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Ecological, Economic and Practical Aspects of Water Treatment in the Galvanic Industry

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ABSTRACT

The galvanic industry and the production of printed circuit boards are a significant source of environmental pollution, they pose a threat comparable to the chemical industry. They pollute both the atmosphere, the biosphere and the hydrosphere. The paper presents an assessment of the negative impact on the environment, galvanic production and the resulting post-production waste. It was proposed to use the technology of regeneration of used treating solutions, in which the recovered metal can be reused as a secondary raw material for the production of copper products. The regenerated solution, on the other hand, can be used to treat integrated circuit boards. As part of the work, with the use of a microscope, the structural characteristics of the metal surface obtained as a result of the applied regeneration process were carried out. The indicator of the total exposure to substances present in the deposit formed during production was determined, both before (0.045) and after the introduction of the new technology (100). The economic analysis of the planned project based on the new technology showed that the implementation of the presented method of wastewater treatment allows for obtaining significant benefits, both financial and environmental. The analyses performed can be a valuable source of information on how to reduce the impact environment during the production of integrated circuit boards, as well as on the possibilities of obtaining less expensive materials in the form of secondary raw materials.

Keywords: copper, electroplating, sewage, printed circuit board, regeneration, environmental safety, economic effect

INTRODUCTION

The resources of copper ore deposits in the Volyn Oblast of Ukraine constitute, on average, about 1.0% of the content of this metal and are estimated at 28 million tons. The annual demand of Ukrainian enterprises for this metal ranges from 120 to 140 thousand tons. Most of the demand for this raw material is provided by imports from Russia and Poland, and only 20% of the demand comes from the domestic processing of metal objects obtained from recycling [Chervonyy et al. 2014]. Extraction of copper ore by opencast method is characterized by relatively low financial outlays and the possibility of using devices with high processing capacity [Chervonyy et al. 2014; Nester 2016; Pohrebennyk et al. 2019].

Open-pit mining of the deposits contributes to the formation of mining areas with a limited possibility of their use. In addition, this method often causes irreversible geomorphological changes to the terrain, which directly affect the landscape of the environment. As part of field work in opencast mines, specialized geological and drilling work is required. In order to minimize the input of the collected minerals, it is required to use a rational direction of their management. Open-pit mining of deposits generates the necessity to use both the main mineral and the accompanying minerals. Careful management of minerals contributes to the limitation of mining areas and the minimization of other areas. From some of the raw materials obtained, it is possible to obtain pro-ecological materials. In addition, sustainable opencast mining makes it possible to protect resources against their irreversible loss. It has economic significance by increasing the supply of materials made from the obtained minerals [Pękala 2019, 2020].

The second commonly used method of extracting copper ore is underground mining. It is used when there is no economic or technical justification for carrying out the works with the opencast method. The activity of underground mines has a lesser impact on the natural environment than opencast mines. As a result of this type of activity, the demand for iron – 20%, copper – 45%, zinc – 70%, tin and lead – 75% and 100% of the demand for tungsten is ensured. The cost of ore extraction using the underground method is much higher compared to the opencast method [Pashayan et al. 2018, Prolejchik et al. 2018]. The current exploitation of copper deposits in Ukraine by opencast method is carried out at depths of up to 250 m. However, the growing demand for raw materials and the decreasing amount of readily available resources mean that they must be obtained from deeper and deeper deposits, thus increasing the cost of technology. The trend for the dredging of existing mines is observed all over the world. When analysing the resources of global ore extraction, Canada draws attention, where ores containing gold, copper and nickel are mined at depths of 1800–2600 m. In the United States of America, copper and gold are mined at 1,700-3,000 m. In India, gold is obtained from a depth of 3500 m. In South Africa, mining is carried out at depths above 4000 m [Chervonyy et al. 2014, Nester 2016]. The use of Ukrainian land for the extraction of raw materials is regulated by their national mining law. This document imposes mandatory assurance of safe and rational extraction and use of mineral resources [Chervonyy et al. 2014, Nester 2016].

Electroplating production is one of the most dangerous sources of environmental pollution, mainly surface and ground waters. This is mainly due to the formation of large amounts of sewage during production, as well as a large amount of solid waste. Metal compounds that are discharged with wastewater from electroplating production have a very detrimental effect on the environment [Grizzetti et al. 2017, Mitryasova et al. 2016, Makisha et al. 2016, Oliveira et al. 2007].

When using electroplating processes, there is a risk of emergencies related to waste disposal and direct technological processes. In the event of an unfavorable development of crisis situation, preventive measures are introduced to stop the unfavorable development of events. Electroplating processes and improper handling of the generated waste pose a huge threat to humans and the natural environment. The probability of occurrence of adverse changes in the natural environment or long-term negative effects of these changes resulting from the negative impact on the environment is defined as the environmental risk [Karpinski et al. 2018, Nester 2016, Pohrebennyk et al. 2017].

Ukrainian companies in their country produced about 410^3 m^2 of boards per year, which had a negative effect on the production of about 1500-3000 tons of waste per year. Post-production waste stored in containers and plastic bags when exposed to weather conditions poses a threat to the natural environment. During precipitation, chemicals are leached and then get into soils and surface waters [Matukhno et al. 2019, Zaporozhets et al. 2018].

