



Ultrasonic recovery of copper and iron through the simultaneous utilization of Printed Circuit Boards (PCB) spent acid etching solution and PCB waste sludge[☆]

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ABSTRACT

A method was developed to recover the copper and iron from Printed Circuit Boards (PCB) manufacturing generated spent acid etching solution and waste sludge with ultrasonic energy at laboratory scale. It demonstrated that copper-containing PCB spent etching solution could be utilized as a leaching solution to leach copper from copper contained PCB waste sludge. It also indicated that lime could be used as an alkaline precipitating agent in this method to precipitate iron from the mixture of acidic PCB spent etching solution and waste sludge. This method provided an effective technique for the recovery of copper and iron through simultaneous use of PCB spent acid solution and waste sludge. The leaching rates of copper and iron enhanced with ultrasonic energy were reached at 93.76% and 2.07% respectively and effectively separated copper from iron. Followed by applying lime to precipitate copper from the mixture of leachate and rinsing water produced by the copper and iron separation, about 99.99% and 1.29% of soluble copper and calcium were settled as the solids respectively. Furthermore the settled copper could be made as commercial rate copper. The process performance parameters studied were pH, ultrasonic power, and temperature. This method provided a simple and reliable technique to recover copper and iron from waste streams generated by PCB manufacturing, and would significantly reduce the cost of chemicals used in the recovery.

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1. Introduction

The manufacturing of PCB, a basic component used extensively in the electronic equipments, has grown rapidly in the last two decades with a continually increasing demand for electronic products. The vast majority of PCB was made by selective acid etching of the thin copper foil covered on a non-conductive plastic board to reveal desired copper conductor circuits. The etching is a significant source of copper containing spent acid etching solution in PCB industry [1]. Other processes of PCB manufacturing such as board rinsing and electroless copper plating can also generate a significant amount of heavy metals-bearing wastewater that mostly contains mixed copper and iron ions, and this wastewater is normally treated by adding sodium hydroxide and iron salt as coagulants to precipitate copper and iron out of the spent solution forming so-called PCB waste sludge [2]. The precipitation is induced by ferric hydroxide formed from iron ions and hydroxyl ions that aggregates copper and iron ions of the solution. If the aforementioned spent etching solution and wasted sludge generated from

PCB manufacturing are not treated and discharged properly, it will not only have detrimental effects on the environment, but also result in valuable heavy metal resources wasted without further utilization [3]. In order to have both sound environmental protection and sustainable development that highly emphasizes on reuse of valuable resources, it is of great importance to develop a methodology to economically recover the heavy metals from spent etching solution and wasted sludge generated from PCB manufacturing industry.

In recent years, various metal recycling methods have been developed to recover valuable metals focusing separately on either spent solutions or waste sludge generated by PCB manufacturing. Some methods that recover metals from PCB spent etching solution include electrowinning, cementation, solvent extraction, precipitation and biological membrane enrichment [1,4–8]. Many methods have also been developed to recover metals from waste PCB sludge, such as emulsified liquid membranes, co-precipitation, adsorption, cementation, and solid-phase extraction have also been developed [9–14]. However, unacceptable treatment costs, highly complicated processes, and potential adverse environmental impacts limit these methods to be applied at industrial scale.

Recent studies have demonstrated that ultrasonic power could enhance either the extraction or leaching rates of metals [15–21], while metals themselves, even if leached more efficiently, were still

[☆] Patent-pending technique.

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co-dissolved in an aqueous solution and were not separated. As a result, the leached metals in these studies could not be effectively recovered as reused resource materials. Seeking an efficient way for metals separation and recovery from multiple metals containing waste sludge, Xie et al. [22] developed a lab-scaled ultrasonically-assisted acid leaching technique for separation of copper and iron from sulfuric acid-dissolved PCB waste sludge. The test indicated that ultrasound energy enhance the copper ions leaching into acidic aqueous phase, while iron ions still remained in solid phase. The leaching rate of copper was measured at 97.83% and iron at 1.23%. Without ultrasonic assistance, it also showed that copper and iron could not be completely separated. The test provided an acceptable separation of copper and iron from heavy metal bearing PCB waste sludge. Xie et al. [23] applied this lab-originated technique to an industrial scale metal recycling process and treated PCB waste sludge generated from electronic manufacturing. The process separated copper and iron of the sludge. The separated copper was produced as copper sulfate after concentrating and crystallizing the acidic aqueous phase which contained only copper ions. The separated iron, as ferric hydroxide in solid phase, was dissolved by hydrochloric acid converting to ferric chloride which could be reused for treatment of the rinse water generated from the board rinsing process. The ultrasonically enhanced metal recovery process generates no pollution to the environment and is fully in compliance with all local environmental regulations. Xie et al. [24] then developed an ultrasonically enhanced two-stage acid leaching process on extracting and recovering multiple heavy metals from electroplating sludge in lab tests. The results showed that all recovery rates of Cu, Ni, Zn, Cr and Fe from electroplating sludge could reach 97.42%, 98.46%, 98.63%, 98.32% and 100% respectively.

