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## ARTICLE

# Recycling Gold and Copper from Waste Printed Circuit Boards Using Chlorination Process

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Yuchen He and Zhenming Xu\*

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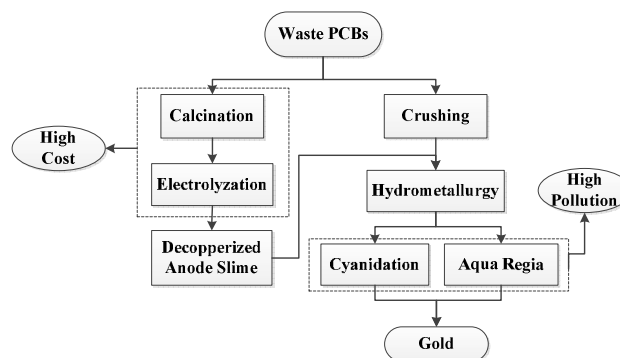
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Waste electric and electronic equipment (WEEE) usually contains many recoverable and valuable elements, including gold and copper. Primitive technologies like aqua regia leaching and calcination are still widely used in China which has caused the serious pollution to local environment. Chlorination is a feasible alternative for the recovery of metallic elements due to the higher dissolution rate, non-polluting character and selective leaching of different metals by controlling the redox potential. In the present study, an efficient and less-polluted chlorination process to recycle gold and copper from waste PCBs was investigated. This work based on a physical processing with a crush-pneumatic separation-corona electrostatic separation dealing with waste PCBs which provided the raw material for chlorination process. The influences of different pretreatments and experimental parameters were studied. The result showed that more than 90% of copper could be selective recovered by controlling the Eh of leaching solution at 400 to 800mV. The supercritical process had a better effect with a leaching yield of metallic elements over 99% percent both for gold and copper. Ball milling process had different influence on gold and copper based on milling time. The leaching yield of copper increased with the increasing of ball milling time. For gold there was an optimum time around 10min at 20s-1 frequency of milling. The leaching yield of gold could reach more than 99% after a pretreatment of ball milling for 10min when the leaching time was 90min, the leaching temperature was 40°C and the initial concentration of sulfuric acid was 100g/L. This study could contribute significantly to metallic elements recycling of high value added WEEE and provide technological parameters for the industrial application in the future.

## Introduction

With the rapid development of electronic industries, large amount of waste electric and electronic equipment (WEEE) is constantly generated worldwide<sup>1</sup>. WEEE usually contains many recoverable and valuable elements, including gold and copper that has the highest value and recoverable amount respectively. The treatment of WEEE is not only an issue about environmental protection, but also an important way to resources recycle. Generally the electronic components are fixed onto a printed circuit board (PCB) in every piece of electronic equipment virtually. It was reported that PCBs in personal computer contain gold amount to 80g/t<sup>2</sup>, which is higher than that in some gold ores. Due to the shortage of high-grade gold resources with large-scale gold ore mining<sup>3,4</sup>, the recoverable gold in WEEE will become one of the important sources of gold. Gold is generally plated on printed circuit board contact in order to increase the hardness of contact and take advantage of the good conductivity of gold to minimize contact resistance of the circuit. The main part of the contact is copper foil. There is only a thin layer of gold plated on the copper foil. Hence, the separation of gold and copper needs to be taken into account in leaching process. Presently, a physical processing with a crush-pneumatic separation-corona electrostatic separation has been proved to be a feasible method for industrialization of waste PCB recycling<sup>5</sup>. A metal concentrate could be generated after the process. But this process cannot achieve the purpose to separate gold or copper from other metal materials.

Hydrometallurgy is widely used in gold extraction<sup>6</sup>. Cyanidation process is the most frequently used method in conventional<sup>7</sup>. But this process couldn't achieve the selective leaching of copper and gold<sup>8</sup> and has environmental-related disadvantage such as highly toxic effluent<sup>9</sup>. As shown in Figure 1, in China, primitive technologies are still widely used in family-run workshop to recover gold from PCBs. The electrolytic process has high cost that prevented the application for small-scale treatment. The leaching process with *aqua regia* would produce large amount of strong acid waste liquid which results in the serious pollution on local environment<sup>10-12</sup>.



