Leaching of copper from metal powders mechanically separated from waste printed circuit boards in chloride media using hydrogen peroxide as oxidant

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Abstract

The dissolution of copper from waste printed circuit boards in chloride media using hydrogen peroxide as oxidant was carried out. The effects of stirring speed, temperature, solid/liquid ratio and concentrations of HCl and H2O2 on the leaching of copper were investigated. The copper extraction increased significantly with the increase of HCl concentration. H+ and Cl− ions both improved the leaching of copper from waste printed circuit boards and had the synergetic effect on copper dissolution. The H2O2 was the main reagent which made possible the leaching of metallic copper from waste printed circuit boards in acidic chloride solutions. The copper extraction also increased with the increase of stirring speed, temperature and solid/liquid ratio. Finally, a reaction mechanism was proposed as well.

Keywords: Copper; Waste printed circuit boards; Leaching; Hydrogen peroxide

1. Introduction

Printed circuit boards (PCBs) are the main constituents of most electric and electronic equipment. PCBs contain not only the valuable metals such as gold, silver and copper but also the hazardous materials such as tin, lead and brominated flame retardants. Therefore, the recycling of waste PCBs gained more and more attentions not only from

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the aspect of waste treatment, but also with respect to the recovery of valuable materials\textsuperscript{1-5}. Leaching is one of the processes for the recovery of metals from waste PCBs\textsuperscript{6-9}. Zhu et al. reported that the leaching of copper by electro-oxidation from metal powders of waste PCBs was accelerated, where the electro-generated chlorine not only as a complexing agent but also as an oxidant made the reaction speed up to 3.5 h to reach 100% leaching rate\textsuperscript{10}. The leaching of copper from waste PCBs using electro-generated chlorine in hydrochloric acid solutions was also investigated, where various parameters such as current density, agitation speed, temperature were explored to understand the leaching mechanism\textsuperscript{11-13}. Havlik et al.\textsuperscript{14} investigated the impact of thermal treatment on the subsequent hydrometallurgical recovery of copper and tin from PCBs using HCl solutions at 80 °C. The previous literatures revealed that the main advantage of chloride hydrometallurgical processes for the leaching of copper is the high solubility of metal complexes, stability of monovalent copper and high leaching rates\textsuperscript{15-17}. However, the solubility of chlorine in solutions is low and decreases with increase in temperature\textsuperscript{18}, which would limit the reaction speed of copper leaching and even generate atmospheric pollution through the release of chlorine.

In our previous paper, the metallic copper dissolution systems were investigated in detail according to the composition characteristic of these systems, which are a judicious combination of oxidants and complexants. These chemicals, depending on their nature, play the role of oxidizer and complexant in the dissolution processes of metallic copper, respectively\textsuperscript{19}. This conclusion extends the range of chloride leaching systems for copper dissolution, which allows us to search for alternative oxidants in order to not only make use of the advantage of chloride leaching systems but also eliminate the shortcoming of chlorine as oxidant.

The hydrogen peroxide is widely used in hydrometallurgical processes due to its very good properties\textsuperscript{20-22}. Moreover, H\textsubscript{2}O\textsubscript{2} is safe, effective, powerful and versatile oxidant. In acidic solution, H\textsubscript{2}O\textsubscript{2} is one of the most powerful oxidant known stronger than chlorine, chlorine dioxide and potassium permanganate. The oxidizing capacity of hydrogen peroxide is so strong that it is considered a highly reactive oxygen species. The oxidation and dissolution of copper was investigated using hydrogen peroxide as oxidizer and glycine as a complexing agent\textsuperscript{23-24}. The dissolution behavior of copper in citric acid solutions with the presence of hydrogen peroxide were studied\textsuperscript{25-26}. Pandija et al.\textsuperscript{27} investigated aqueous solutions of oxalic acid and hydrogen peroxide for copper dissolution and proposed a reaction scheme describing the chemical effects of oxalic acid and hydrogen peroxide. The primary objective of the work discussed in this paper was to study the dissolution characteristics of copper from waste PCBs in acidic chloride solutions using H\textsubscript{2}O\textsubscript{2} as oxidant and to propose a mechanism for the dissolution.

