### **UDC 669**

A. A. Nester<sup>1</sup>, orcid.org/0000-0002-1276-6068, O. O. Nikitin<sup>1</sup>, orcid.org/0000-0002-0842-3505, O. V. Romanishina<sup>1</sup>, orcid.org/0000-0003-2029-1004, L. O. Mitiuk<sup>2</sup>, orcid.org/0000-0003-4914-2387, Yu. O. Polukarov<sup>2</sup>, orcid.org/0000-0002-6261-3991

## https://doi.org/10.33271/nvngu/2020-6/115

1 — Khmelnytskyi National University, Khmelnytskyi, Ukraine, e-mail: <a href="mailto:nesteranatol111@gmail.com">nesteranatol111@gmail.com</a>
2 — National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine

# ACHIEVING ENVIRONMENTAL SECURITY WITH ECONOMIC IMPACT

Dumping and storing spent pickling solutions on the territory of enterprises leads to environmental pollution, requires significant costs for their neutralization at the enterprise and at treatment facilities at the production sites.

**Purpose.** To clarify the previously known, but insufficiently studied processes of wastewater treatment and to present the results of research and tests conducted to obtain copper from wastewater and create environmentally friendly equipment.

**Methodology.** The paper studies individual processes of regeneration of copper-ammonia etching solutions using electrochemical technology to obtain dense copper deposits, whose release sharply reduces the formation and storage of sludge on the territory of enterprises.

**Findings.** It is noted that the chemical correction of etching solutions leads to the formation of a significant amount of wastewater, sludge which contains heavy metals that adversely affect soils, groundwater, the plant world and humans as the top of the food chain. To avoid the accumulation of sludge on the territory of enterprises, it is proposed to use the technology of regeneration of spent etching solutions, in which sludge is not formed, and the isolated metal is reused as a secondary raw material for copper production. In this case, the regenerated etching solution is reused for etching printed circuit boards. The creation of equipment for the regeneration of used solutions with the release of metal in a form suitable for melting becomes an important element in preserving the environment and obtaining raw materials for non-ferrous metallurgy in Ukraine.

**Originality.** For the first time, comprehensive studies have been carried out which made it possible to create promising wastewater treatment equipment based on them. The research-based etching line for printed circuit boards provides for the reuse of rinsing waters in the technological process after its regeneration. At the same time, the use the line rinsing water is available to replenish the withdrawn pickling solution.

**Practical value.** The use of the process with the separation of copper by dense deposits makes it easier to remove metal by simple mechanical operations and to avoid a complex structure for removing copper in the form of metal powders.

**Keywords:** regeneration, sludge, pickling solution, copper, cathode, rinsing water

Introduction. In Ukraine, there is an urgent need for copper, which is used widely in the electrical industry and other industries. At the same time, there are no known deposits of copper ores in Ukraine. Prospective and predicted resources of copper ores have been estimated: in the Volyn region, in the Donbas and in the Dnipro and Donetsk hollow within the Ukrainian shield in the Middle Dnipro and Volyn regions. The total ore resources of the Volyn region with an average copper content of 1.0 % are estimated at 28 million tons of metal. All of the above indicates a lack of copper ore deposits in Ukraine. Ukraine's annual demand for this metal is approximately 120—140 thousand tons, twenty percent of which is provided by its own copper scrap. The rest of the demand in the form of blister copper has to be imported from neighboring Russia and Poland.

In Ukraine, the mineral resource base of non-ferrous metallurgy is insufficient, and many enterprises in this industry work on imported raw materials or melt non-ferrous scrap metal. At the same time, according to some estimations, the total costs of copper production from secondary raw materials are 35–40 % lower than from primary ones.

When locating these enterprises, consumer, transport and environmental factors are also taken into account. Non-ferrous metallurgy is an environmental pollutant and the main source of heavy metals.

The specificity of solid production wastes is that in small quantities they do not have a noticeable effect on the environment, and in large concentrations they become an ecological

© Nester A.A., Nikitin O.O., Romanishina O.V., Mitiuk L.O., Polukarov Yu.O., 2020

disaster. The problem of utilization of industrial and domestic waste is now becoming more and more acute due to the fact that the volume of waste generation is constantly increasing, while the rate of their processing is incomparably low. As a result, hundreds of millions of tons of various solid wastes (including those with heavy metals) have been accumulated by now, which must be processed and neutralized.

