>2</sub> O   | 25.5                   |                                |   |
| Cuprum                 | CuCl <sub>2</sub>  | 0.7                    | 19.35                          | Before the limit of complete hydration (there are both chemically bound water and hydrated water) |
|                        | NH <sub>4</sub> Cl | 0.725                  |                                |   |
|                        | NH <sub>4</sub> OH | 0.7625                 |                                |   |
|                        | H <sub>2</sub> O   | 42.2                   |                                |   |

Note:  $v_{\text{HOH}}$  is the number of moles of water and  $v_{\text{el}}$  is the number of moles of electrolytes

Table 3  
Chemical composition of cuprum-ferrum-containing WTS and products of their processing

| Type of suspension                | Substance           | C, g/dm <sup>3</sup> | C <sub>v</sub> , m/dm <sup>3</sup> | $v_{\text{HOH}}/v_{\text{el}}$ |
|-----------------------------------|---------------------|----------------------|------------------------------------|--------------------------------|
| Output WTS                        | FeCl <sub>3</sub> + | 108                  | 0.65                               | 12.05                          |
|                                   | FeCl <sub>2</sub>   | 171.45               | 1.35                               |                                |
|                                   | CuCl <sub>2</sub>   | 134.5                | 1.457                              |                                |
|                                   | H <sub>2</sub> O    | 750                  | 41.65                              |                                |
| Filtrate                          | FeCl <sub>2</sub>   | 0.12638              | 0.00089                            | 27                             |
|                                   | CuCl <sub>2</sub>   | 0.1883               | 0.0014                             |                                |
|                                   | NaCl                | 87.75                | 1.5                                |                                |
|                                   | NaOH                | 18                   | 0.45                               |                                |
|                                   | H <sub>2</sub> O    | 952.2                | 52.9                               |                                |
| Clarified liquid (after settling) | FeCl <sub>2</sub>   | 0.00381              | 0.00003                            | 34                             |
|                                   | CuCl <sub>2</sub>   | 0.0538               | 0.0004                             |                                |
|                                   | NaCl                | 65.52                | 1.12                               |                                |
|                                   | NaOH                | 14                   | 0.35                               |                                |
|                                   | H <sub>2</sub> O    | 960.45               | 53.35                              |                                |

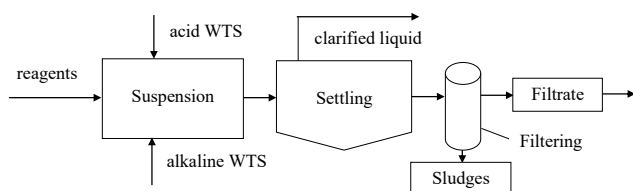


Fig. 5. General scheme of processing of HCMW with obtaining of sludges

Thus, all galvanic sludges belong to the heavy-separable suspensions. They are conditioned by the method of adding of a coagulant, in particular salts of ferrum, after obtaining of precipitates for easier separation. It is proposed to obtain sludge with the ferrum content already in the presented technology. Thus, we exclude the operation of conditioning. As an example, the coprecipitation of cuprum-containing WTS together with ferrum-containing WTS of galvanic and PCB production. It becomes possible to reduce the cost of expensive reagents and improve the efficiency of purification significantly this way. Such precipitations will be ready for transportation. We propose using this method to obtain cuprum-ferrum, zinc-ferrum and chromium-ferrum sludges, which are easily dehydrated.

## 5. 2. Results of studies of the technology of neutralization of WTS with obtaining of a precipitate, which is ready for further utilization by processing

The most important prerequisite for creation of new resource-saving non-waste processes is a clear understanding of the theoretical foundations of a technology. Thus, thermodynamic and technological analysis of division of a complex system of substances makes it possible to create perfect technologies of division of mixtures with high environmental parameters.

Fig. 6 shows the scheme of division of the obtained cuprum-ferrum-containing precipitate formed during the coprecipitation of cuprum-containing and ferrum-containing solutions of galvanic production for further utilization.