In this study, sulfuric acid that was used in the two prior studies [22,23] is substituted with copper containing acidic PCB spent etching solution as an acid leaching solution to extract metals from PCB waste sludge. It also substitutes sodium hydroxide that was used in [22,23] with lime as the alkaline precipitating agent to precipitate iron from leachate generated from the mixed acidic spent etching solution and PCB waste sludge. With ultrasonic assistance, the proposed approach enhances copper leaching to aqueous solution from the sludge and retains iron inside the sludge. This results in a separation between copper and iron, and it is the first step of the recovery process. Ferric hydroxide generated as solids in the separation is taken out, and further dissolved by hydrochloric acid to ferric chloride as one of end-products of the process that are commercially reusable. To make reusable copper products, copper ions in the aqueous solution generated at the first step are added with lime and precipitated into solid cupric hydroxide. The copper ions, which entered the aqueous solution with the assistance of ultrasound, were originally contained by the acidic spent etching solution and waste sludge. The precipitated cupric hydroxide could be further dissolved by sulfuric acid and crystallized as commercial rated copper sulfate. As demonstrated in this study, the utilization of PCB acid spent etching solution instead of sulfuric acid, and the utilization of PCB waste sludge and lime instead of sodium hydroxide could recover copper and iron from PCB spent etching solution and waste sludge simultaneously. Fig. 1 shows raw materials and major products of the study carried experiment. The study would significantly reduce cost of chemicals used in copper and iron recovery from PCB manufacturing generated waste streams.

2. Materials and methods

2.1. Materials and experimental device

Copper containing acidic PCB spent etching solution and PCB waste sludge samples tested in the study were supplied by Dingfu



Fig. 1. Raw materials and major products of the study carried experiment.

Electrical Co. Ltd. at Huizhou, China. The spent etching solution appeared greenish with pH of 0.1 and contained mainly hydrochloric acid, copper chloride, and sulfate radical, the content of other components was very low that can be neglected. Copper of the solution was measured by an Atomic Absorption Spectrometry (AAS) (Z-2000, Hitachi Ltd.) at 114.1 g/l. The sludge appeared blackish with a pH of 6.8 and it contained mainly copper hydroxide, ferric hydroxide, and ferrous hydroxide. Moisture content of the sludge was measured by an Infrared Moisture Meter (IMM) at 79.40%. Principal metals of the sludge were analyzed by AAS as 3.19% copper and 4.65% iron in wet weights. The sludge was also accompanied by trace amounts of various kinds of other metallic impurities in the form of soluble compounds with overall weight <0.1%, which was measured by X-ray fluorescence (XRF) (PANalytical Axios, The Netherlands), and these impurities were negligible in this study. Lime used in the study was supplied by a local firm with a pH of 11.5.

Ultrasound produced by an ultrasonic generator (Guangzhou KEPU Ultrasonic Electric Technological Ltd.) has exerted on tested materials inside a beaker through an immersed titanium probe. Ultrasound had a frequency set at 20 kHz and its power was adjusted at 100 W, 200 W and 300 W during the study. The beaker was stirred with a thermostatic magnetic stirrer under a preset temperature. pH inside the beaker was measured by a calibrated PHB-3 pH-meter (Shanghai San-Xin Instrumentation, Inc.). Copper



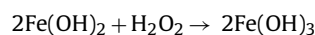
Fig. 2. The ultrasonically enhanced leaching experiment device.

and iron in both solid and liquid phases were measured by AAS. The ultrasonically assisted leaching experiment device is shown in Fig. 2.

2.2. Copper and iron separation for PCB spent etching solution and waste sludge

2.2.1. PCB waste sludge preparation

Replicate subsamples of PCB waste sludge (50.00 g each) were made. Each sample was weighed and put into a 250-ml beaker. Water was added, and diluted the sludge until it was up to 90% water. 20 ml 30% of H₂O₂ was then added and stirred at a speed of 300 rpm for 60 min at room temperature (25 °C). It made all ferrous irons inside the beaker oxidized to ferric irons. The reaction could be described as:



All the PCB sludge used in the experiment discussed below was the prepared sludge that contained iron salt hydroxide precipitate near-neutral with a pH around 7.0.

