



# Application of Cementation Technology in a Chemical Recycle Plant Treating Waste Copper-Bearing Solution from Micro-Etching Processes

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## Abstract

Waste copper-bearing solution generated from the micro-etching process of printed circuit boards (PCBs) was studied using cementation technology in a chemical recycle plant. Operation parameters include initial copper ion concentrations (15, 23, 30 g/L) and pH values (pH = 1, 2, 3, 4) were assessed. Results showed that, within the range from 15 to 30 g/L of copper ion concentration, the reaction rate decreased with increasing the initial concentration. In addition, the higher the pH value the slower the copper cementation rate. And at pH = 4, the rate is as low as about 40 %, compared to the other pH values. It is attributed that, presumably as the pH of the solution increases, the copper hydroxide may be deposited onto the iron sheet surface to form a passivation layer, resulting in the blocking of solid-liquid interface mass transfer. Results from mass balance calculations indicated that the unit operation of the plant was quite in agreement with expectations. However, the average resource conversion rate (RCR) was at 58.7%. In order to increase the resource conversion rate, it is suggested that either a reduction of water consumption or a water recycling program to the process should be taken into consideration to increase the RCR. The result of this study is beneficial to shorten the gap between theoretical research and practical operations for chemical recycle plant that is positive to industrial waste reduction and resource sustainability.

**Keywords:** Micro-etching, cementation technology, passivation, mass balance, resource conversion rate

## 1 Introduction

Electronic products are widely used in various fields of life, and have been linked to instant and mobile devices, making the manufacturing process of printed circuit boards (PCBs) more prosperous in recent years. According to the survey report [1], up to 2018, the global PCBs output value will increase to US\$ 68 billion, and the average annual compound growth rate is 3.9%.

High-precision and effective micro-etching is an important process to enhance the productivity of PCBs [2~3]. The micro-etching process can be divided into three sections: inner layer etching, plated through hole and line etching, and outer layer etching. Among them, the plated through hole and line etching process generates a waste copper-bearing solution with copper content less than 30 g/L. However, partially due to this low concentration of copper in the waste liquid, most of the chemical plants lack of incentives to recycle. As the PCB factory discharged this waste liquid into the wastewater treatment system, the

result is not only a large amount of copper-bearing hazardous sludge, but also increase the environmental loading.

For waste copper-bearing solution, chemical treatment methods such as precipitation, electrolysis, and cementation are commonly used in industry [4-5]. The advantage of precipitation and electrolysis is that the reaction rate is speedy, while the major disadvantage is that the post-treated liquid is still in large quantity and needs to be subsequently processed. As for the cementation method, it is theoretically to use iron having a lower reduction potential to recover copper metal having a higher reduction potential in waste liquid [6-9]. Although the reaction rate of cementation is generally slower than precipitation and electrolysis, both the products after solid-liquid separation procedure are industrial reusable.

Although there have been many investigations on the copper-iron cementation, the results using waste liquid from the PCBs factories were mostly laboratory scale, let alone employed a chemical recycle plant to evaluate the control parameters. The objective of this study is to assess the effect of the initial copper content and pH value on cementation technology using the waste copper-bearing solution produced by the PCBs micro-etching process. This study has been carried out in a chemical recycle plant,

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and the results are capable of direct application to benefit both industrial waste reduction and resource sustainability.

## 2 Experimental section

### 2.1 Procedure

The testings were carried out using a stirring drum reactor schematized in Figure 1. The reactor is mainly composed of two parts: (1) a stainless-steel drum coated with PE-inliner film, and (2) an automatic programmable mortar mixer. The waste copper-bearing solution, tank-truck delivered from a PCBs factory, was added in 2.0 m<sup>3</sup> each time in batch process. The ionic sheets (5 cm × 5 cm × 0.01 cm) were obtained from a recycling plant specializing in waste vehicle bumper. The testing procedure is as follows:

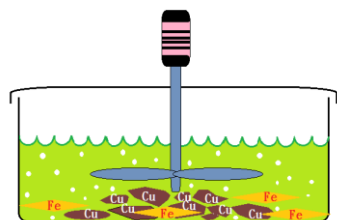


Figure 1: Schematic of the Cu-Fe Cementation Reactor.

