Importance of chemical pretreatment for base metals remotion and its effect on the selective extraction of gold from Printed Circuits Boards (PCBs)

Importancia del pretratamiento químico para la remoción de metales base y su efecto en la extracción selectiva de oro de tarjetas de circuito impreso (PCBs)

B. Segura-Bailón*, G. Lapidus-Lavine
Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, Av. Ferrocarril San Rafael Atlíxco, 186, Colonia Leyes de Reforma 1ª sección, Alcaldía de Iztapalapa, Ciudad de México 09310, México.

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Abstract
Printed Circuit Boards (PCBs) are constituted of multiple materials, which contributes to the complexity of the metal extraction process. In this work, a methodology for removing base metals and selectively extracting gold from a PCB sample was proposed; the sample tested contained ~200 g Au per ton. Two pretreatment stages were introduced (Na3C6H3O7-(NH4)3PO4-H2O2 and H2SO4-H2O2 systems), removing >90% of Cu, Ni, Zn, Fe, and Al. Subsequently, in the precious metal leaching stage, the thiourea-hydrogen peroxide-oxalic acid system (CS(NH2)2-H2O2-C2H4O4), was employed. To achieve elevated gold extraction, the oxalate ion (C2O42-, Ox) was used as a masking agent, forming stable species with remaining base metals in the leach liquors. Furthermore, this also contributed to H2O2 and CS(NH2)2 stability, permitting a gold dissolution of 92%.

Keywords: Selective leaching of gold, Chemical pretreatment, Base metal removal.

Resumen
Las tarjetas de circuito impreso (PCBs, por sus siglas en inglés) están constituidas por múltiples materiales, los cuales contribuyen a un proceso de extracción de metales complejo. En este trabajo se propuso una metodología para la remoción de metales base y la extracción selectiva de oro de una muestra de PCB, la cual, contenía ~200 g Au por tonelada. Se emplearon dos etapas de pretratamiento (sistemas: Na3C6H3O7-(NH4)3PO4-H2O2 y H2SO4-H2O2), eliminando >90% de Cu, Ni, Zn, Fe y Al. Posteriormente, en la etapa de lixiviación de metales preciosos, se empleó el sistema tiourea-peróxido de hidrógeno-ácido oxálico (CS(NH2)2-H2O2-C2H4O4). Para lograr una extracción de oro elevada, se utilizó el ion oxalato (C2O42-, Ox) como agente enmascarante, quien formó especies estables con los metales base remanentes en los licores de lixiviación. Además, contribuyó en la estabilidad de H2O2 y CS(NH2)2, permitiendo la disolución del oro en un 92%.

Palabras clave: Lixiviación selectiva de oro, Pretratamiento químico, Remoción metales base.
1 Introduction

Printed Circuit Boards (PCBs) are an essential part of electronic devices and where metals are concentrated. Commonly, a PCB contains 40% wt metallic materials, 30% wt plastics, and 30% wt ceramics (Rao et al., 2020).

In recent years, the recycling industry has implemented hydrometallurgical techniques, focusing on leaching processes to extract a wide variety of metals (copper, zinc, iron, aluminum, tin, silver, gold, etc.) from PCBs (Li et al., 2018). Therefore, the PCBs have been cataloged as a resource-rich material, which is used to enhance Urban Mining activities (Xu et al., 2016).

The PCBs are composed of layers of metallic and non-metallic material, hindering an effective leaching process. For example, gold is covered by polymeric material and is located under copper, nickel, and iron layers (Alzate, 2017). Consequently, direct extraction of gold is not possible, because metal-leaching agent contact is blocked. For this reason, it is necessary to couple physical and chemical pretreatments, and separate the materials that interfere with an efficient leaching process (Moyo et al., 2022).