2. Materials and methods

Waste PCBs were pretreated in a local machinery manufacturing factory, where those waste PCBs were separated into metal powders and non-metallic part. The metal powders were used as received for the leaching experiment. The composition of the metal powders listed in Table 1 shows that copper is the major metal. All the chemicals in the experiments were purchased from Sinopharm Chemical Reagent Co, Ltd and were used without further purification.

The dissolution experiments were carried out in a 1000 mL glass reaction vessel equipped with a mechanical stirrer having a digital controller unit. The rotational speed of the stirrer was varied from 100 to 1400 rpm. The glass reaction vessel was immersed in a circulating thermostated water bath with a controlling temperature accuracy of±0.1°C. In this work, the leaching solutions were firstly added into the reaction vessel, and then a predetermined amount of metal powders was added to the solutions. This was marked as the beginning of the experiment. After the leaching experiments, the solid residue was filtrated out and was dissolved in aqua regia to determine the quantity of copper present in the residue. The metal concentrations in solutions were determined by a Z-5000 atomic absorption spectrometer (Hitachi Ltd, Tokyo, Japan).

Table 1 Metals content of metal powders mechanically separated from waste printed circuit boards.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Cu</th>
<th>Fe</th>
<th>Zn</th>
<th>Ni</th>
<th>Mn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>73.3</td>
<td>1.44</td>
<td>0.02</td>
<td>1.39</td>
<td>0.13</td>
<td>0.75</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Effect of HCl concentration

The effect of HCl concentration on copper extraction was investigated in the range of 0.05-0.8 mol/L keeping the other parameters constant. The results exhibited in Fig. 1 showed that the copper extraction increased significantly with the increase of HCl concentration. This can be attributed to the synergetic effect of HCl on copper dissolution. In order to illustrate the role of H+ and Cl⁻ ions, the effects of H+ ions concentration and Cl⁻ ions concentration on copper extraction from waste PCBs were further investigated, respectively.

The effect of H⁺ ions concentration on copper extraction from waste PCBs was investigated under the following conditions: Aqueous phase (500 mL): 0.2 mol/L H₂O₂, total Cl⁻ concentration = 0.8 mol/L, S/L = 0.004 g/mL, stirring speed: 500 rpm, temperature: 25°C. H⁺ ions were added in the form of HCl. In order to eliminate the effect of Cl⁻ ions, NaCl was also added simultaneously. Thus, the concentration of Cl⁻ ions in leaching solutions kept constant. Results were presented in Fig. 2. It can be seen from this figure that the leaching of copper from waste PCBs in absence of H⁺ almost was not observed in 90 min. However, the copper extraction increased significantly to 49.7 % in 30 min with the presence of 0.05 mol/L H⁺ in leaching solutions. The copper extraction increased with the increase of H⁺ ions concentration from 0.05 to 0.3 mol/L. This indicated that the H⁺ ions concentration is an important parameter and has a positive effect for copper dissolution from waste PCBs.

The effect of Cl⁻ ions concentration on copper extraction from waste PCBs was investigated under the following conditions: Aqueous phase (500 mL): 0.2 mol/L H₂O₂, 0.1 mol/L HCl, S/L = 0.004 g/mL, stirring speed: 500 rpm, temperature: 25°C. Cl⁻ ions were added in the form of NaCl varied from 0 to 0.5 mol/L. The results exhibited in Fig. 3 showed that the copper extraction increased with the increase of excess Cl⁻ ions concentration. Thus it reinforces the conclusion that the H⁺ and Cl⁻ ions both enhance the leaching of copper from waste PCBs and have the synergetic effect on copper dissolution.

