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Manivannan Sethurajan, Eric D. van Hullebusch. Metals Leaching and Selective Recovery of Cu from Printed Circuit Boards. Metals, 2019, 9 (10), pp.1034. 10.3390/met9101034 . insu-02548981

**HAL Id: insu-02548981**

**https://insu.hal.science/insu-02548981**

Submitted on 21 Apr 2020

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# Leaching and Selective Recovery of Cu from Printed Circuit Boards

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Received: 4 September 2019; Accepted: 21 September 2019; Published: 24 September 2019




**Abstract:** Printed circuit boards (PCBs), a typical end-of-life electronic waste, were collected from an E-waste recycling company located in the Netherlands. Cu and precious metal concentration analyses of the powdered PCBs confirm that the PCBs are multimetallic in nature, rich, but contain high concentrations of Cu, Au, Ag, Pd, and Pt. Ferric sulfate concentration (100 mM), agitation speed (300 rpm), temperature (20 °C), and solid-to-liquid ratio (10 g·L$^{-1}$) were found to be the optimum conditions for the maximum leaching of Cu from PCBs. The ferric sulfate leachates were further examined for selective recovery of Cu as copper sulfides. The important process variables of sulfide precipitation, such as lixiviant concentration and sulfide dosage were investigated and optimized 100 ppm of ferric sulfate and (copper:sulfide) 1:3 molar ratio, respectively. Over 95% of the dissolved Cu (from the multimetallic leachates) was selectively precipitated as copper sulfide under optimum conditions. The characterization of the copper sulfide precipitates by SEM-EDS analyses showed that the precipitates mainly consist of Cu and S. PCBs can thus be seen as a potential secondary resource for copper.

**Keywords:** copper recovery; E-waste; hydrometallurgy; printed circuit boards; selective recovery; sulfide precipitation

## 1. Introduction

Copper is the second most important nonferrous metal (after aluminum) and is being used in many industries ranging from healthcare to construction, machineries to electronics, and telecommunication [1]. Chalcopyrite ($CuFeS_2$) is the most predominant ore of copper and most often used as the raw material for the extraction of Cu. Other Reduced ores such as chalcocite ($Cu_2S$) and covellite (CuS) are alternative sources for Cu production [2]. Oxide minerals bearing low-grade ores are also used in extractive metallurgies of copper. Generally, copper is produced from the primary sulfidic ores by pyrometallurgy because the hydrometallurgy processes are less successful [3]. The demand for copper is constantly increasing, but, on the other hand, natural resources have been decreasing. In order to overcome this issue, metallurgical industries have started utilizing metal-bearing solid wastes for the recovery of metals [4,5]. Almost 10%–15% of Cu is currently produced from secondary Cu resources such as alloys and scraps [3]. Of late, a lot of waste materials (metallurgical sludges, residues and slags, etc.) have been used for the extractive metallurgy of Cu [1,6–10].

Not only metallurgical wastes contain a significant concentration, but waste printed circuit boards (PCBs) also contain a very high concentration of Cu. PCB is one of the major parts present in all types of electrical and electronic devices. Nonconductive circuits and electrical components (which include metals, polymers, and ceramics) are the major components of a PCB. Typically, PCBs are made of metals (40%), ceramic (30%), and plastics (30%). Metal fractions of PCB contain many base (such as Cu,

Ni, and Fe) and precious metals (such as Au, Ag, and Pt). Even though PCBs are made of various metals, the driving force for recycling the PCB is its Cu and Au concentration [11]. The concentrations of Cu and precious metals present in the PCBs are higher than the concentrations of Cu and precious metals in their natural primary ores. Enormous amounts of waste printed circuit boards (PCBs) have been discarded annually. A research report [12] states that approximately 1.5 million tons of PCBs were discarded every year.

Many researchers have reported the Cu leaching from waste printed circuit boards using various lixiviants. Inorganic acids, organic acids, ionic liquids, and even microbes (such as bacteria and fungi) have been proposed for the solubilization of Cu from the printed circuit boards [12–19]. Even though Fe(III) salts were found to be a good leachant of Cu from other different minerals [20–22], only Yazici and Deveci [23] reported the effect of Fe(III) salts on Cu leaching from PCBs. Also, most of the studies (including Yazici and Deveci [23]) had not discussed the recovery of Cu from the polymetallic (ferric ion-dominated) leachate [20–23]. Final leachate from the ferric ion-mediated leaching process results in polymetallic solutions and thus, a selective recovery of the desired metal (Cu) is mandatory. Cu recovery from the PCB leachates has been studied using different techniques such as solvent extraction, adsorption, electrolysis, and chemical precipitation. Metal sulfide precipitation (MSP) processes are useful, especially for selective recovery of metals from polymetallic leachates, and are also simple in operation and offer more stable precipitates than hydroxide precipitation [24,25].