2.2.2. Lime preparation

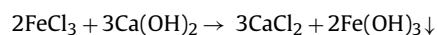
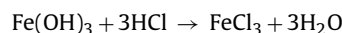
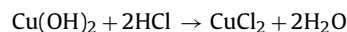
3.00 kg of lime were put into a 5-l bucket. 1.5 l of water was added and stirred for 30 min and then the slurry samples were filtered through to a 600-mesh sieve. Lime cream that passed down through the sieve was collected in another 5-l bucket that would be used later. The lime used hereafter was the prepared lime as described in this section.

2.2.3. Copper and iron separation test

With temperature maintained at 25 °C, the prepared PCB sludge was poured into a 250-ml beaker and stirred at 300 rpm. Acidic spent etching solution was then added into PCB sludge to adjust its pH down to 1.5 with an added spent etching solution of 55 ml; at this point both copper and iron were leached out as aqueous solution. Lime was then added in to increase pH of the solution and precipitate dissolved iron ions. Complete mixing tests were carried out in different scenarios: one with no ultrasound impact and others under different ultrasonic powers of 100 W, 200 W and 300 W respectively. Subsequently, the beaker containing mixed slurry was forced through a filter and the filtered sludge was rinsed three times each with 200 ml water. All rinsing water and filter filtrates were collected. Copper and iron inside both the filtered sludge and the collected aqueous solution were then measured.

2.2.4. Criteria of copper and iron separation

The reactions occurred in the above described test could be presented as following:



In the test, the separation of copper and iron could be determined by the amount of metal that stayed in distinguishable solid or liquid phase in the final products. A leaching rate that is the percentage of a metal dissolved into an aqueous solution was used in this study to define the separation of copper and iron as presented by:

$$\text{Copper leaching rate}(\%) = \frac{C_{\text{Cu},l}(\text{g/l}) \times V_1(l) - W_{\text{Cu}(\text{WES})}}{W_{\text{Cu}(\text{WS})}} \times 100\%$$

Iron leaching rate(%)

$$= \frac{C_{\text{Fe},l}(\text{g/l}) \times V_1(l)}{W_{\text{Fe},s}(\text{g/kg}) \times M_s(\text{g})/1000 + C_{\text{Fe},l}(\text{g/l}) \times V_1(l)} \times 100\%$$

where V_1 is the liquid volume of all rinsing water and filter filtrates that were collected in the test, and M_s is its mass weight; metal contents inside both filtered sludge and collected aqueous solution were measured by AAS. $W_{\text{Fe},s}$ is iron in solid phase (measured through dissolution with hydrogen chloride), $C_{\text{Cu},l}$, $C_{\text{Fe},l}$ in liquid phase respectively. $W_{\text{Cu}(\text{WES})}$ is the copper initially contained in the tested spent etching solution ($W_{\text{Cu}(\text{WES})} = 114.1 \text{ g/l} \times 55 \text{ ml} = 6.276 \text{ g}$). $W_{\text{Cu}(\text{WS})}$ is the copper initially contained by the tested waste sludge ($W_{\text{Cu}(\text{WS})} = 50 \text{ g} \times 3.19\% = 1.595 \text{ g}$).

2.3. Copper and calcium separation test

After copper and iron separation, most of the copper became copper chloride in aqueous solution while most of the iron was precipitated as iron (III) hydroxide sludge. To covert soluble copper chloride to reusable copper sulfate end-product, lime needs to be added into the solution to precipitate soluble copper as basic copper chloride first. With subsequent sulfuric acid addition, precipitated copper could be dissolved as copper sulfate.

This test was carried out with 100 ml solution taken out from the mixture of rinsing water and filter filtrates produced from the prior discussed copper and iron test, and poured into a 250-ml beaker. Impacts of ultrasonic power, pH, and temperature on addition of lime to the 100 ml solution were then studied.

