

## Literature Review of Hydrometallurgical Recycling of Printed Circuit Boards (PCBs)

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### Abstract

This study provides an up-to-date review of recycling of printed circuit boards (PCBs), specifically in hydrometallurgical treatment. Waste printed circuit boards, which are rich in base and precious metals, are the essential component of end-of-life electrical and electronic equipment. From the economic and environmental perspectives, the efficient recycling of PCBs is of importance. For the extraction of metals from PCBs, a large amount of work has been done to establish an environmentally friendly and economic way to recover metals from PCBs based on physical, pyrometallurgical and hydrometallurgical processes. Among those processes, hydrometallurgy is a promising treatment due to its low capital cost, high selectivity and lower environmental impact. This review emphasizes the recycling of PCBs by physical and hydrometallurgical treatments.

**Keywords:** PCBs; Recycling; Physical separation; Hydrometallurgical treatment

### Introduction

Due to the rapid development of technology and incredible market growth, electronic equipment has an ever shortening lifespan, which contributes to the fastest increase of e-waste. The definition of e-waste is the end-of-life electric and electronic equipment without the intent of reuse [1]. E-waste generally consists of six categories, including lamps, small IT, screens, temperature exchange equipment and small equipment, as well as large equipment, such as LED lamps, cell phones, refrigerators, printers and dryers, as shown in reference [1]. According to data in 2014, there are approximately 41.8 million tonnes of e-waste generated through the world, and it is expected that the amount of e-waste will reach 49.8 million tonnes in 2018, with an annual growth rate of four to five percentages [1]. Figure 1 shows the trend of e-waste generation in the world from 2010 to 2018. The management options of e-waste are involved in reuse, refurbishment and repairs of electronics, and the end-process for recovering metals, as well as disposal [1]. Since e-waste has high content of base and precious metals and toxic substances, such as mercury, lead and plastic additives, how to efficiently recover those metals is of importance, not only because of its high economic potential, but also due to potential environmental and human health risks. Table 1 [2] shows that the content of the metals that contain iron and steel, copper, aluminum and printed circuit boards, as well as other non-ferrous metals are almost 60%, which could contribute to the fact that e-waste could be regarded as the secondary sources for those metals [3-6].

Printed circuit boards, the essential part of electronics, contain more abundant base and precious metals than their ores, respectively. Table 2 shows the content of PCBs. Therefore, the main driving forces of developing metal recovery methodologies are high contents of base and precious metals and stringent environment regulations. Other than metals, a large number of polymers and ceramics can be found in PCBs as well. It is reported that plastics in PCBs commonly contain isocyanates and phosgene from polyurethanes, acrylic and phenolic resins, epoxides and phenols such as chip glass [7]. Presently, incineration and landfill are the only ways on a large scale to practically treat the non-metallic fraction physically separated from PCBs, which results in a severe consequence where some organic matters can either produce hazardous substance as the composition of off-gas or convert into some poisonous compounds [8,9].

A major challenge for metal recovery is the heterogeneity and complexity of PCBs, which includes metal diversity and their liberation. Generally, a schematic process of recycling PCBs, shown in Figure 2 [10], is involved in disassembly, upgrading and refining [11]. Disassembly is used for separation of a target component, particularly metals, from their organic substance. Upgrading includes mechanical, pyrometallurgical and hydrometallurgical treatments. Refining is a final step to get high purity metals. The industrial treatment of E-scrap is carried out via mainly pre-treatment and pyrometallurgy. Aurubis, one of the largest copper producers in the world, also efficiently processes a variety of recycling raw materials including: electronic scrap, precious metal-bearing copper scrap, copper-iron material, as well as tin/lead-bearing recycling raw materials, etc. [12]. The Kayser Recycling System (KRS) is well suited at the Aurubis unit in Lünen, Germany, to recycle materials with low levels of copper and precious metals [13]. The main pyrometallurgical operations are two reduction processes in a submerged lance furnace and top blown rotary converter, respectively, and an oxidation process in an anode furnace. The final product that contains 99% copper is cast into copper anodes. Due to the fact that precious metals can be resolved in copper, lead and matte [14], electrowinning is always utilized as the refining process to further purify copper and remove and recover precious metals in the anode slimes [13]. Likewise, as shown in Figure 3, Umicore [15] built up an integrated metals smelter and refinery at Hoboken Plant, Antwerp, Belgium, and used copper as a solvent to separate precious metals from other metals that are collected in a lead slag. After leaching and electrowinning, precious metals are obtained as residues that require being refined. The lead slag is sent to the base metals operation in order to be transformed to the impure lead bullion that is sent to refinery.

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Received December 16, 2015; Accepted January 05, 2016; Published January 18, 2016

Citation: Cui H, Anderson CG (2016) Literature Review of Hydrometallurgical Recycling of Printed Circuit Boards (PCBs). J Adv Chem Eng 6: 142. doi:10.4172/2090-4568.1000142

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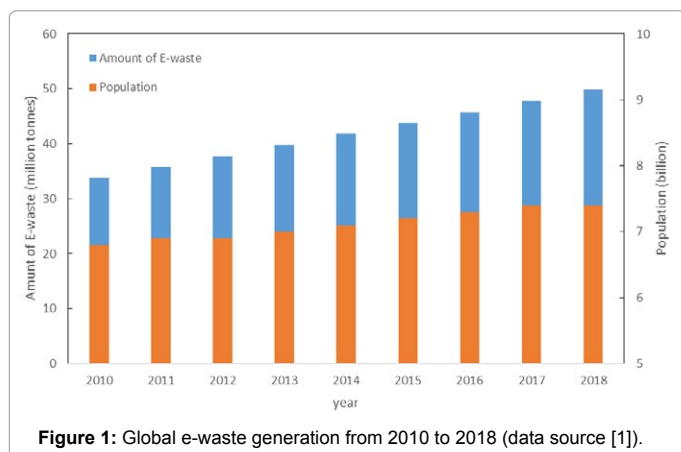


Figure 1: Global e-waste generation from 2010 to 2018 (data source [1]).

Material	Composition (Wt%)
Iron and steel	47.9
Non-flame retarded plastic	15.3
Copper	7
Glass	5.4
Flame retarded plastic	5.3
Aluminum	4.7
Printed circuit boards	3.1
Other	4.6
Wood and plywood	2.6
Concrete and ceramics	2
Other metals (non-ferrous)	1
Rubber	0.9

Table 1: E-waste material composition [2].

