# Development of Innovative and Sustainable Methodologies Applied To the Recovery of Gold and Critical Elements in Integrated Circuit Boards

**Lídia Cunha[1,2]\*, Joana Monteiro[1,2], Andreia Azevedo[1], Aurora Futuro[1,2], José Soeiro[1,2], Rui Sousa[1,2]**
[1]Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2]CERENA—Polo FEUP—Centre for Natural Resources and the Environment, Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal
*\*Corresponding authors: Lídia Cunha, E-mail: up20140672@fe.up.pt*

**Abstract -** This study aimed to present the physical and hydrometallurgy processes using an eco-friendlier leaching method to extract iron (Fe), copper (Cu), zinc (Zn), gold (Au) and silver (Ag) from wasted printed circuit boards (PCBs). The physical processing study allowed to obtain a sample manly composed of metals to proceed with the hydrometallurgical process. For the hydrometallurgical process, selective leaching was studied, and the optimized results for the 1st and 2nd steps will be presented. In the 1st step, it was possible to extract the most amount of Fe, more than 80%, with a low extraction of Cu. In the 2nd step, the remaining Cu (>80%) was extracted. Au and Ag present unique properties, such as electrical conductivity and high resistance to corrosion, making them ideal candidates for electrical devices. Last years, electronic waste (e-waste) has grown significantly, with a large portion ending up in landfills, including spent PCBs that contain these valuable metals. Therefore, a study of the 3rd leaching step will be presented to extract Au and Ag from PCBs. Preliminary results demonstrate that it is possible to extract 54% of Au and 55% of Ag using thiourea and Fe (III).

**Keywords**: electronic waste, printed circuit boards, physical processing, iron extraction, copper extraction, gold extraction, silver extraction, green leaching.

## 1. Introduction

E-waste is one of the fasted-growing wasted segments in the world. Each year, approximately 50 million tonnes of e-waste is produced, and only 20% is formally recycled [1]. By this way the e-waste will more than double by 2050, to 120 million tonnes annually. One of the most valuable and complex components in e-waste is PCBs.

PCBs contain high concentrations of precious, and critical metals compared to primary mining deposits.

Cu, Fe and Zn are the most representative metals [2,3]. The connectors and contact points are mainly composed of Au and Ag due to their high electrical conductivity and corrosion resistant properties [4,5]. PCBs have Au concentrations nearly 100 times higher than those found in natural ore [6]. In 2018, it was estimated that 9533 tons of Ag were used in the electronic industry. Despite Au and Ag not being the most abundant metals in PCBs, as visualized in Table 1, they are the most valuable. For example, in 2022, it was estimated that $15 billion worth of Au was embedded in e-waste [7].

Additionally, recovering Au it would reduce the environmental and societal impact of mining, along with potential savings of 17 000 tons per ton in carbon dioxide emissions [8]. Therefore, due to the low abundance of these metals in ores, connected with the economic and social issues associated with mining and separation operations, PCBs are a potential source for Au and Ag recovery.

**Table 1** Precious metals content in PCBs.

| | Precious metal content of PCB (mg/ kg) | | | Reference |
|---|---|---|---|---|
| | **Au** | **Ag** | **Pd** | |
| **Mobile phone** | 1500 | 3800 | 300 | [2,9] |
| **Television** | 250 | 500 | - | |
| **Laptop** | 240 | 570 | 150 | [2,3,10,11] |

The commonly used processes for its extraction are cyanidation and aqua regia, which are toxic reagents harmful to humans and the environment [4,12]. In order to overcome these disadvantages, recent literature suggests the thiourea leaching process as a greener hydrometallurgical process.

