

ETCHING LINE WITH INTEGRATED ELECTROCHEMICAL REGENERATION FOR COPPER RECOVERY AND SLUDGE REDUCTION

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Abstract. Pollution of surface and groundwater by heavy metals, including copper, is currently a global environmental problem. Elevated concentrations of heavy metals in wastewater and soil contamination degrade the quality of water used for the supply of cities, rural settlements, and industrial facilities. The discharge and on-site storage of spent etching solutions at industrial enterprises lead to environmental pollution and require substantial costs for their neutralization both at the enterprise itself and at wastewater treatment facilities located in production areas. We have developed a technology for the recovery of heavy metals (copper) and the corresponding reduction of sludge accumulation on the premises of printed circuit board manufacturing enterprises. The proposed etching line with integrated electrochemical regeneration provides a technologically and environmentally efficient alternative to conventional printed circuit board etching systems. By redirecting rinsing waters and spent etchants into a closed-loop regeneration unit, the process eliminates wastewater discharge and substantially reduces the formation of hazardous sludge, thereby minimizing environmental impact. The line ensures a constant etching rate of printed circuit boards (substrates) within the range of 35–38 $\mu\text{m}/\text{min}$. The recovered copper can be sent for remelting and subsequent use in industrial applications. At a productivity of the printed circuit board (substrate) etching line of 14 m^2/h , the regeneration unit recovers around 7 kg of copper per hour of operation (11,856 kg per year on average), while practically no waste (sludge) is generated.

Keywords: etching line, electrochemical regeneration, copper recovery, sludge reduction

LINIA DO GRAWROWANIA Z ZINTEGROWANĄ REGENERACJĄ ELEKTROCHEMICZNĄ SŁUŻĄCĄ DO ODZYSKIWANIA MIEDZI I OGRANICZANIA ILOŚCI OSADU

Streszczenie. Zanieczyszczenie wód powierzchniowych i podziemnych metalami ciężkimi, w tym miedzią, stanowi obecnie globalny problem środowiskowy. Podwyższone stężenia metali ciężkich w ściekach oraz zanieczyszczenie gleb prowadzą do pogorszenia jakości wody wykorzystywanej do zaopatrzenia miast, osiedli wiejskich oraz obiektów przemysłowych. Odprowadzanie oraz magazynowanie na terenie zakładów zużytych roztworów trawiących powoduje zanieczyszczenie środowiska i wiąże się ze znacznymi kosztami ich neutralizacji, zarówno w samych przedsiębiorstwach, jak i w oczyszczalniach ścieków zlokalizowanych na obszarach przemysłowych. Opracowaliśmy technologię odzysku metali ciężkich (miedzi) oraz odpowiadającego jej ograniczenia akumulacji osadów na terenie zakładów produkujących płytki drukowane. Zaproponowana linia trawienia z wbudowaną regeneracją elektrochemiczną stanowi technologicznie i ekologicznie efektywną alternatywę dla konwencjonalnych systemów trawienia płytek drukowanych. Poprzez skierowanie wód płuczących oraz zużytych trawiaczy do zamkniętego obiegu jednostki regeneracyjnej proces eliminuje zrzut ścieków i znacząco ogranicza powstawanie niebezpiecznych osadów, minimalizując tym samym oddziaływanie na środowisko. Linia zapewnia stałą szybkość trawienia płytek drukowanych (substratów) w zakresie 35–38 $\mu\text{m}/\text{min}$. Odzyskana miedź może być kierowana do przetopienia i dalszego wykorzystania w zastosowaniach przemysłowych. Przy wydajności linii trawienia płytek drukowanych (substratów) wynoszącej 14 m^2/h , jednostka regeneracyjna odzyskuje około 7 kg miedzi na godzinę pracy (średnio 11 856 kg rocznie), przy jednoczesnym praktycznym braku wytwarzania odpadów (osadów).

Słowa kluczowe: linia trawienia, regeneracja elektrochemiczna, odzysk miedzi, redukcja osadów

Introduction

Currently, the most widely used reagent-based technologies for metal removal from water do not provide sufficient purification for water reuse [6, 7]. Moreover, they lead to the formation and accumulation of toxic sludge, which continues to build up both at operating enterprises of the former USSR and at newly established facilities [16, 24]. A critical unresolved issue is the disposal of regeneration solutions produced during ion-exchange processes, which could otherwise enable the implementation of closed-loop water use systems in electroplating operations [2, 8].

Among the available methods, electrochemical regeneration of spent etching solutions is considered the most economically advantageous [3, 12]. This process simultaneously allows the recovery of pure copper and the restoration of the solution's etching capacity [10, 15]. Its economic efficiency stems from the significant reduction of chemical consumption, decreased waste disposal costs, and the return of copper to the production cycle [22]. Electrolysis may occur with gas evolution at the anode; however, a gas-free process is preferable because it removes only copper from the solution and eliminates the need for solution adjustment [13, 17].

1. Motivation

Figure 1 presents a typical modern production line scheme employed in printed circuit board manufacturing [4, 19]. The diagram highlights distinct wastewater discharge streams generated during equipment operation. This scheme is currently widely used in industrial practice [20].