Metallic Element	Birloaga et al. [3]	Yang et al. [4]	Oishi et al. [5]	Behnamfard et al. [6]
Cu (wt%)	30.57	25.06	26	19.19
Al (wt%)	11.69	4.65	3.2	4.01
Fe (wt%)	15.21	0.66	3.4	1.13
Sn (wt%)	7.36	1.86	4.9	0.69
Ni (wt%)	1.58	0.0024	1.5	0.17
Zn (wt%)	1.86	0.04	2.6	0.84
Pb (wt%)	6.70	0.80	3.0	0.39
Mn (wt%)	-	-	0.11	0.04
Sb (wt%)	-	-	0.16	0.37
Au (ppm)	238	-	-	130.25
Ag (ppm)	688	-	-	704.31

Table 2: Representative material composition of PCBs.

## Pre-Treatment

Both disassembly and mechanical processes are used for the liberation and separation of the metallic components from waste PCBs in order to expose the metals for subsequent chemical processes. The mechanical process is considered the most environmentally friendly methodology to recover metals. Generally, a mechanical process could contain shredding, grinding, magnetic separation and electrostatic separation. However, the major challenge for the physical process is poor recovery of base and precious metals.

Many studies have been conducted on the physical process. A study was performed to investigate the feasibility of the mechanical process flowsheet proposed by Yoo et al. [16], which consists of milling by a stamp mill, size classification, gravity separation and two-step magnetic

separation. The results showed that the metallic elements, such as Fe, Cu, Ni and Al, could be concentrated, even though further optimization of the parameters was required. Li et al. [17] also investigated a process that contained a two-step crushing, corona electrostatic separation and recovery. It appeared that an effective separation of metals from base plates could be accomplished. In the study done by Veit et al. [18], 43% of iron on average in whole PCBs was in the fraction of the magnetic concentrate. After electrostatic separation, the concentrate of electrostatic components contained 50% copper, 25% tin and 7% lead, which could be further processed by chemical processes. A novel mechanical process [19] looked into the effect of wet impact crushing and falcon centrifugal machine on upgrading the metal grade. The study indicated that the grade of the metal concentrate was up to 92.36% with the recovery of 97.12%. Furthermore, the water medium in the wet impact crushing cannot only cool the machine, but help the discharge of the crushed materials in order to control the over-crushing. Although physical separation is a concern due to low cost and high environmental friendliness, the high metal loss (10%-35%) [20] can cause a negative effect in economics. For instance, Yazici et al. [20] indicated that the magnetic separation could recover up to 96% Fe and 93% Ni, while more than 60% losses of copper, gold and palladium occurred because of their association with iron alloy.

A gravity separation was studied by Huge Marcelo Veit et al. [21] to investigate the utilization of Mozley concentrator for pre-extraction of metals from PCBs. The Mozley concentrator consists of a flat tray and separation V-shaped tray for fine and coarse particles, respectively. The water flow rate and tilt-tray angle were considered as parameters to be optimized. It is reported that the material size fraction of  $-1+0.25$  mm is used in the gravity process, after taking the loss of materials and interference of fine particles in the gravity process into consideration. It appeared that it was possible to pre-concentrate 85% copper, 95% tin, 96% nickel, and 98% silver, while aluminum and gold could not be recovered due to its density and lamellar form, respectively [21].

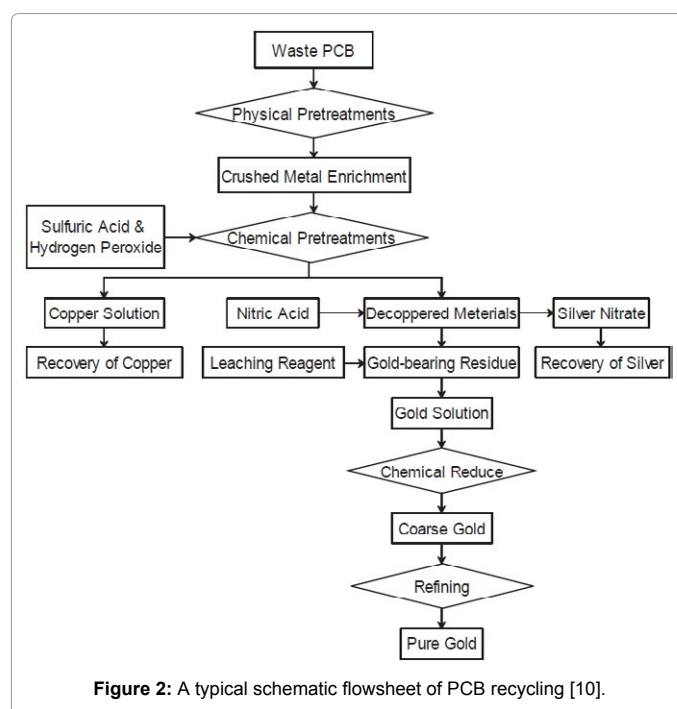
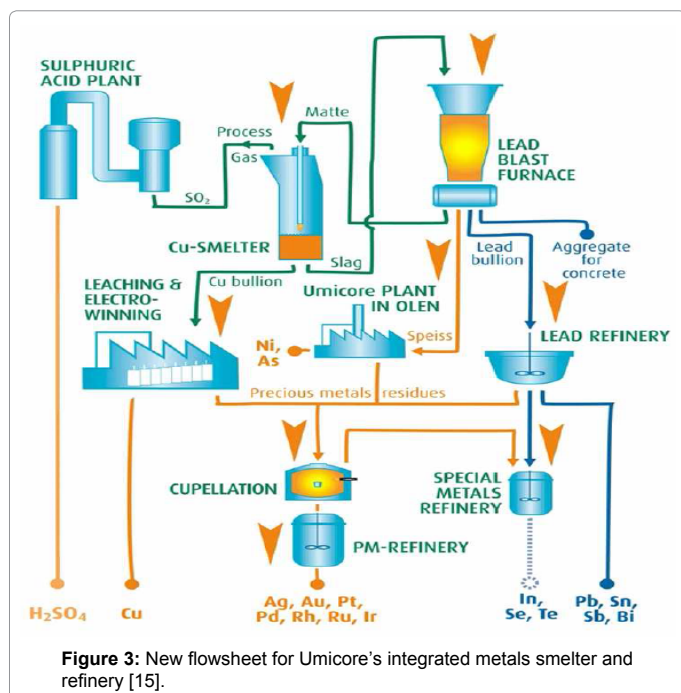


Figure 2: A typical schematic flowsheet of PCB recycling [10].



