

## EVALUATING THE METHODS USED FOR THE REGENERATION PROCESS OF COPPER-ZINC SOLUTIONS

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**Abstract.** The purpose of this study was to investigate the physicochemical particularities of the regeneration processes that occur in spent sulphate copper-zinc solutions using the reagent methods of crystallization, cementation, and sedimentation. The obtained results show that the method of crystallization is easy-to-implement, though it fails to provide a required level of efficiency during the regeneration process in the solution to extract heavy metal ions (the extraction of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions was 97.2% and 49.7%, respectively). The displacement (cementation) method does not require additional chemical reagents to implement the stages of processing, the percentage of extraction of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions were higher in comparison to crystallization method, 99.9% and 95.4%, respectively. The advantages of the sedimentation method are the high rates of chemical transformations at technological process stages, complete deposition of heavy metal ions from spent electrolytes (99.9%) and the energy saving due to the shortened time of the regeneration process.

**Keywords:** waste, heavy metal, regeneration, reagent method, treatment efficiency.

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### Introduction

The formation of substantial volumes of liquid and solid wastes is considered to be one of the most topical ecological problems faced by the companies where the industrial cycle includes galvanic processes [1-5]. The ecological problems that arise due to the activity of such companies can be solved by applying regeneration processes in spent solutions and the recovery of precious components instead of the decontamination of concentrated spent etching solutions (SES) with the formation of galvanic sludge [4] that is usually the source of secondary environmental pollution [6-15]. The main methods used for the industrial sewage water treatment, in particular those of coagulation, adsorption, oxidation, ion exchange, membrane filtration and hydrodynamic cavitation were discussed in detail by Ranade Vivek, V. *et al.* [1].

Regeneration is considered to be the most important method used by SES treatment technologies, because it provides a considerable increase in electrolyte life time and an efficient decrease in the quantity of reagents required for the adjustment and preparation of fresh process solutions and also for the decontamination of salvo discharges [1,7,10-12]. The choice of the methods for the SES regeneration in galvanic

production is mainly defined by the level of their pollution and the content of heavy metals (HMe) that affect the metal dissolution rate. Hence, in practice, spent sulphate etching solutions are usually discharged into the industrial sewage system during the process of the electrochemical brass etching when critical concentrations in the etching solution amount to  $C_{\text{Zn}^{2+}} = 30-40$  g/L,  $C_{\text{Cu}^{2+}} = 10-15$  g/L and the brass etching rate is substantially decelerated [5]. The ingress of the untreated or insufficiently treated sewage water, and other types of wastes containing HMe into water bodies results in the economic and environmental problems not only because of the loss of metals used by the production but also due to a pollution on natural ecosystems [4-6].

Nowadays, the environment protection requirements regarding the industrial electroplating waste severely restrict the concentrations of contaminants contained in the wastes. Many methods have been described for the treatment of concentrated spent solutions, including chemical, physicochemical, biological and electrochemical methods [3,6-15]. Various methods are used for the industrial sewage water treatment in an attempt to reduce the concentration of heavy metals and afford the reuse of water resources. These technologies

include membrane filtration, chemical deposition, nanotechnology-based treatments, electrochemical processes, coagulation-flocculation, floatation and upgraded oxidation processes [7,10,13]. Shah, M.P. has well described the important technologies used for the environmental bioremediation and also their specific use for the treatment of industrial sewage water [9]. In a study presented by Geraskin, V.V. *et al.*, it was shown that the Chelyabinsk zinc plant uses the zinc powder to remove such admixtures as copper, cadmium, cobalt, nickel, arsenic, antimony, *etc* from sulphate solutions by the cementation method [12]. Whilst, another study has shown that the copper cementation processes that occur on the zinc powder that was obtained from the scrap of carbon-zinc batteries with the subsequent use of copper powder to produce copper(II) oxychloride [11].

The prospective physical and chemical methods used for the treatment of industrial sewage water discharged by the electroplating industry and other promising methods used for the recirculation and reuse of treated water were described in the literature [7-11]. The methods of regeneration used by industrial companies, in particular those of coagulation, adsorption, ion exchange, oxidation, membrane separation and chemical deposition, were discussed in detail. These methods allow treating the industrial wastewater containing HMe ions and provide for the disinfection of wastewater before its discharge into a reservoir. It was shown that the wastewater treatment can be carried out by any of the above-mentioned methods or a set of methods, depending on the extent of pollution [9,11].

Certain attention should be paid to the review of the methods used for the sewage water treatment by low waste output companies [12-15]. In particular mechanical, physicochemical and biological methods that take into consideration the volume and the extent of waste water pollution. The most efficient method of the treatment of industrial waste with the purpose of HMe ions extraction is the reagent method. This method allows to deposit HMe ions and separate the sludge from the treated water. It is a high-speed process that is easy-to-perform and it requires no complicated technological equipment. A special attention is paid to the four key methods that are used for the regeneration of concentrated SES, in particular these are the methods of the metal displacement (cementation); deposition, electrolysis and crystallization under different conditions [14,15].