Several companies are responsible for the production of printed circuit boards in Ukraine, including: “ETAL” Kirovograd, which produces about 4–5 thousand m^2 of boards per year, and its production capacity is estimated up to 50,000 m^2 of boards; “Galvanotechnics”, Kiev plant “Radar”, “Novator” (Khmelnytsky) with a capacity of 0.9 thousand m^2; “Concern-Elektron” – 0.8 thousand m^2.

Thus, only one company can discharge up to 5-6 tonnes of copper per year along with sewage or collected sludge, contributing to a negative environmental impact. In Kiev, until 1992, over 20 tonnes of copper were generated annually as waste. For example, the plant “Electronmash” etched 15,000 m^2 of plates per year (which leads to the release of 7,500 kg of copper) [Nester 2016].

The use of technology for the regeneration of used etching solutions would avoid the accumulation of problematic sediments on the enterprise areas. Its aim is to reuse copper as a secondary raw material. The regenerated solution, on the other hand, could be reused in the etching process of printed circuit boards [Nester and Drapak 2008, Nester and Evgrashkina 2017, Girnychyy and Zakon 1999].

The complexity and severity of the problem results from the fact that Ukrainian consumers, in order to meet the demand for this raw material, are forced to purchase a significant part of copper outside their country. Unfortunately, the production capacity of rolled copper and its alloys in Ukraine is limited due to a lack of raw materials. Additionally, a significant proportion of copper scrap and waste is exported. Although the export of rolled copper and its alloys is much more profitable compared to the export of copper scrap and waste. For each ton of exported rolled products, up to $ 1,000 can be obtained, while the annual figure is around $ 30-40 million. However, the analysis of patent and technical sources showed that due to the lack of raw materials intended for the smelting of non-ferrous metals, the issue of copper recovery from wastewater is not sufficiently profitable [Nester 2016, Prolejchik et al. 2018].

The production technology of non-ferrous metals has its own specificity, resulting from the low content of non-ferrous metals in the ore compared to the amount of iron (in non-ferrous ores - the content is only a few percent), as well as the presence of other metals in the ore. In particular, ores with an average metal content of 2-3% are used for the production of copper. However, the transport of the raw material is impractical. Consequently, copper smelting must take place close to where it is mined. In the first step, the copper ores are enriched to obtain a copper concentrate with a metal content of 35%. The material is then melted and cleaned. The last stage of this process involves the removal of impurities from the product (the so-called refining) [Nester 2016]. In addition, other non-ferrous metals can be obtained from copper ore using a special technology. During the smelting process, the specific electricity consumption is between 230 and 350 kWh per 1 ton of copper. Thus, the technological process requires relatively large amounts of electricity. On the other hand, the production of non-ferrous metals from scrap is 25 times cheaper, and the costs of transporting raw materials are several times lower by even 5-6 times. Electricity consumption is much lower, which has a direct impact on the quality of the environment [Nester 2016].

However, the resource base of non-ferrous metals in Ukraine is insufficient and does not meet the demand for these products. Consequently, many companies use imported raw materials or processed scrap of non-ferrous metals for their production. Plate production and electroplating can also be a source of non-ferrous scrap [Pashayan et al. 2018, Prolejchik et al. 2018, Nester 2016, Bloomberg 2014].

Currently, the most popular technologies for recovering metals from the water phase do not provide the necessary efficiency of water treatment for its reuse. These processes lead to the formation of toxic sludge, which is collected on the areas of the Ukrainian enterprises. Non-ferrous metallurgy is primarily a source of environmental pollution with heavy metals [Prolejchik et al. 2018, Bloomberg 2014, Klyachkin et al. 2019]. The use of the ion exchange process in the plating industry enables the creation of closed water reuse systems. However, unresolved questions regarding the application of possible regeneration methods remain [Vershinina and Martynenko 2019, Pohrebennyk and Petryk 2017].

MATERIALS AND RESEARCH METHODS

Ukrainian companies producing printed circuit boards generate waste containing metals such as copper, iron, nickel, chromium and others. For example, during the year, during the operation of one technological line with a capacity of 14 m^2/h, almost 28,000 m^2 of semi-finished products are created. On the other hand, copper is obtained in the etching process in the amount of about 14 tons. Assuming a unit profit of 3.2 $/kg, you get an annual recovery of about $ 4,500. The industrial production of plates (one-shift production, the number of lines in operation at the level of 350 pieces) generates this metal in the form of waste in the amount of 4,900 tons. However, this metal can be reused.

As a result, the use of copper recovery methods from electroplating and plate production wastewater can provide part of the domestic copper demand. The methods of treating wastewater from galvanic production are presented in Figure 1 [Bazrafshan et al. 2015, Voloshkina et al. 2015].