**Fig. 1** Widely-used process for recycling gold from waste PCBs in China.

Due to the higher dissolution rate<sup>13</sup>, non-polluting character<sup>14, 15</sup> and selective leaching of different metals by controlling the redox potential, chlorination is a feasible alternative method for gold recovery<sup>16, 17</sup>. Thus far, some research efforts have been done to use chlorination as an alternative method. Donmez, B. et al.<sup>18, 19</sup> have studied the chlorination of gold from decopperized anode slime. The extraction yield can reach more than 90%. Baghalha<sup>13</sup> used chloride/hypochlorite solutions in the leaching of oxide gold ore which reached 67% gold extraction in 4h. Nam, K. S.<sup>20</sup> used chloride/hypochlorite to recover gold from tailing and reached 80% gold extraction. The studies indicated that raw material played a big role in the chlorination leaching. However, few studies focused on the chlorination leaching of gold from PCBs.

Meanwhile, pretreatment is an important method to improve the leaching yield and purity of metal. However, the traditional pretreatment methods as roasting, acid leaching, alkaline leaching and bio-oxidation<sup>3</sup> will generate large amount of waste water or gas with high pollution<sup>20, 21</sup>. Different from refractory gold ores, there is no sulfide or carbonate in PCB. The oxidation is not the key process in the pretreatment of PCBs. Hence, ball milling as a physical method with low pollution and cost should be taken into consideration in the pretreatment process. In recently years, supercritical water ( $T \geq 374^\circ\text{C}$ ,  $P \geq 22.1\text{MPa}$ ) has been known as an environment-friendly method in many academic sectors. As the dissociation constant ( $K_w$ ) for water is about three orders of magnitude higher at the critical point<sup>22</sup>, supercritical water is both a strong acid and alkali. It is an ideal pretreatment method due to the utilization of non-toxic reactant<sup>23, 24</sup>. There are many influencing factor in chlorination process such as temperature, reaction time, acidity, chloride concentration, agitation rate, etc. Some of the influencing factors should be investigated for the optimization of the gold leaching process.

In this work, we try to establish an efficient and less-polluted process to selectively recycle gold and copper from metal concentrate which comes from waste PCBs after a crushing-electrostatic separation process. The objectives of this research are: (1) to evaluate the effectiveness of crushing and supercritical water pretreatment on gold and copper recovery; (2) to evaluate the effectiveness and feasibility of the selective leaching of gold and copper by chlorination process and optimize the experimental parameters to increase the leaching yield.

## Experimental

### Materials

In this study, the waste memory stick collected from WEEE recycling factory in Shanghai was used as the representation of waste PCBs. The gold plated parts had been sheared from the waste memory sticks for the experiment. The metal concentrate was collected after the crushing-electrostatic separation process and regarded as raw materials in the following experiments. The mass fraction of mainly metallic elements was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) after acid digestion and presented in Table 1. The non-metal part of raw material was mainly consisted of glass fiber and reinforced resin.

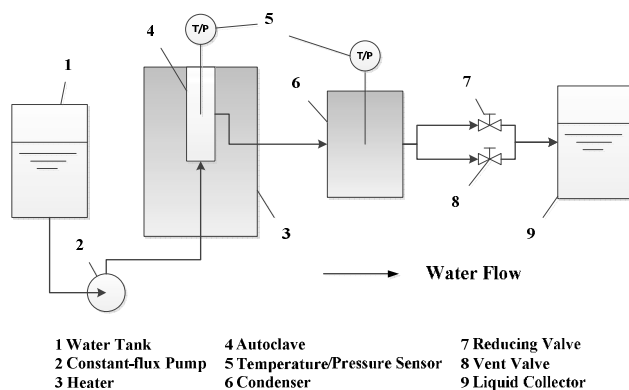
**Table 1** The Mass Fraction of Mainly Metals of Raw Material  
wt%

Au	Cu	Al	Fe	Ni	Pb
0.2339	20.78	0.8529	0.1424	0.1478	0.0868

In this experiment, sodium chlorate was taken as chlorinating agent. The reagents used in this study ( $\text{NaClO}_3$ ,  $\text{NaCl}$  and  $\text{H}_2\text{SO}_4$ ) were of analytical grade and the solutions were pre-made separately.

### Apparatus

The leaching experiments were carried out in a glass Erlenmeyer flask immersed in a thermostatically controlled water bath with a constant temperature circulator which equipped with an adjustable speed magnetic stirrer. The Eh of the solution was monitored and controlled using a Mettler Toledo experimental pH meter FE20 with ORP probe in all experiments. The particles needed pretreatment were ball milled with a Retsch mixer mill MM400. The size of particles was measured by a Laser Particle Size Analyzer MAE-3000. The surface morphology of particles was observed with a Nove NanoSEM 230 scanning electron microscope. A semi-batch reactor was used for the supercritical pretreatment process in the present study. The schematic diagram of the reactor was shown in Figure 2.