In some cases, the physical pretreatments are not enough to remove the polymeric material, so chemical reagents such as sodium hydroxide (NaOH), chlorohydric acid (HCl), methanesulfonic acid (CH₃SO₃H), dimethyl sulfoxide (C₂H₆OS, DMS) are employed; however, at high concentrations (>1.0 M), they are unsafe (Jung et al., 2017; Li et al., 2018). Furthermore, the presence of principal metals, such as copper and iron, in the solution promote the leaching agent and oxidant degradation, impeding precious metals extraction (Calla et al., 2016). Consequently, the base metals should be removed prior to precious metal leaching.

Segura and Lapidus (2023) developed a methodology focused on the analysis and comparison of two chemical pretreatments for base metals extraction, and the subsequent selective extraction of gold. To achieve a selective process, these authors proposed combined systems: leaching agent-masking agent-oxidant. The first system consisted of sodium citrate, ammonium phosphate, and hydrogen peroxide (Na₃C₆H₅O₇·(NH₄)₃PO₄·H₂O₂). Sodium citrate and ammonium phosphate are considered non-toxic and environmentally friendly compounds, and recently, have been used to coordinate a wide variety of base metals (Anzures et al., 2022; Ruiz et al., 2023). In the second system, sulfuric acid and hydrogen peroxide (H₂SO₄·H₂O₂) were employed. For the subsequent gold dissolution, thiourea, oxalic acid, and hydrogen peroxide (CS(NH₂)₂·C₂H₂O₄·H₂O₂) were used. It was found that the remnants of copper, tin, iron, and aluminum after the pretreatments, contributed to the reagent species degradation. For example, copper and iron promote the formation of elemental sulfur and cyanamide (CN(NH₂)), causing oxidative thiourea degradation (Calla et al., 2016). Aluminum chemically reacts with gold, contributing to its cementation, therefore the gold dissolution efficiency is affected (Jeon et al., 2019; Segura and Lapidus, 2023).

In the present work, a methodology for the processing of an Electronic Waste Printed Circuit Boards (EWPCB) sample to selectively extraction of gold is proposed. This study is based on the process described by Segura and Lapidus (2023), and it is supported by a theoretical thermodynamic analysis. To complement the study carried out by Segura and Lapidus (2023), the present work proposes an analysis of the effect of two coupled chemical pretreatments. The overall process consists of the following stages: a physical pretreatment, two chemical pretreatments, and the gold leaching phase (Figure 1). Combining the two pretreatment phases will contribute to a more quantitative extraction/removal of base metal traces, ensuring gold selective extraction.

![Figure 1. Hydrometallurgical process for metal recovery from EWPCB.](www.rmiq.org)
2 Methodology

2.1 Physical pretreatment of the Electronic Waste Printed Circuit Boards (EWPCB)

Approximately 800 cellphones were manually disassembled, and the PCBs were separated and crushed to 6 mm employing a hammer mill (Schutte-Buffalo, W Series Laboratory Scale Industrial Hammer Mill), which operated at 150 rpm. Subsequently, the plastic material was partially removed by the float-sink method. Finally, a granulometric analysis was carried out, using a mechanical sieving (Tyler series); the following particle sizes were obtained:

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;500 µm</td>
<td>50%</td>
</tr>
<tr>
<td>500-250 µm</td>
<td>30%</td>
</tr>
<tr>
<td>250-150 µm</td>
<td>10%</td>
</tr>
<tr>
<td>150-75 µm</td>
<td>5%</td>
</tr>
<tr>
<td>&lt;75 µm</td>
<td>5%</td>
</tr>
</tbody>
</table>

The following solid particles were obtained: 0.1 g each fraction (>500 µm, 500-250 µm, 250-150 µm, 150-75 µm and <75 µm) were digested in 100 mL of aqua regia (HCl:HNO3 3:1 v/v) with constant magnetic agitation (200 rpm) during 3 h. Subsequently, the solution was cooled at ambient temperature, was vacuum filtered and diluted to 100 mL with deionized water (Millipore Milli-Q). Finally, the metal content was determined by Atomic Absorption Spectrometry (AAS, Varian SpectrAA 220FS) and Atomic Emission Spectrometry coupled to Microwave-generated Plasma (MP-AES, Agilent 4210). The metal composition of the fraction with the highest gold content was reported in Table 1; the other fractions contained negligible quantities of gold.

