SEPARATION OF COPPER FROM A LEACHING SOLUTION OF PRINTED CIRCUIT BOARDS BY USING SOLVENT EXTRACTION WITH D2EHPA

Mónica Maria Jiménez Correa1*, Flávia Paulucci Cianga Silvas1,2, Paula Aliprandini1, Viviane Tavares de Moraes1, David Dreisinger3 and Denise Croce Romano Espinosa1

1Universidade de São Paulo, Escola Politécnica, Departament of Chemical Engineering. do Lago, 250, 05424-970, PO 61548, São Paulo, Brazil. 
2Vale Institute of Technology-Mining, Av. Juscelino Kubitschek, 31, 35400-000, Ouro Preto, Minas Gerais, Brazil. 
3Department of Materials Engineering, University of British Columbia, 309-6350 Stores Road, Vancouver, B.C., Canada V6T 1Z4. 

*Corresponding author. monicamariajimenezc@gmail.com; flavia.silvas@itv.org; tavares.vivi@gmail.com; david.dreisinger@ubc.ca; espinosa@usp.br

Abstract - Global generation of waste electrical and electronic equipment (WEEE) is increasing quickly. Metals from WEEE can be recovered by using unit operations of chemical engineering. This paper describes a combined hydrometallurgical route (sulfuric oxidant leaching + solvent extraction) to recover copper from printed circuit boards (PCBs). A non-magnetic fraction from comminuted PCBs was used to perform leaching tests at 75°C for 6 hours in an oxidizing media (sulfuric acid + hydrogen peroxide). In order to separate zinc, aluminum, and copper from the leaching liquor, solvent extraction tests were carried out using D2EHPA. Parameters that influence the process, such as pH, extractant concentration, and the aqueous/organic (A/O) ratio were investigated. Solvent extraction experiments were carried out in two stages: i) separation of zinc, aluminum, and residual iron, and ii) copper separation. The results showed that the leaching obtained around 60% aluminum, 94% copper, 76% zinc, 50% nickel and residual iron from the non-magnetic fraction of PCBs. With the solvent experiments, in the first stage, 100 wt.% zinc, iron and aluminum were extracted at pH 3.5, 2:1 A/O, 10 % (v/v) D2EHPA, while, in the second stage 100% of the copper was extracted at pH 3.5, 1:1 A/O, 20 % (v/v) D2EHPA. 

Keywords: Waste electrical and electronic equipment (WEEE), recycling, printed circuit boards (PCBs), leaching, solvent extraction.

INTRODUCTION

Waste of electrical and electronic equipment (WEEE) is increasing quickly. In 2014 alone, the global generation of WEEE was 41.8 million tons (5.9 kg per inhabitant), while in 2010 the electrical and electronic equipment (EEE) discarded was 33.8 million tons (5.0 kg per inhabitant) (Baldé et al., 2015; Kane, 2015).
WEEE recycling can help minimizing the environmental impacts caused by primary metal extraction (Flandinet et al., 2012; Hall and Williams, 2007). Several studies have shown that PCBs contain valuable metals, such as gold, silver, palladium, nickel and copper which can make the metals recovery economically viable (Jiménez Correa et al., 2014; Park and Fray, 2009; Yamane et al., 2011).

Processes for metal extraction from WEEE based on mechanical, physical, pyrometallurgical and hydrometallurgical techniques have been developed (Chen et al., 2015; Fogarasi et al., 2013; Hagelüken, 2006). In pyrometallurgical processing, the matrix is incinerated, while target metals are smelted. Hydrometallurgical processing already consists of leaching, separation, purification and electrowinning of the metals of interest (Cui and Zhang, 2008; Tuncuk et al., 2012). Compared with pyrometallurgical processing, hydrometallurgical methods present a relatively low capital cost, and are also more easily controlled and more predictable and the recovery of metals is large for small scale applications. Pyrometallurgical processing operates at high temperatures (usually greater than 1000°C), consumes a lot of energy and produce hazardous gasses that must be treated with cleaning systems (Cui and Zhang, 2008; Rochetti et al., 2013; Tuncuk et al., 2012).

