

## Article

# Study of Metal Leaching from Printed Circuit Boards by Improved Electrochemical Hydrochlorination Technique Using Alternating Current

Vera Serga <sup>1</sup>, Aleksey Zarkov <sup>2,3</sup>, Andrei Shishkin <sup>4,5,\*</sup>, Edgars Elsts <sup>2</sup>, Maksims Melnichuks <sup>1</sup>, Mikhail Maiorov <sup>6</sup>, Ervins Blumbergs <sup>4,6,7</sup> and Vladimir Pankratov <sup>2</sup>

- <sup>1</sup> 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
- <sup>2</sup> Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street., LV-1063 Riga, Latvia
- <sup>3</sup> Institute of Chemistry, Vilnius University, 24 Naugarduko Street, LT-03225 Vilnius, Lithuania
- <sup>4</sup> ZTF Aerkom SIA, 32 Miera Street., Salaspils nov., LV-2169 Salaspils, Latvia
- <sup>5</sup> Rudolfs Cimdinis 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
- <sup>6</sup> Institute of Physics, University of Latvia, 32 Miera Street, LV-2169 Salaspils, Latvia
- <sup>7</sup> Faculty of Civil Engineering, Riga Technical University, 21/1 Azenes Street, LV-1048 Riga, Latvia
- \* Correspondence: andrejs.siskins@rtu.lv

**Abstract:** This paper presents the results of the leaching of metals from computer PCBs by electrochemical hydrochlorination using alternating current (AC) with an industrial frequency (50 Hz). Leaching was carried out with a disintegrator-crushed computer motherboard with a particle size ( $d$ ) of  $<90 \mu\text{m}$ . In the course of the research, the leaching efficiency of metals including Fe, Sn, Mn, Al, Cu, Zn, Pb, Ni, Ti, Sb, Cr, Co and V was evaluated depending on process parameters, such as AC density, experiment duration, hydrochloric acid concentration in the electrolyte solution, solid/liquid ratio, electrolyte temperature, and the loading option of raw material (loading option 1 involving loading into the electrolyte solution, and loading option 2 involving loading into the filter containers attached to electrodes). The research results showed that AC superimposition significantly intensifies the leaching of metals. It was established that the complete leaching of metals including Al, Mn, Sn, Ti and Zn, under experimental conditions (loading option 2,  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ,  $i = 0.80 \text{ A}\cdot\text{cm}^{-2}$ ,  $S/L = 8.6 \text{ g}\cdot\text{L}^{-1}$ ), is reached after 1.5 h, and that of Cu and Ni is reached after 2 h from the beginning of the experiment. At the same time, the degree of leaching of other metals after 2 h is Co-78.8%, Cr-84.4%, Sb-91.7%, Fe-98.9%, V-98.1% and Pb-5.1%. The paper also reports the results on the leaching of all abovementioned metals, as well as Ag and Pd, with disintegrator-crushed mixed computer PCBs with  $d < 90 \mu\text{m}$  and loading option 1.



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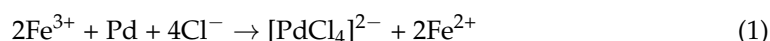
## 1. Introduction

Currently, active scientific research on the recycling of waste PCBs is ongoing within the framework of hydrometallurgical technologies. Moreover, a significant part of these studies is related to extracting the most valuable components of PCBs—noble metals (mainly gold) and copper [1–6].

Leaching with cyanide solutions is the main method of the hydrometallurgical recycling of noble metal ores [7]. However, the exceptional toxicity of cyanides has led to the long-term search for alternative leaching agents that can be used to recover gold from both different ores [8,9] and secondary raw materials, i.e., e-waste [10–12]. Thiosulfate, thiourea

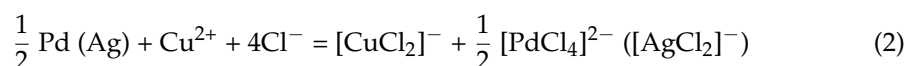
and various halides, including chlorine/chloride leach systems, are considered the most promising replacement for cyanide [13].

Halide leaching is used to leach platinum metals from such secondary raw materials as spent automotive catalysts. Chloride leaching of palladium from spent catalysts has been studied using various oxidants ( $\text{Fe}^{3+}$  or  $\text{Cu}^{2+}$  ions) [14,15]. The research results showed [14] that in the absence of oxidant at 60 °C and with an experiment duration of 120 min, the degree of Pd leaching ( $R_{\text{Pd}}$ ) increases from 18.0% to 41.2% with an increase in HCl concentration from 2.0 mol·L<sup>-1</sup> to 6.0 mol·L<sup>-1</sup>. The results also showed that, using a chloride solution with the composition 2.0 mol·L<sup>-1</sup> HCl, 4.0 mol·L<sup>-1</sup> NaCl and 0.67 mol·L<sup>-1</sup>  $\text{Fe}^{3+}$  at 80 °C for 90 min,  $R_{\text{Pd}}$  reached 99.5%. Pd leaching using  $\text{Fe}^{3+}$  as an oxidant is represented as a reaction:



A significant increase in the rate of dissolution of palladium from spent catalysts in a 2 mol·L<sup>-1</sup> HCl solution was also observed in the presence of  $\text{Cu}^{2+}$  ions [15].

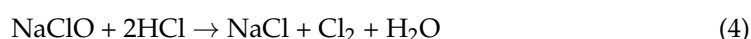
A process for cuprous chloride synthesis and the simultaneous leaching of Ag and Pd from PCBs was developed [16]. In the chloride system, cupric ions also played the role of an oxidant. Metal leaching efficiency was 93.9%, 95.3% and 98.5% for Ag, Pd and Cu, respectively, in the two stages of the process. The dissolution of Ag and Pd is presented by the authors as the following reaction:



A combination of sodium chloride and calcium hypochlorite as the lixiviant was proposed for silver leaching from a magnetic fraction of PCBs [17]. Under experimental conditions, the degree of silver leaching was about 95%. The dissolution of silver is represented by the equation:



Authors [18] have also studied the dissolution of metallic copper with molecular chlorine, generated in situ as a result of the chemical reaction between sodium hypochlorite and hydrochloric acid:



The presented results showed that the rate of metal dissolution is mainly determined by the concentration of chlorine.

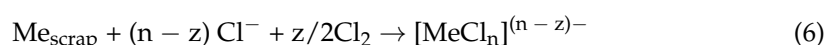
Chlorine, bromine and iodine are well-known lixiviants for leaching gold [19,20]. The solubility of chlorine increased in relatively concentrated HCl solutions due to the formation of tri-chloride ions as follows [21]:



Moreover, in a solution of hydrochloric acid at pH < 2, the dominant species of chlorine are  $\text{Cl}_{2(\text{aq})}$  and  $\text{Cl}_3^-$ , but at pH > 2, HClO is the dominant species. The distribution of chlorine species in a solution depends on HCl concentration and temperature [22].

To avoid the release of chlorine into the atmosphere during the hydrochlorination of both ore and secondary raw materials, it is preferable to perform a process with low consumption of chlorine to increase the environmental friendliness of the process. Therefore, in connection with the possibility of the complex recycling of raw materials with a low content of valuable components, new directions in hydrochlorination have been outlined in recent years. A separate leaching reactor connected to the anode chamber of a chlorine gas generator was used when studying the leaching process of both copper plates [23] and

the non-magnetic fraction of PCBs [24]. The degree of metal leaching from PCBs into a  $2 \text{ mol}\cdot\text{L}^{-1}$  HCl solution at the temperature of  $50 \text{ }^\circ\text{C}$  in 4 h was 98, 96, 96 and 71% for Zn, Sn, Pb and Cu, respectively. Gold leaching from mobile phone PCBs was also investigated in a separate leaching reactor [25]. The results showed that copper and gold could be separated in two leaching stages by adjusting the solution's acidity and chlorine concentration. In the 1st stage of leaching in a  $2 \text{ mol}\cdot\text{L}^{-1}$  HCl solution, the degree of copper leaching was 97%, while the gold leaching was below 5%. High leaching of gold (93%) was obtained along with residual copper ( $770 \text{ mg}\cdot\text{L}^{-1}$ ) in the second stage of leaching with a diluted acid solution ( $0.1 \text{ mol}\cdot\text{L}^{-1}$  HCl). The metal leaching process from scrap PCBs with chlorine in the hydrochloric acid medium in a leaching reactor coupled to an electrochemical reactor was also studied in [26]. As a result, a multi-component solution containing nearly all of the available metals in the scrap was obtained. The reaction of metals dissolution in this process is described in general form:



Here, the composition of chloride complexes of metals varies depending on the concentration of chloride ions in the solution [27]. In a recent study [28], electro-generated chlorine produced in a separate electrochemical cell was also used as an oxidising agent to leach Cu, Sn, Pb, Zn and Al from PCBs into an HCl solution ( $3 \text{ mol}\cdot\text{L}^{-1}$ ). To increase the efficiency of chlorine utilisation, it is proposed to use a series of sequentially connected leaching cells. As a result, in 100 min of the experiment, the maximum degree of Cu leaching, 87.22%, was achieved, while the degree of Zn, Sn, Al and Pb leaching was more than 90%.

