The 7th International Conference on Waste Management and Technology

Current status on leaching precious metals from waste printed circuit boards

Yanhua Zhang\textsuperscript{a,*}, Shili Liu\textsuperscript{a}, Henghua Xie\textsuperscript{a}, Xianlai Zeng\textsuperscript{b}, Jinhui Li\textsuperscript{b}

\textsuperscript{a}Dongjiang Environmental Company Limited, Shenzhen 518057, China
\textsuperscript{b}School of Environment, Tsinghua University, Beijing 100084, China

Abstract

Current research on leaching precious metals from waste printed circuit boards (PCBs) in the world is introduced. In the paper, hydrometallurgical processing techniques including cyanide leaching, thiourea leaching, thiosulfate leaching, and halide leaching of precious metals are addressed in detail. In order to develop an environmentally friendly technique for recovery of precious metals from Waste PCBs, a critical comparison of main leaching methods is analyzed based on three-scale analytic hierarchy process (AHP). The results suggest that thiourea leaching and iodide leaching make more possible to replace cyanide leaching.

© 2012 Published by Elsevier B.V.

Selection and/or peer-review under responsibility of Basel Convention Coordinating Centre for Asia and the Pacific and National Center of Solid Waste Management, Ministry of Environmental Protection of China.

Open access under CC BY-NC-ND license.

Key Words: waste printed circuit board; leaching; recovery; precious metals; analytic hierarchy process.

1. Introduction

Nowadays, the amount of scrap materials generated in the process of molding and machining of printed circuit boards (PCBs) reach 100,000 tons every year in China. Taking into account PCBs from the large quantities of waste electrical and electronic products imported abroad and dismantling of end-of-life electrical and electronic equipments, each year more than 500,000 tons waste PCBs need to be treated in China mainland [1], which contain about 150,000 to 200,000 tons of metals. Table 1 gives examples of the metal composition of waste PCBs from literatures [2-15]. As can be seen from Table 1, metals contents of PCBs are varied in different literatures. The reason for this is that metals contents especially precious metals contents of PCBs are varied with age, origin and manufacturer. But even calculating with the minimum content of gold in Table 1, there will be 40 tons of gold in 500,000 tons of waste PCBs.

* Corresponding author. Tel.: +86 755 2726 4217; fax: +86 755 2726 4217.
E-mail address: zhyh@dongjiang.com.cn
To develop a clean and environment-friendly technology for recovery of resources from waste PCBs as soon as possible is not only to raise the utilization rate of resources, but also to reduce pollution, to protect environment, and to achieve energy saving and emission reduction. Therefore, this work is of great significance for national construction, and at the same time it can bring economic benefits to the enterprise.

At present, there are a lot of techniques of recycling waste PCBs in the world. Researchers has proposed many methods including physical and mechanical separation technology, pyrometallurgical method, hydrometallurgical processing, bio-technology, microwave treatment and supercritical fluid technology to recycle PCBs from different point of view. However, “mechanical crushing + hydrometallurgical” processing is still the most competitive technology for waste PCBs recycling, and it is the most commonly used technology to recycle PCBs abroad [16].

Although a few reviews have been provided on resource recycling progress of waste PCBs by researchers [2,16-27], some of these reviews involve many aspects, and the summary and discussion of hydrometallurgical technology is not deep enough, the others have been finished for a few years, and it’s necessary to add some new literatures. With the amount of waste PCBs growing faster and faster, it’s very important to accelerate the step of developing a kind of process which is economically feasible and environmentally friendly to recycle resources from waste PCBs.

Leaching is the initial step in a hydrometallurgical process, it is also the most important key during the precious metal recovery from waste PCBs. Therefore, discussion and summarization on hydrometallurgical technology progress especially on progress of leaching process have been provided in this paper.