2.3.1. Impacts of ultrasonic power and pH

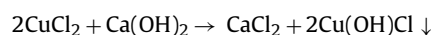
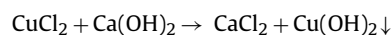
Prior prepared lime was slowly added into the 100 ml solution stirred at 300 rpm with a temperature at 25 °C. As a result, pH of the solution was adjusted by the added lime. pH was continually measured and the solution was continually stirred under ultrasonic enhancement. After stirring for 30 min, final pH of the solution was booked. Subsequently, the beaker containing mixed slurry was forced through a filter and filtered solids were rinsed three times each with 200 ml of water. All rinsing water and filter filtrates were collected. Copper and calcium inside both filtered solids and collected aqueous solution were then measured. The same tests were repeated for several different ultrasonic powers and pHs. Different copper and calcium contained by aqueous solution and solids at different ultrasonic powers and pH values were then compared. A set of an ultrasonic power and a pH with most of copper inside aqueous solution and most of calcium inside solids was determined.

2.3.2. Impacts of temperature

Prior prepared lime was slowly added into the 100 ml solution stirred at 300 rpm at the temperature of 25 °C to adjust ultrasonic power and pH to the ones being chosen in prior section. The rest of test procedure was identical to that of Section 2.3.1 except temperatures were investigated. A temperature with the most copper inside aqueous solution and the most calcium inside solids was determined.

2.3.3. Criteria of copper and calcium separation

The reactions occurred in the above-described tests on the separation of copper and calcium could be presented as following:



The percentage of a metal either precipitating or remaining as solids was used in this study to define the separation of copper and calcium as presented by:

Rate of copper transferring into solid phase(%)

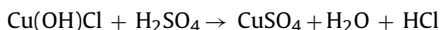
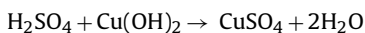
$$= \frac{W_{\text{Cu,s}}(\text{g/kg}) \times M_{\text{S}}(\text{g})/1000}{W_{\text{Cu,s}}(\text{g/kg}) \times M_{\text{S}}(\text{g})/1000 + C_{\text{Cu,l}}(\text{g/l}) \times V_{\text{l}}(\text{l})} \times 100\%$$

Rate of calcium remaining in solid phase(%)

$$= \frac{W_{\text{Ca,s}}(\text{g/kg}) \times M_{\text{S}}(\text{g})/1000}{W_{\text{Ca,s}}(\text{g/kg}) \times M_{\text{S}}(\text{g})/1000 + C_{\text{Ca,l}}(\text{g/l}) \times V_{\text{l}}(\text{l})} \times 100\%$$

where V_{l} is the liquid volume of all rinsing water and filter filtrates that were collected in the test, and M_{S} is its mass weight. Metal contents inside both filtered solids and collected aqueous solution were measured by AAS, and copper and calcium were $W_{\text{Cu,s}}$, $W_{\text{Ca,s}}$ in solid phase (measured through dissolution with hydrogen chloride), $C_{\text{Cu,l}}$, $C_{\text{Ca,l}}$ in liquid phase respectively.

After the separation of calcium in aqueous solution and copper in solids, sulfuric acid was added into filtered solids that contained mainly cupric hydroxide and basic copper chloride stirred for 60 min. After pH reached 1.5, solids containing copper were converted into copper sulfate solution. Followed by 24 h of natural crystallization, copper sulfate crystals were formed as end-products. The occurred reactions could be presented as:



3. Results and discussion

3.1. Results and discussion for separation of copper and iron

As shown in Figs. 3 and 4, at pH 1.5 almost all PCB waste sludge contained copper were leached out to an aqueous solution by the addition of acidic spent etching solution. As pH increased, leaching efficiencies of both copper and iron decreased. When pH increased to 3.0, leaching rate of iron became to zero. Leaching efficiencies of copper increased as ultrasonic power increasing at same pH and temperature, while leaching efficiencies of iron decreased with ultrasonic power increasing at same pH and temperature. The trend was strengthened at higher pHs where better separation between

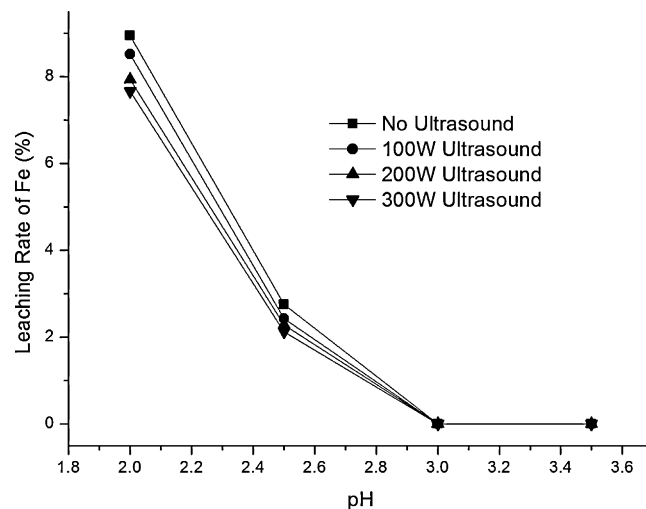


Fig. 4. Impacts of ultrasonic power on Fe leaching rates with different pHs during Cu and Fe separation (with lime, 25 °C and 300 rpm).

