metals

Article

Investigation of the Impact of Electrochemical Hydrochlorination Process Parameters on the Efficiency of Noble (Au, Ag) and Base Metals Leaching from Computer Printed Circuit Boards

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Abstract: The development of environmentally friendly and energy-saving processes for recycling electronic waste (e-waste) is still relevant today. The research presented in this work relates to hydrometallurgy, namely, the electrochemical leaching of metals from e-waste under the action of alternating current (AC) into hydrochloric acid solutions of electrolytes, and can be used for leaching both noble and non-ferrous metals from secondary raw materials. The main object of the study was disintegrator-crushed mixed computer PCBs metal-rich powders with a particle size (d) of <90 µm. The impact of such leaching process parameters as temperature (T_{el}) and composition of the electrolyte solution, AC density (i) on the electrodes, experiment duration (t_{ex}) while maintaining a constant electrolyte temperature (60 °C, 70 °C, and 80 °C) on the metal (Au, Ag, Cu, Al, Ni, Pb, Sn, Ti, Zn, and Fe) leaching efficiency has been studied. In addition, under similar experimental conditions, but without external control of T_{el}, the kinetics of metal leaching from raw material powders obtained via PCBs single and double crushing in a disintegrator has been also presented. Comparison of raw material powders obtained from different batches of the source material showed both the variability of its chemical composition and the different kinetics of Au and Ag leaching under the same experimental conditions. The optimal conditions for pretreatment of the raw material obtained by single crushing in a disintegrator (C_{HCl} = 6 mol·L^{-1}, i = 0.88 A·cm^{-2}, t_{ex} = 1 h, solid-to-liquid ratio—8.6 g·L^{-1} and without external control of T_{el}) were determined. It has been shown that this electrochemical pretreatment is accompanied by transition of only base metals into the electrolyte solution, making it possible to significantly reduce their concentration in the final solution. Under pretreatment conditions, the following degree of metal leaching (R_{Me}) has been established: R_{Cu} = 98.2%, R_{Al} = 62.8%, R_{Ni} = 53.4%, R_{Pb} = 93.2%, R_{Sn} = 98.0%, R_{Ti} = 88.5%, R_{Zn} = 61.6%, and R_{Fe} = 78.8%. As a result of a subsequent two-hour electrochemical treatment of a solid residue, the degree of leaching of gold and silver was 73.6% and 86.7%, respectively. The presented results provide a broader understanding of the possibility of using the proposed electrochemical hydrochlorination method for noble and base metals leaching from waste PCBs. The novelty and practical value of this research is a validation of the developed technology in laboratory conditions using the real batch of the PCBs. This approach may also be useful to researchers involved in the recycling of other types of secondary raw materials.

Keywords: electrochemical leaching; alternating current; mixed printed circuit boards; base metals; gold; silver

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1. Introduction

Vast quantities of waste electrical and electronic equipment (WEEE) have been increasingly produced in recent years. Based on recent data from the European Union statistics institute [1] the quantity of electrical and electronic equipment introduced into the EU market saw a progression from 7.6 million tons in 2012 to a peak of 13.5 million tons in 2021. Notably, in 2013, the recorded amount hit its lowest point at 7.3 million tons. Throughout the entire period spanning from 2012 to 2021, the influx of EEE in the market exhibited a 77.1% increase. Correspondingly, the total collected WEEE augmented from 3.0 million tons in 2012 to 4.9 million tons in 2021, marking a rise of 65.1%. Figure 1 reflects the statistical data for small equipment and small IT and telecommunication equipment in absolute value in tons, by country, in the 2019–2021 period.

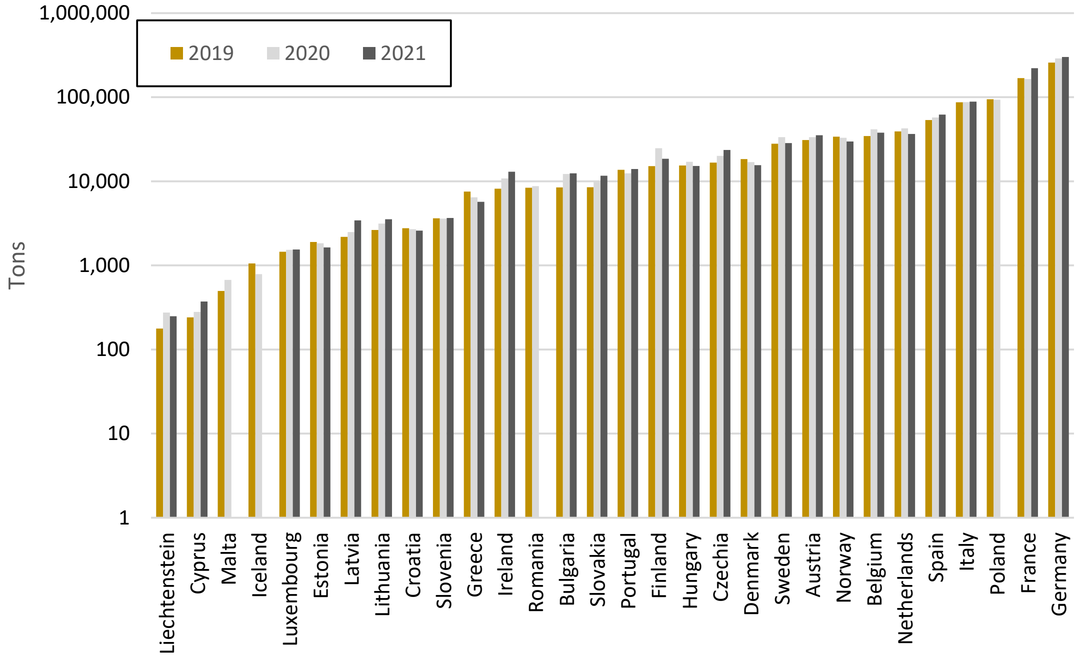


Figure 1. Waste electronic equipment (small equipment with no external dimension greater than 50 cm and small IT and telecommunications equipment with no external dimension greater than 50 cm) waste collection statistics. Reprinted/Adapted from Ref. [2].

Printed circuit boards (PCBs) are estimated to account for 3 to 5% of total WEEE by weight [3]. The composition of PCBs includes such non-conductive materials as a laminate, including a polymer binder (epoxy or phenolic resins) and reinforcing fillers (glass, paper, polyester fiber fabrics), as well as ceramics and plastics located in components mounted to PCBs. The metal (conductive) part contains both base metals (copper, aluminum, tin, lead, zinc, nickel, and iron) and expensive noble metals (gold, silver, and palladium) [4,5]. Therefore, efficient recycling of waste PCBs is important both for conserving metal resources and preventing environmental pollution.

In PCBs recycling, the predominant commercial process is the pyrometallurgical process, which focuses on the recovery of precious metals and copper [6,7] The main disadvantages of this technology are high energy consumption, environmental hazards, insufficient selectivity, and the need for additional operations (usually hydrometallurgical).

Hydrometallurgy for recycling e-waste is a sustainable alternative to pyrometallurgy. The hydrometallurgical process involves two main steps: transferring metals from the solid matrix into the aqueous phase (leaching) and separating the target metals from the produced solution. To separate and concentrate target metals from leaching solutions, liquid–liquid extraction, ion exchange, and precipitation are most often used in hydrometallurgical processes [7,8]. Before leaching precious metals from waste PCBs, pretreatment is usually performed, including physical (crushing and various operations to enrich the metal component of scrap: pneumatic separation, magnetic separation, screening, eddy current separation, and electrostatic separation) and chemical pretreatments (with mineral acids) [9]. It is noted that, as a result of physical pretreatment, the precious metals present in the raw material in small or trace quantities are partially lost both in the mass of metal dust and plastic particles [3,10]. Cyanides, thiosulfates, thiourea, and halides are used in hydrometallurgical techniques [9,11]. The mechanisms of the reactions of precious metal leaching from PCBs with these reagents, and progress in hydrometallurgical technologies, are presented in a number of reviews published in the last decade [12–17].

Cyanide (sodium or potassium), as a gold leaching agent, dominates in the mining industry due to its high leaching efficiency, low consumption, and its ability to carry out the process in an alkaline environment [18,19]. However, this reagent is extremely toxic.

In terms of toxicity and environmental impact, the use of chelating agents, including thiosulfates (sodium and ammonia) [20] and thiourea [21] to leach precious metals from PCBs is less hazardous. The use of these reagents makes it possible to achieve a high degree of leaching of Au and Ag. However, both hydrometallurgical processes using thiosulfate and thiourea require large amounts of reagent due to the slow kinetics of thiosulfate and the low stability of thiourea [22].

Thiourea has a higher dissolution rate of gold than cyanide [23]. This reagent is considered as an alternative to cyanide for the leaching of gold from refractory ores [24]. Research results on the use of thiourea for leaching gold from waste PCBs [21,25,26] and different types of random-access memory (RAM) sticks [11] are also reported. The selectivity of the leaching of gold by thiourea increases in the absence of base metals. Therefore, when leaching this metal from e-waste, pre-leaching of base metals is mandatory.

PCBs include different components containing Au: microchips (processors, RAM) and electric contacts. Typically, in gold leaching studies, separate gold-rich components are used. In real cases, waste PCBs containing gold only in non-dismantled components are used for recycling. The use of thiourea as a leaching agent of Au from such PCBs, in our opinion, has the following disadvantages: (i) part of the gold-plated contacts mounted on PCBs are located under a layer of solder, which inevitably leads to the loss of valuable metal and (ii) the selectivity of gold leaching is difficult to control during the process. The use of the preliminary leaching of base metals, on the one hand, can lead to an increase in the Au leaching efficiency and, on the other hand, to losses of valuable metal at the stages of its subsequent filtering and washing.

The chlorine method (blowing chlorine through molten unrefined gold) and the hydrochlorination method (chlorination in hydrochloric acid solution) are used for gold and platinum group metal refining, respectively [27].

The use of halogen/halide systems (chlorine, bromine, iodine/chloride, bromide, iodide) to dissolve gold preceded cyanidation [28]. Gold forms both Au(I) and Au(III) complexes with chloride, bromide and iodide, depending on the concentration of the solution. However, among the halides, only chlorine/chloride was used on an industrial scale [29]. The use of chlorine instead of oxygen as an oxidizing agent, and chloride instead of cyanide as a complexing agent, significantly increases the rate of gold dissolution [28,30]. However, chlorine leaching of gold is more difficult to use than cyanide leaching for two main reasons: (i) special stainless steel and rubber-lined equipment is required that is resistant to highly aggressive acidic and oxidizing conditions; (ii) chlorine gas is a highly toxic substance, and therefore, both during storage and when working with it, special safety measures must be observed.

Therefore, in situ production of chlorine is proposed to minimize the risks associated with the use of chlorine in chloride leaching systems [31,32]. The main advantage of this approach is that there is no need for its separate production, storage, and handling [31]. The kinetics of the hydrochlorination of pure gold with molecular chlorine, generated in situ as a result of the chemical reaction between sodium hypochlorite and hydrochloric acid, has been studied by various authors [32]. The presented results show that the rate of metal dissolution is mainly determined by the concentration of the trichloride ion (Cl_3^-) in the solution.