The hydrochlorination method was used for gold leaching from the solder-removed PCBs fraction with a particle size 4–5 mm pretreated in  $4.0 \text{ mol}\cdot\text{L}^{-1}$  of an HCl solution with the addition of 5 vol%  $\text{H}_2\text{O}_2$  [29]. Chlorine, as in the studies mentioned above [23–26,28], was produced by the electrolysis of an HCl solution in a separate electrochemical cell. The research results showed that in  $2.0 \text{ mol}\cdot\text{L}^{-1}$  of NaCl solution ( $\text{pH} = 1.0$ ) at a chlorine supply rate of  $0.62 \text{ mmol}\cdot\text{min}^{-1}$ , a solution temperature of  $50 \text{ }^\circ\text{C}$  and an experiment duration of 75 min, more than 99% of Au was leached into the solution. Under these experimental conditions, the leaching degree of copper and nickel was 71.6% and 59.6%, respectively.

The authors of [30] proposed a scheme for leaching critical and valuable metals from scrap mobile electronics. This scheme consisted of two stages: the first stage was the dissolution of Cu, Sn, Ag and magnetic materials, using  $\text{Fe}^{3+}$  formed in an acid sulfate solution; the second stage was the dissolution of Pd and Au, using  $\text{Cl}_2$  electro-generated in an HCl solution in a separate electrochemical cell.

When a direct electric current (DC) is passed through an electrochemical system with hydrochloric acid electrolyte, metal ionisation occurs at the anode: the anode material is electrically dissolved, chlorine and oxygen are released, and hydrogen is released at the cathode [31]. Feasible reactions of the metal oxidation process on alternating current (AC) differ from DC processes in that the electrodes change their polarity with a given frequency (50 Hz). Both oxidation and reduction processes take place on the same electrode. 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. In addition, the use of AC makes it possible to eliminate the diffusion limitations that arise during electrolysis [32,33].

A study of the electrochemical behavior of Pt in hydrochloric acid solutions under AC polarisation conditions, using titanium as an auxiliary electrode, showed [34] that a significant increase in the current efficiency of platinum dissolution is observed in HCl concentrations ranging from  $5 \text{ mol}\cdot\text{L}^{-1}$  to  $7 \text{ mol}\cdot\text{L}^{-1}$ . When using two iron electrodes in the anode half-cycle of the AC, active dissolution of the electrode material is observed with the formation of  $\text{Fe}^{2+}$  ions in a solution of hydrochloric acid electrolyte; in the cathode half-cycle, the hydrogen ion reduction reaction occurs on the electrode. The process is characterised by a high iron dissolution rate of  $88 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  at  $C_{\text{HCl}} = 80 \text{ g}\cdot\text{L}^{-1}$  [35]. The stability of pairs of graphite–graphite electrodes during AC polarisation makes it possible

to carry out processes at high currents and potentials on electrodes that cannot be used with DC [32].

In a previous work [36], the possibility of producing an oxidising agent—chlorine and leaching metals (with the examples of Au and Cu) from PCBs powders in one electrochemical cell by passing an AC of industrial frequency (50 Hz)—was demonstrated for the first time. The main advantages of the proposed scheme for leaching metals from PCBs are simplicity (the absence of any thermal or chemical pretreatment) and minimal environmental risk: chlorine is produced and consumed directly in the process (in situ), meaning there is no need for its production, transportation and storage. In this scheme, disintegrator-crushed PCBs powders with a non-conductive matrix content ~50 wt% were loaded into electrolyte and a suspension was created using a stirrer (loading option 1). With this loading option of raw materials, the oxidation of metals occurred in the volume of the hydrochloric acid electrolyte by, predominantly, forms of dissolved chlorine such as  $\text{Cl}_{2(\text{aq})}$  and  $\text{Cl}_3^-$ .

In this paper, to implement the process of electrochemical hydrochlorination, another loading option of raw material powders is proposed: a metal-rich fraction of PCBs (the content of non-conductive matrix ~5 wt%) is loaded into filter containers attached to the electrodes (loading option 2). With this loading option, the metal particles present in the PCB powder are in contact with the graphite electrodes. Therefore, in the anodic half-cycles of AC, both the electrooxidation (electrodissolution) and the electrochlorination of metals during the oxidation of chloride ions on their surface will occur. In this case, the efficiency of metal oxidation will not depend on the concentration of free chlorine in the volume of electrolyte, which is not the case with loading option 1. This technique (loading option 2) could increase the completeness of the leaching of both base and noble metals from PCB powders.

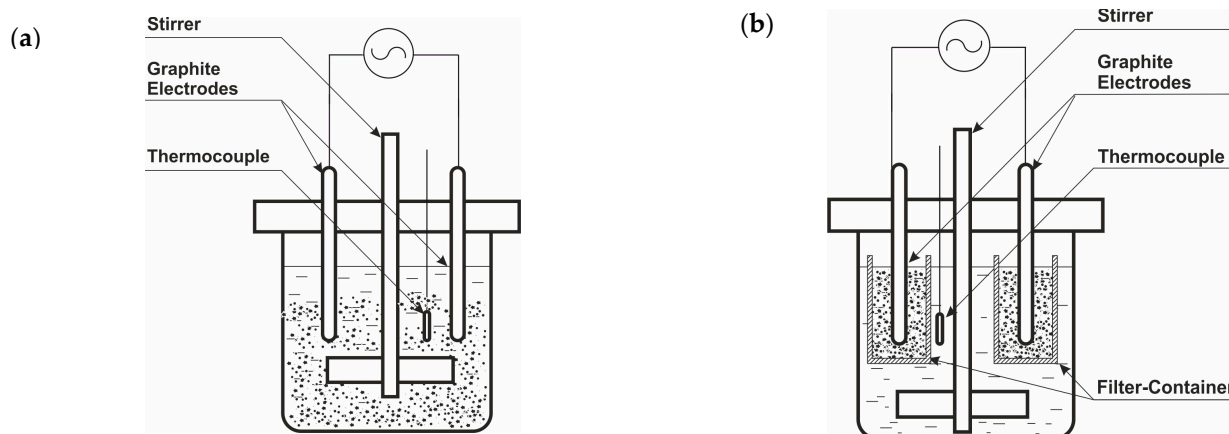
The results of studies on the influence of process parameters, such as the AC density, experiment duration, concentration of hydrochloric acid in an electrolyte solution, and solid/liquid ratio, on the leaching efficiency of metals, including Al, Co, Cr, Cu, Mn, Ni, Sb, Sn, Ti, Zn, Fe, Pb and V, are presented. For comparison, for these metals, and additionally for Pd and Ag, the results of leaching under the experimental conditions described in our previous paper [36] are also presented.

## 2. Materials and Methods

Computer motherboards and, for comparison, mixed computer PCBs were used as the source materials. Preliminary preparation of raw materials included dismantling the PCBs, double crushing in a hammer mill (for computer motherboards) and single crushing (for mixed computer PCBs) using the high-energy semi-industrial disintegration-milling system (disintegrator DSL-350, Tallinn University of Technology, Tallinn, Estonia) and subsequent sieving using FRITTSCH ANALYSETTE 3 PRO Vibratory Sieve Shaker (FRITTSCH GmbH, Weimar, Germany). A detailed description of the new method of disintegration-crushing of PCBs is given in [37]. For research, powders of the finest fraction of raw material powders of disintegrator-crushed computer motherboards (raw material 1) and mixed computer PCBs (raw material 2) with a particle size ( $d$ ) of  $<90 \mu\text{m}$  were used.

Experimental setup and experimental technique for electrochemical hydrochlorination of PCBs powders using AC of industrial frequency (50 Hz) are presented in previous work [36]. Within the framework of the proposed experimental technique, the raw material powder under study was loaded into the electrolyte solution (loading option 1) (Figure 1a). Another loading option was also used in this study: the raw material powder was loaded into filter containers attached to graphite electrodes (loading option 2) (Figure 1b). The containers were made of polyethylene terephthalate (PET) cloth (average mesh size  $135 \times 65 \mu\text{m}$ ). This material has good chemical resistance and sufficient mechanical strength. Equal weights of the raw material were loaded into the containers. The experiments used two types of electrochemical cells: a square-shaped diaphragmless polypropylene cell (cell 1) and a water-jacketed glass cell (cell 2). An AC with a density ( $i$ )

of 0.40, 0.72 and 0.80 A·cm<sup>-2</sup> (raw material 1 powder, loading option 2) and 0.88 A·cm<sup>-2</sup> (raw material 2 powder, loading option 1) on the visible surface of graphite electrodes were used. The duration of the experiments was from 0.5 to 5 h.



**Figure 1.** Schematic representation of an electrochemical cell with different loading options of the raw material: (a) loading option 1; (b) loading option 2.

During the process, the electrolyte temperature ( $T_{el}$ ) was controlled using a thermocouple (chromel–alumel). Solutions of hydrochloric acid in distilled water with concentrations of 4, 6 and 8 mol·L<sup>-1</sup> were used as electrolytes. The ratio of solid (PCB powder) and liquid (electrolyte) phases (S/L) in the experiments was 5.7, 8.6, 11.4 and 14 g·L<sup>-1</sup>.

