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Leaching of Gold and Copper from Printed Circuit Boards under the Alternating Current Action in Hydrochloric Acid Electrolytes

Vera Serga [1], Aleksej Zarkov [2,3], Ervins Blumbergs [4,5,6], Andrei Shishkin [4,7], Janis Baronins [4,7,8,*], Edgars Elsts [2] and Vladimir Pankratov [2]

[1] Institute of Materials and Surface Engineering, Faculty of Materials Science and Applied Chemistry, Riga Technical University, 3/7 P. Valdena Street, LV-1048 Riga, Latvia
[2] Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street, LV-1063 Riga, Latvia
[3] Institute of Chemistry, Vilnius University, 24 Naugarduko Street, LT-03225 Vilnius, Lithuania
[4] ZTF Aerkom SIA, 32 Miera Str., LV-2169 Salaspils, Latvia
[5] Institute of Physics, University of Latvia, 32 Miera Street, LV-2169 Salaspils, Latvia
[6] Faculty of Civil Engineering, Riga Technical University, 21/1 Azenes Street, LV-1048 Riga, Latvia
[7] Rudolfs Cimdins Riga Biomaterials Innovations and Development Centre of RTU, Institute of General Chemical Engineering, Faculty of Materials Science and Applied Chemistry, Riga Technical University, 3 Pulka Street, LV-1007 Riga, Latvia
[8] Latvian Maritime Academy, 12 k-1 Flotes Street, LV-1016 Riga, Latvia
* Correspondence: janis.baronins@gmail.com

Abstract: Modern technologies for recycling electronic waste (e-waste) have high economic efficiency and environmental safety requirements. Among the existing technologies, hydrometallurgy is considered to be the most promising technology for e-waste recycling. Increasing attention paid to the chlorination method is associated with the complex recycling of low-grade ores containing noble metals and the raw materials of secondary polymetallic. In this paper, we propose a new scheme for leaching metals from computer printed circuit boards (PCBs) pre-crushed in a disintegrator: The processes of chlorine production and hydrochlorination are implemented in one reactor under the action of an alternating current (AC) of industrial frequency (50 Hz). Three fine fractions of raw material powders with particle size d < 90 μm, d = 90–180 μm, and d = 180–350 μm were used as research objects and the finest fraction of the raw material (d < 90 μm) was studied in more detail. It was found that complete leaching of gold is achieved from fractions of raw materials with a particle size d = 90–180 μm and d = 180–350 μm, containing 277 ppm and 67 ppm of the gold, respectively, at an experiment duration (t_{ex}) of 2 h, a current density (i) of 0.66 $A{\cdot}cm^{-2}$, and a solid/liquid (S/L) ratio of 8.6 $g{\cdot}L^{-1}$. Under the same conditions of the electrochemical leaching process from the fraction of raw materials with a particle size of d < 90 μm and a gold content of 824 ppm, the degree of metal leaching is 80.5%. At the same time, with an increase in particle size in the raw material fractions from d < 90 μm to d = 180–350 μm and a copper content in the raw material from 1.40% to 6.13%, an increase in the degree of its leaching from 81.6% to 95.2%, respectively, is observed. In the framework of the preliminary study presented in this work, for the finest raw material fraction with d < 90 μm the highest gold leaching degree (86.3%) was achieved under the following experimental conditions: t_{ex}= 4 h, C_{HCl} = 6 M, i = 0.88 $A{\cdot}cm^{-2}$, S/L ratio—8.6 $g{\cdot}L^{-1}$ and the highest copper leaching degree (94.2%) was achieved under the following experimental conditions: t_{ex} = 2 h, C_{HCl} = 6 M, i = 0.64 $A{\cdot}cm^{-2}$, and S/L ratio—2.9 $g{\cdot}L^{-1}$.

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

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Citation: Serga, V.; Zarkov, A.; Blumbergs, E.; Shishkin, A.; Baronins, J.; Elsts, E.; Pankratov, V. Leaching of Gold and Copper from Printed Circuit Boards under the Alternating Current Action in Hydrochloric Acid Electrolytes. *Metals* **2022**, *12*, 1953. https://doi.org/10.3390/met12111953

Academic Editor: Stefano Ubaldini

Received: 4 October 2022
Accepted: 11 November 2022
Published: 15 November 2022

1. Introduction

The volume of electronic waste (e-waste) suitable for recycling in order to recover precious and non-ferrous metals is rapidly growing worldwide. Personal computers is the largest source of electronic waste [1]. Computer printed circuit boards (PCBs) are manufactured using complex technologies. The composition of PCBs includes a non-conductive substrate (glass fibre/paper reinforced with epoxy/phenolic resin) or laminate, polymer and ceramic materials [1], and metals, including copper, aluminium, tin, lead, zinc, nickel, iron and noble metals (gold, silver and palladium [2–4]). The content of individual metals in PCBs, given in the literature [3,5], varies widely, and is associated not only with the manufacturer and the 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 [2,6–10]. Pyrometallurgy is mainly used industrially for recycling large volumes of primary (ore) and secondary raw materials [9]. Biotechnological techniques are commercially applied to process mineral raw materials [10]. The use of bioleaching for the recovery of valuable metals from e-waste is currently one of the rapidly developing areas [8]. However, hydrometallurgy is mainly associated with research, development, and application potential. Therefore, hydrometallurgical electronic scrap recycling possibilities have been actively studied [11–16]. 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 [14,17,18]. Within the framework of hydrometallurgical technology, there are many methods of gold leaching, including cyanide, aqua regia, halogen-halide, thiosulfate, thiourea, among others. [9]. Cyanidation is the primary method of hydrometallurgical recovery of gold and silver from ores, which consists of the leaching of metals using an alkaline cyanide solution (NaCN and KCN) in the presence of atmospheric oxygen [19]. The use of cyanidation for leaching gold from PCBs showed that this method is only effective 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 [20].

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+} [21,22], acting as an oxidizing agent. The dissolution reaction examples can be expressed, as in Equations (1) and (2):

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

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

Leaching with the use of chlorine, bromine, and iodine is characterized by a high rate [23,24]. In this case, gold forms both Au^+ and 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 Equations (3) and (4) [21,25]:

$$Au + 0.5Cl_2 + Cl^- \rightarrow [AuCl_2]^- \tag{3}$$

$$Au + 1.5Cl_2 + Cl^- \rightarrow [AuCl_4]^- \tag{4}$$

Chlorination of gold and copper in chloride solutions is characterized by the high solubility of metal complexes with chlorine and a high leaching rate [26].