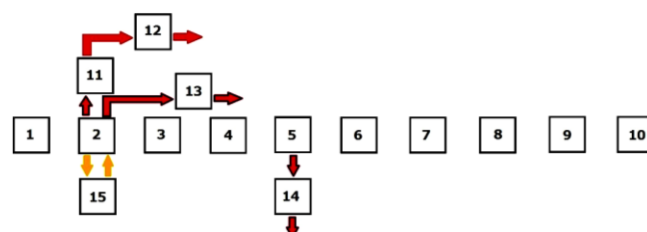


Fig. 1. Modern printed circuit board etching line with wastewater discharge points: 1 – loading module, 2 – etching module, 3 – lighting module, 4 – inspection module, 5 – third cascade rinsing module, 6 – second cascade rinsing module, 7 – first cascade rinsing module, 8 – hot drying module, 9 – cold drying module, 10 – unloading module, 11 – plant treatment facilities, 12 – municipal treatment facilities, 13 – treatment facilities (dilution stage), 14 – plant treatment facilities, 15 – filtration facilities

The line is designed to etch copper from non-print areas, thereby forming the printed circuit pattern, under conditions ranging from experimental and small-batch production to serial manufacturing. It is also employed to refine and test technological processes. In the presented scheme, following the etching operation and the saturation of the solution with copper compounds in the etching module (module 2), the etching rate decreases. Consequently, the spent solution must be replaced with fresh solution capable of maintaining adequate etching speed.

The spent solution is then directed to the plant's treatment facilities (module 11) for preliminary purification. Once treated to meet the standards established by the municipal water authority, the residual solution may be discharged into the city sewer system.

Pollution of surface and groundwater by heavy metals, including copper, is currently a global environmental problem that must be addressed at every high-technology enterprise. Elevated

concentrations of heavy metals in wastewater and soil contamination degrade the quality of water used for the supply of cities, rural settlements, and industrial facilities. The discharge and on-site storage of spent etching solutions at industrial enterprises lead to environmental pollution and require substantial costs for their neutralization both at the enterprise itself and at wastewater treatment facilities located in production areas. The presented results of certain methods and testing schemes indicate the possibility of utilizing the recovered copper for substrate metallization in appropriate technological processes or, after remelting, for electrotechnical applications.

Chemical adjustment of etching solutions results in the formation of significant volumes of wastewater containing heavy metals, which have a negative impact on soils, groundwater, vegetation, and humans as the apex of the food chain. Nonetheless, sludge remains on the enterprise site after wastewater treatment, posing a risk to the surrounding environment, the facility itself, and the local population.

As an example, let us consider the formation of sludge during the operation of printed circuit board etching lines. At an etching line productivity of 14 m²/h, the amount of sludge generated over 8 hours of operation exceeds 110 kg, which, under single-shift monthly operation, amounts to 2,400–2,500 kg.

Modern enterprises that, during their most productive periods, manufactured approximately 4·10³ m² of printed circuit boards have accumulated on their sites 1,500–3,000 tonnes or more of sludge. These sludges are stored in containers or polyethylene bags and are exposed to atmospheric precipitation. Under the action of precipitation, salts are leached and migrate into soils and surface waters, thereby contaminating the environment [9, 26].

Studies conducted at individual enterprises where such sludges are stored have shown that the waste toxicity index, calculated using the median lethal dose of a chemical substance upon oral intake for laboratory animals, classifies electroplating sludges precipitated with alkali or soda as highly hazardous wastes (toxicity class II). The hazard index exceeded 1, indicating that this level of risk is unacceptable. Consequently, pollutants contained in electroplating sludge that enter environmental compartments as a result of accidental releases can adversely affect human health. Therefore, emergency situations associated with the loss of integrity of storage facilities (containers, bags, etc.) and the subsequent release of electroplating sludge into the environment lead to atmospheric air pollution and increase risks to human health [1, 18, 23].

Some researchers have conducted studies on wastewater treatment [2, 3, 7, 18, 21]; however, the treatment results generally culminate in the formation of sludge [11, 14, 25]. Other modern wastewater treatment methods have proven to be poorly suited for implementation on an industrial scale; therefore, the authors of the present study have chosen the approach of etching solution regeneration [5, 19].

To reduce risks to the population associated with the storage of waste from printed circuit board etching, the authors propose a production line that ensures continuous regeneration of the etching solution and its repeated use in the manufacturing process. Copper deposited on the cathodes of the regeneration unit can be recovered by remelting and reused in the electrical engineering industry.

However, a modern production line must be automated; this requires the development of a schematic model that ensures the regeneration process operates simultaneously with the primary process, which is the etching.

The advantages of such a line include the following:

- 1) increased productivity (continuous operation, high processing speed, and high throughput in printed circuit board manufacturing);
- 2) reduced manual labour, leading to fewer errors and defects;
- 3) improved occupational safety due to reduced manual handling;
- 4) adaptability to various types of printed circuit boards;

- 5) near-complete elimination of sludge formation during the etching process.

The potential disadvantages of such a line include:

- 1) high initial capital investment;
- 2) the need for highly qualified specialists [14].

2. Etching line scheme with diversion for regeneration

The authors proposed and investigated a scheme for regenerating wastewater from etching and rinsing operations, with the recovery of copper in sheet form for possible remelting at metallurgical plants. The etching line scheme, including the diversion of part of the spent solution and rinsing water for regeneration, is presented in Figure 2.