2.2 Chemical analysis of the EWPCB sample

Three EWPCB samples (0.1 g) of each fraction (>500 µm, 500-250 µm, 250-150 µm, 150-75 µm, and <75 µm) were digested in 100 mL of aqua regia (HCl:HNO3 3:1 v/v) with constant magnetic agitation (200 rpm) during 3 h. Subsequently, the solution was cooled at ambient temperature, was vacuum filtered and diluted to 100 mL with deionized water (Millipore Milli-Q). Finally, the metal content was determined by Atomic Absorption Spectrometry (AAS, Varian SpectrAA 220FS) and Atomic Emission Spectrometry coupled to Microwave-generated Plasma (MP-AES, Agilent 4210). The metal composition of the fraction with the highest gold content was reported in Table 1; the other fractions contained negligible quantities of gold.

2.3 Chemical pretreatment of the EWPCB sample: extraction/remotion of base metals

The chemical pretreatment consisted of two stages, both based on the methodology proposed by Segura and Lapidus (2023). In the first pretreatment, 1.2 M sodium citrate (Na3C6H5O7) and 0.5 M ammonium phosphate ((NH4)2HPO4) were used. The pH was adjusted at 4 with nitric acid (HNO3, 68-70%). As an oxidant, hydrogen peroxide (H2O2, 30% w/v) was employed, dosing a solution (0.2 M) each hour throughout the experiment due to its consumption by the chemical reactions. All chemical solutions (pretreatment and leaching) were prepared with analytical grade reagents MEYER®. 100 g EWPCB per liter of the solution was considered, and all experiments operated at ambient temperature (25°C) with constant magnetic agitation (600 rpm) for 6h. Once the first pretreatment phase was completed, the solutions were vacuum filtered, and the solid residue (dry) was pretreated in a second phase.

In the second chemical pretreatment, 1.0 M acid sulfuric (H2SO4, 95-98%) and 0.3 M H2O2 (30% w/v) solutions were prepared. The solid residue was leached in 1 liter of this solution, where the oxidant was added every 15 minutes throughout the experiment. These experiments were performed at 60°C with constant mechanical agitation (600 rpm) for 1 h. When the second chemical pretreatment phase concluded, the remaining solids were leached with thiourea solutions for gold extraction.

2.4 Leaching of the EWPCB sample with thiourea-hydrogen peroxide (CS(NH2)2-H2O2) solutions for gold extraction

The solid residue from the second chemical pretreatment was leached in 1 liter of 0.1 M thiourea (CS(NH2)2) and 0.2 M H2O2 (30% w/v) solution. In some cases, oxalic acid (C2H2O4) was employed as a masking agent in different concentrations: 0.1 M, 0.3 M, and 0.5 M. The pH was adjusted to 3 with nitric acid (HNO3, 68-70%). The leaching process operated at ambient temperature (25°C) with constant mechanical agitation (600 rpm) for 1 h.

Throughout the experiments, pH and Oxidation Reduction Potential (ORP) were monitored, employing HANNA® Instruments electrodes. All liquid samples and digested solids (residues) were analyzed by AAS and MP-AES to calculate the extraction percentages in the chemical pretreatment and leaching stages.

2.5 Chemical titration tests to quantify the thiourea (CS(NH2)2) concentration

Chemical titration tests were carried out according the method proposed by Calla and Nava (2020). 2%wt starch was completely dissolved in deionized water (Millipore Milli-Q) at boiling temperature and then was cooled. A 0.005 M potassium iodate (KIO3) solution was prepared and placed into a glass burette for titration. 0.5 mL of a sample of the leach solution, 6 mL of 1 M sulfuric acid (H2SO4), and 1 mL of starch solution were placed into an Erlenmeyer flask with constant magnetic agitation (150 rpm). The KIO3 solution was added until the endpoint of the titration (blue starch-iodine complex formation).