- (1) Pump the waste copper sulphate liquid to the cementation reactor.
- (2) Adjust the pH to the testing conditions using liquid NaOH or sulfuric acid ( $\text{pH} = 1.0 \sim 4.0 \pm 0.1$ ), then add iron sheets to the reactor and start mortar mixer.
- (3) Take samples to analyse copper and iron concentration at 2-hour intervals over a period of 14 hours, then terminate the stirring pump.
- (4) Wait for 10 hours for copper precipitation, then pump the supernatant liquid from the cementation reactor to the storage tank of the ferrous sulphate solution.
- (5) Add 1 m<sup>3</sup> of tap water to flush the cementation. The residual liquid cleaning work was carried out, and the stirring pump was again turned on for about 10 minutes, and then left to stand for 10 hours.
- (6) Pump the supernatant liquid in the cementation reactor to the wastewater treatment facility, and remove the cemented copper manually into press filter to dewatering operations.
- (7) After dewatering, the copper cake is weighed and analysed in the plant laboratory.

### 2.2 Analytical Methods

All samples were stored in amber glass bottles to prevent metal ions from being attached to the bottle wall, and were analyzed immediately after each batch of test to avoid any potential interference. The analyses of metal ions were carried out using flame atomic absorption spectrometry (AAS 932Plus, GBC Scientific Equipment). The analytical method was adapted according to the National Institute of Environmental Analysis (NIEA M111.01C) [10].

## 3 Results and Discussion

### 3.1 Composition of Waste Copper-Bearing Solution

The constancy of the waste liquid component plays an important role on the progress of this study. The waste copper-bearing solution has a total of 3 trips of tank-truck entering plant for testing. The analytical results of the composition are summarized in Table 1. As shown in Table 1, the content of copper is between 25.8 and 30.2 g/L. There is no significant difference in the remaining composition of the waste liquid. This waste copper-bearing solution from micro-etching process of PCBs is classified as hazardous waste solution as its  $\text{pH} \leq 2.0$  in Taiwan.

Table 1: Analysis of waste copper-bearing solution.

| Item             | unit | Tank Truck Entering Chemical Plant |      |      |
|------------------|------|------------------------------------|------|------|
|                  |      | 1                                  | 2    | 3    |
| Specific Gravity | -    | 1.10                               | 1.14 | 1.19 |
| pH               | -    | 1.4                                | 1.4  | 1.2  |
| Cu               | g/L  | 18.3                               | 25.8 | 30.2 |
| Hg               | mg/L | ND                                 | ND   | ND   |
| Pb               |      | 0.03                               | 0.04 | 0.04 |
| Cd               |      | ND                                 | ND   | 0.01 |
| Cr               |      | 0.05                               | 0.05 | 0.06 |
| Cr <sup>6+</sup> |      | 0.01                               | 0.02 | 0.02 |
| As               |      | ND                                 | ND   | ND   |
| Se               |      | ND                                 | ND   | ND   |
| Ba               |      | ND                                 | ND   | ND   |

### 3.2 Effects of Initial Copper Ion Concentration

In this study, three different initial concentrations of copper ions were prepared to investigate the effect of initial copper ion concentration on the cementation reaction. The initial concentrations were prepared for 15, 23, and 30 g/L, respectively. The stirring speed was set at 60 rpm during the test. The pH value is chosen to be fixed at 3.0 first. Figure 2 shows the change of the copper ion concentration in the cementation reactor with the change of reaction time. From the figure it is obvious that the copper ion concentration decreases with the reaction time, while at the end of the reaction the residual copper ion concentration increases with the increase of the initial concentration. It is noted that from Figure 3, the result at 30 g/L is different from the other two initial concentrations.