In hydrometallurgical processing, metals from PCBs are solubilized by different methods acid leaching or bioleaching and the liquor can be purified by solvent extraction, selective precipitation and electrowinning (Ghosh et al., 2015; Tuncuk et al., 2012). Copper is the main metal present in PCBs and its leaching can be performed using sulfuric acid and hydrogen peroxide as an oxidant agent. Nickel, zinc and iron leaching can already be carried out using sulfuric acid. Several studies have evaluated the PCB leaching process and studied conditions, such as the solid-liquid ratio, acid concentration and temperature (Birloaga et al., 2013; Oh et al., 2003; Yang et al., 2011).

Yang et al. (2011) analyzed copper leaching from spent PCBs. The study reported copper extraction higher than 90 wt.% using sulfuric acid, hydrogen peroxide and a solid: liquid ratio of 1:10(g/mL), after 3h at 23°C. According to Birloaga et al. (2013) 90 wt.% of copper can be leached from PCBs after two leaching stages with sulfuric acid and hydrogen peroxide. Silvas et al. (2015) investigated copper leaching with sulfuric acid + hydrogen peroxide and 1:10 solid/liquid ratio at 75°C over 4h. After two successive leaching stages, 100% of the copper in comminuted PCBs was leached.

The separation of metals contained in a liquor from acid leaching can be achieved by a solvent extraction technique. The extractant di-2-ethylhexyl phosphoric acid (D2EHPA) belongs to the organic phosphonic acid class and its main characteristic is the formation of a hydrogen bond between extractant molecules, causing the formation of dimeric structures (Figure 1) (Pereira, 2006).

The solvent extraction process has been widely used in hydrometallurgical metal recycling from WEEE (Kumari et al., 2016). Provazi et al., 2011) studied metal separation from a leaching liquor of spent batteries using Cyanex 272 versus selective precipitation. The results showed that solvent extraction was more efficient in metal separation than selective precipitation. Meanwhile, Oishi et al., 2007) investigated the recovery and purification of copper from printed circuit boards using LIX 26. Solvent extraction tests found that it is possible to achieve a metal extraction rate of lead, manganese, aluminum, iron, zinc and copper higher than 92% using LIX 26.

Several solvent extraction works have been developed to recover metals from WEEE (Dorella and Mansur, 2007; Kumari et al., 2016; Long Le et al., 2011; Nayl et al., 2015; Provazi et al., 2011). Table 1 shows some of the studies performed by different authors for metal recovery from WEEE using solvent extraction.

In this paper, a combined hydrometallurgical route was studied in order to recover and separate copper from discarded computer video PCBs using D2EHPA as extractant.
**MATERIALS AND METHODS**

Printed circuit boards used in this research were collected by a waste electronics recycling center in the city of São Paulo - Brazil. Initially, the manual dismantling of the printed circuit boards was performed using pliers and a screwdriver for the removal of heat sinks, screws, and electrolytic capacitors. With the aid of a manual guillotine, the boards were cut into smaller pieces so that they could fit into the opening of the mill.

The comminution was made primarily by grinding the PCBs in a blade mill with a 6 mm grid, followed by grinding in a hammer mill with a 2 mm grid. According to Tuncuk et al. (2012), the full release of copper happens with a particle size smaller than 2 mm as, in larger particles, there can be tunneling of Cu on the pins of the plastic components.

The magnetic separation of the sample was performed after grinding by the hammer mill. A dry drum magnetic separator was used at the following settings: magnetic roller speed of 27 rpm; vibration percentage of the feed 25%. In the present study, the material used was the non-magnetic fraction of PCBs. The sample was characterized by inductively coupled plasma optical emission spectrometry (ICP-OES) in equipment of the Agilent brand, model axial 710, in order to quantify the concentration of metals present in the liquors leached from acid digestion with aqua regia (1 HNO₃: 3HCl; 24 hours; 25 ºC). The composition is shown in Table 2.