According to the results of the X-ray fluorescence analysis of the ammonium acetate extract of the investigated sludge with pH 4.5, carried out by the ElvaX Light SDD spectrometer, chromium, iron, nickel, copper and zinc were found among the mobile forms of heavy metals. An S115-M1 atomic absorption spectrophotometer was used to determine the quantitative content of these compounds in the slime of board production and electroplating.

The environmental hazard of heavy metals lies in the fact that they are actively absorbed by Phytoplankton, and then get to humans through the food chain.

At the same time, industrial enterprises, as a rule, are significant consumers of water from water bodies. Wastewater generated at enterprises after treatment is used in water circulation cycles (if possible) or after preliminary treatment at enterprises and reaching the maximum permissible concentrations of pollutants, it is discharged into the municipal sewage system.

In the world practice, considerable experience has been accumulated in preventing the adverse impact of waste on the environment. Such activities include their burial at specially prepared landfills, as well as their use as secondary raw materials in the national economy. Burial of certain types of waste at landfills is unprofitable due to pollution of the lithosphere (oc-

cupation of arable and other lands), as well as the construction of special landfills.

Due to the increasing load on wastewater treatment plants and the creation of new ones, Ukraine allocates significant capital costs for environmental protection (Table 1).

The impact of industrial wastewater on the deterioration of the environmental situation in Ukraine is increasing. This is due to the ineffective functioning of most treatment facilities, the lack of modern equipment and technologies for the treatment of industrial wastewater. So, over the past 19 years (1990–2019), the volume of water consumption in Ukraine has decreased from 35 615 million m³/year to 11 296 million m³/year, and the amount of specific pollutants discharged has increased [1].

Galvanic production is one of the most dangerous sources of environmental pollution, mainly of surface and underground water bodies, through the formation of a large volume of wastewater, as well as a large amount of solid waste, especially from the reagent method for neutralizing wastewater [1]. Compounds of metals, which are carried away by wastewater from galvanic production, have a rather harmful effect on the ecosystem of soil-plant-animal world-man [2]. This necessitates the creation of such a system of environmental protection which would exclude the possibility of copper connections getting outside the enterprise. In other words, the organization of production should be built in such a way that all solutions are used for a long time, and the water is circulating [3].

**Literature review.** Analysis of the patent and technical literature has shown that the solution to the problem of waste solutions is the transition to a production process based on a closed cycle in a single technological operation.

At the same time, waste water from enterprises has not been properly investigated; reliable designs and technologies have not been developed. They could provide special treatment to remove heavy metals [4].

Taking into account the current situation, we carried out several studies, which should serve as a basis for obtaining raw materials for copper smelting and improving environmental safety. Some of these tests and suggestions are outlined below.

Unsolved aspects of the problem. The etching characteristics of solutions, including copper-rolling ones, decrease as etched copper accumulates in them, which leads to a deterioration in the characteristics of the manufactured printed circuit boards (in this work, printed circuit boards are considered in which copper covering the base is widely used). At a high concentration of etched copper, the etching rate becomes so low that the subsequent use of this solution becomes impossible [4].

Discharge of 'depleted' pickling solutions serves as a source of environmental pollution; there is a need to spend

Table 1
Capital investments for environmental protection
(thousand of UAH)

		Including		
Year	Total	cleansing of return water	waste management	protection of soil, water
2014	7 959 853	1 122 149	783 965	359 925
2015	7 675 597	848 881	737 498	388 259
2016	13 390 477	1 160 029	2 208 676	419 988
2017	11 025 535	1 276 530	2 470 969	1 284 502
2018	10 074 279	1 692 640	1 182 045	1 444 291

<sup>&</sup>lt;sup>1</sup> Data for 2014–2018 are given without taking into account the temporarily occupied territories of the Autonomous Republic of Crimea, the city of Sevastopol and part of the temporarily occupied territories in Donetsk and Luhansk regions

quite large funds for the neutralization of wastewater. In addition, copper, which has passed into the solution during the pickling process, is lost irrevocably, and a large amount of valuable chemicals is needed to make a fresh pickling solution. All this leads to deterioration in the efficiency of the production of printed circuit boards and environmental pollution.