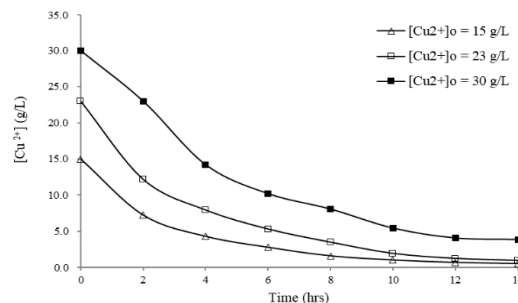


Figure 2: Effects on initial copper ion concentration to the cementation reactions.

As the cementation reaction proceeds, the order of the reaction can be evaluated by analysing the change of the

concentration of copper ions with respect of the change of reaction time. Previous studies have suggested that copper-iron cementation reactions as first-order reaction [11~13], and can be expressed as Equation (1):

$$-\frac{d[Cu^{2+}]}{dt} = k \left( \frac{A}{V} \right) [Cu^{2+}] \quad (1)$$

where the  $-\frac{d[Cu^{2+}]}{dt}$  is the rate of change of copper ion concentration with respect to reaction time (t), k is the reaction rate constant, A is the total area of the iron piece, and V is the volume of the waste copper sulfate solution in the reactor. Integrate Equation (1) and let t = 0, the initial copper ion concentration  $[Cu^{2+}] = [Cu^{2+}]_0$ , the reaction rate can be expressed as Equation (2):

$$\ln \frac{[Cu^{2+}]}{[Cu^{2+}]_0} = -k \left( \frac{A}{V} \right) \cdot t \quad (2)$$

Since each batch of this study keeps constant in volume and in weight of the iron at the same pH, the (A/V) can be regarded as a constant value. Figure 3 shows the cementation reaction constant (k) obtained by changing the reaction time with  $\ln([Cu^{2+}]/[Cu^{2+}]_0)$ . Comparing the slopes of the reaction straight lines of each initial concentration in Figure 4, it is clear that the slopes of the initial concentration of 15 g/L and 23 g/L are larger and closer. As concentration increases to 30 g/L, the slope is lower than 15 g/L and 23 g/L.

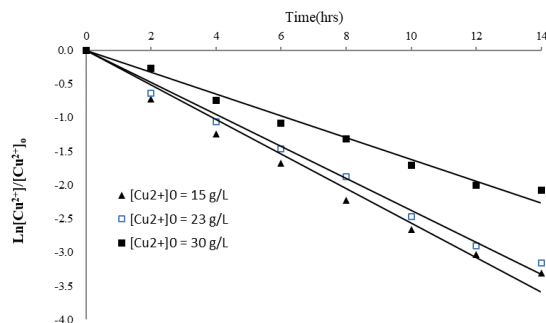


Figure 3: Change of  $\ln([Cu^{2+}]/[Cu^{2+}]_0)$  in the cementation reactor with respect to time.

The rate of chemical reaction is often affected by the initial concentration of the reactants. In order to explore the extent of the effect, this study formulated three sets of initial concentrations for cementation reactions. Figure 4 shows the cementation reaction rate constant (k) plotted against the initial copper concentration  $[Cu^{2+}]_0$ . From the figure, the cementation rate constant decreases as from 0.257 hr<sup>-1</sup> to 0.234 hr<sup>-1</sup>, with the increases of initial concentration from 15 g/L to 23 g. This change of k is slightly minor. But the change of k becomes obviously greater, that is reduced from 0.234 hr<sup>-1</sup> to 0.162 hr<sup>-1</sup>. It is postulate that, since the cementation of metal is heterogeneous reaction, the higher the initial concentration of copper ions, the higher the activity of the solution in the

concentration tank, so as increased the viscosity coefficient and the diffusion layer between solid and liquid. An increase in these parameters may lead to a decrease in the diffusion rate of copper ions in the solution, which eventually result in a decrease in the rate of cementation reaction, and is relatively in agreement with previous studies [14~15].

