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Current status and future perspective of recycling copper by hydrometallurgy from waste printed circuit boards

Yan Xu[a]，Jinhui Li[a,]*, LiliLiu[a]

State Key Joint Laboratory ofEnvironment Simulation andPollution Control, School ofEnvironment, Tsinghua University, Beijing, 100084, China

Abstract

The current replacement of electronic products is speeding up, resulting in a growing number of e-waste. Electronic waste, especially waste print circuit boards contain large amounts of copper, which not only bring greater ecological threat, but also cause a serious waste of copper resources. Therefore, the study on clean, effective copper leaching technology has a very important practical significance to reduce environmental hazards of waste print circuit board and resources recycling. Hydrometallurgical is a better technology for recycling copper from waste print circuit boards. In this article, hydrometallurgical copper recovery system is divided into four categories: acid leaching, ammonia - ammonium leaching, chloride leaching, as well as other ways of leaching. The advantages and disadvantages of leaching of copper system are analyzed in the process of copper resource utilization. Studies abound on recycling copper from copper-containing waste with citric acid and other complexing agents as the leaching reagent, but studies on recycling copper from waste print circuit boards are rarely reported, which can be used for reference. The trends of the research are using environmentally friendly reagent as leaching agent, selecting the appropriate leaching solution at a certain temperature and pressure and optimizing the subsequent separation procedure. Recycling of waste gas and waste leachate generated in the hydrometallurgical processcan further reduce chemical costs and meet increasingly exacting environmental requirements.

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*Keywords:*Waste printed circuit boards; Copper; Leaching; Recovery; Hydrometallurgy

1. Introduction

The amount of global e-waste - discarded electrical and electronic equipment - reached 41.8 million tonnes in 2014, according to a new United Nations University report. According to the report, just two countries - the US and China - discarded nearly one-third of the world's total e-waste in 2014[1].

* Corresponding author. Tel.: +86-10-6279 4143; fax: +86-10-6277 2048.
E-mail address: jinhui@tsinghua.edu.cn

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The discarded e-waste contained about iron, (16,500 kilotons), copper (1,900 kilotons), and gold (300 tonnes) also significant quantities other metals such as silver, aluminium, palladium, and other potentially reusable resources, and estimated value about US$52 billion. It may also contains amounts of health-threatening metals and substances such as mercury, cadmium, chromium, and ozone-depleting chlorofluorocarbons [2].If not properly disposed of, it will cause great harm to environment and human health. The metal content in the waste circuit board is much higher than the metals in the ore. For example, the average grade for copper in China is 0.8%，while the content of copper in waste circuit board copper taste is more than 20%. As an important nonferrous metals，because of its unique physical and chemical properties：good ductility, high thermal conductivity， electrical conductivity and corrosion resistance，copper is widely used in electrical, light industry, machinery manufacturing, construction industry, defense industry and other fields. With the continuous development of society and increasingly demand for copper, although China's copper reserves is more, but on the whole, copper resources, especially rich copper is still poor. Therefore, no matter for environmental protection, or for resources recycling, the comprehensive recycling of waste printed circuit boards has important social and economic significance[3,4].

Recently different recycling methods are used for circuit boards such as mechanical [5], pyrometallurgical [6], hydrometallurgical[7.8] and biological treatment[9], etc. Besides, supercritical fluid[10], microwave pyrolysis[11] and plasma melting[12]are also reported, but in other hand these process have their own certain limitation such as level of research at laboratory scale, small recycling capacity. Although, mechanical recovery method can effectively separate the metal and non-metal, but can't get the pure metal products at last and the following must be combined with hydrometallurgy process. In addition, this method is become an important step in terms of pre-treatment of electronic waste recycling. In another hand, pyrometallurgy technological process is short, but the equipment investment is large, metal recycling cannot achieve at significant level. In addition , high possibility for secondary pollution. However, biological metallurgy with environmental protection, small investment, is a potential way of recycling, but less strain, hard to cultivate and long leaching cycle limiting its large-scale application. It also has some drawbacks, including leaching agent consumption and greater pollution. But by optimizing the process, choosing less toxic leaching agent and leaching leachate recycling process, these problems can be better solved. It is a viable method for large-scale processing[13.14].

Recovery of metals from electronic waste by hydrometallurgical technology began in the western developed countries in the late 1960s[15.16]. The basic principle is to scrap printed circuit board in an acidic or alkaline leaching solution, so there is a separation of valuable metals and other materials. Then by using solvent extraction, precipitation, displacement, ion exchange, distillation, filtration to recovery of precious metals and other base metals from the liquid phase[17].The processing steps are as follows: (1) Heating the waste printed circuit board to a certain temperature, when organic matter of the substrate part occurs pyrolysis in high temperature，in order to reduce the consumption of acid and simplify the subsequent process.(2)Leaching the waste printed circuit boards in strong acid or strong oxidizer solution can obtain acid solution containing copper and other lower value metals and sediment containing precious metal strip.(3) Treating stripping sediment containing precious metals by using aqua regia or other caustic acid to recycling platinum, gold, silver and other precious metals.(4) Adopting ion exchange, solvent extraction or chemical precipitation method processing metal leaching solution can extract metal or metal compounds[18].