To avoid chlorine emissions into the atmosphere during the hydrochlorination of secondary raw materials, it is also preferable to conduct a process with low chlorine consumption to improve the environmental friendliness of the process. To implement the hydrochlorination process for leaching metals from PCBs, the authors [33–37] proposed a different approach.

In these studies, chlorine was produced in a separate electrochemical cell with an anion exchange membrane via electrolysis of an HCl solution and supplied to a leaching reactor. In this case, the products of dissolution of $Cl_{2(gas.)}$ in the leaching solution such as: $Cl_{2(aq),}$ Cl_3^-, and HClO acted as metal oxidizer [38]. The leaching behavior of base metals, such as Cu, Zn, Pb, Sn [33], and Au only [34], and the mixture of the metals: Ag, Au, Cu, Pb, Pd, and Sn [35] from shredded PCB's, have been detailed studied.

Within the framework of our proposed technique [39,40], the process of generating chlorine and the leaching of metals from PCBs are combined in one reactor. Moreover, chlorine is produced under conditions of non-stationary electrolysis of hydrochloric acid solutions, using alternating current (AC). An innovative high-energy semi-industrial disintegration-milling system was used to crush the PCBs [41].

The main idea that guided us when choosing the disintegrator and hydrochlorination scheme was to minimize the loss of noble metals at the stages of physical pretreatment of the source material (computer PCBs) and ensure the completeness of their transfer into solution at the leaching stage. The transfer of all metals into the solution within the framework of the proposed approach makes it possible, on the one hand, to obtain a solid residue free of metals, which creates the possibility of its further use and does not create problems with its disposal, which is important from an environmental point of view. On the other hand, the resulting electrolyte solutions can be further used for complex recycling, because they contain not only expensive noble metals, but also non-ferrous metals.

As a result of the proposed process, all metals contained in the PCBs powder transferred into the electrolyte solution. The main feature of produced multicomponent solutions is not only the low content of noble metals in the background of the high content of base metals, but also a high concentration of hydrochloric acid. Therefore, at the stage of metal separation, special requirements are imposed on sorbents and extractants: selectivity in relation to the target metal and stability in a strongly acidic environment.

Gold (III) halide complexes are easily extracted from acidic solutions with various types of known organic extractants. But selective extraction is easily achieved only from weakly acidic solutions [42].

Currently, effective and economical methods for the selective extraction of noble metals, based on the use of nitrogen- and sulfur-containing sorbents, are being developed. It has been demonstrated that the S,N-rich MOF (metal–organic framework) has a high adsorption capacity, fast adsorption rate, and good selectivity under acidic conditions for gold recovery [43]. To isolate noble metals from acidic chloride solutions obtained as a result of the leaching of computer PCBs in aqua regia, mesoporous carbons and sulfur-impregnated mesoporous carbon have been proposed. It has been shown that the efficiency of Au(III) adsorption in the concentration range of from 1 to 5 M HCl is noticeably higher than for Pd(II) and Pt(IV) [44]. In addition, for the selective adsorption of precious metals from hydrochloric acid solutions, it has been proposed to use such sorbents as nanosized $Fe_3O_4@SiO_2\text{-}NH_2$ [45].

One of the most common methods for removing iron (III) from chloride solutions is its hydrolytic precipitation [46]. However, when recycling acidic solutions to avoid acid neutralization, the liqui–liquid extraction method is used. The possibility of selective extraction of Fe^{3+} ions from acidic chloride solutions ($C_{HCl} > 6\ mol\cdot L^{-1}$) with 2-octanone in the presence of macro amounts of nickel chloride as well as the trace impurities of Co and Cu has been demonstrated [47]. In turn, the results presented in the paper [48] showed that the use of a solution of hydrazides of Versatic acids (fraction C_{15}–C_{19}) in kerosene as an extractant with the addition of tributyl phosphate (TBP, 10%) makes it possible to selectively extract copper in the presence of Fe^{3+}, Ni^{2+}, and Co^{2+} at $C_{HCl} > 1$ mol·L^{-1}.

It should be noted that studies on the isolation of metals from the resulting electrolyte solutions are not the subject of the studies presented in this work, and will be carried out in the future at the next stage of research.

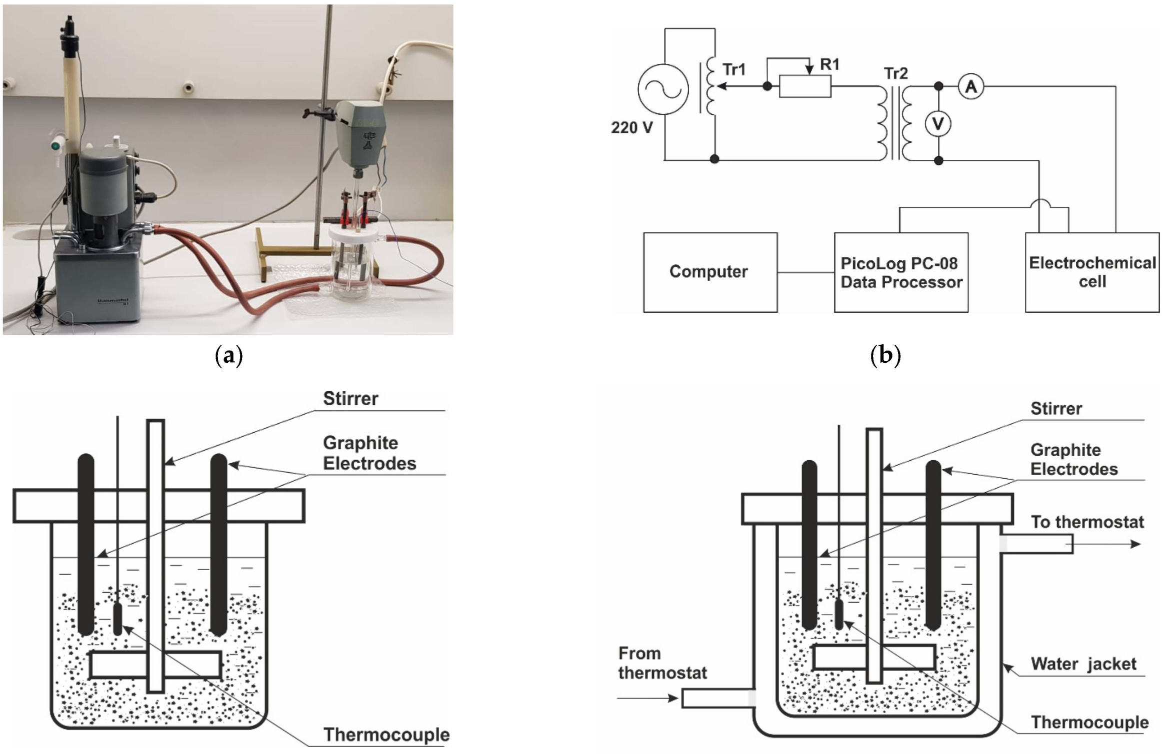
The purpose of this work is to study the influence of the most important parameters of the metal leaching process from fine raw material powders obtained from disintegrator-crushed mixed computer PCBs at a controlled electrolyte temperature within the previously proposed electrochemical hydrochlorination technique [39]. Continuation of the search for optimal process conditions for the most complete leaching of metals from the raw materials under study and the production of electrolyte solutions suitable for further recovery of valuable metals is also presented.

2. Materials and Methods

Preliminary preparation of raw materials (mixed computer PCBs) includes: PCB dismantling; double crushing in a hammer mill; single or double crushing using the high-energy semi-industrial disintegration-milling system (disintegrator DSL-350, Tallinn University of Technology, Tallinn, Estonia) [41]; and subsequent sieving using a FRITSCH ANALYSETTE 3 PRO Vibratory Sieve Shaker (FRITSCH GmbH, Weimar, Germany). As a result, the finest fraction of the obtained powders with a particle size (d) < 90 µm was selected as a research material.

The experimental setup is represented in Figure 2—a common view Figure 2a. It consisted of an alternating current (AC) circuit (Figure 2b) and an electrochemical cell. The AC circuit included a step-down transformer, a laboratory autotransformer, and a rheostat, as well as an AC ammeter and AC voltmeter to measure current and voltage, respectively (Figure 2b) [39]. Graphite rods (d = 8 mm) were used as electrodes. During the electrochemical leaching process, the required current value was maintained constant.

A polypropylene reactor—cell 1 (Figure 2c) and a water-jacketed glass reactor—cell 2 (Figure 2d) were used as an electrochemical cell. Cell 1 was used in experiments without adjusting the electrolyte temperature (at ambient temperature) during the electrochemical process. When studying the influence of parameters of the electrochemical process on the efficiency of metal leaching, experiments were carried out in cell 2 while maintaining a constant electrolyte temperature. The choice of temperature was based on the maximum temperature that the electrolyte reaches during the electrochemical process at a given current density (i) in the absence of external control of electrolyte temperature. During experiments, the electrolyte temperature (T_{el}) was measured using a chromel–alumel thermocouple. Powders of the raw material were used in the form of a dispersed (solid) phase in the electrolyte solution (liquid phase). The solid-to-liquid (S/L) ratio in the suspension was 8.6 g·L^{-1}. In all experiments, the volume of the electrolyte was 350 mL, and the concentration of the hydrochloric acid was 4, 6, and 8 mol·L^{-1}. After filling the reactor with the initial components (PCB powder and electrolyte solution) 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. To produce chlorine, an alternating current (AC) of industrial frequency (50 Hz) with a density (i) of 0.21 A·cm^{-2}, 0.42 A·cm^{-2}, 0.63 A·cm^{-2}, 0.84 A·cm^{-2}, and 0.88 A·cm^{-2} was used. The duration of the experiments (t_{ex}) varied from 0.5 to 6 h. When carrying out a two-stage leaching process, chemical or electrochemical pretreatment of the raw material was first carried out. Then, after removing the leach solution and adding a fresh portion of electrolyte to the wet residue of the raw material, electrochemical leaching was performed. Chemical pretreatment of the raw material powder was carried out at a constant electrolyte temperature (T_{el} = 70 °C) under conditions of stirring of reaction mixture for an hour. Electrochemical pretreatment was also carried out for an hour under the same experimental conditions as the subsequent electrochemical leaching process.



(**a**) (**b**)

(**c**) (**d**)

Figure 2. Experimental setup: a common view without power supply and control (**a**), AC circuit, where Tr1—laboratory autotransformer, R1—rheostat, Tr2—step-down transformer, V—AC voltmeter, A—AC ammeter (**b**), and schematic representation of electrochemical cells: polypropylene cell—cell 1 (**c**) and a water-jacketed glass cell—cell 2 (**d**). The (**b**) section is Reprinted/Adapted from Ref. [39] (CC BY Open Access, MDPI).

To establish the metal content in the raw material, the chemical treatment (leaching) of three representative samples (0.500 g each) was carried out. This treatment included sequentially boiling the sample in a solution of HCl (1:1) and two portions of aqua regia until a wet residue was formed. During the boiling process in aqua regia, HNO_3 excess was removed by adding several portions of concentrated HCl. The resulting wet residue was transferred to the filter with a 3 $mol \cdot L^{-1}$ HCl solution and washed accurately. Filtrate was diluted to a volume of 100 mL with 3 $mol \cdot L^{-1}$ HCl solution. Quantitative determination of the metals in the prepared solutions 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). Based on the results of the analysis, an average concentration of each metal under study was calculated. Solid residues after leaching were washed with distilled water to pH 5–6, dried at a temperature of 105 °C in one hour, and weighed.