**Acid leaching in an oxidizing medium**

The non-magnetic fraction of PCBs was leached for 6h using 1M sulfuric acid, 1:10 solid/acid ratio (25g PCBs:250mL H₂SO₄) at 75°C. An oxidizing media was induced by the addition of 10 mL of 30% (v/v) hydrogen peroxide every 30min into the system (H₂O₂ total added 120 mL) (Silvas et al., 2015). The liquor from the leaching process was used in solvent extraction tests.

**Solvent extraction**

Parameters like the pH effect, extractant concentration levels the aqueous/organic ratio (A/O) and extraction isotherms were evaluated. Temperature and time were maintained constant at 25°C and 10 min, respectively.

The aqueous phase in solvent extraction was prepared by diluting copper sulfate pentahydrate (CuSO₄·5H₂O); nickel sulfate hexahydrate (NiSO₄·6H₂O); zinc sulfate heptahydrate (ZnSO₄·7H₂O), ferrous sulfate heptahydrate (FeSO₄·7H₂O), and aluminum sulfate hydrate (Al₂(SO₄)₃·18H₂O) in deionized water. All the chemicals used were of analytical grade and purchased from Casa Americana (Brazil).

The extractant used was di-(2-ethylhexyl) phosphoric acid (D2EHPA) from Sigma-Aldrich. The diluent was kerosene of analytical grade from Cromoline Química Fina Ltda (Brazil).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extractant</th>
<th>Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric acid liquor from PCB waste</td>
<td>1st step: D2EHPA (10%) diluted in Kerosene; 2nd step: D2EHPA (20%) diluted in Kerosene.</td>
<td>1st step: t = 10 min; T = 25 ºC; pH = 3.5; A/O = 2/1; 2nd step: t = 10 min; T = 25 ºC; pH = 3.5; A/O = 1/1.</td>
<td>This paper</td>
</tr>
<tr>
<td>Sulfuric acid from battery waste</td>
<td>CYANEX 272 (0.72M) diluted in Exxol D-80</td>
<td>t = 20 min; T = 50 ºC; pH = 5.5; A/O = 1/1.</td>
<td>Dorella and Mansur (2007)</td>
</tr>
<tr>
<td>Sulfuric acid liquor from battery waste</td>
<td>CYANEX 272 (0.6M) diluted in Kerosene</td>
<td>t = 20 min; pH = 3, 6.5.</td>
<td>Provazi et al. (2011)</td>
</tr>
<tr>
<td>Sulfuric acid liquor from battery waste</td>
<td>1st step: Acorga M5640 (20%) diluted in Kerosene; 2nd step: CYANEX 272 (0.04M) diluted in Kerosene.</td>
<td>1st step: t = 5 min; T = 30 ºC; O/A = 1/1; 2nd step: pH = 5; t = 10 min; T = 25ºC; O/A = 1.</td>
<td>Nayl et a. (2015)</td>
</tr>
<tr>
<td>Sulfuric acid liquor from PCB waste</td>
<td>1st step: TEHA (70%) diluted in kerosene; 2nd step: LIX 84IC (10%) diluted in kerosene; 3rd step: LIX 84IC (1%) diluted in kerosene.</td>
<td>1st step: t = 5 min; T = 30 ºC O/A = 2/1; 2nd step: pH = 2.5; t = 5 min; O/A = 1/1; 3rd step: t = 15 min; pH = 4.58; O/A = 2/1.</td>
<td>Kumari et al. (2016)</td>
</tr>
<tr>
<td>Nitric acid liquor from PCB waste</td>
<td>LIX 984 (50%)</td>
<td>T = 50 ºC; pH = 1.5; A/O = 1/1.5.</td>
<td>Long Le et al. (2011)</td>
</tr>
</tbody>
</table>

**Table 2. Characterization of PCBs non-magnetic fraction**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Al</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Zn</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>2.0</td>
<td>33.9</td>
<td>0.2</td>
<td>0.2</td>
<td>3.8</td>
<td>7.6</td>
</tr>
</tbody>
</table>
a) Experiments

The pH was monitored with a pH meter and specific glass electrode for solvents. Agitation was maintained constant during all the tests using a mechanical agitator.