The value of electronic waste is the largest component of precious metals. While, with the reduction in precious metal content in electronic products, as well as the increasingly stringent environmental requirements, research on hydrometallurgical method is not only limited to the extraction of precious metals, but also turned to the precious metals and common metals recycling[19].

Because of the obvious advantages in recycling metal from waste printed circuit boards, a large number of hydrometallurgical leaching are carried out at home and abroad. Due to the highest content of copper in the waste printed circuit board, the base metal recycling is mainly for hydrometallurgical leaching of copper[20].

In hydrometallurgy, the disposal of waste printed circuit board of the leaching process is critical, the current method of hydrometallurgical leaching of waste printed circuit board can be divided into four types: acid leaching, ammonia leaching, ammonium salt leaching, chloride leaching, and other ways of leaching, some of the leaching methods have had certain industrial applications in different ranges[21].

2. Leaching of copper from waste print circuit boards

2.1Acid leaching method

2.1.1Nitric acid leaching method

Copper can be directly oxidized to generate copper nitrate by dilute nitric acid at normal temperature, so it doesn't need additional oxidizer. The leaching process can produce acidic gas. Copper nitrate cannot be directly applied to the preparation of high purity copper by electroplating, which needs to translate into pure copper sulfate solution by extraction- reverse extraction technology before electro-deposition[22-25]. The relative reaction equation is as follows:

$$3Cu + 8HNO_3(dilute) = 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O \quad (1)$$

$$Cu + 4HNO_3(concentrated) = Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O \quad (2)$$

Zhang[26] used two kinds of recycling leaching system ,H_2SO_4-HNO_3-H_2O-NaOH and H_2SO_4-HNO_3-H_2O-NOX ,for electronic waste pretreatment. Lix84I was used as extraction agent, sulfuric acid as extraction agent, and got the copper purity of more than 99.9%, current efficiency is above 90%.

Andrea[27]found that nitric acid is good preprocessing agent, by which tin can be converted into tin acid precipitation, while lead and copper transformed into ions state to separate with tin. Tin acid was dissolved in hydrochloric acid after filtration and then electrolytic recovery of metal tin, while lead and copper transformed into metallic copper and $PbO_2$by electrolysis process, all process of electrolytic current efficiency was as high as 95% above. This process, by nitric acid leaching, realized the recycling of three kinds of basic metals tin, lead and copper; through an electrolytic realized the regeneration of nitric acid and hydrochloric acid; obtained efficient metal recovery. But the process also had some of shortcoming that declined the efficiency, such as required a large amount of NaOH for neutralization and also increased the strength of the subsequent electrolytic regeneration, at the time duration may leads to produce sodium accumulation, then we needed to use membrane equipment in the process of electrolytic regeneration, large-scale application needed high investment.

2.1.2Sulfuric acid and hydrogen peroxide leaching method

In fact diluted sulphuric acid is not able to directly solubilize the copper from waste printed circuit boards in the form of copper sulfate solution, in addition oxidizing agent need to be added to achieve the leaching of copper.

Chi[28] used mechanical and physical methods for sorting out the nonmagnetic metal from waste printed circuit board, and then soaked the rest for leaching of copper, iron, zinc, nickel and aluminium with sulfuric acid and hydrogen peroxide in 85℃. The leaching rate was higher than 95%, and the rest of the solid can recovery of gold and silver by ammonium sulfate, copper sulfate and ammonia. Zhang[29] used sulphuric acid and hydrogen peroxide as reaction reagent leaching of copper, and then used electrolysis - electrodialysis method recycling copper from leaching liquid, copper recovery rate was 88.07%.Marcelo[30]adopt crushing-electrostatic separation - magnetic separation to isolate non-conductor, magnetic materials and magnetic materials from waste printed circuit boards and other electronic components; nonmagnetic metal enrichment dissolved respectively with sulfuric acid and aqua regia; then by electrolytic method to recycle the copper from the dissolved liquid, electrolytic recovery of copper can reach more than 98%, the purity of copper can reach99.5%.

Generally, acid leaching method has very short reaction time, high efficiency (99%), but the sulfuric acid corrosion is stronger, puts forward higher requirements to the reactor; as a result of the existence of the impurity ions at the same time, make the follow-up of each metal ion separation process is complicated. The various acid leaching methods were compared in the table 1.