**Fig. 2** Schematic diagram of the semi-batch reactor.

### Methods

In the typical run of experiment, for leaching copper, the known weight of sample particles and 150g/L sulfuric acid solution were added into the reactor. When the temperature achieved  $80^\circ\text{C}$ , sodium chlorate was added continuously into the reactor to maintain the Eh of the solution at a range of 400 to 600 mV. After 8 hours leaching, the samples were filtered. The filtrate and chlorination residue were collected separately. The filtrate  $L_1$  was diluted with distilled water to a certain volume. The chlorination residue and 150g/L sulfuric acid solution were added back to the reactor for leaching gold. 25g/L sodium chlorate and 75g/L sodium chloride were added into the reactor after achieving the desired temperature. The initial Eh of the solution was between 1000 to 1200mV. The remainder samples were filtered after the leaching for 2 hours. The filtrate  $L_2$  was also diluted with distilled water to a certain volume. Finally the concentration of metallic elements of copper and gold leachate was determined by ICP-OES. In the process, the agitation was set at a certain speed and the solid-liquid ratio was 1:8.

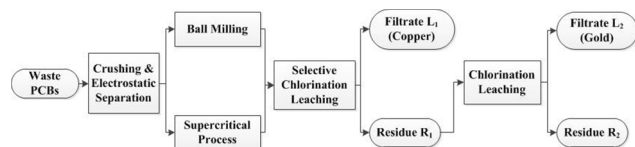
The parameters in gold leaching experiment would be optimized, including initial concentration of sulfuric acid, reaction time and temperature. The parameter settings in the optimization experiment were presented in Table 2.

**Table 2** Parameter Settings of the optimization experiment

Time	Temperature	Initial Acidity
t=30,60,90,120,180,240, 300;	T=30,40,50,60, 70;	C=50,100,150,200,2 50;
T=40; C=150	t=120; C=150	T=40; t=120

t (min): leaching time; T (°C): leaching temperature; C (g/L): initial concentration of sulfuric acid.

The flowchart of leaching process was shown in Figure 3.

**Fig. 3** The flowchart for leaching of waste PCBs.

The metallic elements leaching yield (R) is calculated by the following equation:

$$R = \frac{C \times V}{M_0} \times 100\% \quad (1)$$

Where R is the leaching yield of metallic elements,  $M_0$  is the initial amount of metallic elements in sample, V is the volume of the leaching solution after distilling, C is the concentration of the metallic elements in the leaching solution.

## Results and discussion

### Pretreatment Experiment

In this experiment, the leaching yield of copper was calculated by the copper concentration in  $L_1$ , the leaching yield of gold is calculated by the gold concentration in  $L_2$ .

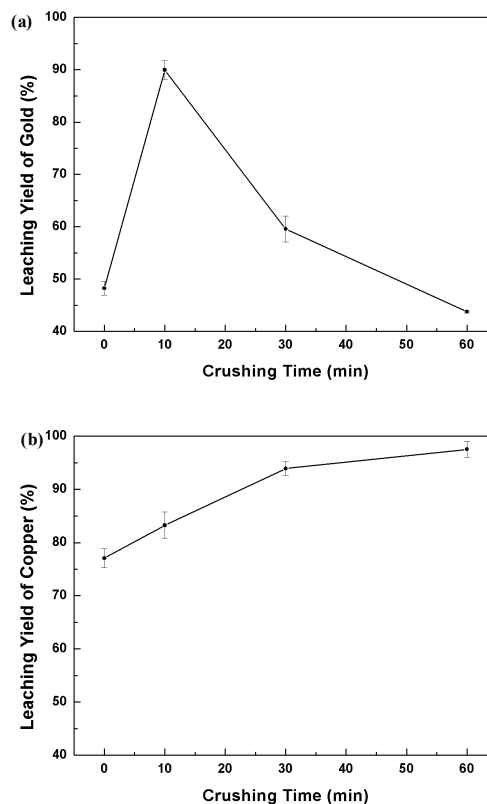
**Effect of Ball Milling.** The raw materials were ball-milled by the MM400 mixer mill for 10, 30 and 60 minutes respectively. The frequency of mixer mill was set at  $20s^{-1}$ . The size distribution of crushed particles was presented in Table 3.

**Table 3** The Size Distribution of Crushed Particles

Fine Crushing Time (min)	Dx (10) ( $\mu m$ )	Dx (50) ( $\mu m$ )	Dx (90) ( $\mu m$ )
0	14.7	325	1490
10	8.56	177	639
30	5.69	86.5	338
60	5.14	60.6	242

where  $D_x(n)$  is the particle size at the cumulative frequency of n%.