The purpose of this research was to study the physicochemical peculiarities of the regeneration processes that occur in spent copper-zinc sulphate solutions using the reagent methods of crystallization, displacement (cementation), and sedimentation. Brief description of each method, and the advantages and drawbacks have been presented. The laboratory and experimental data obtained during the investigation of treatment processes in the present research paper enable the evaluation of the specific features and the efficiency of their application. The choice of simulated solutions and their initial concentrations was conditioned by the composition of actual wastewater resulting from the  $\alpha$ -brass treatment processes. The investigation of copper and zinc ions recovery was carried out because of their considerable content in wastewaters.

## Experimental

### Materials

Analytically pure reagents were used, in particular  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (produced by LabWorld) and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (produced by ReaChim). Other reagents corresponding to the national standards of Ukraine were  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  (from Reagen),  $\text{H}_2\text{SO}_4$  (from Reagen),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (produced by ChemElements),  $\text{NaOH}$  (from Reakhimdevice), concentrated  $\text{H}_2\text{O}_2$  (produced by Newkhim), and two types of commercial zinc powder with the particle size ( $d_{Zn}$ ) of 0.063-0.2 mm and 0.25-0.5 mm (from Grand Lada).

### Instrumentation

The concentration of copper and zinc ions in the solution was checked by the *atomic absorption spectroscopy* using the Saturn spectrophotometer (Japan) at the wavelength of 213.9 and 324.8 nm for zinc and copper, respectively.

Sediment components were defined after the deposition by the *X-ray diffraction* method using the Siemens D-500 diffractometer (Germany) in the copper radiation equipped with the graphite monochromator. The full-profile diffraction pattern was measured for the angle interval of  $5 < 2\theta < 80^\circ$  with the pitch of  $0.02^\circ$  and the exposure time of 40 seconds. The first phases were defined using [16] with the subsequent computation of the X-ray pattern using the Rietveld method and the FullProf program [17].

The elemental and mineral composition of the sediment were studied using the *electron-probe microanalysis* (EPMA) and the JSM-6390 LV *scanning electron microscope*

(SEM) (Japan) with the X-ray microanalysis system INCA. The measurement error of the weight percent of chemical elements contained in the samples varied in the range of 1.5 to 8.5%.

#### Methods of reagent regeneration

In this study, the most widely used chemical methods were selected for the reagent regeneration in concentrated solutions *i.e.* the crystallization, cementation and deposition methods. These are easy-to-implement and do not require complicated technological equipment and, thus, are the most promising for the companies with low waste water output volumes.

#### Composition of the simulated systems

Copper and zinc sulphate solutions were used to prepare simulated electroplating wastes of  $C_{Cu^{2+}} = 25.85$  g/L and  $C_{Zn^{2+}} = 77.0$  g/L, accordingly, and subjected to the treatment by crystallization method;  $C_{Cu^{2+}} = 55.68$  g/L and  $C_{Zn^{2+}} = 53.3$  g/L were treated by the displacement method; and  $C_{Cu^{2+}} = 52.25$  g/L and  $C_{Zn^{2+}} = 59.85$  g/L were treated by the deposition method.

#### Regeneration of the sulphate copper-zinc solutions using the crystallization method

The crystallization method consists in adding to the solution a reagent that reduces the solubility of the salt, followed by cooling the solution. In this study, the crystallization of copper compounds was performed according to a previously described method, using sulphuric acid and sodium sulphate as precipitators and simultaneously cooling the solution [18]. Briefly, the copper sulphate crystallization was enhanced by cooling the spent solution subjected to regeneration throughout a period of 5 days to achieve the temperature of  $+5^{\circ}\text{C}$  at the precipitator ratio of  $\text{Na}_2\text{SO}_4:\text{H}_2\text{SO}_4 = 1:3$ .

The content of the components separated by the crystallization was controlled by the mass balance of the components distributed in liquid and solid phases, see Eq.(1).

$$C \cdot V = C' \cdot V' + m' \quad (1)$$

where,  $V$ – volume of the simulated solution, L;

$C$ – concentration of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in the simulated solution, g/L;

$V'$ – volume of the solution after the crystallization, L;

$C'$ – concentration of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in the solution after the crystallization, g/L;

$m'$ – content of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in the sediment after the crystallization, g.

#### Regeneration of the sulphate copper-zinc solutions by the displacement (cementation) method

Contact displacement of metals (cementation) is a method of precipitating metals from aqueous solutions by other, more electronegative metals. In this study, the contact displacement of copper by the zinc powder was carried out in simulated solutions at a constant temperature and mixing, according to a previously described method [19]. The zinc powder (standard electrode potential of Zn is  $E^0 = -0.763$  V [20]) was selected as a cementing reagent. In addition,  $\text{Zn}^{2+}$  ions were present in the initial solution, thus simplifying the regeneration process. The process was monitored through the changes in values of thermodynamic parameters including the equilibrium constant ( $K_{eq}$ ) and the Gibbs thermodynamic potential ( $\Delta G$ ) which were calculated using the Eqs.(2,3) [19].

$$K_{eq} = \frac{C_{Zn^{2+}}}{C_{Cu^{2+}}} \quad (2)$$

$$\Delta G = -2.3RT \lg K_{eq} \quad (3)$$

where,  $K_{eq}$ – equilibrium constant;

$\Delta G$ – a change in Gibbs thermodynamic potential, kJ/mol;

$T$ – temperature, K;

$R$ – gas constant, 8.314 J/K·mol.