The greatest danger to the environment is possessed by mobile forms of chemical compounds, which determine the degree of toxicity and harmfulness of sludge waste from the production of boards and electroplating. The substances that make up the waste affect the cytogenetic characteristics of soil, water and ecosystems. A complete assessment of the intensity of soil pollution provides for an analysis of the combined action of factors of influence during the accumulation and accounting of the migration capacity of pollutants.

The main directions of the effect of the reagents on the soil are the phytotoxic effect of anions, the direct phytotoxic effect of water-insoluble reagents, changes in the composition of the absorbing complex of the soil, and the destruction of the soil structure [5].

In places of waste disposal, there is an established structure of technogenic lithochemical areas, which is manifested in different contents of heavy metals: zinc, nickel, iron and copper, depending on the characteristics of technological processes. At a distance of up to 0.3 km from the sites of sludge placement, the background concentration of zinc, nickel and copper in the soil may be exceeded, which leads to soil and water pollution, and a deterioration in the quality of life of the population. The biggest disadvantage of the neutralization process is the formation of sludge and the practice of storing them in sludge collectors. The components of sludge have a significant effect on human health [4].

**Purpose.** One of the most desirable ways to solve the problem of restoring the etching properties of solutions is to maintain their constant components during the entire etching process, waste water disposal and removal of etched copper, and electrochemical regeneration of etching solutions. The ability to electrochemically regenerate the properties of solutions based on ferric chloride and copper chloride has been proven by the works of foreign and domestic researchers [6].

Nowadays, devices for electrochemical regeneration of these solutions have been designed and introduced into production, which exclude harmful discharges and remove copper in the form of powder [4].

The issue of electrochemical regeneration of copper-ammonia pickling solutions with the release of copper in the form of a dense precipitate is relevant nowadays, which makes it possible to simplify the design of the regenerator electrolyzer: there is no need for a powder removal unit, which has a complex design.

The patent literature describes a variety of means of regeneration of pickling solutions that can reduce the cost of chemicals and waste disposal. Regeneration methods, that is, the resumption of the working characteristics of pickling solutions can be roughly divided into two methods: chemical and electrochemical. The possibility and effectiveness of this or that method depends on the solution that is used. Solutions based on chloride copper and copper sulfate (alkaline) have the ability to regenerate. The etching process in them can be expressed by the following equation

$$Cu + Cu(NH_3)_4^{++} \rightarrow 2Cu(NH_3)_2^{+}$$
 (1)

Chemical regeneration can be expressed by the following equation

$$2[Cu(NH3)2]+ + O2 + 4NH3 + 2H2O \rightarrow$$

$$\rightarrow 2[Cu(NH3)4]++ + 4OH-$$
(2)

Here, cuprous ions are oxidized by atmospheric oxygen or another oxidizing agent to a bivalent state. To maintain a constant composition of the solution in terms of the components that are included in its composition, in addition to the divalent copper salt, they are introduced into the solution in a calculated amount, and then the solution is diluted.  $NH_4OH$  is added to the solution to maintain the pH.

Although the solution regains its pickling characteristics, in the chemical regeneration process it is necessary to constantly remove the solution from the process, which leads to the cost for neutralizing the waste water and to the loss of copper. In addition, the adjustment of the solution for all components is associated with its constant analysis and does not always return the solution to its initial properties. With this type of chemical regeneration, although the cost of valuable chemicals for solution preparation is reduced, the etched copper is still lost [7].

Methods. The most economically viable method for regenerating depleted pickling solutions is the electrochemical method, in which there is a simultaneous release of etched copper in its pure form and the recovery of the pickling characteristics of the solution [8]. With this method, economic efficiency is due to a significant reduction in the cost of chemicals, a decrease in the cost of waste disposal and return of copper to production [9]. The electrolysis process can occur with and without the release of gases at the anode. A non-gassing process is more desirable because only copper is released from the pickling solution and there is no need to adjust the solution. In such a scheme, after the operation of etching and saturation of the solution with copper compounds in the etching module, the etching rate decreases and the etching solution should be replaced with a fresh one, capable of etching at a sufficient rate. The spent solution is sent to the factory treatment facilities for previous treatment, in which the residue can be discharged into the city sewer (after reaching the maximum permissible concentrations of pollutants established by the city water utility). After the sewage passes through the treatment facilities of the enterprise, sludge remains on its territory, which harms the environment of the state (and, naturally, the population) [10].