The leaching experiments were conducted with 10g of metal concentrate with different ball milling time respectively. The results were presented in Figure 4.

**Fig. 4** Leaching yield of particles with different fine crushing time: (a) gold; (b) copper.

As shown in Figure 4, with the increasing of ball milling time, the leaching yield of copper increased from 77.06% to 97.54%. The leaching yield of gold increased from 48.25% to 89.98% after 10 minute ball milling. However, the leaching yield of gold decreased from 89.98% to 43.75% when the ball milling time increased from 10 minutes to 60 minutes.

In order to improve the separation rate of gold and copper, an experiment of two-stage leaching with the controlling of redox potential was conducted for the particles with 10min ball milling. After the typical run, the residue and sulfuric acid were added back to the reactor for another 8h leaching at a range of 400 to 600mV. The result showed an additional 6.99% of copper was leached out from residue.

**Effect of supercritical process.** The supercritical pretreatment process was conducted with 10g of metal concentrate without ball milling. Supercritical conditions were set at 400°C and 23MPa with a holding time for 60min. After supercritical process, the particles remained in the reaction tube were collected for the leaching process. The leaching yields of metallic elements were presented in Figure 5 with the comparison of that after 10 and 60min ball milling and the raw material.

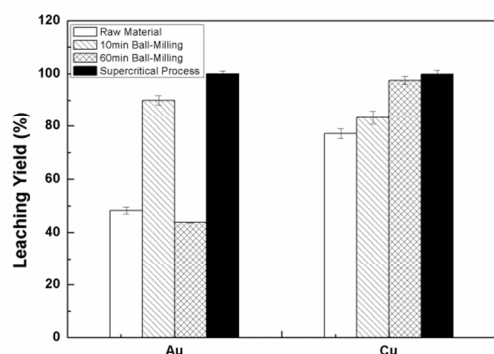


Fig. 5 Comparison of leaching yield of metallic elements.

As shown in Figure 5 and, the supercritical process had an advantage of higher leaching yield of metallic elements. Both the leaching yield of gold and copper could reach more than 99%.

**SEM Photograph.** The scanning electron microscope photographs for particles with different pretreatments were presented in Figure 6.

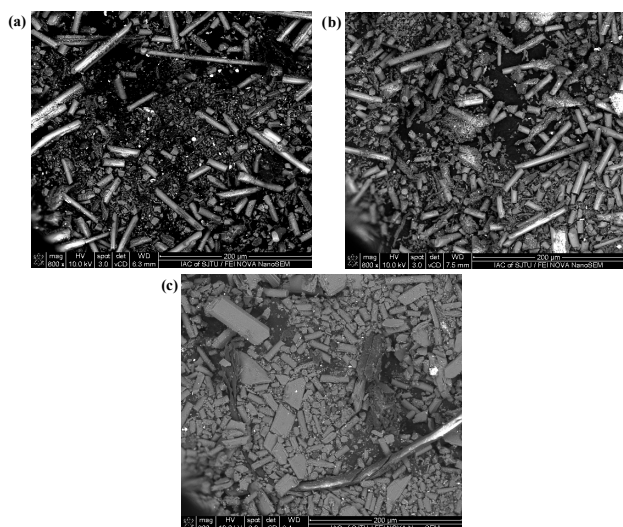


Fig. 6 Surface Morphology of Different Particles ( $800 \times$  magnification): (a) raw material; (b) particles after 10 minutes ball milling; (c) particles after supercritical process.

**Analysis for pretreatment.** The Figure 6 showed that, the ball milling process was only a changing of particle size. On the one hand, the ball milling could achieve the separation of metallic and metalloid parts and enlarge the specific surface area of metallic particles. On the other hand, with the decreasing of particle size, the surface energy of particles will increase which resulted in the agglomeration of particles. The metallic particles were partly wrapped by reinforced resin which is the main composition of the substrate of PCBs. In the PCBs, most of copper existed as copper foil, while gold mostly existed as a plated metal on contact. Due to the small amount and the thin thickness of gold clad layer, it was much easier for gold to be crushed into smaller particle size. Hence, the wrapping of reinforced resin had a greater influence on gold which led to the decreasing of leaching yield of gold with longer

ball milling time, while the leaching yield of copper was still increasing.

However, Figure 6 also showed that, the particle surface was totally different after the supercritical process. Due to the change of dissociation constant at the critical point, supercritical water became a strong oxidizing agent. Supercritical water is a solvent to recycle organic polymers due to its low viscosities, high mass transportation coefficient, diffusivity and solubility. On the one hand, the supercritical process changed the surface morphology of particles. On the other hand, the non-metal parts of PCBs were resolved into low molecular weight organic matter after the supercritical process, which means a more complete separation of metal and non-metal parts. Hence, the leaching yield of metallic elements increased after supercritical process. However, supercritical process is high energy consumption due to the reaction condition of high temperature and pressure, which might hamper the industrial application.