#### Regeneration of the sulphate copper-zinc solutions by the sedimentation method

The selected reagent method is based on the reactions of  $\text{H}_2\text{O}_2$  and iron ions [15]. The soluble  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  salt was used for a more efficient oxidation process. The addition of this salt to the deposition process in the amount of 0.06 to 0.08 per unit of the content of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in the solution enabled the obtaining of eco-friendly products at minimum reagent consumption.

The pH value is one of the defining parameters for the process optimization in the  $\text{H}_2\text{O}_2\text{--Fe}^{2+}(\text{Fe}^{3+})$  system [15,21]. For this purpose, the residual  $\text{Na}^+$  ion concentration in the solution was determined after precipitation was carried out using the 5% NaOH solution. After the HME deposition, the regeneration of alkaline solution was performed with the simultaneous formation of the closed cycle for the NaOH solution. The obtained solution after the sedimentation contained 48 g/L to 50 g/L of  $\text{Na}^+$  ions (determined by titrimetry), which was insufficient to return into the recycle.

Therefore, crystalline NaOH was added to attain the concentration values of 20 to 25% required for the subsequent return to the production cycle.

**Evaluating the methods used for the regeneration**

The efficiency of the reagent regeneration methods evaluated in this study was monitored through the value of the extraction degree (ED) of HMe ions, which was calculated using Eq.(4).

$$ED = \frac{C_{HMe} - C'_{HMe}}{C_{HMe}} 100\% \quad (4)$$

where,  $C_{HMe}$ — concentration of metal ions in the simulated model solution, g/L;

$C'_{HMe}$ — concentration of metal ions in the solution after the regeneration process, g/L.

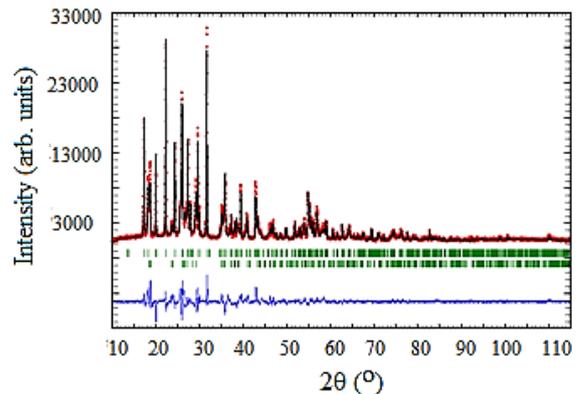
**Results and discussion**

**Regeneration by the crystallization method**

The obtained results showed that the separation of copper and zinc ions in the concentrated spent solutions was observed during the combined addition of H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> (Table 1). The content of the components separated by the crystallization method was checked by the mass balance, which showed that the discrepancies in the content of copper were within 2 to 12%, and those for zinc were within 0.1 to 10%. At the precipitator ratio of Na<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>SO<sub>4</sub>= 1:3, the concentration of metal ions was  $C_{Cu^{2+}} = 5.7$  g/L and  $C_{Zn^{2+}} = 48.0$  g/L for the supernatant and  $C_{Cu^{2+}} = 13.57$  g/L and  $C_{Zn^{2+}} = 12.1$  g/L for the sediment. A similar result was obtained in a different study; however, the authors recommend to use expensive reagents when introducing additional operations (rectification and distillation) [14].

The further investigation of the separation process of copper and zinc ions by crystallization method showed that the ratio of Na<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>, which are used as precipitators, can be optimized for liquid and solid phases (Table 1). However, it was noted that the most complete separation of copper and zinc ions is achieved for the crystallization by H<sub>2</sub>SO<sub>4</sub> only (Table 1, experiment 10). The total concentration of sulphate ions added to the salting out solution is about 288 g/L [18].

The driving factors of the crystallization are a simultaneous decrease of temperature and the addition of H<sub>2</sub>SO<sub>4</sub> that result in the decreased salt solubility. The mechanism of the process consists in a decrease of the salt solubility due to the addition of SO<sub>4</sub><sup>2-</sup> ions and the suppression of salt hydrolysis with an increase in acidity. As a result, CuSO<sub>4</sub> is preferably deposited as a crystalline compound. The composition of the obtained sediment through the crystallization method has been established by the X-ray diffraction technique (Figure 1).