That is, the production of boards and electroplating, where copper is used as a conductive material and is vented in the process of preparing the surface for use (drawing and etching), can partially become a source of replenishment of the resources of scrap non-ferrous metals [11].

Surveys have shown that a range of metals — copper, iron, nickel, chromium, and others are discharged into wastewater by companies that manufacture printed circuit boards. So, with an annual one-shift operation of a PCB etching line with a productivity of 14 m²/hour, almost 28 000 m² of work pieces will be produced, and the amount of metal (copper) recovered will be approximately 14 000 kg, which at a price of 85 UAH/kg will be 14 000 kg  $\cdot$  85 UAH/kg = 1 190 000 UAH. In USD equivalent it is \$ 44 000.

This metal can be reused when using solutions for electrochemical regeneration of pickling solutions simultaneously with the main process. So the amount of metal that will be vented when the industrial production of boards is resumed can be (with one-shift operation and the number of lines in operation 350 pcs)  $14\,000\cdot350=4\,900\,000$  kg.

The negative side of PCB manufacturing is sludge formation. For example, let us consider the condition with the formation of sludge during the operation of the etching lines of printed circuit boards. With a pickling line productivity of  $14 \text{ m}^2/\text{h}$ , the amount of sludge in 8 hours of operation will reach more than 110 kg, which, with a monthly one-shift operation, will be 2400-2500 kg.

Modern enterprises, which, at the best time for production, produced approximately  $4 \cdot 10^3 \, \mathrm{m}^2$  of boards, accumulated on their territory 1500-3000 tons and more in the form of sludge, which are stored in containers, plastic bags and fall under the influence of atmospheric precipitation. In the course of the action of atmospheric precipitation on them, salts are washed out and pass into the ground, surface waters,

polluting the environment and increasing the level of environmental hazard. Therefore, the electrochemical regeneration of solutions is the basis for obtaining copper raw materials and increasing the environmental safety of the areas of production of boards.

For the proposed scheme of regeneration of the spent pickling solution, only solid electrodes as working ones were used. The ones most widely used for such purposes are platinum and graphite. Therefore, in this work, they were taken as a basis for testing. In order to replace expensive platinum, the possibility of using a titanium electrode for analysis was investigated. A preliminary experiment was carried out on the corrosion behavior of titanium in a pickling solution. The mass of a titanium wire sample with a length of 100 mm and a diameter of 0.7 mm (0.2104 g) after 115 hours of exposure in an etching solution did not change when weighed on an analytical balance. This made it possible to use a titanium electrode in the etching solution as a working one.

The temperature of the solution was maintained within 45 °C. To regulate the pH of the solution and its effect on the etching rate, aqueous ammonia (25 %), or synthetic liquid ammonia was used, which was placed in a separate room outside the workshop. The research process was carried out using etching solutions, the composition of which is presented above.

The effect of pH on the etching rate is essential for obtaining the etching rate in the range of  $35-38 \mu m/min$ . Maintaining the pH in the range of 8.3 to 8.55 makes it possible to provide the required etching rate combined with the rate of copper deposition on the cathode system of the regeneration unit.

Tests of the regeneration unit together with the pickling machine and the installation for separating and supplying ammonia solution made it possible to choose batch-type apparatuses (Fig. 1), which are simpler in design and convenient in operation compared to continuous-action apparatuses.

Table 2 Concentrations of the components used in the tests

No.	Component namesx	Indicators, kg/m <sup>3</sup>
1	ammonia complex of copper dichloride (for metal)	40-60
2	ammonium chloride	50-100
3	ammonia water (25 %), or synthetic liquid	fluent
4	orthophosphoric acid	20-30
5	pH solution	fluent

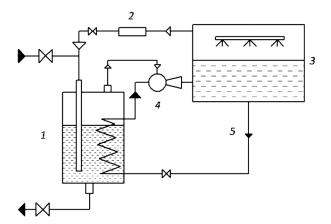


Fig. 1. Scheme of the ammonia installation for feeding of periodic action for an aqueous copper and alkaline solution.