Only very few manuscripts discussed the effect of $Fe^{3+}$ on leaching of Cu from other minerals, and except Yazici and Deveci [23], no other articles were found with respect to waste electrical and electronic equipment (WEEE) leaching (95% confidence level). Finally, to the best of the author's knowledge (95% confidence level), no other articles were found to investigate and discuss the effect of lixiviant concentration ($Fe^{3+}$) in the metal sulfide precipitation process. In the present study, selective Cu recovery from waste printed circuit boards was investigated. The ultimate aim of this study was to investigate Cu leaching characteristics and the selective recovery of Cu from the polymetallic leachate from PCBs. The parameters that influence leachability, such as (i) ferric sulfate concentration, (ii) pulp density and (iii) temperature, (iv) particle size, and (v) agitation were optimized for the maximum Cu leaching. Further in this study, selective copper sulfide recovery was also examined from the multimetallic PCB leachate. Important precipitation parameters such as (i) effect of initial lixiviant concentration and (ii) copper:sulfide ratios were also optimized for the maximum recovery of Cu from the leachate.

## 2. Materials and Methods

### *2.1. Samples*

PCB samples were collected from an E-waste recycling company located in Eindhoven, the Netherlands. The PCBs were cut into pieces and ground (size reduced to less than 2 mm in diameter) by using a cutting mill (SM 2000 mill, Retsch, Haan, Germany). The powdered PCBS were then sieved and sorted into three groups: (i) particle size less than 500 µm, (ii) particles sizes between 500 and 800 µm, and (iii) particles sizes between 800 and 2000 µm. Cu and precious metal contents of the powdered PCBs were determined with the help of Activation Laboratories Ltd (Actlabs, Ancaster, ON, Canada, which is ISO 17025 accredited and/or certified to 9001: 2008). The results are shown in Table 1.

**Table 1.** Cu and precious metals content of printed circuit boards (PCBs).

| Metals | Particle Size 0–500 µm | Particle Size 500–800 µm | Particle Size 800–2000 µm |
|---|---|---|---|
| Cu (wt. %) | 16.6 | 29 | 31.5 |
| Ag (ppm) | 2110 | 2840 | 1240 |
| Au (ppb) | 409,000 | 532,000 | 537,000 |
| Pd (ppb) | 61,100 | 82,300 | 38,700 |
| Pt (ppb) | 1400 | 1440 | 1130 |

### 2.2. Leaching Experiments

All the leaching studies were conducted in 100 mL Erlenmeyer flasks. The working volume was always maintained at 50 mL. Ferric sulfate (Merck, 97%) was used as the lixiviant. The factors influencing the leaching rate, such as (i) ferric sulfate concentration (10 ppm, 50 ppm, 100 ppm, and 1000 ppm), (ii) temperature (20 °C, 30 °C, and 40 °C, ±2 °C), (iii) agitation (75 rpm, 150 rpm, and 300 rpm), and (iv) pulp density (10 g·$L^{-1}$, 20 g·$L^{-1}$, 50 g·$L^{-1}$, and 100 g·$L^{-1}$) were studied. All the flasks (containing the lixiviant and the powdered PCBs) were agitated using a platform shaker (New Brunswick Digital Platform Shaker Innova 2100, Eppendorf AG, Hamburg, Germany). The samples were withdrawn at regular time intervals (15, 30, 60, 120, and 240 min) and analyzed for soluble metal (Cu) concentration by atomic absorption spectroscopy (AAnalyst 200, PerkinElmer, Waltham, MA, USA).

### 2.3. Copper Sulfide Precipitation

The PCB leachates were collected in glass beakers and filtered using 0.45 µm nitrocellulose filters to remove any suspended solids. The total metal concentrations (Cu and Fe) in the leachates were analyzed. MSP investigations were conducted in septum closed glass bottles. The effect of the lixiviant concentration was investigated in the 10 ppm to 1000 ppm ferric sulfate concentration range (at 1:10 and 1:5 Cu to sulfide molar ratio). 10 mL of the PCB leachates was transferred to an airtight glass bottle, followed by the addition of 10 mL of $Na_2S{\cdot}9H_2O$ solution. Prior to the addition of $Na_2S{\cdot}9H_2O$, the headspace was filled up by using $N_2$ gas to ensure anaerobic conditions. The glass bottles were placed in a platform shaker and agitated at 150 rpm at room temperature (20 ± 2 °C) for 60 min.

The influence of the copper to sulfide dosage was also studied by varying the concentration of soluble sulfide against copper concentration, therefore, soluble moles of copper to soluble moles of sulfide ratios of 1:1, 1:2, 1:3, 1:5, and 1:10 (at 100 ppm ferric sulfate leachate). After 60 min, the precipitate was separated from the leachate by filtration using 0.45 µm on nitrocellulose filters, and the precipitate free leachate was analyzed for soluble Cu and Fe concentration. The precipitates (i.e., copper sulfides) were subjected to scanning electron microscope–energy-dispersive X-ray spectroscopy analyses (SEM-EDS, JSM 6010LA, Jeol, Tokyo, Japan) at 10–20 KeV and high-vacuum conditions to understand about their elemental composition and surface morphology.

### 2.4. Analytical Methods and Statistical Analysis

All experiments were conducted in triplicates, the average was reported, and controls were also performed. Samples were filtered on 0.45 µm nitrocellulose filters and acidified using 5% $HNO_3$ prior to analyzing the soluble metals concentration using atomic absorption spectroscopy (AAnalyst 200, PerkinElmer, Waltham, MA, USA).