The research material was obtained from the regeneration of waste from metallurgical plants. The obtained metal is characterized, which can be used as a secondary raw material in metallurgical

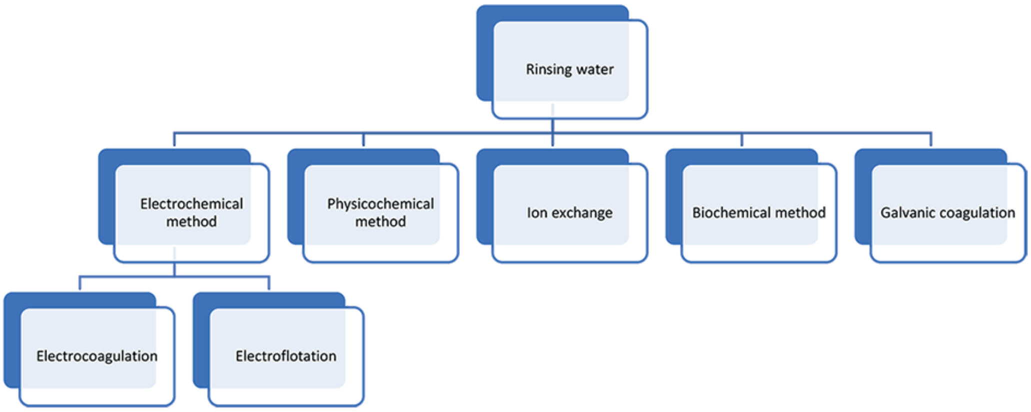

Fig. 1. Methods of wastewater treatment from galvanic production

plants or can be directly used for the production of printed circuit boards. When using electrodes with copper as a secondary raw material, its new characteristic properties should be taken into account. Above all, the composition of the cathode material and the cleanliness of the surface after treatment are important. For this purpose, the influence of surface roughness on the value of the force causing the desorption of the Cu metal layer from the electrode (cathode) surface was analysed.

Measurements were made using an LH-3m dynamometer with a sediment thickness of 1.5 mm. The width of the strip was 0.025 m, the length was 0.15 m. In order to maintain a constant separation angle during the analysis, the dynamometer was moved in an inclined plane. The adhesion of the deposited copper to the electrode surface was assessed on the basis of the value of the force causing the desorption of the Cu metal layer from the electrode surface. The measurement of the arithmetic mean of the roughness profile Ra for the electrodes was carried out by the contact method using a profilometer (model 283).

In the process of continuous operation of the regenerators, the reactive surface of the electrodes increases, which reduces the actual current density and causes the electrode with the deposited copper to melt. As a result, the efficiency of the copper separation process from the electrode is reduced. It is then necessary to ensure reprocessing of the electrodes. An important aspect is also the decreasing density of the cathode material resulting from the original surface roughness. Consequently, copper powder particles appear on the electrode surface, which increase the cathode surface area and at the same time reduce the current density. The same process contributes to an increase in the micro-density at some points on the surface, which results in a further increase in roughness, resulting in the formation of cathode deposits that are released in the form of powders.

Cleaning or electropolishing of electrodes allows to improve the quality of process parameters, among others by increasing the current output power. The research confirms that after cleaning the electrodes, the initial value of the output current and the efficiency of the process are restored. The quality of the separated copper was assessed using microstructural tests. The microscopic analysis of the microstructure was performed on the cross-sectional and longitudinal sections of the sample taken from the most characteristic parts of the tested plate. Samples in the shape of parallelepipeds with dimensions of 0.01x0.01x0.02 m were tested. In order to completely remove any unevenness, the surface of the specimens was polished with sandpaper with a gradual change in the grain size in the range of 125–20 μm to the grain size within 28–3.5 μm. Polishing is carried out with diamond pastes on a metal disc covered with felt. Examination of the surface of the blanks immediately after polishing revealed dark pore areas in the light field. The samples were digested to obtain a complete picture of the microstructure. First, the surface of the samples was degreased with alcohol, and then immersed for a few minutes in a reagent with the following composition: hydrogen peroxide (H_2O_2) and aqueous ammonia solution (NH_3).

The microstructure of the deposited copper was examined using a metallographic microscope, model MIM-7.

The risk characterization for a given site is based on the integration of the results of the toxicity assessment and the exposure assessment. The risk is determined separately for carcinogenic and non-carcinogenic substances in the developed exposure scenarios. The exposure factor for copper compounds discharged with sludge is determined as follows [Ukrainian State Sanitary Rules and Regulations 2.2.7.029-99]:

$$K_i = \frac{MPC_{\text{з}}}{(S + C_w)_{\text{з}}} \qquad (1)$$

where: K_i – exposure index;
MPC_i – the maximum permissible content in the soil of the chemical substance introduced with the waste, mg/kg;
S – the solubility of the chemical in water;
C_w – the content of a chemical substance in the mass of waste, mg/kg.

In turn, the indicator of the total exposure to these substances was determined using the formula:

$$K = \frac{1}{n^2} \sum\nolimits_{i=1}^{n} K_i \qquad (2)$$

where: n – number of hazardous substances present in sludges from plate production and electroplating.

The toxicity factor of an individual chemical component in a waste is calculated using the formula:

$$K_c = \frac{\lg(LD_{50})i}{(S + 0{,}1F + C_w)i} \qquad (3)$$

where: LD_{50} – the mean dose which causes the death of 50% of the organisms used in the experiment after a single administration of the analysed substance;
S – the solubility of the chemical in water;
F – the volatility of the chemical;
C_w – chemical content in the mass of waste or its share t/t.

Assessing the risk of exposure to heavy metals requires the calculation of the Average Daily Dose (LADD), averaged over the life expectancy (70 years) according to formula (4). LADD is used to assess the exposure of substances with no threshold activity, ie substances that may cause adverse health effects independent of the concentration in which they occur.

$$LADD = \frac{C \cdot CR \cdot ED \cdot EF}{BW \cdot AT \cdot 365} \quad (4)$$

where: $LADD$ – average daily dose, mg/(kg×d);
C – the content of the analysed substance in the soil, mg/kg;
CR – the amount of contact with a given environmental medium per unit of time, kg/d;
ED – the lifetime of the subject during which the exposure has occurred, years;
EF – frequency of exposure, days/year;
BW – average body weight, kg;
AT – averaged exposure time (days, years, in the so-called chronic lifetime exposure, most often taken as AT = 70 years);
365 – the number of days in the year.