**Figure 1. The X-ray pattern of the sediment obtained by the crystallization method. (Table 1, experiment 10)**

Table 1

**Optimizing the ratio of precipitators for the regeneration process in the spent copper-zinc sulphate solutions by crystallization method.**

Experiment	Na <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> SO <sub>4</sub> precipitator ratio		The content of metal ions					
			in the simulated solution, g/L		in the solution, g/L		in the sediment, g/kg	
	Na <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
1	2.0	1.0	25.85	77.0	7.1	21.4	15.71	31.5
2	1.0	1.0	25.85	77.0	5.7	31.0	14.29	28.5
3	1.0	2.0	25.85	77.0	5.7	40.5	11.43	20.5
4	1.0	3.0	25.85	77.0	5.7	48.0	13.57	12.1
5	1.0	–	25.85	77.0	Complete salting out in the absence of solution			
6	1.0	4.0	25.85	77.0	15.85	75.0	10.00	4.0
7	1.0	4.3	25.85	77.0	13.75	73.5	11.25	3.5
8	1.0	4.5	25.85	77.0	14.15	70.0	11.65	3.5
9	1.0	4.7	25.85	77.0	15.00	75.0	11.25	3.5
10	–	1.0	25.85	77.0	13.35	74.0	25.85	12.5

The obtained results (Figure 1) showed that the composition of the initial specimen is CuSO<sub>4</sub>·3H<sub>2</sub>O– 61% and ZnSO<sub>4</sub>·H<sub>2</sub>O– 39%. On the diffractogram, the rows of vertical bars (in the middle) correspond to the lines of CuSO<sub>4</sub>·3H<sub>2</sub>O and ZnSO<sub>4</sub>·H<sub>2</sub>O phases from the top downward. In terms of copper and zinc content in the crystalline hydrates of CuSO<sub>4</sub>·3H<sub>2</sub>O and ZnSO<sub>4</sub>·H<sub>2</sub>O, the content of Cu makes up 18.24%, and that of Zn is 14.16%. According to SEM-EPMA results, the elemental composition of the sediment is as follows: Cu– 32.8%; Zn– 5.4%; O– 40.9%; and S– 20.9%. The difference in the X-ray diffraction data and the SEM-EPMA of the composition of the sediment specimen can be explained by the fact that the CuSO<sub>4</sub>·3H<sub>2</sub>O compound is initially deposited in the amorphous state and then it crystallizes, whilst the ZnSO<sub>4</sub>·H<sub>2</sub>O compound is deposited immediately in the crystalline state.

To provide a low waste process, the solution that is formed after the crystallization and that contains zinc ions ( $C_{Zn^{2+}} = 74.0 \text{ g/L}$ ) is delivered to the electrolyzer to carry out the electrochemical zinc deposition process. At this stage, the residual concentration of Zn<sup>2+</sup> ions in the solution is 38.7 g/L.

Based on the obtained experimental data, the stages of the regeneration process in the spent copper-zinc sulphate solution by the crystallization method were determined and optimized as follows:

- separation of copper and zinc ions from the spent solution by crystallization can be optimized by the combined addition of H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>, followed by cooling to +5°C. The total concentration of SO<sub>4</sub><sup>2-</sup> ions is of 288 g/L;
- separation of the sediment and the solution is done by decantation after 10-15 min;
- performing the electrochemical extraction of residual zinc and copper amounts on the cathode;
- returning the solution that contains SO<sub>4</sub><sup>2-</sup> ions into the production process:

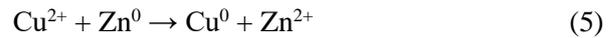
treatment of anolyte solution with SO<sub>4</sub><sup>2-</sup> ions in a vacuum evaporator with its subsequent recycling into the production process;

- use of the copper sulphate with a slight admixture of zinc sulphate in the production process.

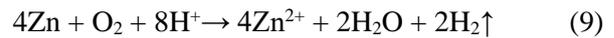
**Regeneration by the displacement (cementation) method**

A mechanism of the copper cementation by zinc is determined by a combination of the electrochemical and parallel chemical reactions, Eqs.(5-12) [19]:

- the main process



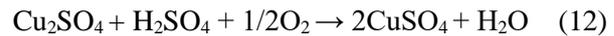
- electrochemical reactions  
anodic:



- cathodic:



- parallel chemical reactions



The process of the cementation of copper by zinc shows that the developed cathode surface is required for an increased process efficiency by contributing to the removal of gas bubbles that prevent the contact of zinc with the copper-containing solution and the cementing metal, *i.e.* zinc should be present in a small surplus [11,12].

Table 2

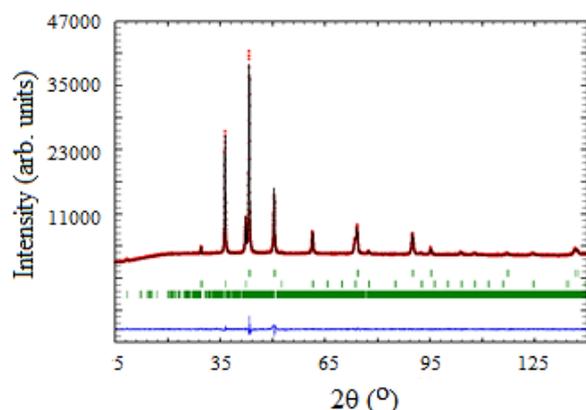
**Basic characteristics of the copper cementation process depending on the metal-cementing reagent of a zinc particle size.**