Table 1 Weight composition of metals from different waste PCBs

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/%</td>
<td></td>
<td>23.73</td>
<td>23.47</td>
<td>20</td>
<td>20</td>
<td>26.8</td>
<td>10</td>
<td>15.6</td>
<td>22</td>
<td>17.85</td>
</tr>
<tr>
<td>Al/%</td>
<td></td>
<td>4.7</td>
<td>1.33</td>
<td>5</td>
<td>2</td>
<td>1.9</td>
<td>7</td>
<td>—</td>
<td>—</td>
<td>4.78</td>
</tr>
<tr>
<td>Pb/%</td>
<td></td>
<td>4.48</td>
<td>0.99</td>
<td>1.5</td>
<td>2</td>
<td>—</td>
<td>1.2</td>
<td>1.35</td>
<td>1.55</td>
<td>4.19</td>
</tr>
<tr>
<td>Zn/%</td>
<td></td>
<td>0.75</td>
<td>1.51</td>
<td>—</td>
<td>1</td>
<td>1.5</td>
<td>1.6</td>
<td>0.16</td>
<td>—</td>
<td>2.17</td>
</tr>
<tr>
<td>Ni/%</td>
<td></td>
<td>3.32</td>
<td>2.35</td>
<td>1</td>
<td>2</td>
<td>0.47</td>
<td>0.85</td>
<td>0.28</td>
<td>0.32</td>
<td>1.63</td>
</tr>
<tr>
<td>Fe/%</td>
<td></td>
<td>7.47</td>
<td>1.22</td>
<td>7</td>
<td>8</td>
<td>5.3</td>
<td>12</td>
<td>1.4</td>
<td>3.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Sn/%</td>
<td></td>
<td>3.65</td>
<td>1.54</td>
<td>—</td>
<td>4</td>
<td>1.0</td>
<td>—</td>
<td>3.24</td>
<td>2.6</td>
<td>5.28</td>
</tr>
<tr>
<td>Sb/%</td>
<td></td>
<td>1.82</td>
<td>—</td>
<td>—</td>
<td>0.4</td>
<td>0.06</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Au/ppm</td>
<td></td>
<td>800</td>
<td>570</td>
<td>250</td>
<td>1000</td>
<td>80</td>
<td>280</td>
<td>420</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Pt/ppm</td>
<td></td>
<td>30</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>4.6</td>
</tr>
<tr>
<td>Ag/ppm</td>
<td></td>
<td>800</td>
<td>3301</td>
<td>1000</td>
<td>2000</td>
<td>3300</td>
<td>110</td>
<td>1240</td>
<td>—</td>
<td>1300</td>
</tr>
<tr>
<td>Pd/ppm</td>
<td></td>
<td>210</td>
<td>294</td>
<td>110</td>
<td>50</td>
<td>—</td>
<td>—</td>
<td>10</td>
<td>—</td>
<td>250</td>
</tr>
<tr>
<td>Total/%</td>
<td></td>
<td>~50</td>
<td>~33</td>
<td>~35</td>
<td>~40</td>
<td>~40</td>
<td>~21</td>
<td>~22</td>
<td>~30</td>
<td>~38</td>
</tr>
</tbody>
</table>

Table 1 shows that recovery of precious metals from waste PCBs is most attractive. Research on recovery of metals from waste PCBs by hydrometallurgical processing began in 1970s [31], the initial goal of that is exactly the recovery of such precious metals as gold and/or silver.
2. Leaching of precious metals from waste PCBs

2.1. Pretreatment

Pretreatment is of necessity prior to leaching of precious metals from waste PCBs including physical pretreatments and chemical pretreatments. Physical pretreatment is to mechanically break and crush PCB scrap after dismantling the electronic components, and then according to the differences of physical characteristics of metals and nonmetals, to use one of the methods, including pneumatic separation, magnetic separation, screening, eddy current separation, and electrostatic separation, to obtain the enrichment of metals and nonmetals. Chemical pretreatment is to dissolve base metals such as copper, lead and tin in solution, leaving precious metals in residue, and then to isolate and purify precious metals from the residue. The commonly used chemical pretreatment is nitric acid pretreatment or sulfuric acid & hydrogen peroxide pretreatment. Fig. 1 shows typical flow chart of recovery of precious metals from waste PCBs.

Mecucci [28] used nitric acid of 1 - 6 mol/L to extract copper and lead from PCBs. Precipitation of tin as \( \text{H}_2\text{SnO}_3 \) (metastannic acid) occurred at acid concentrations above 4 mol/L. And preliminary galvanostatic electrolysis from simulated leaching solutions had investigated the feasibility of electrodeposition of copper and lead at different concentrations of \( \text{HNO}_3 \).