Assessment of the risk related to exposure to toxic substances with a threshold effect (the toxic effect is observed above a certain concentration (threshold), and below this threshold their harmfulness is not identified) is expressed by comparing the actual or potential exposure to the reference level determined for a given substance according to the formula:

$$HQ = AD/RfD \qquad (5)$$

where: HQ – hazard factor;
AD – average dose, mg/kg;
RfD – reference dose (safe), mg/kg.

If HQ is greater than 1, there is a certain risk of non-carcinogenic toxic effects from exposure to the substance. The hazard index (HI) using formula (6) is calculated if the exposure is caused by more than one substance:

$$HI = \sum_{i}^{n} HQ_i, \qquad (6)$$

where: HQ_i – hazard factors for individual substances.

If the hazard index is greater than 1, an exposure sensitivity analysis for the individual doses is necessary. The risk of substances with teratogenic and carcinogenic properties is determined by giving the value of the probability of cancer occurrence. Consequently, the carcinogenic risk is estimated as the lifetime probability of developing cancer as a result of exposure to a given carcinogen (in the analyzed case for nickel) by a given exposure route. For this purpose, the following formula is used:

$$CR = LADD \cdot SF \qquad (7)$$

where: SF – slope factor appropriate to the route of exposure, (mg/(kg×day)).

It is a factor for converting the absorbed dose of a carcinogenic substance to the health effect, i.e. the probability of cancer occurrence, the so-called carcinogenic potency coefficient of the analyzed substance.

The total carcinogenic risk is calculated by summing the calculated risk for individual carcinogens, then compared with the acceptable (acceptable) risk level, which is most often taken from 1×10^{-6} to 1×10^{-4}.

If the total carcinogenic risk resulting from contamination of a given environmental medium (e.g. soil) is greater than 1×10^{-4} or the total hazard index exceeds 1, then local remediation criteria are determined, necessary to select the appropriate remediation or management method. chemically degraded land, including the assessment of the economic aspects of planned activities [Alekhya et al. 2013, Bates et al. 2008, Dorokhina and Kharchenko 2017].

RESULTS AND DISCUSSION

Technological scheme for etching and regeneration

In order to prevent the accumulation of deposits on the areas of enterprises, it is proposed to apply the technology of regeneration of spent etching solutions, in which the separated metal is used as a secondary raw material for the production of copper and the regenerated solution is reused to etch printed circuit boards. Figure 2 shows the proposed technological scheme for pickling with the regeneration process [Nester 2016].

Research results of the copper deposition process

Figure 3 shows the measurement data obtained during the copper deposition process on stainless steel electrodes (08X17TM). The deposition of the coatings was carried out at a current density in the range of 15–25 A/dm^2. The required surface roughness was achieved by machining. The influence of the force causing the desorption of the Cu metal layer from the electrode surface (*R*) depending on the surface roughness of the electrode and the influence of the relative deviation δ% depending on the approximate average value of R and surface cleanliness, as well as the effect of the force R depending on the surface cleanliness for the value estimated and experimental studies are presented in Figures 3–5. The analysis of the test results confirms that the lower the surface roughness of the electrodes, the lower the force needed to separate the metal.

The analysis of the microstructure of the precipitated copper in the longitudinal section did not reveal the presence of impurities, electrolyte residues, slag and copper sulphate. The image showed no dendritic growth and no porous copper layer (Fig. 6).

The cross-sectional examination of the sample showed microstructural differentiation of the precipitated copper. It has been shown that the nature of the tested material is two-layered. The first layer is characterized by a fine-grained structure. It is the first generation of material, created at the beginning of the metal layer growth as a result of the high current density. The increase in the cathodic current density leads to the formation of layers that are less and less dense, with increasingly finer grains, reaching the final stage of powder deposits. The width of this layer is 12–14 µm, the grain size does not exceed 1–2 µm. The next generation is formed by a layer in the

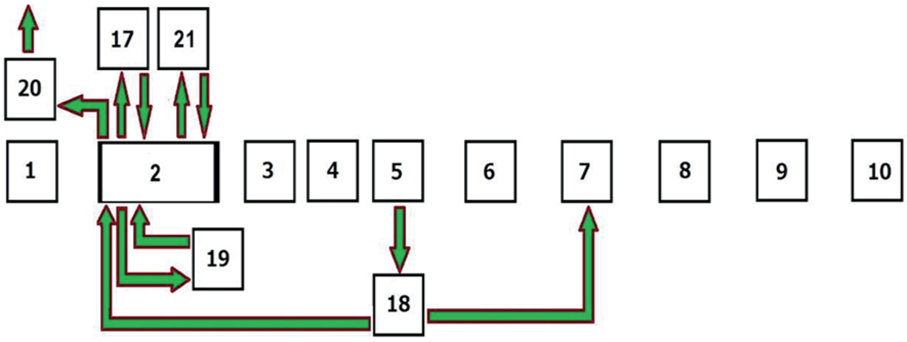

Fig. 2. Block diagram of the etching process of printed circuit boards:
1 - batch module; 2 - etching module; 3 - lighting module; 4 - review module; 5 - third cascade washing module; 6 - second cascade washing module; 7 - first cascade washing module; 8 - hot drying module; 9 - cold drying module; 10 - unloading system; 17 - pickling solution; 18 - water treatment; 19 - filtration installation; 20 - processing equipment; 21 - installation of covers (if necessary)