The first stage in the obtained technology is transformation of cuprum-ferrum-containing precipitate into solution by addition of sulfuric acid:

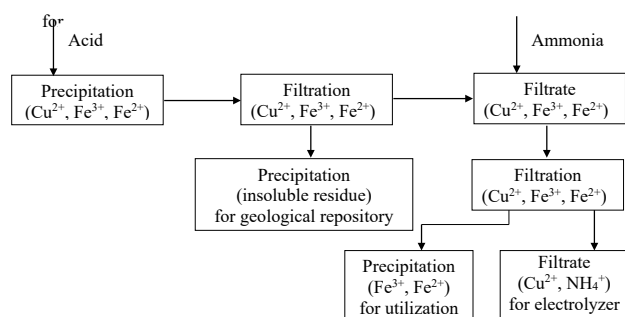
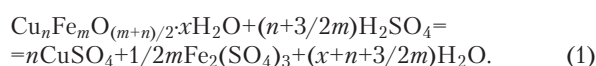
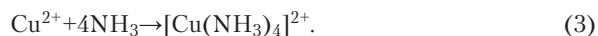
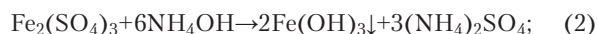


Fig. 6. Scheme of preparation of cuprum-ferrum-containing precipitation for utilization

The precipitate (insoluble residue) sent for disposal contains silica (IV), magnetite (ferric oxide III), gypsum and other chemically stable compounds, which do not have a negative impact on the environment.

The second stage is precipitation of ferrum ions with 25 % ammonia solution to pH=8.2 – obtaining a precipitate of ferric hydroxide (III) and ammonia complex of cuprum:



Then, we filter the ferrum hydroxide precipitate (III) off and send it for further disposal. Finally, we send the obtained cuprum-containing filtrate to obtain copper in the form of foil or for utilization by the reagent method. Metal precipitate is a raw material for non-ferrous metallurgy enterprises.

## 5. 3. Results of studying the technology of utilization of cuprum-containing highly-concentrated waste by the electrochemical method to obtain a product for further use

Electrochemical extraction of metals is a complex process connected with formation of a precipitate on an electrode (cathode). One should consider that transformation of metal ions occurs under the action of electric field voltage, reaction products and combined action of the voltage and products of electrode reactions. The following sequential processes occur during electrochemical extraction on a cathode:

- deformation of a hydration shell with simultaneous displacement of foreign particles from a surface of an electrode;
- release of ions from a hydration shell;
- adsorption and migration of them to active sites of an electrode;
- discharge and incorporation of atoms, which form a crystal lattice [10].

A factor that complicates the study of the electrochemical process of metal extraction is that the process has many stages; the discharge includes an electrochemical electron transfer reaction and chemical transformation.

We carried out studies in diaphragm and non-diaphragm electrolyzers of laboratory and experimental-industrial type to study processes of metal ion extraction. Basic processing parameters are electrode material, electric current density on a cathode, temperature should correspond to the data substantiated in relevant sections of applied electrochemistry, in particular, in electroplating. We considered a degree of transformation and consumption ( $D$ ) of electric current ( $\text{C/mol}\cdot\text{dm}^3$ ) to study the individual processes of influence of electric current on transformation of components of a WTS water system in terms of technological parameters.

As follows from the data shown in Fig. 8, when  $\text{Cu}^{2+}$  concentration is in the range of  $8 \text{ g/dm}^3$  ( $0.125 \text{ mol}$ ) to  $0.75 \text{ g/dm}^3$  ( $0.012 \text{ mol}$ ), which corresponds to an electric current consumption of  $80.103 \text{ C/dm}^3$ , the amount of  $\text{Cu}^{2+}$  ions remaining in the solution does not exceed  $5 \text{ g/dm}^3$  (the extraction efficiency is about 90 %). The change in the ratio of cation:salt anion does not affect the degree of transformation. The current density on a cathode (we used copper as a cathode) has a more significant effect. Thus, reduction of the current density from 200 to  $50 \text{ A/m}^2$  leads to an increase in the consumption of electric current from  $38 \cdot 10^6 \text{ C/mol}\cdot\text{dm}^3$  to  $70 \cdot 10^6 \text{ C/mol}\cdot\text{dm}^3$ . Below we consider the modes, which correspond to the current density  $i_k$  200–500  $\text{A/m}^2$ , which are the optimal parameters [10]. Although more pure precipitations form on a cathode in the form of crystals well bonded to the electrode surface at lower current density.