Table 1 Comparison of acid leaching method

Authors	Leaching agent	Key technology	Results	References
Zhang	H_2SO_4-HNO_3-H_2O-NaOH, H_2SO_4-HNO_3-H_2O-NOX	Acid pretreatment, Lix84I as extraction agent and sulfuric acid as extraction agent	More than 99.9% of the copper	26
Andrea	nitric acid	Using nitric acid as the preprocessing agent	Realizes the recycling of three kinds of basic metals tin, lead and copper	27
Chi	sulfuric acid and hydrogen peroxide	Mechanical and physical methods sorting out the nonmagnetic metal, and then soaking with sulfuric acid and hydrogen peroxide in 85 ℃	The leaching rate was higher than 95%	28
Zhang	sulfuric acid and hydrogen peroxide	Use electrolysis electrodialysis method - recycling leaching liquid of copper	Copper recovery was 88.07%	29
Marcelo	sulfuric acid and aqua regia	Crushing-electrostatic separation- magnetic separation	Electrolytic recovery of copper can reach more than 98%,the purity of copper can reach 99.5%	30

2.2 Ammonia - ammonium salt leaching method

Since the middle of the 20th century, many researchers have evaluated the process of copper solubilisation by

liquid ammonia. In the ammonia - ammonium salt systems, the copper existed in the form of a copper ammonia complex. Copper ammine complex and molecular oxygen dissolved in the solution as the oxidant, to achieve the separation of copper and other metal components[31,32].

With the presence of oxidant, ammonia or ammonium salt can react with copper to form copper ammonia complex ion to dissolve metal copper. Main chemical reaction equations of Ammonia - ammonium salt dissolved metal copper are as shown in the following equations (for hydrogen peroxide as oxidant):

$$Cu+H_2O_2+4NH_3\cdot H_2O=Cu(NH_3)_4^{2+}+2OH^-+4H_2O \quad (3)$$

$$Cu+H_2O_2+4NH_4^+=Cu(NH_3)_4^{2+}+2H^++2H_2O \quad (4)$$

$$Cu+Cu(NH_3)_4^{2+}=2Cu(NH_3)_2^{2+} \quad (5)$$

$$2Cu(NH_3)_2^{2+}+H_2O_2+4NH_3\cdot H_2O+2H^+=2Cu(NH_3)_4^{2+}+6H_2O \quad (6)$$

According to above equation, the pH value of the leaching system affect the reaction equilibrium, and it turn, affect the leaching rate of copper. Hence, a single ammonia or ammonium chloride cannot be efficient leaching of copper from waste printed circuit boards. Because copper ammonia complex ion solution produced cannot be directly used in electroplating, extraction and reverse extraction technology were used to translate into pure copper sulfate solution.

Several studies focused on ammonia/ammonium salt leaching of copper from the waste printed circuit boards. Similarly Zhang[33]used old computer circuit boards particles as raw materials, ammonia and ammonium sulfate as leaching reagents, leaching of copper under the experimental conditions with pumping into the air, copper leaching rate can reach 96.3%.In this regard, Li[34]used the ammonia - ammonium chloride - hydrogen peroxide as leaching agent, can selective leaching of copper from the printed circuit boards. Then they used the extraction agent N910 for extraction separation of copper and sulphate for extraction agent. Also extraction agent and leaching liquid can be recycled. Wang [35]not only optimized the ammonia/ammonium salt system of the leaching conditions from waste computer circuit board, but also explored the leaching kinetics: with carbonic acid, ammonium for copper leaching process followed "unreacted shrinking core model" which didn't produce solid product layer, and leaching reaction was controlled by diffusion.

Koyama [36-40]also conducted a research on recycling of copper from waste printing printed circuit board. They used Ammonia - ammonium salt system containing Cu (I) and Cu (II) ammonia complex ion as leaching agent, preparation of high purity electrolytic copper through three jobs of leaching, purification – electrolysis, which got good results. They also studied the leaching process of alkaline ammonium salt solution from waste circuit boards and the copper was oxidized to Cu (I) complex by Cu (II). With Cu (II) complex ammonium, leaching rate can be improved, the Cu (I) - ammonium complex leaded to inhibition of copper leaching; broken increased the surface area of bare copper, which was benefit for copper leaching； the effects of temperature on leaching was not obvious. They further studied the electro deposition process of alkaline ammonium solution leaching of copper from waste circuit boards, which found that the current efficiency of leaching of copper deposition was close to 100% and Cu (I) - ammonium complex deposition was easier to get plate instead of copper powder.