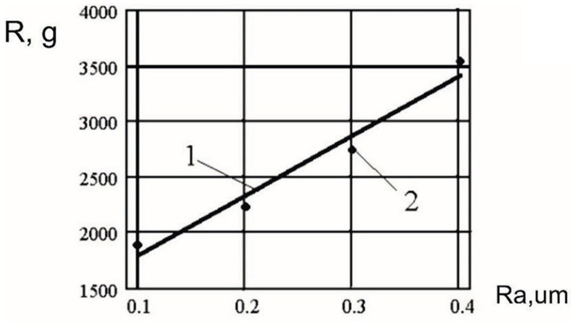

Fig. 3. The average value of the R force depending on the cleanliness of the surface: 1 – model; 2 – experiment

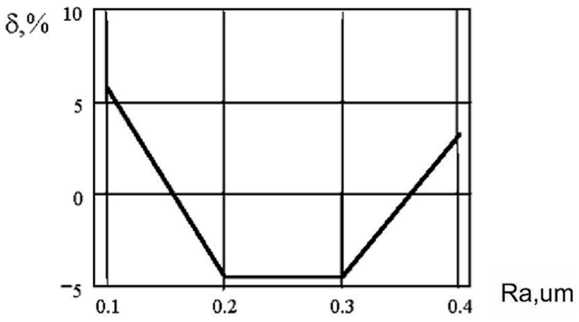

Fig. 4. Relative deviation *δ* (%) depending on the mean value of the *R* force and the cleanliness of the surface

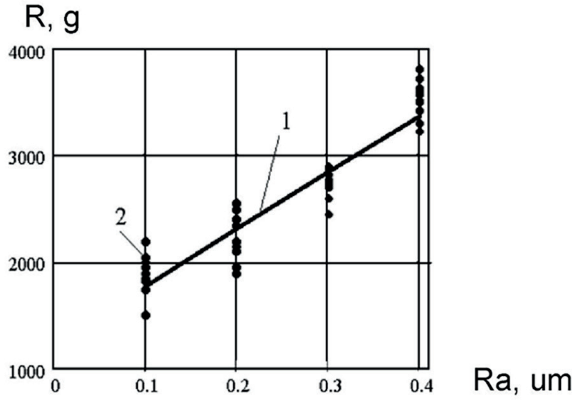

Fig. 5. Distribution of the R force depending on the cleanliness of the surface: 1 – model; 2 – experiment

form of dendritic clusters in the shape of columns (Fig. 7). The branches of the dendrites are 7–8 μm long and 40–50 μm high. When the layers are thick, the dendrites merge. This structure remains unchanged until the dendrites reach a length of 30–35 μm. When this value is exceeded, the layer disappears and perforates with the growth of dendrites. However, this phenomenon does not prevent the use of the precipitated copper as electrodes or as a conductive and structural material after remelting. Consequently, the copper present in the wastewater meets the requirements for use in surface remelting or metallization.

The tests with the use of a metallographic microscope have also shown that the texture of the tested material is microporous. Most of the time, teardrop-shaped pores were visible. Only some of them are shaped like tubules. The pores are evenly distributed over the sample surface, and their diameter does not exceed the value in the range of 10–20 μm.

Economic aspects of wastewater treatment

The conducted analyses made it possible to estimate the economic efficiency of the devices, assuming that they are energy-saving and environmentally friendly. It was necessary to take into account the physicochemical properties of the materials used in the process and technological parameters that make it possible to reuse aqueous solutions without the need to discharge them for disposal [Ishchenko et al. 2018, Magalhaes et al. 2005, Mymrin et al. 2020, Rukovodstvo 2004].

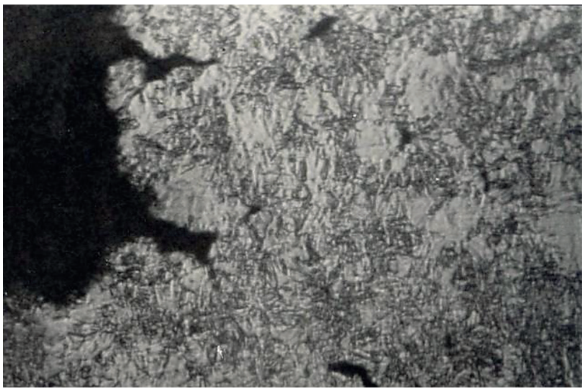

Fig. 6. Microstructure of the precipitated copper (longitudinal section), ×120

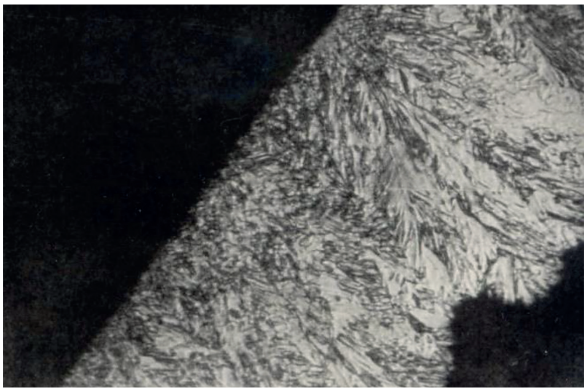

Fig. 7. Microstructure of the precipitated copper (cross-section), ×120

In addition, the existing technological line is adapted to the introduction of wastewater recovery technology without introducing any changes to the etching process of printed circuit boards.