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 [21]. Therefore, reducing chlorine consumption and improving maintenance personnel's safety is crucial when developing a hydrochlorination technology for recovering valuable metals from secondary raw materials.

New technological solutions are proposed to minimize the risks of chlorine/chloride leaching systems, including in situ chlorine production (electrogeneration). Thus, to study the leaching of copper, zinc, lead, and tin from PCBs, the authors [27] 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 min, 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 of cuprous ions, it increases [28]. In this case, the following reactions of leaching in hydrochloric acid solution (Equations (5)–(8)) on the anode took place [29]:

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

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

$$2Cl^{-} \rightarrow Cl_{2(g)} + 2e^{-},\ E^0 = 1.358\ V_{SHE} \tag{7}$$

$$[CuCl_2]^{-} \rightarrow Cu^{2+} + 2Cl^{-} + e^{-},\ E^0 = 0.457\ V_{SHE} \tag{8}$$

The gaseous chlorine released at the anode Equation (7) and dissolves in hydrochloric acid solutions follows the reactions in Equations (9)–(11) [30]:

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

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

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

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 the solution and an increase in the content of Cl_3^{-} are observed. At the same time, the content of HClO remains insignificant [30].

The results of the two-stage leaching process of gold from waste mobile phone PCBs in a separate leaching reactor are also presented in ref. [31]. 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 in 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 reactions in Equations (12) and (13):

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

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

A separate reactor connected with the anode compartment of a chlorine gas generator was also used in ref. [32] to leach gold from waste PCBs. The leaching stage was preceded by treatment in a 4 M HCl with the addition of H_2O_2. It is shown that, with over 75 min of the experiment at a temperature of 50 °C, more than 99% of the 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, Pd, and Au in two stages. In the second stage, Pd and Au are dissolved by chlorine generated on the anode under the action of direct current [33].

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. The AC of various shapes contributes to the intensification of the processes of anodic dissolution/dispersion of metals and the elimination of the passivation of the metal electrode [34]. The authors [35] 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 from noble metals. A method for the dissolution of noble metals (Au, Ir, Pd, Pt, and Rh) and metals resistant to hydrochloric acid (Cd, Cu, In, Ta, and W) under the action of a half-wave or a full-wave AC was also proposed in ref. [36]. The study showed that the rate of dissolution of metals noticeably increases with an 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 an 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.

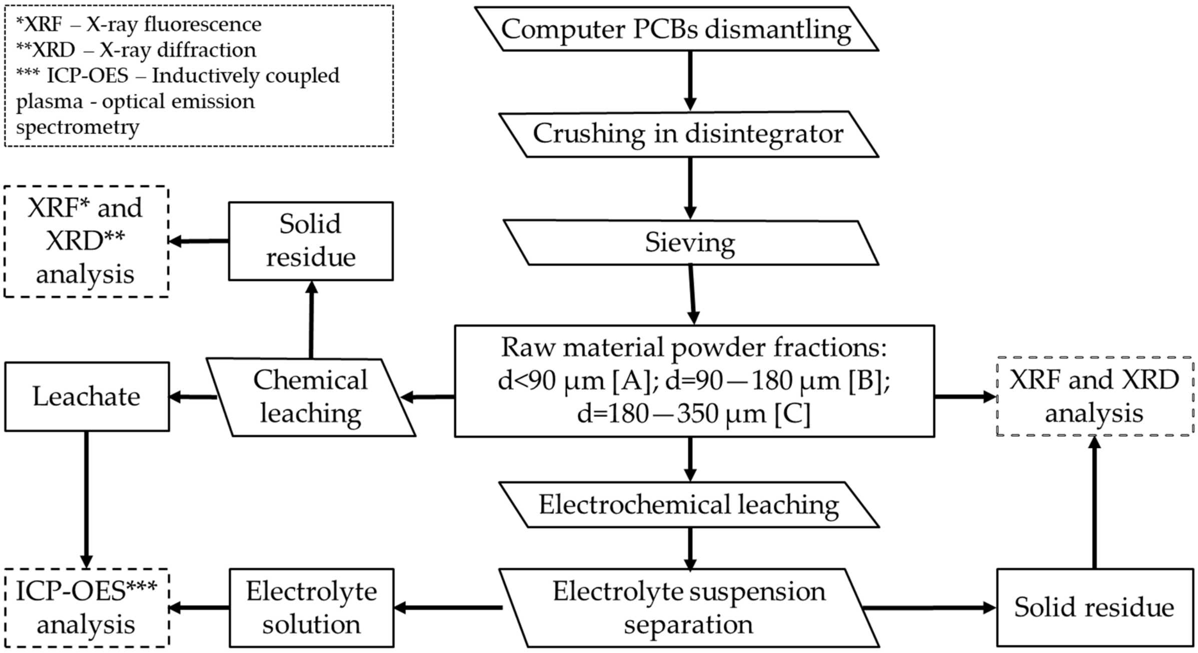


Figure 1. Schematic diagram of the process investigated.

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, Tallinn, Estonia) and subsequent sieving using FRITSCH ANALYSETTE 3 PRO Vibratory Sieve Shaker (FRITSCH GmbH, Weimar, Germany). 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}). A water-jacketed glass cell was only used in separate experiments to study the effect of electrolyte temperature on the efficiency of target component leaching. Powders of the raw material were used in the form of a dispersed (solid) phase in the hydrochloric acid electrolyte (liquid phase). In all experiments, the volume of the electrolyte was 350 mL, and the concentration of the hydrochloric acid was 6 M. The choice of the electrolyte concentration was based on the electrical conductivity data of hydrochloric acid solutions: Specific electrical conductivity of 18–20% (~5–6 M) solutions at 65 °C are 1.2 $Ohm^{-1}\cdot cm^{-1,}$ and at 90 °C is 1.5 $Ohm^{-1}\cdot cm^{1}$ [37].