## 3. Results

### 3.1. Total Metal Concentration in the PCBs

The acid digestion results are presented in the Table 1. Table 1 clearly shows that different particle sizes contain different concentrations of metals, for instance Cu concentration of smaller particle size contained 16%, and larger particle size contained 32%. The acid digestion results also showed that the PCBs contain a high concentration of precious metals such as Ag (1240–2840 ppm), Au (409,000–537,000 ppb), Pd (38,700–82,300 ppb), and Pt (1130–1440 ppb) in the different particle sizes.

### 3.2. Optimization of Process Parameters that Influence Leaching

Various lixiviants such as mineral acids (sulfuric, nitric, and hydrochloric acids) and organic acids like acetic and citric acids and ferric salts (ferric chloride and ferric sulfate) were tested for their Cu-leaching efficiency from PCBs. Based on the initial results obtained, ferric sulfate was chosen as

the lixiviant and 4 h was chosen as the leaching time. Figure 1 shows the effect of particle size on the leaching rate of Cu from the PCBs. The results show that the particle size has a significant effect on the leaching of Cu from PCBs. When the particle size was lower, the leaching efficiency increased. For instance, when the particle size was 0–500 µm in size, the leaching efficiency was 67% after 4 h (50 mM ferric sulfate concentration, 20 °C, and 150 rpm) of leaching, but when the particle size was 500–800 µm and 800–2000 µm, the leaching efficiency was reduced to 43% and 29%, respectively, under the same conditions. Based on the results, particles with size 0–500 µm were found to be optimal particle size, and consequently used in all following experiments.

The effect of the agitation on the leaching rate of Cu from PCBs was studied by varying the agitation from 75 rpm to 300 rpm at room temperature (20 °C), containing a pulp density 10 g·L$^{-1}$ and 50 mM ferric sulfate for 4 h (Figure 2). An increase in agitation (75–300 rpm) resulted in an insignificant increase in the leaching efficiency of Cu from the PCBs (Figure 2). A 42% increase in leaching yield was observed when the agitation rate was increased from 75 rpm to 300 rpm. Figure 2 shows that 300 rpm could be the optimum agitation among the investigated range.

Figure 3 depicts the effect of the ferric sulfate concentration on the leaching of Cu. The ferric sulfate concentration and the leaching of Cu from PCBs were generally directly proportional. The Cu leaching yield from PCB was increased from 25% (±8%) to 99% (±6%) when the ferric sulfate concentration was varied from 10 mM to 1000 mM. The influence of pulp density was studied on the dissolution of Cu from PCBs by varying pulp density as 10, 20, 50, and 100 g·L$^{-1}$. Figure 4 illustrates the effect of pulp density on the leaching of Cu from PCBs (20 °C, 150 rpm, with 50 mM ferric sulfate concentration, for 4 h). Figure 4 reveals that the pulp density and the Cu leaching from PCBs were indirectly proportional. The leaching efficiency was decreased by 50% when pulp density was increased from 10 to 100 g·L$^{-1}$. The effect of temperature (in the range 20–40 °C) was not significant (<5% difference) on the leaching of Cu from the PCBs (data not shown). Based on the experimental results (Figures 1–4), 20 °C, 300 rpm, 100 mM ferric sulfate, and 1% solid-to-liquid phase ratio were selected as optimum conditions for the maximum leaching of Cu from PCBs, and the leaching time was extended to 24 h. The results disclose that more than 95% of Cu can be leached under these conditions (Figure 5).

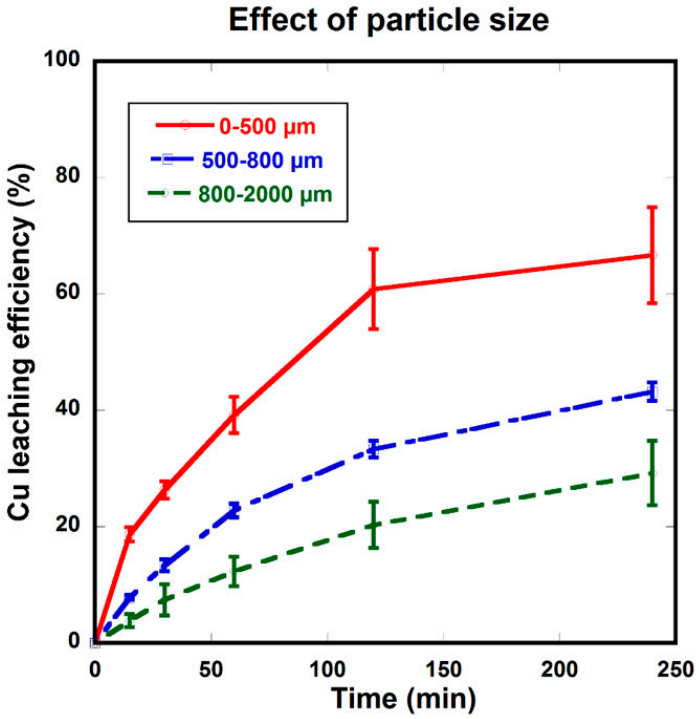



**Figure 1.** Effect of particle size (Ferric sulfate—50 mM, temperature—20 °C, agitation—150 rpm, and pulp density—10 g·L$^{-1}$).