Data required for calculations:

- the price of water and sewage in Kiev from 2019 r. – 21,756 UAH/m^3;
- electricity price in Kiev from 2019 r. - 2,47 UAH/kWh;
- the cost of expanding the installation related to the recovery of wastewater in the technology of etching of printed circuits - 450000 UAH;
- scrap price of copper - 140 UAH/kg.

The economic analysis, taking into account the purchase costs of the necessary equipment for the expansion of the installation, was carried out for the production of products and operation of the equipment in an annual cycle. The annual working time was assumed in the amount of 247 days, while maintaining a single-shift work in the amount of 247×8 = 1976 hours. The number of working hours per the number of products produced will allow to obtain 23,712 m^2 (1976 hours ×12 m^2/h) of semi-finished products and 23,712 m^2 ×0.5 = 11856 kg of copper. The results of the economic analysis are summarized in Table 1. Cost estimate for the billing period (year): basic option: Z_b= 3569351 UAH; option proposed: Z_n = 722192 UAH; economic efficiency $E = Z_b – Z_n$ = 2 877 159 UAH.

Table 1. Results of the economic analysis

The name of the cost item	Basic option	Option proposed
Material costs (basic and additional), UAH	-	55000
Water consumption, m^3/h	4.8	0.8
Water and sewage price, UAH/m^3	21.756	21.756
Annual cost of water, UAH/m^3	206351	34391
The amount of sludge formed, ton	25.2	3
Sludge removal cost (2500 UAH/t), UAH	63000	7500
Increase in the amount of electricity after the introduction of the recovery proces, kW··h	-	14227.2
Electricity price, UAH/kW··h	2.47	2.47
Electricity costs increase, UAH	-	35141
The amount of metal (copper) formed, kg	-	11856
Metal (copper) cost, UAH	-	1659840
Investment cost, UAH	2100000	600000
Total costs, UAH	3569351	722192

Environmental aspects of wastewater treatment

The results concerning the exposure rates to copper compounds that are discharged with the sediments, based on the example of a selected Ukrainian plant, are presented in Table 2. The indicator of the total exposure to copper compounds after their removal from sewage indicates that there is no risk to health at the sites covered by the research (Table 3).

It was observed that with the removal of copper compounds from wastewater (not transformed into sludge), the value of the total hazard index changed. There has been an improvement in environmental and ecological safety. Moreover, raw materials for copper smelting were obtained. The value of the Total Hazard Index for electroplating sludge analyzed for the example enterprise increased from 0.7575 to 100.

The amount of sludge formed and the content of copper compounds in them decreased. As a consequence, ecological and environmental safety has increased. For comparison, the case of an enterprise collecting the resulting sediment for a period of several years was considered (Table 4). Possible consequences in terms of environmental protection and human health for this type of technological solution are presented. The waste generated during production in the analyzed plant consists mainly of sludge and alkalis. Appearance and texture: yellow-green, odorless, dry porous lumps.

The bath of semi-finished products in an alkaline solution generates waste, which after solidification is characterized by a compact consistency. Qualitative composition of waste and the content of hazardous substances in it: sodium hydroxide - 38–65% by weight; sodium nitrate - 24–35% by weight; sodium chloride - 5–6% by weight; insoluble impurities (scale, glass mass) - up to 100%; the pH of the aqueous extract from waste is 11.68.

The degree of risk that pollutants from waste may pose should be determined on the basis of their actual content in the waste and its water solubility. Sodium compounds, especially sodium hydroxide, are characterized by the lowest toxicity index.

Substituting the value into formula (3), we get:

$$Kc = \lg(150)/(1.0 + 0.0 + 0.56) = 1.39 \qquad (8)$$

The analysis of the results shows that in terms of the values of the toxicity coefficient obtained, e.g. for sodium hydroxide ($1.3 < Kc < 3.3$) the

Table 2. Indicators of exposure to copper compounds discharged with sediment

Group of substances	MPC_i, mg/kg	$(S + C_w)_i$, mg/kg	K_i	K
Copper compounds	3	73.98	0.0405	0.7575

Table 3. Exposure rates to copper compounds from plate production and electroplating after removal from wastewater

Group of substances	MPC_i, mg/kg	$(S + C_w)_i$, mg/kg	K_i	K
Copper compounds	3	0.01	300.0	100
		0.03	100.0	

Table 4. Concentration and toxicity of the analysed substances

Form	Content, mg/kg (X), toxicity of the substance						
	Pb(1)	Cd(I)	Zn(1)	Mn	Cu(2)	Cr(2)	Ni(2)
Total content	<0.5	<0.25	6.94	39.64	3.71	<0.1	27.87
Mobile in T=25 °C	<0.5	<0.25	2.39	39.62	0.74	<0.1	9.00
Water soluble at T=25 °C	<0.5	<0.25	0.29	9.38	<0.35	<0.1	2.90
Soluble in the analyzed solution (g/100 g)	-	-	4.1	23.2	He	-	He
Average amount of waste (kg/t)	-	-	0.007	0.04	0.004	-	0.03
MPC in soil (mg/kg) - total content	32.0	1.5	-	1500.0	-	80.0	-
MPC in soil (mg/kg)	-	-	23.0	-	3.0	6.0	4.0

generated waste is a hazardous waste (II toxicity class). Additionally, due to the strongly alkaline reaction of the water extract from waste, it is required to dispose of these substances in accordance with the principles of dealing with hazardous substances. In this case, the risk to human health and the environment may change (decrease) after appropriate neutralization of the solutions [Rukovodstvo 2004].