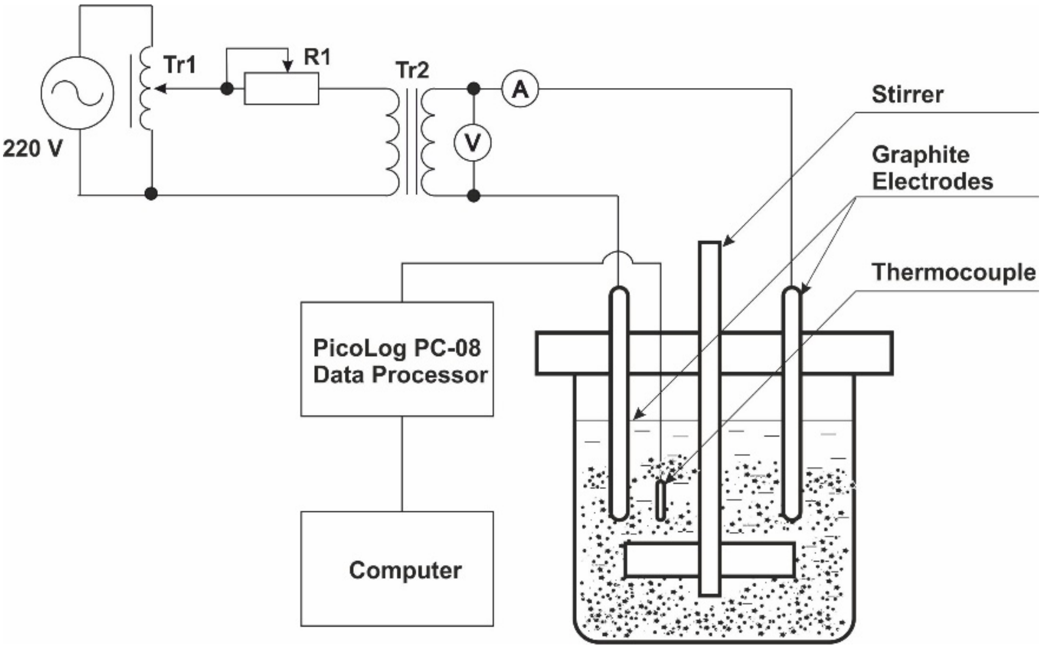


Figure 2. Scheme of the experimental setup: AC circuit (Tr1—laboratory autotransformer, R1—rheostat, Tr2—step-down transformer, V—AC voltmeter, A—AC ammeter) and electrochemical cell.

After filling the reactor with the initial components to create a suspension, the mixture was stirred at a speed of 1200 rpm for 5 min, 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 h. 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 6 M HCl solution and aqua regia solution) and electrochemical (in 6 M 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, Perkin Elmer Inc., Waltham, MA, USA). X-ray diffraction (XRD, diffractometer Rigaku—MiniFlex 600 with CuK_{α} radiation with λ = 1.5418 Å, Rigaku Corp., Tokyo, Japan) and X-ray fluorescence (XRF, analyser EAGLE III XPL, EDAX Inc., Mahwah, NJ, USA) analyses were used to characterize raw materials and solid residues after leaching. The disintegrator-crushed fractions of a raw material microscope (KEYENCE VHX-2000, Keyence Corporation, Osaka, Japan) 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 [38].

The efficiency of electrochemical leaching of metals from raw materials was evaluated by the degree of metal 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 (M_{PCBs}), 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.

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 in refs. [39–41]. The device crushes materials by collisions. Supplied particles collide with the fingers of the milling device and with other particles, which have a moving counter direction. The resulting intensive wave of pressure begins to propagate, and the resulting values of stresses exceed the material strength. The previous work in ref. [42] described a novel single and two-stage PCBs disintegration-milling approach.

Mixed computer PCBs (Figure 3) were used as raw material to imitate wasted PCBs from real landfilled damp, which is essential for commercial technology development. This mixture of PCBs was treated as described in the previous work in ref. [42] 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, and the morphology of these fractions was studied using optical microscopy (Figure 4a–c) and designated [A], [B] and [C], respectively.

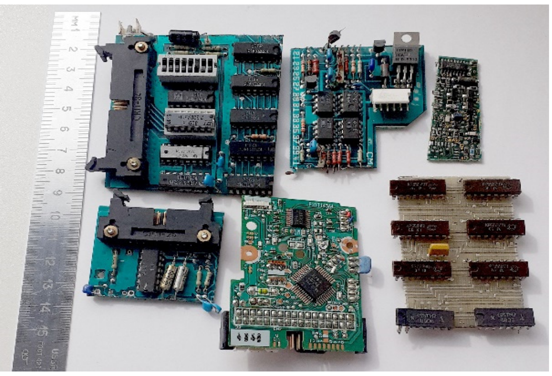


Figure 3. Image of computer PCBs used for the study.

From the presenting data, it can be seen that 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 and Cu electrochemical leaching.

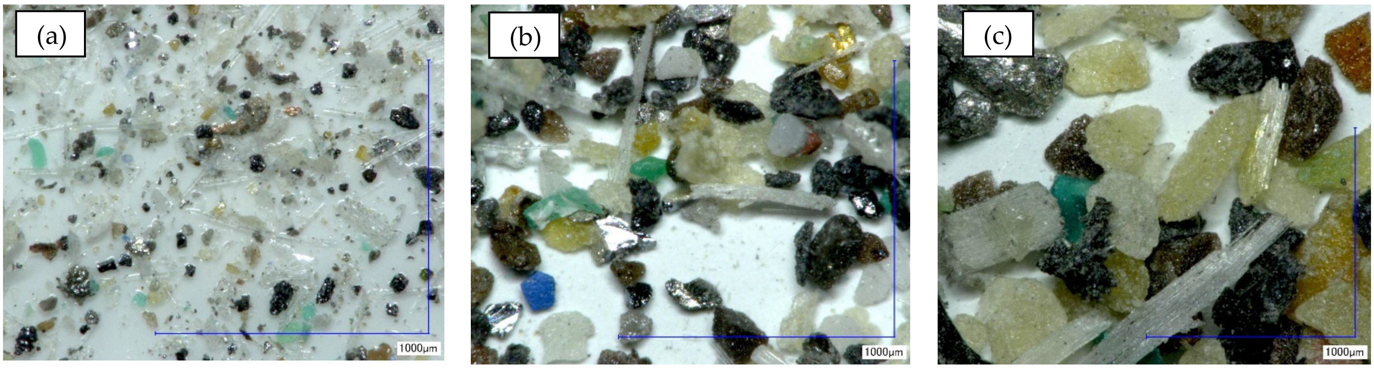


Figure 4. Optical images at magnification ×200 times, of disintegrator-crushed PCBs fractions: (**a**) is d < 90 µm; (**b**) is d = 90–180 µm; and (**c**) is d = 180–350 µm and designated [A], [B] and [C], respectively.