The advantages of ammonia leaching method are good selectivity and high leaching rate. However, because of the volatile of ammoniacal solution, impermeability of leaching device should be noted. And the total nitrogen in the wastewater may be higher. The various ammonia - ammonium salt leaching process were compared in the table 2.

Table 2 Comparison of ammonia - ammonium salt leaching process

Authors	Leaching agent	Key technology	Results	References
Zhang	ammonia and ammonium sulfate	Ammonia and ammonium sulfate as leaching reagents, leaching of copper under the experimental conditions with pumping into the air	Copper leaching rate can reach 96.3%	33
Li	ammonia - ammonium chloride - hydrogen peroxide	Use the extraction agent N910 for extraction separation of copper and sulfate was used as extraction agent,	Extraction agent and leaching liquid can be recycled	34
Wang	ammonia/ammonium	ammonia/ammonium salt system	Ammonium for copper leaching process follow " unreacted shrinking core model" which doesn't make solid product layer, leaching reaction controlled by diffusion	35
Koyama	Ammonia - ammonium salt system containing Cu (I) and Cu (II) ammonia complex ion	Leaching, purification- electrolysis	Current efficiency of leaching of copper deposition is close to 100%.	36-40

2.3 chloride leaching method

Zhu[41]investigated the results of copper recovery from the printed circuit boards in the $CuSO_4$- NaCl - H_2SO_4 solution with and without electro oxidation: with the condition of no electricity, the copper in the printed circuit boards was oxidized to Cu^{2+}, which combined with the Cl^- in solution form copper chloride complex $CuCl^{2-}$. Then $CuCl^{2-}$ was oxidized to $CuSO_4$by O_2, the leaching rate can reach 100%, and $CuSO_4 \cdot 5H_2O$was obtained followed by evaporation crystallization. But due to the limitation of dissolved oxygen in water, the whole process requires 5.5 h; through the electro oxidation reinforcement, the reaction mechanism was:

$$2Cl^- - 2e = Cl_2 \quad (7)$$

$$Cl_2 + H_2O = HClO + HCl \quad (8)$$

$$2H_2O - 4e = O_2 + 4H^+ \quad (9)$$

$$ClO^- + Cu + Cl^- + H^+ = CuCl_2^- + H_2O \quad (10)$$

$$ClO^- + 2CuCl_2^- + 2H^+ = 2CuCl_2^- + H_2O + Cl^- \quad (11)$$

With Cu^{2+}, $O_2$and ClO^- as oxidizing agent, the method improved the limit of low solubility of dissolved oxygen in the process before, and shorten the reaction duration from 5.5 h to 3.5 h. Kim[42]did the study on leaching of copper from the waste circuit board in hydrochloric acid solution by chlorine gas produced by electrolysis, of which the Cl_2, Cl_3^- and Cu^{2+} as oxidant. By measuring the change of oxidation reduction potential ORP of the solution during the reaction process, they probed into the leaching mechanism of copper and copper leaching was divided into three stages: ORP≈1300mVSHE，380mVSHE＜ORP＜490mVSHE，ORP＞490mVSHE.

The copper chloride leaching system has also been studied by many researchers, which can give some guidance for chloride leaching of copper in waste printed circuit boards.

Yu[43] discussed the leaching mechanism and technological process of copper chloride solution (NaCl, HCl, $CuCl_2$) in recycling waste miscellaneous copper. With the $CuCl_2$as oxidizing agent, copper in the miscellaneous copper was oxidized into Cu^+, Cu^+ and Cl^- combined into copper chloride complex, and then copper was recycled through electro deposition. Apparent activation energy of leaching reaction showed that the process of copper chloride salt leaching was a typical diffusion control process.

Masao[44] made a research on dissolved copper with dissolved oxygen molecules in copper chloride-hydrochloric acid solution. The results showed that the effect of concentration of antioxidant $CuCl_2$ and complexing agent Cl^- on the dissolution rate of copper were more significant. Under these experimental conditions, oxygen partial pressure and hydrogen ion concentration had no effect on the dissolution rate of copper, and the reaction mechanism of copper dissolved was given.

Herreros[45,46] studied the dissolution behaviour of copper in Cl_2 / Cl^- system, of which Cl_2 was generated through reaction NaOCl+ 2HCl = Cl2 + NaCl + H_2O. Cl_2 is the oxidant and copper existed in the form of copper chloride complex in solution. Experimental results confirmed the importance of molecules chlorine gas for the process of dissolved. Research on CuSO4, NaCl, HCl system dynamics had shown that $Cu^{2+}$was one of the important reagent in the dissolving process. With C (Cl^-)/C (Cu^{2+}) < 8, the CuCl(s) generated will be attached on the surface of copper and hindered the further dissolution process.