ICP-OES was also used for the quantitative determination of metals under study in electrolyte solutions obtained as a result of electrochemical leaching.

The efficiency of electrochemical leaching of metals from raw materials was evaluated by the degree of metal leaching (R_{Me}), 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 (1):

$$R_{Me}\ (\%) = (M_{el}/M_{PCBs}) \times 100\% \tag{1}$$

The content of metals in the raw material (M_{PCBs}) was calculated from the results of the ICP-OES analysis of the solutions obtained from the chemical leaching of a representative sample of the raw material. The quantity of metals in the solid residue (M_s) after electrochemical leaching of the raw material was estimated using Equation (2):

$$M_s = M_{PCBs} - M_{el} \tag{2}$$

3. Results and Discussion

3.1. Raw Material Characterization and Kinetics of Electrochemical Leaching of Metals

The main object of the research was the raw material 1 powder fraction with a particle size < 90 µm prepared by single crushing in a disintegrator of mixed computer PCBs. The percentage of both metals in this raw material, based on the results of ICP-OES analysis of the solutions prepared by chemical leaching and obtained after chemical leaching of solid residue, is presented in Table 1. The metal content in double-crushed mixed computer PCBs from the same batch of source material (raw material 2) and single-crushed mixed computer PCBs from another batch of mixed PCBs (raw material 3) are also shown.

Table 1. Content of metals in the raw material fraction with a particle size < 90 µm.

	Raw Material Powder Fraction d < 90 µm		
Component, Content	**Raw Material 1**	**Raw Material 2**	**Raw Material 3 [39]**
Fe, (%)	33.38	12.37	7.56
Sn, (%)	2.82	2.52	4.76
Al, (%)	1.74	3.56	1.31
Cu, (%)	1.42	1.57	1.40
Zn, (%)	0.53	0.43	2.00
Pb, (%)	1.07	0.77	7.50
Ni, (%)	1.10	0.53	1.03
Ti, (%)	1.54	0.48	1.74
Sb, ppm	510	1790	1365
Mn, ppm	n/a [2]	760	1698
Cr, ppm	504	144	188
Co, ppm	902	140	224
V, ppm	74	46	29
Mo, ppm	n/a [2]	n/a [2]	17
Ag, ppm	1734	906	8450
Pd, ppm	BDL [1]	BDL [1]	1550
Au, ppm	504	606	824
Solid residue, %	34.1	60.4	45.8

[1] BDL—below the detectable limit. [2] n/a—not analyzed.

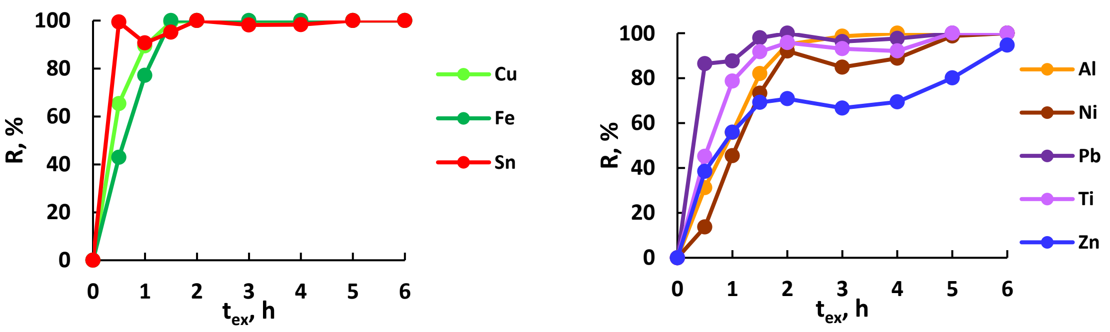
The results obtained show that the content of both metals in the raw material powders and the solid residue obtained as a result of their leaching differ significantly. Thus, the composition of the disintegrator-crushed raw material fractions with a particle size d < 90 µm depends on both the PCB batch and the number of times it is crushed. Moreover, it should be noted that the content of individual metals in PCBs, given in the literature [49], varies widely. It is associated not only with the methods of preliminary grinding of the raw material, but also with the sampling and leaching method for transferring metals into a solution for quantitative analysis.

Under the same conditions of electrochemical leaching, the kinetics of metal leaching from these raw material powders was studied. All experiments were carried out without external regulation of the electrolyte temperature (at ambient conditions).

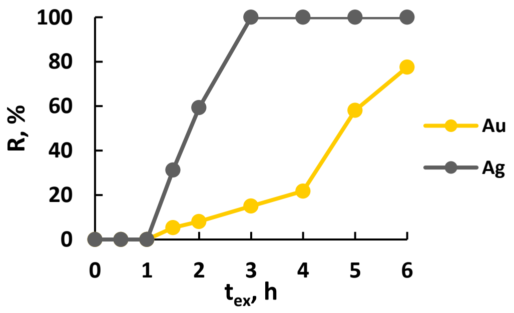
The presented results (Figure 3, Table 1) show that the leaching kinetics from the studied powders of such active metals as Sn is almost identical: complete metal leaching is achieved with an experiment duration of 0.5 h. The leaching efficiency for Pb and Al depends on the metal content in the raw material: with increasing metal content in the raw material, the time for complete leaching also increases. Moreover, the complete leaching of

Al from raw material 2, with the highest content, was not observed under the conditions of a 5 h experiment.

(**A**)



(**a**) (**b**)



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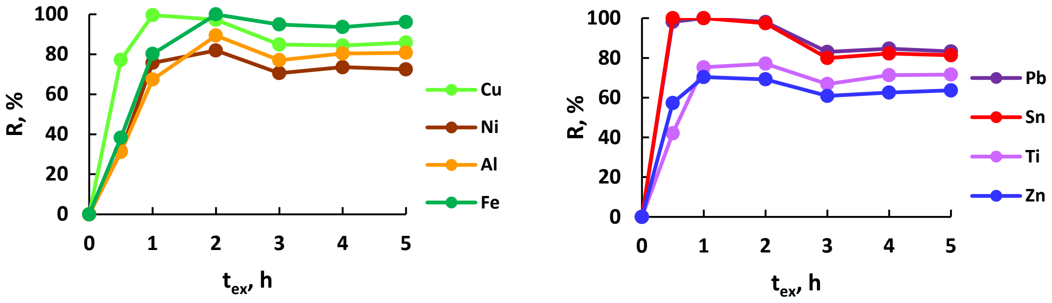

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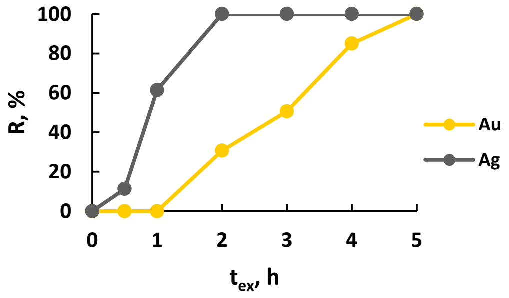
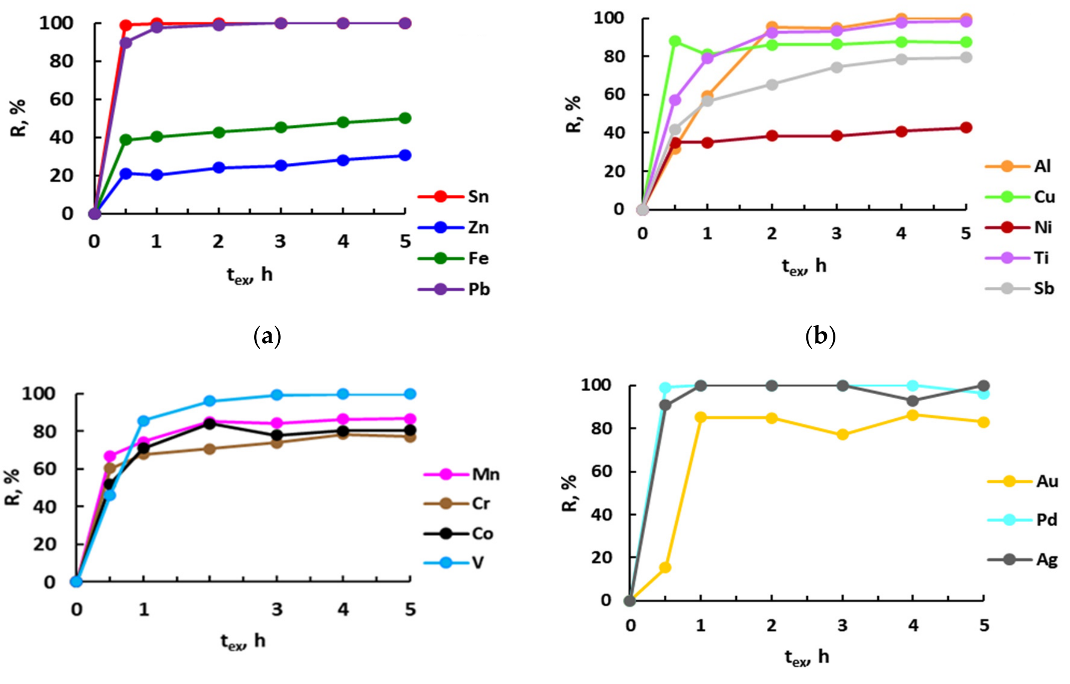


(**c**)

Figure 3. *Cont.*

(**C**)



(**a**) (**b**)

(**c**) (**d**)

Figure 3. Impact of experiment duration on the degree of metal leaching from raw material powders: (**A**) is raw material 1: for Cu, Fe and Sn (**a**); for Al, Ni, Pb, Ti and Zn (**b**); and for Au and Ag (**c**). (**B**) is raw material 2 for Cu, Ni, Al and Fe (**a**); for Pb, Sn, Ti and Zn (**b**); and for Au and Ag (**c**). (**C**) is raw material 3 for Sn, Zn Fe and Pb (**a**); for Al, Cu, Ni, Ti and Sb (**b**); for Mn, Cr, Co and V (**c**); and for Au, Pd and Ag (**d**). Experimental conditions: cell 1, C_{HCl} = 6 mol·L^{-1}, i = 0.88 A·cm^{-2}, S/L = 8.6 g·L^{-1} Reprinted/Adapted from Refs. [39,40].

In the case of Ti, complete metal leaching was achieved with an experiment duration of 5 h for raw material 1 (Figure 3(Ab)) and raw material 3 (Figure 3(Cb)). The efficiency of metal leaching from raw material 2, with the lowest content, was only 71.6% (t_{ex} = 5 h). The maximum degree of Zn leaching after 5 h of the experiment was 80.1% when using raw material 1. From the raw material 2 and the raw material 3, less effective metal leaching was observed—63.6% and 30.8%, respectively. The same regularity was established for Ni leaching (t_{ex} = 5 h): R_{Ni} = 100% from raw material 1, R_{Ni} = 72.5% from raw material 2, and R_{Ni} = 42.6% from raw material 3.