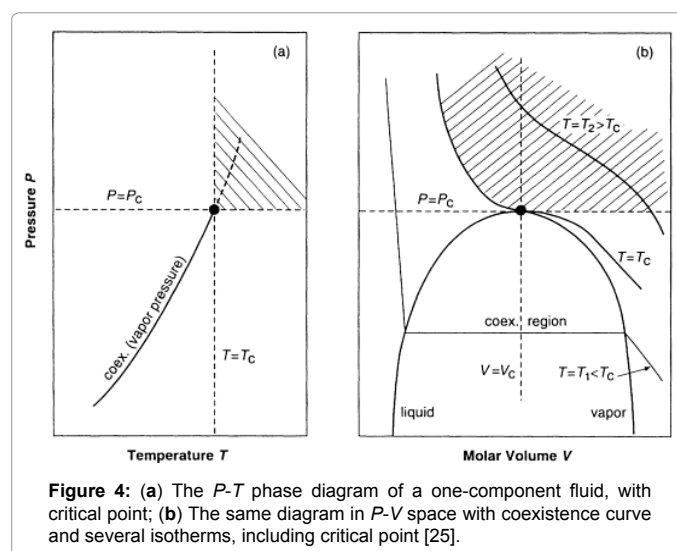
Flotation also has been investigated to reversely separate metals from organic matters with regard to fine particles, since gravity separation, magnetic separation and electrostatic separation could not be effective because of the similar physical qualities when the particles are so fine. The plastic is naturally hydrophobic; thus, an e-waste flotation study without reagents was carried out to mainly investigate following kinetic parameters with the 65% passing 35  $\mu\text{m}$  materials: airflow rate, pulp density and impeller speed. It is found that natural hydrophobicity of the plastic was confirmed by the experiments and the mechanism of the flotation kinetics was the first order kinetics. Gold and palladium could be recovered with 64% recovery at enrichment ratio of 3:1 [22]. Mäkinen et al. [23] showed that even though flotation, without reagents, could produce the concentrated metal products, a relatively large amount of copper, nickel, lead and antimony were found in the froth, which contributed to severe consequences of disposal and loss of metals. Moreover, Vidyadhar et al. [24] reported that under the conditions of a stirrer speed of 1198 rpm, frother dosage of 0.61 kg/ton, and pulp density of 9.02%, as well as air flow of 5.00 lph, 37% metal content with 76% mass yield was obtained, which meant that nearly 95% metal value was recovered [24].

Other than the conventional physical processes mentioned above, attention to supercritical water, whose temperature and pressure are over its critical point (374°C, 218 atm), shown as Figure 4 [25], has been drawn as a technique to pre-treat PCBs before chemical processes. Compared with ambient liquid water, several unique properties, such as lower dielectric constant, lower energy of hydrogen bond, and high solubility of organic compound, were possessed by water near its critical point. Reactions could occur in a homogeneous supercritical phase because of the high miscibility of organic compounds in supercritical water, which contributes to a fact that there are no interphase mass transport limitations to lower reaction kinetics [26]. Moreover, high pressure and temperature of supercritical water provide high enough velocity and temperature rise to destroy particle structure and make particles more porous. These further result in the diffusion of supercritical water through particle structures and the creation of big-hole structures [27,28]. Typically, the supercritical techniques applied

to recycling of PCBs contain supercritical water oxidation (SCWO), which is in the presence of oxygen gas, and supercritical water depolymerization (SCWD) under reducing atmosphere [27].

As for SCWO, it has been studied in decomposing toxic organic substances of PCBs. In the study of Chien et al. [9], the resin conversion in the supercritical water oxidation process of PCBs was 0.90 at 793 K for 10 min. It was determined that NaOH enhanced the supercritical water oxidation of PCBs and entrainment of Br in the liquid phase. The structure of copper in the solid residue was also identified and the results showed that  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$  and  $\text{Cu}(\text{OH})_2$  are the main copper phases, after a supercritical water oxidation. Xiu et al. [27] investigated both SCWO and SCWD with regards to the separation of organic substances from metals and ceramics. The effects of temperature, retention time and initial pressure were studied. It appeared that as temperature increased, the weight loss of solid phase increased for both methods. However, the degradation rate of organic matter on behalf of SCWO was higher than that under the SCWD process, which could be attributed to the combination of hydrolysis and oxidation in the case of SCWO process, compared with SCWD where only hydrolysis occurred. In addition, polymers with high molecular weight were eventually decomposed into low molecular compounds along with SCWD, however, in the process of SCWO, most organic matter was eventually oxidized into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , resulting in high pressure generated in the reactor. The higher final pressure in the process of SCWO also provided an explanation that SCWO was a superior method. Xiu et al. [27] also found HCl could be applied to acid leaching of base metals after the pretreatment of SCWO. That could be explained by the fact that SCWO converted copper metal to copper oxides that could be soluble in HCl, even though HCl is a non-oxidizing acid.

However, since water not only has high critical temperature and pressure, but also unique properties, such as ion product and dielectric point, which could contribute to high requirement of reactors, several alternatives are undertaken. Supercritical methanol was studied by Xiu et al. [28] to separate polymers and metals from printed circuit boards. The reasons for utilizing methanol as a supercritical fluid are that the critical point of methanol is 240°C, 8.09 MPa, which is lower than that of water. Additionally, the boiling point of methanol is lower than that of water. The results indicated that temperature, pressure, reaction time and the solid/liquid ratio affected the performance of supercritical methanol. The highest conversion happened either at 380°C with 120



min or 420°C with 60 min. The difference with the two conditions was that the oil recovery at higher temperature with shorter reaction time was less than that at low temperature with longer reaction time. Based on the elemental analysis of ICP-OES, It turned out that most metals were concentrated after the supercritical methanol process. Particularly, the content of copper after the treatment was approximately three times of that in the original material, and silver were significantly concentrated up to 7902 ppm.

## Recycling of Non-Metallic Fraction

As mentioned, non-metallic fraction in PCBs can be separated from metallic fraction by physical separation, such as magnetic separation, flotation, electrostatic separation and gravity separation. However, some challenges, such as how to get a clean separation between non-metallic and metallic fraction, are still remaining with regards to physical recycling of non-metallic fraction. In addition, there are mainly four methods to chemically recycle non-metallic fraction, including pyrolysis, gasification, supercritical fluid depolymerization and hydrogenolytic degradation [29]. Other than landfill or combustion, the non-metallic fraction can be reused in different fields, such as building materials, additives, *etc.* Li et al. [17] reported that the non-metallic fraction attained from a crushing-corona electrostatic separation could be hot-pressed to the nonmetallic plate with a few additives. The nonmetallic plate could be used as building materials. Guo et al. [30] further reported that the non-metallic plates that had flexural strength of 68.8 MPa and Charpy impact strength of 6.4 kJ/m<sup>2</sup> were obtained, when the nonmetallic plate contained 20 wt% non-metallic materials from PCBs and the particle size of nonmetallic fraction was less than 0.07 mm. Guo et al. [31] also investigated the replacement of non-metallic fraction from PCBs in the production of wood plastic composite. The results indicated that the flexural strength and tensile strength could be enhanced by using the non-metallic fraction, compared with using wood floor.

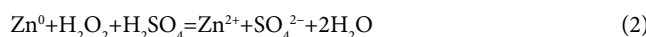
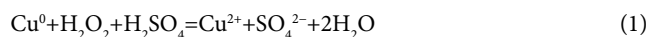
## Hydrometallurgical Treatment

There are a number of monographs on hydrometallurgical treatment with regards to recycling e-waste in recent years because of its low capital cost, low environment impact and easy management, compared with pyrometallurgy [32]. A hydrometallurgical process mainly consists of leaching, purification and recovery of metals.