![Fig. 1. Effect of HCl concentration on copper extraction from waste PCBs. Aqueous phase (500 mL): 0.2 mol/L H₂O₂, S/L = 0.004 g/mL, stirring speed: 500 rpm, temperature: 25°C.](image-url)
3.2. Effect of H$_2$O$_2$ concentration

The effect of H$_2$O$_2$ concentration on copper extraction was investigated in the range of 0-0.4 mol/L keeping the other parameters constant. Results were presented in Fig 4. The copper extraction was only 0.8% in 90 min with the absence of H$_2$O$_2$. The low copper extraction within experimental conditions may be attributed to the facts that the metal copper was dissolved in the presence of oxygen of acidic chloride leaching solutions$^{14}$. With the addition of H$_2$O$_2$ into leaching solutions, the copper extraction increased significantly to 60.8% in 90 min with the presence of 0.05 mol/L H$_2$O$_2$ in leaching solutions and the copper extraction increased significantly with the increase of H$_2$O$_2$ concentration from 0.05 to 0.4 mol/L. As a result of these experiments, a conclusion can be obtained that the H$_2$O$_2$ is
the main reagent and that it makes possible the leaching of metallic copper from waste PCBs for the studied ranges. In this leaching system, H$_2$O$_2$ was oxidant, which oxidized metallic copper to cupric ions in acidic solutions. It was reasonable that the copper extraction increased with the increase of H$_2$O$_2$ concentration.

Fig. 4. Effect of H$_2$O$_2$ concentration on copper extraction from waste PCBs. Aqueous phase (500 mL): 0.3 mol/L HCl, 0.5 mol/L NaCl, S/L = 0.004 g/mL, stirring speed: 500 rpm, temperature: 25°C.

Fig. 5. Effect of stirring speed on copper extraction from waste PCBs. Aqueous phase (500 mL): 0.2 mol/L H$_2$O$_2$, 0.3 mol/L HCl, 0.5 mol/L NaCl, S/L = 0.004 g/mL, temperature: 25 °C.

3.3. Effect of stirring speed

The effect of stirring speed on copper extraction was investigated in the range of 0-500 rpm keeping the other parameters constant. As shown in Fig. 5, the copper extraction increased according to the increase in the stirring speed. This may be contributed to the fact that agitation of the leaching solutions improved the mass transfers and accelerated the leaching of copper.
3.4. Effect of solid/liquid ratio

The effect of solid/liquid ratio was investigated in the range of 0.001-0.006 g/mL keeping the other parameters constant. Increasing solid/liquid ratio increased the copper extraction as presented in Fig. 6. This can be attributed to the increase of the metallic copper per milliliter of leaching solutions, which resulted in the increase of Cu$^{2+}$ ions concentration with the leaching of copper from waste PCBs. The similar phenomena were observed in the dissolution of metallic copper with CuSO$_4$-NaCl-HCl system, where the copper extraction increased with the increase of total copper concentration$^{17}$.

![Fig. 6. Effect of solid/liquid ratio on copper extraction from waste PCBs. Aqueous phase (500 mL): 0.2 mol/L H$_2$O$_2$, 0.3 mol/L HCl, 0.5 mol/L NaCl, stirring speed: 500 rpm, temperature: 25 °C.](image)

3.5. Effect of temperature

The effect of temperature on copper extraction from waste PCBs was studied in the range of 25-65 °C keeping the other parameters constant. The experimental results were shown in Fig. 7. As shown in this graph, the copper extraction was highly sensitive to temperature. About 98% of copper was extracted from waste PCBs at a temperature of 25 °C in 90 min leaching time, while about 96% was extracted at a temperature of 65 °C in only 10 min leaching time. Therefore, higher temperature was in favour of the leaching of copper from metal powders mechanically separated from waste printed circuit boards. The high copper extraction at high temperature may be attributed to the increase of the mass transfer coefficient and diffusivity as the increase of temperature.