Complex Characterisation of Raw Material

From the obtained fractions of [A], [B] and [C], the finest fraction [A] was chosen as the main object of the research. The choice of this faction is due to several reasons. First, the scheme for studying the leaching process involves the use of the reaction mixture in the form of a suspension, and finer particle suspension is more stable than coarse particles (according to Stock's Law). Second, a finer particle powder has a higher specific surface area, which is crucial for leaching reaction intensity. Third, "open" laminated PCBs, small fragments with Cu intermediate layers, are essential. Finally, this fraction has the highest gold content.

The quantitative determination of the elements included in the composition of PCBs is complicated by both the presence of a wide range of elements present in various chemical forms (metals, alloys, and 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 the complex investigation of raw material.

In this work, XRF analysis was used to qualitatively/semi-quantitatively determine the composition of the raw material sample. According to the results obtained (Figure 5), metals such as Fe, Ca, Zn, Cu, Ni, Al, Ti, Mn, and 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 in the region of the gold (AuL) peak (about 9.50 keV), overlapping with a second zinc peak (ZnK), indicated by the arrow in Figure 5.

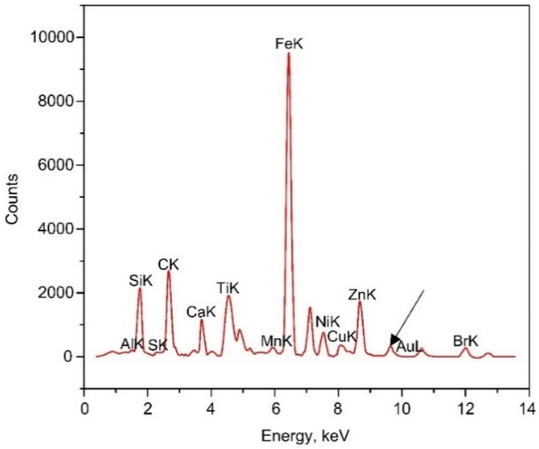


Figure 5. Fluorescence spectrum of the raw material fraction [A].

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 [43]. The phase composition of the solid residue obtained after the 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 the identified phase composition, except the crystalline phase of the magnetite

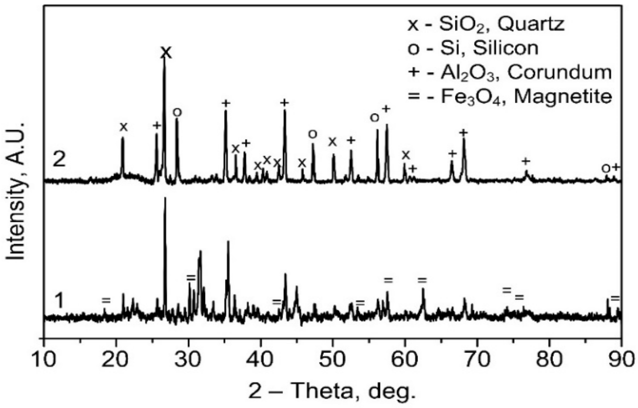


Figure 6. XRD patterns: 1—raw material fraction [A]; 2—solid residue after chemical leaching of a raw material fraction [A].

The solution obtained after chemical leaching of the raw material sample—leachate—was analyzed by ICP-OES. A quantitative determination was carried out not only on metals identified in a solid sample using XRF analysis (Figure 5), but also on some others, usually included in PCBs, including tin, lead, antimony, nickel, and cobalt. The results are presented in Figure 7. According to the results of weighing, the content of the solid residues after chemical leaching raw material fractions [A], [B] and [C] is 45.76 wt.%, 61.28 wt.% and 68.20 wt.% of the mass of raw material, respectively. It should be noted that 26.53 wt.% are elements of a fraction [A], 19.08 wt.% of a fraction [B] and 15.81 wt.% of a fraction [C], whose quantitative determination in the solution was not carried out and/or could not be identified by the ICP-OES method. A comparison of the results of ICP-OES obtained for three fractions shows that, with an increase in the particle size of the raw material, a decrease in the content of all analyzed elements is observed, except the copper. For this metal, an inverse relationship is established. More significant amounts of copper are most likely present in larger disintegrator-milled fractions (d > 350 μm). Thus, the content of target metals in fraction A was established: Gold—824 ppm and copper—1.40 wt.%.

According to the results of the ICP-OES analysis of the leachates obtained after chemical leaching of the raw material fractions B and C, the gold content is 277 ppm, 67 ppm, 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 show that the degree of gold leaching slightly increased from 77.3 wt.% at S/L = 2.9 $g \cdot L^{-1}$, reaching a maximum of 80.5 wt.% at S/L = 8.6 $g \cdot L^{-1}$. With a further increase in the S/L ratio, there is a significant decrease in R to 46.9 wt.% (S/L = 14.3 $g \cdot L^{-1}$). This could be because, at a higher S/L ratio 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 oxidizing agent—chlorine—but also a complexing agent that forms soluble complex ions with metal ions [30]. To increase the degree of gold leaching by an increasing S/L ratio, it is also necessary to raise the concentration of the oxidizing agent. The chlorine concentration in the electrolyte solution can be raised by increasing the chloride ions' concentration and the current density [44]. At the same time, with an increase in the S/L ratio from 2.9 g·L^{-1} to 14.3 g·L^{-1}, the degree of copper leaching increased linearly from 82.1 wt.% to 87.3 wt.%, respectively.