The focus of the present research was divided in two phases as visualized in Figure 1. The first stage involved the disassembly and mechanical processes to liberate and separate the metallic parts from PCBs, resulting in a metallic-enriched product for the subsequent hydrometallurgical process. In the second stage, the hydrometallurgy process was divided in three steps (selective leaching), where reagents with less environmental impact and high extraction rates were studied. The results for the optimized conditions of the 1st and 2nd steps will be presented, with a significant amount of Fe being extracted in the 1st step and a high content of Cu in the 2nd step. For the extraction of these metals, the traditional reagents used are hydrochloric acid (HCl) and nitric acid (HNO3) due to their efficiency and fast dissolution rates [13,14]. However, due to their high corrosion potential, which cause equipment damage in large-scale operations, and their negative impact on the environment, a sulfuric acid ($H_2SO_4$) - hydrogen peroxide ($H_2O_2$) system was used to overcome these drawbacks [15,16].

The 3rd leaching step involves the extraction of Au and Ag using thiourea leaching. The main reason for its lack of application at an industrial level is the excessive consumption because of its fast decomposition [4]. Therefore, preliminary experiments will be presented in order to understand the thiourea and Fe (III) effect on the extraction of Au, as well as Ag.
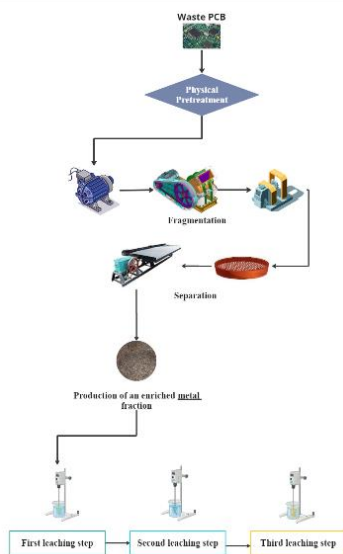


**Figure 1** PCBs physical and hydrometallurgical processing.

## 2.    Details experimental

### 2.1. Materials

The PCBs samples were obtained from André Redondo Gouveia Unipessoal Lda (ARG). H2SO4 95-98% (batch 0002307670) from PanReac AppliChem (ITW Reagents). H2O2 30% brought from VWR Chemicals (batch 22A254127). Thiourea, 99%, extra pure (lot A0325071) from Acros Organics. Fe (III) sulfate hydrate, reagent grade (lot N10G016) brought from Alfa Aesar. HNO3 70% pure, in water purchased from Thermo Scientific.

## 2.2 Equipment

Samples separator (PT 100), griding mill and sieves from Retsch company. Shredder acquired from Erdwich company. Overhead stirrer from Hei-TORQUE 100. Chemical analysis of Fe, Cu, Zn, Au and Ag were performed by atomic absorption in an Analityk Jena ZEEnit70 equipment. The control of pH of the experiments was carried by a meter from the Metrohm company (model 913 pH Meter). X-ray fluorescence (XRF) equipment from the Oxford Instruments.

## 2.3 Procedure
## 2.3.1 Samples preparation

The PCBs samples were transformed into small pieces using a guillotine. After using the shedder, they were subjected to a griding mill to liberate the plastic matrix and achieve a significant size reduction. The samples with sizes between 2.36/0.106 mm were separated using a shaking table. This allowed for the separation of concentrates from the middle and tailings samples. The concentrated samples, which are mainly composed of metal fractions, were then subjected to XFR analysis. The schematic process for obtaining the required samples to perform the leaching experiments is presented in **Error! Reference source not found.**.
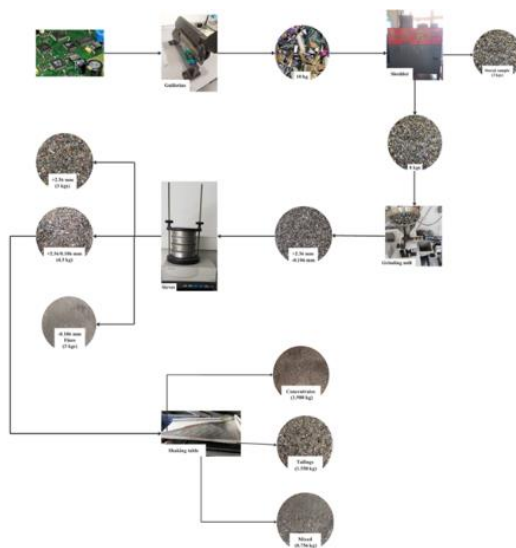