The nitric acid solutions with different concentration were employed [29] for leaching metals from the waste printed circuit boards. The effects of nitric acid concentration on disassembling times of the electric components and dissolving rate of metals were investigated. Results indicated that the metals were apt to dissolve in solution with higher nitric acid concentration; they all dissolved quickly except Cu, which did not dissolve in the leachate when nitric acid concentration was lower than 2.73 mol/L. The dissolution rate of Cu, Fe and Zn could reach to 50%, 80% and 93% when the nitric acid concentration was 4.55 mol/L.
The recovery of gold and copper from waste PCBs with H$_2$O$_2$-H$_2$SO$_4$ solution was studied by Zhu [30]. The influence of concentration and amount of sulfuric, solid-liquid ratio, the amount of hydrogen peroxide and reaction time on the reaction were investigated. The result indicated that it is unfavorable for recovering rate of gold and copper when acidity is too high or too low. For 10 g waste material, under the condition of 1:2 solid-liquid ratio, 20 ml hydrogen peroxide 20 ml sulfuric acid (1:3), all of the gold and copper were almost recovered. Desquamation rate of gold and recovering rate of copper reaches 98.75% and 99.43%.

2.2. Cyanide leaching

Cyanide as lixiviant for gold has dominated in the mining industry for more than one century for its advantages such as cheaper reagent, less dosage, operating in an alkaline solution. Its principle is to dissolve gold and silver of the PCB surface into the solution by alkali metal cyanide, and then to recover gold and silver by reduction from the cyanide solution.

Cyanide leaching is only effective to leach gold and/or silver at the surface of PCBs. Those gold and/or silver wrapped inside PCBs are hard to dissolve by cyanide process [31].

Although cyanide leaching is still dominant in the gold mining industry, plenty of wastewater containing cyanide is produced in the leaching process, which is harmful for both operators and surrounding environment. And cyanidation has a long production cycle for its slow leaching rate. Therefore, metallurgical researchers have provided multiple non-cyanide leaching processes in recent years, and some of these processes have made significant progress that they are almost to be used in commercial production.

Currently, more attention has been paid to the study of several non-cyanide leaching process, including thiourea leaching, thiosulfate leaching and halide leaching.

2.3. Thiourea leaching

Thiourea was first synthesized in 1868, also known as sulfurized urea. It is an organic complexing agent with reducibility, being able to form white crystal of complexes with many metal ions. Under acidic conditions, with the presence of oxidant (usually Fe$^{3+}$), thiourea and gold will form soluble cationic complexes.

Comparing with other leaching reagent, thiourea shows much poorer stability. It is easy to decompose to sulfide and cyanamide in alkaline solution, and cyanamide can be further converted to urea; and it is easy to be oxidized into disulfide formamidine and elemental sulfur and other various products in acidic solution. Therefore, it’s very important to select suitable oxidant and the oxidant concentration so that gold is oxidized as much as possible into the solution but thiourea is oxidized as little as possible. Although disulfide formamidine, as the product of the initial stage of oxidation, is help to accelerate leaching rate. However, with the increase of disulfide formamidine concentration, it is prone to irreversible decomposition to generate elemental sulfur, which will form a stable passivation layer on the surface of gold particles, hindering gold dissolution. At the same time, a great deal of chemical reagent is consumed. That is the very reason why acidic thiourea leaching has not been used widely and industrially up to now [32].

Thiourea leaching gold and silver from waste circuit boards was carried out by Xu [33], and the influence of leaching time, react temperature, thiourea concentration, Fe$^{3+}$ concentration and material particle size on gold leaching rates were investigated. The results showed that, gold and silver leaching rates can reach 90.87% and 59.82% respectively under the best conditions.
Research by Wu [34] also showed that selectively leaching gold and silver from PCB scrap in acid thiourea solution is possible and effective. The optimal leaching condition was: the ratio of solid to liquid is 1:10, stirring condition 300 rpm, leaching temperature 20 - 25 °C, leaching time 1 h, thiourea concentration 12 g/L, Fe\(^{3+}\) concentration 0.8%, pH =1.5. The leaching yields of gold and silver were 91.4% and 80.2%, respectively.

Results of the experiment of leaching gold from waste PCBs with thiourea by Zhong [35] showed that suitable leaching conditions are as follows: solid-liquid 1:5, leaching temperature 35 °C, thiourea concentration 10 g/L, Fe\(^{3+}\) concentration 0.3%, H\(_2\)SO\(_4\) concentration 5%, leaching period 1h.