2.6 Thermodynamic diagrams construction

A theoretical thermodynamic study of the different systems (Metal-leaching agent and Metal-masking agent) was elaborated. For the construction of predominance and species distribution diagrams, the Software MEDUSA© (Making Equilibrium Diagrams Using Simple Algorithms) (Puigdomenech, 2004) was employed. Thermodynamic data reported in the NIST (National Institute of Standards and Technology) database (NIST, 2004), Lothenbach et al., (1999) and Smith and Martell (1982) were considered.

Table 1. Average metallic content of the EWPCB sample (particle size <75 µm).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Cu</th>
<th>Fe</th>
<th>Sn</th>
<th>Ni</th>
<th>Zn</th>
<th>Al</th>
<th>Pb</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg/t</td>
<td>58±0.84</td>
<td>55±0.28</td>
<td>22±1.47</td>
<td>4.4±0.04</td>
<td>14±0.17</td>
<td>32±0.12</td>
<td>2.9±0.1</td>
<td>1.0±0.4</td>
<td>200±0.33</td>
</tr>
</tbody>
</table>

*s/g/t
3 Results and discussion

3.1 Thermodynamic analysis

The EWPCB sample consisted of different base metals (Table 1); for their extraction, previous studies (Segura, 2022) demonstrated the citrate ion’s (Cit) capacity to form soluble stable complexes with most of them, especially with the principal metals in the EWPCB sample: copper, iron, and aluminum. The soluble species Metal-Citrate are formed in wide intervals of potential (-1.0 to 1.0 V) and pH (2 to 8), as shown in Figure 2.

The addition of masking agents into the leach solutions (combined systems) allows the selective recovery of metals. For example, the addition of phosphate ion (PO$_4^{3-}$) into sodium citrate solutions at pH 4, assures the precipitation of metals such as iron, lead, and tin (Segura and Lapidus, 2021). With iron, insoluble species are formed with potentials greater than 0.1 V (Figure 3A), with lead from -1.0 V (Figure 3B) and from -0.5 V for tin (Figure 3C).

The presence of copper ions and aluminum metal are detrimental to gold extraction, due to the formation of insoluble species with thiourea (Cu(CS(NH$_2$)$_2$)$_2$)$_2$) in acid media (Donna and Stanbury, 1996), and gold cementation by aluminum (Free, 2013); they therefore should be removed from the leach liquors. In the second pretreatment phase, acid sulfuric (H$_2$SO$_4$), an excellent leaching agent for base metals (Jadha et al., 2016), was employed to extract these metals (Figure 4).

Figure 2. Predominance diagrams. A. Cu (0.84 M)-Cit, B. Fe (0.1 M)-Cit, C. Al (0.04 M)-Cu-Cit, with 1.2 M Cit, at 25°C. MEDUSA© software site. The concentrations of ions used to elaborate the diagrams correspond to the values found in the leach liquor.
C. Sn-Cit-PO$_4^{3-}$

Figure 3. Species distribution diagrams. A. Fe (0.1 M)-Cit-PO$_4^{3-}$, B. Pb (1 x 10$^{-4}$ M)-Cit-PO$_4^{3-}$, C. Sn (0.02 M)-Cit-PO$_4^{3-}$, with 1.2 M Cit and 0.5 M PO$_4^{3-}$, at 25°C. MEDUSA© software site (Segura and Lapidus, 2021).

Finally, thiourea (CS(NH$_2$)$_2$) was employed as the leaching agent for gold dissolution. Thiourea and gold form a stable complex Au(CS(NH$_2$)$_2$)$_2^{+}$ at pH values from 1 to 3 (Figure 5). This reagent is a non-toxic alternative to substitute the cyanide processes (Li et al., 2012).