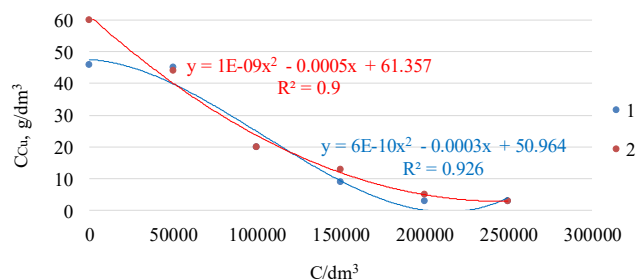


Fig. 7. Changes in  $\text{Cu}^{2+}$  concentration during processing in the diaphragm electrolyzer of WTS of operations: 1 – glittering coppering; 2 – matt coppering

The presented study results evidence that an increase in the initial concentrations of  $C_{\text{start}}$  cuprum ions leads to a decrease in the current consumption. Thus,  $D$  current consumption decreases from  $17280 \cdot 10^3 \text{ C/mol}\cdot\text{dm}^3$  to  $6400 \cdot 10^3 \text{ C/mol}\cdot\text{dm}^3$  at  $C_{\text{start}} = 0.02 \dots 0.0125 \text{ mol/dm}^3$ , that is, the reduction of  $C_{\text{start}}$  in 1.6 times leads to the increase of electric current costs in 2.7 times. To determine the dependence of the influence of the change of the processing parameters on current consumption, completeness of a flow and speed of electrolytic processes, we approximated the obtained results with determination of the deviation coefficients ( $R^2 > 0.94$ )

shown in Fig. 7–12. Since the curves in Fig. 7, 9, *b*, 11, 12 do not have linear dependences, we selected second-order polynomial curves.

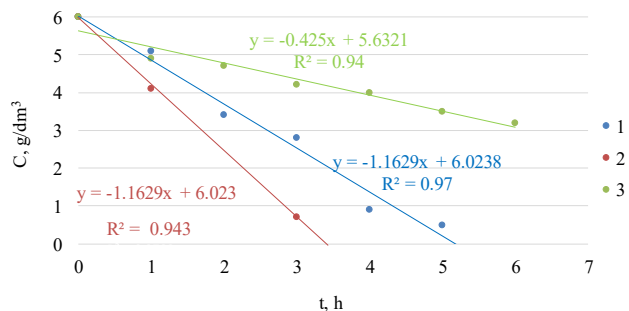


Fig. 8. Changes in Cu<sup>2+</sup> concentration during processing in the diaphragm electrolyzer of WTS of operations of acidic coppering at different values of current density on cathodes (*j*): 1 – *j*=200 A/m<sup>2</sup>; 2 – *j*=150 A/m<sup>2</sup>; 3 – *j*=100 A/m<sup>2</sup>

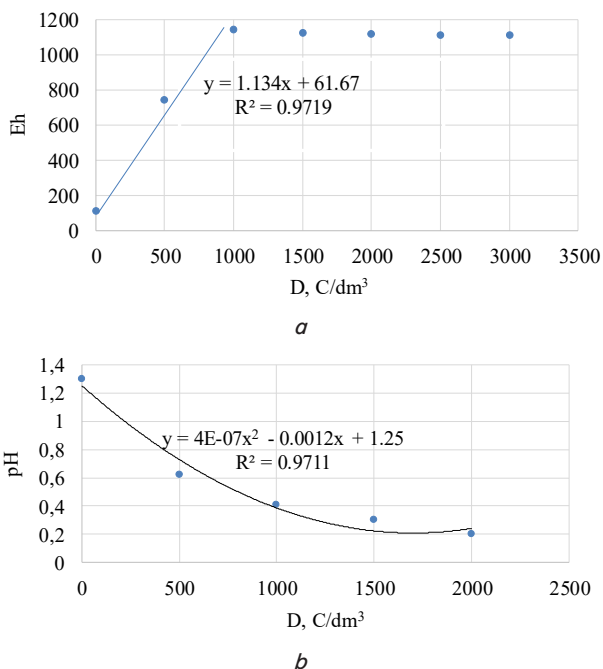


Fig. 9. Changes in properties of WTS of operations of acid coppering during processing in a diaphragm electrolyzer: *a* – redox (Eh); *b* – acid-base (pH)