Iron was almost completely leached from raw material 1 and raw material 2 with experiment durations of 1.5 h and 2 h, respectively. In the case of raw material 3, the degree of leaching was significantly lower and R_{Fe} = 50.0%. After 2 h of electrochemical leaching, Cu was leached completely from raw material 1 (R_{Cu} = 100%). From raw material 2 and raw material 3, 97.2% and 86.3% of metal was leached, respectively. Complete leaching of Ag was observed with experiment durations of 3 h, 2 h, and 1 h (Figure 3(Ac,Bc,Cd)) from raw material 1, raw material 2, and raw material 3, respectively. Au was completely leached from raw material 2 at t_{ex} = 5 h; from raw material 3 the maximum degree of metal leaching was 86.3% at t_{ex} = 4 h; and from raw material 1—77.5% at t_{ex} = 6 h. The observed differences in the kinetics of the leaching of gold and silver from the materials studied are probably associated both with the mass content of the active metals relative to Au and Ag, and with the location of thr noble metals in the microparticles of the raw material. Thus, from the presented data, it is clear that the composition of the raw material most significantly affects the leaching of such metals as Au, Ag, Ni, Zn, and Fe.

3.2. Impact of Electrochemical Process Parameters on the Degree of Metal Leaching

The passage of AC through the system causes the heating of the electrolyte solution. Moreover, the temperature of the electrolyte depends both on the current density and the duration of the experiment [39,40]. Therefore, when studying the influence of such process parameters as the composition and temperature of the electrolyte and the current density on the efficiency of metal leaching from the raw material, experiments were carried out while maintaining the electrolyte at a constant temperature.

3.2.1. Electrolyte Composition

Study of the impact of the concentration of hydrochloric acid in the electrolyte solution on the degree of metal leaching from raw material 1 was carried out at a constant electrolyte temperature (T_{el}) of 80 °C.

The results obtained showed (Figure 4) that the increase in hydrochloric acid concentration in the electrolyte solution from 4 mol·L^{-1} to 8 mol·L^{-1} leads to a significant increase in the degree of Ni, Zn, and Ag leaching. The complete leaching of Cu is achieved at C_{HCl} = 6 mol·L^{-1}. It should be noted that the presence of gold in the obtained electrolyte solutions was not established under these experimental conditions.

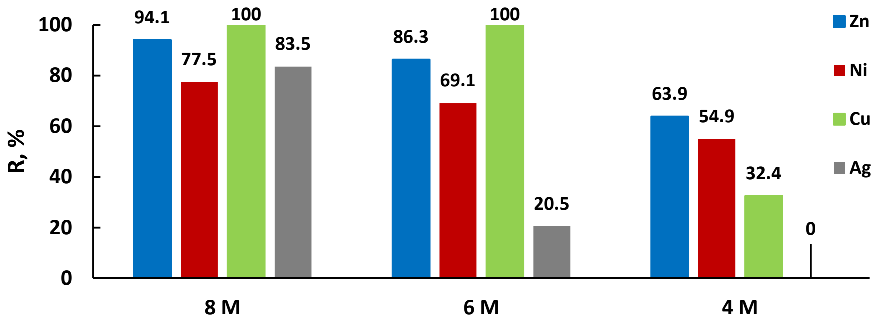
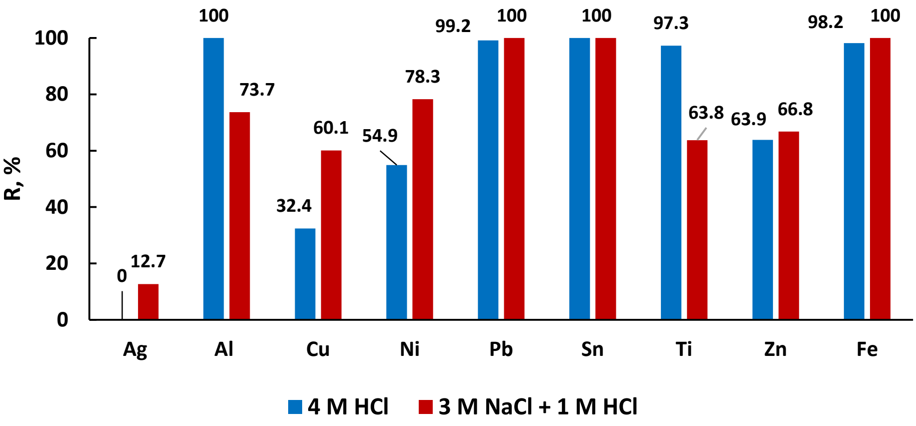


Figure 4. Impact of HCl concentration on the degree of metal leaching. Experimental conditions: cell 2, raw material 1; i = 0.84 A·cm^{-2}; t_{ex} = 1 h; S/L = 8.6 g·L^{-1}; T_{el} = 80 °C.

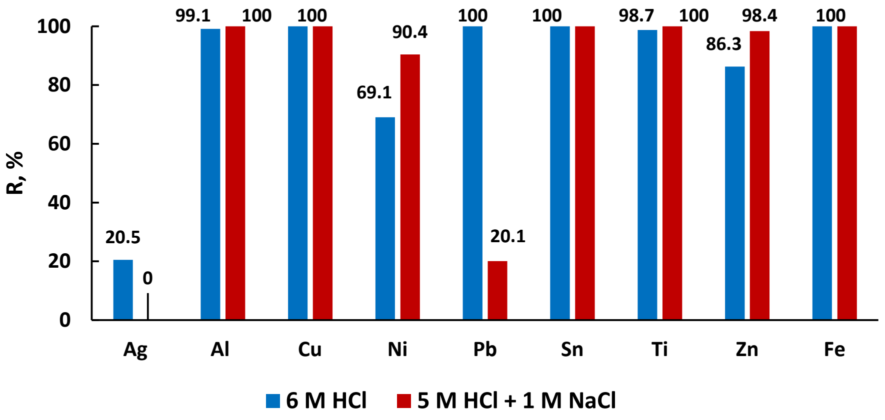
To reduce the acidity of the electrolyte solution, hydrochloric acid solutions with the addition of sodium chloride were also used. Figure 5a,b demonstrate the results of these studies.

For comparison, the results of the electrochemical leaching of metals into pure hydrochloric acid solutions (without NaCl) with the same concentration of chloride ions are also presented.

Figure 5a demonstrates that the complete leaching of Al and Sn was achieved at C_{HCl} = 4 mol·L^{-1}. The other metals (Pb, Ti, and Fe) are characterized by a high degree of leaching at this concentration of hydrochloric acid in the electrolyte solution, but their complete leaching from the raw material was not achieved. At the same concentration of chloride ions (4 mol·L^{-1}) in the electrolyte solutions, the presence of sodium chloride leads to a decrease in the degree of Al and Ti leaching and an increase in the degree of Cu and Ni leaching. In the case of other metals, this effect is less significant. The presence of sodium chloride (C_{NaCl} = 1 mol·L^{-1}) in a hydrochloric acid solution with a concentration of chloride ions of 6 mol·L^{-1} leads to an increase in the degree of Ni and Zn leaching (Figure 5b). At the same time, a significant decrease in the efficiency of Pb leaching is observed. This is probably due to the peculiarities of the formation of lead chloride complexes in this environment [50]. Silver is leached in a small amount (20.5%) into the hydrochloric acid electrolyte in the absence of NaCl and does not leach at all in the presence of sodium chloride. The degree of the leaching of other metals is characterized by high values and practically does not depend on the composition of the electrolyte. The presence of gold in the studied electrolytes was not established.



(**a**)



(**b**)

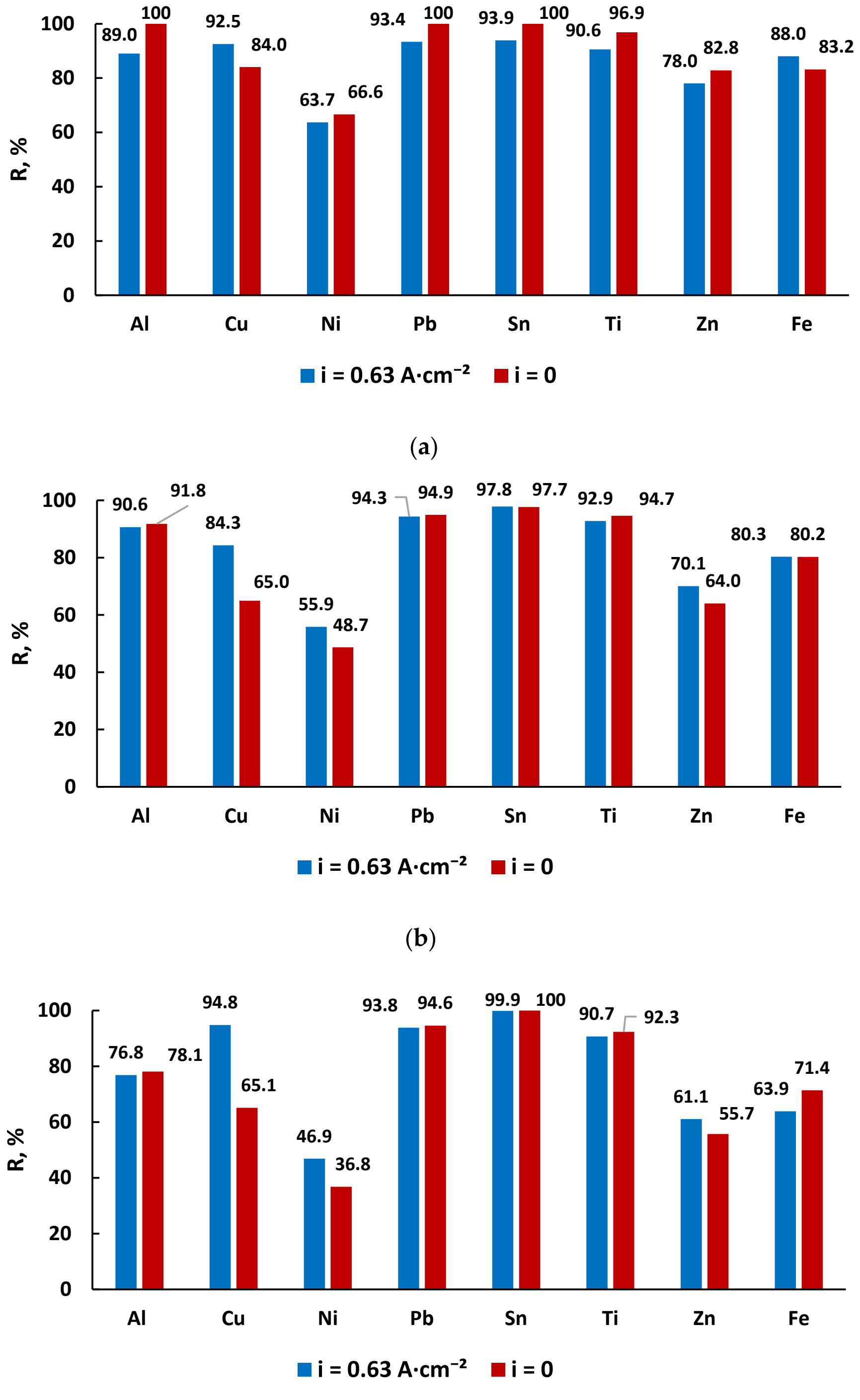
Figure 5. Impact of the presence of NaCl in hydrochloric acid electrolyte on the degree of metal leaching: C_{NaCl} = 3 mol·L^{-1} in 1 mol·L^{-1} HCl solution (**a**); C_{NaCl} = 1 mol·L^{-1} in 5 mol·L^{-1} HCl solution (**b**). Experimental conditions: cell 2; raw material 1; t_{ex} = 1 h, i = 0.84 A·cm^{-2}; S/L = 8.6 g·L^{-1}; T_{el} = 80 °C.