### Extraction of base metals

A large amount of base metals, such as copper, lead, zinc and cadmium, *etc.* can be found in waste printed boards. Generally, leaching, as the first step of hydrometallurgical treatment, is to dissolve the constituents of the e-scrap to form a pregnant solution by a suitable lixiviant. Acid leaching with an oxidant reagent is widely used for the first stage leaching of base metals from PCBs. The base metal leaching, particularly, copper, was generally conducted by using acid such as H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, aqua regia and HClO with various oxidants including H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, Fe<sup>3+</sup> and Cl<sub>2</sub>.

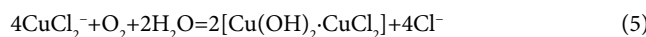
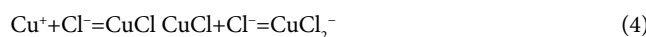
Hydrometallurgical extraction of copper has been well-established with regards to copper ore, however, there is no flowsheet that could be applicable to recycle copper from PCBs on the industrial scale. Typically, copper is dissolved in sulfuric acid to produce impure copper bearing pregnant solution, and then the pregnant solution goes through solvent extraction to upgrade copper purity. Eventually, pure copper is obtained by further electrowinning. A sulfuric acid leaching with H<sub>2</sub>O<sub>2</sub> is shown in Equations (1) and (2).



In the study of selective leaching of valuable metals from PCBs, it was found that 100% of the copper and zinc were leached out within 8 h by employing 2M H<sub>2</sub>SO<sub>4</sub> and 0.2M H<sub>2</sub>O<sub>2</sub> at 85°C, meanwhile, 95% of the iron, nickel and aluminum were dissolved within 12 h. Whereas lead had low dissolution rate in the H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-CuSO<sub>4</sub>-NH<sub>4</sub>OH systems, thus, the solid residue, mainly lead sulfate, undertook NaCl leaching solution to form PbCl<sub>2</sub>, followed by a solid/liquid separation [33]. In the investigation by Deveci et al. it was clear that concentration of H<sub>2</sub>O<sub>2</sub> and temperature were the most significant factors through a 2<sup>3</sup> full factorial design [34]. Yang et al. studied the effects of particle size, temperature and initial copper concentration with regards to leaching of copper. The results indicated that the fine particle which was smaller than 1 mm was efficiently treated, and temperature and initial copper concentration had insignificant effects on copper leaching [35]. Moreover, a negative effect was mentioned that the high stirring rate decreased the copper extraction, which could be attributed to the fact that the increasing stirring speed caused H<sub>2</sub>O<sub>2</sub> degradation [3].

In acidic sulfate solution, even though H<sub>2</sub>O<sub>2</sub> was extensively used as the oxidant as mentioned above, it suffers from its remarkably high consumption due to its decomposition and high temperature. Thus, ferric ion is regarded as an oxidant alternative because of its low cost and regeneration [36]. The downstream can be purified by goethite and jarosite precipitation before electrowinning [37,38]. An environmental assessment was investigated by Fogarasi et al. to evaluate two copper processes which were the direct electrochemical oxidation and mediated electrochemical oxidation using the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couples [39]. Unfortunately, there was no leaching data reported. Furthermore, Yazici and Deveci investigated the effect of ferric ions on sulfate leaching of metals from PCBs. The study indicated that high extractions of copper and nickel were obtained, and increasing temperature, ferric concentration and acid concentration positively affected the metal extraction, while the increase of solid ratio was an adverse effect on leaching of metals. The addition of air or hydrogen peroxide could maintain the high ratio of Fe<sup>3+</sup>/Fe<sup>2+</sup> [36].

The H<sub>2</sub>SO<sub>4</sub>-CuSO<sub>4</sub>-NaCl system has attracted attention not only because of the fact that chloride solution has higher solubility and activity of metals compound compared with in sulfate phase, but also due to the advantage of copper ions, which means the usage of copper can avoid the contamination of Fe<sup>3+</sup> and decrease the high cost when H<sub>2</sub>O<sub>2</sub> is used [40,41]. The mechanism in H<sub>2</sub>SO<sub>4</sub> system is shown in Equations (3)-(7). Ping et al. showed that in the electro-oxidation conditions, the recovery of Cu was 100% within 3.5 h [40].



Further investigation was performed with regard to other metals such as Fe, Ni, Ag, and Au. The experimental results indicated that the Cl<sup>-</sup>/Cu<sup>2+</sup> ratio is the influential factor for the extraction process. At 1% solid ratio, more than 90% Fe, Ni and Ag could be recovered with 58%, under the condition of a Cl<sup>-</sup>/Cu<sup>2+</sup> ratio of 21 and 80°C. Furthermore, the addition of oxygen could increase the recovery of the metals even at a higher solid ratio [41].

In addition to the sulfuric acid treatment of copper, other acids are also employed. Kasper et al. studied copper extraction by using aqua regia, followed by electrowinning. The material fed to the acid leaching was a metal concentrate by the mechanical process containing 60% copper. 95% of the copper purity was obtained on the cathodes [42]. Havlik et al. proposed a method that hydrochloric acid was used as the leaching solution to leach the sample thermally treated by either pyrolysis or burning. An improvement of the copper extraction was accomplished, when the burning temperature increased, which could be explained by the fact that copper is released from the PCBs and is oxidized. At the pyrolysis temperature of 900°C, the highest extraction of copper was achieved because copper oxide was more efficiently leached out in a non-oxidizing environment than pure copper metal [43]. Kim et al. [44] were highly interested in electro-generated chlorine in a hydrochloric acid solution. The effect of cuprous ions and leaching kinetics of copper from PCBs were investigated. It appears that depression of cuprous ions is helpful for increasing the leaching rate of copper, which is due to the fact that the chloride generation preferably occurs in the anode [44]. Moreover, a comparison was made to differentiate the performances in a combined reactor, which could be used as both the chlorine generator and metal leaching, and in two separated reactors. The results showed that current and temperature were of importance in terms of the kinetics of copper dissolution and metals leaching. The generation of cuprous ions has a negative effect on the leaching efficiency of the metals. Furthermore, it was observed that the surface layer diffusion was the kinetics law of copper dissolution, which meant that from the viewpoint of kinetics, the rate control step of copper leaching was the diffusion of the lixiviant through the porous product layer [45]. In a recent study, Yazici and Devci further studied cupric chloride leaching of copper as well as other metals (Fe, Ni, Ag, Pd and Au) from PCBs. The study showed that almost complete extraction of copper, nickel and iron were achieved over a leaching period of 120 minutes at 79mM initial  $\text{Cu}^{2+}$ . Increasing the initial copper concentration remarkably enhanced the metal extraction except for gold. Increasing temperature and oxygen supply could also increase the extraction of palladium and silver to 90% and 98%, respectively, which could be attributed to maintaining the high ratio of  $\text{Cu}^{2+}/\text{Cu}^+$  and thermodynamically favorable reaction between palladium/ silver and dissolved oxygen [46].