copper and iron was resulted with a stronger ultrasound. The possible mechanism behind may be the collapse of cavitation bubbles will form liquid jets with the speeds close to 400 km/h driving into the solid surface [25]. The liquid jets can break down the particle size and increase the surface area of the solid. Moreover, the collapse of cavitation bubbles causes a dramatic partial thermal increase, which can activate the surface of the solid, ejects material into solution, thus increasing ion movement from surface of copper hydroxide into liquid phase and enhancing the leaching of copper into the leachate from the sludge. At the same time, ultrasonic wave can also enhance the settlement of ferric hydroxide.

During the tests, it was found, without adding lime, that ferric hydroxide colloid would be formed at pH around 1.5–2.5. However, with the addition of lime there were almost no colloidal particles even with pH over 2.0. The possible mechanism behind may be when acidic spent etching solution was added into PCB sludge, electronegative charged colloidal particles of ferric hydroxide would be formed under a condition started from near neutral PCB sludge environment (more or less alkaline), and lime addition created positive charged divalent calcium ions that coalesced negative charged colloidal particles of ferric hydroxide and reduced ferric hydroxide colloid in suspension. Another advantage of adding lime during copper and iron separation was the fact that it also precipitated sulfate radical anion out of the leachate solution. This would prevent the following copper and calcium separation from co-precipitation among calcium sulfate and copper hydroxide or basic copper chloride, and produce end-product copper sulfate with less calcium sulfate impurities.

As shown in Fig. 5, when the pH was 2.5, with ultrasonic power of 300 kW the leaching rate of copper was 93.79% and iron was 2.07%. When the pH value was 3.0, the leaching rate of copper was 90.92% and iron was basically zero. In a prior study [22], concentration of aqueous solution after PCB waste sludge was dissolved by sulfuric acid was at 30.6 g/l. Dissolving same type PCB sludge, this experiment used PCB acidic spent etching solution, and the resulting concentration of copper ions was about 63.0 g/l. Since PCB spent etching solution originally contained quite an amount of copper (114.1 g/l) by itself, the resulted solution from applying etching solution to dissolve PCB sludge contained more copper ions than the one was investigated in the study [22]. The high copper concentration in the spent etching solution limited leaching of copper from the waste sludge into liquid solution. As a result, ultrasonic enhancement has smaller impacts on the copper leaching rates in

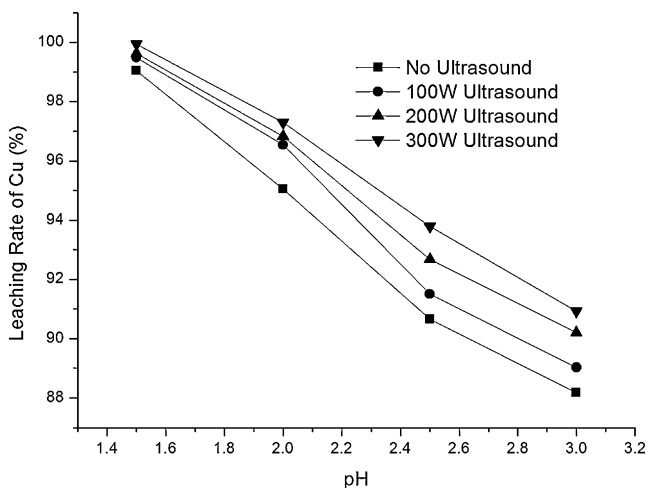


Fig. 3. Impacts of ultrasonic power on Cu leaching rates with different pHs during Cu and Fe separation (with lime, 25 °C and 300 rpm).