3.2.2. Current Density and Electrolyte Temperature

The influence of AC superimposition on the system was studied at electrolyte temperatures of 60 °C, 70 °C, and 80 °C (Figure 6).

The presented results show that an increase in electrolyte temperature in the absence of current leads to an increase in the degree of leaching of almost all of the studied metals. At i = 0.63 A·cm^{-2}, an increase in the electrolyte temperature leads to an increase in the degree of Ni, Zn, Fe, and Al leaching. Effective leaching of Sn, Pb, Ti, and Cu was observed at 60 °C and a further increase in the electrolyte temperature has practically no positive effect. At the same electrolyte temperature, the effect of electrical current superimposition on the system was most noticeable in the leaching of Cu, Ni, and Zn. The transition of Au and Ag into the electrolyte solution under experimental conditions was not established.

At an electrolyte temperature of 70 °C, the effect of electrical current superimposition with a higher value (I = 0.84 A·cm^{-2}) on the system was also studied.



(a)

(b)

(c)

Figure 6. Impact of current superimposition on the degree of metal leaching. Experimental conditions: cell 2; raw material; t_{ex} = 1 h; S/L = 8.6 g·L^{-1}; C_{HCl} = 6 mol·L^{-1}, (**a**)—T_{el} = 80 °C, (**b**)—T_{el} = 70 °C and (**c**)—T_{el} = 60 °C.

The results obtained show (Figure 7) that electrical current superimposition leads to an increase in the leaching efficiency of all metals, except for Al and Ti, compared to the experiment without current superposition on the system. The leaching of Au and Ag into the electrolyte solution under experimental conditions was also not observed. Comparison of the results obtained at different current densities (Figures 6 and 7) shows that increasing the current density promotes more efficient leaching of almost all metals from the raw material. An increase in the current density leads to promotion of the current efficiency of chlorine and, as a consequence, to an increase in the concentration of the oxidizing agent in the electrolyte solution [36].

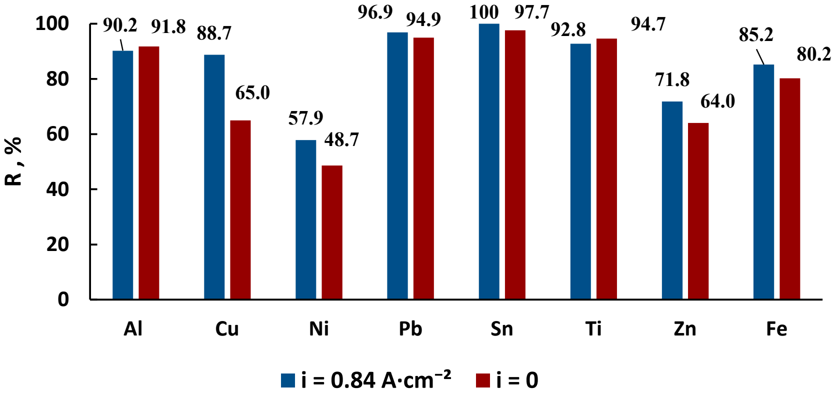
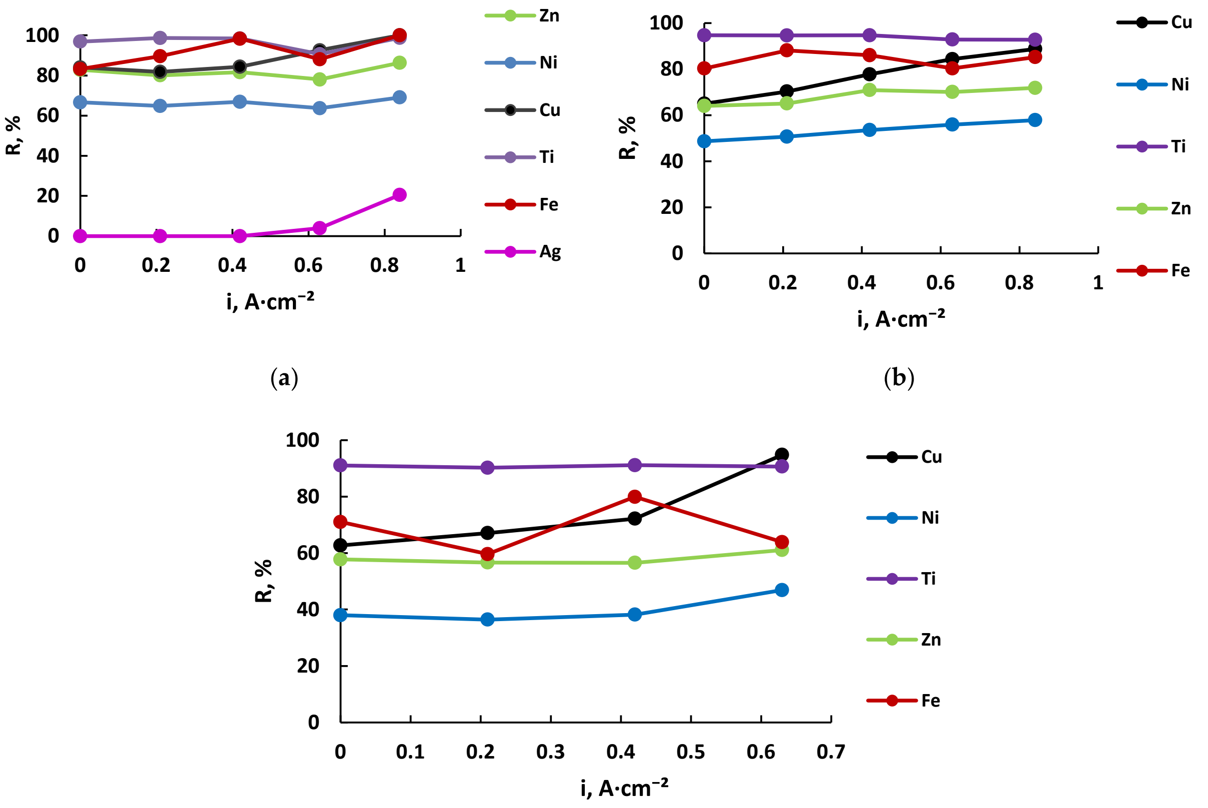


Figure 7. Impact of alternating current superimposition on the degree of metal leaching. Experimental conditions: cell 2; raw material 1; S/L = 8.6 g·L^{-1}; C_{HCl} = 6 mol·L^{-1}; t_{ex} = 1 h; T_{el} = 70 °C.

The results of studies on the effect of current density on the efficiency of metal leaching at different electrolyte temperatures (60 °C, 70 °C and 80 °C) are presented in Figure 8.



(**a**) (**b**)

(**c**)

Figure 8. Impact of current density on the degree of metal leaching. Experimental conditions: cell 2; raw material 1; t_{ex} = 1 h; S/L = 8.6 g·L^{-1}; C_{HCl} = 6 mol·L^{-1}; (**a**)—T_{el} = 80 °C, (**b**)—T_{el} = 70 °C, (**c**)—T_{el} = 60 °C.

At an electrolyte temperature of 80 °C, an increase in the degree of leaching of Cu and Ag begins at i > 0.42 A·cm^{-2}, and of other metals at i > 0.63 A·cm^{-2} (Figure 8a). With a decrease in the electrolyte temperature (T_{el} = 70 °C), an increase in current density leads to a gradual increase in the degree of Ni, Cu, and Zn leaching and practically does not affect the leaching of other metals. At a temperature of 60 °C and i > 0.42, an increase in the degree of leaching of Ni, Cu, and Zn was also observed. Moreover, in the case of Cu, this effect was most significant. It should be noted that Ag leaching is observed only at the electrolyte temperature of 80 °C at i > 0.42 $A \cdot cm^{-2}$. The leaching of Au into the electrolyte solution under experimental conditions was not observed.

Thus, the presented results show that an increase in electrolyte temperature from 60 °C to 80 °C, both in the absence of electrical current and under electrical current superimposition on the system, leads to an increase in the degree of leaching of almost all of the studied metals. An increase in current density has the most significant effect on the efficiency of leaching of all metals at an electrolyte temperature of 80 °C. However, the transition of Au into the electrolyte solution under experimental conditions was not established.

For comparison, hydrochloric acid solutions with the addition of sodium chloride were used as an electrolyte in the experiments at an electrolyte temperature of 80 °C (Figures 9 and 10).

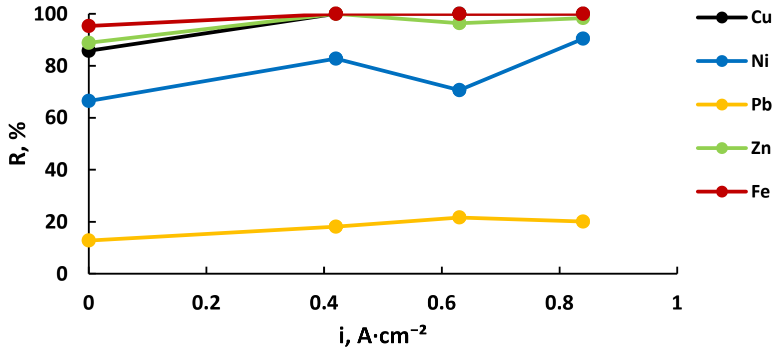


Figure 9. Impact of current density on the degree of metal leaching. Experimental conditions: cell 2; raw material 1; t_{ex} = 1 h; S/L = 8.6 $g \cdot L^{-1}$; electrolyte composition: C_{HCl} = 5 $mol \cdot L^{-1}$, C_{NaCl} = 1 $mol \cdot L^{-1}$; T_{el} = 80 °C.

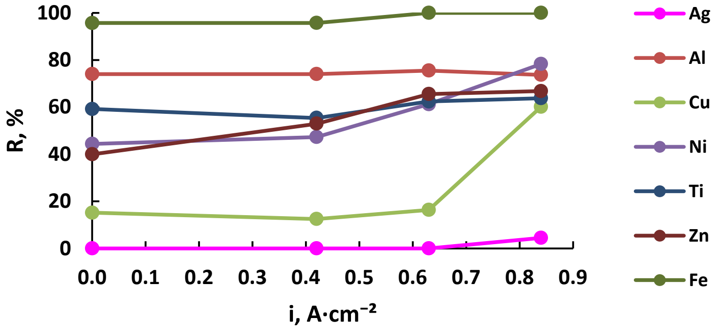


Figure 10. Impact of current density on the degree of metal leaching. Experimental conditions: cell 1; raw material 1; t_{ex} = 1 h; S/L = 8.6 $g \cdot L^{-1}$; electrolyte composition: C_{HCl} = 1 $mol \cdot L^{-1}$, C_{NaCl} = 3 $mol \cdot L^{-1}$; T_{el} = 80 °C.