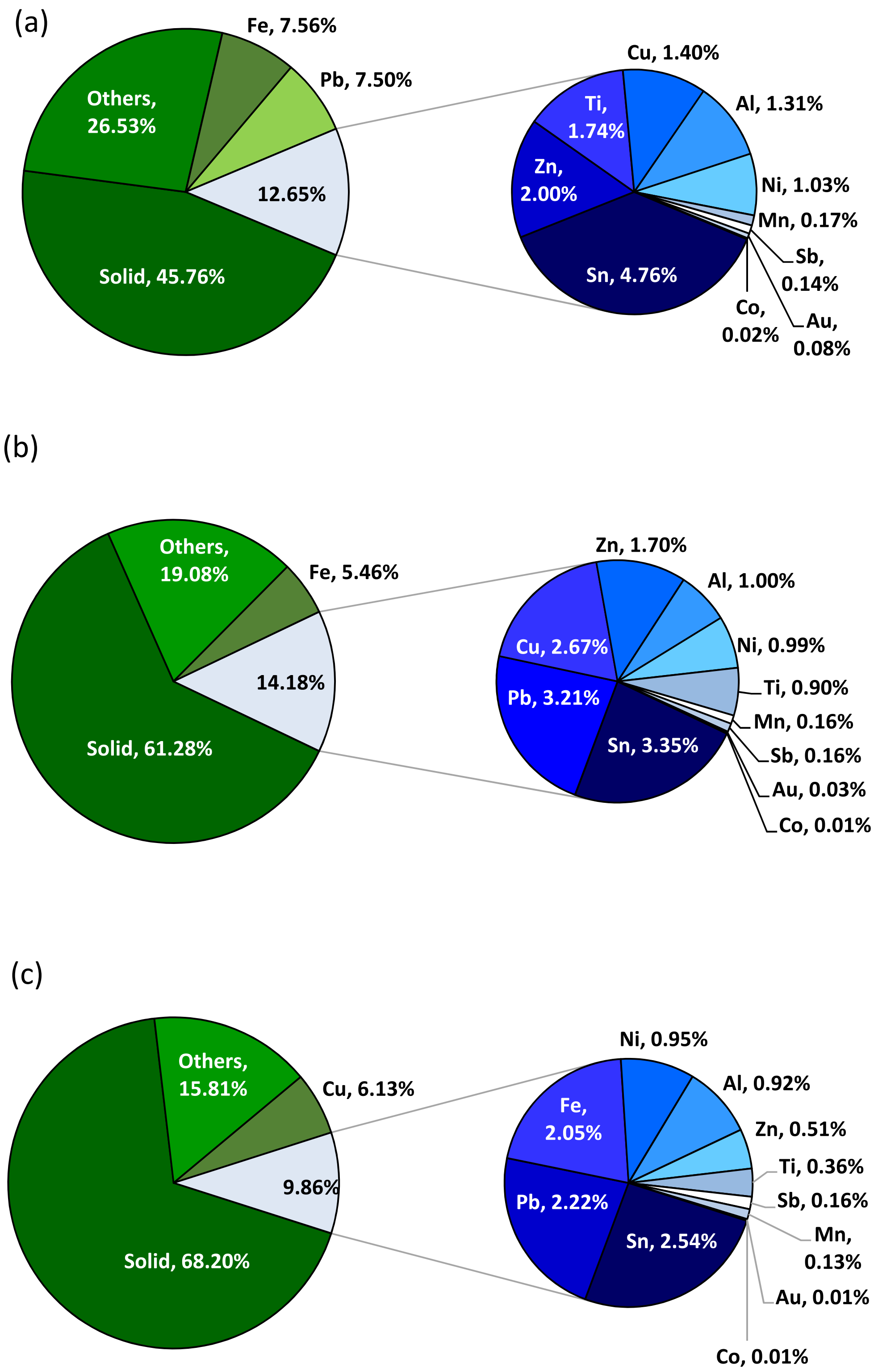


Figure 7. Content of metals in raw materials according to the results of ICP-OES analysis of the leachates prepared by chemical leaching: (**a**)—Fraction [A]; (**b**)—fraction [B]: and (**c**)—fraction [C].

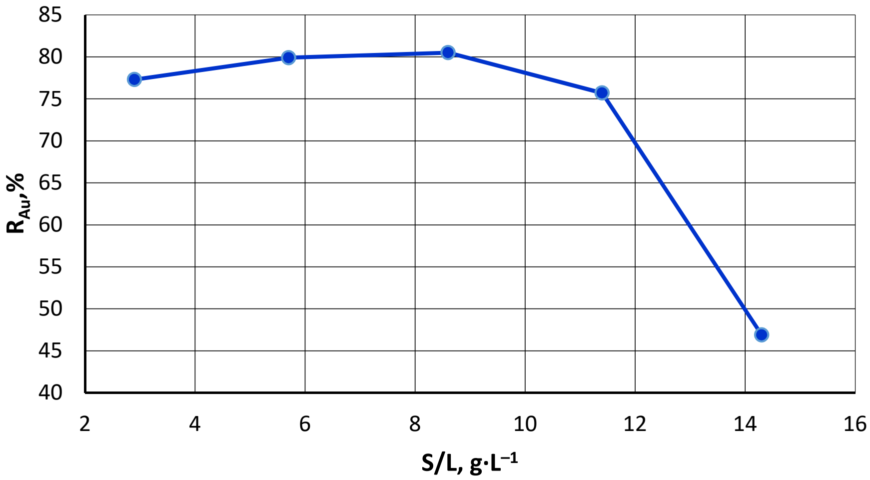


Figure 8. Impact of S/L ratio on the degree of gold leaching. Experimental conditions: Raw material fraction [A], C_{HCl} = 6 M, i = 0.66 A·cm^{-2}, and t_{ex}= 2 h.

3.2.2. Raw Material Particle Size

The particle size of the PCBs obtained after crushing is one of the essential factors determining the efficiency of metal leaching, but this effect is not the same for all elements [45]. 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,c). The degree of copper leaching also increases with the particle size, but complete leaching was not achieved.

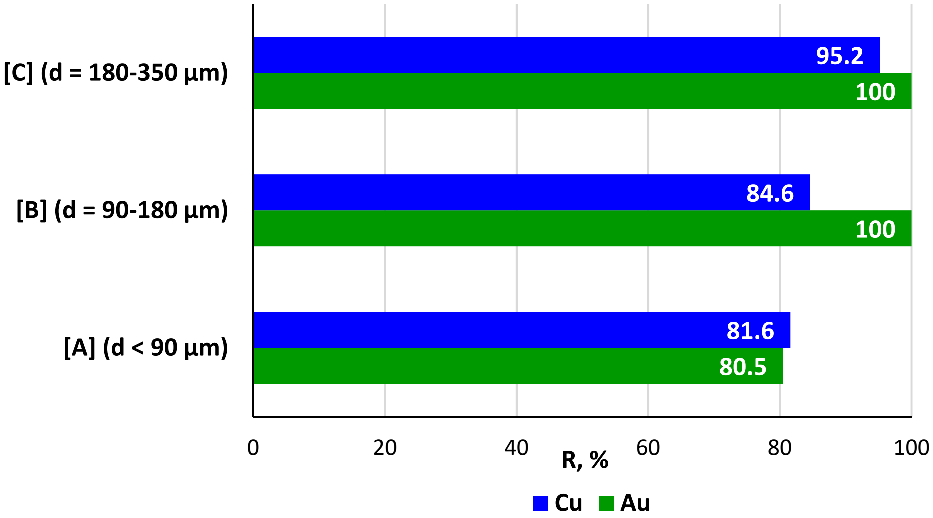


Figure 9. Impact of raw material particle size on the degree of gold and copper leaching. Experimental conditions: i = 0.66 A·cm^{-2}, t_{ex} = 2 h, S/L = 8.6 g·L^{-1}, and C_{HCl} = 6 M.