Metal extraction (%E) was calculated from a mass balance (1) of each system studied. Equation 2 was used to calculate the extraction percentage (%E) for all A/O ratio experiments.

\[
(C_{\text{aq}} - C_{\text{f,aq}}) V_{\text{aq}} = (C_{\text{f,org}} - C_{\text{f,org}}) V_{\text{org}}
\]

Extraction percentage = \( \frac{C_{\text{org}} + C_{\text{f,aq}}}{V_{\text{aq}} + V_{\text{org}}} \times 100\% \)

where \( C_{\text{org}} \) and \( C_{\text{f,org}} \) are the initial and final concentrations of metal in the organic phase, respectively, while the initial and final metal concentrations in the aqueous phase are defined as \( C_{\text{f,aq}} \) and \( C_{\text{f,org}} \). Furthermore, \( V_{\text{aq}} \) and \( V_{\text{org}} \) are the volumes of the aqueous and organic phases, respectively.

b) Extractant concentration and pH effect

Initially, the aqueous phase was added to the reactor and mechanical stirring was turned on. The pH was adjusted to the target value with the addition of 3M H₂SO₄ and 5M NaOH. Then, the organic phase was mixed with the aqueous phase and the pH was maintained constant during the experiments.

Mixture separation was achieved in a separation funnel. The aqueous phase was collected and analyzed by the energy dispersive X-ray fluorescence spectrometry (EDX) technique.

In order to evaluate the extractant concentration effect, solvent extraction experiments with 10, 15 and 20% (v/v) of the extractant D2EHPA were performed. The described procedure was repeated for the pH values: 1.0; 1.5; 2.0; 2.5; 3.0; and 3.5.

c) Organic/Aqueous ratio (A/O)

To evaluate the A/O ratio, experiments using 1:1 and 2:1 A/O were realized at 25°C for 10min. A 10% (v/v) concentration of the extractant D2EHPA was used, diluted in 90% (v/v) kerosene, with pH modified to between 0.5-3.5.

d) Extraction isotherms

For determining the metal extraction isotherms, the aqueous phase was mixed with the organic phase at different A/O ratios. The extraction stage of the individual metal solutions was divided into two parts:

i. Initially, zinc and aluminum were separated from the solution with copper and nickel. Tests were conducted at pH 3.5, using 10% (v/v) D2EHPA and 90% (v/v) kerosene. The A/O ratio was modified to between 1:5 and 5:1.

ii. The new aqueous phase (solution with copper and nickel) was stirred with an organic phase comprising 20% (v/v) D2EHPA and 80% (v/v) kerosene. The A/O ratio varied between 1:5 and 5:1 at pH 3.5.

The A/O ratio was varied between 1:5 and 5:1 to determine the number of countercurrent stages, known as McCabe-Thiele Method.

RESULTS AND DISCUSSION

After hydrometallurgical processing, it was possible to leach zinc, aluminum, copper, nickel and residual iron from video PCBs. Also, with the solvent extraction experiments variables such as the extractant concentration, pH effect, and A/O ratio were evaluated.

Acid leaching in an oxidative medium

In order to leach copper, other authors (Birloaga et al., 2013; Jha et al., 2011; Yang et al., 2011) also used sulfuric acid and hydrogen peroxide to leach metals from PCBs. The operational conditions used in the present study obtained around 60% aluminum, 94% copper, 76% zinc, 50% nickel and residual iron from the non-magnetic fraction, while the solution pH and ORP after the test were 0.5 and 673mV, respectively.

