Article

Leaching of gold and copper from printed circuit boards under the alternating current action in hydrochloric acid electrolytes

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Abstract: Modern technologies for recycling electronic waste (e-waste) impose high economic efficiency and environmental safety requirements. Among existing technologies, hydrometallurgy is considered the most promising technology for e-waste recycling. Increasing attention to the chlorination method is associated with the complex recycling of low-grade ores containing noble metals and secondary polymetallic raw materials. In this paper, we propose a new scheme for leaching metals from computer printed circuits (PCBs) pre-crushed in a disintegrator: the processes of chlorine production and hydrochlorination are implemented in one reactor under the action of alternating current (AC) of industrial frequency (50 Hz). It was found that complete leaching of gold is achieved from fine fractions of raw materials containing 0.03% and 0.01% of the gold at an experiment duration of 2 hours, a current density of 0.66 $A \cdot cm^{-2}$, and a solid/liquid ratio of 8.6 $g \cdot L^{-1}$. Under the same conditions of the electrochemical leaching process from the fraction of raw material with a gold content of 0.08%, the degree of metal leaching is 80.5%. At the same time, with an increase in the copper content in the raw material from 1.40% to 6.13%, an increase in the degree of its leaching from 84.6% to 95.2%, respectively, is observed. These results will serve as a foundation for developing a complex technology for recovering valuable metals from PCBs.

Keywords: printed circuit boards, gold, copper, electrochemical leaching, alternating current

1. Introduction

The volume of electronic waste (e-waste) suitable for recycling to recover precious and non-ferrous metals is rapidly growing worldwide. Personal computers are the largest sources of electronic waste [1]. Computer printed circuit boards (PCBs) are manufactured using complex technologies and contain metals, polymers, and ceramics [2]. The content of individual metals in PCBs, given in the literature [3], varies widely, which is associated not only with the manufacturer and date of production of computers but also with the methods of preliminary grinding of the raw material, sampling, and leaching method for transferring metals into a solution for quantitative analysis.

There are three leading technologies for recycling electronic waste - pyrometallurgy, hydrometallurgy, and bio-metallurgy [4]. Pyrometallurgy requires significant capital investments and is characterized by high energy consumption compared to the hydrometallurgical process and is used mainly for recycling large volumes of primary (ore) and secondary raw materials [5]. The particular importance of hydrometallurgical technology is determined by economic efficiency and environmental safety. Therefore, hydrometallurgical electronic scrap recycling possibilities have been actively studied [6]–[11]. Leaching is the initial stage of the hydrometallurgical process and the most critical stage in recovering valuable metals from waste PCBs. Usually, for the enrichment of raw materials, a preliminary acid treatment (H_2SO_4, HCl or HNO_3) is carried out [9], [12], [13]. Within the framework of hydrometallurgical technology, there are many ways of gold leaching – cyanide, aqua regia, halogen-halide, thiosulfate, thiourea, etc. [9]. Cyanidation is the primary method of hydrometallurgical recovery of gold and silver from ores, which consists of the leaching of metals using alkaline cyanide solution (NaCN, KCN) in the presence of atmospheric oxygen [14]. The use of cyanidation for leaching gold from PCBs showed that this method is effective only for dissolving gold and/or silver from the surface of PCBs. In addition, this process has a low leaching rate and generates a large amount of wastewater containing cyanide [15].

Gold dissolves in aqua regia to form chloroauric acid $H[AuCl_4]$. Similarly, gold dissolves in hydrochloric acid solutions in the presence of Fe^{3+} [16], [17], acting as an oxidizing agent. The dissolution reaction examples can be expressed as in Equation (1) and (2):

$$Au + 2Cl^- + Fe^{3+} \rightarrow [AuCl_2]^- + Fe^{2+} \quad (1)$$

$$[AuCl_2]^- + 2Cl^- + 2Fe^{3+} \rightarrow [AuCl_4]^- + 2Fe^{2+} \quad (2)$$

Leaching with the use of chlorine, bromine, and iodine is characterized by a high rate [18]. In this case, gold forms both Au+ and Au3+ complexes with halide ions, depending on the chemical composition of the solution. The reaction of dissolving metallic gold in a chlorine-saturated solution of hydrochloric acid (hydrochlorination process) proceeds according to the equations (3) and (4) [16], [19]:

$$Au + 0.5Cl_2 + Cl^- \rightarrow [AuCl_2]^- \quad (3)$$

$$Au + 1.5Cl_2 + Cl^- \rightarrow [AuCl_4]^- \quad (4)$$

Chlorination of gold and copper in chloride solutions is characterized by the high solubility of metal complexes with chlorine and a high leaching rate [20].

Chlorination processes for recovering gold from ores and concentrates have been used since the second half of the 19th century and preceded cyanide leaching technology. A significant release of chlorine characterizes industrial methods of hydrochlorination into the atmosphere [16]. Therefore, it is crucial to reduce chlorine consumption and improve maintenance personnel's safety when developing a hydrochlorination technology for recovering valuable metals from secondary raw materials.

New technological solutions are proposed to minimize the risks of using chlorine/chloride leaching systems, including the production (electrogeneration) of chlorine *in situ*. Thus, to study the leaching of copper, zinc, lead, and tin from PCBs, the authors [21] proposed two reactor designs: a combined reactor (with an anion-exchange membrane) with simultaneous formation of chlorine under the action of direct current and metal leaching, and a separate metal leaching reactor connected with the anode compartment of the chlorine gas generator. The non-magnetic fraction of crushed PCBs was used as a dispersed phase in a hydrochloric acid solution. The results obtained showed that the efficiency of copper leaching in a combined reactor is lower than in a separate reactor. In the separate reactor at 50 °C and experiment duration of 240 minutes, the degree of Zn, Sn, Pb and Cu leaching in a 2M HCl solution is 98, 96, 96 and 71%, respectively. The impact of copper ions in solution on the rate of copper leaching using electrogenerated chlorine in a combined reactor showed that with an increase in the concentration of cuprous ions in the solution, the share of current for the release of chlorine decreases. For the oxidation

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of cuprous ions, it increases [22]. In this case, the following reactions of leaching in hydrochloric acid solution Equations (5) and (6) and Equations (7) and (8) on the anode take place [23]:

$$Cu + Cl_{2(aq)} \rightarrow Cu^{2+} + 2Cl^{-} \quad (5)$$

$$Cu^{2+} + 4Cl^{-} + Cu \rightarrow 2[CuCl_2]^{-} \quad (6)$$

$$2Cl^{-} \rightarrow Cl_{2(g)} + 2e^{-},\ E^0 = 1{,}358\ V_{SHE} \quad (7)$$

$$[CuCl_2]^{-} \rightarrow Cu^{2+} + 2Cl^{-} + e^{-},\ E^0 = 0{,}457\ V_{SHE} \quad (8)$$

The gaseous chlorine released at the anode equation (7) and dissolves in hydrochloric acid solutions as follows reaction Equations (9)-(11) [24]:

$$Cl_{2(g)} \leftrightarrow Cl_{2(aq)} \quad (9)$$

$$Cl_{2(aq)} + H_2O \leftrightarrow HCl + HOCl \quad (10)$$

$$Cl_{2(aq)} + Cl^{-} \leftrightarrow Cl_3^{-} \quad (11)$$

The product distribution depends on the HCl concentration, pH, and temperature. At electrolyte temperatures of 50 °C, 60 °C, and 70 °C, with an increase in the HCl concentration from 3 $mol{\cdot}L^{-1}$ to 7 $mol{\cdot}L^{-1}$, a decrease in the content of $Cl_{2(aq)}$ in solution and an increase in the content of Cl_3^{-} are observed. At the same time, the content of HClO remains insignificant.