$d_{Zn} = 0.063-0.2 \text{ mm}$				$d_{Zn} = 0.25-0.5 \text{ mm}$			
$Cu^{2+}:Zn^0$ ratio	The content of metal ions, g/L		Time, min	$Cu^{2+}:Zn^0$ ratio	The content of metal ions, g/L		Time, min
	in the simulated solution	in the solution after the cementation			in the simulated solution	in the solution after the cementation	
	Cu <sup>2+</sup>	Zn <sup>2+</sup>			Cu <sup>2+</sup>	Zn <sup>2+</sup>	
1:1.34				1:1.07			
1:1.36	55.68	53.30	15	1:1.08	55.68	53.30	60–120
1:1.38				1:1.09			

The formation of slightly soluble compounds on the zinc surface and the progress of concurrent cathode processes result in the additional consumption of the active metal. The effect of these factors can be reduced through the use of zinc with the well-developed surface at a minor surplus in comparison to the stoichiometric amount. The main results of the cementation process depending on the  $\text{Cu}^{2+}:\text{Zn}^0$  ratio and the size of metallic zinc particles are shown in Table 2. It was established that the process efficiency can be improved within 15 minutes by using zinc powder (with the particle diameter of 0.063 to 0.2 mm) within the ratio of  $\text{Cu}^{2+}:\text{Zn}^0 = 1:1.36$  (Table 2) as a cementing agent.

Similar studies were performed using the zinc powder with an average size of particles of 10, 20, 30  $\mu\text{m}$  for the sulphate solution cementation evaluated in this study; this contributed to decrease the content of iron in the eluate to  $5.0 \cdot 10^{-4}$ -0.3 g/L [12]. However, these values are significantly lower than those achieved in the present study.

The main components contained by the specimen were Cu,  $\text{Cu}_2\text{O}$  and  $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_5$ . According to the SEM-EPMA the elemental composition of the sediment is as follows: Cu– 97.27%; Zn– 2.44%; S– 0.29%, and it is in agreement with the X-ray diffraction data (Figure 2). On the diffractogram the rows of vertical bars (in the middle) correspond to the lines of Cu,  $\text{Cu}_2\text{O}$  and  $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_5$  phases from the top downward.



**Figure 2. The X-ray pattern of the sediment obtained by the cementation method. (Table 2, experiment  $\text{Cu}^{2+}:\text{Zn}^0 = 1:1.34$ )**

The estimated thermodynamic parameters for the contact displacement of copper by zinc (Table 3) show that the temperature influences the process and that a more complete extraction of copper from the spent solution occurs at a 298 K.

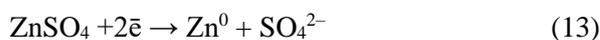
Table 3

**The equilibrium constant ( $K_{eq}$ ) and the Gibbs thermodynamic potential ( $\Delta G$ ) for the contact displacement of copper by zinc as a function of temperature.**

Temperature, K	$K_{eq}$	$\Delta G$ , kJ/mol
295	270.92	-13.62
298	861.05	-19.62
303	866.07	-19.97
308	876.82	-20.34

To ensure a low-waste process, the solution obtained after cementing ( $C_{\text{Zn}^{2+}} = 90.4\text{-}91.0$  g/L) was fed into the electrolyzer to carry out the process of electrochemical zinc deposition. The deposition of zinc ions occurs on the cathode (according to Eq.(13)) and sulphuric acid is formed in the anode space according to Eqs.(14-16).

Cathode reaction:



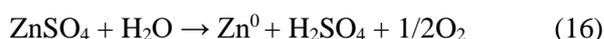
Anode reaction:



In the anode space, a sequential reaction of the formation of sulphuric acid takes place, according to Eq.(15)



Lumped reaction:



At this stage, the residual concentration of  $\text{Zn}^{2+}$  ions in the solution is 2.47 g/L. In addition, at the stage of the electrochemical extraction of zinc, sulphuric acid is formed in the anode space due to the formation of  $\text{H}^+$  ions Eqs.(14,15) and the migration of  $\text{SO}_4^{2-}$  ions when exposed to the action of the electric field. The acid concentration increases over time. To reduce the volume of acid, low-temperature evaporation is carried out to attain an appropriate volume. When the pH of 1 to 1.3 is attained, the acid solution is returned to the production cycle. The collected water vapor can be used for subsequent process operations.

Based on the obtained results, the stages of the regeneration in the spent sulphate copper-zinc solution by the displacement (cementation) method were determined and optimized as follows:

- separating copper and zinc ions by the copper displacement using the zinc powder as the cementing reagent with the particle diameter of 0.063-0.2 mm and a ratio of

$Cu^{2+}:Zn^0 = 1:1.36$ . At 298 K the process takes 15 minutes;

– separating the sediment and the solution; the solution is allowed to settle for 10-15 minutes and then it is decanted;

– performing the electrochemical extraction of  $Zn^{2+}$  ions from the solution to return it into the cementation process;

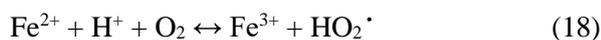
– returning the solution that contains  $SO_4^{2-}$  ions into the production process: the anolyte solution that contains  $SO_4^{2-}$  ions is treated in the vacuum evaporator to get the values required by process regulations to return it to the production process.