Pressure leaching of copper has been extensively investigated in recent years due to two benefits: high concentration of oxygen in solution and fast kinetics [47]. However, a limited amount of literature mentioned the application of pressure oxidation leaching in recycling PCBs. In the study of Jha et al. [48], it was found that at 150°C with 2M  $\text{H}_2\text{SO}_4$  and 15%  $\text{H}_2\text{O}_2$  under the oxygen pressure of 20 bar, 97.01% copper could be recovered from the liberated metal sheets, which was pretreated by organic swelling.

Some efforts were made in recycling copper by employing the Cu(I)-ammine complex [5,49]. On the basis of the thermodynamic prediction, the oxidation-reduction potential of  $\text{Cu}(\text{NH}_3)_4^{2+}/\text{Cu}(\text{NH}_3)_2^+$  was greater than that of  $\text{Cu}(\text{NH}_3)_2^+/\text{Cu}$ , and the oxidation-reduction potential of  $\text{Cu}(\text{I})/\text{Cu}$  was greater than hydrogen potential, which meant, in this case, that  $\text{Cu}(\text{NH}_3)_4^{2+}$  could be regarded as an oxidant and  $\text{Cu}(\text{I})$  could be reduced to metallic copper. The theoretical power consumption was lower than the conventional electrowinning process. The results indicated that the Cu(II)-ammine complex had the positive effect on the leaching rate of copper [49]. Oishi et al. found that the Cu(I) ammine contained the impurities, such as Zn, P, Mn and some Ni, in the both ammonium sulfate and chloride systems. However, Zn, Pb, Ni and Mn could be removed in the sequent purification process

by using LIX 26 (alkyl substituted 8-hydroxy-quinoline). The main impurity for copper concentrate was lead, which was due to similar potential between copper and lead [5].

In addition, the application of ionic liquid was studied to recycle copper from PCBs because of its outstanding properties, such as negligible volatility and high conductivity. Zhu et al. [50] reported that  $[\text{EMIM}^+][\text{BF}_4^-]$  could completely separate electronic components and solders from printed circuit boards at 240°C due to the hydrogen bond of  $[\text{EMIM}^+][\text{BF}_4^-]$ . Zeng et al. [51] investigated the utilization of water soluble ionic liquid  $[\text{BMIm}]\text{BF}_4$  in dismantling electronic components and tin solder from PCBs as functions of temperature, retention time and turbulence. The results indicated that approximate 90% of the electronic components could be separated at 250°C, 12 minutes and 45 rpm. And this study also reported that due to high efficiency and reusability of ionic liquids,  $[\text{BMIm}]\text{BF}_4$  dismantling is more favorable than mechanical dismantling, when the capacity of the plant is over 3,000 tons/day. In 2007, Dong et al. [52] investigated the behaviors of  $[\text{bmim}]\text{HSO}_4$  in leaching of chalcopyrite. The results suggested that  $[\text{bmim}]\text{HSO}_4$  acted as an acid and catalyst to facilitate the dissolution of chalcopyrite. In the study by Huang et al.  $[\text{bmim}]\text{HSO}_4$  was further studied to recycle copper from PCBs. Particle size, ionic liquid concentration,  $\text{H}_2\text{O}_2$  dosage and solid-liquid ratio, as well as temperature were considered as the parameters. It was observed that 99.92% copper could be reached under the conditions of 25 mL 80% (v/v) ionic liquid, 10 mL 30%  $\text{H}_2\text{O}_2$ , solid/liquid ratio of 1/25 at 70°C within 2 retention hours. Moreover, diffusion through a product layer was the controlling step, using the shrink core model [53].

There is a scenario that leaching is not necessary if metals obtained from PCBs have been concentrated to high purity (60%-80%) [54] from physical separation. Under this circumstance, electrometallurgy could be superior to produce copper. Xiu et al. [55] reported that after the strong SCWO process, recoveries of copper and lead approached to 100%. In the electrokinetic process, as shown in Figure 5, the solid residue was suspended in 1M HCl solution. The anode and cathode, two platinum-coated plates, were isolated by two porous glass frits. The results indicated that the increase of current density promoted the rise of copper recovery, however, the excessively high current density led to high potential gradient that resulted in more side reactions. Thus, 97.6% of copper concentration with recovery of 84.2% was obtained at 20 mA/cm<sup>2</sup> current density and 11 h reaction time. More than 74% copper recovery was attained by cathode deposition as two phases: Cu and  $\text{Cu}_2\text{O}$  [55]. The same electrokinetic set-up was also applied in the extraction of heavy metals (Cd, Cr, As, Ni, Zn and Mn) with different acids [56]. It appeared that HCl could recover 70% Cd, which could be attributed to the conjugation of low pH and Cd-Cl complexes. The high extraction of Cr, Zn, and Mn was found in the presence of citric acid [56]. Chu et al. [54] also investigated the electrolysis process as

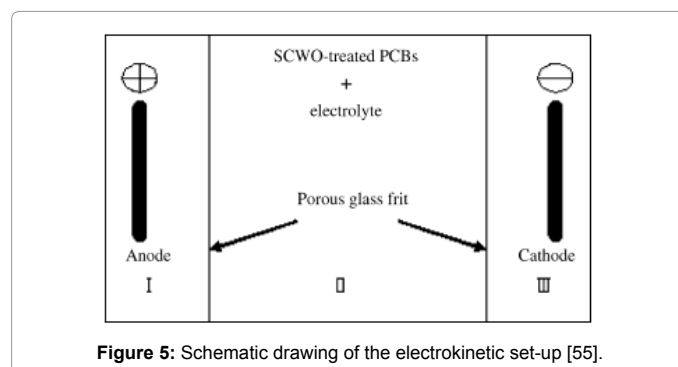


Figure 5: Schematic drawing of the electrokinetic set-up [55].

functions of the concentrations of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{NaCl}$ , current density and time with regards to the concentrated metal scraps containing 83.42% copper. It was found that the increase of the concentration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  simultaneously increased the current efficiency and particle size of copper powder in the cathode. Increasing the concentration of  $\text{H}_2\text{SO}_4$  and current density were effective at the increase of current efficiency. The optimization indicated the copper purity of 98.06% was obtained under the optimal conditions of 50 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 40 g/L  $\text{NaCl}$ , 118 g/L  $\text{H}_2\text{SO}_4$ , and 80 mA/cm<sup>2</sup> with 3 h.