The results of the two-stage leaching process of gold from waste mobile phone PCBs in a separate leaching reactor are also presented in [25]. It was demonstrated that at the first stage of the process, 97% copper and 5% gold are leached into a 2 M HCl solution, and at the second stage, 93% of gold is leached into a 0.1 M HCl solution. In this case, the reactions of gold dissolution in the reactor are presented in the form of the following reaction Equations (12) and (13):

$$Au + Cl^{-} + 3/2Cl_2 \rightarrow [AuCl_4]^{-}_{(aq)} \quad (12)$$

$$Cl_{2(aq)} + H_2O \leftrightarrow HCl + HOCl \quad (13)$$

A separate reactor connected with the anode compartment of a chlorine gas generator was also used in [26] to leach gold from waste PCBs. The leaching stage was preceded by treatment in a 4M HCl with the addition of H_2O_2. It is shown that over 75 minutes of the experiment at a temperature of 50 °C, more than 99% of gold passes into a 2.0 M NaCl solution (pH 1.0) at a feed rate of electrogenerated Cl_2 of 0.62 $mmol{\cdot}min^{-1}$.

An electrochemical process is also proposed to separate Cu, Sn, Ag, and Pd, Au in two stages. Wherein at the second stage, Pd and Au are dissolved by chlorine generated on the anode under the action of direct current [27].

Thus, the above-mentioned studies have shown that the electrogenerated chlorine leaching process can be successfully used to leach metals from electronic waste.

At the same current densities, the voltage using alternating current (AC) is almost two times lower than when using direct current, which makes the process energetically more favorable. AC of various shapes contributes to the intensification of the processes of anodic dissolution/dispersion of metals and the elimination of passivation of the metal electrode [28]. The authors [29] demonstrated that the electrochemical dissolution of platinum group metals in hydrochloric acid solutions using AC is an effective and promising way to obtain pure salts of noble metals. A method for the dissolution of noble metals (Au, Ir, Pd, Pt, Rh) and metals resistant to hydrochloric acid (Cd, Cu, In, Ta, W) under the action of a half-wave or a full-wave AC was also proposed in [30]. The study showed that the rate of dissolution of metals noticeably increases with increasing current density and HCl concentration in the electrolyte solution from 3.2 M to 12 M.

This work aims to study some regularities of the process of copper and gold leaching from disintegrator-crushed PCBs under the action of alternating current in hydrochloric acid electrolytes. In the proposed scheme, the processes of producing an oxidizing agent - chlorine and leaching of metals- occur in one electrochemical cell. The production of chlorine occurs on the electrodes under the action of AC.

2. Materials and Methods

The scheme of studies presented in this paper is shown in Figure 1.

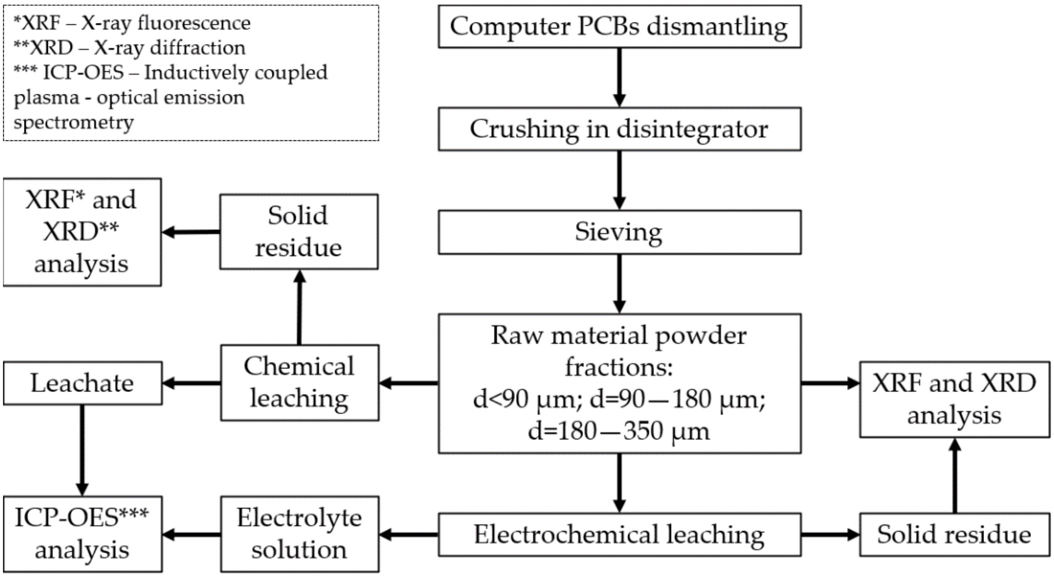

Figure 1. Schematic diagram of the process investigated.

Preliminary preparation of raw materials included only stages of PCB dismantling, double crushing in a hammer mill (DS-A) and single crushing using the high-energy semi-industrial disintegration-milling system (disintegrator DSL-350, Tallinn University of Technology, Estonia) and subsequent sieving (FRITSCH ANALYSETTE 3 PRO Vibratory Sieve Shaker). As a result, the three finest fractions of the obtained powders with different particle sizes (d) were selected as raw research materials: <90 μm, 90-180 μm and 180-350 μm.

The electrical circuit and the electrochemical cell used are shown in Figure 2. The electrochemical cell was a square-shaped diaphragm-less polypropylene reactor with a tight-fitting lid, on which two cylindrical graphite electrodes (for spectral analysis, d=0.8 cm) were mounted. The lid also had two holes for a glass paddle stirrer, loading the raw material, filling the electrolyte, and installing a chromel-alumel thermocouple to measure the electrolyte temperature (T_{el}). Powders of the raw material were used in the form of a dispersed phase in a volume (V) of hydrochloric acid electrolyte (C_{HCl}=6M, V=350 ml). After filling the reactor with the initial components to create a suspension, the mixture was stirred at a speed of 1200 mim^{-1} for 5 minutes, then the stirring speed was reduced to 700 rpm, and the power was turned on. The solid to liquid (S/L) ratio in the suspension was 2.9 $g \cdot L^{-1}$, 5.7 $g \cdot L^{-1}$, 8.6 $g \cdot L^{-1}$, 11.4 $g \cdot L^{-1}$ and 14.3 $g \cdot L^{-1}$. To produce chlorine, an alternating current (AC) of industrial frequency (50 Hz) with a density (i) of 0.66 $A \cdot cm^{-2}$ and 0.88 $A \cdot cm^{-2}$ was used. The duration of the experiments (t_{ex}) varied from 0.5 to 5 hours. Solid residues after leaching were washed with distilled water to pH 5-6, dried at a temperature of 105 °C and weighed.

Quantitative determination of metals in solutions resulting from chemical (sequentially boiling in 6M HCl solution and aqua regia solution) and electrochemical (in 6M HCl solution) leaching of raw materials was carried out by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 7000 DV ICP-OES). X-ray diffraction (XRD, diffractometer Rigaku – MiniFlex 600 with CuK_{α} radiation with λ=1.5418Å) and X-ray fluorescence (XRF, analyzer EDAX-EAGLE III XPL) analyses were used to characterize raw materials and solid residues after leaching. The disintegrator-crushed fractions of raw material microscope (KEYENCE VHX-2000) were used for optical imaging. For the quantitative determination of free chlorine in the electrolyte solution, the method of titration with methyl orange was used [31].

The efficiency of electrochemical leaching of metals from raw materials was evaluated by the degree of metals leaching (R), which was defined as the ratio of the quantity of metal transferred into the electrolyte solution (M_{el}) to the quantity of metal contained in the raw material (MPCBs), as demonstrated in Equation (14):

$$R(\%) = (M_{el} / M_{PCBs}) \times 100\% \quad (14)$$

The content of metals in the raw material (MPCB) was calculated from the results of the ICP-OES analysis of the leachates obtained from the chemical leaching of a representative sample of the raw material.