1 – desorber; 2 – filter; 3 – pickling machine; 4 – ejector; 5 –

To exclude the loss of ammonia into the environment, the air from the working chamber of the pickling machine 3 through filter 2, where drops of pickling solution are captured, enters the desorber 1 and is saturated with ammonia. The ammonia-air mixture is sucked in by the ejector 4, the working fluid of which is the pickling solution. In the ejector, ammonia is absorbed by the pickling solution, and air is returned to the working chamber of the pickling machine. To intensify the desorption process, the aqueous-ammonia solution in the stripper is heated with an aqueous pickling solution. The desorption process stops when the ammonia water in the desorber reaches 5 % by weight, after which the ammonia solution is replaced with a fresh one. For the research, a line for etching printed circuit boards with an aqueous copper-alkaline solution was used. In this case, the regenerator used to recover the solution is set for a copper productivity in the range of 3-4 kg/h.

The rate of desorption of ammonia was calculated by the formula (g/hour)

$$G = \frac{(V_H \cdot C_H) - (V_K \cdot C_K)}{\tau},\tag{3}$$

where,  $V_H$ ,  $V_K$  are the initial and final volumes of the solution;  $C_H$ ,  $C_K$  are the initial and final concentrations of ammonia, g/l;  $\tau$  is time of desorption, h.

Based on the test results, it was proposed to use the correction device in conjunction with an electrochemical recovery (regeneration) installation. This fact makes it possible to create equipment that can operate in an automatic mode and introduce a low-waste energy-saving technological process for aqueous solutions, which in turn will reduce the burden on the environment due to a sharp decrease in the discharge of spent pickling solutions and improve environmental safety.

Another, no less important, circumstance is the fact that through the roughness of the initial surface, respectively, the density of the cathode deposit is constantly decreasing. As a result, grains of copper powder appear on the electrode surface, which increase the cathode surface and reduce the current density.

The same process contributes to an increase in micro densities at individual points of the surface, which leads to a further increase in roughness and, as a consequence, the formation of powders.

Additional cleaning or electro polishing of electrodes allows improving the parameters of the processes (to increase the current efficiency). After cleaning the electrodes, the original current efficiency and performance are restored.

The dependence of the average value of the breakout force P on the surface cleanliness is shown in Fig. 2, and the dependence of the relative deviation  $\delta$ , % on the average value of the breakout force and the cleanliness of the electrode surface is shown in Fig. 3.

The quality assessment of the deposited copper was determined by conducting micro structural studies. Two plates  $10 \times 10$  mm in size were cut from the deposited plate and filled in with epoxy resin.

The microstructure of the deposited copper was investigated on a MIM-7 microscope and photographed. Fig. 4 shows the microstructure of deposited copper (longitudinal section). When examining the samples, a microstructure was found that allows the samples to be characterized as follows. The outer surface is clean, well washed from electrolyte residues and slags, does not have a coating of copper sulfates. No mushroom-shaped dendritic outgrowths or large porous copper outgrowths were found.

Fig. 5 shows the microstructure of the plate surface (a micro section is cut across the plate), which makes it possible to reveal the pores, the overwhelming majority of which have a teardrop shape. Some of them look like end-to-end channels. The pores are evenly distributed on the sample surface. Their diameter does not exceed 10–20 microns. The study of a mi-

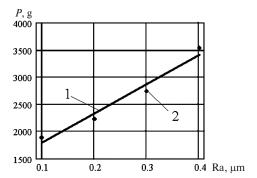


Fig. 2. Dependence of the average value of the breakout force P on the surface cleanliness

 $1-approximated\ value;\ 2-experimental\ value$ 

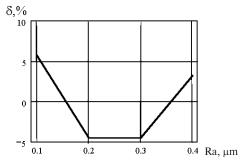


Fig. 3. Dependence of the relative deviation  $\delta$ , % of the average value of the breakout force and the cleanliness of the electrode surface

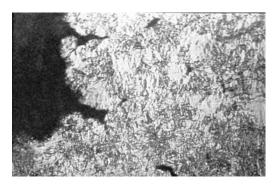


Fig. 4. Microstructure of deposited copper (longitudinal section), enlarged ×120

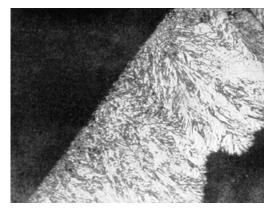


Fig. 5. Microstructure of deposited (cross-section) copper, enlarged ×120

cro section cut in the transverse direction of a copper plate made it possible to reveal the presence of dense layers, which differ in their structure. The first layer was formed at the beginning of the nucleation of the growth zone at a high initial current density and has a fine-grained structure. The width of this zone is 12–14 microns. The grain size does not exceed 1–2 microns.