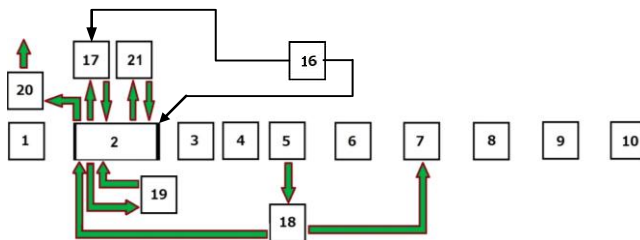


Fig. 2. Printed circuit board etching line scheme with diversion for regeneration: 1 – loading module, 2 – etching module, 3 – lighting module, 4 – inspection module, 5 – third cascade rinsing module, 6 – second cascade rinsing module, 7 – first cascade rinsing module, 8 – hot drying module, 9 – cold drying module, 10 – unloading module, 16 – hydrometer, 17 – etching solution regenerator, 18 – rinsing water regenerator, 19 – filtration unit, 20 – plant treatment facilities, 21 – coating application unit (if required)

The developed scheme enables the regeneration of solutions during the etching process while maintaining a constant concentration of elements, and therefore, a stable etching rate for the boards. Simultaneously, this line configuration allows the recovered copper to be used in metallization processes without wastewater discharge, thereby preventing environmental contamination. Copper can also be deposited on titanium cathodes for use as secondary metal during remelting. Titanium cathodes proved most suitable as electrodes, as they provide the easiest removal of deposited copper from the spent solution, requiring the least mechanical effort compared to copper or steel electrodes.

Investigations of the pilot-industrial electrochemical regeneration unit were conducted to determine optimal operating conditions for different solution concentrations. At constant flow rates (1–2 cm/s) and a solution temperature of +40°C, the yield of dense copper deposits was determined as a function of current density. The following requirements were established:

- 1) stability of etching characteristics during operation;
- 2) feasibility of electrochemical regeneration.

The aim of this part of the study is a comprehensive testing and examination of the pilot-industrial unit, evaluation of its capabilities, and determination of its technological operating modes.

The unit designated as module 17 operates under the following supply conditions:

- 1) Potable water purified in accordance with sanitary requirements, at a pressure of 0.1–0.3 MPa (1–3 kg/cm²), with a volumetric flow rate of at least 0.8 m³/h.
- 2) Recirculated water supplied to the cooling system, at a pressure of 0.1–0.3 MPa (1–3 kg/cm²), a temperature of 10–20 °C, and a volumetric flow rate of not less than 0.8 m³/h.

Water supply is routed through a sensor to the etching module 2 and to the first cascade rinsing module 7. In the event of insufficient water pressure, a signal is generated to shut down the line. During operation, the regeneration unit (module 17) is connected to the exhaust ventilation system with a minimum air flow rate of 250 m³/h. Therefore, a sensor is installed to monitor the presence and operation of the exhaust ventilation system.

The same exhaust ventilation system is also connected to the hot drying module 8 and the cold drying module 9, where an additional ventilation presence sensor is installed (Figure 3).

The etching capacity of the solution is maintained by the built-in regeneration unit operating either in manual or automatic mode. Control is based on readings from a hydrometer (module 16) and a pH cell installed in the etching module. According to the signals from these sensors, the regeneration control system generates control commands for the actuators of the regeneration system.

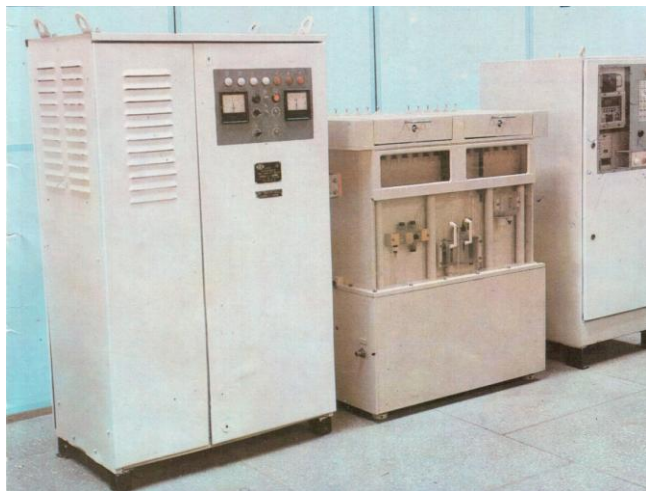


Fig. 3. The regeneration unit (the rectifier is on the left)

Filling of the etching module tank (module 2) with solution is carried out up to a specified level, after which operation of the line becomes possible.

The list of sensors installed in the modules is given as follows (for reference). The sensors in etching module 2 are:

- 1) level sensor for water (etching solution);
- 2) pressure sensor for water (etching solution);
- 3) potable water sensor for the cooling system;
- 4) hydrometer for the electrolyte, used to measure relative density, concentration, and specific gravity of the liquid;
- 5) pH meter, a device for measuring the hydrogen ion concentration (pH value) in solutions;
- 6) temperature sensor for the etching solution.

The sensors in first cascade rinsing module 7 are:

- 1) water level sensor;
- 2) water pressure sensor.