The separation rate of copper could achieve over 90% after the result of two-stage leaching. But the results also indicated that the reaction rate in the second stage leaching had a significant decline due to the decreasing of leachable metal. Hence, leaching with multiple times was not an efficient way to increase the separation rate and leaching yield of metallic elements without the change of other experimental conditions.

### Optimization Experiment

The experiments were conducted with 100g of particles after 20 s-1 ball milling for 10 minutes. After the typical procedure for the leaching of copper, 5g of the residue ( $R_1$ ) was used in each experiment for the gold leaching. The parameter settings were presented in Table 2. The leaching yields were calculated by the concentration of metallic elements in  $L_2$ . The concentration of metallic elements was presented in Table S1.

### Effect of Leaching Time

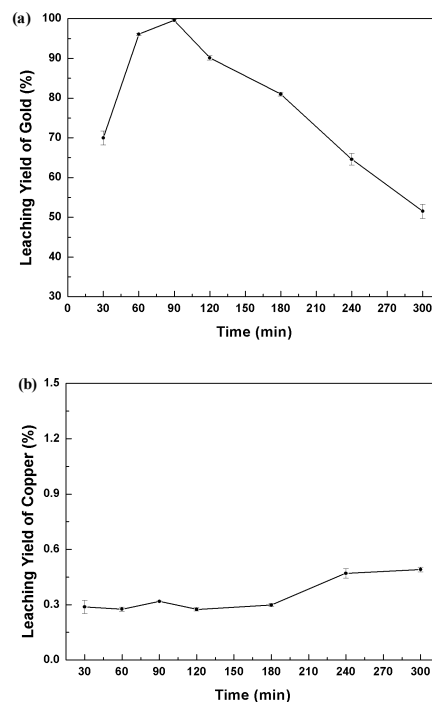
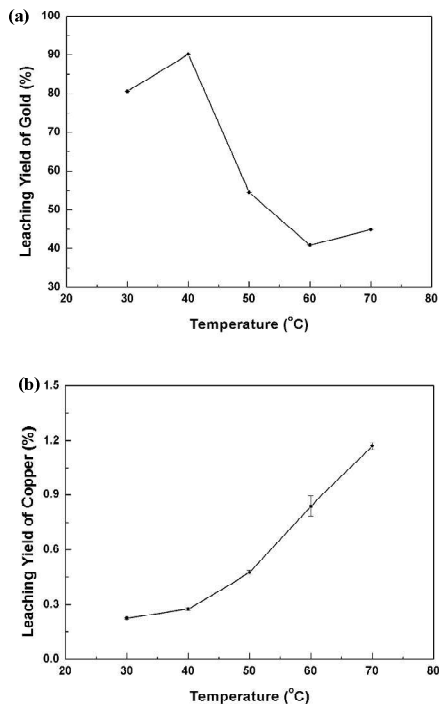


Fig. 7 Leaching yield of different leaching time: (a) gold; (b) copper.

As shown in Figure 7, with the increasing of leaching time from 30min to 90min, the leaching yield of gold increased from 69.97% to 99.60%. However, when the leaching time continuously increased from 90min to 300min, the leaching yield of gold decreased from 99.60% to 51.52%. For copper, when the time increased from 30min to 180min, the leaching yield is about 0.3% of the total raw material and the leaching time has little influence on the leaching of copper. The copper remained in the residue was hard to leach without the change of experimental parameters. Meanwhile, the leaching yield of copper showed an increasing from 0.30% to 0.49% when the leaching time increased to 300min.