The value of the average daily dose for nickel was calculated according to the formula (4):

$$LADD = \frac{C \cdot CR \cdot ED \cdot EF}{BW \cdot AT \cdot 365} = \frac{10 \cdot 0.2 \cdot 5 \cdot 365}{70 \cdot 70 \cdot 365} = 2 \cdot 10^{-3}\ \mu g/(kg \cdot day) \quad (9)$$

Carcinogenic risk is estimated as the likelihood of developing cancer as a result of exposure to a carcinogen. This value for nickel is as follows (7):

$$CR = LADD \cdot SF = 2 \cdot 10^{-3} \cdot 0.84 = 1.68 \cdot 10^{-3} \quad (10)$$

The hazard index (HI) was also determined for the most important pollutants present in the analyzed waste, in particular for cadmium, nickel, lead, and chromium:

$$HI = \sum_{1}^{4} HQ_i = \frac{0.002}{0.0005} + \frac{0.01}{0.02} + \frac{0.027}{0.0035} + \frac{0.005}{0.005} = 82.5 \quad (11)$$

The obtained value of the hazard index is> 1. In this case, there is a risk of toxic effects due to exposure (eg during an accident) to the analyzed substances – the degree of risk does not correspond to the acceptable conditions.

CONCLUSIONS

The paper proposes a technology for the regeneration of spent etching solutions, in which the separated metal can be used as a secondary raw material for the production of copper, while the regenerated solution can be reused for etching printed circuit boards.

The research confirmed that the copper recovered from wastewater meets all the requirements that allow it to be used for surface remelting or metallization in appropriate technological processes.

An economic analysis of the implementation of the new wastewater treatment technology and the reduction of the amount of sludge generated on an annual basis showed a revenue effect of UAH 2,847,159 (USD 105,000). The use of a new technology of wastewater treatment by introducing only one installation can bring a significant economic effect. The increase in electricity consumption in the process of wastewater regeneration is balanced by an increase in the level of environmental safety in the areas of such enterprises. The condition of the natural environment in this area can be significantly improved. Research confirms that it is possible to implement an environmentally friendly process of copper utilization from galvanic wastewater.