We obtain the same final concentration of Cu<sup>2+</sup>=0,007 mol/dm<sup>3</sup>, which corresponds to the degree of transformation *a*=0.4–0.7. The increase in the initial concentration of cuprum ions to 0.1 mol/dm<sup>3</sup> (which corresponds to the structure of a concentrated aqueous system) makes it possible to provide a degree of transformation *a*=0.9 for Cu<sup>2+</sup> – H<sub>2</sub>O type of ions with 80 % of current yield.

When the electrochemical extraction of metals occurs from highly concentrated aqueous systems (the concentration of C<sub>Cu</sub>=1–0.5 mol/dm<sup>3</sup> with a current yield of 90 %), we can assume that the discharge of ions occurs from complex compounds of Cu<sup>2+</sup> – a ligand – water. Bonds of water are weak. Thus, one can consider that the most energy-efficient is extraction of metals from complex compounds of metal-ligand-water ions type.

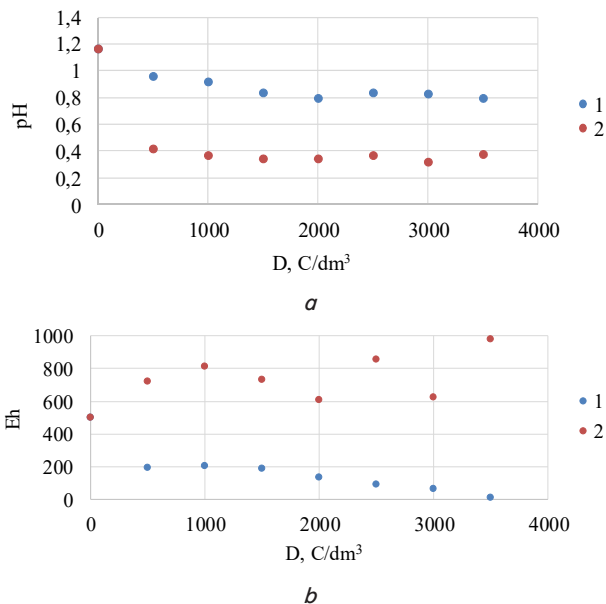


Fig. 10. Change of redox (Eh) and acid-base (pH) properties of WTS of acidic coppering operations during processing in a diaphragm electrolyzer: *a* – cathode chamber; *b* – anode chamber

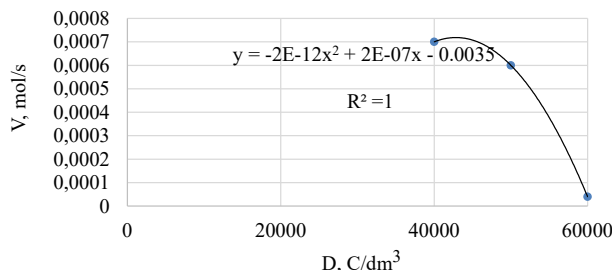


Fig. 11. Speed of electrochemical extraction of Cu<sup>2+</sup> in a cathode chamber of the diaphragm electrolyzer

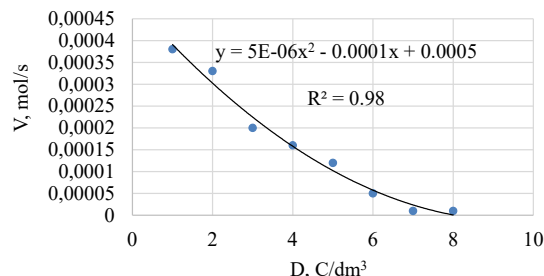


Fig. 12. Speed of electrochemical extraction of Cu<sup>2+</sup> in a non-diaphragm electrolyzer