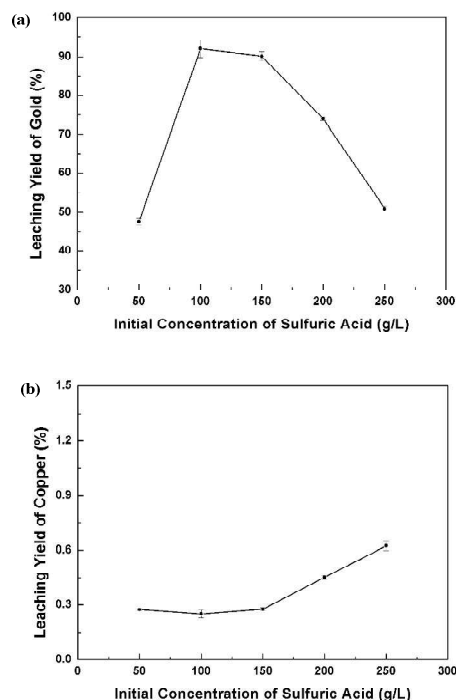
### Effect of Leaching Temperature



**Fig. 8** Leaching yield of different leaching temperature: (a) gold; (b) copper.

As shown in Figure 8, while experiment temperature increased from 30°C to 40°C, the leaching yield of gold rose from 80.57% to 90.12%. When temperature continuously increased to 60°C, there is a significant decline of leaching yield. However, there is a rising trend of leaching yield of gold while the leaching temperature increased to 70°C. Meanwhile, the leaching yield of copper increased with the increasing of temperature. It can be found that the trend of rising is more remarkable at high temperature.

### Effect of Initial Concentration of Sulfuric Acid

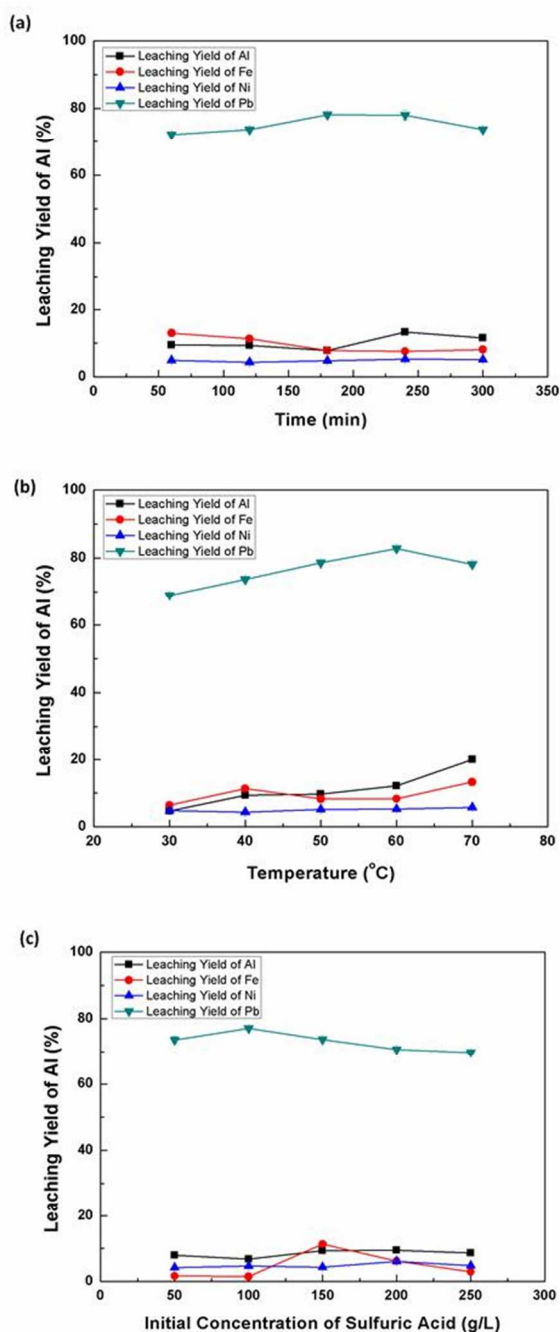


**Fig. 9** Leaching yield of different initial concentration of acid: (a) gold; (b) copper.

As shown in Figure 6, the leaching yield of gold peaked among 100g/L to 150g/L of the concentration of sulfuric acid. When concentration of acid decreased to 50 g/L or increased to 250g/L, there are both presented a significant decline of leaching yield of gold. For the leaching of the copper, the leaching yield increased gradually with the increasing of the concentration of acid. However, the influence was unobvious, especially when the concentration of acid was from 50g/L to 150g/L.

### Interaction of other metals

As waste PCB has complicated composition including many other metals, the interaction of metals should be studied. According to the Table 1, Al, Fe, Pb and Ni were chosen for further study. The leaching yields were calculated by the concentration of metallic elements in  $L_2$ .



**Fig. 11** Leaching yield of Al, Fe, Ni and Fe in different experiment condition: (a)time; (b)temperature; (c)initial concentration of sulfuric acid.

As shown in Figure 11, with the increasing of leaching time, neither Al nor Fe presented obvious change of leaching yield that the fluctuation was less than 3%. However, both Al and Fe showed a significant increasing of leaching yield with the increasing of leaching temperature. Compared with Figure 8, it was the same trend as copper. The figure 11(c) indicated that Fe was more sensitive to the change of acidity of solution.