The chemical treatment of a representative sample was carried out to establish the metal content in raw material powders. In preparing a representative sample, the rolling method was used to mix the powders, and the quartering method was used to reduce the sample. Chemical leaching of the sample included sequentially boiling 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<sub>3</sub> excess was removed by adding several portions of concentrated HCl. The resulting wet residue was transferred to the filter with a 3 mol·L<sup>-1</sup> HCl solution and washed accurately. Filtrate was diluted to a volume of 50 mL with 3 mol·L<sup>-1</sup> HCl solution.

The quantitative determination of metals in solutions resulting from the chemical and electrochemical leaching of raw materials was carried out by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 7000 DV ICP-OES, Perkin Elmer Inc., Waltham, MA, USA).

Solid residues of PCBs after both chemical and electrochemical leaching were washed on a filter with distilled water until the pH of the filtrate was ~5–6, dried at 105 °C for an hour, weighed and ground in an agate mortar. X-ray diffraction (XRD, diffractometer Rigaku—MiniFlex 600 with CuK $\alpha$  radiation with  $\lambda = 0.15418$  nm, Rigaku Corp., Tokyo, Japan) and X-ray fluorescence (XRF, analyser EAGLE III XPL, EDAX Inc., Mahwah, NJ, USA) analyses were used to characterise solid materials (raw material, solid residue after leaching and precipitate from electrolyte). A microscope (KEYENCE VHX-2000, Keyence Corporation, Osaka, Japan) was used for optical imaging of the disintegrator-crushed powder of raw material 1.

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 (7):

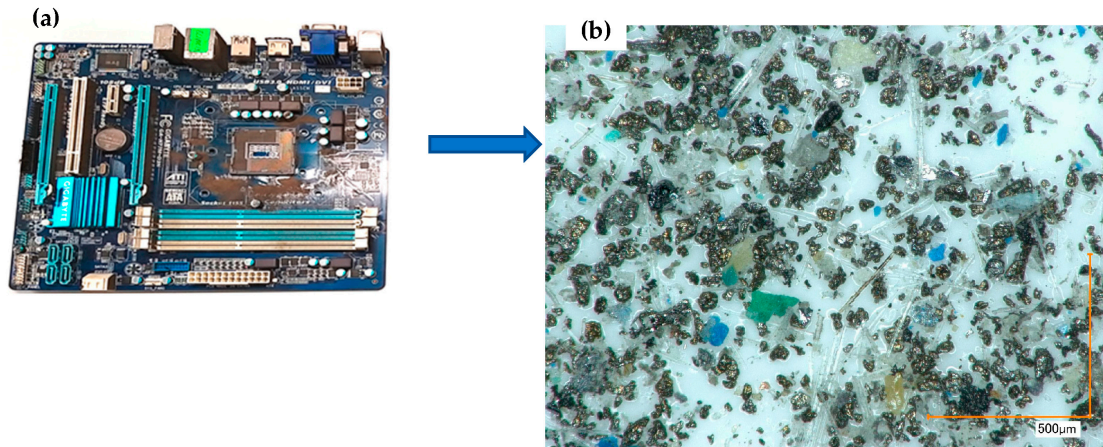
$$R (\%) = (M_{el}/M_{PCBs}) \times 100\% \quad (7)$$

The content of the metals in the raw material ( $M_{PCBs}$ ) 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 materials.

### 3. Results and Discussion

#### 3.1. Raw Material Characterisation

A fine fraction of raw material 1 with  $d < 90 \mu\text{m}$  is the main object of this research. Therefore, the powder obtained after crushing and subsequent sieving is relatively homogeneous and contains only a small amount of plastic and fibreglass fragments (Figure 2b).



**Figure 2.** Image of computer motherboard (a) and optical image at magnification  $\times 200$  of disintegrator-crushed fraction of raw material 1 with  $d < 90 \mu\text{m}$  (b).

Table 1 shows the results of the ICP-OES analysis of leachates, obtained from the chemical treatment of raw material 1 and raw material 2, which characterised in detail in our previous study [36]. Based on the presented data, it can be concluded that iron is the most significant component of the raw material 1 sample, while the content of each of the other metals does not exceed one per cent. The presence of precious metals (Au, Pd and Ag) in the leachate is not detected. Element content in the raw material 2 sample is significantly different and contains a broader range of elements. Predominantly present are Fe, Pb and Sn. Moreover, the content of iron is  $\sim 10$  times smaller than in the raw material 1 sample. In addition, the presence of noble metals (Au, Pd, and Ag) and, in trace amounts, Mo, is established.

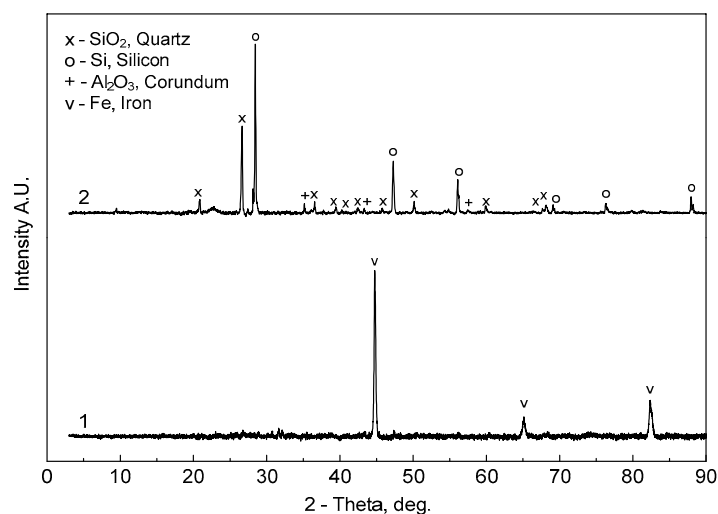
Table 1 also shows the content of solid residue after the chemical treatment of raw materials and the overall scope of elements (other) that were not determined and/or could not be determined in solutions with the ICP-OES method.

Based on the XRD analysis results of the solid residue obtained from the chemical treatment of raw material 1, such crystalline phases as  $\text{SiO}_2$  (PDF 00-046-1045), Si (PDF 00-027-1402) and  $\text{Al}_2\text{O}_3$  (PDF 00-046-1212) (Figure 3, curve 2) were identified in the sample. The presence of the crystalline phase of  $\alpha\text{-Fe}$  (PDF 00-006-0696), the dominant crystalline phase in raw material 1 (Figure 3, curve 1), was not established. It should be noted that the phase composition of the solid residue obtained under similar chemical leaching conditions of raw material 2 is identical [36]. However, iron is present in different forms in the raw materials: the crystalline phase of  $\alpha\text{-Fe}$ , in raw material 1; and the crystalline phase of magnetite  $\text{Fe}_3\text{O}_4$ , in raw material 2.

**Table 1.** Content of metals in raw materials according to the results of ICP-OES analysis of the solutions prepared by chemical leaching.

Component, Content	Raw Material 1	Raw Material 2 [36]
Fe, wt. %	81.4	7.56
Sn, wt. %	0.887	4.76
Mn, wt. %	0.665	0.170
Al, wt. %	0.488	1.31
Cu, wt. %	0.386	1.40
Zn, wt. %	0.220	2.00
Pb, wt. %	0.208	7.50
Ni, wt. %	0.206	1.03
Ti, wt. %	0.208	1.74
Sb, wt. ppm	129	1365
Cr, wt. ppm	102	188
Co, wt. ppm	19	224
V, wt. ppm	18	29
Mo, wt. ppm	BDL *	17
Ag, wt. ppm	BDL *	8450
Pd, wt. ppm	BDL *	1550
Au, wt. ppm	BDL *	824
Solid residue, wt. %	4.84	45.8
Other, wt. %	10.4	26.5

\* BDL—below the detectable limit.

**Figure 3.** XRD patterns: 1: raw material 1; 2: solid residue after chemical treatment of a raw material 1 sample.

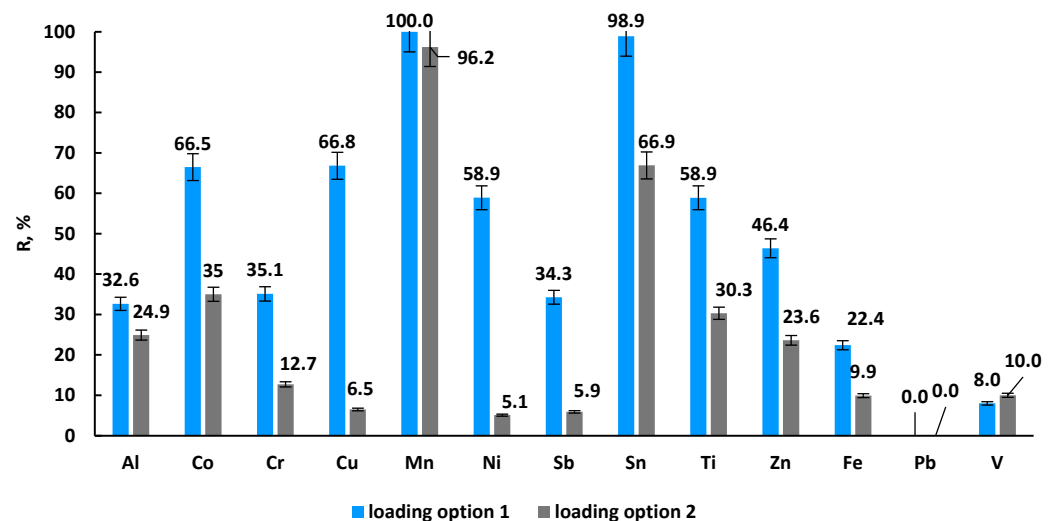
### 3.2. Influence of Process Parameters on the Efficiency of Metal Leaching from Raw Materials

When raw materials are treated with hydrochloric acid solutions, active metals are dissolved, even in the absence of an oxidising agent. The low dimensionality ( $d < 90 \mu\text{m}$ ) of the raw materials chosen for the research contributes to an increased dissolution rate. Chlorine, being a strong oxidising agent, interacts with metals and almost all metal oxides to form chlorides and hydrocarbons [38]; therefore, the transition of base metals into solutions within the framework of the proposed method is reasonably expected. The leaching research of all identified metals in raw material 1 and raw material 2 (Table 1) are shown below, both with and without an oxidising agent.