In the proposed process organization scheme (Figure 2), the oxidizing agent – chlorine, is produced during the anodic half-cycles of the passage of AC through the cell on graphite electrodes, and raw material leaching occurs mainly in the volume of the electrolyte solution. This process does not require special conditions or additional reagents, and the process can be carried out in batch mode. This dramatically simplifies chlorination technology and makes it more environmentally friendly.

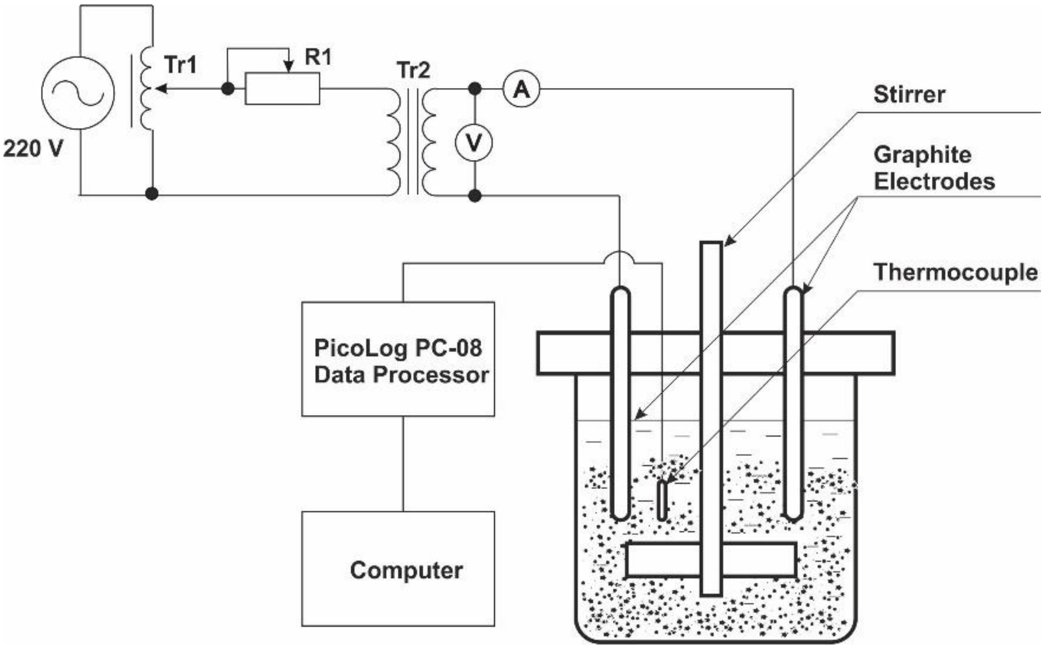

Figure 2. Scheme of the experimental setup: the electrical part (AC circuit): Tr1 - laboratory autotransformer, R1 - rheostat, Tr2 - step-down transformer, V - AC voltmeter, A - AC ammeter.

3. Results and discussion

3.1. Raw material treatment and characterisation

The high-energy semi-industrial disintegration-milling system, specially designed for processing mechanically durable materials was used to grind fragments of PCBs into finer particles. The detailed disintegration-milling system is described in the works [32]–[34]. The device is grinding materials by collisions. Supplied particles collide with a wall (target, grinding body) from the point of contact. The resulting intensive wave of pressure begins to propagate, and the resulting values of stresses exceed material strength. In the previous work [35], a novel single and two-stage PCBs disintegration-milling approach was described.

A mixture of various computer PCBs (Figure 3) was treated as described in previous work [35], and was used as an object of this research. As a result of crushing and subsequent sieving, three fine powder fractions of the raw material were obtained (Figure 4a, 4b and 4c) and designated [A], [B] and [C] respectively. The morphology of the three finest fractions of raw material powders was studied using optical microscopy (Figure 4a, 4b and 4c).

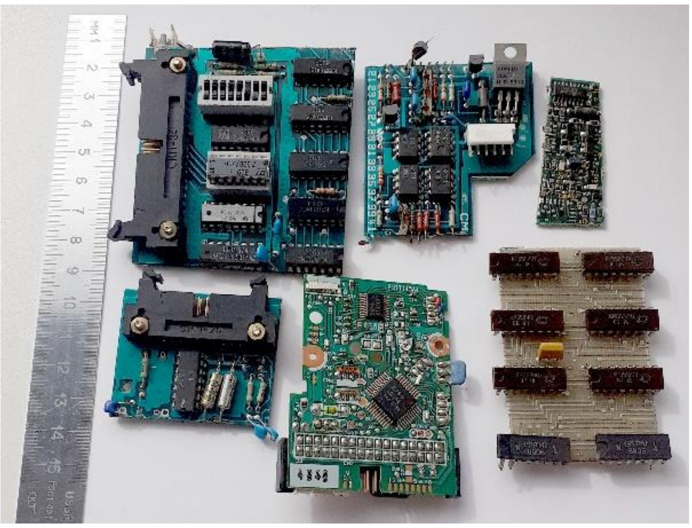

Figure 3. Image of computer PCBs used for the study.

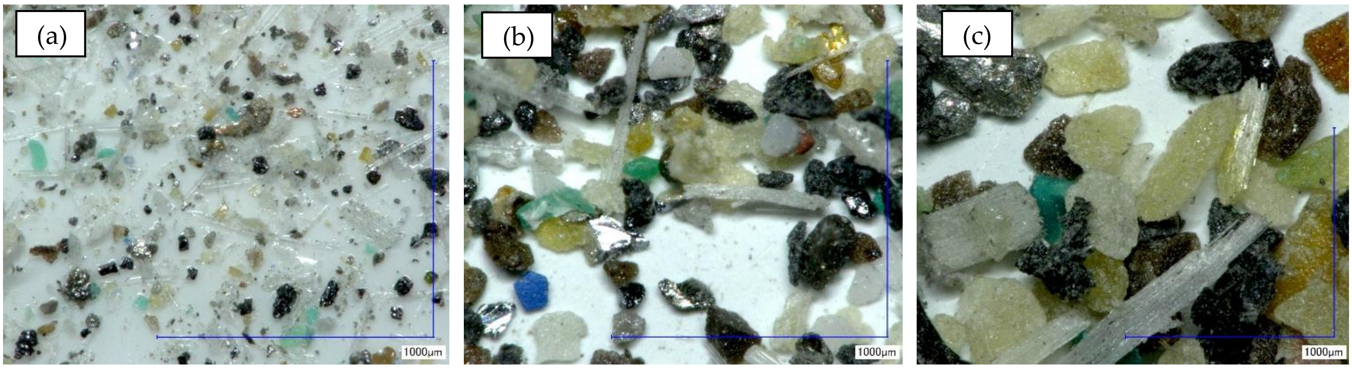

Figure 4. Optical images at magnification ×200 times, of disintegrator-crushed PCBs fractions: (a) is d<90 μm; (b) is d=90–180 μm; (c) is d=180–350 μm and designated [A], [B] and [C] respectively.

From the presenting data it can be seen the obtained powders are heterogeneous and consist of irregularly shaped particles (Figure 4). It should be noted that these raw material powders without any additional physical and/or chemical pre-treatment were used in the study of Au Cu electrochemical leaching.

3.1.1. Complex characterization of raw material fraction [A]

From the obtained fractions [A], [B] and [C], the finest fraction [A] was chosen as the major object of the research.