Hot drying module 8 has only one sensor — the air temperature sensor.

The sensors in etching solution regenerator (module 17) are:

- 1) hydrometer with specified density measurement range for the etching solution ($\rho = 1.06\text{--}1.12\text{ g/cm}^3$);
- 2) electromagnetic valve for supplying solution to the section from the pressurized line of the module, and a regeneration controller.

The operation of the whole unit is based on the principle of double-sided jet treatment of printed circuit board blanks with processing solutions and rinsing water as they move along a roller conveyor. The unit enables implementation of the technological process comprising the following stages:

- 1) feeding of blanks onto the conveyor by manual loading;
- 2) etching of copper from non-print areas of printed circuit boards using an alkaline solution to form the printed circuit pattern;
- 3) ammonia rinsing of the blanks after etching;
- 4) rinsing of the blanks with potable tap water supplied from the water network;
- 5) unloading of the blanks from the conveyor (manually).

When the modules forming the unit are interconnected, their transport systems constitute a single roller conveyor.

The processing solution is contained in the tank of module 2, from which it is supplied by a recirculation pump through a pressurized pipeline to spray manifolds with nozzles directed at the printed circuit board blanks moving along the conveyor.

The processing chambers of adjacent modules are separated by partitions and squeeze rollers to prevent the transfer of processing solution and rinsing water from one module to another. During transportation through the processing zones, the printed circuit board blanks are subjected to jet treatment in accordance with the stages of the technological process.

The etching capacity of the solution is maintained by introducing the required components based on laboratory analysis results or by replacing the solution as its service life is exhausted. To improve etching quality, the spray manifold in module 2 performs oscillatory motion in the horizontal plane perpendicular to the direction of board movement along the conveyor. The etching capacity of the solution is also maintained by the built-in regeneration unit operating in either manual or automatic mode, based on readings from the hydrometer and pH cell installed in module 2. According to the signals from these sensors, the regeneration control system generates control commands for the actuators of the regeneration system.

The integrated regeneration and adjustment section operates jointly with the printed circuit board etching section. Therefore, regeneration and adjustment processes proceed in parallel with the etching process. During combined operation of the regeneration and adjustment section and the etching section, a constant etching capacity of the solution is ensured by maintaining the copper material balance through electrolysis, while the ammonia balance is maintained by periodic chemical adjustment.

Adjustment of the etching solution with respect to ammonium chloride content is performed periodically in accordance with a separate instruction. Thus, the etching speed is not constant (Figure 4). Ammonia rinsing of the blanks is carried out in module 3, while rinsing with tap water from the municipal supply is performed in the inspection module 4 (Figure 5). The water flow rate is adjusted manually by a valve installed on the pipeline supplying module 3.

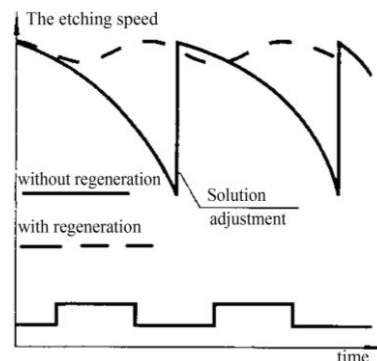


Fig. 4. The etching speed sketch with electrochemical regeneration and without, where the meander shows regeneration cycles

Figure 5 shows that ammonia is supplied by means of an ejector to maintain the pH level. When pH adjustment in the regenerator (module 1 in Figure 5) is required, the pump (module 3 in Figure 5) is switched on and transfers the solution through the ejector (module 2 in Figure 5). Due to the pressure reduction created in the ejector, ammonia is drawn into the regenerator. The ejector operates according to the Bernoulli principle, in which a high-velocity jet of the working medium (gas, vapor, or liquid) passes through a narrowed nozzle, creating a low-pressure region (vacuum). This pressure reduction causes another medium (the passive flow) to be sucked in.

The supply voltage from the workshop power network is fed to the input terminal block located in module 2. Through the main circuit breaker, intermediate terminal blocks, and connecting four-core cables, electrical power is supplied

to the power panel of module 2. The module is equipped with a power supply unit with an output voltage of 24 V (not shown), which is used for control and signaling circuits. Control of module 2 is carried out from the control panel located in the loading area.

The control system provides two operating modes of the whole unit:

- 1) parameter maintenance mode with transition to the temperature operating regime;
- 2) operating mode.

Switching between the modes is performed using a selector switch on the control panel. The parameter maintenance mode ensures activation of the heaters and the recirculation pump in module 2. This mode is used during system start-up at the beginning of a shift to reach the required temperature regime or to maintain readiness during breaks. In this mode, the solution temperature is maintained after reaching the preset value. The operating mode ensures simultaneous operation of all actuators of the modules while maintaining the preset temperature values and conveyor speed. Temperature is set on module 2 via the temperature controller panel. Maintenance of the preset temperature is achieved by switching the electric heaters on and off, as well as by activating the supply of cooling water to the cooling coil. Conveyor speed is adjusted using a variable resistor located on the module control panel.