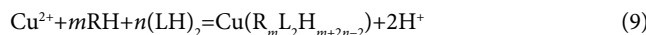
Additionally, recycling of other valuable base metals, including lead, tin, nickel and zinc, is also of significance in terms of economic and environmental perspectives. Studies on recycling of lead and tin from solder are reported using alkaline [57,58], nitric [58-60], hydrochloric [58] or fluoroboric acids [61] as leaching reagents. Ranitović et al. [58] reported that  $\text{NaOH}$  was not a reliable leaching reagent to extract lead and tin due to the dissolution and precipitation of metal hydroxides.  $\text{HNO}_3$  is capable of extracting lead, yet, tin could not be extracted resulting from the fact that tin is oxidized to insoluble form. On the contrary, it is also shown that 90% of tin could be extracted using  $\text{HCl}$  at high temperature; however, the precipitation of  $\text{AgCl}$  resulted in an unacceptable loss of  $\text{Ag}$  [58]. In the investigation of lead leaching from solder, Jha et al. [59] reported that 99.99% lead could be leached out from the swelling liberated solder under the conditions of 90°C, 0.2M  $\text{HNO}_3$  and S/L ratio of 1:20 (g/mL) in 120 min. Meanwhile, 98.74% tin could also be recovered at 90°C with 3.5M  $\text{HCl}$  for 120 min. Mecucci et al. [60] proposed the flowsheet, shown as Figure 6, to selectively separate copper, lead and tin. The flowsheet contains shredding, nitric acid leaching and electrodeposition, as well as electrolyte regeneration. It was found that copper and lead could be completely dissolved in the nitric acid of 6M, whereas at the high concentration of  $\text{HNO}_3$ , the formation of metastannic acid resulted in the fact that tin was able to be removed as a precipitate (metastannic acid). The reaction was shown in Equation (8).



The results indicated the feasibility of simultaneous recovery of lead and copper through electrodeposition, and tin could be recovered by electrodeposition after the dissolution of metastannic acid in the presence of hydrochloric acid. Park et al. studied the separation of zinc and nickel ions in a diluted aqua regia using TBP, Cyanex 272 and Cyanex 301. It appeared that over 99% zinc could be recovered using Cyanex 301 at low pH (pH<6), while 20% nickel could be extracted. The separation factor was approximately 21,700 at pH 6 [62]. As mentioned above, there are some potential leaching reagents that are capable of extracting base metals. Table 3 summarizes the advantages and disadvantages of four reagents for base metal extraction.

The copper leaching solution after solid-liquid separation can be either treated by purification or directly taken to the final process, where precipitation or electrowinning is involved to recover copper or its compounds [47,63]. Solvent extraction is considered to concentrate copper from dilute acidic leaching liquors. The common extractants are hydroxyl oximes (such as LIX984N [64]) and alkyl phosphinic acids (such as CYANEX 301 and CYANEX 302 [65]). Fouad [66] investigated solvent extraction of copper by the mixture of Cyanex 301 (RH) and LIX 984N (LH). The extraction could be expressed by Equation (9). The results indicated that the mixture of RH and LH with the ratio of 1:1 had the higher extraction efficiency, compared with using RH or LH, individually, which could be attributed to the formation of  $\text{CuRL}_2\text{H}$  complex. Moreover, 90.65% of stripping percentage of copper(II) from the organic phase was obtained by the addition of 6 M

$\text{HCl}$ . Other than solvent extraction, cementation is employed to extract copper as well. Behnamfard added metallic iron to copper solution, then metallic copper precipitated [6]. Kumari et al. [67] also reported that in a process of pyrolysis-beneficiation-leaching-solvent extraction, after recovering sulfuric acid and iron from the leach liquor using 70% TEHA in kerosene and air sparging, respectively, 99.99% copper could be extracted using 10% LIX 841C in two stages at pH 2.5 and O/A ratio 1/1. Similarly, nickel could be completely recovered from the raffinate in two stages when 1% LIX 841C was used at pH 4.58 and O/A ratio 2/1.



### Extraction of precious metals

Precious metals have been used in electric and electronic industries due to their excellent electrical conductivity, low contact electrical resistance and corrosion resistance [68], even though rare earths have started partially replacing precious metals in electronic industry. Therefore, a large number of e-waste contains significant amount of precious metals, particularly gold, silver, and palladium. It is of importance to recycle precious metals from e-waste. For instance, the gold content in PCBs is 35-50 times higher than gold ore [68], even though it has been noticed that the gold content in printed circuit boards is decreasing. Extraction of precious metals from PCBs, including leaching, purification and recovery, is the second stage after the recovery of base metals. The most common leaching reagents for precious metal leaching include cyanide, thiourea and thiosulfate because of the stable metal complex formed [32]. Table 4 [69] and Table 5 summarize the alternatives to cyanide and make a comparison of several common reagents for gold extraction. Senanayake [70] summarized a series of equations to illustrate the mechanism of gold complex formation regarding different lixiviants, and also showed the linear correlations of stability constants of Au(I)-complexes, following the order:  $\text{CN}^- > \text{HS}^- > \text{S}_2\text{O}_3^{2-} > \text{SC}(\text{NH}_2)_2 > \text{OH}^- > \text{I}^- > \text{SCN}^- > \text{SO}_3^{2-} > \text{Br}^- >$

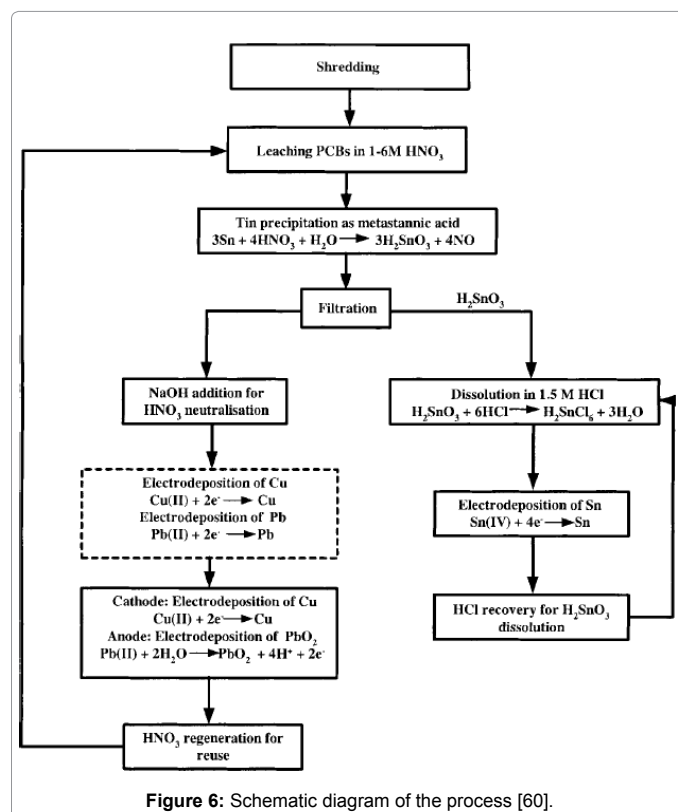


Figure 6: Schematic diagram of the process [60].