Figure 9 demonstrates results obtained for electrolyte with a total content of chloride ions $C_{Cl}{}^{-}$ = 6 $mol \cdot L^{-1}$.

It should be noted that the presence of NaCl in the electrolyte solution does not affect the leaching efficiency of Al, Sn, and Ti: the degree of metal leaching reaches 100% in the absence of electrical current. That is why the results for these metals are not shown in Figure 9.

Comparison of the results presented in Figures 9 and 10 demonstrates that the addition of NaCl into hydrochloric acid electrolyte has practically no effect on the efficiency of Fe leaching under studied range of current densities. At the same time, the leaching efficiency of Zn, Cu, and Ni increases: complete leaching of Zn was achieved at i = 0.42 A·cm^{-2} instead of R_{Zn} = 86.3% at i = 0.84 A·cm^{-2}; complete leaching of Cu was observed at a lower current density (i = 42 A·cm^{-2} instead of i = 0.84 A·cm^{-2}) and an increase in the degree of leaching of Ni at i = 0.84 A·cm^{-2} from 69.1% to 90.4% was achieved. The maximum leaching of Fe, Cu, and Zn into the NaCl-containing electrolyte was observed at i = 0.42 A·cm^{-2}. However, the presence of sodium chloride significantly decreases the efficiency of Pb leaching. An increase in current density leads only to a slight increase in the degree of Pb leaching. The maximum value of R_{Pb} reaches only 21.7% at i = 0.63 A·cm^{-2}. The transition of Ag and Au into the electrolyte solution with NaCl additive was not established.

A similar study, but with a higher content of sodium chloride (C_{NaCl} = 3 mol·L^{-1}) with a lower total content of chloride ions (C_{Cl^-} = 4 mol·L^{-1}) was carried out (Figure 10).

From the presented data, it can be seen that the active transition of copper into the electrolyte solution and the onset of silver leaching occurs at a higher current density (i = 0.63 A·cm^{-2}) compared to the hydrochloric acid electrolyte (Figure 8a). The degree of Pb and Sn leaching reaches 100% in the absence of current. That is why the content of these elements in the electrolyte solutions obtained as a result of electrochemical leaching was not determined.

3.2.3. Experiment Duration

Studies of the effect of experiment duration on the efficiency of metal leaching were carried out at a constant electrolyte temperature of 70 °C.

The results obtained show (Figure 11) that an increase in the duration of the experiment from 1 h to 3 h leads to an increase in the degree of all metal leaching, except for Sn (the metal is completely leached at the end of a one-hour experiment).

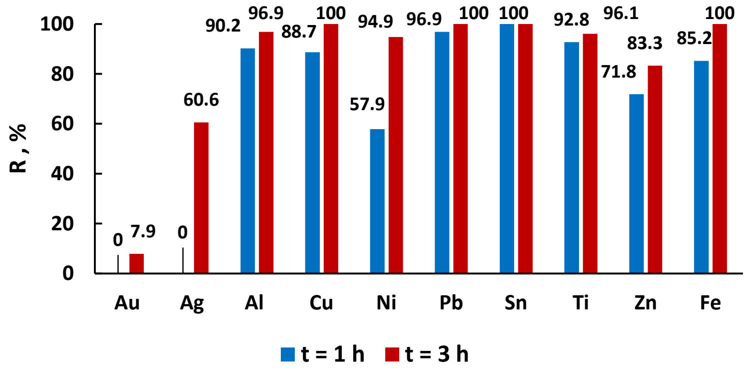


Figure 11. Impact of experiment duration on the degree of metal leaching. Experimental conditions: cell 2; raw material 1; S/L = 8.6 g·L^{-1}; i = 0.84 A·cm^{-2}; C_{HCl} = 6 mol·L^{-1}; T_{el} = 70 °C.

The kinetics of metal leaching from raw material 1 was also studied at a constant electrolyte temperature of 70 °C, both without power supply (Figure 12) and under conditions of alternating current superimposition (Figure 13).

The comparison of the results obtained shows (Figures 12 and 13) that current superimposition has practically no effect on the efficiency of Sn, Ti, Pb, and Zn leaching, but leads to an increase in the degree of leaching of such metals as Ni, Cu, and Ag. Under similar experimental conditions (t_{ex} = 3 h) in the absence of current, R_{Ag} = 14.4% and R_{Ni} = 73.0%, and in conditions of current superimposition, R_{Ag} = 69.6% and R_{Ni} = 95.4%. As a result of electrochemical leaching after 1.5 h of the experiment, R_{Cu} = 96.5%, and chemical leaching—R_{Cu} = 91.8% after 2 h of the experiment. In addition, under current superimposition, slow leaching of Au begins after 0.5 h of the experiment, and after 3 h, RAu achieves only 5.1%.

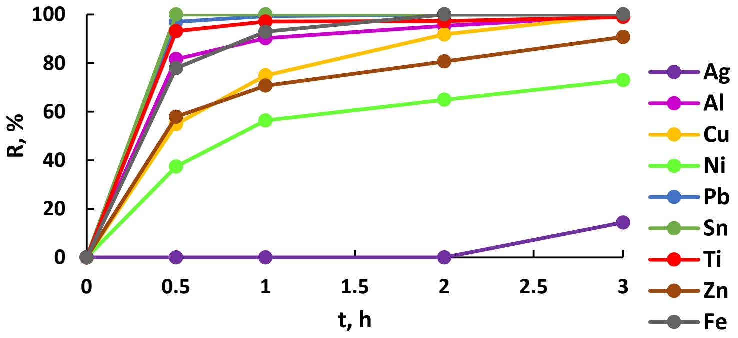


Figure 12. Impact of experiment duration on the degree of metal leaching. Experimental conditions: cell 2; raw material 1; S/L = 8.6 g·L^{-1}; i = 0; C_{HCl} = 6 mol·L^{-1}; T_{el} = 70 °C.

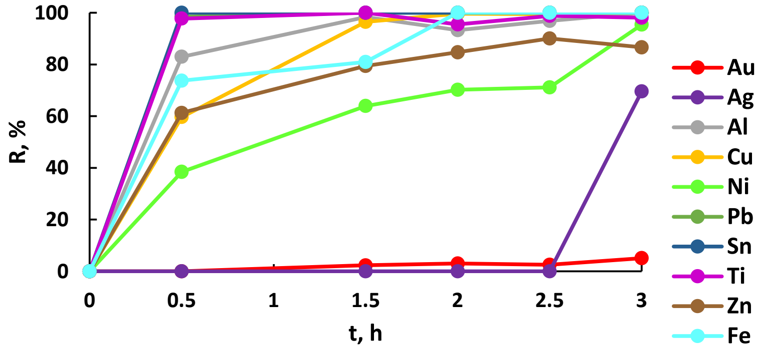


Figure 13. Impact of experiment duration on the degree of metal leaching. Experimental conditions: cell 2; raw material 1; S/L = 8.6 g·L^{-1}; i = 0.63 A·cm^{-2}; C_{HCl} = 6 mol·L^{-1}; T_{el} = 70 °C.

Thus, in the process of electrochemical hydrochlorination, high current density and concentration of chloride ions in the electrolyte solution, as well as elevated temperature, contribute to the high efficiency of the leaching of base metals. In addition, leaching time also affects the completeness of base metal leaching.

Unfortunately, a correct comparative analysis of the results presented above with the results of studies on the hydrochlorination leaching of base metals presented by other authors [33–36] is difficult. This is due to both the different metal content in the materials under study and the particle size of the crushed PCBs (from 0.15 mm to 5.0 mm), as well as the concentration of chloride ions in the leaching solution, its temperature, and experiment duration.

3.3. Impact of Chemical/Electrochemical Pretreatment on the Efficiency of Metal Leaching

Two methods were used for the pretreatment of the raw material, keeping experiment time at 1 h, based on the results (Figures 3(Ac) and 12), where Ag and Au leaching into solution was not determined.

- Electrochemical pretreatment—pretreatment 1. Experimental conditions: polypropylene cell, C_{HCl} = 6 M, i = 0.88 A·cm^{-2}, t_{ex}= 1 h, S/L = 8.6 g/L. The treatment was carried out without regulation of the electrolyte temperature (T_{el}) and during the process T_{el} increased from 20 °C to 68 °C;
- Chemical pretreatment—pretreatment 2. Experimental conditions: glass cell, C_{HCl} = 6 M, i = 0, t_{ex}= 1 h, S/L = 8.6 g/L. The pretreatment was carried out at a constant electrolyte temperature (T_{el} = 70 °C).

The results obtained show (Figure 14) that the use of electrochemical pretreatment of raw material 1 makes it possible to significantly intensify the process of gold leaching at an experiment duration of ≥1 h. It should be noted that, as a result of the use of chemical pretreatment (pretreatment 2), the leaching of gold under similar conditions of the electrochemical process was not observed.

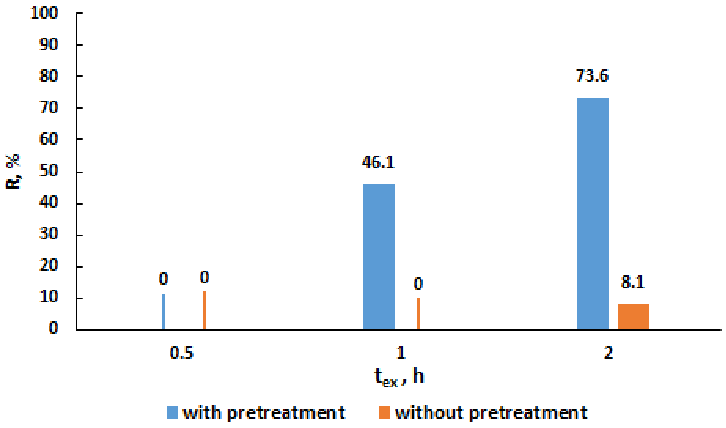


Figure 14. Impact of pretreatment 1 of raw material 1 on the efficiency of Au electrochemical leaching. Experimental conditions: cell 1, fresh portion of electrolyte (C_{HCl} = 6 M), i = 0.88 A·cm^{-2}.

Figure 15 demonstrates that electrochemical pretreatment significantly increases the degree of leaching of Ag in the process of electrochemical leaching. Silver leaching under similar conditions of the electrochemical process is less effective using chemical pretreatment of the raw material (pretreatment 2) in comparison with pretreatment 1. After 0.5 h of the experiment, the degree of Ag leaching was 1.6%, and after 1 h—62.6%. According to the results obtained (Figures 14 and 15), the leaching efficiencies of Au and Ag as a result of the electrochemical leaching process (t_{ex}= 2 h, i = 0.88 A·cm^{-2}) using pretreatment 1 of raw material 1 were 73.6% and 86.7%, respectively.

