Regeneration of etching solution used in the production of printed circuit boards

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Abstract. Some waste waters containing copper are formed during the production of printed circuit boards. When these effluents are discharged into the reservoir, they must be diluted 140,000 times, and the treatment of these copper-containing effluents causes the copper loosing. The paper presents the results obtained during the study of electrochemical processing of copper-containing effluents formed at the stage of PCBs etching. The spent solution processing was realized in a membrane electrolytic cell. An increase in current density results in an increase in process speed. Along with a decrease in copper concentration in the solution, the hydrochloric acid was concentrated. It is shown that it is possible to regenerate the etching solution and obtain a metallic copper.

1 Introduction

The circuit boards are used in many industries [1]. One of the solutions used in the PBCs production is a solution containing: CuCl2 65 - 140 g/dm^3 (in terms of Cu), HCl 90 - 160 g/dm^3, H_2O_2 25 - 30 g/dm^3 [2, 3].

Copper chloride oxidizes metallic copper in solution by reaction:

$$CuCl_2 + Cu \rightarrow 2CuCl.$$

The resulting copper chloride CuCl is insoluble and can be a source of nozzle clogging in etching plants. In the presence of chlorine ions in the form of HCl, well-soluble complexes are formed, dissociating in solution to form $CuCl^-$ [4] ion. Oxidation of the resulting univalent copper compounds is accomplished by exposure to hydrogen peroxide [5]:

$$2CuCl + H_2O_2 + 2HCl \rightarrow 2CuCl_2 + 2\,H_2O.$$

During the circuit board treatment, the copper content in the solution increases. When the concentration of copper in the etching solution reaches more than 140 g/dm^3 the electrolyte is considered to be spent. It also contains about 65.7 g/dm^3 HCl and 14 g/dm^3 H_2O_2.

The MAC of copper in waters of fishery importance makes of 0.001 mg/dm^3. When discharging this effluent into the water bodies, it should be diluted for 140000 times [6].

The treatment of copper-containing wastewaters by alkaline reagents to obtain a copper hydroxide sediments [7] and other methods of treatment [8, 9, 10] causes the copper losses. So during the work of the only one line for circuit boards etching with productivity of 14 m^2/hour the copper losses may reach about 1,2 tons/month [11].

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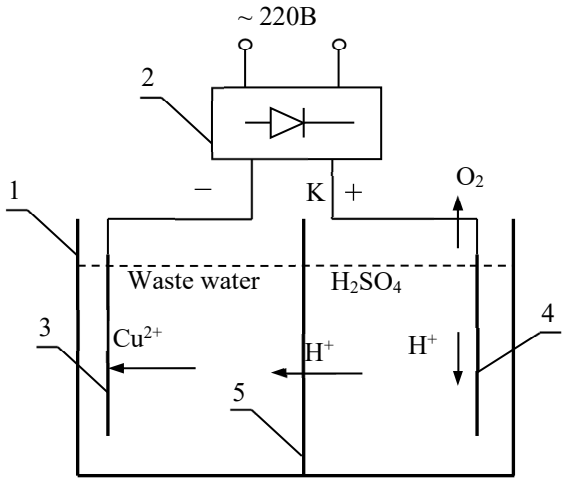
The paper presents the results obtained in the study of electrochemical treatment of copper-containing effluents generated at the stage of PCBs etching. It is shown that it is possible to regenerate the etching solution and obtain metallic copper.

2 Materials and methods

The scheme of the pilot plant, consisting of an electrolyzer and a power source, is shown in the Figure 1. The electrolyzer consists of two chambers separated by a cation-exchange membrane MK-40. A titanium plate coated with ruthenium oxide served as the anode, a copper plate with a working surface of 9 cm^2 served as the cathode.

For the experiment was used the waste generated after etching baths with the content of $CuCl_2$ 140 g/dm^3 (per copper), HCl 65.7 g/dm^3, H_2O_2 14 g/dm^3.