	Pros	Cons
Sulfuric acid	Highly selective, low reagent cost, well established process for copper ore	At elevated temperature, corrosive
Chloride	Fast kinetics at room temperature, high solubility and activity of base metals, low toxicity	Excessive corrosion, difficult electrowinning of copper, poor quality of copper
Aqua regia	Fast kinetics, effective	High reagent cost, highly corrosive, low selectivity
Ionic liquids	Thermally stable, environmentally friendly	High cost, excessive dosage

**Table 3:** Comparison of potential leaching reagents for base metals [32,36,46,50].

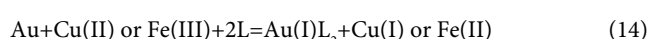
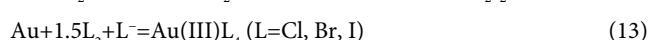
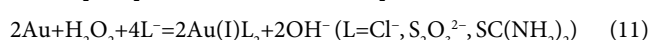
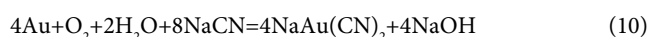
Reagent	Concentration range	pH range	Basic chemistry	Research level	Extent of commercialization
Ammonia	High	8-10	Simple	Low	Pilot
Ammonia/cyanide	Low	9-11	Simple	Extensive	Cu/Au ores
Ammonium thiosulfate	High	8.5-9.5	Complex	Extensive	Semi-commercial
Hypochlorite/chloride	High chloride	6-6.5	Well-defined	Extensive	Historical and Modern
Bacteria	High	7-10	Fairly complex	Low, growing	None
Natural organic acids	High	5-6	Fairly complex	Low	None
Thiourea	High	1-2	Well-defined	Fairly popular	Some concentrates
Thiocyanide	low	1-3	Well-defined	Low	None
Aqua regia	High	<1	Well-defined	Low	Analytical and refining
Acid ferric chloride	High	<1	Well-defined	Low	Electrolytic Cu slimes

**Table 4:** Suggested alternatives to cyanide [69].

	Pros	Cons
Cyanide	Highly effective, low reagent dosage and cost	Difficult to process wastewater, environmental risk, low kinetics
Thiourea	Less toxic, high reaction rate, less interference ions	Poorer stability, high consumption, more expensive than cyanide, downstream metal recovery
thiosulfate	High selectivity, non-toxic and non-corrosive, fast leaching rate	High consumption of reagent, downstream metal recovery
Halide	High leaching rate, high selectivity, relatively healthy and safe except for bromine	Highly corrosive for chlorine, high consumption for iodine
Aqua regia	Fast kinetics, low reagent dosage	Strongly oxidative and corrosive, difficult to deal with downstream

**Table 5:** Comparison of potential leaching reagents for gold [10,32,76].

Cl<sup>-</sup>.



(L = Cl<sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, SC(NH<sub>2</sub>)<sub>2</sub>, SCN<sup>-</sup>, NH<sub>2</sub>CH<sub>2</sub>COO<sup>-</sup>, NH<sub>2</sub>CH(CH<sub>3</sub>)COO<sup>-</sup>).

For over a century, cyanide has been extensively used as the leaching lixiviant to treat both gold mines and secondary gold source due to

its high efficiency and low cost [68]. Most cyanide leaching processes occur at pH 10, because of the fact that cyanide ion is stable at pH 10.2. Below pH 8.2, cyanide exists as hydrogen cyanide that is highly volatile [71], which results in cyanide loss and harmfulness of operators' health. Recently, the slow cyanidation rate and severe environmental impact of cyanide gold leaching accelerate the development of a substitute that is more effective and environmental-friendly.

Thiourea, NH<sub>2</sub>CSNH<sub>2</sub>, is considered a most promising alternative to cyanide regarding leaching of precious metals due to its fast leaching rate and non-toxicity. The thiourea leaching is conducted at pH=1.5 following the reaction shown as Equation (14). The demerits of thiourea leaching are high cost and consumption because of its poor stability. Li et al. [72] examined the thiourea leaching of gold and silver from PCBs as functions of particle size, temperature, and thiourea concentration, as well as Fe<sup>3+</sup> concentration. It appeared that the optimum condition for gold leaching happened when 24 g/L thiourea and 0.6% of Fe<sup>3+</sup> were used within 2 h. It is also proved that thiourea is less toxic and highly efficient [72]. Birloaga et al. reported that 69% of gold was extracted under the conditions of 20 g/L thiourea, 6 g/L Fe<sup>3+</sup>, and 10 g/L H<sub>2</sub>SO<sub>4</sub>, as well as 600 rpm. Furthermore, under the same reagent condition, a multistage cross current leaching was used to reduce the consumption of thiourea and improve the efficiency of gold leaching from PCBs [73]. Yin et al. compared thiourea leaching with iodine leaching of gold from PCBs. It appeared that 93.5% gold was able to be leached out directly by iodine without pretreatment, while thiourea leaching of gold was carried out after copper leaching, which resulted in the high consumption of thiourea [74].

Several studies highlighted thiosulfate leaching of gold. Thiosulfate leaching is operated in alkaline condition to prevent thiosulfate decomposition [75]. An evaluation [76] was conducted to compare thiosulfate with cyanide and nitric acid. Nearly 65% of gold was leached in the cyanide solution, and almost 100% of silver was leached in HNO<sub>3</sub> solution. However, in the case of thiosulfate leaching, only around 15% gold could be extracted, which gave a negative indication of thiosulfate leaching of gold. Further, in this study, it was suggested that the presence of copper ions promoted gold extraction in the sodium thiosulfate system. Ficeriová et al. found that 98% of gold and 93% of silver were recovered from pretreated PCBs under the conditions of 0.5M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 0.2M CuSO<sub>4</sub>·H<sub>2</sub>O, and 1M NH<sub>3</sub> at 40°C after 48 h. Up to 90% of palladium was also extracted by leaching in aqua regia solution with 2 h [77]. Ha et al. [78] reported that 98% gold could be recovered using a solution containing 20 mM copper, 0.12M thiosulfate and 0.2M ammonia. The reaction happening in the thiosulfate leaching is shown in Equation (15).



Park et al. proposed a process of recycling precious metals such as gold, silver and palladium using aqua regia. The results showed that 98% silver could be recovered without any additives and 93% palladium was recovered as Pd(NH<sub>4</sub>)<sub>2</sub>Cl<sub>6</sub>, which was a red precipitate. A solvent extraction was employed to recover gold as nanoparticles, where toluene, dodecanethiol and sodium borohydride were used [79]. However, the application of aqua regia in extraction of precious metals is limited in a lab scale because aqua regia is strongly oxidative and corrosive, and the waste water from leaching is too acidic to be dealt with [76].