**Figure 2** Schematic representation of the samples preparation

## 2.3.2 1st and 2nd leaching step

The 1st and 2nd leaching process was conducted using 3M $H_2SO_4$ and 4M of $H_2O_2$ under the same operating conditions. Subsequently, the mixture was filtered using a vacuum filter, and the leachate was analyzed for Fe, Cu, and Zn using the AAS. The remaining residue was digested with aqua regia for instrumental reading, allowing the re-calculation of the initial Cu, Fe and Zn concentration in the feed.

## 2.3.3 3rd leaching step

Four experiments were conducted using thiourea, Fe (III), and $H_2SO_4$. As visualized in Table 2, the concentrations of the reagents and the S/L ratio varied. All experiments were performed at a stirring speed of 900 rpm and a leaching time of 3h. Subsequently, the mixture was filtered using a vacuum filter, and the leachate was analyzed for Au and Ag using the AAS. The remaining residue was digested with aqua regia for instrumental reading, to execute the re-calculation of the initial Au and Ag concentration.

**Table 2** Experimental Au leaching.

| Experiment | Thiourea | Fe (III) | $H_2SO_4$ | Ratio S/L |
|------------|----------|----------|-----------|-----------|
| | | **M** | | |
| **1** | 0.52 | 0.214 | 0.22 | 1/10 |
| **2** | 0.52 | 0.214 | 0.22 | 1/7 |
| **3** | 0.26 | 0.214 | 0.22 | 1/10 |
| **4** | 0.52 | 0.107 | 0.11 | 1/10 |

## 3.    Results and discussion
### 3.1 Samples preparation

Table 3 presents the metal distribution in these products obtained by XRF analysis. The shaking table was used for the fraction 2.36/0.106 mm to separate the metals by density to obtain a final sample containing only metals without any plastic material. This method allows for the separation of three products: concentrates (high density), middles (intermediate density), and tailings (low density). As expected, the concentrates contain a significant amount of Cu (93%), as this metal is the primary electric current conductor [17], and of Zn (94%), Fe (83%), Sn (97%), Pb (98%), Ni (99%) and Ag (81%).

**Table 3** Metal distribution of the obtained samples from the shaking table.

| Wilfley Shaking Table | Cu | Fe | Zn | Ag | Au |
|-----------------------|----|----|----|----|----|
| | | | **%** | | |
| **Concentrates** | 93 | 83 | 94 | 81 | 0 |
| **Middling** | 5 | 4 | 1 | 19 | 33 |
| **Tailings** | 2 | 13 | 5 | 0 | 67 |

Figure 3 illustrates the concentrate from the physical processing, which will proceed to the hydrometallurgical process, where it is possible to visualize its very heterogenous nature.



**Figure 3** Concentrate obtained from the physical processing.

## 3.2 1st and 2nd leaching Step

The main importance of extracting Fe and Cu is to avoid interfere with the extraction of Au and Ag. As visualized in Figure 4A, a green leaching solution was obtained from the 1st step, which may indicate the predominant presence of Fe.

In the 2nd step, as observed in Figure 4B, the blue leaching solution indicates the presence of Cu.

In both steps, an extremely acid solution resulted. In the 1st leaching step, the Eh values are lower compared to the 2nd step, which maintains values higher than 650 mV.

In the 1st step, it was possible to extract the most content of Fe (>80%) with a low extraction of Cu and Zn.

In the 2nd step, approximately 50% of Zn was extracted, along with more than 80% of Cu. Therefore, the aim of these leaching steps was achieved, obtaining a final Cu-enriched solution.