The quantitative determination of the elements included in the composition of PCBs is complicated both by the presence of a wide range of elements present in various chemical forms (metals, alloys, their corrosion products) and the range of their concentrations and by the significant content of the base. Therefore, atomic spectral analysis methods such as X-ray fluorescence (XRF), optical emission analysis with inductively coupled plasma (ICP-OES), as well as X-ray diffraction (XRD) were used for complex investigation of raw material.

In this work, XRF analysis was used to qualitatively/semiquantitatively determine the composition of the raw material sample. According to the results obtained (Figure 5), such metals as Fe, Ca, Zn, Cu, Ni, Al, Ti, Mn, and also Si are present in the sample. However, based on the obtained spectrum, it is impossible to unequivocally judge the presence of gold in the sample under study since in the region of the gold (AuL) peak (about 9.50 keV), overlapping with a second zinc peak (ZnK), on the figure an indicated by arrow.

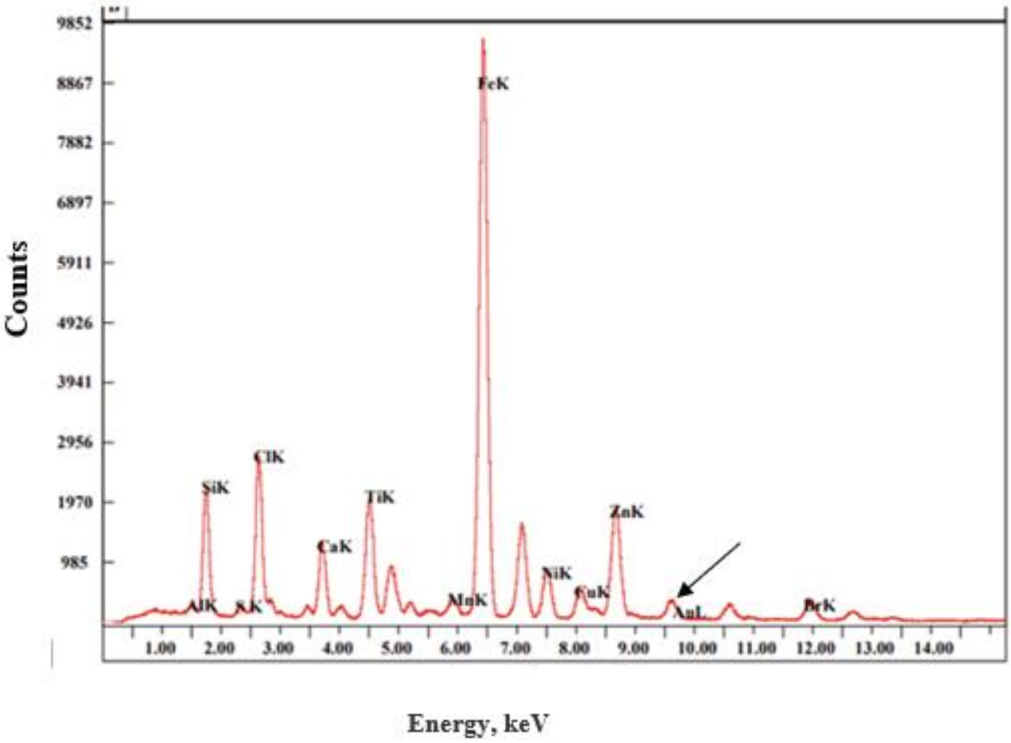

Figure 5. Fluorescence spectrum of raw material

In turn, the X-ray phase analysis data (Figure 6, curve 1) demonstrate the presence of such basic crystalline phases as SiO_2, Si, Al_2O_3 and Fe_3O_4. Established compounds are included in PCB materials such as fiberglass, ceramics, and semiconductor materials [36]. The phase composition of the solid residue obtained after chemical leaching of a raw material sample was also studied (Figure 6, curve 2). A comparison of the obtained results (Figure 6) shows that the chemical leaching of the raw material has practically no effect on its phase composition. In the solid residue obtained after chemical leaching, only the crystalline phase of magnetite was not detected.

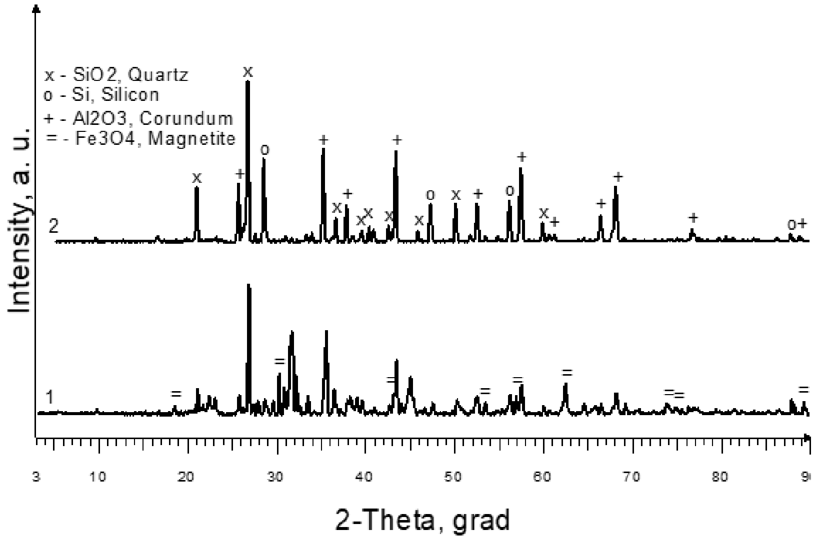

Figure 6. XRD patterns: 1 – raw material; 2 - solid residue after chemical leaching of raw material.

The solution obtained after chemical leaching (leachate) of the raw material sample was analyzed by ICP-OES (Figure 7). Wherein a quantitative determination was carried out not only of metals identified in a solid sample using XRF analysis (Figure 5) but also of some others, usually included in PCBs, - tin, lead, antimony, nickel, and cobalt. The results are presented in Figure 7. According to the results of weighing, the content of the solid residue after chemical leaching is 45.76 wt.% of the mass of raw material. It should be noted that 26.52 wt.% are elements whose quantitative determination in the solution was not carried out by the ICP-OES method. Thus, the content of target metals in fraction A was established: gold - 0.08 wt.% and copper - 1.40 wt.%.

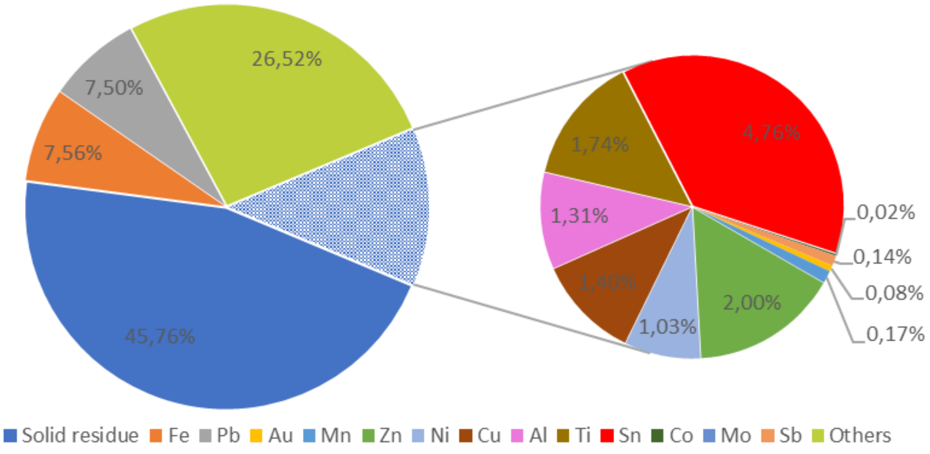

Figure 7. Content of metals in raw material according to the results of ICP-OES analysis of the leachate.