Comparing with cyanide leaching, thiourea leaching gold has the advantages of quick leaching speed, low-toxic, high efficiency, environmental friendly and less interference ions.

Commercial application of thiourea leaching has been hindered by the following three factors [36]: (1) it is more expensive than cyanide; (2) its consumption in gold processing is high because thiourea is readily oxidized in solution; and (3) the gold recovery step requires more development. However, it was implied that the high costs attached to leaching are likely due to the thiourea process still being in an infancy stage.

2.4. Thiosulfate leaching

There are two kinds of thiosulfate commonly used in leaching gold, one is sodium thiosulfate, the other is ammonium thiosulfate. Gold and thiosulfato will form a stable complex with the presence of oxygen. Thiosulfate is stable in alkaline medium, because tetrathionate, the oxidation product of thiosulfate, will turn into thiosulfate again under alkaline conditions in about 60%. But the pH of the solution cannot be too high, otherwise it is prone to disproportionation reaction turning thiosulfato into sulfidion.

The behavior of cathodic process of leaching gold with thiosulfate has been investigated by Jiang [37]. Results show that ammonia reacts with gold ions on anodic surface of gold; the formed Au(NH\(_3\))\(^{2+}\) is substituted by S\(_2\)O\(_3\)\(^{2-}\) after entering solution to form more stable Au(S\(_2\)O\(_3\))\(^{2-}\).

The kinetics of sodium thiosulfate leaching gold was studied by Moore [38], results show that it is linear relationship between gold solubility and temperature when temperature between 45 to 85 °C. Taking into account that thiosulfate will be prone to decomposition at high temperature, the suitable temperature is between 65 to 75 °C.

The kinetics of electrochemical reaction of thiosulfate leaching under ammonia medium was researched by Heath [39], results show that leaching rate depends on the concentration of thiosulfate, Cu\(^{2+}\) and ammonia. The higher the concentration of reagents, the faster the leaching reaction goes. Yen [40] found that the dissolution of copper minerals is the main reason for the increase of thiosulfate consumption.

Thiosulfate leaching process, whose solution is an ammoniacal solution, is suitable for handling gold mine rich of alkaline components, especially for gold ore or gold concentrate containing copper, manganese and/or arsenic which is sensitive to cyanide leaching.

Thiosulfate leaching has the advantages of high selectivity, nontoxic and non-corrosive. The principal problem with thiosulfate leaching is the high consumption of reagent during extraction. It is reported a loss of up to 50% of thiosulfate in ammoniacal thiosulfate solutions containing copper. High reagent consumption renders most thiosulfate systems uneconomical overall, in spite of their potential environmental benefits.
2.5. Halide leaching

Halide leaching includes chloride leaching, bromide leaching and iodide leaching. Their common merits are high leaching rate. Gold forms both Au⁺ and Au³⁺ complexes with chloride, bromide and iodide depending on the solution chemistry conditions. Only chlorine/chloride has been applied industrially on a significant scale of the halides. But chloride leaching requires special stainless steel and rubber-lined equipments to resist the highly corrosive conditions.

The vapor pressure of bromine is 10kPa at 0 °C and 28kPa at 35 °C. Special equipment is required for safety and health risks in bromide leaching process, and that restricts it from industrial application [41].

Iodide leaching has the following advantages: (1) quick leaching; (2) good selectivity, less leaching of base metal; (3) easy to regenerate iodide, iodine being reduced while recovering gold in anode region; (4) no corrosion, for iodide leaching in a weakly alkaline medium; (5) no toxicity. Moreover, the complexes formed by gold and iodine are the most stable complexes formed by gold and halogen [42].

Research on iodide leaching gold from discard PCBs was carried out by Xu [43]. According to the result, the rational parameters for iodide leaching gold are 1.0%~1.2% iodide concentration, n(I₂) : n(I⁻) =1:8 ~ 1:10, H₂O₂ concentration 1%~2%, leaching time 4 hrs, solid to liquid 1:10, leaching gold at normal temperature (25°C), solution pH=7. Gold leaching rate can reach at about 95%.

Iodide leaching is a promising technology in non-cyanide leaching process. However, iodide leaching consumes a great deal of reagent, and iodine is relatively expensive, and efficiency of electrolytic deposition of gold needs to be improved. All these problems must be solved before iodide leaching gold is applied in industry.