$Fe^{3+}$of $Fe_2(SO_4)_3$, $FeCl_3$ had a strong oxidizing, usually be used as the oxidant of leaching process. $Fe_2(SO_4)_3$ than $FeCl_3$ not only be easy to get, but also can provide Cl^- and form complex with metal so as to accelerate the dissolution of metal. Acidulated $FeCl_3$ solution was widely used for the treatment and recycling of metals. Cakir[47] used $FeCl_3$, $CuCl_2$ solution as chemical etching effect on copper and contrast the results ,which showed that chemical etching rate was high with $FeCl_3$ as etching agent. The reason is: with ferric chloride as oxidant, chemical reactions happened as follows:

$$FeCl_3 + Cu \rightarrow FeCl_2 + CuCl \quad (12)$$

$$FeCl_3 + CuCl \rightarrow FeCl_2 + CuCl_2 \quad (13)$$

$$CuCl_2 + Cu \rightarrow 2CuCl \quad (14)$$

So the reaction has two etchant $FeCl_3$ and $CuCl_2$, when copper chloride for oxidizer, there is only one etching agent $CuCl_2$. The various chloride leaching method were compared in the table 3.

The chloride hydrometallurgy based recycling of copper has a lot of advantages than traditional mixed copper regeneration process; such as, short process, simple equipment, less investment, low energy consumption, high metal recovery rate, low processing cost, pollution-free advantages in the environment.

Table 3 Comparison of chloride leaching method

Authors	Leaching agent	Key technology	Results	References
Zhu	$CuSO_4$—NaCl—H_2SO_4	Electro oxidation	Leaching rate can reach 100%	41
Kim	chlorine gas produced by electrolysis of hydrochloric acid solution	Leaching of copper in the waste circuit board in hydrochloric acid solution by chlorine gas produced by electrolysis	Copper leaching process is divided into three stages	42
Yu	NaCl—HCl—$CuCl_2$	$CuCl_2$ as oxidizing agent, copper in the miscellaneous copper oxidizes into Cu^+, Cu^+ and Cl^- combined into copper chloride complex, and then copper is recycled through electro deposition	Apparent activation energy of leaching reaction shows that the process of copper chloride salt leaching is a typical diffusion control process	43
Masao	copper chloride-hydrochloric acid	The effect of concentration of antioxidant $CuCl_2$ and complexing agent Cl^- on the dissolution rate of copper is more significant.	The effect of concentration of antioxidant $CuCl_2$ and complexing agent Cl^- on the dissolution rate of copper is more significant	44
Herreros	$CuSO_4$—NaCl—HCl	Cu^{2+} is one of the important reagent in the dissolving process	The dissolution behaviour of copper in Cl_2 / Cl^- system	45-46
Cakir	$FeCl_3$	$FeCl_3$ as etching agent, the reaction has two etchant $FeCl_3$ and $CuCl_2$	$FeCl_3$ as etching agent ,chemical etching rate is high	47

2.4 Other leaching method

2.4.1Through the own redox reaction to enrich copper with elements exist in the raw materials

At present, dismantling, crushing and sorting slice can only get crumbs mixture, the content of the copper is low. According to this, Yao[48,49]did the research on leaching Pb and Sn with the oxidant, Cu fall off surface only, which make the separation of copper and lead and tin. Further by the flotation separation of slag phase fibber board substrate, pure copper products of copper content more than 99.7% was obtained.

The main metal elements in waste print circuit boards are copper, lead, tin and other metals. Seeking out an A-1 oxidizing agent among a number of reagents and leaching amount of copper conditionally based on the lead and tin in raw materials, the reaction equation is:

$$Cu+[O] \rightarrow Cu \quad (15)$$

When Cu^{2+} in the solution reaches a certain amount, the following reaction can automatically happen:

$$Pb(Sn)+Cu^{2+} \rightarrow Cu + Pb^{2+} + Sn^{2+} \quad (16)$$

To control the amount of A - 1 oxidant in the solution, the end results of the reaction were: lead and tin were dissolved; copper was reduction, retention, and separated with lead, tin.[Pb^{2+}] [Sn^{2+}] obtained by displacement reaction can easily generate $PbCl_2$ or $SnSO_4$ precipitation and residue in the copper in acid solution. Therefore, A - 3 reagent wad added in material to make the transformation of precipitation , then the precipitation dissolved in dilute acid aqueous solution in 70-80℃, and further separation of copper, which made copper was purified. Copper scrap obtained through the process of drying operations such as filtering and washing, the copper content was over 99.7% and the content of impurities such as lead, tin can meet the second copper industry requirements. For further comprehensive utilization of this kind of material, copper chemical products of $CuSO_4 \cdot 5\ H_2O$, CuO and $CuC1_2$ can be obtained by conventional methods in experimental conditions. By the analysis of measurement, related indicators met the requirements of industrial grade one. The technological process was simple, convenient operation, low cost and high economic efficiency.