Table 3 shows the liquor concentration obtained after the video PCB leaching process.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.20</td>
</tr>
<tr>
<td>Cu</td>
<td>31.72</td>
</tr>
<tr>
<td>Fe</td>
<td>0.003</td>
</tr>
<tr>
<td>Ni</td>
<td>0.11</td>
</tr>
<tr>
<td>Zn</td>
<td>2.91</td>
</tr>
</tbody>
</table>

After the leaching test, a solid fraction can be used to extract other metals or materials and then it has to be disposed of in landfills. In a study developed by Muniyandi et al. (2013) the non-metallic fraction was used as a filler material in recycled High-Density Polyethylene (HDPE), recycled high-density polyethylene (rHDPE) and in the production of rHDPE/PCBs composites. The environmental regulation (balance in strength, stiffness, and toughness) for
Separation of copper from a leaching solution of printed circuit boards by using solvent extraction with D2EHPA

Composite materials was attained with the incorporation of a 30 wt% non-metallic fraction PCBs and 6 phr MAPE (maleic anhydride modified linear low-density polyethylene) compatibilizer (Muniyandi et al., 2013).

**Solvent extraction**

Concentration of the synthetic aqueous feed solution is shown in Table 3. The initial pH of the synthetic solution was adjusted to 0.5 with additions of sulfuric acid.

e) **Extractant concentration and the pH effect.**

The extractant concentration effect has been investigated by several authors to analyze metal extraction efficiency from sulfate solutions (Lee et al., 2010; Mohapatra et al., 2007; Vahidi et al., 2009). In this paper, the influence of the D2EHPA concentration was examined in solvent extraction.

As shown in Figure 2, zinc, residual iron, copper and aluminum extractions increased upon increasing the extractant concentration. Also, metal pH isotherms were displaced to the left with the increase in extractant concentration. As can be seen in Figure 2 (a), the higher metal extractions were achieved when a mixture of 20% (v/v) D2EHPA and 80% (v/v) kerosene was used. This reflects the fact that the system with 20% (v/v) D2EHPA has more extractant molecules than systems with 10% (v/v) and 15% (v/v) D2EHPA. The metal extraction order found for this system was: Fe>Zn>Al>Cu>Ni, which is consistent with the results achieved by Sole and Hiskey (1992).

It is known that acid extractants release hydrogen ions during metal extraction and, when metallic cations are extracted, the extractant (D2EHPA) releases hydrogen ions. Metal extraction reactions, equilibrium constants (Keq) and distribution coefficients (D) for divalent and trivalent ions are described in Table 4 (Mansur et al., 2002; Mohapatra et al., 2007).

For divalent and trivalent metals, the distribution coefficient can be calculated by Equation 7. Therefore, considering that the extractant concentration is constant, it follows that:

\[
D = \frac{K_{eq}}{[H^+]^n}
\]  

Taking the logarithm of Equation 7 and rearranging,

\[
\log D = -n \log[H^+] + \log K_{eq}
\]  

The values of log \( K_{eq} \) and \( n \) are related to the extraction of the metals. Thus, only the metals extracted were considered for the determination of both parameters. Then, the values of log \( K_{eq} \) and \( n \) were calculated for aluminum, zinc and iron in the systems that used 10%v/v D2EHPA, 15% v/v D2EHPA, and 20%v/v D2EHPA (see Table 5). Since copper only
showed increasing extraction with 20% v/v D2EHPA, the equilibrium values were only calculated for this system (Table 5).

The results showed that pH can directly influence metal extraction capacity. An estimated number of hydrogen ions generated by each metal molecule extracted could be calculated with the experimental data of D and pH. Equation 4 shows that metal extraction produces hydrogen ions; therefore, the pH decreases and the metal extraction percentage also decreases.

Figure 3 shows the pH variation effect in the distribution coefficient of aluminum, copper, iron and zinc.

**f) Aqueous/organic ratio (A/O)**

In solvent extraction tests with D2EHPA at an A/O ratio of 1:1 extractions of zinc, aluminum and copper higher than an A/O ratio of 2:1 (Figure 4) were achieved. However, aluminum and zinc were the metal cations most affected in the solution. For example, at pH 3.5 and an A/O ratio of 1:1, the extraction percentages for zinc and aluminum were 100% and 78%, respectively, while at pH 3.5 and an A/O ratio of 2:1 the E% decreased to 84% and 59%, respectively.