### Regeneration by the sedimentation (deposition) method

The combination of consecutive processes is considered to be a mechanism of sedimentation, Eqs.(17-19): i) the introduction of  $FeSO_4$  reagent into the copper-zinc sulphate solution; ii) the precipitation of  $Zn(OH)_2$  and  $Cu(OH)_2$  by NaOH solution; iii) further introduction of  $H_2O_2$  into the chemical system. Oxygen and  $H^+$  are formed upon  $H_2O_2$  decomposition, according to Eq. (17) [15].



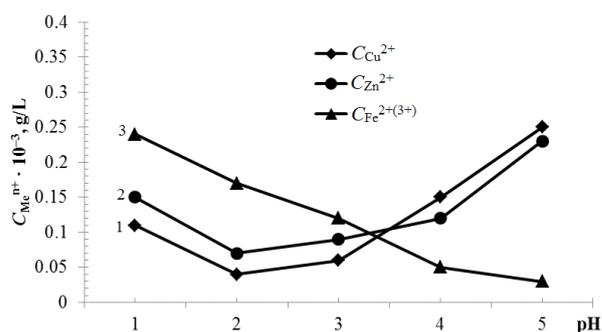
A decrease of the pH in the medium contributes to the final transformation of  $Zn(OH)_2$  and  $Cu(OH)_2$  into the corresponding oxides. The  $Fe^{2+}$  ions contribute to the regeneration of  $H_2O_2$ , which increases the time of ZnO and CuO precipitation, Eqs.(18,19)



The pH value is one of the defining parameters for  $Zn(OH)_2$  and  $Cu(OH)_2$  precipitation by NaOH. For this purpose, the residual concentrations of  $Zn^{2+}$ ,  $Cu^{2+}$  and  $Fe^{2+}$  ions in the solution were determined after their hydroxides precipitation (Figure 3). Optimum pH values for a complete sedimentation of HME hydroxides by alkaline solution:  $Fe^{3+}$  (pH 8),  $Zn^{2+}$  and  $Cu^{2+}$  (pH 10),  $Fe^{2+}$  (pH 11) were given in the literature [21]. Taking these data into consideration, the process of HMe deposition was carried out using a 20-25% NaOH solution.

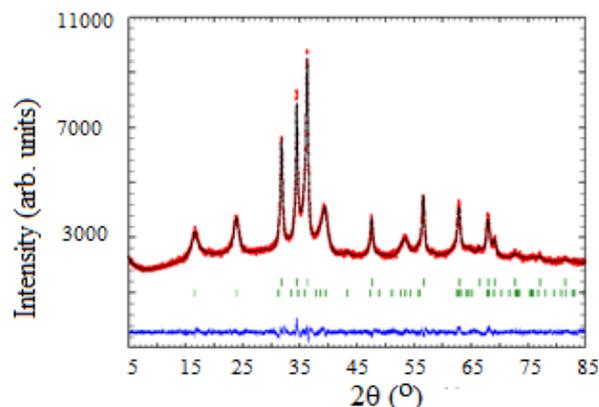
According to Figure 3, the residual concentration of HME in the solution after the deposition was  $C_{Cu^{2+}} = 0.04 \cdot 10^{-3}$  g/L;  $C_{Zn^{2+}} = 0.07 \cdot 10^{-3}$  g/L; and  $C_{Fe^{2+}(Fe^{3+})} = 0.17 \cdot 10^{-3}$  g/L when pH 9 was reached. At the pH value of 10.5 the solution composition is changed:  $C_{Cu^{2+}} = 0.15 \cdot 10^{-3}$  g/L;  $C_{Zn^{2+}} = 0.12 \cdot 10^{-3}$  g/L; and  $C_{Fe^{2+}(Fe^{3+})} = 0.05 \cdot 10^{-3}$  g/L. It should be noted that

an increase in the pH value of the solution results in an increase of concentration of  $Cu^{2+}$  and  $Zn^{2+}$  ions, however the content of  $Fe^{2+}(Fe^{3+})$  decreases. It means that the co-deposition of the metals at the same pH value allows enhancing an individual deposition of one or several metals; however, it is impossible to provide their total co-deposition. This is conditioned by the individual properties of metal ions and the ability of their compounds to dissolve in alkaline medium; therefore, it is recommended to conduct the HMe deposition process using the NaOH solution until the pH value of 9 to 10.5 is attained.