2.4.2Other oxidant and complexing agent for copper leaching

In the presence of other antioxidants and complexing agent, copper can also be dissolved, such as citric acid, sodium sulfate, 2, 2 '- pyridine, etc. At present, many researchers adopt complexing agent such as citric acid as the leaching reagent to recover copper from copper scrap, but the study on the recovery of copper from the PCBs is rarely reported, which can be used for reference[50].

Yang[51]adopted the hydrogen peroxide - ammonium citrate to stripping Cu, which was economical and environmentally friendly. And the copper stripping mechanism of the system was also discussed: the hydrogen peroxide oxidant was oxidizing agent; hydrolysis of ammonium citrate, which was double complexing agent for copper ion, can produce citric acid and ammonium hydroxide. Chemical reactions occurred as follows:

$$H_2O_2 \rightarrow H_2O + O \quad (17)$$

$$O + Cu \rightarrow CuO(NH_4) \quad (18)$$

$$3Cit + 3H_2O \rightarrow 3NH_4OH + H_3Cit \quad (19)$$

$$2CuO + 8NH_4OH \rightarrow 2Cu(NH_3)_4^{2+} + 8H_2O + O_2 \quad (20)$$

$$2H_3Cit + CuO + H2O \rightarrow Cu(OH)_2(H_3Cit) \quad (21)$$

Zhu[52] selected sodium persulfate as the oxidant, which is stable and strong oxidizing in the air, to analyse the principle of brass chemistry etching and the etching solution was composed of sodium thiosulfate and sodium bicarbonate. The results showed that copper was oxidized to copper ion by sodium thiosulfate，copper ion react with ammonia produced by sodium bicarbonate and form complex ion to achieve the dissolution of copper.

Duda[53]studied the dissolution process of copper with alkaline 2, 2 '- al pyridine as complexing agent, which found only in the presence of oxidants , O_2 for example, dissolution could occur, and the influence on the reaction of $O_2$was significant. With the existence of oxygen, copper and 2, 2 '- pyridine happened complex reactions, generated the Cu (I) - dipy complex. Then, under different pH of the solution, continue to be oxidation for Cu (dipy) x^{2+}, to realize the dissolution of copper.

Jui[54]added the oxidant H_2O_2 and Fe $(NO_3)_3$to the citric acid solution, studied the dissolution behaviour of copper is both cases, and examined the influence of rotating speed. The results showed that the content of hydrogen peroxide had dual effects on the dissolution of copper, the existence of the low concentration of hydrogen peroxide was beneficial to the dissolution of copper powder, but high concentration of hydrogen peroxide will form passivation membrane on the surface of copper, however, Fe $(NO_3)_3$ will not form passivation membrane in copper surface. With the addition of H_2O_2 and Fe $(NO_3)_3$, following the increase of electrode speed, copper dissolution rate were increased.

Huang[55]investigated the dissolution of copper foil in hydroxylamine solution, results showed that hydroxylamine also acted as an oxidizing agent and a complexing agent, no additional oxidizing agent was added.

3. Conclusions

Except for using acid leaching, ammonia - ammonium salt leaching, chloride leaching, through their own redox reaction to enrich copper with elements that exist in the raw materials, is also a cheap way of recycling copper from waste circuit boards. Studies abound on recycling copper from copper-containing waste with citric acid and other complexing agents as the leaching reagent, in another hand, recycling copper from waste printed circuit boards are rarely reported, which can be used for further reference. The trends of the research are using environmentally friendly reagent as leaching agent, selecting the appropriate leaching solution at a certain temperature and pressure and optimizing the subsequent separation procedure. The recycling of waste gas and waste leachate generated in the hydrometallurgical process can also reduce the chemical costs and meet increasingly exacting environmental requirements.

References

[1]Global E-Waste Volume Hits New Peak in 2014: UNU Report, 2015, 04, 20.http://unu.edu/.

[2] Liu P，Peng XC，Yang YB, et al．Study on the overseas electronic waste．*Recyclable Resources Circular Economy*, 2010, 3(2): 41-44(in Chinese).

[3]Zhao YM, Duan CL, Wang HF. The physical separation theory and technology of electronic waste. *Science Press*, 2009.4 (in Chinese).

[4]Brett H. Robinson. E-waste: An assessment of global production and environmental impacts. *Sci Total Environ*, 2009, 408: 183-191.

[5]Wen XF, Li JH, Zhu FF, et al．Review of the physical treatment of waste printed wiring boards in China. *Mining Metallurgy*, 2005, 14(3):58-63 (in Chinese).