*Table 4. Solvent extraction reactions, equilibrium constants (Keq) and distribution coefficients for divalent and trivalent ions (adapted from Mansur et al., 2002 and Mohapatra et al., 2007).*

<table>
<thead>
<tr>
<th>Ion</th>
<th>Extraction Reaction</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Divalent metal (Adapted from Mansur et al., 2002)</td>
<td>$M^{n+} + n(RH)<em>2 \rightleftharpoons MH</em>{2(n-1)}R_{2n} + 2H^+$</td>
<td>$K_{eq} = \frac{[MH_{2(n-1)}R_{2n}][H^+]^2}{[M^{n+}][n(RH)_2]}$ Equation 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D = \frac{[MH_{2(n-1)}R_{2n}]}{[M^{n+}]}$ Equation 4</td>
</tr>
<tr>
<td>Trivalent metal (Adapted from Mohapatra et al., 2007)</td>
<td>$M^{n+} + n(RH)<em>2 \rightleftharpoons MH</em>{2(n-3)}R_{2n+3} + 3H^+$</td>
<td>$K_{eq} = \frac{[MH_{2(n-3)}R_{2n}][H^+]^3}{[M^{n+}][n(RH)_2]}$ Equation 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D = \frac{[MH_{2(n-3)}R_{2n}]}{[M^{n+}]}$ Equation 6</td>
</tr>
</tbody>
</table>

*Table 5. Equilibrium value for different organic concentrations (contact time = 10 min, A/O ratio = 1:1 and temperature = 25 °C)*

<table>
<thead>
<tr>
<th>Concentration of D2EHPA (% v/v)</th>
<th>Metal</th>
<th>log Keq</th>
<th>n</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Al</td>
<td>-1.21</td>
<td>0.5</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>-1.91</td>
<td>2.07</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>-2.82</td>
<td>2.09</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-1.32</td>
<td>0.6</td>
<td>0.98</td>
</tr>
<tr>
<td>15</td>
<td>Fe</td>
<td>-1.78</td>
<td>2.27</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>-2.91</td>
<td>2.35</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-1.54</td>
<td>0.88</td>
<td>0.98</td>
</tr>
<tr>
<td>20</td>
<td>Cu</td>
<td>-2.36</td>
<td>3.05</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>-2.71</td>
<td>2.66</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>-2.24</td>
<td>0.66</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Separation of copper from a leaching solution of printed circuit boards by using solvent extraction with D2EHPA

Separation parameters

In solvent extraction, the separation factor is a measure of the selectivity of a solvent for one component over another one. A separation factor higher than one indicates that the separation is favored and can occur.

The separation factors of aluminum, zinc, and residual iron over copper are listed in Table 6. It was found that the selectivity of the solvent for Al, Fe, and Zn over copper increased with increasing pH. At the same time, it was observed that the separation factor of Fe and Zn increased with increasing extractant concentration as a result of the strongest affinity of D2EHPA for iron and nickel over the other metals in solution.

After evaluation of the separation factors, the variables chosen to carry out the separation of zinc, aluminum and residual iron from the aqueous solution were: pH of 3.5, an A/O ratio of 2:1 and 10% (v/v) D2EHPA diluted with kerosene.

The solvent selectivity for copper over nickel is given in Table 7. It was observed that the extraction of copper over nickel was improved with the increase in the pH and in the D2EHPA concentration. For copper extraction, the parameters adopted were: pH of 3.5, A/O ratio of 1:1 and 20% (v/v) D2EHPA.

Table 6. Separation factors of aluminum, iron, and zinc over copper at different pH values, A/O ratios and at various extractant concentrations.