As one can see from the conducted studies (Fig. 7–10), separation of cathode and anode products by means of an inert semi-permeable membrane (a diaphragm) contributes to the efficiency of transformation due to cathode processes. If a diaphragm is absent, a high concentration of oxygen (the major product of anode processes) leads to inhibition of recovery processes. Thus, the redox potential increases from 725 MW to 1100 MW. Presence of a diaphragm near a cathode produces an excess of recovering agent (H<sub>2</sub>), which corresponds to a decrease in Eh to –125 MW. Thus, we create optimal conditions for recovery processes, which lead to a decrease in current consumption (Fig. 11, 12).

**5. 4. Results of studies of the technology for utilization of cuprum-containing highly-concentrated waste by the reagent method to obtain a product, which is ready for further use**

Table 6 presents the composition of minerals [11] with the most thermodynamically stable state. There are known suitable methods of their processing into a finished product [12, 13]:

1) we can obtain any copper compounds depending on the desired field of use of Cu(OH) hydroxide and Cu<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub> hydrocarbonate. A hydroxide transforms into a hydrocarbonate under the influence of carbon monoxide;

2) cuprum citrate is used in the national economy and as a component for production of anti-corrosion coatings.

Therefore, we investigated conditions for extraction of Cu cuprum in the form of Cu<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>, which has the lowest solubility and is subject to further utilization (processing) for production of cuprum-containing compounds or citrate chelate, in our study.

The proposed technology [14] involves extraction of cuprum from complex compounds, including pre-regulation of pH and Eh of WTS (which ensures the destruction of complex Cu<sup>+</sup> oxidation compounds) of etching operations, which makes it possible to reduce consumption of a reagent for precipitation and to increase purity of a product.

The process of chemical deposition includes:

- chemical transformations and onset of solid phase particles;
- chemical transformations and formation of solid phase particles throughout the deposition and coprecipitation volume.

Fig. 13 shows the general scheme of disposal.

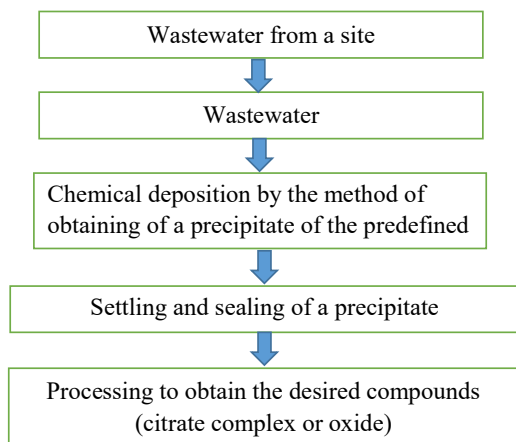


Fig. 13. Structural scheme for disposal of aqueous systems, which contain Cu<sup>2+</sup> + cuprum ion

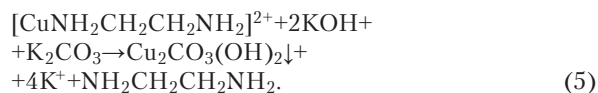
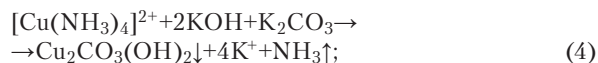
The prevailing form in solution at pH=5.6–10 and presence of ammonium ions is [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> tetra-amino-cupro ion, a sufficiently large proportion of Cu(NH<sub>3</sub>)<sub>3</sub><sup>2+</sup> ions, and values of equilibrium concentrations of other complexes, in particular, hydroxocompounds of cuprum, are small.

The correct choice of the main parameter is especially important in the batch process. Thus, an excess of one or another reagent has the determinant value for chemistry of the process in Cu<sup>2+</sup>– OH<sup>–</sup>–H<sub>2</sub>O system, so the main parameter under these deposition conditions is the molar ratio of reagents in the reaction medium. If you want to get a precipitate of copper hydroxide, the main parameter of precipitation is the ratio of Cu<sup>2+</sup>– OH<sup>–</sup>–H<sub>2</sub>O, which is possible to achieve by direct dosing of a solution of Cu<sup>2+</sup> salt in alkali solution, since excess of OH<sup>–</sup> in the reaction medium limits chemistry of the process by interaction with formation of only Cu(OH)<sub>2</sub> copper hydroxide.