### 3.2.1. Raw Material 1

#### Impact of Loading Option on the Degree of Chemical Leaching of Metals

Figure 4 demonstrates the results of metal leaching from raw material 1 in the absence of an electric current with two different loading options of the raw material. With loading option 1, the effective leaching of Mn ( $R_{Mn} = 100\%$ ) and Sn ( $R_{Sn} = 98.9\%$ ) is observed. Moreover, the change from loading option 1 to loading option 2 has a less significant effect on the leaching efficiency of Mn in comparison with Sn. For elements such as Co, Cr, Cu, Ni, Sb, Ti, Zn and Fe, the change in the loading option leads to a significant decrease in the leaching efficiency. The loading option practically does not affect the degree of V leaching into the hydrochloric acid solution. Similarly, the effect is also not very significant for aluminium. Regardless of the loading option used, the transition of lead into a hydrochloric acid solution has not been established. The decrease in the efficiency of metal leaching due to the change from loading option 1 to loading option 2 is associated with diffusion restrictions arising from the presence of a separating diaphragm (container material) between the pulp and the electrolyte volume.



**Figure 4.** Leaching degree of metals depending on the loading option of the raw material. Experimental conditions: raw material 1; electrochemical cell 1;  $C_{HCl} = 6 \text{ mol}\cdot\text{L}^{-1}$ ;  $i = 0$ ;  $S/L = 8.6 \text{ g}\cdot\text{L}^{-1}$ ;  $t_{ex} = 2 \text{ h}$ ; ambient temperature.

#### Impact of Solid/Liquid Ratio on Metal Electrochemical Leaching Degree

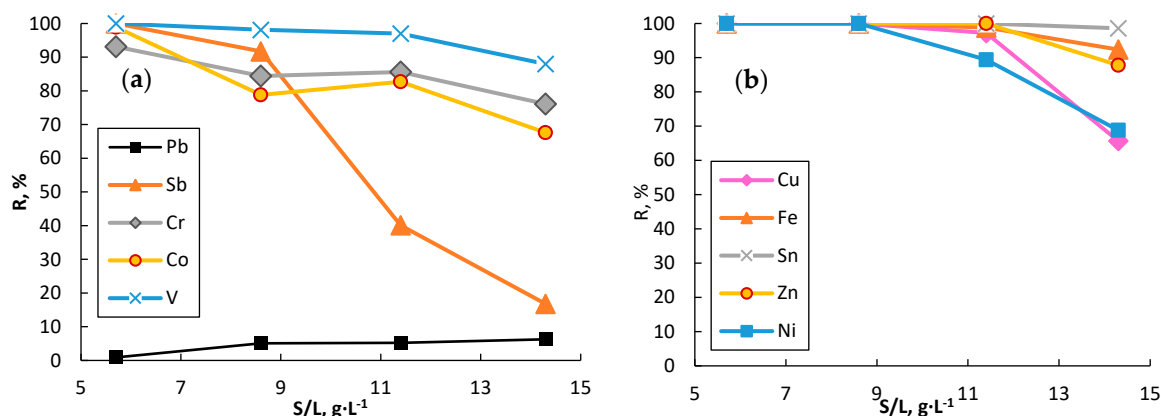
Because of the low content of the non-conductive matrix and the high content of the highly conductive material—metallic iron (Table 1, Figure 3, curve 1)—loading option 2 was used to load this material into the electrochemical cell. In this case, when an AC passes through an electrochemical system with hydrochloric acid electrolyte, during the anode half-cycles, basic reactions such as the ionization of metals that have electrical contact with graphite electrodes, the release of chlorine (both on the surface of graphite electrodes and metal particles of the raw material) and the oxygen evolution reaction will occur. It is known [18] that molecular chlorine at the moment of release upon direct contact with the chlorinated substance is more active than gaseous chlorine supplied from outside. With loading option 2 in the anodic half-cycles of AC, the electrooxidation of  $\text{Cl}^-$  ions with the formation of atomic chlorine occurs directly on the surface of the electrically conductive particles of raw material 1, and this provides a high metal dissolution rate in the electrochemical process [39]. It should be noted that the true current density, with this loading option, will be less than the calculated one.

To test this loading option, Au powder (99.99%, Premion, Germany) was used as the raw material, and cell 1 was used as the electrolyser. During the tests, 0.250 g of gold powder was placed in each filter container and attached to graphite electrodes, and the



cell was filled with  $6 \text{ mol}\cdot\text{L}^{-1}$  of HCl. The process of electrochemical leaching was carried out at  $i = 0.88 \text{ A}\cdot\text{cm}^{-2}$  for 2 h. According to the results of the ICP-OES analysis, after the completion of the experiment, the gold concentration in the electrolyte solution reached  $212.1 \text{ mg}\cdot\text{L}^{-1}$ , corresponding to a metal recovery of 14.9%. The process was accompanied by electrolyte heating from  $20 \text{ }^\circ\text{C}$  to  $67 \text{ }^\circ\text{C}$ .

To select the optimal S/L ratio for research on the electrochemical leaching of metals from raw material 1, a series of experiments were carried out with different S/L ratios. The results showed (Figure 5a) that with an increase in the S/L ratio, a gradual decrease in the leaching efficiency of Cr, Co and V is observed. In the case of Sb, an increase in the S/L ratio from  $8.6 \text{ g}\cdot\text{L}^{-1}$  to  $11.4 \text{ g}\cdot\text{L}^{-1}$  leads to a more than twofold decrease in the degree of leaching. Lead leaching occurs with very low efficiency, but is characterised by a gradual increase in the degree of leaching in the studied range of the S/L ratio. It should be noted that metals such as Al, Mn and Ti are leached completely regardless of the S/L ratio. The leaching of Cu, Fe, Ni and Zn deteriorates at an S/L ratio  $> 8.6 \text{ g}\cdot\text{L}^{-1}$ , and for Sn, there is only a slight decrease in the degree of leaching, with an S/L ratio =  $14.3 \text{ g}\cdot\text{L}^{-1}$  (Figure 5b).



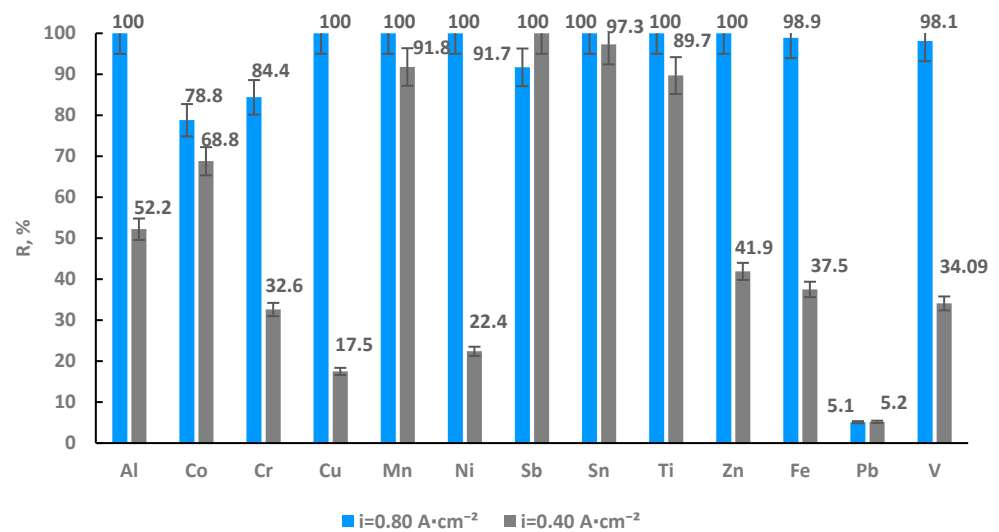
**Figure 5.** Impact of S/L ratio on the degree of metal leaching. Experimental conditions: electrochemical cell 1; loading option 2; raw material 1;  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ;  $i = 0.80 \text{ A}\cdot\text{cm}^{-2}$ ;  $t_{\text{ex}} = 2 \text{ h}$ . The electrolyte temperature during the processes increased from  $20 \text{ }^\circ\text{C}$  to  $79 \text{ }^\circ\text{C}$ .

Considering the obtained results and the application of loading option 2 of the raw material, the S/L ratio of  $8.6 \text{ g}\cdot\text{L}^{-1}$  was chosen for the study of the electrochemical leaching processes of the metals.