In the case of Au, the efficiency of metal leaching depends more on the content of the metal in the raw material, but not on raw material particle size. An increase in the degree of copper leaching with an increase in the particle size of the raw material is probably due to an increase in the content of not only copper, but also the product of its corrosion formed during the storage of electronic waste in humid air—dicopper dihydroxo carbonate $(CuOH)_2CO_3$—which reacts with an HCl solution [46]. Unfortunately, the results obtained are complicated to compare with the literature data since, as a rule, larger fractions of raw materials, a different method of preparing raw material and crushing, and other leaching agents are used in the studies.

3.2.3. Alternating Current

Applying AC has resulted in a noticeable improvement in the degree of gold leaching compared to the experiment without AC. In contrast, the degree of copper leaching does not seem to significantly benefit from AC (Figures 9 and 10).

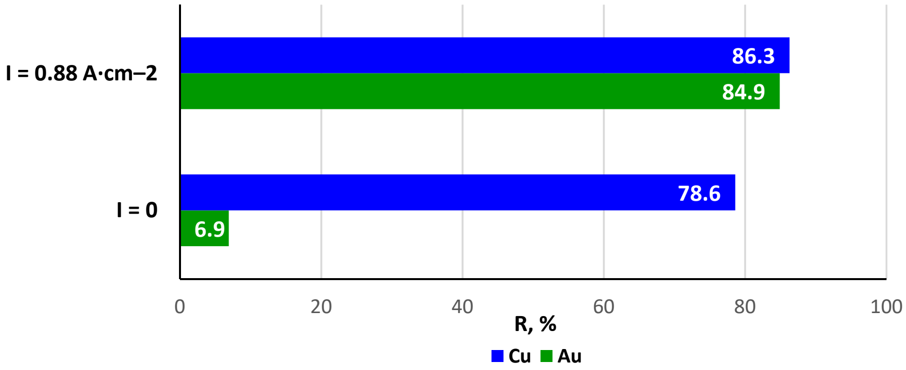


Figure 10. Effect of AC applying on gold and copper leaching degree. Experimental conditions: Raw material—fraction [A], t_{ex}= 2 h, S/L = 8.6 g·L^{-1}, and C_{HCl} = 6 M.

Increasing the current density from 0.66 A·cm^{-2} to 0.88 A·cm^{-2} leads to a slight increase in the gold and copper degree of leaching (above 4%).

From the presented data (Figure 10), it can be seen that 6.9% of gold and 78.6% of copper at ambient temperature passes into a hydrochloric acid solution that does not contain chlorine. On the one hand, this phenomenon is due to the reaction of oxidation of these metals by iron ions (Equations (1) and (2)) [21,22,47], 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 $(CuOH)_2CO_3$ [POD]. Thus, these results show that acid pre-treatment 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 min 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).

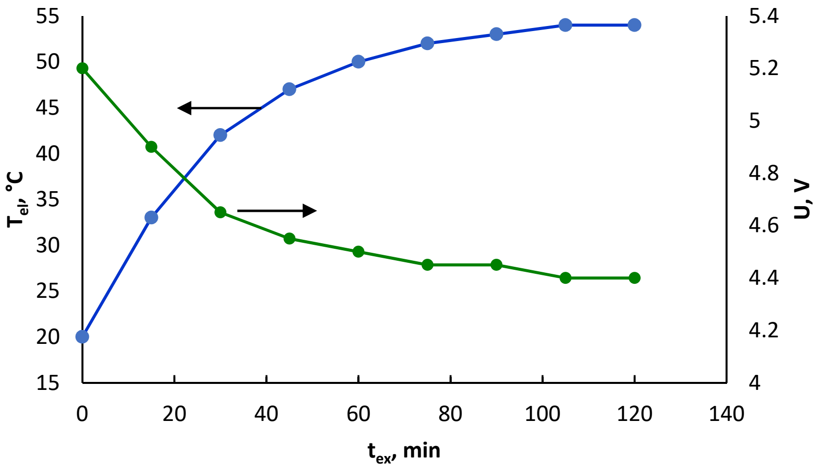


Figure 11. Electrolyte temperature and cell voltage versus the experiment duration. Experimental conditions: Raw material—fraction [A], C_{HCl} = 6 M, i = 0.66 A·cm^{-2}, and S/L = 8.6 g·L^{-1}.

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 12).