The solution volume of 70 ml was placed in the cathode chamber of the electrolyzer. 70 ml of 0.1 n sulfuric acid was poured into the anode chamber. The wastewater recycling process was investigated at the cathode current densities from 68 mA/cm^2 to 134 mA/cm^2, the current load was from 0.61 A to 1.21 A. The electrolyzer process resulted in the water decomposition with the release of oxygen and generation of hydrogen ion sat the anode. Hydrogen ions migrated through the membrane into the cathode chamber by the action of the electric field. Copper ions were discharged at the cathode, forming metal. As a result, a hydrochloric acid solution appears and the concentration of copper chloride decreases.



1 – electrolyze,
2 – power source,
3 – cathode,
4 – anode,
5 – cation -exchange membrane.

Fig. 1. Schematic diagram of the pilot plant.

After each hour of the unit operation, the concentration of copper and hydrochloric acid in the treated solution was determined.

3 Results and discussion

The dependence of copper concentration in the recycled solution on the electrolysis time is presented in Figure 2. The current passed through the electrolyzer has a significant effect on the rate of copper extraction from wastewater. The highest rate of copper extraction is observed at current density 134 mA/cm^2 and is 16.67 g/h, at current density 68 mA/cm^2 the rate of copper extraction is 5.56 g/h. The experiments duration was determined by the copper ions concentration in the solution equal to 40 g/dm^3. As a result, the wastewater treatment at the current density 68 mA/cm^2 will take 18 hours, at current density 134 mA/cm^2 will take 6 hours.

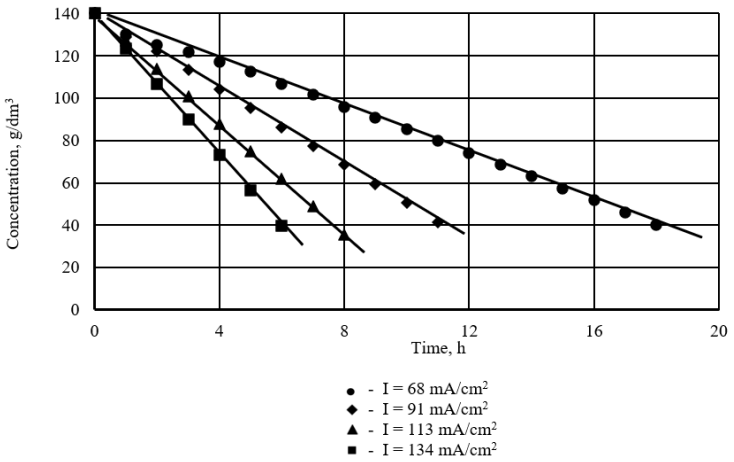


Fig. 2. Dependence of copper concentration in the recycle solution on the electrolysis time.

Figure 3 shows the dependence of current efficiency on current density. When the current density increases from 68mA/cm^2 to 134 mA/cm^2, the current efficiency increases from 54% to 81%.

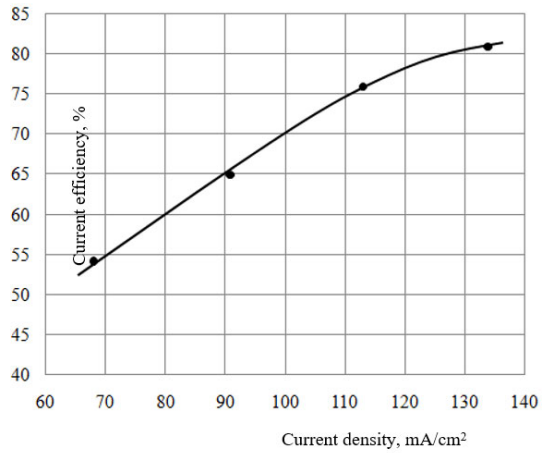


Fig. 3. Current efficiency versus current density.