**Figure 4** Leaching solutions from **A)** 1st step **B)** 2nd step.

## 3.3 3rd leaching step

In the previous steps, the operating conditions are optimized, but the 3rd leaching step is still under study. Therefore, the preliminary results for this section will be presented. In Figure 5A, it is possible to visualize the PCBs used for the 3rd leaching step, and in Figure 5B, the final PCBs residue obtained, which consisted of powder. After the filtration, a yellow solution was obtained as shown in Figure 5C.
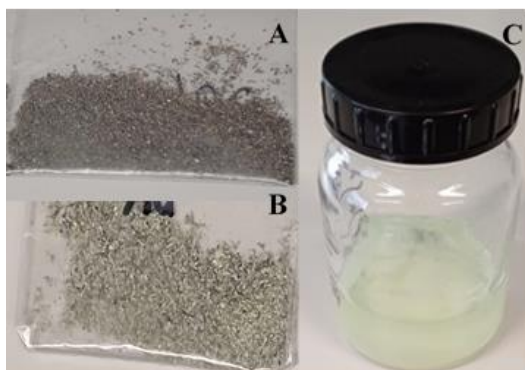


**Figure 5** Residue obtained from: **A)** 2nd step, **B)** 3rd step; **C)** Au leaching solution.

The pH and Eh of the four experiments were measured, as visualized in Figure 6. For pH, there was no significant difference, as most values were near 2 despite the variation in reagent concentrations and the S/L ratio. However, in experiment 1, the pH was around 2.5, where the highest reagent concentrations and S/L ratio were used. In the case of Eh, experiment 3 had the highest value, corresponding to an S/L ratio of 1/10 and the lowest regent concentrations. Further experiments need to be executed in order to understand the effects of the operating process on the pH and Eh during the leaching.
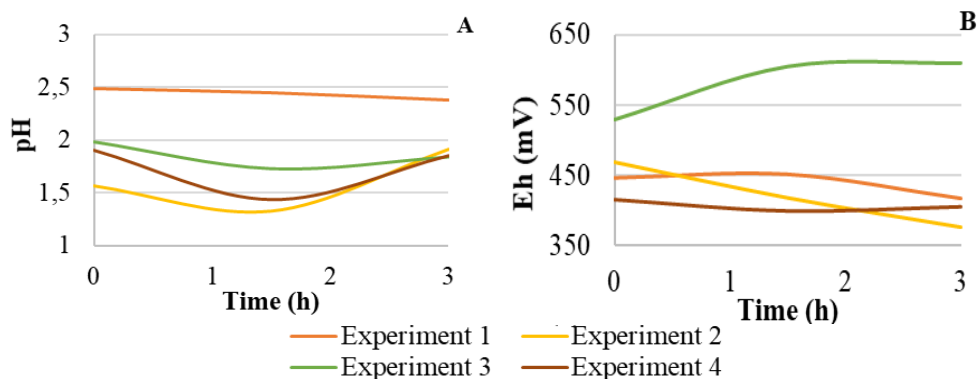
**Figure 6** pH and Eh variation during 3h of leaching time.

As visualized in Figure 7, for experiment 1, using the highest reagents concentration and a S/L ratio of 1/10 48% of Au and 61% of Ag were extracted.

In experiment 2, where the same reagent concentrations were used but with a lower S/L ratio (1/7) compared to experiment 1, a lower extraction of Au (44%) and Ag (52%) was obtained. Therefore, for the subsequent experiments, the S/L ratio of 1/10 was fixed, and the concentrations of other reagents were varied to study their impact on the extraction rates.

In experiment 3, where the thiourea concentration was decreased from 0.52M to 0.26M, the lowest extraction rates were obtained, 25% for Au and 10% for Ag.

For experiment 4, the concentration of Fe (III) was reduced from 0.214M to 0.107M, and $H_2SO_4$ from 0.22M to 0.11M. Under these operating conditions, it was possible to increase the Au extraction from 48% to 54%. However, the Ag extraction decreased from 61% to 55%.