According to the results of ICP-OES analysis of the leachates obtained after chemical leaching of the raw material fractions B and C, the gold content is 0.03 wt.%, 0.01wt.% and the copper content is 2.67 wt.%, 6.13 wt.%, respectively.

3.2. *Impact of electrochemical leaching process parameters on the leaching degree of gold and copper*

3.2.1.Solid/liquid ratio

The results presented in Figure 8 shows that the degree of gold leaching varies according to a parabolic law, reaching a maximum at S/L=8.6 g/L. With a further increase in the S/L ratio, there is a significant decrease in R to 46.9 % (S/L=14.3 g/L). This could be because at a higher S/L under these experimental conditions, chlorine concentration in the electrolyte solution is insufficient for complete metal dissolution. Since in the process under study, chlorine ions are not only a precursor for the production of an oxidising agent - chlorine but also a complexing agent that forms soluble complex ions with metal ions [30]. With an increase in S/L, an increase in the degree of leaching can be achieved both by increasing the concentration of chloride ions in the electrolyte solution and by increasing the current density [37]. Whereas with an increase in the S/L ratio from 2.9 g/L to 14.3 g/L, the degree of copper leaching increased linearly from 82.1 wt.% to 87.3 wt.%, respectively.

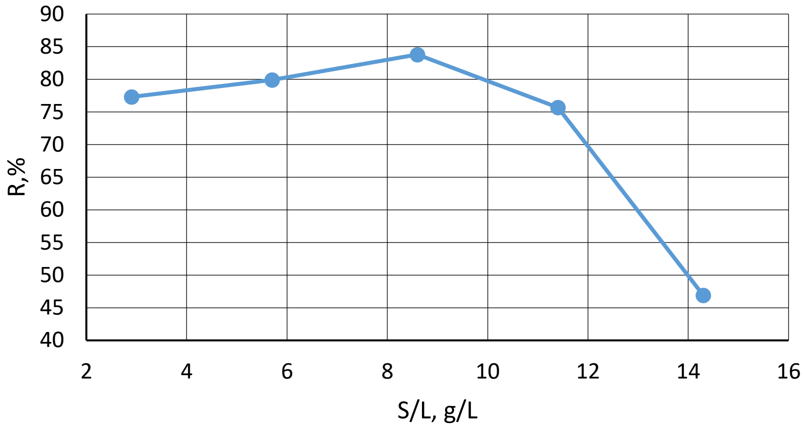

Figure 8. Impact of S/L ratio on the degree of gold leaching. Experimental conditions: raw material - fraction [A], CHCl=6 M, i=0.66 A/cm2, tex= 2h.

3.2.2. Raw material particle size

According to Figure 9, complete leaching of gold is achieved at a larger particle size of raw material and lower gold content (fractions [B] and [C], Figure 4b and 4c). The degree of copper leaching also increases with the particle size, but complete leaching was not achieved.

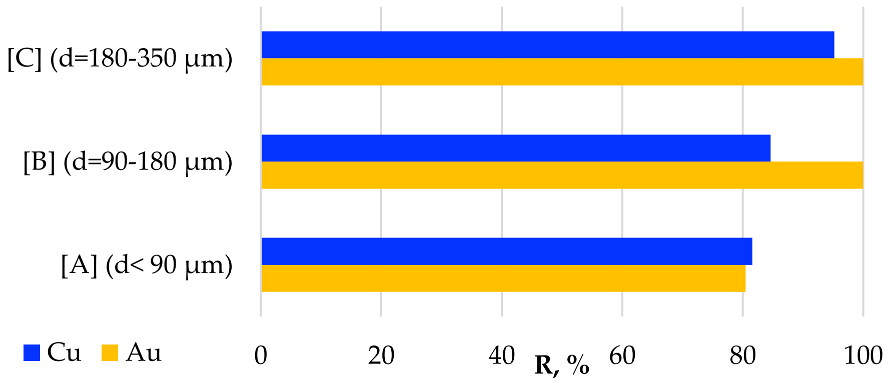

Figure 9. Impact of raw material particle size on the degree of gold and copper leaching. Experimental conditions: i=0.66 A/cm^2, t_{ex}=2h, S/L=8.6 g/L, C_{HCl}=6 M.

3.2.3.Alternating current

Applying AC (i=0,66 A/cm^2) has resulted in a noticeable improvement in the degree of gold leaching compared with the experiment in the absence of AC. In contrast, the degree of copper leaching does not seem to benefit from AC (Figure 9, 10) significantly.

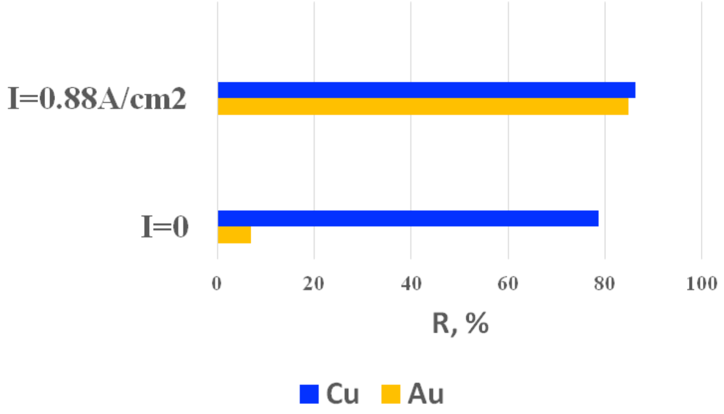

Figure 10. Effect of AC applying on gold and copper leaching degree. Experimental conditions: raw material - fraction [A], tex= 2h, S/L=8.6 g/L, CHCl=6 M.

Increasing the current density from 0,66 A/cm2 to 0,88 A/cm2 leads to a slight increase in the gold and copper degree of leaching (about 4%).

From the presented data (Figure 10), it can be seen that 6.9% of gold and 78.6% of copper at room temperature passes into a hydrochloric acid solution that does not contain chlorine. On the one hand, this is due to the reaction of oxidation of these metals by iron ions (equations (1) and (2)) [16], [17], [38], which are formed as a result of the dissolution of iron or its compounds in a solution of hydrochloric acid. On the other hand, such a significant transition of copper into the solution under these conditions is also probably associated with substantial amounts of its corrosion products, which occurs during the storage of electronic waste in the humid air. Thus, these results show that acid pretreatment of finely dispersed raw material with hydrochloric acid solutions, which are used in certain hydrometallurgical technologies for pre-leaching of active metals, can lead not only to losses of copper but also of gold.

3.2.4. Electrolyte temperature

With the passage of alternating current during the first 30 minutes of the process, a noticeable increase in the temperature of the electrolyte and a decrease in the voltage on the cell are observed. A further increase in the duration of the experiment leads to a gradual stabilisation of these parameters. (Figure 11).

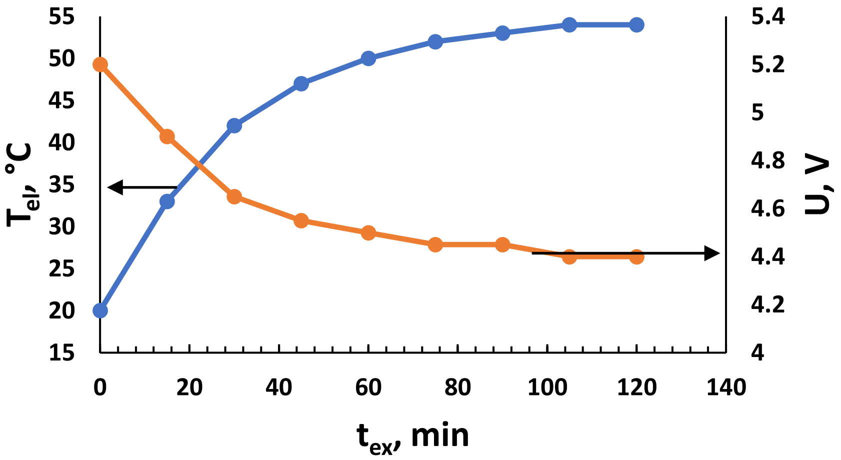

Figure 11. Electrolyte temperature and cell voltage versus the experiment duration. Experimental conditions: raw material – fraction [A], CHCl=6 M, i=0.66A/cm2, S/L=8.6 g/L.