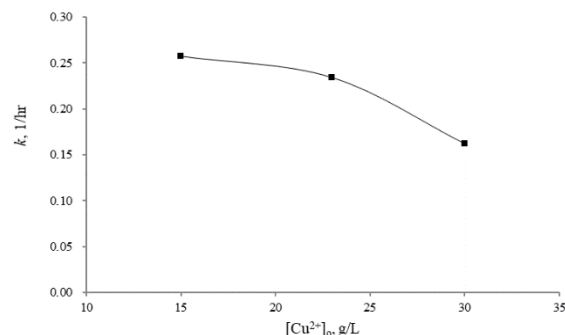


Figure 4: Change of reaction rate constants (k) respect to initial copper ion concentrations.

### 3.3 Effects of pH Value

As stated in previous section, the pH of the waste copper sulfate solution produced by the micro-etching process is usually less than 2.0. Factors including number of plated holes, number of layers of the circuit board, and frequency of cleaning, may result in the variation of pH in the waste copper sulfate solution discharged from batch to batch. Therefore, it is necessary to evaluate the effect of pH on the cementation reaction for the recycling plant operation. In this study, the range of pH was set from 1.0 to 4.0, and the initial copper ion concentration was controlled at 23 g/L. Figure 5 shows the copper ion concentration in the solution decreases with the increase of the reaction time. It is obvious that the cementation rate of pH=4 is much lower than that of the other pH=1~3. The copper ion concentration is reduced from 23 g/L to 14 g/L, indicating the change of cementation is about 40%.

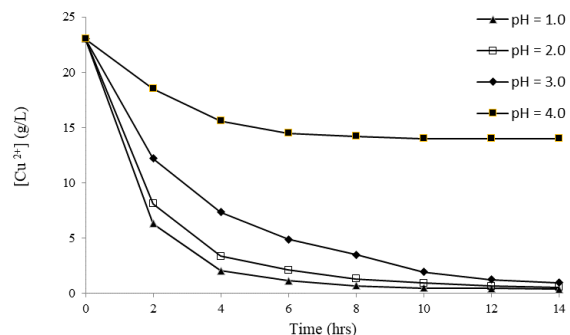


Figure 5: Change of copper ion concentration respect to pH value.

Figure 6 shows the emerge of ferrous ions in the cementation reactor with pH=1~4. It can be seen that the concentration of ferrous ion at pH=4 is only 7.7 g/L, which is significantly lower than the other pH=1~3 (up to 19.5 g/L). In comparison with the other groups of pH=1~3, the

copper-iron cementation rate at a pH=4 is only about 40%. Previous research results have suggested that the increase of pH in cementation reactor may result in reducing the reaction rate [16~17].

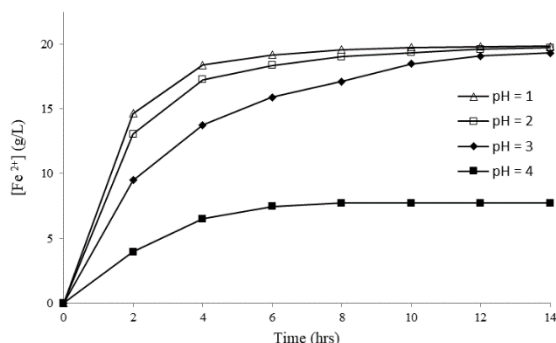


Figure 6: Change of ferrous ion concentration respect to time.