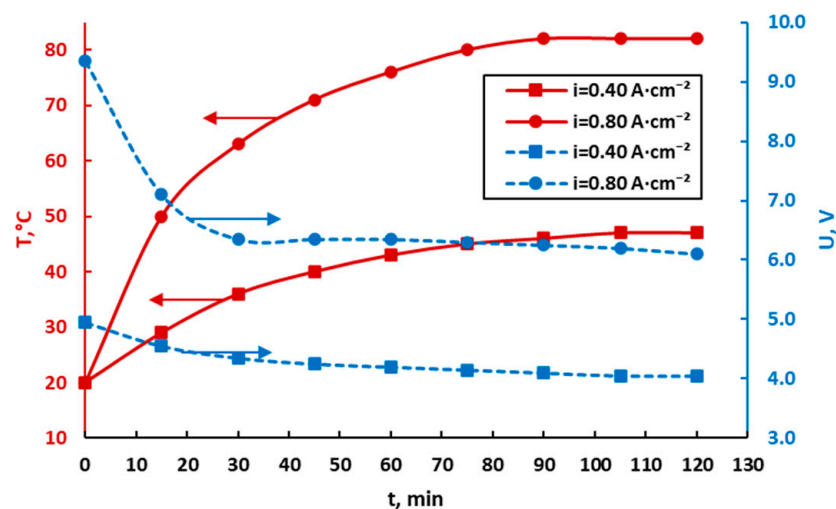
#### Impact of Current Density on Metal Leaching Degree

A comparison of the results of the electrochemical (Figure 6) and chemical leaching (Figure 4), obtained under the same experimental conditions, shows that the superimposition of an AC ( $i = 0.40 \text{ A}\cdot\text{cm}^{-2}$ ) on the studied system significantly intensifies the transition of almost all metals into the hydrochloric acid solution. A twofold increase in AC density has the same effect, except for Sb and Pb. Compared to chemical leaching using raw material loading option 1, the impact of AC is more noticeable at  $i = 0.80 \text{ A}\cdot\text{cm}^{-2}$ .

As a result of the current passage, the electrolyte's heating is observed. The final temperature of the electrolyte solution (reaction mixture) depends both on the duration of the experiment at a fixed current density and on the current density on the graphite electrodes (Figure 7).



**Figure 6.** Impact of current density on the degree of metal leaching. Experimental conditions: raw material 1; electrochemical cell 1; loading option 2;  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ;  $S/L = 8.6 \text{ g}\cdot\text{L}^{-1}$ ;  $t_{\text{ex}} = 2 \text{ h}$ .

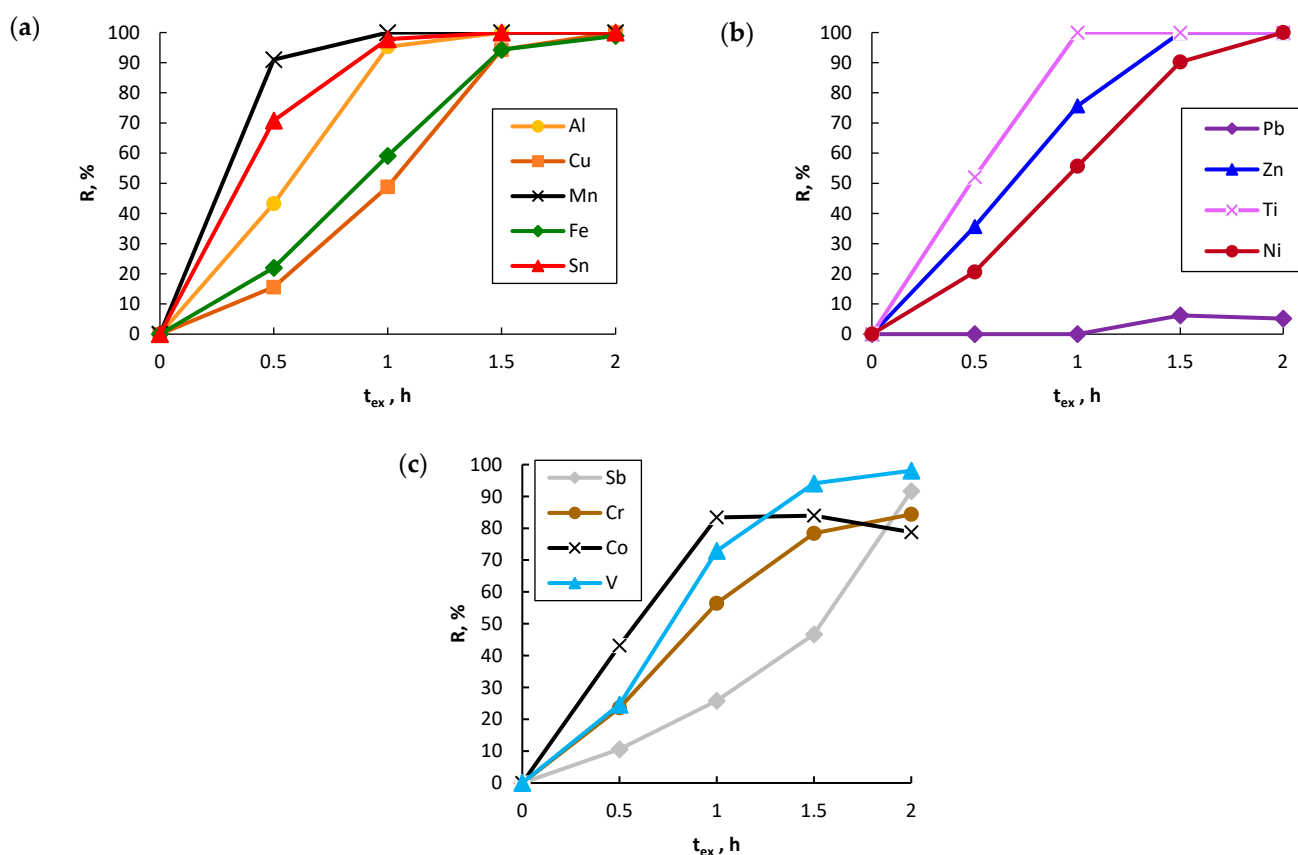


**Figure 7.** Electrolyte temperature and cell voltage versus the experiment duration. Experimental conditions: raw material 1; electrochemical cell 1; loading option 2;  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ;  $S/L = 8.6 \text{ g}\cdot\text{L}^{-1}$ .

#### Impact of Experiment Duration on Metal Electrochemical Leaching Degree

According to the results of the ICP-OES analysis of the solution obtained from the chemical treatment of raw material 1 (Table 1), the metals, listed by the amount that their content decreased in the raw material, are arranged as follows:  $\text{Fe} > \text{Sn} > \text{Mn} > \text{Al} > \text{Cu} > \text{Zn} > \text{Pb} > \text{Ti} > \text{Sb} > \text{Cr} > \text{Co} > \text{V}$ . Based on this series, metals are divided into three groups and the kinetic curves of their electrochemical leaching are shown in Figure 8. The presented data show (Figure 8a) that the complete leaching of Mn is achieved with an experiment duration of 1 h and that the complete leaching of Sn and Al is achieved at 1.5 h. Copper, the least active element of this group, completely dissolves in the electrolyte solution in 2 h. Ti, Zn and Ni are completely leached in 1, 1.5 and 2 h, respectively (Figure 8b). The behaviour of lead is significantly different: the slow leaching of the metal into the electrolyte solution begins only an hour after the beginning of the experiment when the electrolyte temperature reaches  $76 \text{ }^\circ\text{C}$  (Figures 7 and 8b). At the end of the investigation, the degree of lead leaching is only 5.1%. This behaviour is probably because the lead, in this study, is in the form of a mixed oxide,  $\text{PbO}\cdot\text{TiO}_2$ , which is non-conductive. The transition of metals (Co, Cr, Sb and V) present in the raw material in microquantities into the solution is characterised by high values of leaching degree, but it is not possible to completely leach

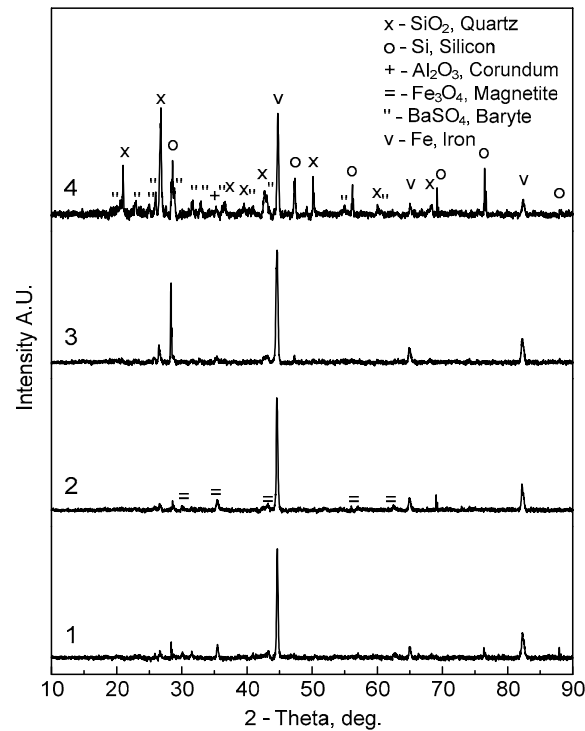
them into the electrolyte solution within 2 h of the experiment (Figure 8c). On the one hand, the incomplete leaching of metals may be related to the chemical form in which the metals are present in the raw material. On the other hand, due to a feature of loading option 2, during the leaching process, the amount of the metal component of the sample decreases and the non-conductive matrix content increases, ultimately leading to the loss of electrical contact between the remainder of the conductive material and the electrode. Thus, after completion of the 2 h leaching, the following content of metals remains in the solid residue of raw material 1: Pb—94.9; Co—21.2; Cr—15.6; Sb—8.3; Fe—1.1; and V—1.9%. At the same time, the following content of metals ( $\text{mg}\cdot\text{L}^{-1}$ ) is established in the electrolyte solution: Al—41.8; Cu—33.0; Mn—56.9; Ni—17.6; Ti—17.8; Zn—18.8; Co—0.135; Cr—0.752; Fe—6903; Pb—0.919; Sb—1.01; V—0.148; and Sn—76.0. It should be noted that in comparison with chemical leaching (Figure 4), an increase in the efficiency of all metal leaching is observed under the conditions of electrochemical leaching.