[6]Yang X N, Sun L S, Xiang J,et al. Pyrolysis and dehalogenation of plastics from waste electrical and electronic equipment (WEEE): A review[J]. *Waste Manage*, 2013, 33(2): 462-473.

[7] Ortiifio N,Conesa JA, Molto J, et al. Pollutant emissions during pyrolysis and combustion of waste printed circuit boards, before and after metal removal. *Sci Total Environ*,2014,499: 27-35.

[8] Kinoshita T, Akita S, Kobayashi N, et al. Metal recovery from non-mounted printed wiringboards via hydrometallurgical processing. *Hydrometallurgy*, 2003, 69(1-3):73 -79

[9] Zhou PG, Zheng Z, Peng XC, et al.Leaching of copper from printed circuit board by Thiobacillus ferrooxidans. *Environ Pollut Control*, 2007,29(2):119-122 (in Chinese).

[10]Hu ZX. Researchon experimentand mechanismof discarded PCB reutilization based on super critical fluid technology. *Hefei University of Technology*,2007 (in Chinese).

[11]Liu H. Controlled pyrolysis of the printed circuit boards assisted by microwave. *Dalian University of Technology*,2009 (in Chinese).

[12] Yan JS, Chen ZW,Ch F, et al. The dealing and call back application of plasma melting gasification disposal to electron solid cast off. *Applied Energy Technology*,2012,03:1-4 (in Chinese).

[13]Lambert F,Gaydardzhiev S, Léonard G, et al. Copper leaching from waste electric cables by biohydrometallurgy. *Miner Eng*, 2015,76: 38-46.

[14] Zhi S, Xiao Y,SietsmaJ, et al. A cleaner process for selective recovery of valuable metals from electronic waste of complex mixtures of end-

of-life electronic products. *Environ Sci Technol*, 2015: 150619125513003.
[15] Kiver C. Proceedings of the technical programme-interneuron：international electronic packaging and production conferences. Surbiton,1978,Oct 17-19,15-20.
[16]Sum，Elaine YL. Recovery of metals from electronic scrap. JOM，43（4）：1991，53-61，1047-4838.
[17]Tan Q, Li J. Recycling metals from wastes: a novel application of mechanochemistry. *Environ Sci Technol*,2015. 49(10): 5849-5861.
[18]Tong HQ, Yu X, Development and application on waste printed circuit boards recycling technology. *Electronic Test*, 2013(09): 252-254 (in Chinese).

[19]Bryan CG, Watkin E,McCredden TJ,et al. The use of pyrite as a source of lixiviant in the bioleaching of electronic waste. *Hydrometallurgy*, 2015. 152: 33-43.