Other than gold and silver, palladium is also considered as a valuable metal to be recycled. Zhang et al. [80] proposed the process to recover palladium, including enrichment and dissolution of palladium, and extraction and stripping of Pd(II). Copper was leached out in

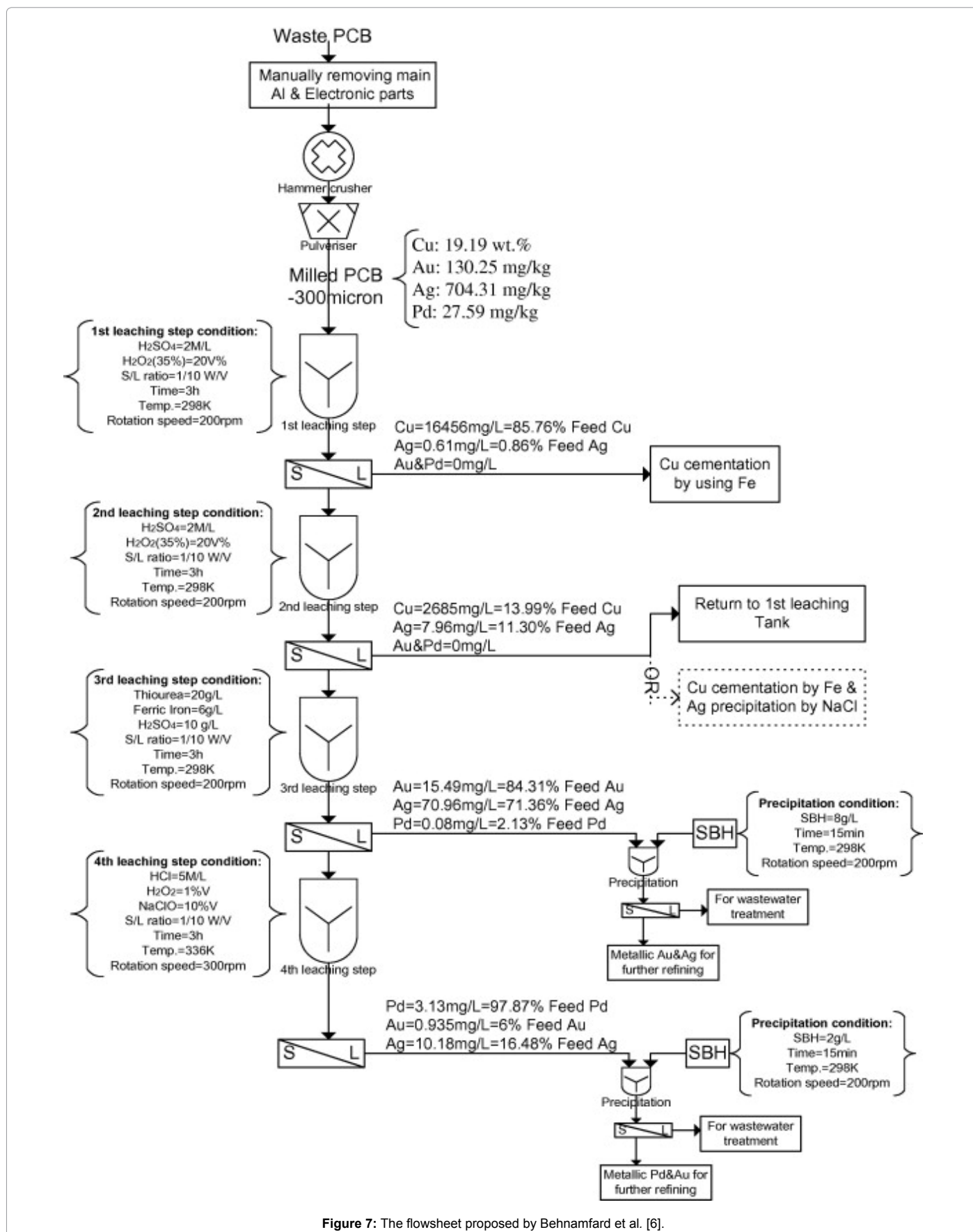


Figure 7: The flowsheet proposed by Behnamfard et al. [6].



the solution of  $\text{CuSO}_4$  and  $\text{NaCl}$ . The overall reaction was shown as Equation (16).



When the ratio of  $[\text{Cu}]/[\text{Cu}^{2+}]$  was more than 1.4, palladium was leached out along with  $\text{CuCl}$ . Thereafter, palladium was further dissolved in the solution of  $\text{CuSO}_4$  and  $\text{NaCl}$ , where the ratio of  $[\text{Cu}]/[\text{Cu}^{2+}]$  was less than 0.9. The reaction of palladium dissociation was shown as Equation (17). Diisoamyl sulfide (S201) was applied to extract 99.4% palladium from leaching solution, then a two-step stripping was accomplished using dococene with 0.1M  $\text{NH}_3$ . Therefore, 96.9% palladium was obtained with negligible effect of copper ions.



In the gold industry, gold is recovered from gold-rich leaching solution by carbon adsorption, following precipitation with zinc dust or electrowinning [81,82]. Behnamfard et al. [6] proposed the flowsheet, shown in Figure 7, involving a two-step sulfuric acid leaching, acidic thiourea leaching with ferric ions, and  $\text{HCl-NaClO}_2\text{-H}_2\text{O}_2$  leaching, as well as precipitation with sodium borohydride (SBH). Approximate 99% copper could be recovered. It was found that 84.31% of gold and 71.36% of silver could dissolve in acidic thiourea with ferric ions, while palladium could not be dissolved in thiourea solution. In this study, SBH was used as a reducing reagent to selectively precipitate gold from silver. The optimal precipitation of gold and silver happened at 8 g/L SBH in 15 min.

## Conclusion

Printed circuit boards (PCBs) contains various valuable materials, such as copper, gold and silver. From the economic point of view, recycling of those valuable materials is extremely attractive. Increasing generation of PCBs and the severe environmental impacts of landfills promote the development of recycling methodologies. The mechanical process is of importance for following chemical processes, because of the need for metal liberation. The hydrometallurgical process has been studied in terms of its advantages, such as low capital cost and less environmental impact. The work done shows the promising future in the world of PCBs recycling. Both ionic liquid and chlorine-based media have the potential for the extraction of base and precious metals. However, the flowsheets proposed are limited in lab-scale. Thus, larger scale studies should be concentrated on to achieve commercialization.

## Acknowledgements

This work was funded by the NSF CR3 consortium through collaboration with Kroll Institute for Extractive Metallurgy in the George S Ansell, Department of Metallurgical and Materials Engineering, Colorado School of Mines, USA.

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