**Figure 8.** Impact of the experiment duration on the degree of metal leaching. Experimental conditions: raw material 1; electrochemical cell 1; loading option 2;  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ;  $i = 0.80 \text{ A}\cdot\text{cm}^{-2}$ ;  $S/L = 8.6 \text{ g}\cdot\text{L}^{-1}$ ;  $t_{\text{ex}} = 2 \text{ h}$ .

The solid residue after completion of 0.5, 1, 1.5 and 2 h experiments is 69.8%, 39.3%, 11.7% and 5.3%, respectively. Figure 9 presents the results of the X-ray phase analysis of solid residues of PCBs after the experiments on the kinetics of the electrochemical leaching of raw material 1 (Figure 8). With the duration of the experiments increased from 0.5 to 1.5 h, the phase composition of solid residues almost does not change and is a mixture of  $\text{SiO}_2$ ,  $\text{Fe}_3\text{O}_4$  (PDF 00-019-0629), Si and  $\alpha$ -Fe crystalline phases. After the 2 h experiment, the iron was almost completely leached into the electrolyte solution (Figure 8a), and the crystalline phases of  $\text{Al}_2\text{O}_3$  and  $\text{BaSO}_4$  were also identified in the solid residue, but the presence of magnetite was not established. The main difference in the phase composition of the sample obtained as a result of chemical treatment (Figure 3, curve 2) and the sample obtained as a result of a two-hour experiment (Figure 9, curve 4) is the presence in the latter

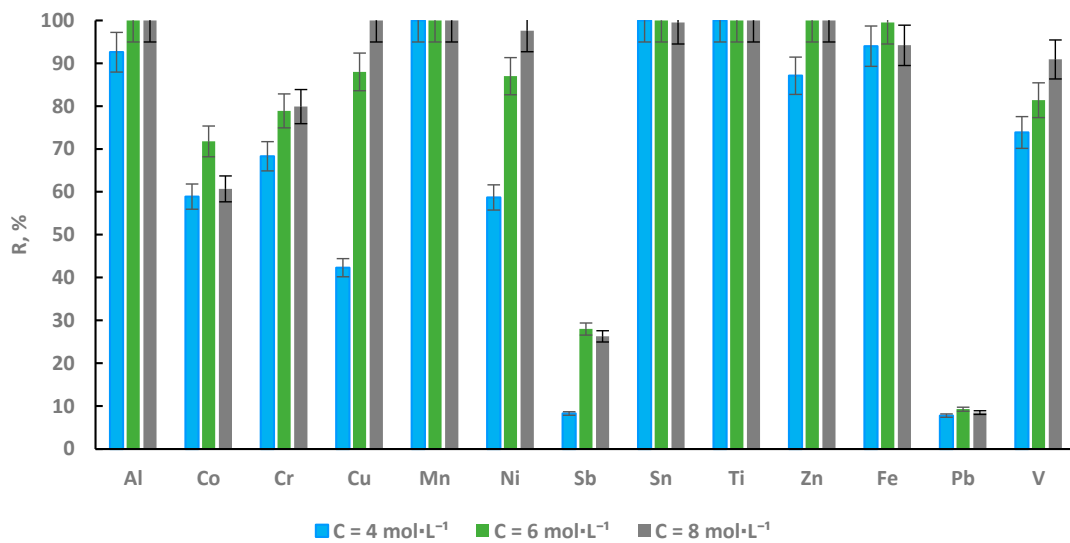
of the crystalline phases of  $\text{BaSO}_4$  (PDF 00-024-1035) and  $\alpha\text{-Fe}$ . The crystalline phase of  $\text{BaSO}_4$  was probably not found in the solid residue after chemical leaching due to the small amount of the material under study. The presence of a residual amount of iron in the solid residue indicates the incomplete leaching of metal from raw material 1. This result is also confirmed by the result of the ICP-OES analysis of the electrolyte solution: the degree of iron leaching under the experimental conditions is 98.9% (Figure 8a).



**Figure 9.** XRD patterns of solid residues from the experiments at different experiment duration: 1—0.5 h; 2—1 h; 3—1.5 h; and 4—2 h. Experimental conditions: electrochemical cell 1; loading option 2;  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ;  $S/L = 8.6 \text{ g}\cdot\text{L}^{-1}$ ;  $i = 0.80 \text{ A}\cdot\text{cm}^{-2}$ .

#### Impact of HCl Concentration in Electrolyte Solution on the Degree of Metal Electrochemical Leaching

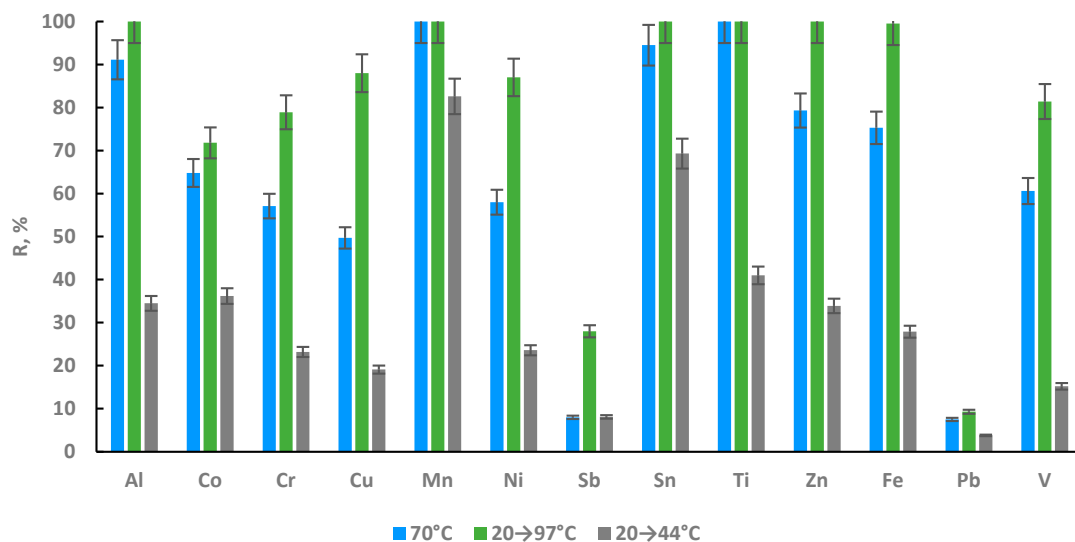
When studying the effect of the HCl concentration in the electrolyte solution on the leaching efficiency, it was found (Figure 10) that the degree of Mn, Ti and Sn leaching reaches its maximum value at  $C_{\text{HCl}} = 4 \text{ mol}\cdot\text{L}^{-1}$ . A further increase in the concentration of hydrochloric acid in the solution to  $6 \text{ mol}\cdot\text{L}^{-1}$  leads to an increase in the leaching efficiency of all other metals, and, for Al and Zn in particular, it leads to maximum leaching efficiency. With a further increase in the HCl concentration to  $8 \text{ mol}\cdot\text{L}^{-1}$ , the degree of Cu, Ni, V, and Cr leaching continues to increase; however, in the case of Co, Sb, Fe and Pb, a slight decrease in the dissolution efficiency is observed. This is probably due to a reduction in the solubility of complex salts of these metals.



**Figure 10.** Impact of HCl concentration on the degree of metal leaching. Experimental conditions: electrochemical cell 2; loading option 2; raw material 1;  $i = 0.72 \text{ A}\cdot\text{cm}^{-2}$ ;  $t_{\text{ex}} = 2 \text{ h}$ . The electrolyte temperature during processes increased from  $20 \text{ }^\circ\text{C}$  to  $97 \text{ }^\circ\text{C}$ .

#### Impact of Electrolyte Temperature on the Degree of Metal Electrochemical Leaching

To study the effect of electrolyte temperature on the efficiency of metal leaching, experiments were carried out under the following three conditions: temperature control of the electrolyte at  $70 \text{ }^\circ\text{C}$ , without forced temperature control ( $20\text{--}97 \text{ }^\circ\text{C}$ ) and with water cooling of the electrolyte ( $20\text{--}44 \text{ }^\circ\text{C}$ ). According to the results obtained (Figure 11), an increase in the electrolyte temperature contributes to an increase in the leaching efficiency of all studied metals.