[20]ChancerelP, MeskersC,HagelükenC,et al. Assessment of precious metal flows during preprocessing of waste electrical and electronic equipment. *J Ind Ecol*, 2009. 13(5): 791-810.
[21]Zeng XL, Zheng LX, Xie HH, et al. Current status and future perspective of waste printed circuit boards recycling. *Procedia Environ Sci*, 2012. 16: 590-597.
[22]Nikhil D, Manih W, Vinay K. Recovery of metals from electronic crap by hydrometallurgical route[J],*J Hazard Mater*,2001,(19):23-26
[23]Tang QY. A new method of recovery of tungsten and copper metal from tungsten-copper alloy scraps by nitrate method. *J Central South Forestry University*,1997，17(2)：88-92 (in Chinese).
[24] Hülya D, Cengiz Ö, M.Muhtar K, et al. Determination of semi empirical kinetic model for dissolution of metallic copper particles in HNO_3 solutions. *Chem Eng Process*,2004, 43(8): 1095-1100.
[25] Hülya D, Ö.zkan K, Cengiz Ö, et al. Derivation of semi-empirical model for copper dissolution in HNO_3solutions with rotating disc technique. *Chem Eng Process*, 2005,44(8): 895-900.
[26] Zhang WX. Pretreatment of electronic wastes and preparing copper by electrodeposition. *Donghua University*, 2007,107 (in Chinese).
[27] Andrea M, Keith S. Leaching and electrochemical recovery of copper，lead and tin from scrap printed circuit boards. J *Chem Technol Biot*, 2002, 77(4): 449-457
[28] Chi JO，Sung OL. Selective leaching of valuable metals from waste printed circuit boards. *J Air &Waste Management Assoc*. 2003，53：897-902.
[29]Zhang ZJ，Zhou LN. Study on recovering copper from waste printed circuits plate. *Liaoning Chem Industy*，2005，34(3)：93-95 (in Chinese).
[30] Hugo MV，Andrca M B，Jane Z F，et a1. Recovery of copper from printed circuit boards scraps by mechanical processing and electrometallurgy[J]. *J Hazard Mater*，2006，B137：1704-1709.
[31]Rudnik E, Pierzynka M, Handzlik P. Ammoniacal leaching and recovery of copper from alloyed low-grade e-waste. *J Mater Cycles Waste*, 2014.
[32]Yao YW. Study on the leaching of copper by ammoniacal solution from copper-containing waste, 2010, Shandong University. 63 (in Chinese).
[33]Zhang GP. The hydrometallurgy process research for metal recovery from WPCB. *East China University Sci Tech*, 2005 (in Chinese).
[34]Li JY. Experimental research on recovery of copper from waste computer circuit boards. *Hydrometallurgy*, 2009, 28(4):225-228 (in Chinese).
[35]Wang M, Cao HB, Zhang Y. Selective recovery of copper, zinc and nickel from printed circuit boards by ammonia leaching under press. *Environ Sci*,2011(02): 596-602 (in Chinese).
[36] Koyama K, Tanaka M, Lee JC. Copper leaching behaviour from waste printed circuit board in ammonniacal alkaline solution. *Mater. Trans.*, 2006, 47(7): 1788-1792
[37] Koyama K, Tanaka M, Lee JC. Electrolytic copper deposition from ammoniacal alkaline solution containing Cu(I). *Mater. Trans.*, 2006, 47(8): 2076-2080
[38] Oishi T, Koyama K, Tanaka M, et al. Influence of electrolyte on an energy-saving copper recycling process using ammoniacal alkaline solution. *Mater. Trans*., 2006,47(11): 2871-2876
[39] Oishi T, Koyama K, Tanaka M, et al. Influence of ammonium salt on electro winning of copper from ammoniacal alkaline solution. *Electrochemical Acta*, 2007, 53:127-132
[40] OishiT, KoyamaK, AlamS, et al. Recovery of high purity copper cathode from printed circuit boards using ammoniacal sulfate or chloride solutions. *Hydrometallurgy*, 2007, 89: 82-88
[41]Zhu P, Gu GB. Recovery of gold and copper from waste printed circuits. *Chinese J Rare Metals*, 2002, 26(3): 214-216 (in Chinese).
[42] Kim EY, KimMS, LeeJC, et al. Leaching behaviour of copper using electro-generated chlorine in hydrochloric acid solution. *Hydrometallurgy*, 2010. 100(3-4): 95-102.
[43]Yu ZX, Zhou BN, Lu ZH, et al. Hydro-electro metallurgical process for recovering scrap from cuprous chloride solution .*Shanghai nonferrous metals*, 1999(02): 24-28+35 (in Chinese)..
[44]Masao Iwai, Zhang BL. Dissolved of copper in hydrochloric acid solution by dissolved oxygen molecules. *Hydrometallurgy*,1990,02:54-58+47 (in Chinese).
[45]Herreros O, Quiroz R, Viñals J. Dissolution kinetics of copper, white metal and natural chalcocite in Cl_2/Cl^- media. *Hydrometallurgy*, 1999, 51(3):345-357.
[46]Herreros O, Quiroz R, Restovic A, et al. Dissolution kinetics of metallic copper with $CuSO_4$–NaCl–HCl[J]. *Hydrometallurgy*, 2005, 77:183-190.
[47] Cakir O. Copper etching with cupric chloride and regeneration of waste etchant. *J Mater Process Tech*,2006:63-68.
[48] Yao H,Lin GY,Wang HT. Disassemble and recovery of copper in the circuit board and the preparation of chemical products. *China National Resources Recycling*，1998 (in Chinese).
[49]He YQ. The recycling of the electronic waste. *Chemical Industry Press*,2006.7 (in Chinese).
[50]Wang ZK, Che JT, Ye CL. Application of ferric chloride both as oxidant and complexant to enhance the dissolution of metallic copper.

Hydrometallurgy, 2010, 105: 69-74.
[51]Yang GL.Stripping Cu by hydrogen peroxide-ammonium citrate in the electroplating process. *Environ Che*, 1989(04): 69-73 (in Chinese).
[52]Zhu RX.Study on chemistry etching of brass superficial. *Applied Chem Industry*, 2005(05): 277-279 (in Chinese).
[53]Duda LL. Kinetics of the dissolution of copper in aqueous alkaline 2,2′ -dipyridyl solutions. *Corros Sci*, 2002,44 (5), 989-995.
[54]Chen JC, Lin SR, Tsai WT. Effects of oxidizing agent and hydrodynamic condition on copper dissolution in chemical mechanical polishing electrolytes. *Appl Surf Sci*, 2004, 233 (1-4), 80-90.
[55]Huang W, Tamilmani S, Raghavan S, et al. Dissolution of copper thin films in hydroxylamine-based solutions. *Int J Miner Process*, 2003, 72(1-4): 365-372.