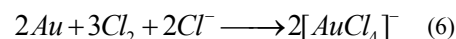
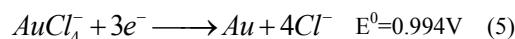
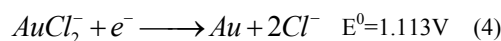
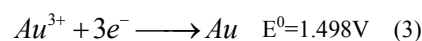
The leaching yield of Pb was significantly higher than other metals. Due to the low solubility of  $PbSO_4$ , Pb was hardly leached in the first stage leaching process. The figure 11(b) and (c) showed that the temperature and acidity had influence on

the leaching yield of Pb with an optimized leaching condition. However, the influence was limited. The leaching yield of Ni didn't have an obvious change in different experimental condition. Furthermore, the concentration of Ni was low in the leaching liquor  $L_2$ . Hence, the interaction between Pb, Ni and gold was not the main influence factor for the leaching efficiency of gold.

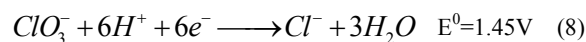
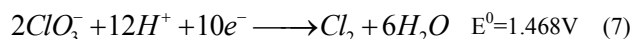
The results proved that the interaction of gold and other metals leaching was obvious in high temperature. The competitive relationship of gold and other base metals would result in the decreasing of gold leaching yield with the increasing of temperature. However, as the amount of these metals was much less than copper, the interaction was very limited in the leaching system, especially in low temperature.

### Principle and Thermodynamic Analysis

Main chemical reactions that occur in gold extraction process could be described by the following equation<sup>25, 26</sup>:

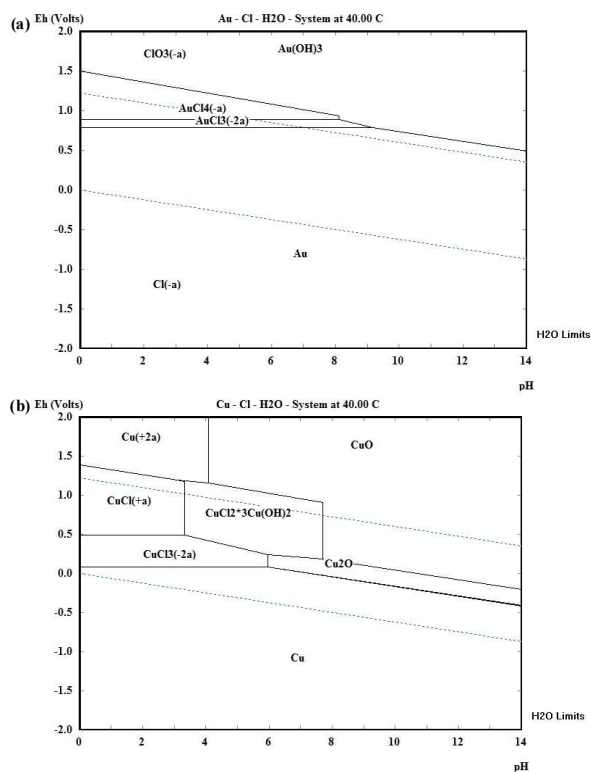


As sodium chlorate was the chlorinating agent in this experiment, the reactions in leaching solution could be described as following equations:



The chemical equation indicated that, the gold ion could only exist in solution after the formation of complex ions with chloride ion as the complex ion decreased the electrode potential of gold from 1.498V to 0.994V. The leaching solution should be in the acidic condition and the hydrogen ions would be consumed in the leaching process.

The Eh-pH diagram for the Au-Cl-  $H_2O$  system (25g/L  $NaClO_3$ , 75g/L  $NaCl$  and 0.29g/L Au) and the Cu-Cl- $H_2O$  system (25g/L  $NaClO_3$ , 75g/L  $NaCl$  and 25.96g/L Cu) used in this study were typically shown in Figure 10 (calculated by HSC Chemistry 7.0).



**Fig. 10** Eh-pH diagram for: (a) Au-Cl-H<sub>2</sub>O system (25g/L NaClO<sub>3</sub>, 75g/L NaCl and 0.29g/L Au); (b) Cu-Cl-H<sub>2</sub>O system (25g/L NaClO<sub>3</sub>, 75g/L NaCl and 25.96g/L Cu).