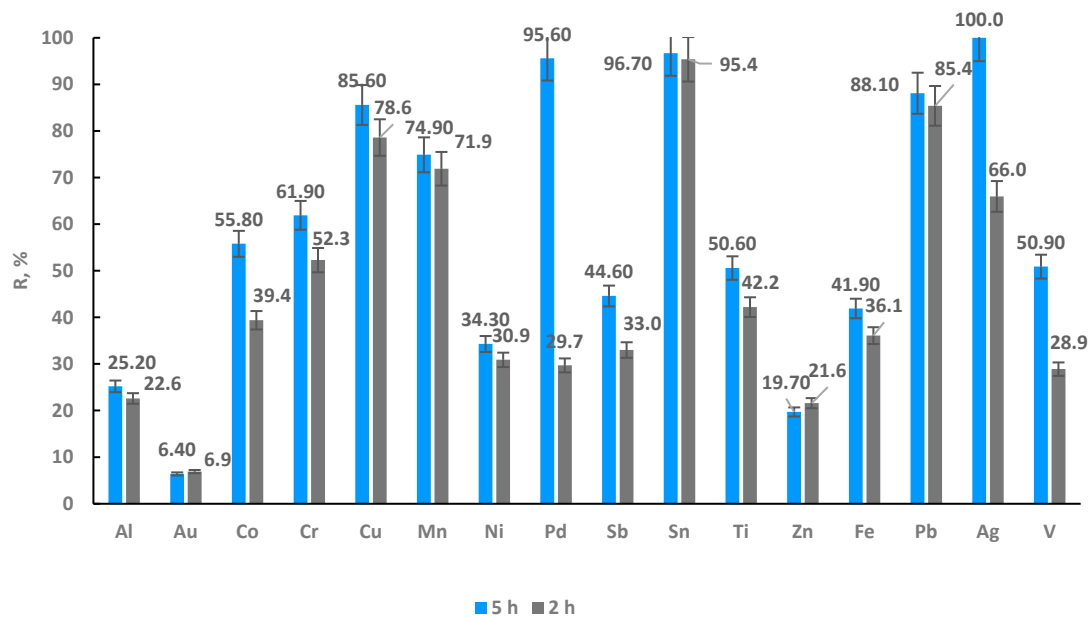
**Figure 11.** Impact of electrolyte temperature on the degree of metal leaching. Experimental conditions: electrochemical cell 2; loading option 2;  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ; raw material fraction 1;  $i = 0.72 \text{ A}\cdot\text{cm}^{-2}$ ;  $t_{\text{ex}} = 2 \text{ h}$ .

#### 3.2.2. Raw Material 2

##### Impact of Experiment Duration on Metal Chemical Leaching Degree

In the study on metal leaching from raw material 2, only loading option 1 was used (Figure 1a). Increasing the experiment duration from 2 to 5 h in the absence of an electric current led to an increase in the degree of extraction of almost all metals (Figure 12).

Moreover, after a 2 h experiment in the electrolyte solution, the presence of such noble metals as Au [36], Ag and Pd were also established. A further increase in the experiment duration has practically no effect on the degree of gold leaching, but leads to a noticeable increase in the efficiency of Ag leaching from 66.0 to 100% and Pd leaching from 29.7 to 95.6%. At the same time, an increase in the degree of Cu leaching from 78.6 to 85.6% is also observed. Under the conditions of these experiments, cupric ions can play the role of an oxidising agent for silver and palladium (Equation (2)) [15,16].



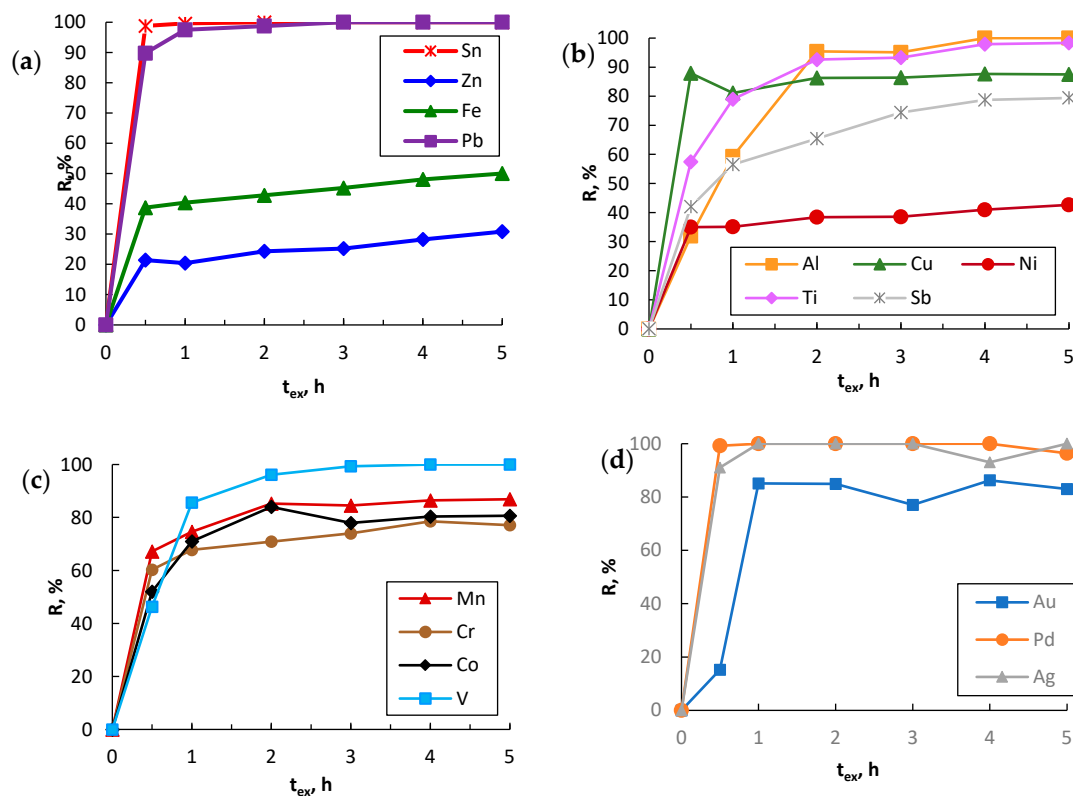
**Figure 12.** Impact of the experiment duration on the degree of metal leaching. Experimental conditions: raw material 2; electrochemical cell 1; loading option 1;  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ;  $i = 0$ ;  $S/L = 8.6 \text{ g}\cdot\text{L}^{-1}$ ; ambient temperature.

A comparison of these results with those presented above using raw material 1 (Figure 4) under similar experimental conditions ( $t_{\text{ex}} = 2 \text{ h}$ , loading option 1) demonstrates differences in metal leaching efficiency. In the case of raw material 2, the degree of Pb leaching reaches 85.4%, while metal leaching from raw material 1 is not observed at all. The lead content, however, in the latter is less than  $\sim 8$  times, which is likely because, in raw material 2, lead is a component of a tin–lead alloy (solder), while in raw material 1, it is a part of the  $\text{PbO}\cdot\text{TiO}_2$  mixed oxide. Meanwhile, for such metals as Cr, Cu and V, despite their higher content in raw material 2 compared to raw material 1 (Table 1), higher leaching degrees are established. In all other cases, with a lower content of metals in the raw material, higher values of the degree of metal leaching are also observed.

#### Impact of Experiment Duration on Metal Electrochemical Leaching Degree

The active electrochemical leaching of all metals is observed during the first 30 min of the experiment (Figure 13). A further increase in the experiment duration has a different effect on the efficiency of metal leaching. In the case of V and Co, an active transition of metals into the solution is observed within 1 h from the beginning of the experiment (Figure 13c), and, for Al, within 2 h (Figure 13b). Complete leaching of Ag is achieved in 1 h of the process and of Pd in 2 h (Figure 13d). Sn and Pb thoroughly leach into the solution in 3 h (Figure 13a), and Al and V in 4 h. A relatively low efficiency of leaching characterises Ni, Zn and Fe, which take 5 h to leach into the electrolyte solution, with leaching degrees of  $R_{\text{Ni}} = 42.6\%$ ,  $R_{\text{Zn}} = 30.8\%$  and  $R_{\text{Fe}} = 50\%$ , respectively. During this time, the degree to which other metals leach reaches sufficiently high values ( $\geq 80\%$ ); however, their complete leaching is not achieved. As a result of a 2 h experiment, the concentrations of metals in the electrolyte solution ( $\text{mg}\cdot\text{L}^{-1}$ ) are Al—107.2; Cu—103.6; Mn—12.4; Ni—33.8; Ti—137.7; Zn—