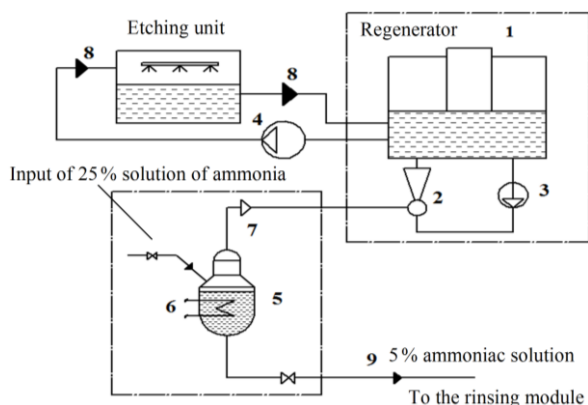


Fig. 5. Technological scheme of the aqueous solution regeneration unit (it is shown here that ammonia is supplied via the ejector to maintain the pH level): 1 – electrolyser; 2 – ejector; 3, 4 – pump; 5 – tank; 6 – electric heater; 7 – electromagnetic valve; 8, 9 – shut-off valves

The control and electrical automation systems provide the following functions:

- 1) switching on and off of actuators,
- 2) monitoring and maintaining the solution temperature with an accuracy of $\pm 1^\circ\text{C}$,
- 3) smooth regulation of conveyor speed within the range of 0.2 to 1.2 m/min,
- 4) monitoring of the minimum solution level,
- 5) monitoring of the position of protective covers enclosing the processing zones of the module,
- 6) interlocking of the recirculation pump and electric heaters when the solution level in module 2 drops to an emergency level,
- 7) interlocking of the recirculation pump when the covers of module 2 are open,
- 8) interlocking of the recirculation pump in module 2 during opening of the ventilation damper.

The control system of the regeneration and adjustment section also provides two operating modes: manual and automatic. Mode switching is performed using a selector switch located on the regenerator control panel. In manual mode, the operator initiates a continuous regeneration process by pressing the "Start" button, activating the solution recirculation pump through the electrolyser and rectifier. The duration of the regeneration process is selected by the operator and is terminated by pressing the "Stop" button.

In automatic mode, the regeneration control system generates control signals for the operation of the recirculation pump through the electrolyser, the rectifier, and the metering pump supplying the aqueous ammonia solution (see Figure 5). The electrochemical regeneration section consists of the following main components: an electrolyser and a common solution tank. For the etching and regeneration sections, the units are interconnected by a connecting pipeline, shut-off and control valves, and ventilation ducts. For operation in automatic mode, the regeneration section is additionally equipped with a density sensor unit for the etching solution. This unit includes a hydrometer (module 16) with specified density measurement limits for the etching solution ($\rho = 1.06\text{--}1.12\text{ g/cm}^3$), an electromagnetic valve for supplying the solution to the section from the pressurized main of the module, and a regeneration controller.

During operation of the etching module, the density of the etching solution changes due to the copper dissolved during etching. This density, which we denote by ρ_{etch} , is measured by the hydrometer. When the permissible density limit is exceeded, the regeneration unit is automatically activated. In the regenerator, copper is recovered, and the regenerated (restored) solution is returned to the etching module. Thus, if

$$\rho_{\text{etch}} \geq \rho \text{ by } \rho \in [1.06; 1.12]$$

then the regenerator is switched on automatically; if

$$\rho_{\text{etch}} < 1.06$$

then the regenerator is turned off automatically.

The electrolyser is the main functional unit of the regeneration section. It ensures the regeneration process through the deposition of copper etched from the surface of printed circuit board blanks and the oxidation of etching products. The electrolyser housing is made of vinylplast and represents a flow-through bath with slots in the side walls for electrode installation. In the lower part of the electrolyser housing, an inlet nozzle and a distribution manifold are located. The manifold is designed as a grid system and ensures uniform supply of the etching solution into the interelectrode spaces.

Windows for draining the regenerated solution into drainage pockets are arranged in the side walls of the electrolyser. These pockets are interconnected and, via a drain pipeline, are connected to the solution tank. The electrolyser is covered on top by two covers: an internal fixed cover and an external hinged cover. The gas space of the electrolyser is connected to the ventilation system of module 2 through openings located in its rear wall between the covers. One of the side walls of the drainage pockets is made transparent to allow visual monitoring of the solution level and adjustment of the flow rate. The etching solution enters the electrolyser through the inlet manifold, rises through the interelectrode space to the upper part of the unit, and overflows into the drainage pockets. From there, it returns to the solution tank through the drain pipeline. The volumetric flow rate of the solution is regulated by the inlet valve.

Sheet-type electrodes made of titanium alloy VT1-0 are installed in the electrolyser. Each electrode has cathodic (Figure 6) and anodic (Figure 7) sides. The anodic side of the electrodes (black-coloured) is coated with a special anticorrosion layer. Copper is deposited on the cathodic sides of the electrodes, while oxidation of etching products occurs on their anodic sides. The electrodes are equipped with vinylplast handles, which allow their periodic removal from the electrolyzer for stripping of the deposited copper (Figure 8).

After the start of solution supply, the electrolyser automatically activates a rectifier unit of type VG-TPE-200-24-0-UKhL4 operating in current stabilization mode. As the electrolyser fills with solution, the current load gradually increases to the operating value, which is preset manually by the operator. Switching the regenerator on and off is performed automatically by commands from the controller or manually in manual mode.

