A hydrometallurgical process for the recovery of copper metal and nickel hydroxide from the aqua regia leaching solutions of printed circuit boards

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Abstract: Leaching solutions of printed circuit boards (PCBs) contain noble and base metal ions. The precious metal ions present in the leaching solutions of PCBs could be separated by cementation with copper metal. After recovery of precious metal ions by cementation, the filtrate contains Cu(II) together with base metal ions like Al(III), Fe(III), Fe(II), Ni(II), Sn(II), and Zn(II). In this work, separation experiments were conducted to recover Cu(II) and Ni(II) from the filtrate. First, copper ions were completely separated from the filtrate by chemical reduction with hydrazine at the following conditions: a molar ratio of 8 for hydrazine to Cu(II), 20°C, 500 rpm, and 20 mins. By adding sodium oxalate to the solution after separation of Cu(II), most of the Ni(II) and 38% of the Zn(II) were co-precipitated at 20°C, 60 mins, 500 rpm, and a molar ratio of 20 for sodium oxalate to nickel. After dissolving the co-precipitates of Ni(II) and Zn(II) oxalates in a 0.5 M HCl solution, the Zn(II) was completely removed from the solution by a five-stage cross-current extraction with 2.5 M Cyanex 272. Nickel hydroxides were then recovered from the raffinate by precipitation with NaOH. The purity of the copper metal and nickel hydroxides was higher than 99%. A process was proposed to recover Au(III), Pd(II), Cu(II), and Ni(II) from the leaching solutions of PCBs.

Keywords: e-waste recycling, separation, recovery, copper metal, nickel hydroxide

1. Introduction

The widespread use of electronic devices in recent decades has led to a growing issue of the disposal of waste electrical and electronic equipment (e-waste) (Hadi et al., 2013; Hao et al., 2020). Printed Circuit Boards (PCBs) are crucial components of electronic devices, facilitating electrical connections through conductive pathways onto a non-conductive substrate. Additionally, PCBs consisted of a complex mixture of metals and non-metals are indispensable to the functionality of modern electronic devices. The fundamental composition of PCBs includes 30–35% by weight of metals, 24–30% of resins, and 32–35% of refractories. PCBs are economically valuable due to the high metal content, especially precious metals like Au (150–2000 ppm Au) and Pd (30–350 ppm Pd) along with some major metals like 11–28 wt% Cu and 1–4 wt% Ni, etc. (Jadhav, et al., 2015; Oke and Potgieter, 2024 Oliveira et al., 2021). Gold and palladium are in high demand for various industrial applications, especially in electronics and jewelry (Ramesh et al., 2008; Awual et al., 2015). Additionally, copper is an excellent conductor of electricity and is widely used in electronics (Topcu et al., 2023), while nickel is commonly used in electroplating and lithium-ion batteries (Jeon and Cha, 2015). With the increasing demand for these metals, it has become necessary to recover Au, Pd, Cu, and Ni contained in PCBs. Various methods such as thermal (Kaya, 2016), eddy current (Cui and Forssberg, 2003), magnetic separation (Khaliq et al., 2014), and pyrolysis (Hsu, et al., 2019) have been applied for the separation of ferrous metal from PCBs. Afterward, the metals in the pre-treated PCB are dissolved by using aqua regia solution. Therefore, it is necessary to recover the above-mentioned ions from the leaching solutions of PCBs.

The precious metal ions present in the leaching solutions of PCBs can be separated by cementation with copper metal owing to their higher reduction potentials. Recently we have reported a process to

recover gold metal powder and Pd(II) compounds from the leaching solution of PCBs containing Al(III), Cu(II), Fe(III), Ni(II), Sn(II), and Zn(II) (Nguyen and Lee, 2023). In this process, the Au(III) and Pd(II) in the leaching solutions were separated from other metal ions by cementation with copper metal. The filtrate after cementation contains Al(III), Cu(II), Fe(III), Fe(II), Ni(II), Sn(II), and Zn(II). Since copper metal is employed as a reducing agent for Au(III) and Pd(II), the concentration of Cu(II) in the filtrate is high. Therefore, it is necessary to recover Cu(II) in the filtrate in order to complete the mass balance of the process. Considering that the demand for pure nickel compounds is rapidly increasing due to the manufacture of electrode materials for lithium-ion batteries, it is necessary to recover the Ni(II) present in the filtrate.

Among the metal ions in the filtrate (Al(III), Cu(II), Fe(III), Fe(II), Ni(II), Sn(II), and Zn(II)), the reduction potentials of Fe(III)/Fe(II) and Cu(II)/copper metal are higher than those of other ions. By utilizing the difference in the reduction potential between Cu(II) and other metal ions, Cu(II) can be separated from other metal ions by chemical reduction. Although the reduction potential of Sn(II) is a little higher than that of Ni(II), cementation would separate Ni(II) from other metal ions. Moreover, the solubility of Ni(II) oxalate is very low, and thus precipitation would lead to the separation of Ni(II) from other metal ions.