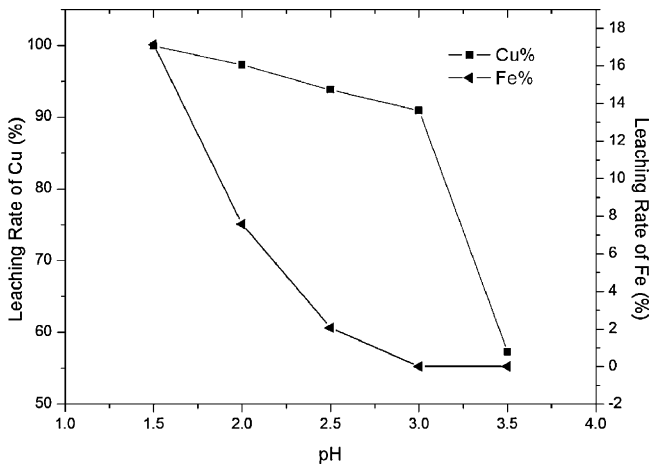


Fig. 5. Leaching rates of Cu and Fe during Cu and Fe separation (with lime, 300W ultrasound, 25 °C and 300 rpm).

this study than the ones in the prior study [22]. Commercial rate copper sulfate, an end-product of this experiment, was required with at least 95% copper so that pH of 2.5 was selected for copper and iron separation for the proposed recovery process in this study.

3.2. Results and discussion for separation of copper and calcium

As shown in Figs. 6 and 7, at pH 5.5, temperature 25 °C and stirring 300 rpm there are less calcium and copper in solid phase with a 100W ultrasound enhancement in comparison to the one with no ultrasound. Ultrasound strengthens the dissolution of calcium the same way it strengthens the dissolution of copper. As a result, it has no enhancement on separation of copper and calcium.

Copper entered solid phase from aqueous solution while calcium remained in solids with alkaline increased. With no ultrasound and temperature at 25 °C and stirring at 300 rpm, 99.99% of copper and 1.29% of calcium were in solid phase when pH gets up to 5.5 as presented in Fig. 8. pH 5.5 was selected as the pH set point for copper and calcium separation in the proposed process. As long as the temperature is higher than 20 °C, Fig. 9 shows that temperature has limited impacts on copper and calcium separation.

Based on the above discussions and tested process parameters, a treatment process, which is capable of recovering copper and iron

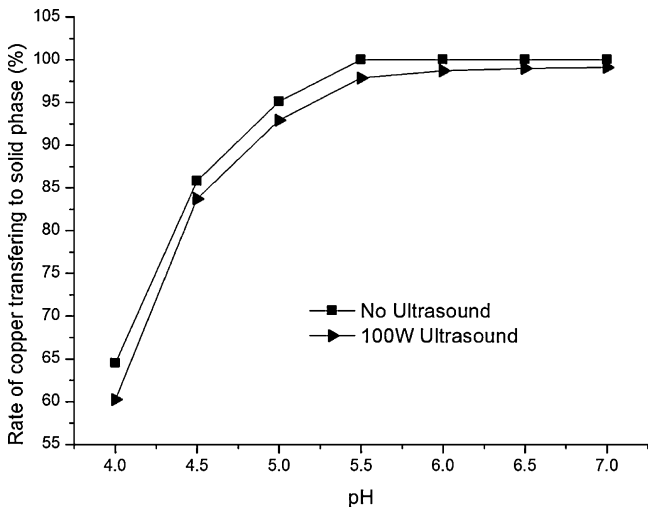


Fig. 6. Impacts of ultrasound on rates of copper transferring to solid phase (25 °C and 300 rpm).

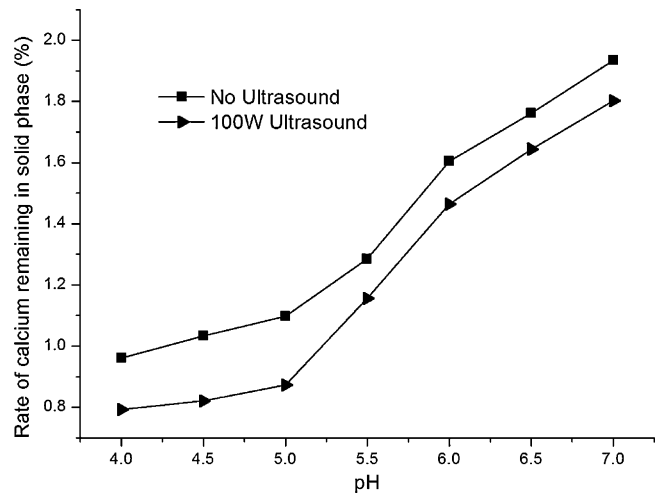


Fig. 7. Impacts of ultrasound on rates of calcium remaining in solid phase (25 °C and 300 rpm).