3.6. Reaction mechanism

According to the results from the leaching tests, it can be concluded that the copper extraction from waste PCBs with acidic chloride solutions containing H$_2$O$_2$ as oxidant was feasible, where the copper extraction increased with the increase in HCl, H$_2$O$_2$ concentration, stirring speed, solid/liquid ratio and temperature. The H$^+$ and Cl$^-$ ions both accelerate the leaching of copper from waste PCBs and have the synergetic effect on copper dissolution. As shown in Eq. (1), metallic copper was oxidized by H$_2$O$_2$ to cupric ions in acidic solutions. The Cu$^{2+}$ concentration in solutions increases with the leaching of metallic copper from waste PCBs in acidic solutions of H$_2$O$_2$, and then the other reaction between metallic copper and Cu$^{2+}$ in chloride media occurs as illustrated in Eq. (2).

\[
\text{Cu} + \text{H}_2\text{O}_2 + 2\text{H}^+ = \text{Cu}^{2+} + 2\text{H}_2\text{O}
\]  

(1)
\[ \text{Cu}^{2+} + \text{Cu} = 2\text{Cu}^+ \]  
\[ \text{Cu}^+ + \text{nCl}^- = \text{CuCl}_n^{(n-1)-} \]  
\[ 2\text{CuCl}_n^{(n-1)-} + 2\text{H}^+ + \text{H}_2\text{O}_2 = 2\text{Cu}^{2+} + 2\text{H}_2\text{O} + 2\text{nCl}^- \]  

Thermodynamically, Eq. (2) proceeds from left to right by increasing the concentration of \( \text{Cu}^{2+} \) and/or decreasing the concentration of \( \text{Cu}^+ \). Increasing the solid/liquid ratio would result in the increase of \( \text{Cu}^{2+} \) concentration in leaching solutions, which enhanced the copper extraction as exhibited in Fig 6. As shown in Eq. (3), \( \text{Cu}^+ \) is steadily removed by the formation of complex ions \( \text{CuCl}_n^{(n-1)-} \). The complex ions \( \text{CuCl}_n^{(n-1)-} \) are also oxidized as shown in Eq. (4), and subsequently, generated \( \text{Cu}^{2+} \) enhanced the leaching of copper to generate \( \text{Cu}^+ \) ions through Eq. (2), which could account for the accelerating effecting of \( \text{Cl}^- \) and \( \text{Cu}^{2+} \) on the leaching of metallic copper from waste PCBs in \( \text{H}_2\text{O}_2\)-\( \text{HCl}\)-\( \text{NaCl} \) solutions. Consequently, the leaching reaction is accelerated through Eq. (2) by \( \text{Cu}^{2+} \) as well as through Eqs. (3) and (4) by \( \text{Cl}^- \) and \( \text{H}_2\text{O}_2 \).

**Fig. 7.** Effect of temperature on copper extraction from waste PCBs. Aqueous phase (500 mL): 0.2 mol/L \( \text{H}_2\text{O}_2 \), 0.3 mol/L \( \text{HCl} \), 0.5 mol/L NaCl, \( S/L = 0.004 \text{ g/mL} \), stirring speed: 500 rpm.

### 4. Conclusions

The dissolution of copper from waste PCBs in acidic chloride solutions using \( \text{H}_2\text{O}_2 \) as oxidant was feasible. \( \text{H}^+ \) ions concentration is an important parameter and has a positive effect for copper dissolution from waste PCBs and the copper extraction also increased with the increase of excess \( \text{Cl}^- \) ions concentration. The \( \text{H}^+ \) and \( \text{Cl}^- \) ions have the synergetic effect on copper dissolution. The \( \text{H}_2\text{O}_2 \) is the oxidant which makes possible the leaching of metallic copper from waste PCBs for the studied ranges. The \( \text{Cl}^- \), \( \text{H}_2\text{O}_2 \) and generated \( \text{Cu}^{2+} \) also accelerated the dissolution of copper from waste PCBs. The copper extraction increased with the increase in concentrations of \( \text{HCl} \) and \( \text{H}_2\text{O}_2 \), stirring speed, solid/liquid ratio and temperature within experimental conditions.

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References