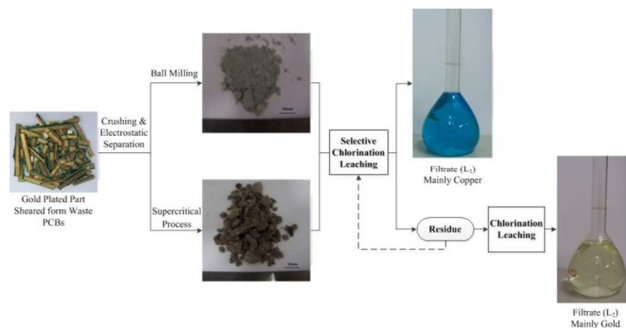
The information from Au-Cl-H<sub>2</sub>O system model indicated that, gold in the leaching solution is mostly stable as AuCl<sub>4</sub><sup>-</sup> complex and the stability zone for AuCl<sub>3</sub><sup>2-</sup> is narrow. Generally speaking, when the Eh of solution is between the range of 900mV to 1500mV and the pH of solution is below 8, the gold can be leached into solution as AuCl<sub>4</sub><sup>-</sup> complex. However, if the Eh potential is too high (say above 1200mV) and the pH of solution is above 5, the gold chloride will convert to a more stable Au(OH)<sub>3</sub><sup>27</sup>. Hence, in order to maintain gold in the solution, the leaching condition should be controlled with the 800-1200mV of Eh range and the pH below 4. The Cu-Cl-H<sub>2</sub>O system model showed that, when the Eh of solution is above 0mV and the pH of solution is below 4, copper can be leached into solution. The lower pH and higher Eh were better for the leaching of copper. The selective leaching of copper could be achieved if the Eh of leaching solution was controlled between 0 to 800mV and the pH of solution is below 4.

The Figure 10 showed that, the gold and copper had a competitive relationship in the leaching system. Due to the complicated composition of PCBs, the leaching yield of gold will be influenced by copper the other metallic elements remained in the residue. As presented in chemical reaction formula Eq. (7), with the time increasing, the H<sup>+</sup> in the leaching solution would be expended and the emission of Cl<sub>2</sub> might occur due to the open system. As a result, the concentration of chlorinating agent will decrease and the pH of solution would increase which had a greater influence on the leaching of gold due to the stability of AuCl<sub>4</sub><sup>-</sup>. The Au<sup>3+</sup> in leaching solution would tend to convert to Au(OH)<sub>3</sub> at this condition, which resulted in a significant decreasing of leaching yield of gold and an increasing of leaching yield of copper after 180min leaching.

Generally speaking, the increasing of temperature would accelerate the reaction rate and presented as an increasing of leaching yield of metallic elements. However, as the leaching system was not closed, if the leaching temperature was too high, the gas emission of Cl<sub>2</sub> would increase which led to the decreasing of the concentration of chlorate and leaching yield of gold. When the temperature increased from 50 °C to 70 °C, the temperature had a more significant influence of the leaching of metal, which resulted in a recovery of leaching yield of gold at 70 °C as shown in Figure 8. Due to the competitive relationship of metallic elements in the leaching system, the leaching yield of gold was influenced by the leaching of other metallic elements like copper at the same time. Hence, the leaching yield of gold decreased within a certain range of temperature.

Chlorate has many existence forms in the aqueous solution. The acidity of solution played a big role in the amount of different forms. Due to the high standard electrode potential of gold, the gold leaching process was more sensitive to the changes of the chlorate form. As shown in Figure 10, if the pH of the leaching solution was too high, the gold chloride would tend to be converted to Au(OH)<sub>3</sub>. However, if the pH of the leaching solution is too low, the solubility of Cl<sub>2</sub> would decrease due to the movement of solubility equilibrium to the direction of producing gas, which resulted in the decreasing of chlorinating agent and led to the decreasing of leaching yield of gold. Meanwhile, a lower pH had a positive influence on the leaching of copper. As the concentration of chlorinating agent was not the main influence factor, the leaching yield of copper would increase continuously with the increasing of acidity, which would have a negative influence on the leaching of gold due to the competitive relationship. Hence, there is an optimum condition for gold leaching around 100g/L of sulfuric acid.

## Conclusions



**Fig. 12** The flowchart of chlorination leaching process for the selective recovery of gold and copper.

The chlorination leaching could achieve the selective leaching of gold and copper in the waste PCBs. The pretreatment could contribute a lot to increase the leaching yield of metallic elements. The supercritical process and the ball milling with appropriate time both had a positive influence on the leaching of metallic elements from waste PCBs. The supercritical process had a better effect but with higher cost. Compared to conventional gold leaching method, this method can recover copper and gold respectively with high purity. Low hazardous waste gases or liquids were produced during the whole process. This process provides a less-polluted, economic and efficient way for recycling gold and copper from waste PCBs.

## Acknowledgements



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