Towards this end, these preliminary results suggest that using 0.52M of thiourea and a lower concentration of Fe (III) at 0.107M may lead to higher Au extraction. On the other hand, the highest Ag extraction rate was in experiment 1, where the highest reagent concentrations were used, suggesting that a higher level of thiourea and Fe (III) may lead to more Ag extraction rates. Therefore, further studies need to be performed in order to study in more detail the impact of Fe (III) as a catalyst in the reaction.
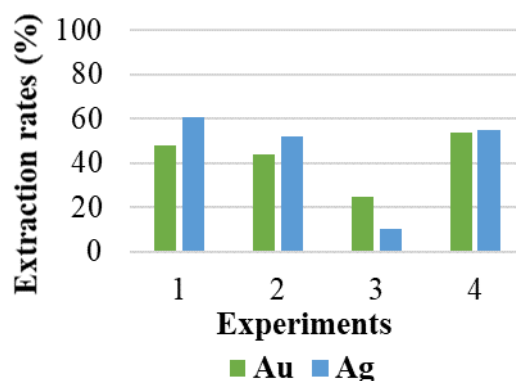


**Figure 7** Extraction rates of Au and Ag from the 3ʳᵈ leaching step.

Additionally, XRF analysis of the leaching solution from experiment 4 was executed. As expected, it is possible to visualized in Figure 8, the Au and Ag presence.
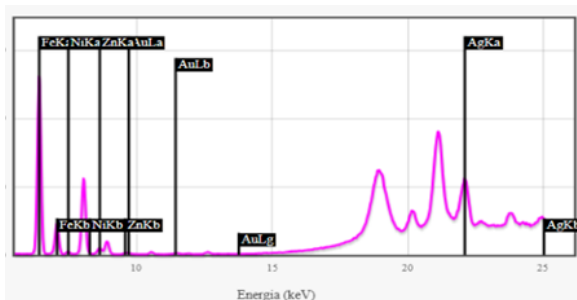


**Figure 8** XRF analysis of the leaching solution of experiment 4.

## 4. Conclusion

The physical processing method allow to obtain an enriched-metal product composed of various metals.

The heterogenous PCBs material requires selective leaching. The obtained results indicate that it is feasible to extract different metals from PCBs.

The 1$^{st}$ step allowed for the extraction of Fe at more than 80% and 20% of Zn, and the 2$^{nd}$ step resulted in a significant amount of Cu (>80%) and approximately 50% of Zn.

PCBs are an attractive source for Au and Ag extraction. The leaching performed indicates that a greener leaching approach could be feasible for extracting Au and Ag from PCBs. Until the moment, thiourea, Fe (III), and $H_2SO_4$, along with varying the S/L ratio, have been experimentally studied. The preliminary results demonstrate that these parameters significantly affect leaching efficiency. The highest Au extraction rate was obtained using 0.52M of thiourea, 0.107M of Fe (III), 0.11M of $H_2SO_4$ for an S/L ratio of 1/10, resulting in 54% of Au and 55% of Ag.

Towards this end, as future work, to understand thiourea decomposition and ensure the maximum concentration of active species available for leaching, the influence of thiourea and Fe (III) will be further studied. Additionally, experiments will be conducted at a pH close to 1, as literature suggests that this pH can improve Au extraction rates, along with other parameters such as an S/L ratio of 1/20, stirring speed, and leaching time. Triplicates for the optimized operating conditions will be performed.

## References

1. *A New Circular Vision for Electronics Time for a Global Reboot*; 2019;
2. Hsu, E.; Barmak, K.; West, A.C.; Park, A.H.A. Advancements in the Treatment and Processing of Electronic Waste with Sustainability: A Review of Metal Extraction and Recovery Technologies. *Green Chemistry* 2019, *21*, 919–936.
3. Priya, A.; Hait, S. Characterization of Particle Size-Based Deportment of Metals in Various Waste Printed Circuit Boards towards Metal Recovery. *Cleaner Materials* 2021, *1*, doi:10.1016/j.clema.2021.100013.
4. Ray, D.A.; Baniasadi, M.; Graves, J.E.; Greenwood, A.; Farnaud, S. Thiourea Leaching: An Update on a Sustainable Approach for Gold Recovery from E-Waste. *Journal of Sustainable Metallurgy* 2022, *8*, 597–612.