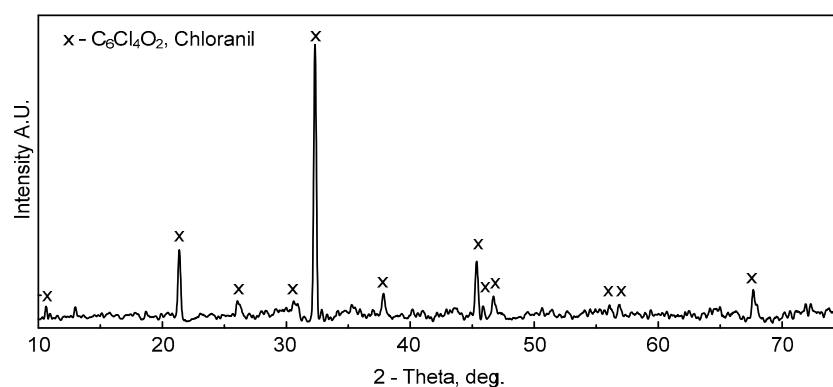
41.7; Co—1.41; Cr—1.16; Fe—265.3; Pb—652.2; Sb—8.14; V—0.236; Au—5.99; Pd—13.2; and Sn—408.1. Following a 5 h experiment, the concentrations are Al—113.3; Cu—105.0; Mn—12.6; Ni—37.5; Ti—146.4; Zn—52.9; Co—1.54; Cr—1.24; Fe—324.4; Pb—684.1; Sb—9.28; V—0.269; Au—5.86; Pd—13.2; and Sn—408.1. A comparison of these results (Figure 13) and the results obtained under similar experimental conditions, but in the absence of AC (Figure 12), allows us to conclude that the AC superimposition on the system under study intensifies the process of leaching metals from raw material 2.



**Figure 13.** Impact of the experiment duration on the degree of metal leaching. Experimental conditions: raw material 2; electrochemical cell 1; loading option 1;  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ;  $i = 0.88 \text{ A}\cdot\text{cm}^{-2}$ ;  $S/L = 8.6 \text{ g}\cdot\text{L}^{-1}$ .

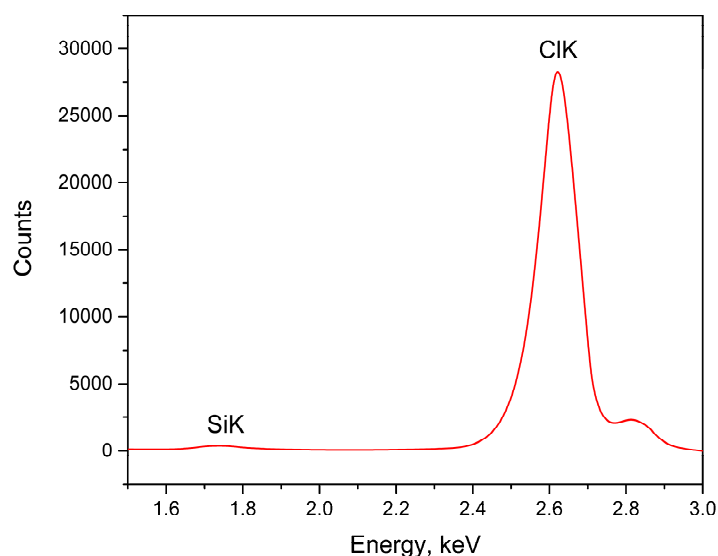
A comparison of the results of 2 h experiments carried out using different loading options and different raw materials (Figures 8 and 13) showed that the degree of all metal leaching from raw material 1 with loading option 2 (Figure 8) is higher than in the case of raw material 2 and loading option 1, except for Pb (Figure 13). The significant difference in the lead leaching efficiency of Pb ( $R_{\text{Pb}} = 98.7\%$  for loading option 1 and  $R_{\text{Pb}} = 5.1\%$  for loading option 2) is most likely due to the different chemical forms of the metal in which it is present in the raw materials.

During the research, after completing all experiments and separating the electrochemically treated powders of PCBs, the transparent electrolyte solutions were obtained. However, when spent electrolytes (after experiments with a duration from 3 to 5 h using raw material 2) were stored in a closed glass container, a flaky lemon-coloured precipitate gradually appeared in them. A month later, the mass of precipitate in electrolyte solutions after completing 4 and 5 h experiments was 0.005 g each. The amount of precipitate in the electrolyte from the 3 h experiment was significantly less and was not weighed. The result of the X-ray phase analysis of the precipitate (Figure 14) showed the presence of a crystalline phase of chloranil.



**Figure 14.** XRD pattern of a precipitate formed in the electrolyte solution during storage (1 month after the experiment). Experimental conditions: raw material 2; electrochemical cell 1; loading option 1;  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ;  $t_{\text{ex}} = 4 \text{ h}$ ;  $S/L = 8.6 \text{ g}\cdot\text{L}^{-1}$ ;  $i = 0.88 \text{ A}\cdot\text{cm}^{-2}$ .

The results of the XRF analysis of the precipitate presented in Figure 15 do not contradict the XRD analysis data. The presence of any metals in the sample was not established. Chloranil can be formed during an electrochemical process due to the interaction of phenol in the PCB's material with chlorine [40]. It should be noted that the precipitate was easily separated from the solution, and its formation in the electrolyte solution was not observed during further storage.



**Figure 15.** Fluorescence spectrum of the precipitate formed in an electrolyte solution during storage (1 month after the experiment). Experimental conditions are provided in the Figure 14 caption.

Thus, as a result of the experiments carried out, multicomponent solutions containing all the studied metals were obtained. It is shown that, under the same conditions of the electrochemical hydrochlorination process, the loading option of the raw material affects the efficiency of Fe, Sn, Mn, Al, Cu, Zn, Pb, Ni, Ti, Sb, Cr, Co and V leaching. The use of loading option 2 increases the completeness of the extraction of almost all metals compared to loading option 1. However, loading option 2 for raw material 2 is limited by a significant amount of non-conductive matrix. Therefore, to reduce its content in the raw material prior to leaching, pretreatment is required (electrostatic or air separation).

Nevertheless, regardless of the composition of the raw material and its loading option, the application of AC intensifies the metal leaching process. According to the results obtained, in the absence of current for 5 h of the experiment, 100% of Ag and 95.6% of Pd are leached into a solution of  $6 \text{ mol}\cdot\text{L}^{-1}$  of HCl from raw material 2. Under the conditions



of AC superimposition ( $i = 0.88 \text{ A}\cdot\text{cm}^{-2}$ ), complete leaching of silver and palladium is achieved in 1 h and 2 h, respectively. The transition of these metals into a chloride multicomponent solution in the absence of chlorine does not contradict the results of studies presented in the research [14–16].

#### 4. Conclusions

The results of the research have shown that the process parameters with the most significant impact on the leaching degree of such metals as Fe, Sn, Mn, Al, Cu, Zn, Pb, Ni, Ti, Sb, Cr, Co and V from powders of the raw material with  $d < 90 \mu\text{m}$ , obtained from the twofold crushing of computer motherboards in a disintegrator, during the process of electrochemical hydrochlorination, were the AC density on the graphite electrodes, electrolyte temperature, and hydrochloric acid concentration. An increase in the electrolyte temperature contributes to a rise in the leaching efficiency of all the studied metals. In contrast, an increase in the AC density from  $0.40$  to  $0.80 \text{ A}\cdot\text{cm}^{-2}$  enhances the degree of all metal leaching, except for Sb and Pb. Under the same experimental conditions ( $i = 0.72 \text{ A}\cdot\text{cm}^{-2}$ ,  $t_{\text{ex}} = 2 \text{ h}$ ), the use of an electrolyte with the concentration of HCl  $4 \text{ mol}\cdot\text{L}^{-1}$  leads to the complete leaching of Mn, Ti and Sn, while an increase in the concentration of hydrochloric acid to  $6 \text{ mol}\cdot\text{L}^{-1}$  allows complete leaching of Al and Zn and increases the leaching efficiency of other metals. A further increase in hydrochloric acid content in the solution to  $8 \text{ mol}\cdot\text{L}^{-1}$  not only raises the leaching efficiency of Cu, Ni, V and Cr but also leads to some decrease in the leaching efficiency of Co, Sb, Fe and Pb.

A study on the impact of the raw material loading option on the leaching efficiency of all the metals above, with powders obtained from different source materials (computer motherboards and mixed PCBs), showed that loading the samples into filtering containers is preferable.

Based on this research, the results have determined the experimental conditions needed to ensure the complete leaching of Ag and Pd ( $t_{\text{ex}} = 1 \text{ h}$  and  $t_{\text{ex}} = 2 \text{ h}$ , respectively) from the powders of the raw material, with  $d < 90 \mu\text{m}$  obtained as a result of a single crushing of mixed PCBs in a disintegrator, and loading the raw material into the electrolyte volume,  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ,  $i = 0.88 \text{ A}\cdot\text{cm}^{-2}$ ,  $S/L = 8.6 \text{ g}\cdot\text{L}^{-1}$ . It has been established that the complete leaching of Cu from the raw material obtained from computer motherboards is observed under the following experimental conditions: the loading of the raw material into filter containers;  $C_{\text{HCl}} = 6 \text{ mol}\cdot\text{L}^{-1}$ ;  $i = 0.80 \text{ A}\cdot\text{cm}^{-2}$ ;  $S/L = 8.6 \text{ g}\cdot\text{L}^{-1}$ ;  $t_{\text{ex}} = 2 \text{ h}$ .

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

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