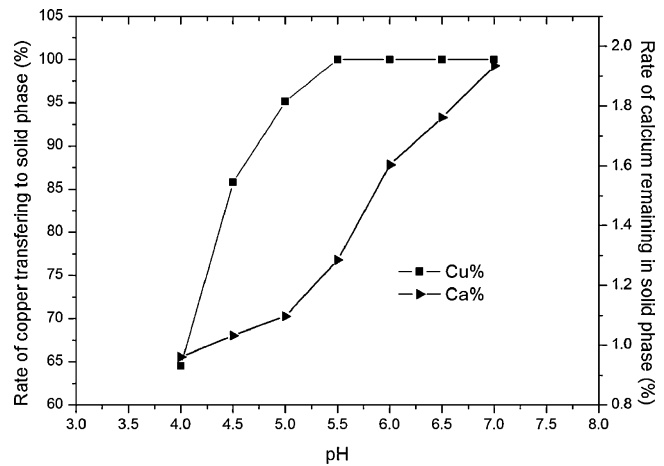


Fig. 8. Impacts of pH on rates of copper and calcium in solid phase (25 °C and 300 rpm).

from the simultaneous utilization of PCB spent etching solution and PCB waste sludge, was designed and could be presented in a schematic process flow sheet as shown in Fig. 10.

Using PCB spent etching solution and PCB waste sludge presented in Section 2.1 as raw material, a lab-scale pilot study

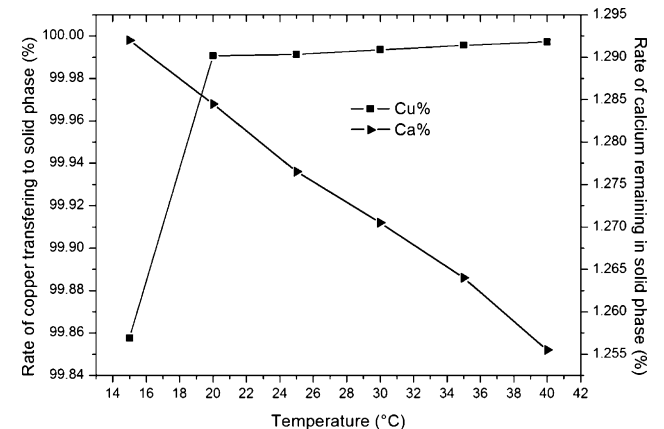


Fig. 9. Impact of temperature on percentage of copper and calcium in solid phase (pH 5.5 and 300 rpm).