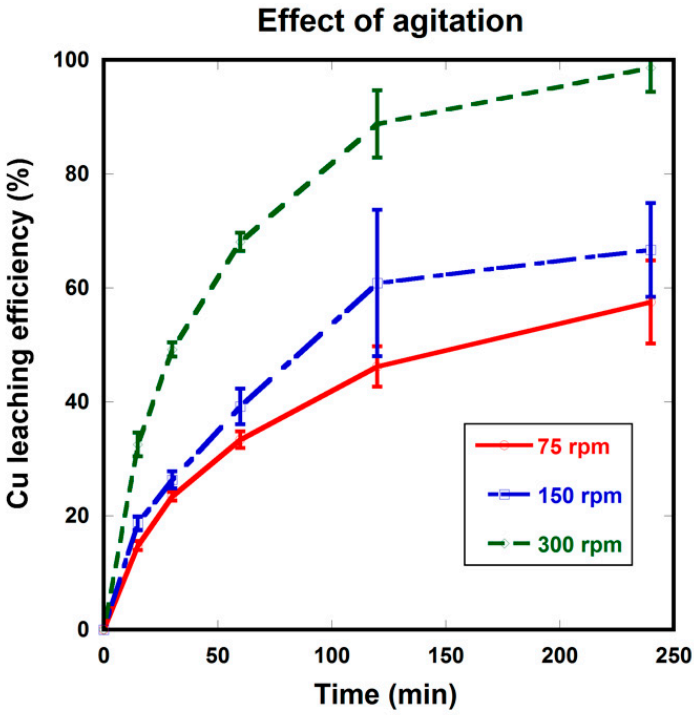



**Figure 2.** Effect of agitation (Ferric sulfate—50 mM, temperature—20 °C, and pulp density—10 g·L$^{-1}$).

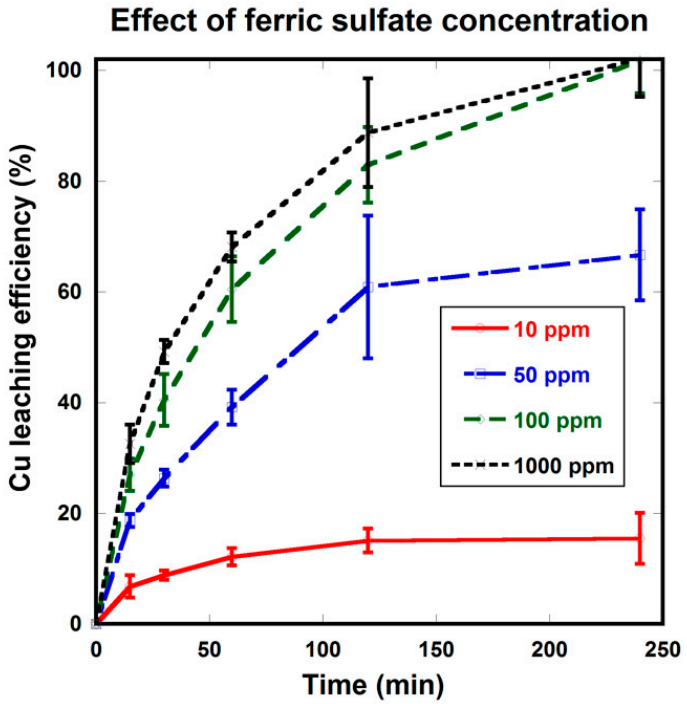



**Figure 3.** Effect of ferric sulfate concentration (Temperature—20 °C, agitation—150 rpm, and pulp density—10 g·L$^{-1}$).