However, a large excess of a reagent is not expedient, so it will be advisable to obtain the basic salt of Cu<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub> composition to obtain an efficient extraction. The main extraction parameter of the basic salt extraction is the ratio of OH<sup>–</sup>/Cu<sup>2+</sup> in the reaction mixture. One can achieve it by the direct simultaneous introduction of an alkali solution with a carbonate.

The process chemistry:

1) Precipitation deposition of the predefined composition with a mixture of KOH and K<sub>2</sub>CO<sub>3</sub> at pH 9.5–10, which destroys chelate and ligand complexes of copper (EDTA and ethanoldiamine) and precipitates copper in the form of hydroxocarbonate:



The supply of reagents occurs in three stages, which gives possibility to reduce supersaturation of the solution with cuprum, and to provide favorable conditions for formation of the solid phase in the metastable region [14]. As a result, there is formation of larger solid phase particles. Their formation also causes a decrease in the content of impurities capable of adsorbing on their surface. Thus, we ensure conditions for an increase in the yield of a product and reduction of its degree of contamination with formation of porous easily separable precipitation. The approximated equation (6) characterizes the dependence of the percentage content of the final amount of cuprum ions on pH of the solution during deposition (Fig. 14).

Table 6

Characteristics of copper and its substances – recycling products

| pH of transformation into insoluble state | Formula and form of precipitation Hydrocompounds  | Minerals in nature (analogues to utilization products)                                      | Compounds used in the economy and industry  | Optimal product of utilization  |
|---|---|---|---|---|
| 7.4–9.1                                   | Cu(OH) <sub>2</sub> Suspension<br>K <sub>sp</sub> =2.2·10 <sup>-20</sup> Cu <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub><br>Suspension K <sub>sp</sub> =2.8·10 <sup>-23</sup> | CuS covellite,<br>Cu <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub> azurite | Cu <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub> azurite,<br>CuO oxide, Cu <sub>x</sub> (C <sub>6</sub> H <sub>8-y</sub> O <sub>7</sub> ) <sub>z</sub> copper citrates | Cu(OH) <sub>2</sub> hydroxide,<br>Cu <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub> hydroxocarbonate,<br>Cu <sub>x</sub> (C <sub>6</sub> H <sub>8-y</sub> O <sub>7</sub> ) <sub>z</sub> copper citrates |



$$n_{\text{Cu}} = 100 - 4,18x^2 + 41,35x + 5,12; \quad (6)$$

2) The second stage after separation of the precipitate is its processing with citric or hydrochloric acids to obtain a finished product of processing in the form of a precipitate of insoluble copper chelate citrate (6), which is dissolved by addition of ammonia (7) or 3-substituted soluble green citrate (8):

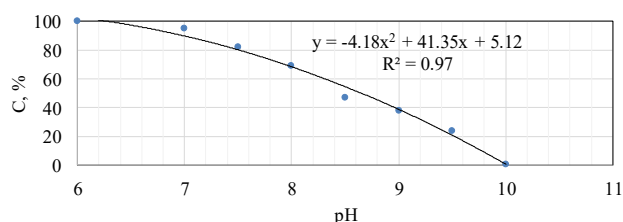
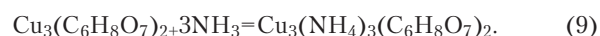
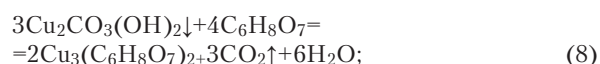
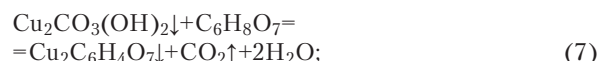


Fig. 14. Content of  $\text{Cu}^{2+}$  copper ions in the solution during processing while adding a mixture of  $\text{K}_2\text{CO}_3$  and  $\text{KOH}$  reagents for  $\text{Cu}^{2+}$  deposition in EDTA complex

Thus, we established the possibility of extraction of copper of highly-concentrated suspensions of galvanic production using a mixture of reagents to obtain precipitates of the predefined composition, which are suitable for further utilization or to obtain ready-to-use products, which can be a final stage of galvanic production and provide complete extraction of copper.