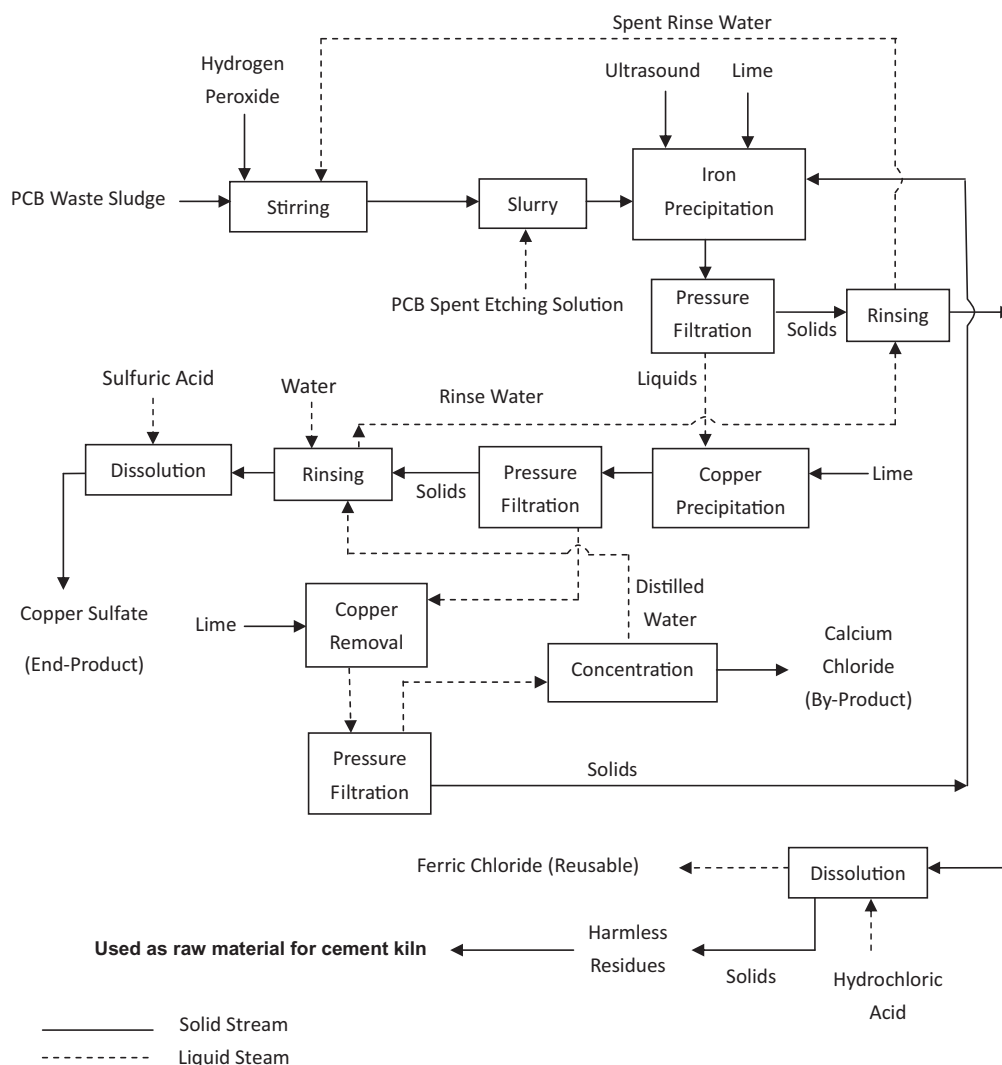


Fig. 10. A schematic process flow diagram for an ultrasonic enhanced process for copper and iron recovery through the simultaneous utilization of PCB spent etching solution and PCB waste sludge.

Table 1
Characteristics of produced copper sulfate.

	Copper sulfate	Water insoluble residues	Free acids
Contents (%)	98.35	0.036	0.2

followed the process described above produced copper sulfate with a quality listed in Table 1.

4. Conclusions

The study presented a method that recovered copper and iron through simultaneous utilization of PCB acid spent etching solution

Table 2
Impacts of ultrasonic power, pH value on leaching rates of Cu and Fe (with addition of lime at 25 °C and 300 rpm).

pH	Without ultrasound		Ultrasound (100W)		Ultrasound (200W)		Ultrasound (300W)	
	Cu%	Fe%	Cu%	Fe%	Cu%	Fe%	Cu%	Fe%
1.5	0.96	18.04	0.51	18.26	0.38	17.74	0.06	17.13
2.0	5.16	8.95	3.46	8.31	3.17	7.78	2.70	7.58
2.5	9.28	2.76	8.49	2.35	7.33	2.21	6.21	2.07
3.0	11.94	0.00	10.97	0.00	9.80	0.00	9.08	0.00

Table 3
Impacts of pH value on transferring rates of copper and calcium into solid phase (at 25 °C and 300 rpm).

pH	4	4.5	5	5.5	6	6.5	7
Cu (%)	64.52	85.81	95.12	99.99	99.99	99.99	99.99
Ca (%)	0.96	1.03	1.10	1.29	1.60	1.76	1.93

and PCB waste sludge with ultrasonic enhancement in a laboratory test. It demonstrated that with ultrasonic enhancement, PCB copper containing spent acid etching solution could be used as acidic leaching solution to leach copper from PCB waste sludge. It also revealed that lime could be used in this process as an alkaline precipitating

agent to precipitate iron from the mixture of PCB spent etching solution and waste sludge. The process recovered copper was converted to commercially rated copper sulfate, and the recovered iron was converted to reusable ferric chloride for the PCB manufacturing. Using PCB spent etching solution and waste sludge provided by Dingfu Electrical Co. Ltd. at Huizhou of China, the following results were demonstrated in the lab test:

- (1) As shown in Table 2, at 25 °C, stirring at 300 rpm and ultrasonic power at 300 W, using spent acid etching solution to regulate the pH value of PCB waste sludge to 1.5 then added lime to tune its pH value to 2.5. The leaching rates of copper and iron reached 93.76% and 2.07% respectively. Copper and iron were effectively separated as the former stayed in aqueous solution and the latter remained in solid phase.
- (2) As shown in Table 3, at 25 °C, stirring at 300 rpm with pH 5.5, lime was used to precipitate copper from the mixture of leachate and rinsing water produced during the separation of copper and iron. The percentage of copper and calcium precipitated and settled as solids were 99.99% and 1.29% respectively. Thus, copper and calcium were effectively separated with most of the copper stayed in solid phase and most of the calcium remained in aqueous solution. The precipitated copper could be made further as commercial rate end product.
- (3) Copper and iron could be recovered by simultaneous utilization of PCB acid spent etching solution and PCB waste sludge with ultrasonic enhancement.

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