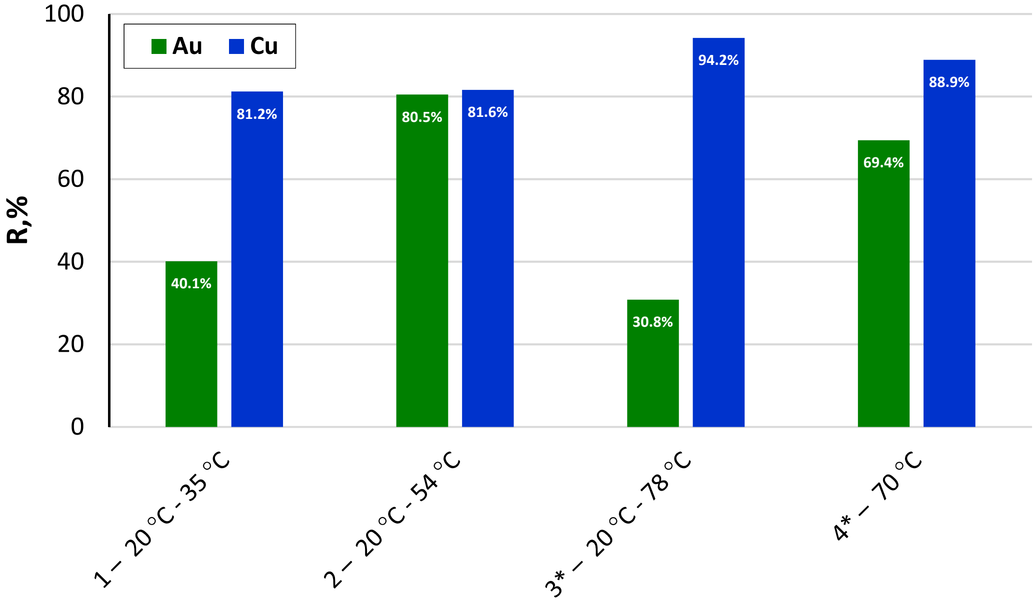


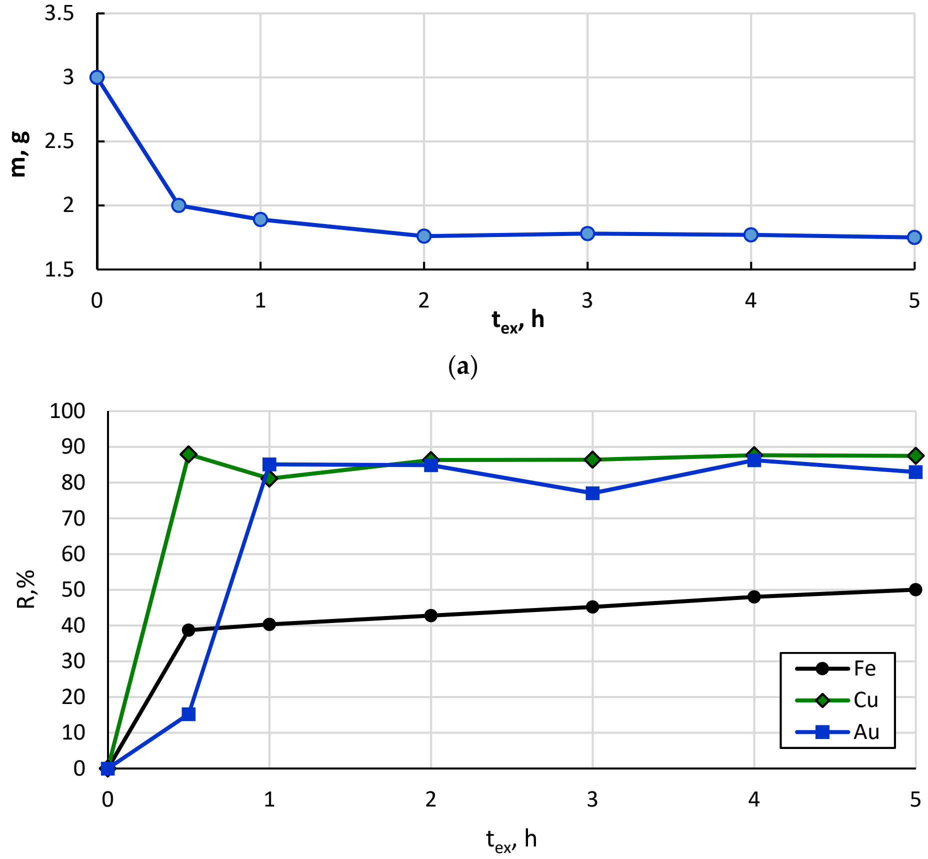
Figure 12. Effect of the electrolyte temperature on the degree of gold and copper leaching from the raw material fraction [A]: 1—Forced electrolyte air cooling; 2—without cooling; 3*—without thermostatic; and 4*—thermostatic at 70 °C. Experimental conditions: 1, 2, 3* and 4*—C_{HCl} = 6 M, 1, 2—I = 0.66 A·cm^{-2}, t_{ex} = 2 h, S/L = 8.6 g·L^{-1}; 3*, 4*—i = 0.64 A·cm^{-2}, t_{ex} = 2 h, and S/L = 2.9 g·L^{-1}. * Water-jacketed electrochemical cell.

The results showed that the electrolyte temperature practically does not affect the copper leaching efficiency in the polypropylene cell. However, the degree of copper leaching increases in the water-jacketed cell when the electrolyte heats during the electrochemical process compared to the process while maintaining a constant temperature of 70 °C by 5%. Such an impact is probably because, in the first case, the final temperature of the electrolyte exceeds 70 °C. In turn, increasing the electrolyte temperature twice improves the gold leaching efficiency.

3.2.5. Experiment Duration

The dependence of all metal leaching on the experiment duration (Figure 13a) was investigated, as well as 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 of the iron leaching are also presented for comparison. The choice of this metal is because iron (III) ions in hydrochloric acid solutions also act as an oxidizing agent for gold [21,22] and copper [47]. The presented results show that the most significant increase in the degree of gold leaching is observed in the range of 0.5–1 h and reaches 85.1 wt.% after 1 h. In this case, after 0.5 h from the beginning of the experiment, the concentration of iron ions in the solution reaches 251.1 mg·L^{-1}. 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 h 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 (15) that occurs in the leaching solution with a decrease in the concentration of dissolved chlorine [21,25].

$$3[AuCl_2]^- \rightarrow [AuCl_4]^- + 2Au + 2Cl^- \quad (15)$$



(**a**)

(**b**)

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·cm^{-2}, and S/L = 8.6 g·L^{-1}.

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

It should be noted that, after the completion of the four-hour experiment, the degree of copper leaching was 87.7%. In addition, 48.0% Fe, 86.4% Mn, 28.2% Zn, 41.0% Ni, and 97.0% Ti also pass into the electrolyte solution. Additionally, for metals such as Al, Pb and Sn, complete leaching from the raw material is achieved.

Solid residues from the experiments at different durations: 0.5 h, 2 h, 4 h and 5 h (Figure 13a) were studied using the XRD method (Figure 14).

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 SiO$_2$, Al$_2$O$_3$, Fe$_3$O$_4$ and Si crystalline phases. Thus, the results of the XRD analysis showed that chemical leaching could dissolve all magnetite (Figure 6, curve 2), not electrochemical leaching.

The XRD analysis of solid residues does not contradict the results of the ICP-OES analysis of the electrolyte solutions (Figure 13b).