The second layer consists of columnar dendrites. Dendrite branches are  $7{-}8$  microns long, and the height of the dendrites reaches  $40{-}50$  microns. With a large thickness of the sediment, complete accretion of dendrites occurs. A layer of columnar dendrites remains compact until the dendrites reach a length of  $30{-}35~\mu m$ , after which, with the growth of dendrites, the layer's density is lost and it acquires perforation.

The physicomechanical properties of electrolytic coatings were investigated by metallography, by measuring the extreme contact angle, by flexible cathode, swinging pendulum and scanning electron microscopy, by measuring micro roughness. The study on surface morphology, including the study on the fine structure of galvanic copper was carried out.

The texture of copper coatings was studied by metallographic etching. To identify the etching figures, a solution of the composition was used:

 $FeCl_3 \cdot 6H_20 - 5 g; \\ HCl - 30 ml; \\ H_2O - 100 ml.$ 

Etching time is 2.5-3 min. The etching pattern was observed using an optical microscope MMU with a magnification of 370 and a scanning electron microscope SEM. Identification of the microstructure of copper coatings by etching metallographic sections and determining the micro roughness of the coating was carried out. The sediment growth coefficient was determined by the optical method by measuring the width of the conductor before and after coating with galvanic copper with a thickness of 15  $\mu$ m. The growth rate was calculated using the formula

$$K_h = \frac{\Delta d}{2h}$$

where  $\Delta d = d_2 - d_1$ ;  $d_2$  is conductor width after coating,  $\mu$ m;  $d_1$  is the width of the conductor to the coating,  $\mu$ m; b is coating thickness, microns.

Internal stresses were determined by the flexible cathode method. A thin metal plate several centimeters long was taken as a cathode, which was fixed in the upper part, while its lower end moved freely.

The cathode on the side opposite to the anode was covered with a thin layer of insulating varnish so that the metal was deposited on one side only. As the metal was deposited under the action of internal stresses arising in the deposit, the cathode plate was bent, the value of which changed depending on the change in internal stresses.

The value of internal stresses was calculated using the formula (kg/cm²)

$$b = \frac{E \cdot d^2 \cdot \Delta}{3 \cdot \ell^2 \cdot h},$$

where E is the elastic modulus of the cathode material, kg/cm<sup>2</sup>; d is the thickness of the cathode, cm;  $\Delta$  is cathode deviation, cm; h is cover of thickness, cm.

The pendulum method was used to determine the hardness of galvanic deposits.

The studies performed and their results do not prevent the use of deposited copper as electrodes, or its remelting with subsequent use as a conductive and structural material.

To assess the tests conducted, the initial data and the calculation of the total hazard index of sludge from the production of boards and electroplating were carried out for one of the enterprises in the city of Khmelnytskyi.

After the implementation of the proposals suggested in the work, the amount of copper compounds, which were released in the form of sludge, dropped sharply. The performed calculation showed an increase in the total safety index.

The amount of separated sludge that will be stored at the treatment facilities of the enterprise will reach minimum values, the value of which can be calculated from the following provisions:

- the solution will work unchanged for 2-3 months;
- the average value of the mass of sludge per month will be 1 kg from one installation

Taking into account the fact of creating equipment that seems environmentally friendly and energy-saving, we have the opportunity to assess how the economic indicators of equipment created on the basis of this study are provided. At the same time, we must take into account the specific parameters of installations that create the possibility of reusing aqueous solutions without being discharged to treatment facilities of both enterprises and cities.

When determining economic feasibility, we must proceed from the criterion of reducing the damage to the environment. The calculation of the economic efficiency from the introduction of new equipment was carried out for the annual program for the production of billets and in dollar terms amounted to \$63 000. After removing copper compounds from wastewater (not converted to sludge), the overall hazard index becomes more acceptable.

The introduction of a new wastewater treatment technology with only one unit, in addition to the economic effect, will improve the environment and make it possible to implement an environmentally friendly process of copper utilization.

#### Conclusions.

- 1. Regeneration of the pickling solution will make it possible to obtain copper which can be used for subsequent remelting at metallurgical enterprises, metallization of boards.
- 2. The use of the correction device together with the installation of electrochemical recovery (regeneration), allows creating equipment that can operate in an automatic mode and introduce a low-waste energy-saving technological process for aqueous solutions.
- 3. The created equipment improves the ecological situation in the area where the enterprise is located.