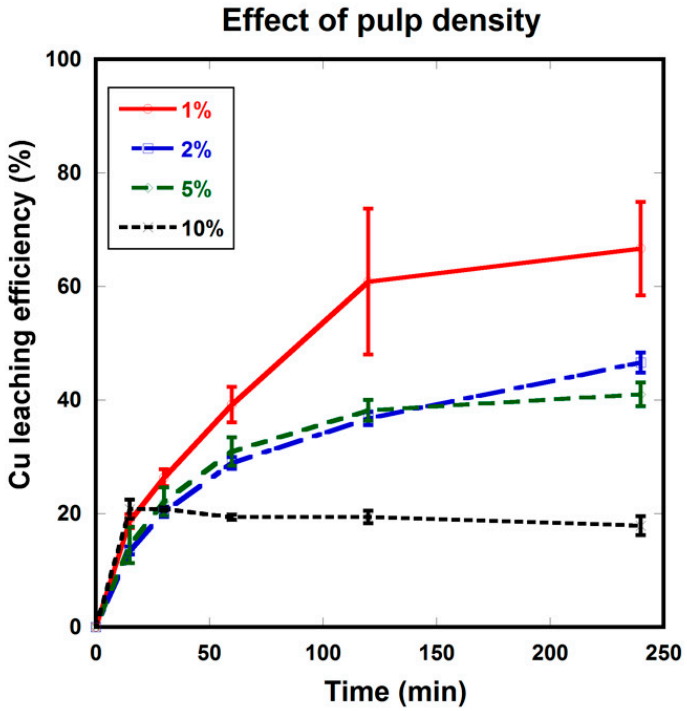



**Figure 4.** Effect of pulp density (Ferric sulfate—50 mM, Temperature—20 °C, and agitation—150 rpm).

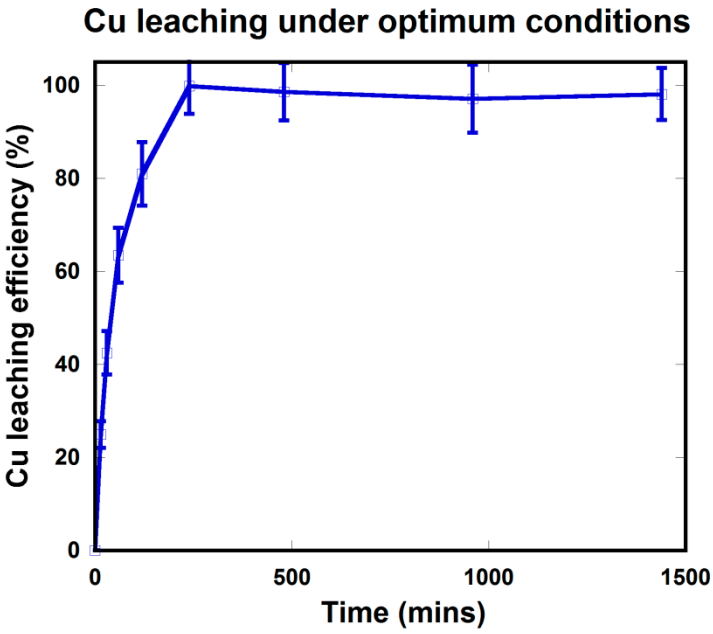



**Figure 5.** Leaching of Cu from PCBs under optimum conditions.

### *3.3. Copper Sulfide Precipitation*

The influence of the lixiviant concentration on the copper sulfide precipitation by dissolved sulfide is shown in Figure 6. It was observed that the more $Fe^{3+}$ concentration present in the leachate, the selective recovery of Cu from the leachate was less. For instance, when the $Fe^{3+}$ was 500–1000 ppm in the leachate, the copper sulfide precipitation was as low as 0%–25%, along with 1%–7% of Fe co-precipitation. Figure 6 states that over 98% of the soluble Cu can be precipitated from 100 ppm ferric sulfate mediated leachate. Approximately 5% of Fe is also found precipitating alongside at this ferric sulfate concentration. At slightly higher $Fe^{3+}$ concentration (330 ppm), the Cu precipitation efficiency

is high (>98%), but higher Fe co-precipitation (13 (±3) %) was also observed. Hence, 100 ppm ferric sulfate leachate was chosen for further copper:sulfide dosage optimization studies.

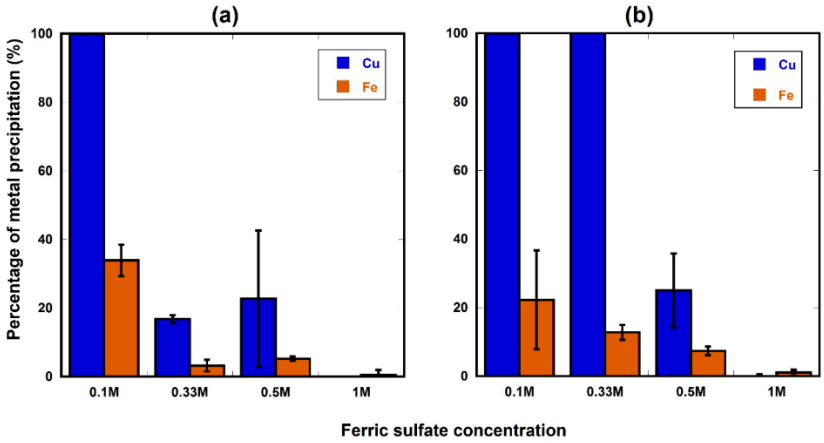



**Figure 6.** Effect of ferric sulfate concentration on copper sulfide precipitation. (**a**) Copper to sulfide ratio—1:5 and (**b**) Copper to sulfide ratio—1:10.

Figure 7 shows the influence of the copper to sulfide dosage ratio on the selective copper recovery. Copper to sulfide molar ratios of 1:1; 1:2; 1:3, 1:5, and 1:10 were studied. The results showed that more than 98% of Cu could be precipitated at a molar ratio of 1:3 of copper to sulfide. Additionally, 5 (±1) % of Fe was also co-precipitating in parallel. On the other hand, 73%–77% of Cu could be precipitated with no detectable level of Fe co-precipitation. At higher copper sulfide molar ratios (1:5 and 1:10), maximum copper sulfide precipitation was observed, however Fe co-precipitation was also found at higher levels. The copper sulfide precipitation process was so quick that in less than a minute most of the soluble Cu was precipitated. The precipitation studies were also conducted for 24 h, and it was observed that there was no or less dissolution of the precipitated copper sulfide.