<table>
<thead>
<tr>
<th>pH</th>
<th>10% v/v D2EHPA, A/O 1:1</th>
<th>15% v/v D2EHPA, A/O 1:1</th>
<th>20% v/v D2EHPA, A/O 1:1</th>
<th>10% v/v D2EHPA, A/O 2:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>6.6</td>
<td>6.3</td>
<td>5.4</td>
<td>4.5</td>
</tr>
<tr>
<td>1.0</td>
<td>6.7</td>
<td>6.4</td>
<td>6.3</td>
<td>2.1</td>
</tr>
<tr>
<td>1.5</td>
<td>15.1</td>
<td>9.1</td>
<td>12.6</td>
<td>2.4</td>
</tr>
<tr>
<td>2.0</td>
<td>20.2</td>
<td>19.1</td>
<td>18.8</td>
<td>4.2</td>
</tr>
<tr>
<td>2.5</td>
<td>21.4</td>
<td>20.1</td>
<td>20.1</td>
<td>8.1</td>
</tr>
<tr>
<td>3.0</td>
<td>23.3</td>
<td>20.9</td>
<td>20.8</td>
<td>15.1</td>
</tr>
<tr>
<td>3.5</td>
<td>23.5</td>
<td>21.8</td>
<td>21.6</td>
<td>25.6</td>
</tr>
</tbody>
</table>

Table 7. Separation factors of copper over nickel at different pH values, A/O ratios and at various extractant concentrations.

<table>
<thead>
<tr>
<th>pH</th>
<th>10% v/v D2EHPA, A/O 1:1</th>
<th>15% v/v D2EHPA, A/O 1:1</th>
<th>20% v/v D2EHPA, A/O 1:1</th>
<th>10% v/v D2EHPA, A/O 2:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
<td>0.7</td>
<td>0.29</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>1.3</td>
<td>0.5</td>
<td>1.37</td>
</tr>
<tr>
<td>1.5</td>
<td>1.0</td>
<td>1.3</td>
<td>0.7</td>
<td>1.56</td>
</tr>
<tr>
<td>2.0</td>
<td>1.6</td>
<td>1.4</td>
<td>3.2</td>
<td>1.63</td>
</tr>
<tr>
<td>2.5</td>
<td>2.4</td>
<td>1.4</td>
<td>2.9</td>
<td>1.76</td>
</tr>
<tr>
<td>3.0</td>
<td>3.1</td>
<td>1.8</td>
<td>5.6</td>
<td>1.93</td>
</tr>
<tr>
<td>3.5</td>
<td>4.9</td>
<td>3.7</td>
<td>14.3</td>
<td>1.81</td>
</tr>
</tbody>
</table>
McCabe-Thiele isotherms

To plot the extraction isotherms of metals, experiments were performed in two steps: i) the extraction of zinc, residual iron and aluminum, and ii) solvent extraction trials to separate copper from nickel.

g) Zinc, residual iron and aluminum extraction

The synthetic solution simulating the oxidant acid liquor (Table 2) was put in contact with a solution of 10% (v/v) D2EHPA diluted with kerosene and using A/O ratios between 1:5 and 5:1. To construct McCabe-Thiele diagrams for aluminum and zinc extraction (see Figure 5), the pH was maintained constant at 3.5. It was possible to verify that both zinc and aluminum can be extracted with two theoretical stages, although zinc, residual iron and aluminum cannot be separated from each other, as shown in Figure 2(a). Extraction of residual iron was achieved with one countercurrent stage. Therefore, in this case, a McCabe-Thiele diagram is not necessary.

Figure 5 (a) shows that two theoretical stages were needed to separate zinc from a synthetic solution using a 2:1 A/O ratio, and Figure 5 (b) shows that two theoretical stages were needed to extract aluminum from the aqueous phase using 2:1 A/O.

D2EHPA is commonly used to separate zinc from solutions that contain metals. Pereira et al., 2007) investigated the extraction of 11.9g/L of zinc from a solution with other metals like iron, magnesium, manganese and calcium. The work reported that zinc extraction using 20% (v/v) D2EHPA and an A/O ratio was possible with two theoretical stages.

Furthermore, D2EHPA can separate aluminum from solutions with other metals. Mohapatra et al. (2007) studied aluminum extraction from a solution by 0.3M D2EHPA. The investigation found that two theoretical stages were required to extract aluminum from the aqueous phase.

h) Copper extraction

To determine the number of theoretical stages to separate copper from a solution with nickel, 20% (v/v) D2EHPA diluted with 80% (v/v) kerosene was mixed with the aqueous phase at pH 3.5. As shown in Figure 6, at an A/O ratio of 1:1, with two theoretical stages, copper was completely separated from nickel.