To study the effect of electrolyte temperature on the efficiency of metal leaching, the processes were carried out with forced air cooling of the electrolyte while maintaining a constant electrolyte temperature in a polypropylene reactor and a jacketed glass cell, respectively (Figure 11).

The results showed that the electrolyte temperature practically does not affect the copper leaching efficiency. In turn, increasing the electrolyte temperature twice improves the gold leaching efficiency.

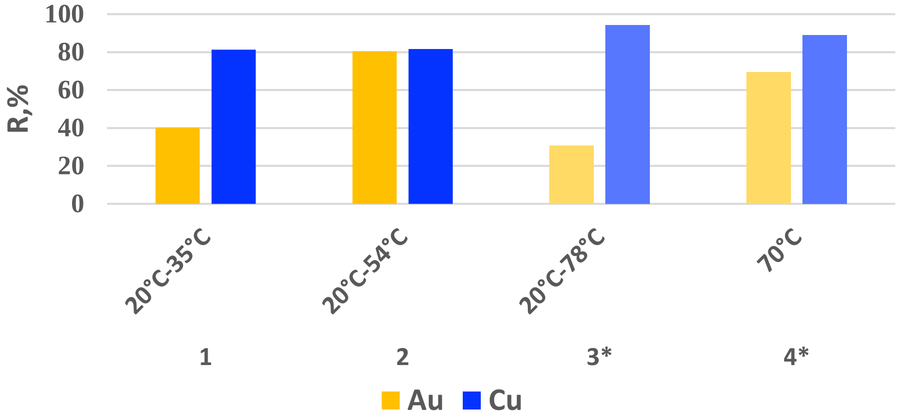

Figure 12. Effect of the electrolyte temperature on the degree of gold and copper leaching from the raw material fraction [A]: 1 – forced electrolyte air cooling; 2 – without cooling; 3* - without thermostatic 4* - thermostatic at 70 °C. Experimental conditions: 1, 2 – i = 0.66 A/cm², t_{ex}= 2 h, S/L=8,6 g/L ; 3*, 4* - i = 0.64 A/cm², t_{ex}= 2 h, S/L=2,9 g/L. *water-jacketed electrochemical cell.

3.2.5 Experiment duration

The dependence of the metal leaching on the experiment duration (Figure 13a) was investigated, as well studies on the effect of the experiment duration on the efficiency of gold and copper leaching were studied and shown in Figure 13b. The results for iron leaching are also presented for comparison. The choice of this metal is due to the fact that iron (III) ions in hydrochloric acid solutions also act as an oxidizing agent for gold [16], [17], and copper [38], The presented results show that the most significant increase in the degree of gold leaching is observed in the range of 0.5 - 1 hour and reaches 85.1%. In this case, after 0.5 hours from the beginning of the experiment, the concentration of iron ions in the solution reaches 87.89 mg/L. With a further increase in the experiment duration, periodic changes in the content of gold ions in the solution are observed, reaching a maximum of 86.3% within 4 hours of the experiment. This phenomenon may be associated with the formation of so-called ‘secondary’ gold, formed on the surface of gold particles as a result of the reaction of disproportionation (14) that occurs in the leaching solution with a decrease in the concentration of dissolved chlorine [16], [19].

$$3[AuCl_2]^- \rightarrow [AuCl_4]^- + 2Au + 2Cl^- \quad (14)$$

To eliminate this phenomenon, it is necessary to adjust the concentration of chloride ions in an electrolyte solution during the process.

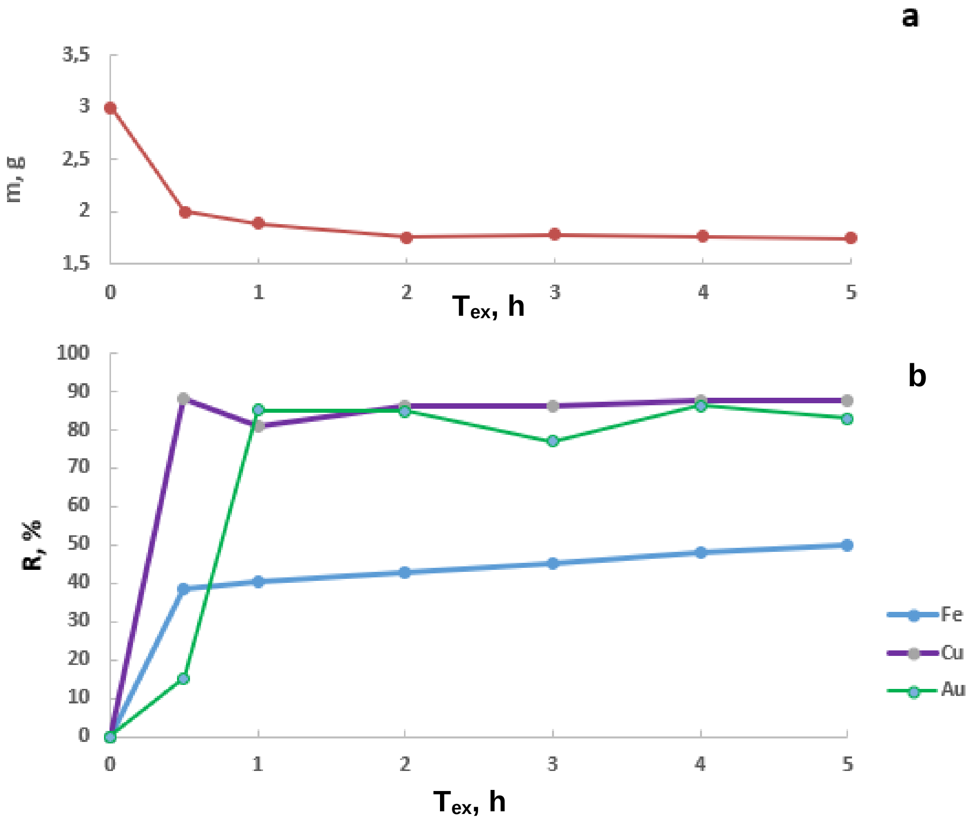

Figure 13. Impact of the experiment duration on the weight of solid residue (a) and the degree of gold, copper, and iron leaching (b). Experimental conditions: raw material fraction [A], C_{HCl} = 6 M, i = 0,88 A/cm2, S/L=8.6 g/L.

It should be noted that after the completion of the four-hour experiment, the degree of copper leaching was 87.7%. In addition, 48% Fe, 86.4% Mn, 28.2% Zn, 41.0% Ni, and 97.0% Ti also pass into the electrolyte solution. And for metals such as Al, Pb and Sn, complete leaching from the raw material is achieved.

Solid residues after the completion of experiments (Figure13a) were studied by the XRD method (Figure 14).