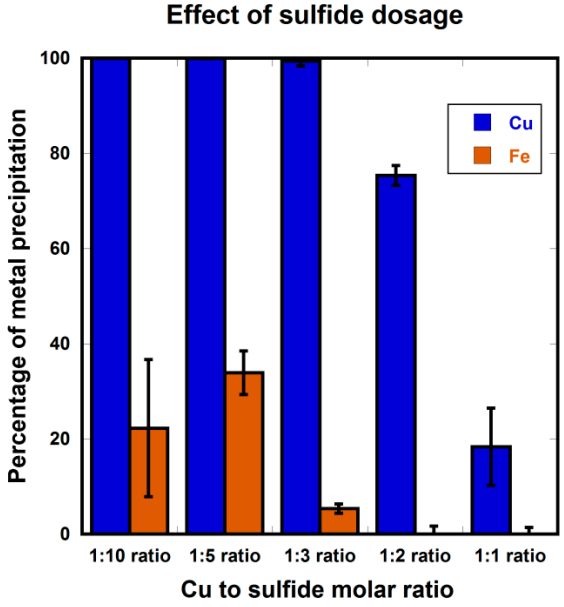



**Figure 7.** Effect of sulfide dosage on copper sulfide precipitation.

### *3.4. Characteristics of Precipitated Copper Sulfide*

SEM-EDS image of the CuS precipitate (precipitated at an initial pH 1.0–2.0, 100 mM of $Fe^{3+}$ (lixiviant) concentration, and 1:3 copper to sulfide molar ratio) is shown in Figure 8. It can be seen from

the EDS analysis that the precipitate mainly contained copper and sulfide and some traces of iron. EDS quantification also revealed that the precipitate contained 20% (±11%) of Cu, 18% (±12%) of S, and 8% (±2%) of Fe (data not shown), and the rest was constituted by carbon and oxygen. The precipitate was black in color.

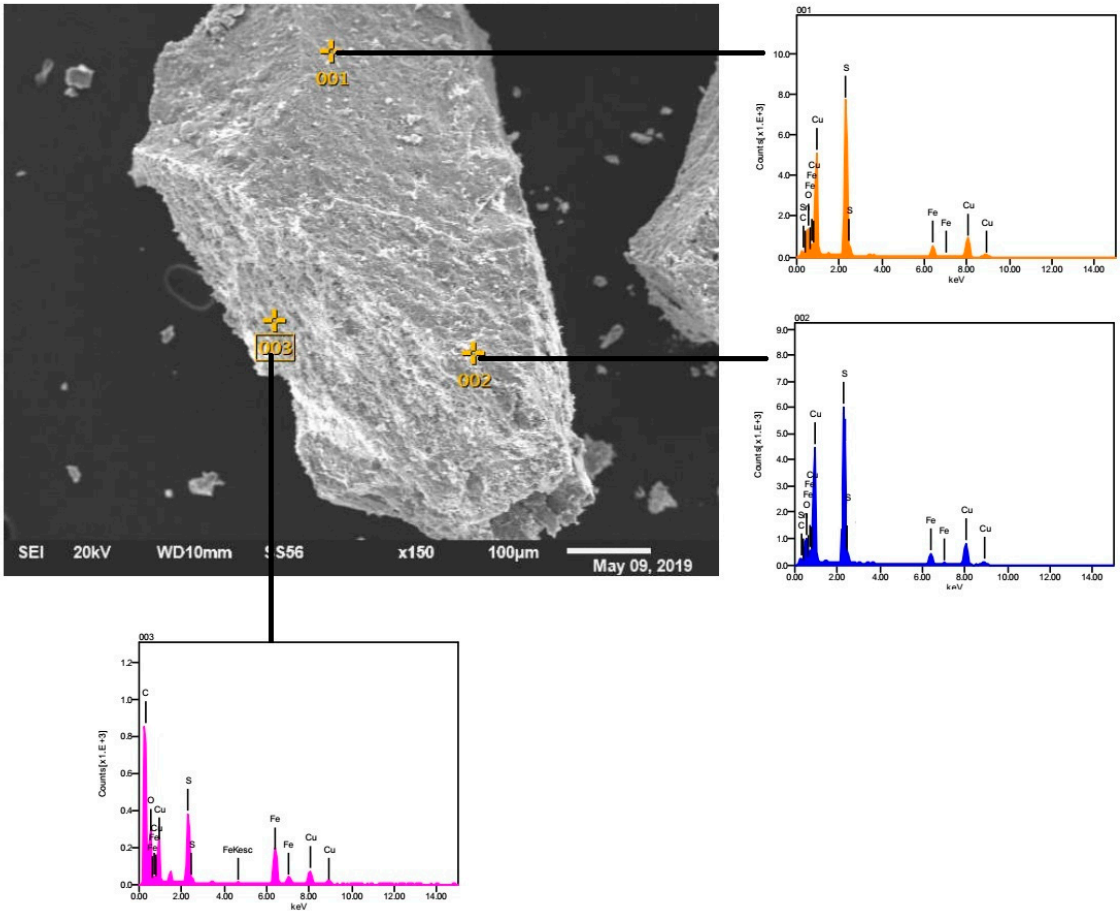



**Figure 8.** Scanning electron microscope–Energy dispersive X-ray spectroscopy (SEM-EDS) spectra of copper sulfide precipitate.

## 4. Discussion

### *4.1. PCB–Secondary Source for Copper Production*

This study demonstrated that PCBs can be used as an alternative feed stock for Cu production. Hydrometallurgical flow route (Figure 9) resulted from this study, showing that Cu can be selectively recovered from PCBs as copper sulfide. These PCBs can be hydrometallurgically reprocessed and can be used as a potential secondary resource for Cu production. Thereby, the depletion of Cu primary ores can be addressed. Under optimum conditions (20 °C, 10 g·L$^{-1}$ pulp density at 300 rpm), 169 (±10) g·kg$^{-1}$ of Cu could be leached from the PCBs by 100 mM ferric sulfate within 4 h. Further, a maximum of 91% of the total Cu content (152 (±8) g·kg$^{-1}$ of Cu) could be recovered as copper sulfides from the PCB ferric sulfate leachates (Figure 7). The copper sulfide precipitation results from the PCB leachates were very much in agreement with those from other PCB leachates [18,26], synthetic polymetallic solutions [27], multimetallic acid mine drainage [28,29], and metallurgical residue leachates [30].