In the copper-iron cementation system, increasing the pH value indicates that the concentration of  $[\text{OH}^-]$  in the solution is increased, and it is intended to cause a reaction of forming a hydroxide precipitate with the copper ion, as expressed in the following reaction equation:



In case that a large amount of copper hydroxide precipitates and accumulates on the surface of the iron sheet, then it is intended to form a passivation phenomenon [18~19]. From the viewpoint of reaction kinetics, as indicated in the Equation (1), the reduction of the active area (A) of the iron sheet may directly decrease the cementation reaction. In addition, the passivation of the surface of the iron sheet, as shown in Figure 7, may highly hinder the outward transfer of electrons. As in Figure 8, the mechanism of the cementation reaction can be subdivided into five main steps. It is noted that in the third step, if the iron sheet is subjected to surface passivation, the iron ions may be ineffectively entering the electric double-layer and diffuse outward, causing a limit to the electrons delivering to copper ion. The rate of cementation reaction will eventually be greatly reduced. Therefore, by evaluating from the results of this study, the waste copper-bearing solution should be controlled to  $\text{pH} \leq 3.0$  for operation in chemical recycling plant.

### 3.4 Calculations of Resource Conversion Ratio

The assessment of mass balance is important to understand the flow of raw materials and products, and to improve the efficiency of unit operations. In this study, the copper-iron cementation reaction is carried out in a recycling plant, and the overall mass balance calculation is presented as a result of the batch testings as shown in Equation (4):

$$\sum \text{Total Input} = \sum \text{Total Output} \quad (4)$$

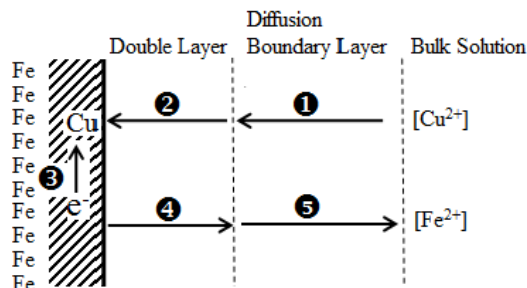


Figure 7: Schematic diagram of mechanism for copper-iron cementation reaction. (1) =  $\text{Cu}^{2+}$  ions entering liquid-solid diffusion boundary layer from bulk solution; (2) =  $\text{Cu}^{2+}$  ions precipitated from electric double-layer interface to form Cu metals; (3) = Fe metal transfers electron to  $\text{Cu}^{2+}$  ions and become  $\text{Fe}^{2+}$ ; (4) =  $\text{Fe}^{2+}$  ions diffuse outward from electric double-layer interface; (5) =  $\text{Fe}^{2+}$  ions entering bulk solution from liquid-solid diffusion boundary layer.)

Table 2: Mass balance and resource conversion rate.

| Items                     |                               |                                  | Unit           | pH=1    | pH=2    | pH=3    |
|---------------------------|-------------------------------|----------------------------------|----------------|---------|---------|---------|
| Total Input               | Waste Copper-Bearing Solution | Weight                           | Kg             | 2280    | 2280    | 2280    |
|                           |                               | Volum e                          | m <sup>3</sup> | 2.0     | 2.0     | 2.0     |
|                           |                               | [Cu <sup>2+</sup> ] <sub>0</sub> | g/L            | 23.00   | 23.00   | 23.00   |
|                           |                               | Copper                           | Kg             | 46.00   | 46.00   | 46.00   |
|                           | pH Adjuster                   | NaOH                             | Kg             | 0.00    | 64.10   | 398.31  |
|                           |                               | H <sub>2</sub> SO <sub>4</sub>   | Kg             | 36.92   | 0.00    | 0.00    |
|                           | Iron Sheets Weight            | Kg                               | 75.09          | 79.20   | 92.12   |         |
|                           | Cleaning Water                | Kg                               | 1000           | 1000    | 1000    |         |
| Sum                       |                               | Kg                               | 3392.01        | 3423.30 | 3770.43 |         |
| Total Output              | Ferrous Sulfate Solution      | Weight                           | Kg             | 1912.77 | 1944.20 | 2163.96 |
|                           |                               | Copper                           | Kg             | 0.21    | 0.22    | 0.23    |
|                           |                               | Iron                             | Kg             | 72.82   | 76.77   | 90.01   |
|                           | Cemented Copper               | Weight                           | Kg             | 64.92   | 65.08   | 64.44   |
|                           |                               | Copper                           | Kg             | 45.67   | 45.63   | 45.49   |
|                           | Cleaning Water                | Weight                           | Kg             | 1414.3  | 1414.0  | 1542.0  |
|                           |                               | Copper                           | Kg             | 0.12    | 0.15    | 0.28    |
|                           |                               | Iron                             | Kg             | 2.27    | 2.43    | 2.11    |
|                           | Sum                           |                                  | Kg             | 3392.01 | 3423.30 | 3770.43 |
| Resources Conversion Rate |                               |                                  | %              | 58.30   | 58.69   | 59.10   |