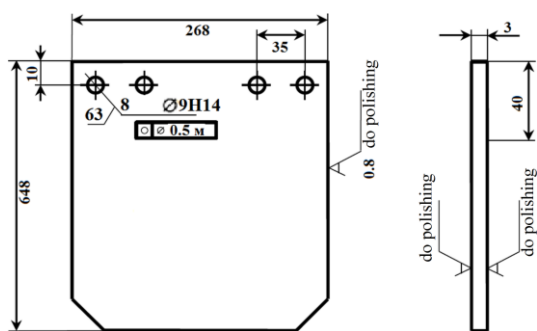


Fig. 6. Cathode for the regeneration unit

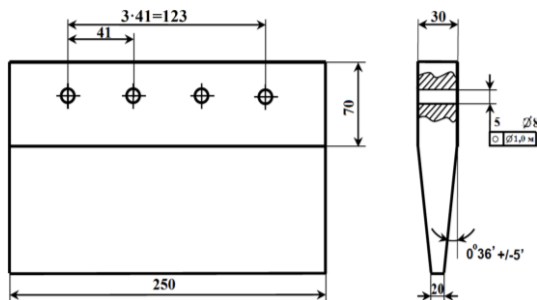


Fig. 7. Anode for the regeneration unit

The pump unit is intended to supply the solution from the solution tank to the electrolyser. The etching solution density sensor, installed on the upper cover of module 2 and supplied with etching solution via an electromagnetic valve and a pump under the control of the density controller, is adjusted to monitor changes in the concentration of copper (Cu^{2+}) ions within the range of 40–60 g/L. When the copper concentration decreases to the lower limit (40 g/L), the regenerator is switched off. When the concentration increases to the upper limit (60 g/L), the regenerator is switched on again. The copper (Cu^{2+}) ion concentration control limits can be adjusted by the operator.

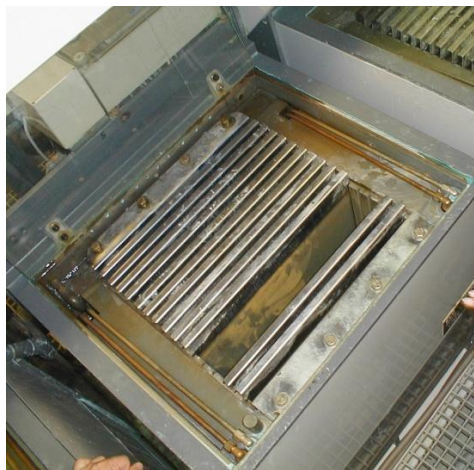


Fig. 8. Cathode sheets inside the regeneration unit

The chemical adjustment section operates in parallel with the electrochemical regeneration section and maintains the ammonia material balance by periodic dosing of an aqueous ammonia solution from an auxiliary tank. This section includes a dosing controller and a pH measurement cell with an electrode (not shown in the diagram).

The pH measurement cell with an electrode for monitoring the pH of the etching solution is installed on top of the etching module. The allowable pH range of the etching solution is set during commissioning. When the pH reaches the minimum preset value, the controller generates a signal to dose aqueous ammonia

solution from the tank into the solution reservoir. When the maximum preset pH value is reached, dosing is stopped. The pH control accuracy is ± 0.1 pH units.

Control of the electrochemical regeneration and chemical adjustment sections is performed from the control panel. Additional regeneration and adjustment parameters, such as current, voltage, and pH limit values, are set on the control panels of the rectifier and the dosing controller.

The jet treatment module with recirculation (module 3) is intended for rinsing blanks with an ammonia solution. It consists of a housing welded from sheet PVC, which contains an electrical automation compartment, a transport system, and upper and lower spray manifolds equipped with fan-type nozzles. The manifolds are covered with lids. A drain valve and a level sensor are installed in the lower part of the housing. A submersible pump (module 8) is mounted on the rear plate of the housing and is connected to the manifolds via a pipeline with a filter.

Jet treatment modules 5, 6, and 7 are designed for rinsing processed blanks with water supplied from the municipal water network. Each jet treatment chamber contains upper and lower spray manifolds with fan-type nozzles. A transport system similar to that of the etching module passes through the chamber. The spray zone is enclosed by transparent internal covers. In the unloading zone, transport rods are provided for moving printed circuit board blanks. A pair of squeeze rollers is installed at the outlet of the jet treatment chamber. Fresh rinsing water is supplied to module 7 through an inlet pipeline with a valve connected to the workshop or section water supply network.

3. Off-cathode post-electrolysis copper

The purpose of the proposed mathematical model is to estimate the amount of copper recovered on titanium cathodes during the electrochemical regeneration of etching solutions in a printed circuit board production line. The copper amount is a function of the electrical operating parameters of the regenerator and the productivity of the printed circuit board etching line. The recovered copper is considered a secondary raw material suitable for further use in metallization processes or for sale to external consumers.

The model is developed under the following assumptions:

- 1) Copper is present in the etching solution predominantly in the form of divalent ions (Cu^{2+}).
- 2) Electrochemical regeneration proceeds under steady or quasi-steady operating conditions.
- 3) The electrolysis current is either constant or varies slowly over time.
- 4) Side reactions are negligible or accounted for by an overall current efficiency coefficient.
- 5) Copper deposited on the cathodes is completely removed from the electrolyte and can be collected as a solid product.