### References.

- **1.** *National report on the state of the environment in Ukraine* (2018). Retrieved from <a href="https://mepr.gov.ua/files/docs/Zvit/2020">https://mepr.gov.ua/files/docs/Zvit/2020</a>.
- **2.** Petryk, A., Chop, M., & Pohrebennyk, V. (2018). The assessment of the degree of pollution of fallow vegetation with heavy metals in rural administrative units of Psary and Płoki in Poland. *18th International multidisciplinary scientific geoconference SGEM Ecology and environmental protection: proceedings 2018*, (pp. 921-928).
- **3.** Pohrebennyk, V., Karpinski, M., Dzhumelia, E., Kłoswitkowska, A., & Falat, P. (2018). Water bodies pollution of the mining and chemical enterprise. *18<sup>th</sup> International multidisciplinary scientific geoconference SGEM Ecology and environmental protection: proceedings 2018, (pp. 1035-1042).*
- **4.** Nester, A.A. (2016). *Wastewater treatment of printed circuit board production: monograph*. Khmelnytskyi: Khmelnytskyi National University.
- **5.** Nester, A. A., & Evgrashkina, G. P. (2017). Forecast of contamination of the machine-building enterprise with slimes in the production of boards and electroplating. *News of the Tul-State University. Technical science*, (6), 193-200.
- **6.** Klyachkin, V. N., Shirkunova, K. S., & Bart, A. D. (2019). Analysis of the Stability of the Chemical Composition of Wastewater in the Production of Printed Circuit Boards. *Ecology and Industry of Russia*, *23*(5), 47-51. <a href="https://doi.org/10.18412/1816-0395-2019-5-47-51">https://doi.org/10.18412/1816-0395-2019-5-47-51</a>.
- 7. Pashayan, A.A., & Karmanov, D.A. (2018). Recycling of Electroplating Wastes without Formation of Galvanic Sludges. *Ecology and Industry of Russia*, 22(12), 19-21. https://doi.org/10.18412/1816-0395-2018-12-19-21.
- **8.** Prolejchik, A.Y., Gaponenkov, I.A., & Fedorova, O.A. (2018). Extraction of Heavy Metal Ions from Inorganic Waste-

water, *Ecology and Industry of Russia*, 22(3), 35-39. <a href="https://doi.org/10.18412/1816-0395-2018-3-35-39">https://doi.org/10.18412/1816-0395-2018-3-35-39</a>.

- **9.** Dorokhina, E. Y., & Kharchenko, S. G. (2017). Circular Economy: Problems and Ways of Development. *Ecology and Industry of Russia*, *21*(3), 50-55. <a href="https://doi.org/10.18412/1816-0395-2017-3-50-55">https://doi.org/10.18412/1816-0395-2017-3-50-55</a>.
- **10.** Vershinina, I.A., & Martynenko, T.S. (2019). Problems of Waste Recovery and Socio-Ecological Inequality. *Ecology and Industry of Russia*, *23*(5), 52-55. <a href="https://doi.org/10.18412/1816-0395-2019-5-52-55">https://doi.org/10.18412/1816-0395-2019-5-52-55</a>.
- 11. Pohrebennyk, V., Cygnar, M., Mitryasova, O., Politylo, R., & Shybanova, A. (2016). Efficiency of sewage treatment of company "Enzyme". *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM, 2*, 295-302.

# Досягнення екологічної безпеки з економічним ефектом

А. А. Нестер<sup>1</sup>, О. О. Никитин<sup>1</sup>, О. В. Романишина<sup>1</sup>, Л. О. Мітюк<sup>2</sup>, Ю. О. Полукаров<sup>2</sup>

1 — Хмельницький національний університет, м. Хмельницький, Україна, e-mail: nesteranatol111@gmail.com
2 — Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського», м. Київ, Україна

Скидання та збереження на території підприємств відпрацьованих травильних розчинів призводить до забруднення навколишнього середовища, вимагає значних витрат при їх знешкодженні на підприємстві й на очисних спорудах у місцях розташування виробництв.

**Мета.** Уточнення відомих раніше, але недостатньо вивчених процесів очищення стічних вод і представлення результатів дослідження, проведених випробувань для отримання міді зі стічних вод і створення екологічно безпечного обладнання.