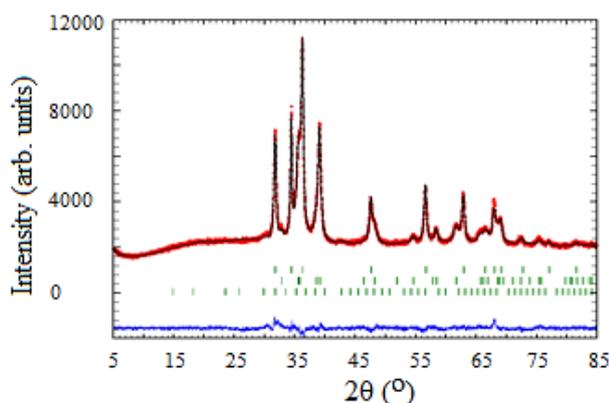
**Figure 3. The concentration of metal ions ( $C_{Me^{n+}}$ ) in the solution after the sedimentation from the simulated solution containing of  $C_{Cu^{2+}} = 55.68$  g/L and  $C_{Zn^{2+}} = 53.3$  g/L in the  $H_2O_2$ - $Fe^{2+}(Fe^{3+})$  system depending on the pH value.**

The sediment obtained after the deposition of HMe with a NaOH solution was studied using the X-ray diffraction method (Figure 4). The composition of sediment determined by SEM-EPMA is as follows:  $Cu(OH)_2$ – 57.5% and ZnO– 42.5%. On the diffractogram (Figure 4) the rows of vertical bars (in the middle) correspond to the lines of  $Cu(OH)_2$  and ZnO phases from the top downward.



**Figure 4. The X-ray pattern of the sediment obtained by the deposition method. (the sediment after precipitation of HMe with a solution NaOH)**

A gradual addition of H<sub>2</sub>O<sub>2</sub> to the solution results in a change of the structural characteristics of the sediment formed after the HMe deposition by the NaOH solution. While the oxidant is added, the sediment diminishes in volume; it becomes more compact and acquires a crystalline structure. The X-ray diffraction analysis (Figure 5) and SEM-EPMA carried out after the H<sub>2</sub>O<sub>2</sub> treatment showed that the sediment is mainly represented by metal oxides modifications: ZnO– 49.5%, CuO– 48.7%, and Fe<sub>2</sub>O<sub>3</sub>– 1.8%. On the diffractogram (Figure 5) the rows of vertical bars (in the middle) correspond to the lines of ZnO, CuO and Fe<sub>2</sub>O<sub>3</sub> phases from the top downward.



**Figure 5. The X-ray pattern of the sediment obtained by the deposition method. (the sediment after treatment with solution H<sub>2</sub>O<sub>2</sub>)**

The presence of ZnO in the obtained precipitate instead of Zn(OH)<sub>2</sub> is an indicative of the chemical reaction given by Eq.(20) in the solution [15].



In other words, particularly ZnO particles are the end products of the reaction between ZnSO<sub>4</sub>·7H<sub>2</sub>O and NaOH. The Zn(OH)<sub>2</sub> is the intermediate compound that is decomposed during the heating and at a specified molar ratio of the reagents [21]. Fe<sup>+2</sup>(Fe<sup>+3</sup>) particles are unavailable in the sediment, because these are present in the solution as suspended hydroxides.

It should be noted that the formation of oxides proceeds with the simultaneous change in the pH value of the mixture attaining the values of 6 to 7 [15]. The shift in the pH value is explained by simultaneous reactions, Eq.(17).

Based on the obtained experimental data, the stages of the regeneration process of the copper-zinc solution sulphate by the deposition (sedimentation) method were determined and optimized as follows:

- adding the catalyst: the water-soluble salt FeSO<sub>4</sub>·7H<sub>2</sub>O in the amount of 0.06-0.08 per unit of the content of Cu<sup>2+</sup> and Zn<sup>2+</sup> ions in the solution. This process is conducted by stirring the mixture at a temperature of 60-70°C;
- deposition of HMe ions: a 20-25% NaOH solution should be added until a pH of 9-10.5 is attained;
- treatment of the resulting sediment must be done by adding the 29-32% NaOH solution, the pH value of 9-10.5 should be controlled and adjusted;
- the conversion of Zn(OH)<sub>2</sub> and Cu(OH)<sub>2</sub> to ZnO and CuO by addition of 30% H<sub>2</sub>O<sub>2</sub> solution;
- separation of the sediment from the solution: the solution is heated for 10-15 minutes at 60-70°C, settled and decanted;
- returning the eluate that contains Na<sup>+</sup> ions to the production process: the eluate is adjusted by the crystalline NaOH until a concentration of 20-25% is reached with its subsequent return to the production cycle.

The regeneration process in question has significant advantages in comparison with similar purification methods [21,22], in particular it is characterized by a high HMe extraction level and it is a low waste process with appropriate cyclicity.

#### **Efficiency of the evaluated regeneration methods**

The comparative analysis data obtained for the regeneration efficiency in concentrated spent solutions using the methods of crystallization, cementation, and sedimentation is presented in Table 4.