3. Comparison of various leaching processes

As one of the most popular methods for multi-criteria decision-making, the analytic hierarchy process (AHP) has been successfully used in a variety of fields [44-47]. Here, three-scale AHP is applied to determine the weight of evaluation indexes of different leaching methods.

Based on the basic score of each leaching method offered in Table 2 and diagram of hierarchical structure in Fig. 2, comparison matrixes are given in Table 3 and judgment matrixes in Table 4. And then the weight of different indexes are calculated in Table 5. Final score in Table 6 is the basic score multiplied by its relevant weight.

Table 2 Basic scores of different evaluation indexes of various leaching methods

<table>
<thead>
<tr>
<th>Leaching method</th>
<th>Leaching rate</th>
<th>Reagent cost</th>
<th>Corrosive</th>
<th>Toxicity</th>
<th>Reliability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanide</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Aqua regia</td>
<td>4</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Thiourea</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Chloride</td>
<td>5</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Bromide</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Iodide</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>
Fig. 2. Diagram of hierarchical structure

Table 3 Comparing matrixes of different hierarchies

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>( \sum_{i=1}^{2} K_i )</th>
<th>B4</th>
<th>C11</th>
<th>C12</th>
<th>C13</th>
<th>( \sum_{i=1}^{3} K_i )</th>
<th>B21</th>
<th>B22</th>
<th>B23</th>
<th>B31</th>
<th>( \sum_{j=1}^{1} K_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>C11 1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>C21 1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>C12 2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>C13 2</td>
<td>0</td>
<td>1</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4 Judging matrixes of different hierarchies

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>T</th>
<th>B1</th>
<th>C11</th>
<th>C12</th>
<th>C13</th>
<th>T</th>
<th>B2</th>
<th>C21</th>
<th>T</th>
<th>B3</th>
<th>C31</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>1</td>
<td>6</td>
<td>7/2</td>
<td>0.627315</td>
<td>C11 1</td>
<td>1/6</td>
<td>2/7</td>
<td>0.086749</td>
<td>C21 1</td>
<td>C31</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>1/6</td>
<td>1</td>
<td>2/7</td>
<td>0.086749</td>
<td>C12 2</td>
<td>C11 1</td>
<td>7/2</td>
<td>0.627315</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>2/7</td>
<td>7/2</td>
<td>1</td>
<td>0.285936</td>
<td>C13 1</td>
<td>7/2</td>
<td>2/7</td>
<td>0.285936</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5 Weight of different indexes about leaching methods

<table>
<thead>
<tr>
<th>Evaluation index</th>
<th>Leaching rate (C11)</th>
<th>Reagent cost (C12)</th>
<th>Corrosive (C13)</th>
<th>Toxicity (C21)</th>
<th>Reliability (C31)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>0.054</td>
<td>0.394</td>
<td>0.179</td>
<td>0.087</td>
<td>0.286</td>
</tr>
</tbody>
</table>

Table 6 Final scores of different leaching methods

<table>
<thead>
<tr>
<th>Leaching method</th>
<th>Cyanide</th>
<th>Aqua regia</th>
<th>Thiourea</th>
<th>Thiosulfate</th>
<th>Chloride</th>
<th>Bromide</th>
<th>Iodide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scores</td>
<td>4.457</td>
<td>3.483</td>
<td>4.000</td>
<td>2.711</td>
<td>3.251</td>
<td>2.249</td>
<td>3.640</td>
</tr>
</tbody>
</table>

The analysis shows that cyanide leaching gains the highest points for its good economic feasibility and research level. But when the toxicity of reagents are taken into account, it is an inevitable trend for non-cyanide leaching to replace cyanide leaching. With further research, thiourea leaching and iodide leaching are both likely to reduce the cost of the process and to be more reliable in technology, so as to replace cyanide leaching.

4. Conclusions

In summary, leaching technologies mentioned above are technically feasible. However, in order to develop an environment-friendly technique for recovery of precious metals from waste PCBs, we should pay more attention to evaluating the environmental impact of techniques. A critical comparison of seven leaching methods is analyzed based on three-scale AHP. The results suggest that thiourea leaching and iodide leaching make more possible to replace cyanide leaching. Along with the further studies on this field, those leaching process with potential environment benefits will be more economically feasible in the future.
Acknowledgements

The work is financially supported by the Environmental Protection Public Welfare Project (grant number 201109035).

References