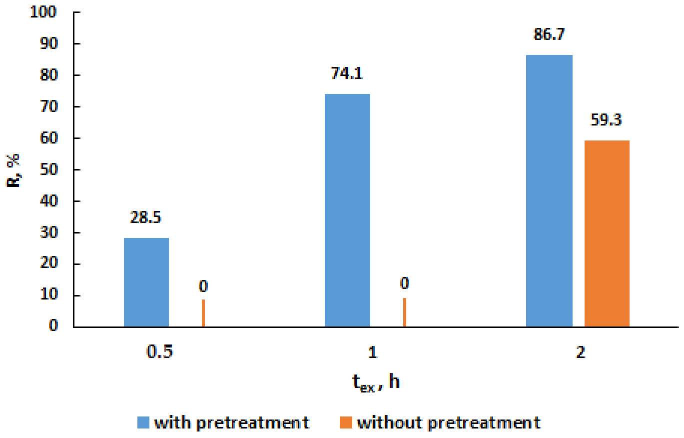


Figure 15. Impact of electrochemical pretreatment of raw material 1 on the efficiency of Ag electrochemical leaching. Experimental conditions: cell 1; pretreatment 1 of raw material 1; fresh portion of electrolyte (C_{HCl} = 6 M), i = 0.88 A·cm^{-2}.

The results of the study of the effect of pretreatment (chemical and electrochemical) on the efficiency of leaching of base metals and Fe are presented in Figure 16.

From the presented data, it is clear that pretreatment 2 resulted in more efficient leaching of almost all base metals compared to pretreatment 1, except for Cu. Copper was leached more effectively with pretreatment 1. It should be noted that, at the stage of both pretreatments of raw material 1, the leaching of noble metals was not observed, which makes it possible to avoid their losses at this stage.

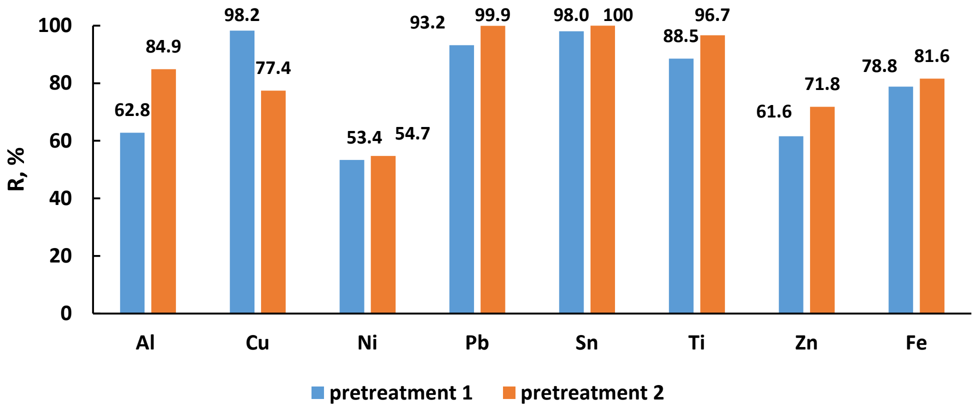


Figure 16. Impact of the pretreatment of raw material 1 on the degree of base metal leaching. Experimental conditions: cell 1, C_{HCl} = 6 M, t_{ex} = 1 h.

The concentration of the metals under study in the solutions obtained, both as result of electrochemical pretreatment (stage 1) and the subsequent electrochemical leaching (stage 2), are presented in Table 2. Additionally, the table presents the estimated quantities (Equation (2)) of each metal in the solid residue after the completion of each stage of the process. Moreover, the results obtained for solid residue after stage 2 are less accurate compared to stage 1, due to incomplete removal of the electrolyte solution after pretreatment (stage 1).

Table 2. Concentration of metals in the electrolyte solution and residual amounts of metals in the solid residue after electrochemical leaching.

Me	Leaching				
	Chemical	Electrochemical			
		Stage 1		Stage 2	
	Metal Concentration in Leach Solution, C_{Me}, mg/L	Metal Concentration in Electrolyte Solution, C_{Me}, mg/L	Metal Content in Solid Residue, m_{Me}, mg	Metal Concentration in Electrolyte Solution, C_{Me}, mg/L	Metal Content in Solid Residue, m_{Me}, mg
Au	4.320	0	1.512	3.18	~0.4
Ag	14.86	0	5.202	12.89	~0.7
Pd	BDL [1]	BDL [1]	-	BDL [1]	-
Al	149.2	96.25	18.52	27.74	~8.8
Cu	121.4	115.1	2.189	6.300	0
Ni	94.34	43.61	17.75	38.96	~4.1
Pb	91.34	85.29	2.117	5.020	~0.4
Sn	242.1	231.3	3.765	3.940	~2.4
Ti	132.4	116.7	5.481	9.150	~2.3
Zn	45.60	27.93	6.189	2.000	~5.5
Fe	2861	2024	293.0	837.0	0

[1] BDL—below the detectable limit.

For comparison, Table 3 presents the same characteristics of the electrochemical leaching process, obtained under similar experimental conditions, but without the pretreatment stage of the raw material. Data for a 6 h experiment are also provided.

The presented data (Tables 2 and 3, Figures 14 and 15) show that the usage of an electrochemical pretreatment stage for raw material 1 makes it possible not only to significantly increase the efficiency of Au and Ag leaching, but also to reduce the content of base metals in the final electrolyte solution. Thus, a gold concentration in the final electrolyte solution in a two-stage electrochemical process (with pretreatment) is almost an order of magnitude higher than in a one-stage process (without pretreatment). In the case of silver, this effect is less pronounced. At the same time, the content of base metals in the solution is significantly lower in comparison with the one-stage experiment.

Table 3. Concentration of metals in the electrolyte solution and residual amounts of metals in the solid residue after electrochemical leaching at different experiment duration.

Me	Leaching				
	Chemical	Electrochemical			
		Experiment Duration			
		t_{ex} = 2 h		t_{ex} = 6 h	
	Metal Concentration in Leach Solution, C_{Me}, mg/L	Metal Concentration in Electrolyte Solution, C_{Me}, mg/L	Metal Content in Solid Residue, m_{Me}, mg	Metal Concentration in Electrolyte Solution, C_{Me}, mg/L	Metal Content in Solid Residue, m_{Me}, mg
Au	4.320	0.350	1.389	3.35	0.339
Ag	14.86	8.820	0	14.87	0
Pd	BDL [1]	BDL [1]	-	BDL [1]	-
Al	149.2	141.7	2.611	149.3	0
Cu	121.4	121.5	0	121.5	0
Ni	94.34	86.85	2.620	94.34	0
Pb	91.34	91.36	0	91.35	0
Sn	242.1	242.3	0	242.2	0
Ti	132.4	126.8	1.946	132.5	0
Zn	45.60	32.29	4.654	43.17	0.850
Fe	2861	2861	0	2862	0

[1] BDL—below the detectable limit.

Increasing the duration of a one-stage experiment leads to an increase in the concentration of all metals, except for those metals whose concentration reaches maximum values within 2 h of the electrochemical process (Cu, Pb, Sn, and Fe). As a result of a 6 h experiment, complete leaching of all metals under study is achieved, except for Au and Zn (Table 3). At the same time, the concentration of Au and Ag in the electrolyte solution is only slightly higher than under the conditions of a 2 h two-stage experiment (Tables 2 and 3).

Thus, for raw material 1, pretreatment 1 is recommended, both to increase the degree of leaching of gold and silver, and to reduce the content of base metals in the final electrolyte solution. But to increase the completeness of leaching of noble metals from the raw material, an increase in the duration of the experiment is required.

The S. Ilyas et al. [37] also carried out preliminary leaching of base metals followed by hydrochlorination of the dry PCBs residue. Under the experimental conditions (hydrochlorination in a leaching reactor with an external supply of chlorine), the degree of gold leaching was more than 99% within 75 min of the experiment. It should be noted that solder removed PCBs with a lower gold content (286 ppm) was used in this study. However, after the finishing of the leaching process using this technique, subsequent neutralization of the excess chlorine is required.

3.4. Electrolyte Reuse in Metal Leaching

The possibility of electrolyte reuse in the process of electrochemical leaching of metals without temperature control of the electrolyte was studied (Figure 17).

The results of the study showed that the electrolyte reuse leads to the complete leaching of Al, Cu, Pb, Sn, and Ti and a slight increase in the efficiency of Zn, Ni, and Fe leaching from a fresh portion of raw material 1. At the same time, a decrease in the electrochemical leaching efficiency of Ag and Au was observed.

The results of electrolyte reuse in the process of chemical leaching (without current superimposition) showed (Figure 18) that a decrease in the efficiency of leaching of all metals, except for Sn, was observed. Moreover, this effect is manifested most significantly in the case of Ag, Au, Al, Cu, and Ni. Thus, the results obtained showed that the electrolyte, after electrochemical leaching, can be reused for metal leaching for a fresh portion of the raw material. Moreover, base metals are leached more efficiently when the electrolyte is reused in an electrochemical leaching process compared to a chemical leaching process. A decrease in the leaching efficiency of Au and Ag was observed in both leaching processes.

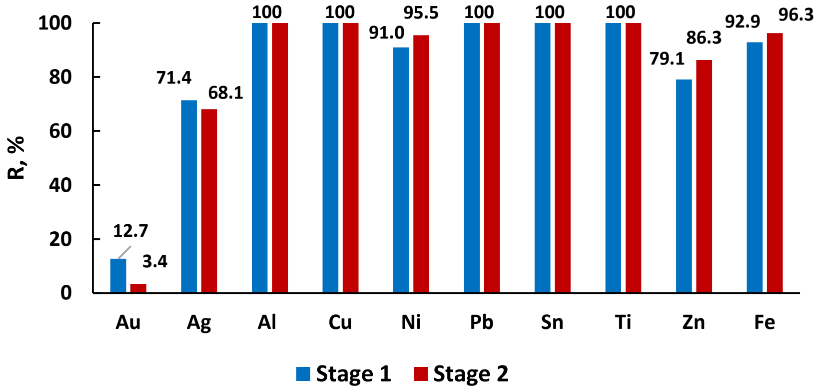


Figure 17. The efficiency of metal leaching under the conditions of a two-stage experiment. Experimental conditions: polypropylene cell, loading option 1; raw material 1; t_{ex} = 3 h. Stage 1—S/L = 8.6 g·L^{-1}; C_{HCl} = 6 mol·L^{-1}, i = 0.88 A·cm^{-2}; stage 2—fresh portion of raw material 1, filtered electrolyte after stage 1, S/L = 9.4 g·L^{-1}, i = 1.0 A·cm^{-2}.

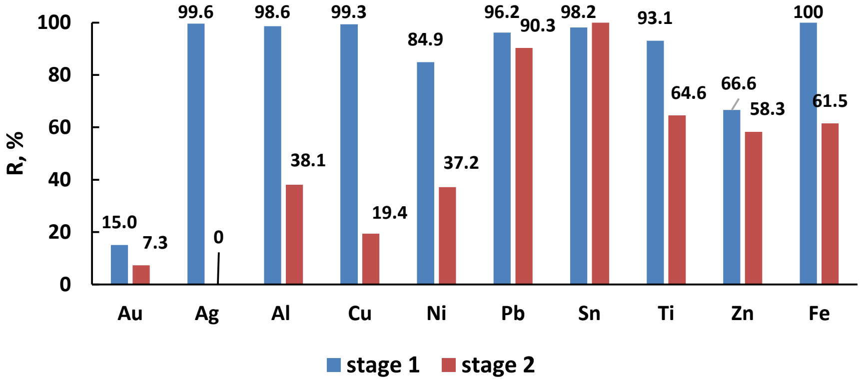


Figure 18. The efficiency of metal leaching under the conditions of a two-stage experiment. Experimental conditions: polypropylene cell, loading option 1; raw material 1. Stage 1—S/L = 8.6 g·L^{-1}; C_{HCl} = 6 mol·L^{-1}, i = 0.88 A·cm^{-2}; t_{ex} = 3 h; stage 2—fresh portion of raw material 1, filtered electrolyte after stage 1, S/L = 9.0 g·L^{-1}, i = 0; t_{ex} = 20 h without stirring of the reaction mixture.