Table 4

**Comparative analysis of the regeneration efficiency of the concentrated spent solutions.**

Regeneration method	The content of metal ions in the solution after the regeneration, g/L		ED, %	
	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
crystallization	13.35	38.70	97.2	49.7
cementation	0.40·10 <sup>-2</sup>	2.47	99.9	95.4
deposition	0.10·10 <sup>-3</sup>	0.10·10 <sup>-3</sup>	99.9	99.9

The results show that the crystallization method is easy-to-perform, however it fails to provide an efficient removal of HMe ions during the regeneration in the spent solution. High residual concentrations of HMe in the solution after the regeneration by the crystallization method result in the need for the introduction of additional stages to the process for the efficient metal extraction. It requires an increased consumption of energy resources and additional economic costs. In addition, the sediments obtained during the decontamination of the electrolytes using this method have relatively high volumes and require additional economic costs for their recycling.

In contrast to the crystallization method, the method of the contact displacement (cementation) of copper by zinc from copper-zinc sulphate solutions has certain advantages, in particular the high rates of chemical conversions at technological process stages, the completeness of the deposition of copper ions from spent electrolytes, and the closed "etching-regeneration cycle". It is a low-waste and cost-effective process because it requires no extra chemical reagents for the realization of the stages. However, the cementation method is only efficient for the extraction of  $\text{Cu}^{2+}$  ions, giving a residual concentration of  $C_{\text{Cu}^{2+}} = 0.4 \cdot 10^{-4}$  g/L in solution after the regeneration using this method, meeting the main requirements set to a maximum permissible concentration for the discharge to the fishery ponds ( $\text{MPC}_w(\text{Cu,Zn}) = 10^{-3}$  g/L [23]). However, a considerably higher dose of the cementing reagent is required to run the process, in comparison to the stoichiometric dose and the introduction of the additional treatment methods is required for the extraction of  $\text{Zn}^{2+}$  ions. The after-cementation solid copper sediment is a valuable product that can be used as a raw material for the powder metallurgy. All that results in high energy and operational costs required for the realization of this method.

The deposition is considered to be the most efficient method used for the regeneration of the concentrated spent etching solutions. Concentrated copper-zinc sulphate solutions are recovered by 99% using this method. The recycling process of the obtained amorphous sediment in the form of the HMe hydroxide salts includes their conversion into the crystalline precipitate in the form of oxides ( $\text{ZnO}$ – 49.5%,  $\text{CuO}$ – 48.7%,  $\text{Fe}_2\text{O}_3$ – 1.8%). This precipitate could be further used for the production of a variety of commercial products (*i.e.* reducing additives for metallurgy companies, pigment

pastes, *etc.*). It should be noted that the addition of supplementary inexpensive reagents ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ ) to the process has certain advantages, in particular HMe-containing solutions are decontaminated to attain  $\text{MPC}_w$  norms; the residual amount of  $\text{H}_2\text{O}_2$  is decomposed spontaneously in the solution; the salt content is stable in the treated solution and the reaction proceeds with no formation of toxic intermediate compounds. Hence, the treatment method of the spent copper-zinc sulphate solutions to extract HMe during the chemical deposition has the following advantages: the high rates of chemical transformations at stages of regeneration process, complete deposition of HMe ions from spent electrolytes, and saving energy resources due to the shortened technological cycle.

#### Research prospects

The obtained research data represent a scientific base that can be used by electroengineering and electrochemical productions, and by etching lines, as well. The set of operational factors, in particular the concentration of metal ions, the admixtures, the solution acidity, temperature, *etc.*, should be taken into account for each individual company. Further, a study is planned on the effect of critical problems on the behaviour of regeneration processes, in particular the fluctuations of operational factors and the rate of their variation. In the future, it will be possible to adjust the obtained data in relation to waste process solutions of a different quality composition.

#### Conclusions

The regeneration processes in the copper-zinc sulphate solution were studied by the methods of crystallization, cementation and deposition that enabled the extraction of metal ions from waste etching solutions and provide the regeneration and return of the reagents into the technological process of the electroplating production.

It was proved that the crystallization method is easy-to-implement, though it fails to provide an efficient treatment of the solution to extract HMe ions. It should be noted that the most complete separation of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions is attained in the case of desalting by  $\text{H}_2\text{SO}_4$ , resulting in large-volume sediments.

It was established experimentally that the efficiency of the process of the contact copper displacement by zinc can be increased within 15 minutes through the use of the zinc powder with the particle diameter of 0.063 to 0.2 mm and

the ratio of  $\text{Cu}^{2+}:\text{Zn}^{0}= 1:1.36$ . It was shown that the contact displacement method requires no extra chemical reagents for the realization of the stages. However, it requires an increased amount of the cementing reagent and the introduction of additional treatment methods, leading to additional operational costs.

It was shown that the addition of the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  salt to the deposition process in the amount of 0.06 to 0.08 per unit of the content of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in the solution enables recovery with a minimum consumption of the reagents.

A comparative analysis of the results of the studies of regeneration processes has shown that the content of the extraction of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions by the crystallization method makes up to 97.2% and 49.7%, respectively; by the contact displacement method to 99.9% and 95.4%, respectively; and by the deposition method it makes up to 99.9% and 99.9%, respectively.

The presented study can be used for improvements in the electroplating productivity.

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