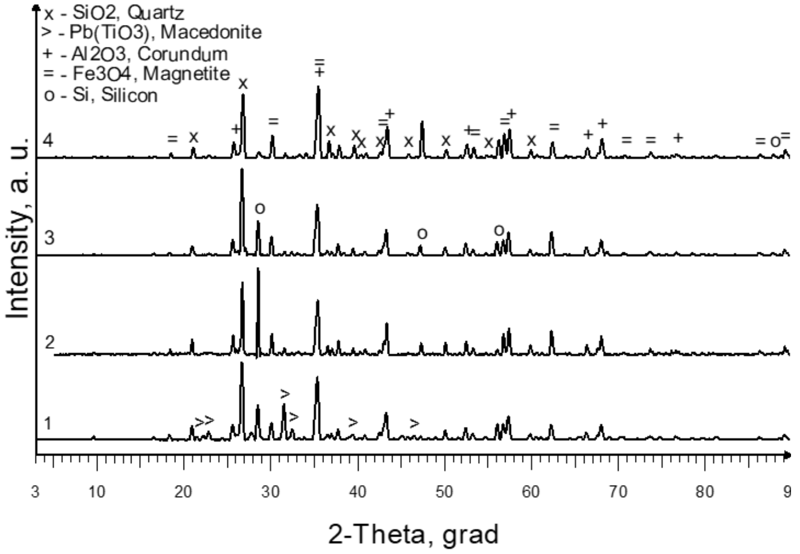

Figure 14. X-ray patterns of solid residues after experiments (according to Figure13a). Duration of the experiment: 1 – 0.5 h, 2 – 2 h, 3 – 3 h and 4 – 4 h.

The presented data show that the Pb(TiO$_3$) crystalline phase is present only in the solid residue obtained after 0.5 h of electrochemical treatment of the raw material (Figure 14, curve 1). With a further increase in the duration of the experiment, the phase composition of solid residues practically does not change (Figure 14, curves 2-4). It is a mixture of crystalline phases of SiO$_2$, Al$_2$O$_3$, Fe$_3$O$_4$ and Si. Thus, the results of XRD analysis showed that, in contrast to chemical leaching (Figure 6, curve 2), it is impossible to achieve complete magnetite leaching in the framework of the presented studies. The XRD analysis of solid residues does not contradict the results of the ICP-OES analysis of the electrolyte solutions (Figure 13 b).

To study the kinetics of the dissolution of chlorine in a solution of electrolyte in the conditions of an experiment corresponding to Figure 13, a series of "idle" experiments (without adding the raw material to the electrolyte) was carried out (Figure 15).

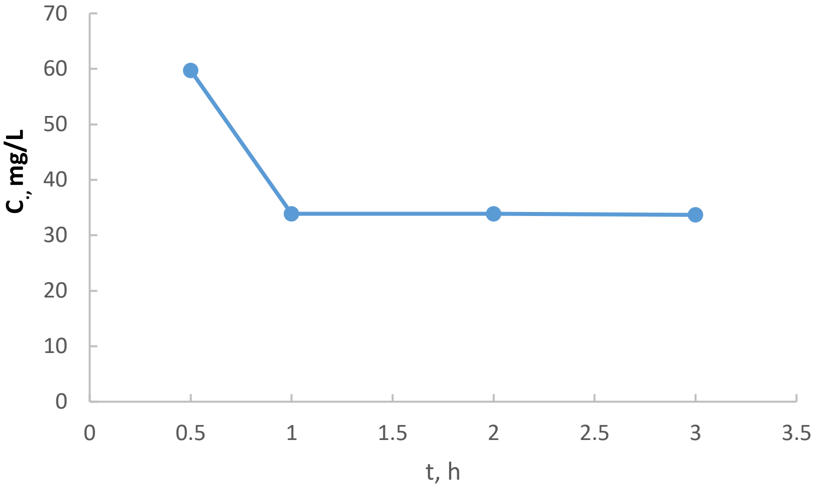

Figure 15. Change of free chlorine concentration in electrolyte solution on the experiment duration. Experimental conditions: $C_{HCl} = 6$ M, $i = 0.88$ A/cm^2.

It can be seen from the presented data that after 0,5 hours of the experiment, the concentration of chlorine in the electrolyte solution reaches 59.72 mg/L. A further increase in the duration of the investigation to 1 hour leads to a decrease in the chlorine concentration in the electrolyte solution by 1.7 times. It remains constant for the next two hours. It has been established that an increase in the duration of the experiment from 0.5 to 3 hours leads to additional heating of the electrolyte from 52 °C to 76 °C, which causes a decrease in the solubility of chlorine in the hydrochloric acid electrolyte solution [39]. It should be noted that these data are in good agreement with the results presented in Figure 13b: active dissolution of gold begins 30 minutes after the beginning of the experiment.

5. Conclusions

The results showed that the developed process of implementing the method applies to leaching gold and copper from the disintegrator-crushed waste PCBs in fine fractions <90 μm, 90-180 μm, and 180-350 μm. According to the results of the ICP-OES analysis, with increasing particle size in the fractions of raw material, the gold content decreases, and the copper content increases. Under the same conditions of the electrochemical leaching process, complete leaching of gold is achieved from raw materials with a particle size of d = 90-180 μm and d = 180-350 μm containing 0.03 wt.% and 0.01 wt.% of gold, respectively. At the same time, an increase in the degree of copper leaching from 84.6% to 95.2% is observed. Applying AC and the increase in the electrolyte temperature have a more significant effect on the gold leaching efficiency than copper.

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References

[1] A. Vidyadhar, "A Review of Technology of Metal Recovery from Electronic Waste," in *E-Waste in Transition - From Pollution to Resource*, 2016. doi: 10.5772/61569.

[2] M. Paola, "Recycling of Printed Circuit Boards," in *Integrated Waste Management - Volume II*, 2011. doi: 10.5772/17220.

[3] J. van Yken *et al.*, "A comparison of methods for the characterisation of waste-printed circuit boards," *Metals (Basel)*, vol. 11, no. 12, 2021, doi: 10.3390/met11121935.

[4] L. Xolo, P. Moleko-Boyce, H. Makelane, N. Faleni, and Z. R. Tshentu, "Status of recovery of strategic metals from spent secondary products," *Minerals*, vol. 11, no. 7. 2021. doi: 10.3390/min11070673.

[5] S. Krishnan *et al.*, "Current technologies for recovery of metals from industrial wastes: An overview," *Environmental Technology and Innovation*, vol. 22. 2021. doi: 10.1016/j.eti.2021.101525.

[6] A. Tuncuk, V. Stazi, A. Akcil, E. Y. Yazici, and H. Deveci, "Aqueous metal recovery techniques from e-scrap: Hydrometallurgy in recycling," *Miner Eng*, vol. 25, no. 1, 2012, doi: 10.1016/j.mineng.2011.09.019.

[7] L. Zhang and Z. Xu, "A review of current progress of recycling technologies for metals from waste electrical and electronic equipment," *Journal of Cleaner Production*, vol. 127. 2016. doi: 10.1016/j.jclepro.2016.04.004.

[8] F. Feng *et al.*, "Study of an environmentally friendly method for the dissolution of precious metal with ionic liquid and iodoalkane," *Metals (Basel)*, vol. 11, no. 6, 2021, doi: 10.3390/met11060919.

[9] Y. Zhang, S. Liu, H. Xie, X. Zeng, and J. Li, "Current Status on Leaching Precious Metals from Waste Printed Circuit Boards," *Procedia Environ Sci*, vol. 16, 2012, doi: 10.1016/j.proenv.2012.10.077.

[10] A. Akcil, C. Erust, C. S. ekhar Gahan, M. Ozgun, M. Sahin, and A. Tuncuk, "Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixiviants--A review," *Waste management (New York, N.Y.)*, vol. 45. 2015. doi: 10.1016/j.wasman.2015.01.017.

[11] A. Birich, S. Stopic, and B. Friedrich, "Kinetic Investigation and Dissolution Behavior of Cyanide Alternative Gold Leaching Reagents," *Sci Rep*, vol. 9, no. 1, 2019, doi: 10.1038/s41598-019-43383-4.