3.2 Effect of coupling two chemical pretreatment phases to extract/remove base metals from the EWPCB sample

The first stage of chemical pretreatment (Na$_3$C$_6$H$_5$O$_7$-(NH$_4$)$_3$PO$_4$-H$_2$O$_2$ system) was carried out at pH 4, according to thermodynamic analysis (Figure 3); the objective was to prevent the dissolution of specific base metals, such as iron, lead, and tin. Figure 6 shows the extraction percentage for each analyzed metal, as a function of time. In this system, the extractions were Cu (96%), Fe (78%), Zn (77%), Ni (55%), Sn (20%), and Al (3%). pH and ORP values were monitored throughout the experimental test. Both values were constant during the 6 hours of the process (pH ~4.1 and ORP ~0.6 V), guaranteeing the extraction of these metals.

A high percentage of copper was extracted (Figure 6). The selectivity of the process allowed the incorporation of a copper recovery stage (direct electrowinning) from the leach liquors (Cu PLS), as a value-addition from this chemical pretreatment.

In sodium citrate solutions, aluminum dissolution was not favored. For that reason, a second pretreatment phase was coupled to achieve the removal of aluminum and other trace base metals. In this case, an inorganic acid was employed (H$_2$SO$_4$-H$_2$O$_2$ system); the results are shown in Figure 7. The metals preferably extracted were Al (55%) and Ni (36%). The other base metals (Cu, Fe, Zn, and Sn) were leached to a lesser degree (<14%). In this system, the pH value was constant during the leaching experiment (pH ~1.0), while the ORP decreased from 0.7 V to 0.5 V by the end of the leach.

Coupling two chemical pretreatment phases allowed the extraction/removal of base metals in percentages greater than 90% (except tin). Although base metals dissolution was not complete, the extraction was considered acceptable. However, it was important to analyze the effect of metallic traces in the leaching process with thiourea solutions.
3.3 Leaching in thiourea-hydrogen peroxide solutions (CS(NH$_2$)$_2$-H$_2$O$_2$) of the pretreated EWPCB sample

The pretreated EWPCB sample (with sodium citrate and acid sulfuric acid) was leached with thiourea and hydrogen peroxide (CS(NH$_2$)$_2$-H$_2$O$_2$ system). The pH of the system was established at 3 (Figure 5). The results are presented in Figure 8, where metal extraction was calculated based on the original (total) EWPCB content. In this system, small amounts of copper, nickel, and tin were dissolved, in addition to gold.

The maximum extraction of gold (~40%) was registered at 15 minutes; after this time, the extraction decreased, and by the end of the experiment, only 25% of the gold remained in solution. Additionally, copper, nickel, and tin were extracted (0.25% Cu, 4.0% Ni y 3.0% Sn). Despite these apparently insignificant percentages, the metallic traces directly affected the gold leaching, because species like copper, form stable complexes with thiourea (Doona and Stanbury, 1996).

3.4 Oxalic acid addition as a masking agent in CS(NH$_2$)$_2$-H$_2$O$_2$ solutions and its effect on gold extraction

The EWPCB sample was pretreated with sodium citrate and acid sulfuric solutions; after the two pretreatments, the following metals were removed: Cu (99%), Fe (91%), Zn (90%), Ni (90%), Al (73%), and Sn (33%).

In the leaching experiments (CS(NH$_2$)$_2$-H$_2$O$_2$ system), the effect of adding and modifying the masking agent (C$_2$H$_2$O$_4$) concentration were tested: 0.1 M, 0.3 M, and 0.5 M. Furthermore, the capacity of oxalate to mask copper, tin, and aluminum was determined. In Figure 10, it may be observed that only nickel and tin were the metals extracted when oxalate ion was added to the leaching solutions (in the three cases: 0.1 M, 0.3 M, and 0.5 M C$_2$H$_2$O$_4$); copper and aluminum registered negligible extraction due to the formation of solid compounds.
despite the presence of masking agent (Segura and Lapidus, 2023). The extraction percentage was 91% when the 0.1 M C$_2$H$_2$O$_4$ was employed. In the other cases (0.3 M and 0.5 M), 1 mL of starch solution (2%wt), 6 mL of H$_2$O$_2$, and 150 rpm.