### 5. 5. Results of the studies of the possibility of safe disposal of residual filtrate obtained after separation of metal-containing precipitate during neutralization of cuprum-containing spent technological solutions by the reagent and electrochemical methods

The filtrate obtained after neutralization of cuprum-containing spent technological solutions by the electrochemical method (section 5.3) contains  $(\text{NH}_4)_2\text{SO}_4$  ammonium sulfate. The filtrate after utilization of cuprum-containing highly-concentrated waste by the reagent method contains  $\text{K}_2\text{SO}_4$  potassium sulfate.

Therefore, the filtrates are suitable for further safe utilization by use as a mineral fertilizer, since ammonium sulfate and potassium sulfate are macro fertilizers, and copper ions and zinc ions will serve as necessary micro elements in the residual concentration.

## 6. Discussion of results of studying the technology of processing cuprum-containing waste of galvanic production with its further use

The presented experimental data gives the technology of processing of cuprum-containing waste of galvanic production with their subsequent use at the level of individual enterprise. The obtained precipitations are suitable for further utilization or obtaining of products, which are ready for

use in industry and the economy. This can be a final stage of galvanic production.

As one can see from the conducted studies (Fig. 8–11), the separation of cathode and anode products by means of an inert semi-permeable membrane (a diaphragm) contributes to the efficiency of transformation due to cathode processes. If a diaphragm is absent, a high concentration of oxygen (the major product of anode processes) leads to inhibition of recovery processes. Thus, the redox potential increases from 725 mV to 1,100 mV. Presence of a diaphragm near a cathode leads to an excess of recovering agent ( $\text{H}_2$ ), which corresponds to a decrease in Eh to  $-125$  mV. Thus, we provide the optimal thermodynamic conditions for recovery processes, which results in approximately twice increase in the speed reaction and a decrease in the current consumption (Fig. 12, 13). The extraction with the concentration of cuprum of at least  $5 \text{ g/dm}^3$  with separation of the electrode space by the diaphragm is the most advantageous energetically.

When extracting cuprum in the form of  $\text{Cu}_2\text{CO}_3(\text{OH})_2$  hydrogen carbonate, the decisive value for the chemistry of the process is the molar ratio of reagents in the reaction medium. Its optimal value is  $\text{Cu}:\text{OH}:\text{CO}_3^{2-}$  equal to  $1:1.1-1.3:0.8-1.2$ . If you want to get a precipitate of copper hydroxide, the main parameter of precipitation is the ratio of  $\text{Cu}^{2+}/\text{OH}^-$ , which we achieve by direct dosing of  $\text{Cu}^{2+}$  salt solution in alkali solution, since  $\text{OH}^-$  excess in the reaction medium limits the chemistry of the process by interaction with formation of only  $\text{Cu}(\text{OH})_2$  copper hydroxide rather than mixed hydroxoanionic complexes due to chemo-aging (for example, hydroxosulfate).

The disadvantages of the studies are:

- the obtained precipitations with a given chemical composition and physical-and-chemical properties are hydroxide and carbonate compounds, and, therefore, they are chemically active. The activity manifests itself in the interaction with chemical environmental factors (chemo-aging), which is a negative factor in their long-term storage, although it facilitates their further processing greatly;
- an effect of changes in the precipitation parameters (temperature, metal concentration, reagent dosing speed, mixing speed) on the chemical composition of the resulting precipitate is insufficiently studied.

The advantages of the conducted studies are:

- technological solutions obtained during the studies provide a closed cycle of resource consumption, which minimizes waste discharges into the environment and expenditures of galvanic and PCB enterprises;
- the obtained technological solutions and technologies make it possible to ensure the ecological safety of galvanic waste by elimination of formation of sludge discharges after neutralization of WTS and WW for this type of production;
- there is a large amount of experimental data on the electrochemical extraction of copper of WTS for obtaining of a precipitate on a cathode in a metallic form.