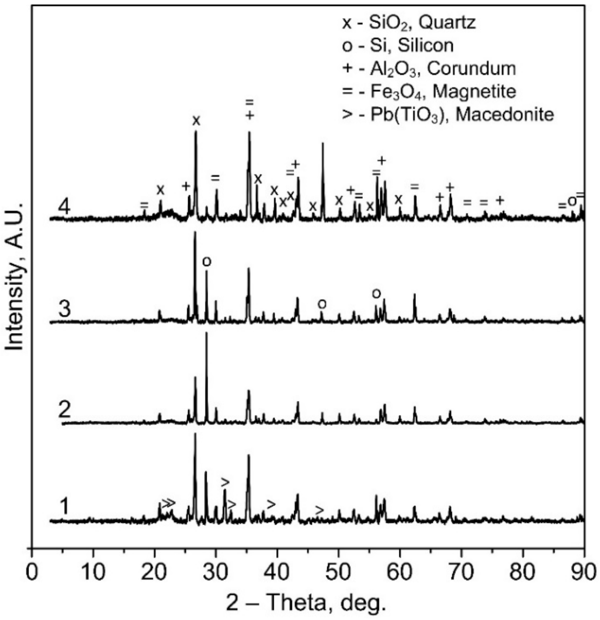


Figure 14. XRD patterns of solid residues from the experiments at different experiment durations: 1–0.5 h, 2–2 h, 3–4 h and 4–5 h. Other experimental conditions are provided in the caption of Figure 13.

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).

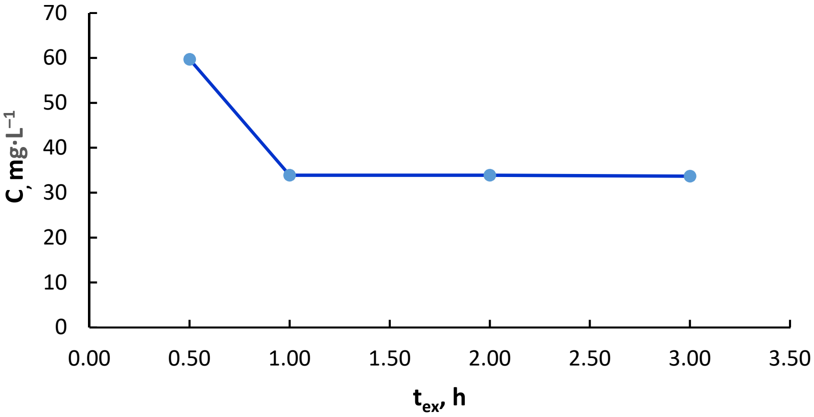


Figure 15. Change of free chlorine concentration in electrolyte solution on the experiment duration. Experimental conditions: C_{HCl} = 6 M, i = 0.88 A·cm^{-2}.

It can be seen from the presented data that, after 0.5 h of the experiment, the concentration of chlorine in the electrolyte solution reaches 59.72 mg·L^{-1}. A further increase in the duration of the investigation to 1 h 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 h 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 [48]. It should be noted that these data are in good agreement with the results presented in Figure 13b, namely that active dissolution of gold begins 30 min after the beginning of the experiment.

Thus, in the framework of the presented study, for the finest raw material fraction with d < 90 μm the highest gold leaching degree (86.3%) was achieved under the following experimental conditions: t_{ex} = 4 h, C_{HCl} = 6 M, i = 0.88 A·cm^{-2}, S/L ratio—8.6 g·L^{-1} and the highest copper leaching degree (94.2%) was achieved under the following experimental conditions: t_{ex} = 2 h, C_{HCl} = 6 M, i = 0.64 $A \cdot cm^{-2}$, and S/L ratio—2.9 $g \cdot L^{-1}$.

4. 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 from 824 ppm to 67 ppm and the copper content increases from 1.40% to 6.13%. Under the same conditions of the electrochemical leaching process, namely, an experiment duration of 2 h, a current density of 0.66 $A \cdot cm^{-2}$, and a solid/liquid ratio of 8.6 $g \cdot L^{-1}$ complete leaching of gold is achieved from raw materials with a particle size of d = 90–180 µm and d = 180–350 µm containing 277 ppm and 67 ppm of gold, respectively. At the same time, increasing the particle size in raw material fractions from d < 90 µm to d = 180–350 µm and the copper content means an increase from 1.40% to 6.13%, respectively, and an increase in the degree of copper leaching from 81.6% to 95.2% is observed. Determine that applying AC (i = 0.66 $A \cdot cm^{-2}$) has resulted in a noticeable improvement in the degree of gold leaching up to 80.5% from the finest fraction of raw material with d < 90 µm compared to the experiment in the absence of AC—6.9%. In contrast, the degree of copper leaching does not seem to benefit from AC significantly. Applying AC leads to an increase in the degree of metal leaching by only 3%. The increase in the electrolyte temperature also has a more significant effect on the gold leaching efficiency than copper. These results could be used as a foundation for developing a complex technology for recovering valuable metals from PCBs.

Author Contributions: Conceptualization, V.S., V.P. and E.B.; methodology, V.S., A.Z. and A.S.; validation, A.S., E.E. and V.P.; formal analysis, E.E. and A.S.; investigation, V.S., V.P., E.E. and A.S.; resources, E.B. and V.P.; data curation, J.B. and A.Z.; writing—original draft preparation, V.S. and A.S.; writing—review and editing, A.S. and J.B.; visualization, A.S. and J.B.; supervision, E.B. and V.P.; project administration, E.B.; funding acquisition, E.B. and V.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by ERDF project no. 1.1.1.1/20/A/139 "Development of sustainable recycling technology of electronic scrap for precious and non-ferrous metals extraction". The project was co-financed by REACT-EU funding to mitigate the effects of the pandemic crisis. The article was published with the financial support from the Riga Technical University Research Support Fund. This research was also supported by the Institute of Solid State Physics, University of Latvia, as the Center of Excellence has received funding from the European Union's Horizon 2020 Framework Program H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART2.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would also like to mention the support from the "Innovation Grants for Maritime Students" performed at Latvian Maritime Academy (Project No: 1.1.1.3/18/A/006, funded by the European Regional Development Fund—ERDF, Republic of Latvia). The article is published with the financial support from the Riga Technical University Research Support Fund.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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