Similar to a study developed by Pranolo et al., 2010), in this study, it was observed that, in the organic phase, the copper concentration increased with the increase in the A/O ratio.

While copper is extracted by the organic phase (20% (v/v) D2EHPA diluted with kerosene), nickel remained in the aqueous phase and can be recovered by an electrolysis process. The organic solution with copper must be forwarded to the stripping stage before copper recovery by the electrowinning technique. Total copper extraction from a liquor produced in the leaching process of the non-magnetic fraction of PCBs was carried out using the present process.
CONCLUSIONS

PCBs from discarded computers of metals such as copper, nickel, zinc, and aluminum can be used as raw materials. At the end of the present study three-metal solutions were obtained: (a) a solution comprising residual iron, aluminum, and zinc, (b) a solution comprising copper, and (c) a solution of nickel. In addition, it was found that:

- In the leaching step using 1M H_2SO_4 and an oxidant medium, at 75°C, 60% aluminum, and 76% zinc, 94% copper, and 50% nickel were leached from the non-magnetic fraction of video PCBs after 6h of reaction.
- It is possible to extract 100% of the zinc and aluminum present in the leaching liquor from the non-magnetic fraction of PCBs using 10% (v/v) D2EHPA diluted with 90% (v/v) kerosene, pH 3.5, 25°C, 10min of reaction time and an A/O ratio of 2:1. The number of theoretical extraction contacts for the countercurrent separation system is two.
- Total copper extraction from a liquor produced in the leaching process of the non-magnetic fraction of PCBs can be carried out in two theoretical contacts at an A/O ratio of 1:1, 25°C, 10min of reaction, pH 3.5 and using 20% (v/v) D2EHPA diluted with 80% (v/v) kerosene, provided that aluminum and zinc are previously extracted.

ACKNOWLEDGMENTS

This work was carried out with financial support from FAPESP (Grants No 2012/20350-3, No 2013/22614-0 and research project 2012/51871-9), CNPq (Research fellowship No 500869/2014-6) and CAPES (PNPD-2010 Program).

NOMENCLATURE

- %E - Extraction percent
- A/O - Aqueous/Organic
- C_{aq} - Final concentration of metal in the aqueous phase
- C_{org} - Final concentration of metal in the organic phase
- C_{i} - Initial concentration of metal in the aqueous phase
- D - Distribution coefficient
- D2EHPA - Di-2-ethylhexyl phosphoric acid
- EDX - Energy dispersive X-ray Fluorescence Spectrometry
- EEE - Electrical and Electronic Equipment
- Keq - Equilibrium constant
- LIX 26 - Alkylated 8-hydroxyquinoline
- M^{2+} - Divalent metal
- M^{3+} - Trivalent metal
- MH_{2n1}R_{2n} - Organic complex formed between the extractant and divalent metal
- MH_{2n3}R_{2n} - Organic complex formed between the extractant and trivalent metal
- n - Stoichiometric constant
- PCBs - Printed Circuit Boards
- (RH)_2 - Dimeric form of extractant
- HDPE - Recycled high density polyethylene
- V_{aq} - Volume of the aqueous phase
- V_{org} - Volume of the organic phase
- WEEE - Waste electrical and electronic equipment

REFERENCES


Mohapatra, D., Hong-In K., Nam C W., and Park K H., Liquid-liquid extraction of aluminium(III) from mixed sulphate solutions using sodium salts of Cyanex 272 and D2EHPA. Separation and Purification Technology, 56(3), 311-318 (2007). doi: http://dx.doi.org/10.1016/j.seppur.2007.02.017
Separation of copper from a leaching solution of printed circuit boards by using solvent extraction with D2EHPA


Nayl, A. A., Hamed, M. M., and Rizk, S. E., Selective extraction and separation of metal values from leach liquor of mixed spent Li-ion batteries. Journal of the Taiwan Institute of Chemical Engineers, 55, 119-125 (2015). doi: http://dx.doi.org/10.1016/j.jtice.2015.04.006