We can recommend the technologies and individual technological solutions obtained in the studies for:

- technologies of utilization of spent technological solutions of galvanic production, eluates of ion-exchange filters, etc.;
- introduction at the level of individual enterprises of galvanic industries for the neutralization of HCMW.

Future studies imply resolving a problem of the effect of changes in parameters of precipitation (temperature, metal concentration, reagent dosing speed, mixing speed) on the chemical composition of the resulting precipitate.

## 7. Conclusions

1. It was established that it is expedient to obtain precipitates with the content of ferrum already for easier separation and elimination of the conditioning operation in the study on cuprum-ammonia sludges obtained by the method of processing of cuprum-containing technological suspensions. Thus, we will reduce costs for expensive reagents, improve efficiency of purification significantly and obtain a precipitate, which is ready to transportation. Thus, the study on cuprum-ferrum sludges obtained by coprecipitation of cuprum- and ferrum-containing WTS, for which  $v_{\text{HOH}}/v_{\text{el}} < 10$ , which corresponds to the structure of an aqueous system, is a boundary after complete hydration. There are compounds of cuprum with ferrum presented in the form of crystalline hydrates only where only bound water remains. The system is easily dehydrated to low-water crystalline hydrates, and it is easy to filter and dehydrate it. The parameters of the resulting precipitate are: humidity – 89.7 %, density – 1.17 kg/dm<sup>3</sup>, specific precipitate resistance a 15–16·10<sup>11</sup>. Thus, such sludge is easily filtered.

2. We developed a method for coprecipitation of cuprum-containing WTS together with ferrum-containing WTS of galvanic and PCB productions. The method involves:

– at the first stage, one transforms a cuprum-ferrum-containing precipitate into a solution by addition of sulfuric acid, a precipitate (insoluble residue) is sent for disposal, it contains silica (IV), magnetite (ferric oxide III), gypsum and other chemically stable compounds, which do not have negative impact on the environment;

– at the second stage, one precipitates ferrum ions with 25 % ammonia solution to pH of 8.5–9, and obtains a ferrum hydroxide precipitate (III) and ammonia complex of cuprum;

– at the third stage, we filter the obtained precipitate of ferrum hydroxide (III) and send it for further utilization, then, we send the obtained cuprum-containing filtrate for electrochemical copper production in the form of copper metal foil or for disposal by the reagent method.

3. We determined the main technological parameters of flow speed and current density in the conducted studies of the electrochemical extraction of cuprum of WTS to obtain a precipitate on a cathode in the metallic form. During processing of cuprous-containing WTS in the diaphragm electrolyzer, it was found that an increase in the initial concentrations of  $C_{\text{start}}$  cuprum ions leads to a decrease in the current consumption. Thus,  $D$  current consumption decreases from 17,280·10<sup>3</sup> C/mol·dm<sup>3</sup> to 6,400·10<sup>3</sup> C/mol·dm<sup>3</sup> at the range of  $C_{\text{start}}=0.02-0.0125$  mol/dm<sup>3</sup>, that is a decrease in  $C_{\text{start}}$  by 1.6 times leads to an increase in the consumption of electric current by 2.7 times. An increase in the initial concentration of cuprum ions to 0.1 mol/dm<sup>3</sup> (corresponding to the structure of a concentrated aqueous system) makes it possible to ensure the degree of transformation of  $a=0.9$  for ions of Cu<sup>2+</sup>–H<sub>2</sub>O type with 80 % of the current yield.

4. It was found that the precipitation of a precipitate of the predefined composition with a mixture of KOH and K<sub>2</sub>CO<sub>3</sub> at pH=9.5–10 is optimal for obtaining of a precipitate of hydroxocarbonate of cuprum, which is by-product for industrial use, for example, for obtaining of citrates of cuprum [14].

5. Filtrates contain ammonium sulfate (the electrochemical method) or potassium sulfate (the reagent method) after neutralization of cuprous-containing spent technological solutions. Therefore, the obtained filtrates are suitable for further safe utilization for using as a mineral fertilizer in agriculture.

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