[12] M. B. Shah, D. R. Tipre, and S. R. Dave, "Chemical and biological processes for multi-metal extraction from waste printed circuit boards of computers and mobile phones," *Waste Management and Research*, vol. 32, no. 11, 2014, doi: 10.1177/0734242X14550021.

[13] I. Masavetas *et al.*, “Production of copper powder from printed circuit boards by electrodeposition,” *Global Nest Journal*, vol. 11, no. 2, 2009, doi: 10.30955/gnj.000595.

[14] Y. Ghorbani, J. P. Franzidis, and J. Petersen, “Heap leaching technology - Current State, innovations, and future directions: A review,” *Mineral Processing and Extractive Metallurgy Review*, vol. 37, no. 2, 2016, doi: 10.1080/08827508.2015.1115990.

[15] Zhou QF and Zhu W, “Recovery of gold from waste computer and its accessories. China Resources Comprehensive Utilization,” *China Resources Comprehensive Utilization*, vol. 7, pp. 31–35, 2003.

[16] Минеев Г.Г. and Панченко А.Ф.(G.G. Mineev and A.F. Panchenko *in Russian*), “Растворители золота и серебра в гидрометаллургии (Solvents of gold and silver in hydrometallurgy- *in Russian*)” *М., Металлургия*, p. 244, p-p 13-22, 1994.

[17] S. Seisko, M. Lampinen, J. Aromaa, A. Laari, T. Koiranen, and M. Lundström, “Kinetics and mechanisms of gold dissolution by ferric chloride leaching,” *Miner Eng*, vol. 115, 2018, doi: 10.1016/j.mineng.2017.10.017.

[18] A. O. Filmer, P. R. Lawrence, and W. Hoffmann, “COMPARISON OF CYANIDE, THIOUREA AND CHLORINE AS LIXIVIANTS FOR GOLD.,” in *Symposia Series - Australasian Institute of Mining and Metallurgy*, 1984, no. 39.

[19] M. A. Diaz, G. H. Kelsall, and N. J. Welham, “Electrowinning coupled to gold leaching by electrogenerated chlorine,” *Journal of Electroanalytical Chemistry*, vol. 361, no. 1–2, 1993, doi: 10.1016/0022-0728(93)87035-t.

[20] R. Winand, “Chloride hydrometallurgy,” *Hydrometallurgy*, vol. 27, no. 3, 1991, doi: 10.1016/0304-386X(91)90055-Q.

[21] E. Y. Kim, M. S. Kim, J. C. Lee, J. Jeong, and B. D. Pandey, “Leaching kinetics of copper from waste printed circuit boards by electro-generated chlorine in HCl solution,” *Hydrometallurgy*, vol. 107, no. 3–4, 2011, doi: 10.1016/j.hydromet.2011.02.009.

[22] E. young Kim, M. seuk Kim, J. chun Lee, M. K. Jha, K. Yoo, and J. Jeong, “Effect of cuprous ions on Cu leaching in the recycling of waste PCBs, using electro-generated chlorine in hydrochloric acid solution,” *Miner Eng*, vol. 21, no. 1, 2008, doi: 10.1016/j.mineng.2007.10.008.

[23] D. Pilone and G. H. Kelsall, “Metal recovery from electronic scrap by leaching and electrowinning IV,” in *Proceedings of the TMS Fall Extraction and Processing Conference*, 2003, vol. 2. doi: 10.1002/9781118804407.ch37.

[24] M. seuk Kim, J. chun Lee, S. woon Park, J. Jeong, and V. Kumar, “Dissolution behaviour of platinum by electro-generated chlorine in hydrochloric acid solution,” *Journal of Chemical Technology and Biotechnology*, vol. 88, no. 7, 2013, doi: 10.1002/jctb.3957.

[25] E. Y. Kim, M. S. Kim, J. C. Lee, and B. D. Pandey, “Selective recovery of gold from waste mobile phone PCBs by hydrometallurgical process,” *J Hazard Mater*, vol. 198, 2011, doi: 10.1016/j.jhazmat.2011.10.034.

[26] S. Ilyas, R. R. Srivastava, and H. Kim, “Gold recovery from secondary waste of PCBs by electro-Cl2 leaching in brine solution and solvo-chemical separation with tri-butyl phosphate,” *J Clean Prod*, vol. 295, 2021, doi: 10.1016/j.jclepro.2021.126389.

[27] T. E. Lister, P. Wang, and A. Anderko, “Recovery of critical and value metals from mobile electronics enabled by electrochemical processing,” *Hydrometallurgy*, vol. 149, 2014, doi: 10.1016/j.hydromet.2014.08.011.

[28] Л. П. Шульгин, “Перенапряжение электродных реакций в растворах при прохождении симметричного переменного тока, (Overvoltage of electrode reactions in solutions during the passage of a symmetrical alternating current, *inRussian*)” *Журн. физич. Химии* (Journal of Physical Chemistry *in Russian)*, vol. 3, pp. 2048–2051, 1979.

[29] A. D. Styrkas and D. Styrkas, “Electrochemical dissolution of metals of the platinum group by alternating current,” *J Appl Electrochem*, vol. 25, no. 5, 1995, doi: 10.1007/BF00260693.

[30] W. D. Box, “Dissolution of Metals by AC Electrolysis,” *Nuclear Applications*, vol. 2, no. 4, 1966, doi: 10.13182/nt66-a27520.

doi:10.20944/preprints202210.0061.v1

[31] M. Taras, "The Micro-Titration of Free Chlorine With Methyl Orange," *J Am Water Works Assoc*, vol. 38, no. 10, 1946, doi: 10.1002/j.1551-8833.1946.tb20088.x.

[32] S. Zimakov, D. Goljandin, P. Peetsalu, and P. Kulu, "Metallic powders produced by the disintegrator technology," *International Journal of Materials and Product Technology*, vol. 28, no. 3/4, p. 226, 2007, doi: 10.1504/IJMPT.2007.013081.

[33] P. Peetsalu, D. Goljandin, P. Kulu, and V. Mikli, "MICROPOWDERS PRODUCTED BY DISINTEGRATOR MILLING," *Powder Metallurgy*, vol. 3, no. 2, pp. 99–110, 2003.

[34] D. GOLJANDIN, H. SARJAS, P. KULU, H. KÄERDI, and V. MIKLI, "Metal-Matrix Hardmetal/Cermet Reinforced Composite Powders for Thermal Spray," *Materials Science*, vol. 18, no. 1, pp. 84–89, Mar. 2012, doi: 10.5755/j01.ms.18.1.1348.

[35] E. Blumbergs *et al.*, "Selective Disintegration–Milling to Obtain Metal-Rich Particle Fractions from E-Waste," *Metals (Basel)*, vol. 12, no. 9, p. 1468, Sep. 2022, doi: 10.3390/met12091468.

[36] Y. Xian, Y. Tao, F. Ma, and Y. Zhou, "Recovery of metals from heat-treated printed circuit boards via an enhanced gravity concentrator and high-gradient magnetic separator," *Materials*, vol. 14, no. 16, 2021, doi: 10.3390/ma14164566.

[37] A. F. Mazanko, G.M Kamaryan, O.P. Romashin, "Industrial membrane electrolysis," *Chemistry, Moscow, Russia*, p. 240, p-p 131-138, 1989.

[38] C. Bryce and D. Berk, "Kinetics of the Dissolution of Copper in Iron(III) Chloride Solutions," *Ind Eng Chem Res*, vol. 34, no. 4, 1995, doi: 10.1021/ie00043a049.

[39] M. Alkan, M. Oktay, M. M. Kocakerim, and M. Çopur, "Solubility of chlorine in aqueous hydrochloric acid solutions," *J Hazard Mater*, vol. 119, no. 1–3, 2005, doi: 10.1016/j.jhazmat.2004.11.001.