These assumptions correspond to the actual operating conditions of pilot-industrial regeneration units and allow the use of classical electrochemical relations.

During the etching of printed circuit boards, metallic copper is transferred from the surface of the boards into the etching solution. In the regeneration unit, this dissolved copper is removed from the solution by electrochemical deposition onto titanium cathodes. Let $M_{\text{Cu}}^{\text{rec}}$ denote the mass of copper recovered during a regeneration period of duration T . According to Faraday's law of electrolysis, the mass of copper deposited on the cathodes is proportional to the total electric charge passed through the electrolyte:

$$M_{\text{Cu}}^{\text{rec}} = \frac{M_{\text{Cu}}}{zF} \eta \int_0^T I(t) dt \quad (1)$$

where M_{Cu} is the molar mass of copper, z is the charge number

of copper ions ($z=2$), F is Faraday's constant, η is the current efficiency of copper deposition, $I(t)$ is the electrolysis current as a function of time t . Expression (1) provides a direct analytical relationship between the electrical operating parameters of the regeneration unit and the amount of copper recovered.

In practical industrial operation (Figure 9), the regeneration unit typically operates at an approximately constant current I_0 . Under this condition, expression (1) reduces to:

$$M_{\text{Cu}}^{\text{rec}} = \frac{M_{\text{Cu}}}{zF} \eta I_0 T \quad (2)$$

This form of the model is particularly convenient for engineering calculations, as all parameters involved are either controlled by the operator or measured directly by the monitoring system.



Fig. 9. A photo of industrial operation of the etching line with integrated electrochemical regeneration at an enterprise, where the power box used for the regeneration unit is seen; the three tanks with solutions are seen in the front along with the pumps mounted above the tanks

The amount of copper entering the etching solution depends on the productivity of the printed circuit board line and the thickness of the copper layer removed during etching. Let S denote the total etched board area during time T , and let h be the average thickness of the removed copper layer. Then the mass of copper transferred into the solution can be estimated as:

$$M_{\text{Cu}}^{\text{etch}} = S \rho_{\text{Cu}} \varphi(S, h) \quad (3)$$

where ρ_{Cu} is the density of copper, $\varphi(S, h)$ is the fraction of etched copper that enters the solution and it is a function of S and h . Function $\varphi(S, h)$ in (3) is nonlinear and it typically satisfies an inequality

$$0.5 < \varphi(S, h) < 0.8$$

where values of fraction $\varphi(S, h)$ slowly grow as S and h increase (Table 1). Figure 10 visualizes the linear trend of this fraction versus the total etched board area of single-sided printed boards, where the parabolic approximation is inconsistent due to the polynomial is badly conditioned. It is clearly seen that the fraction of etched copper that enters the solution has a heavy nonlinear dependence on the total etched board area.

For stable operation without accumulation of copper in the solution or formation of sludge, the regeneration process must satisfy the following material balance condition:

$$M_{\text{Cu}}^{\text{rec}} \leq M_{\text{Cu}}^{\text{etch}} \quad (4)$$

This condition establishes a direct link between the electrical parameters of the regeneration unit and the technological parameters of the etching line (Figure 11).

For practical and economic analysis, it is often convenient to express the recovered copper in terms of volume rather than

mass. The volume of copper deposited on the cathodes is

$$V_{\text{Cu}}^{\text{rec}} = \frac{M_{\text{Cu}}^{\text{rec}}}{\rho_{\text{Cu}}} \quad (5)$$

This quantity represents the total volume of solid deposited copper that can be removed from the cathodes over the considered period and subsequently used as a secondary metal resource (Figure 12).

The proposed mathematical model by (1)–(5) provides a transparent and physically justified framework for estimating the amount of copper recovered during electrochemical regeneration. It can be applied:

- 1) to evaluate the economic feasibility of regeneration-based etching lines;
- 2) to optimize the operating current and regeneration time;
- 3) to assess the reduction of environmental impact through elimination of copper-containing wastewater and sludge.

Table 1. The sorted list of experimental etching cycles on single-sided printed boards

Number of cycle	Total etched board area S , mm ²	Average thickness of the removed copper layer h , mm	Mass of copper transferred into the solution $M_{\text{Cu}}^{\text{etch}}$, g	Fraction $\varphi(S, h)$
1	10000	0.017	0.861	0.56891
2	10000	0.017	0.848	0.56025
3	16000	0.017	1.4701	0.60728
4	16000	0.017	1.4671	0.60602
5	25600	0.017	2.414	0.62333
6	57500	0.035	12.432	0.69411
7	70000	0.035	15.64	0.71727
8	70000	0.035	15.639	0.71722
9	75000	0.035	16.797	0.71899
10	75000	0.035	16.7997	0.71909
11	90000	0.035	20.2847	0.72355
12	120000	0.035	27.8597	0.74531
13	234600	0.07	111.6513	0.76392
14	256500	0.07	120.5368	0.7543
15	270000	0.07	130.1676	0.77384
16	270000	0.07	128.7648	0.7655