Along with the wastewater treatment from copper ions in the cathode chamber the process of hydrochloric acid concentration takes place (Figure 4). As the current density increases from 68 mA/cm^2 to 134 mA/cm^2, the concentration rate of HCl increases from 6.67 g/h to 20 g/h. The hydrochloric acid concentration increases from 67.5 g/dm^3 to 180 g/dm^3. The current density changing from 68 mA/cm^2 to 134 mA/cm^2 reduces the time to reach the maximum hydrochloric acid concentration value from 18 hours to 6 hours.

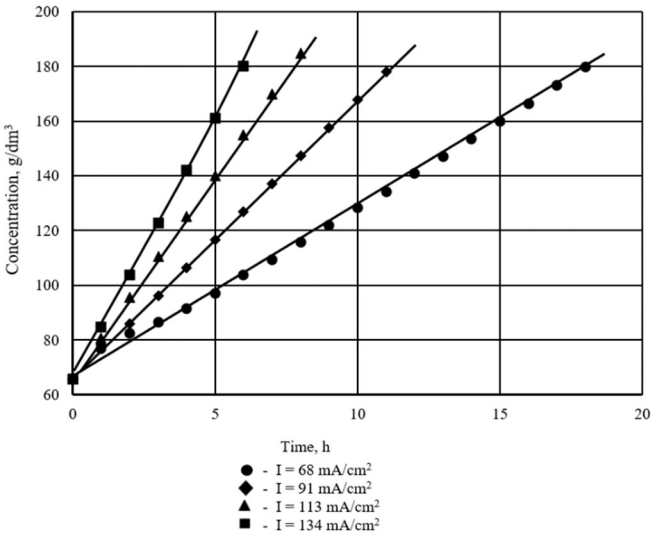


Fig. 4. Dependence of hydrochloric acid concentration in the processed solution on the electrolysis time.

The power consumption increases when the current densityis increased (Figure 5). Thus, an increase in current density from 68 mA/cm2 to 134 mA/cm2 causes an increase in power consumption from 2 kVt·ch/kg to 2.7 kVt·ch/kg.

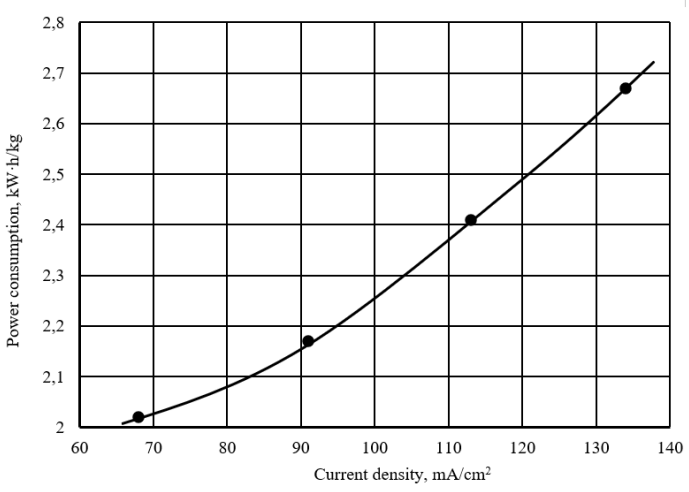


Fig. 5. Dependence of power consumption for copper extraction on current density.

4 Conclusion

The paper refers to the electrochemical treatment of copper-containing effluents generated during the circuit boards etching was investigated. It is shown that the electrochemical treatment of such effluents results in decrease of copper concentration in the waste waters to 40 g/dm3 and of hydrochloric acid concentration to 180 g/dm3. The power quantity affects the speed of processes flowing in the apparatus. The current density increasing from 68 mA/cm2 to 134 mA/cm2 the speed up the process time reducing from 18 to 6 hours, increasing the power efficiency from 54 to 81% and increasing energy consumption from 2 kW·h/kg to 2.7 kW·h/kg. As a result, after the required correction, the resulting solution may be returned to production, thereby creating a closed cycle and reducing the pressure on the environment.

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