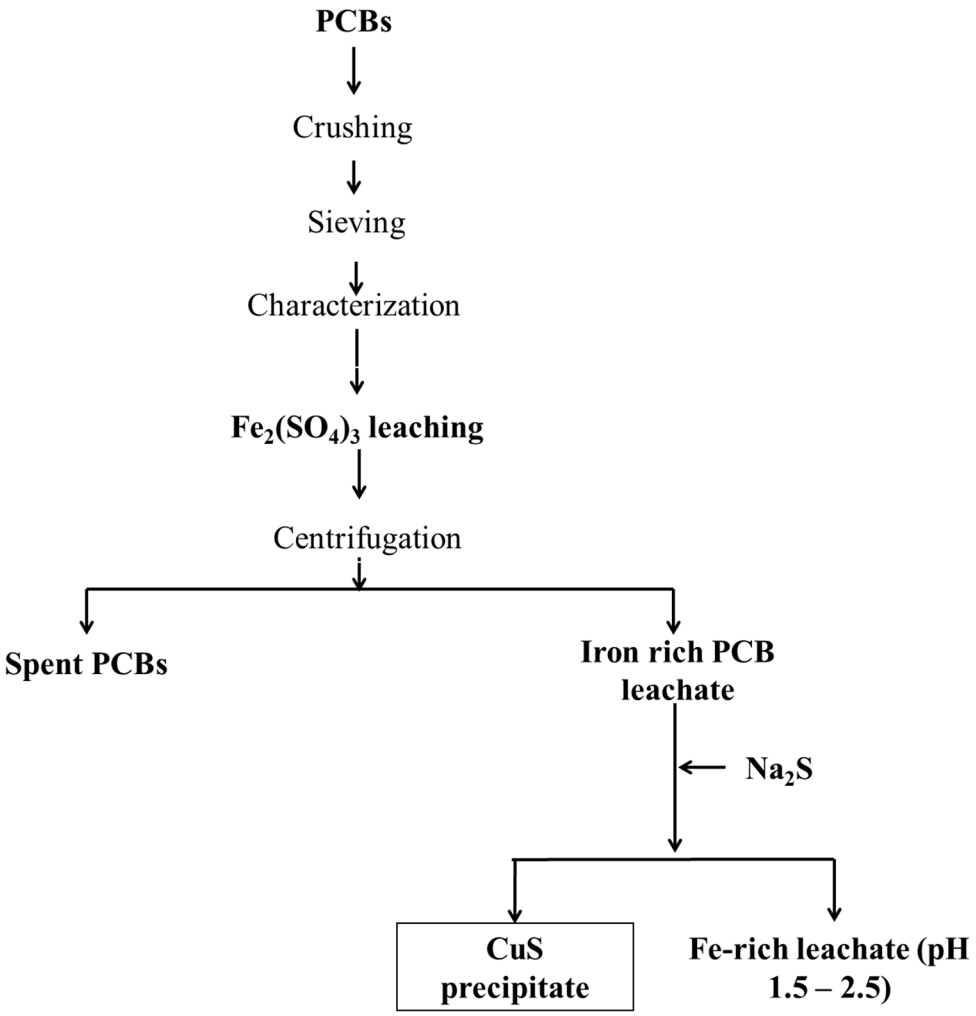



**Figure 9.** Hydrometallurgical flow chart for the selective recovery of Cu from PCBs.

*4.2. Cu Leachability from PCBs*

The results of the study revealed that more than 98% of Cu can be leached from PCBs by ferric sulfate. XRD analysis of powdered PCBs by Işıldar et al. [18], revealed that PCBs contain metallic Cu phase as the major mineral. Hence, Cu leaching by ferric sulfate from PCBs can be explained by Equation (1):

$$Cu^0 + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 \quad (1)$$

Particle size is an important factor in the leaching of Cu from PCBs. The decrease in the Cu leaching rate with an increase in particle size (Figure 1) can be explained by the decrease in the surface area for the leaching reaction. It can be speculated that the mass transfer (of Cu from PCBs) is diffusion-controlled from the linear relation between Cu leaching and agitation speed (Figure 2). The variation in temperature (20–40 °C) did not affect the leaching of Cu significantly (data not shown). However, Yazici and and Deveci [23] reported that Cu leaching efficiency from PCBs is increasing at higher temperatures (40–80 °C) than investigated in this study, which in turn leads to high energy usage and makes the process expensive.