As illustrated in Table 2, the items of total input include waste copper-bearing solution, pH adjuster, iron sheets and cleaning water. The items of total output include ferrous sulfate solution, cemented copper and cleaning water. Each item in total input and total output is measured, respectively. The results show that the total input is equal to output, and in terms of the mass balance in the cementation reaction, it is quite consistent with the theoretical estimates. In addition, the resources conversion rate (RCR) has been calculated using the cementation products, namely ferrous sulfate solution and cemented copper, as expressed in Equation (5):

$$\text{RCR}(\%) = \frac{\text{Weight of ferrous sulfate solution} + \text{Weight of cemented copper}}{\text{Total Input}} \quad (5)$$

It can be seen from Table 2 that the RCR is between 58.3 % and 59.1 %, with the average value at 58.7 %. By

examining the items in Table 2, the cleaning water is the major cause account for this lesser of RCR. Accordingly, the cementation technology may have the application benefit of recycling the waste copper-bearing solution produced by the micro-etching, the water consumption of cleaning the cementation reactor should be further reduced, or the water recycling program be included to improve the RCR.

#### 4 Conclusions

In this study, the cementation technology is applied to an industrial waste treatment plant, and the control parameters of the waste copper-bearing solution produced by the PCB micro-etching process are evaluated. Both initial copper concentration and pH value are the major operational concerns, so as to set as test parameters. All tests were recorded, including input and output amount, copper concentration, weight of iron sheet, and weight of cemented copper. Experimental results were also used to estimate the kinetic rate constants and RCR of the reaction. The conclusions of the study are listed below.

- (1) Three sets of initial copper concentration were tested at 15, 23, 30 g/L, respectively. It was found that the first-order kinetic rate constant decreased with the increase of the initial copper concentration. The increase of copper concentration causes the diffusion layer between solid and liquid to be increased, leading to the decrease of the mass transfer rate.
- (2) Four experiments were carried out with different pH (pH=1~4). The results showed that the cementation rate at pH=4 was much lower than that of the other pH (pH=1~3). It is attributed that as the pH of the solution increases, the surface of the iron sheet is deposited by copper hydroxide. As the passivation phenomenon prevails, the active area of the iron sheet is reduced, resulted in the decrease of cementation reaction. The iron is incapable of effectively transmitting electrons and diffusing into the electric double layer, leading to limit the cementation reaction rate.
- (3) Three sets of pH (pH=1~3) were carried out to perform the mass balance estimation. The results showed that the total input amount and the total output amount are equal, that is within expectations. However, the average RCR is only 58.7%. It is suggested that, either a reduction of water consumption or a water recycling program in the cementation reactor should be considered to increase the RCR.

Though the copper content in the waste copper-bearing solution produced by the through-hole micro-etching process of PCBs is low (< 50 g/L), the cementation technology is capable of recovering the copper and ferrous sulphate solution. Therefore, the result of this study is beneficial to shorten the gap between theoretical and practical operations, as well as to diversify the technology in waste treatment that is positive to industrial waste reduction and resource sustainability.

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#### Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

#### Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

#### Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

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