REFERENCES

1. Alekhya M., Divya N., Jyothirmai G., Rajashekhar K. 2014. Reddy Secured landfills for disposal of municipal solid waste. International Journal of Engineering Research and General Science. 1(1), 368–373.
2. Bazrafshan E., Mohammadi L., Ansari-Moghaddam A., Mahvi A.H. 2015. Heavy metals removal from aqueous environments by electrocoagulation process – a systematic review. Journal of Environmental Health Science and Engineering, 13, 74. DOI: 10.1186/s40201-015-0233-8
3. Bloomberg M., Paulson H., Steyer T. 2014. Risky Business: The Economic Risks of Climate Change in the United States. http://riskybusiness.org/ (access: 26.06.2014).
4. Chervonyy I.F., Bredikhin V.M., Gritsay V.P., Ignatev et al. 2014. Non-ferrous metallurgy of Ukraine, 1, 1: Monograph. Zaporizhzha: ZDIA, 380. (In Ukrainian)
5. Dorokhina E., Kharchenko S. 2017. Circular Economy. Problems and Ways of Development, Ecology and Industry of Russia, 21(3), 50–55. (In Russian) https://doi.org/10.18412/1816-0395-2017-3-
6. Ishchenko V., Pohrebennyk V., Borowik B., Falat P., Shaikhanova A. 2018. Toxic substances in hazardous household waste. International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM, 18 (4.2), 223–230.
7. Girnychyy Zakon Ukraine vid 6.10.1999 No. 1127-XIV. 1999. Vidomosti Verkhovnoy Rady Ukraine (VVR), 50. http://zakon5.rada.gov.ua/laws/show/1127-14
8. Grizzetti B., Pistocchi A., Liquete C., Udias A., Bouraoui F., van de Bund W. 2017. Human pressures and ecological status of European rivers, Scientific Reports, 7. https://www.umwelt-bundesamt/sites/2018_indikatoren-bedeutung-wasser.pdf.
9. Karpinski M., Pohrebennyk V., Bernatska N., Ganczarchyk J., Shevchenko O. 2018. Simulation of Artificial Neural Networks for Assessing the Ecological State of Surface Water, 18th International Multidisciplinary Scientific GeoConference SGEM 2018, Albena, Bulgaria, pp. 693–700.
10. Klyachkin V., Shirkunova K., Bart A. 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. (in Russian) https://doi.org/10.18412/1816-0395-2019-5-47-51
11. Magalhaes J.M., Silva J.E., Castro F.P., Labrincha J.A. 2005. Kinetic study of inmobilization of galvanic sludge in clay based matrix. J. Hazard. Mater., B121, 69–78.
12. Makisha N., Yunchina M. 2016. Methods and solutions for galvanic waste water treatment. Moscow state University of civil engineering, Russia International science conference on smart city, spbwosce. Saint-Petersburg,
13. Matukhno E., Belokon K., Shatokha V., Baranova T. 2019. Ecological aspects of sustainable development of metallurgical complex in Ukraine. Procedia Environmental Science, Engineering and Management, 6(4), 671–680.
14. Mitryasova O., Pohrebennyk V., Cygnar M., Sopilnyak I. 2016. Environmental natural water quality assessment by method of correlation analysis. Proc. International Multidisciplinary Scientific GeoConference, SGEM, 16(50), 2, 317–324.
15. Mymrin V., Borgo S.C., Alekseev K., Avanci M.A., et al. 2020. Galvanic Cr-Zn and spent foundry sand waste application as valuable components of sustainable ceramics to prevent environment pollution. The International Journal of Advanced Manufacturing Technology, 12.
16. National report on the state of the environment in Ukraine. http://old.menr.gov.ua/index.php/dopovidi.
17. Nester A.A. 2016. Wastewater treatment for PCB production. Khmelnitsky National University, monograph, 219.
18. Nester A.A., Drapak G.M. 2008. Microstructure research and recovery copper technology, released from restored water solutions. Polish Journal of Environmental Studies, 17(3A), 423–426.
19. Nester A.A., Evgrashkina G.P. 2017. Forecast of pollution of machine-building enterprise by sludges at manufacture of boards and electroplating. News of the TulState University. Technical science, 6, 193–200.
20. Oliveira A.D., Bocio A., Beltramini Trevilato T.M., Magosso Takayanagui A.M., Domingo J.L., Segura-Muñoz S.I. 2007. Heavy metals in untreated/treated urban effluent and sludge from a biological wastewater treatment plant. Environ Sci Pollut Res, 14, 483–489.
21. Pashayan A., Karmanov D. 2018. Recycling of Electroplating Wastes without Formation of Galvanic Sludges, Ecology and Industry of Russia, 22(12), 19–21. (in Russ.) https://doi.org/10.18412/1816-0395-2018-12-19-21
22. Pohrebennyk V., Dzhumelia E., Korostynska O., Mason A., Cygnar M. 2017. X-Ray Fluorescent Method of Heavy Metals Detection in Soils of Mining and Chemical Enterprises. Proc. 9th International Conference on Developments in eSystems Engineering, DeSE 2016, pp. 323–328.
23. Pohrebennyk V., Koszelnik P., Mitryasova O., Dzhumelia E., Zdeb M. 2019. Environmental monitoring of soils of post-industrial mining areas.

Journal of Ecological Engineering, 20(9), 53–61.

24. Pohrebennyk V., Petryk A. 2017. The degree of pollution with heavy metals of fallow soils in rural administrative units of Psary and Płoki in Poland, International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM, 17(52), 967–974.
25. Prolejchik A., Gaponenkov I., Fedorova O. 2018. Extraction of Heavy Metal Ions from Inorganic Wastewater. Ecology and Industry of Russia, 22(3), 35–39. (in Russian) https://doi.org/10.18412/1816-0395-2018-3-35-39.
26. Pękala A. 2019. The Opoka-Rock from the Mesozoic/Neogene Contact Zone in the Bełchatów Lignite Deposit-Characteristics of a Petrographic Nature and as a Raw Material. J. Ecol. Eng., 20(8), 232–237, DOI: https://doi.org/10.12911/22998993/111714
27. Pękala A. 2020. Rock raw materials from the Mesozoic–Neogene contact zone in the Bełchatów Lignite Deposit – recognition and evaluation of their utility. Gospodarka Surowców Mineralnych – Mineral Resources Management, 36(4), 127–144. DOI: https://doi.org/10.24425/gsm.2020.133943
28. Rukovodstvo P2.1.10.1920-04. 2004. Rukovodstvo po otsenke riska dlya zdorovya naseleniya pri vozdeystvii khimicheskikh veschestv, zagryaznyayuschikh okruzhayuschuyu sredu. M. Federalnyy tsentr gossanepidnadzora Minzdrava Rossii, 144. (in Russian)
29. Ukrainian State Sanitary Rules and Regulations 2.2.7.029-99. 1999. Hygienical Requirements concerning industrial waters management and determination of the class of danger for public health, 29. (in Ukrainian)
30. Vershinina, I., Martynenko, T. 2019. Problems of Waste Recovery and Socio-Ecological Inequality, Ecology and Industry of Russia, 23(5), 52–55. (in Russian) https://doi.org/10.18412/1816-0395-2019-5-52-55
31. Voloshkina O.S., Vasilenko L.O., Bereznitska J.O. 2015. Conformities to law of heavy metals salts migration through absorbent carbon in natural filters, Environmental safety and natural resources, 4(20), 45–48.
32. Zaporozhets A.O., Redko O.O., Babak V.P., Eremenko V.S., Mokiychuk V.M. 2018. Method of indirect measurement of oxygen concentration in the air. Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu, (5), 105–114. https://doi.org/10.29202/nvngu/2018-5/14