3.5. Quantitative Determination of Metals in Solid Residue

Residual amounts of metals in the solid residue after electrochemical leaching were assessed via the results of ICP-OES analysis of both the solution obtained as a result of chemical treatment of the solid residue (leach solution) and of the resulting electrolyte solution. Figure 19 shows the results on the leaching efficiency of Au, Ni, and Zn from raw material 1. The choice of these metals is due to the fact that all other metals under study are almost completely leached at this stage of electrochemical leaching.

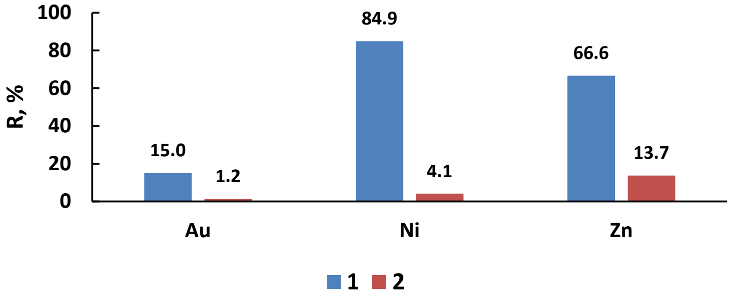


Figure 19. The degree of metal leaching: 1—electrochemical leaching of raw material 1 (experimental conditions: polypropylene cell, loading option 1, C_{HCl} = 6 M, i = 0.88 A·cm^{-2}, t_{ex} = 3 h, S/L = 8.6 g·L^{-1}); 2—chemical leaching of the solid residue produced from the electrochemical process.

From the presented data (Figure 19), it is clear that the total degree of Ni, Zn, and Au leaching from the raw material does not reach 100%. Moreover, in the case of gold, R_{Au} is only 16.2%. This is probably due to the loss of fine particles from these metals, especially Au, at the stages of preparation of the solid residue (washing of the filter, removal from the filter after drying, grinding in a mortar). Thus, to evaluate the effectiveness of the leaching process and the residual amounts of metals in the solid residue, it is recommended to use ICP-OES for quantitative determination of metals directly in the electrolyte solution, but not in the solution obtained as a result of the chemical leaching of solid residue.

3.6. Study of Metal Leaching Process Reproducibility

To assess the reproducibility of the results of the leaching of metals from the raw material into an electrolyte solution, six series of experiments were carried out under the same experimental conditions in each series. The experimental conditions for each series are presented in Table 4.

Table 4. Experimental conditions in all series: cell 1; S/L = 8.6 g/L; C_{HCl} = 6 M; i = 0.88 A·cm^{-2}.

Exp. Series №	**Experimental Conditions**		
	Number of Exp.	**Raw Material**	**Exp. Duration, t_{ex}, h**
1	3	1	1
2	4	1	3
3	3	1	5
4	3	2	1
5	3	2	2
6	3	2	5

Raw material 1 and raw material 2 were used as research objects. The results of the ICP-OES analysis of the obtained electrolyte solutions and the values of the root mean square deviation (RMSD, $S_{\overline{x}}$) of the results obtained for each metal in the experimental series are presented in Table 5.

Table 5. The average amount of each metal leached into the electrolyte solution under the conditions of the experimental series.

Me	**Average Metal Content in Electrolyte Solution, $\overline{m}_{Me}$, mg**					
	Exp. Series 1	**Exp. Series 2**	**Exp. Series 3**	**Exp. Series 4**	**Exp. Series 5**	**Exp. Series 6**
Au	0	0.209 ± 0.020	0.801 ± 0.075	0	0.554 ± 0.340	2.022 ± 0.050
Ag	0	3.986 ± 0.401	3.814 ± 0.220	1.668 ± 0.274	2.949 ± 0.166	3.306 ± 0.280
Al	32.771 ± 0.610	52.602 ± 0.605	51.280 ± 0.780	72.042 ± 0.765	89.460 ± 3.040	86.310 ± 0.423
Cu	41.720 ± 0.720	42.893 ± 0.614	46.120 ± 0.270	46.877 ± 0.260	45.768 ± 1.288	40.413 ± 0.244
Ni	17.617 ± 1.360	29.159 ± 0.419	31.960 ± 0.400	12.025 ± 0.721	13.012 ± 0.454	11.516 ± 0.146
Pb	29.808 ± 0.190	31.608 ± 0.343	33.130 ± 0.400	23.211 ± 0.140	22.502 ± 0.845	19.109 ± 0.209
Sn	83.055 ± 1.260	84.626 ± 0.825	88.840 ± 1.180	76.988 ± 0.375	73.780 ± 3.261	61.577 ± 0.427
Ti	41.008 ± 0.120	45.855 ± 0.931	46.630 ± 0.470	10.935 ± 0.051	11.202 ± 0.339	10.414 ± 0.017
Zn	9.828 ± 0.150	11.544 ± 0.436	12.720 ± 0.031	9.093 ± 0.111	8.940 ± 0.260	8.222 ± 0.177
Fe	788.900 ± 45.130	960.15 ± 17.934	1150.70 ± 27.16	297.700 ± 16.145	375.900 ± 20.127	356.533 ± 1.345

Analysis of the data presented in Table 5 shows that the most reproducible results (standard deviation ≤ 5%) were obtained for Cu in all experimental series. The reproducibility of the results for Au and Ag is significantly worse (red font in Table 5). The most reliable results for Au were obtained in experimental series No. 2, No. 3, and No. 6, and for Ag in series No. 3 and No. 5. In the case of such active metals as Pb, Sn, Ti, and Zn, the most reliable results were obtained in all series of experiments, as well as for iron, except for series No. 1. In the case of Ni, the least reliable results were obtained in series No. 1 and No. 4 (red font in Table 5). Based on the presented data, it is clear that the best reproducibility of results for all metals was obtained in experimental series No. 3. In addition, in experimental series No. 2 and 6, a high reproducibility was also obtained for all metals, except for Ag, and in series No. 5, for all metals except for Au. It should be noted that in these experimental series, different raw materials were used (raw material 1 and raw material 2).

Thus, the reproducibility of the results of electrochemical hydrochlorination of disintegrator-crushed PCB powders with a particle size < 90 μm generally depends on four factors: (i) on the non-metallic part (solid residue Table 1); (ii) the studied metal content; (iii) on the homogeneity of the raw material sample under study, and (iv) on the accuracy of the analytical determination of elements (especially of Ag) in the electrolyte solutions using ICP-OES.

4. Conclusions

The results obtained show that at T_{el} = 80 °C, i = 0.84 $A{\cdot}cm^{-2}$, S/L = 8.6 $g{\cdot}L^{-1}$ and an experiment duration of 1 h, an increase in hydrochloric acid concentration from 4 $mol{\cdot}L^{-1}$ to 8 $mol{\cdot}L^{-1}$ leads to a significant increase in the degree of Ni, Zn, and Ag leaching from single-crushed mixed PCBs. At the same time, the complete leaching of Cu was achieved at C_{HCl} = 6 $mol{\cdot}L^{-1}$.

An increase in electrolyte (C_{HCl} = 6 M) temperature from 60 °C to 80 °C, at an experiment duration of 1 h in the absence of current, leads to an increase in the degree of leaching of almost all base metals and Fe. At i = 0.63 $A{\cdot}cm^{-2}$, an increase in the electrolyte temperature leads to an increase in the degree of Ni, Zn, Fe, and Al leaching but practically does not affect the degree of Cu, Ti, Pb, and Sn leaching. In turn, an increase in AC density from 0.21 $A{\cdot}cm^{-2}$ to 0.84 $A{\cdot}cm^{-2}$ has the most significant effect on the efficiency of leaching of all base metals at an electrolyte temperature of 80 °C. However, under the conditions of all experiments carried out at constant electrolyte temperatures and with a duration of 1 h, the transition of Au into the electrolyte solution was not established.

Comparison of the results on the kinetics of metal leaching into electrolyte solution with T_{el} = 70 °C in the absence AC and under AC superimposition (i = 0.63 $A{\cdot}cm^{-2}$) showed that the current superimposition has practically no effect on the efficiency of Sn, Ti, Pb, and Zn leaching, but leads to an increase in the degree of leaching of such metals as Ni, Cu, and Ag. With an experiment duration of 3 h in the absence of current R_{Ag} = 14.4% and R_{Ni} = 73.0%, and under conditions of current superimposition R_{Ag} = 69.6% and R_{Ni} = 95.4%. As a result of electrochemical leaching after 1.5 h of experiment, R_{Cu} = 96.5%, and for chemical leaching—R_{Cu} = 91.8% after 2 h of experiment. In addition, under current superimposition, slow leaching of Au begins at ~0.5 h from the beginning of the experiment and, after 3 h, R_{Au} achieves only 5.1%.

Comparative study of the metal leaching kinetics from raw material powders under the same experimental conditions (C_{HCl} = 6 mol L^{-1}, i = 0.88 $A{\cdot}cm^{-2}$, S/L = 8.6 $g{\cdot}L^{-1}$, without electrolyte temperature control) showed that after 2 h of the electrochemical process, Cu was leached completely (R_{Cu} = 100%) from single-crushed PCBs. Complete leaching of Ag was observed with experiment durations of 3 h and 2 h from the single-crushed PCBs and the double-crushed PCBs, respectively. Au was completely leached from the double-crushed PCBs at t_{ex} = 5 h, and from the single-crushed PCBs the maximum degree of metal leaching was 77.5% at t_{ex} = 6 h.

It was found that, as the result of a two-stage experiment (one-hour pretreatment at i = 0.88 $A{\cdot}cm^{-2}$ and a subsequent two-hour electrochemical process), the degree of Au and Ag leaching from single-crushed PCBs was 73.6% and 86.7%, respectively. As a result, an electrolyte solution of the following composition ($mg{\cdot}L^{-1}$): Au—3.18; Ag—12.89; Al—27.74; Cu—9.58; Ni—38.96; Pb—5.02; Sn—3.94; Ti—9.15; Zn—2.00; Fe—977.1 was obtained. In the absence of pretreatment of this raw material under similar experimental conditions, the degree of leaching of Au and Ag was 8.1% and 59.3%, respectively. As a result of this process, an electrolyte solution of composition ($mg{\cdot}L^{-1}$): Au—0.35; Ag—

8.82; Al—141.7; Cu—126.1; Ni—86.85; Pb—94.25; Sn—257.0; Ti—126.8; Zn—32.29; Fe—3251.0 was obtained.

Thus, the use of a one-hour electrochemical pretreatment in a two-stage experiment makes it possible to increase the content of gold and silver and significantly reduce the content of background (base) metals in the final electrolyte solution. This in turn will simplify the scheme for the further extraction of noble metals.

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