Lixiviant (ferric ion) concentration is another important parameter that could influence Cu leachability from the PCBs. Higher lixiviant concentration ensures higher leachability of Cu, because of the abundant $Fe^{3+}$ that could solubilize more Cu from the PCBs. However, higher ferric ion in the leachate could be a problem in the selective recovery of Cu. The results were comparable with the findings of Yazici and Deveci [23]. But Yazici and Deveci [23] also used acidic ferric sulfate (i.e., $H_2SO_4$

in combination $Fe_2(SO_4)_3$) and found out that 500 ppm of acidic ferric sulfate could leach a maximum of 99% of Cu within 120 min. However, in the present study, a similar leaching efficiency was observed at even lower ferric sulfate concentration (100 ppm) but at longer leaching time (240 min).

The solid-to-liquid ratio is one of the important parameters which influence Cu leaching from PCBs. The decrease in leaching efficiency of Cu (Figure 4) with respect to increase in solid-to-liquid ratio could be attributed by the lower availability of ferric ions. Based on the stoichiometry of the Equation (1), it can be calculated that 0.1 mM of ferric sulfate could leach out all the 16.6% (by wt. %) of Cu from PCB at 1% pulp density. Also, theoretically 0.2 mM, 0.5 mM, and 1 mM of ferric sulfate could leach all the Cu present in the PCBs at pulp densities 2%, 5%, and 10%, respectively. But the experimental data revealed that 100 mM of ferric sulfate was needed to leach out more than 95% of Cu from 1% pulp density. The difference in the theoretical value and the experimental data could be because of the fact that the PCB not only consists of Cu, but also other metals (like, Fe, Ni, Au, Ag, Pt, and Pd) and other plastic fractions. So, the amount of ferric sulfate added to the PCB will be reacting with Cu and also the other metals and plastics, which in turn leads to the consumption of more ferric sulfate than the theoretical value. pH was also witnessed to increase at higher pulp densities (50 $g{\cdot}L^{-1}$ and 100 $g{\cdot}L^{-1}$). This pH increase might be because of the PCBs high buffering capacity, which in turn results in a decrease in Cu leaching. The decrease in Cu leaching by ferric ions (biogenic ferric and chemical ferric ions) from PCBs with respect to pulp density was also observed in many previous instances [18,23].

### *4.3. Selective Cu recovery from PCB Leachates*

This study demonstrated a proof of concept of selective recovery of Cu (as sulfide precipitate) from PCBs. Lixiviant concentration and pH were found to be the important parameters in copper sulfide precipitation (Figures 6 and 7) [31]. Selective copper sulfide precipitation mostly occurs in the acidic pH range (0.5 to 1.5) [27,30–32]. It can be observed from Figure 7 that more than 98% of soluble Cu can be selectively precipitated at a copper sulfide molar ratio 1:3 (100 ppm ferric sulfate leachate). But, a trace amount of Fe (5%) was also co-precipitating (along with Cu) at this 1:3 molar ratio. On the other hand, no such Fe co-precipitation was witnessed at lower molar ratios of 1:2 and 1:1, but the copper sulfide precipitation was also less. Işıldar et al. [18] reported more than 90% of copper sulfide precipitation at a molar ratio of 1:1 from PCB bioleachates that contained a high concentration of Fe. Hu et al. [26] also reported more than 99% of Cu (and 7% of Fe) could be precipitated from PCB sludge using sulfide precipitation at a molar ratio of 1:0.7. The difference of copper sulfide precipitation efficiency reported in this study and Işıldar et al. [18], could be due to the oxidation state of Fe in the leachate. Energy-dispersive X-Ray spectroscopy analyses (data not shown) also stated that the precipitates mainly consisted of copper and sulfur. Based on the redox state of Cu, copper sulfides are often observed as either covellite (CuS) and/or chalcocite ($Cu_2S$). However, anilite ($Cu_{1.75}S$) and djurleite ($Cu_{1.96}S$) are some other possible crystalline copper sulfides [33]. Most of the copper sulfide precipitation (more than 90%) was observed within 5 min of sulfide addition, and no or less re-dissolution of the formed precipitates was witnessed, even after 24 h (data not shown).

## 5. Conclusions

This study shows that printed circuit boards can be used as a secondary resource for Cu metallurgy. The PCB is polymetallic, rich in Cu (17%), and also contains significant concentrations of precious metals such as Ag, Au, Pd, and Pt. Ferric sulfate leaching was found to be the best lixiviant among the chemicals investigated. Ferric sulfate was able to leach more than 98% of Cu from the PCBs. There was a high 98% of selective recovery of the leached Cu (as copper sulfide) at a copper/sulfide molar ratio of 1:3, initial pH 1.0–2.0, and with 100 ppm of ferric sulfate concentration. Copper could be selectively precipitated as copper sulfide, which can be further pyro/hydrometallurgically processed to produce Cu metal.

**Author Contributions:** Conceptualization, M.S. and E.D.v.H.; methodology, M.S.; validation, M.S.; formal analysis, M.S.; investigation, M.S.; resources, M.S. and E.D.v.H.; data curation, M.S. and E.D.v.H.; writing—original draft preparation, M.S.; writing—review and editing, E.D.v.H.; visualization, M.S.; supervision, E.D.v.H.; project administration, E.D.v.H.; funding acquisition, M.S. and E.D.v.H.

**Funding:** The authors would like to thank the funding agencies European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No 606838.

**Acknowledgments:** The authors would like to thank Sims Recycling Solutions, the Netherlands for generously providing the PCB samples required for this research.

**Conflicts of Interest:** The authors declare no conflict of interest.

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