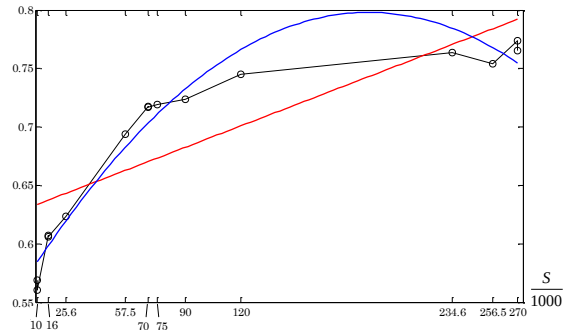


Fig. 10. The linearly approximated fraction of etched copper that enters the solution versus the total etched board area (parabolic approximation is inconsistent due to the polynomial is badly conditioned)



Fig. 11. A photo of the conveyor of circuit boards under acrylic glass, where the worker observes and adjusts the technological parameters of the etching line (the etching module is seen farther in the background)

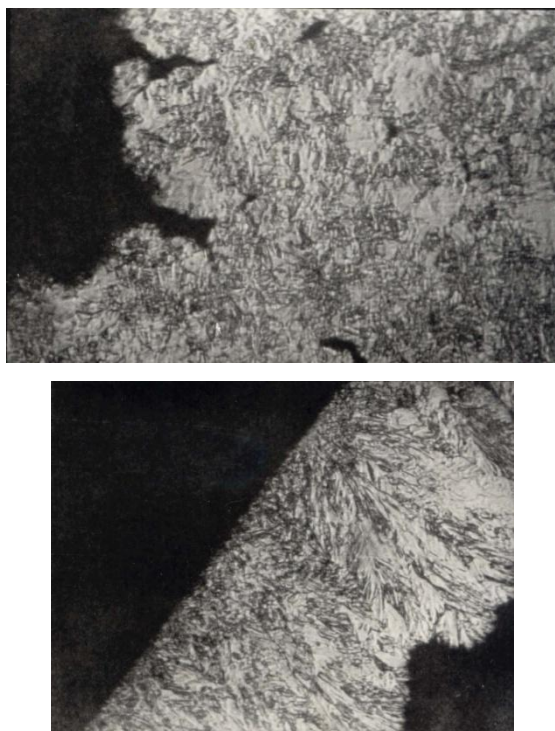


Fig. 12 Frontal (upper) and sectional (lower) views of deposited copper microstructure (120x magnification)

Model by (1)–(5) does not require empirical fitting parameters and is based solely on measurable electrical and technological variables, making it suitable for both design calculations and operational control.

During the operation of a conventional etching line (without regeneration) by Figure 1, under single-shift monthly operation, 2,400–2,500 kg of sludge is transferred to storage facilities (more than 28 tonnes per year). This corresponds to approximately 14 kg of sludge per hour. At the same time, the water consumption required to maintain the process is 4.8 m³/h (Figure 13).

For the line equipped with a regeneration unit by Figure 2, the following results were obtained. At a productivity of the printed circuit board (substrate) etching line of 14 m²/h, the regeneration unit recovers around 7 kg of copper per hour of operation (11,856 kg per year on average), while practically no waste (sludge) is generated (Figure 14). Thus, approximately 0.3 to 0.6 kg of copper is etched from 1 m² of substrate (board). In this case, the water consumption required to support the process is 0.8 m³/h.



Fig. 13. A photo of the whole etching module (in the centre) and its loading module (in the front), rinsing and drying modules at an enterprise; the electrical control system is seen at the loading module (where circuit boards are loaded) with its buttons for turning on and off distinct components of the system, and signaling the system states and issues (for instance, the water consumption rate sustainability)



Fig. 14. A photo of the compact etching solution regenerator (on the right), where parts of the etching module are seen on the left, with a productivity of the printed circuit board (substrate) etching line of 14 m²/h

4. Conclusions

A technology has been developed for the recovery of heavy metals (copper) and the corresponding reduction of sludge accumulation on the premises of printed circuit board manufacturing enterprises. The proposed etching line with integrated electrochemical regeneration provides a technologically and environmentally efficient alternative to conventional printed circuit board etching systems. By redirecting rinsing waters and spent etchants into a closed-loop regeneration unit, the process eliminates wastewater discharge and substantially reduces the formation of hazardous sludge, thereby minimizing environmental impact. The line ensures a constant etching rate of printed circuit boards (substrates) within the range of 35–38 μm/min. The recovered copper can be sent for remelting and subsequent use in industrial applications.

A mathematical framework for estimating the amount of off-cathode copper recovered during electrochemical regeneration has been formulated. The model links the recoverable copper mass to key technological parameters, including the etched board area, copper removal rate per unit surface, electrolyte composition, current efficiency, and operating time. This framework enables predictive assessment of copper recovery volumes and supports economic planning for further utilization or commercialization of the recovered metal.

Industrial operation results confirm the practical validity of the proposed approach. Compared to a conventional line generating significant quantities of copper-containing sludge and consuming large volumes of water, the regeneration-based line achieves near-waste-free operation, markedly lower water consumption, and stable recovery of metallic copper on titanium cathodes. The recovered copper represents a valuable secondary resource suitable for reuse in metallization processes or for sale to external consumers.

Overall, the integration of electrochemical regeneration with a quantitatively grounded estimation model enhances both the sustainability and economic efficiency of printed circuit board etching operations, making the proposed solution attractive for industrial implementation.

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