5.  Mishra, G.; Jha, R.; Rao, M.D.; Meshram, A.; Singh, K.K. Recovery of Silver from Waste Printed Circuit Boards (WPCBs) through Hydrometallurgical Route: A Review. *Environmental Challenges* 2021, *4*.

6.  Rao, M.D.; Singh, K.K.; Morrison, C.A.; Love, J.B. Recycling Copper and Gold from E-Waste by a Two-Stage Leaching and Solvent Extraction Process. *Sep Purif Technol* 2021, *263*, doi:10.1016/j.seppur.2021.118400.

7.  Ruediger Kuehr, S.U.; David Hirsch, I.; Terry Collins Global E-Waste Monitor 2024: Electronic Waste Rising Five Times Faster than Documented E-Waste Recycling.

8.  Doidge, E.D.; Carson, I.; Tasker, P.A.; Ellis, R.J.; Morrison, C.A.; Love, J.B. A Simple Primary Amide for the Selective Recovery of Gold from Secondary Resources. *Angewandte Chemie* 2016, *128*, 12624–12627, doi:10.1002/ange.201606113.

9.  Mao, S.; Kang, Y.; Zhang, Y.; Xiao, X.; Zhu, H. Fractional Grey Model Based on Non-Singular Exponential Kernel and Its Application in the Prediction of Electronic Waste Precious Metal Content. *ISA Trans* 2020, *107*, 12–26, doi:10.1016/j.isatra.2020.07.023.

10. Tecchio, P.; Ardente, F.; Marwede, M.; Clemm, C.; Dimitrova, G.; Mathieux, F. Analysis of Material Efficiency Aspects of Personal Computers Product Group.; 2018.

11. Van Yken, J.; Boxall, N.J.; Cheng, K.Y.; Nikoloski, A.N.; Moheimani, N.R.; Kaksonen, A.H. E-Waste Recycling and Resource Recovery: A Review on Technologies, Barriers and Enablers with a Focus on Oceania. *Metals (Basel)* 2021, *11*.

12. Munganyinka, J.P.; Habinshuti, J.B.; Komadja, G.C.; Uwamungu, P.; Tanvar, H.; Ofori-Sarpong, G.; Mishra, B.; Onwualu, A.P.; Shuey, S. Optimization of Gold Dissolution Parameters in Acidified Thiourea Leaching Solution with Hydrogen Peroxide as an Oxidant: Implications of Roasting Pretreatment Technology. *Metals (Basel)* 2022, *12*, doi:10.3390/met12101567.

13. Barnwal, A.; Dhawan, N. Recycling of Discarded Mobile Printed Circuit Boards for Extraction of Gold and Copper. *Sustainable Materials and Technologies* 2020, *25*, doi:10.1016/j.susmat.2020.e00164.

14. Wu, C.; Awasthi, A.K.; Qin, W.; Liu, W.; Yang, C. Recycling Value Materials from Waste PCBs Focus on Electronic Components: Technologies, Obstruction and Prospects. *J Environ Chem Eng* 2022, *10*.

15. Trinh, H.B.; Kim, S.; Lee, J. Selective Copper Recovery by Acid Leaching from Printed Circuit Board Waste Sludge. *Metals (Basel)* 2020, *10*, doi:10.3390/met10020293.

16. Hao, J.; Wang, X.; Wang, Y.; Wu, Y.; Guo, F. Optimizing the Leaching Parameters and Studying the Kinetics of Copper Recovery from Waste Printed Circuit Boards. *ACS Omega* 2022, *7*, 3689–3699, doi:10.1021/acsomega.1c06173.

17. Cui, H. *Hydrometallurgical Treatment of E-Scrap*; 2018.