**Figure 10.** Metal extraction (%) as a function of time. Leaching process: 0.1 M CS(NH$_2$)$_2$, 0.2 M H$_2$O$_2$, 100 g EWPCB/L, pH 3, 25$^\circ$C, 600 rpm, with different concentrations of C$_2$H$_2$O$_4$ (0.1 M, 0.3 M and 0.5 M).

Further, the gold extraction was analyzed (Figure 11). The extraction percentage was 91% when the 0.1 M C$_2$H$_2$O$_4$ was employed. In the other cases (0.3 M and 0.5 M C$_2$H$_2$O$_4$), 92% of gold was obtained. Furthermore, better stability of the gold dissolution was registered compared to the previous system (CS(NH$_2$)$_2$-H$_2$O$_2$, Figure 8).

Free thiourea concentration was determined as a function of time (Figure 12). In each case, a considerable decrease in concentration was registered, but the reagent had less degradation in the last 30 minutes of the process, as compared to the CS(NH$_2$)$_2$-H$_2$O$_2$ system (Figure 9).

In the proposed systems (CS(NH$_2$)$_2$-H$_2$O$_2$ and CS(NH$_2$)$_2$-H$_2$O$_2$-C$_2$H$_2$O$_4$) the ORP was monitored, and its value was stable throughout the experiments, oscillating around 0.6 V, comparable to the reported by Segura and Lapidus (2023). If the sample is not pretreated, the ORP value decreases to 0.3 V, causing a negligible extraction of gold, despite the presence of masking agent (Segura and Lapidus, 2023).

**Figure 11.** Gold extraction (%) as a function of time. Leaching process: 0.1 M CS(NH$_2$)$_2$, 0.2 M H$_2$O$_2$, 100 g EWPCB/L, pH 3, 25$^\circ$C, 600 rpm, with different concentrations of C$_2$H$_2$O$_4$ (0.1 M, 0.3 M and 0.5 M).

**Figure 12.** Free thiourea concentration as a function of time. Chemical titration conditions: 0.005 M KIO$_3$, 0.5 mL of a sample of the leach solution (0.1 M CS(NH$_2$)$_2$, 0.2 M H$_2$O$_2$, 100 g EWPCB/L, pH 3, 25$^\circ$C, 600 rpm, with different concentrations of C$_2$H$_2$O$_4$: 0.1 M, 0.3 M and 0.5 M)), 1 mL of starch solution (2%wt), 6 mL of H$_2$SO$_4$, 150 rpm.

**Conclusions**

This research demonstrated that two coupled chemical pretreatment phases contributed to the base metal removal from an EWPCB sample. The extraction/removal of copper and aluminum (>90%) especially improved the gold extraction, preventing its cementation and the formation of additional species in the leach liquors.

The accelerated consumption of thiourea was evident in the systems analyzed (CS(NH$_2$)$_2$-H$_2$O$_2$ and CS(NH$_2$)$_2$-H$_2$O$_2$-C$_2$H$_2$O$_4$). However, with the incorporation of acid oxalate, thiourea presented better stability. Furthermore, the oxalate ion masked traces of aluminum, tin, and especially copper, allowing a maximum gold extraction of 92%.

To achieve selectivity in multimetallic material leaching, the use of masking agents is essential. Furthermore, it is important to study the competing chemical reactions,
which probably are generated by the presence of other materials, such as plastics and flame retardants. This analysis will provide useful information to establish efficient extraction and recycling processes. Furthermore, the cost-benefit of the process will be important to analyze, since thiourea and hydrogen peroxide consumption, as well as pretreatment expenditures, would affect the economic feasibility. However, the elevated value of gold more than compensates the added expenses.

References