**Методика.** У даній роботі вивчені окремі процеси регенерації мідно-аміачних травильних розчинів із застосуванням електрохімічної технології для отримання щільних опадів міді, виділення яких різко скорочує утворення та зберігання на території підприємств відходів у вигляді шламів.

Результати. Відзначено, що хімічне коригування травильних розчинів призводить до утворення значної кількості стічних вод, шламів, у складі яких присутні важкі метали, що негативно впливає на грунти, підземні води, рослинний світ і людину, як вершину харчового ланцюга. Щоб уникнути накопичення шламів на території підприємств, запропоновано використовувати технологіями регенерації відпрацьованих розчинів травлення, за яких не утворюються шлами, а виділений метал використовують як вторинну сировину для виробництва міді. При цьому регенерований травильний розчин повторно використовують для травлення друкованих плат. Створення обладнання для регенерації використаних розчинів з виділенням металу у вигляді, придатному для переплавки, стає важливим елементом збереження навколишнього середовища та одержання сировини для кольорової металургії України.

Наукова новизна. Уперше виконані комплексні дослідження, що дозволили створити перспективне обладнання очищення промислових стічних вод. Лінія травлення друкованих плат, створена на основі досліджень, передбачає повторне використання в технологічному процесі використаного водного травильного розчину після його регенерації. Одночасно передбачено використання промивних вод лінії для поповнення виведеного травильного розчину.

**Практична значимість.** Використання процесу з виділенням міді щільними осадами дозволяє полегшити зняття металу простими механічними операціями та

уникнути складної конструкції для вилучення міді у вигляді металевих порошків.

**Ключові слова:** регенерація, шлами, травильний розчин, мідь, катод, промивні води

# Достижение экологической безопасности с экономическим эффектом

 $A. A. Hecmep^1, A. A. Huкитин^1, O. B. Романишина^1,$  $Л. А. Митюк^2, Ю. А. Полукаров^2$ 

1 — Хмельницкий национальный университет, г. Хмельницкий, Украина, e-mail: nesteranatol111@gmail.com
2 — Национальный технический университет Украины «Киевский политехнический институт имени Игоря Сикорского», г. Киев, Украина

Сбрасывание и сохранение на территории предприятий отработанных травильных растворов приводит к загрязнению окружающей среды, требует значительных затрат при их обезвреживании на предприятии и на очистительных сооружениях в местах расположения производств.

**Цель.** Уточнение известных ранее, но недостаточно изученных процессов очищения промышленных сточных вод, представление результатов исследования и проведенных испытаний для получения меди из сточных вод, создание экологически безопасного оборудования.

**Методика.** В данной работе изучены отдельные процессы регенерации медно-аммиачных травильных растворов с применением электрохимической технологии для получения плотных осадков меди, выделение которых резко сокращает образование и хранение на территории предприятий отходов в виде шламов.

Результаты. Отмечено, что химическое корректирование травильных растворов приводит к образованию значительного количества сточных вод, шламов, в составе которых присутствуют тяжелые металлы, что отрицательно влияет на грунты, подземные воды, растительный мир и человека, как вершину пищевой цепи. Чтобы избежать накопления шламов на территории предприятий, предложено использовать технологию регенерации отработанных растворов травления, при которой не образуются шламы, а выделенный металл, используют как вторичное сырье для производства меди. При этом регенерированный травильный раствор повторно используют для травления печатных плат. Создание оборудования для регенерации использованных растворов с выделением металла в виде, пригодном для переплавки, становится важным элементом сбережения окружающей среды и получения сырья для цветной металлургии Украины.

Научная новизна. Впервые выполнены комплексные исследования, которые позволили создать перспективное оборудование очищения промышленных сточных вод. Линия травления печатных плат, созданная на основе исследований, предусматривает повторное использование в технологическом процессе использованного водного травильного раствора после его регенерации. Одновременно предусмотрено использование промывных вод линии для пополнения выведенного травильного раствора.

Практическая значимость. Использование процесса с выделением меди плотными осадками позволяет облегчить снятие металла простыми механическими операциями и избежать сложной конструкции для изъятия меди в виде металлических порошков.

**Ключевые слова:** регенерация, шламы, травильный раствор, медь, катод, промывные воды

Recommended for publication by T. F. Yakovyshyna, Doctor of Technical Sciences. The manuscript was submitted 02.04.20.