Several methods have been reported to recover Cu(II) and Ni(II) from the acidic solutions of secondary resources. These include solvent extraction (Wen and Lee, 2022; Nguyen and Lee, 2022), ion exchange (Kolodynska, et al., 2020), reduction (Li et al., 2019), precipitation (Nguyen, and Lee, 2023). , Recently, some green chemicals such as ionic liquids (Zhang et al., 2018), deep eutectic solvents (Sabzkoohi and Kolliopoulos, 2021), and organic acids (Oke and Potgieter, 2024) are employed for the separation of metal ions. However, the performance of these methods depends on the composition of the acidic solutions and the nature of the metal ions present in the solutions. Among the metal ions in the filtrate (Al(III), Cu(II), Fe(III), Fe(II), Ni(II), Sn(II), and Zn(II)), the reduction potentials of Fe(III)/Fe(II) and Cu(II)/copper metal are higher than those of other ions. By untilizng this difference in reduction potential, there is a possibility that pure copper metal can be recovered by chemical reduction. In general, the separation of Ni(II) from the solutions containing other metal ions like Al(III), iron ion, Sn(II) and Zn(II) is very complicated. The solubility products of Ni(II) and Zn(II) oxalates are smaller than those of other metal oxalates. In this study, the recovery of Cu(II) and Ni(II) from the filtrate after the recovery of precious metals by cementation was investigated through reduction and precipitation. First, hydrazine was employed as a reducing agent and optimum conditions were obtained to recover pure copper metal from the filtrate. Second, mixed oxalates of Ni(II) and Zn(II) were separated from the solution by oxalate precipitation using sodium oxalate after recovering Cu(II). Then the mixed oxlates were dissolved by using HCl solution. Zn(II) was removed from the leaching solution of mixed oxlates by solvent extraction. Optimum conditions for oxalate precipitation, HCl dissolution, and solvent extraction were obtained. The purity of the recovered copper metal and Ni(II) hydroxides was higher than 99%. A hydrometallurgical process was proposed for the recovery of gold, palladium annd copper as well as nickel present in the leaching solutions of PCBs. This process represents a significant advancement in the field of metal recovery from e-waste, offering a practical solution for maximizing the extraction of valuable metals while minimizing waste disposal and environmental impact.

2.   Experimental

2.1. Chemicals and reagents

Iron powders with the size of 150 μm were employed in the cementation reaction. In solvent extraction experiments, Cyanex 272 (Solvay Cytec Industries, 85%) was used as an extractant. The concentration of Cyanex 272 was adjusted by diluting it with reagent-grade kerosene (Dae-Jung Co.). In chemical reduction experiments of Cu(II), hydrazine ($N_2H_4 \cdot H_2O$, Dae-Jung Co., 80%) was used as a reducing agent. Sodium oxalate ($Na_2C_2O_4$, Orient Chemical Industries CO., LTD) and sodium hydroxide (NaOH, Duksan pure chemical CO., LTD, >93%) were used as precipitants. Hydrochloric acid (HCl, Daejung Co., 35%) was used in dissolving the oxalates of Ni(II) and Zn(II). Potassium permanganate ($KMnO_4$, Junsei Chemical Co., Ltd, > 99.3%) was employed in the measurement of the concentration of Fe(II) by titration (Kumar and Ram, 2021). All reagents used were of analytical grade.

2.2. Experimental procedure and analytical methods

2.2.1. The analytical method

The leaching solutions employed in this work were provided by a company in Korea. Waste printed circuit boards together with some wastes containing Au were dissolved by aqua regia at 80°C and at a pulp density of 250 g/L. Table 1 shows the composition of the leaching solution analyzed by ICP-OES (Inductively coupled plasma-optical emission spectrometry, Spectro Arcos, Germany). The pH of the solutions was measured by a pH meter (Orion Star A211, Thermo Fisher Scientific, Waltham, Massachusetts, USA).

Table 1. The concentrations of the metal ions in the leaching solution of printed circuit board (Nguyen and Lee, 2023)

Ions	Au(III)	Pd(II)	Al(III)	Cu(II)	Fe(III)	Na(I)	Ni(II)	Zn(II)	Sn(II)
g/L	32.43	1.31	0.53	1.67	0.12	1.35	0.64	6.43	0.08

2.2.2. Solvent extraction, reduction, and precipitation

The reduction experiments were performed by using a 250 mL three-neck round-bottom flask. In the chemical reduction of Cu(II), adequate amount of the hydrazine was added as a reducing agent to the solution. After reaction, copper powders were separated from the solutions by using filter paper (ADVANTEC No. 2, 110 mm, 100 circles, Toyo Roshi Kaisha, Ltd.).

The precipitation experiments were also performed by using a 250 mL three-neck round-bottom flask. In the precipitation, a certain amount of $Na_2C_2O_4$ was added as a precipitant to the filtrate after recovering Cu(II). The precipitates were separated from the solutions with the filter paper. Then, Zn(II) was separated over Ni(II) from the solution by solvent extraction using Cyanex 272. Solvent extraction experiments were done by shaking equal volumes (20 mL) of organic and aqueous phases in a 100 mL screwed cap bottle within 30 mins using a Burrell wrist action shaker (model 75, USA) at ambient temperature (20 ± 1°C). After the reaction, the mixed solutions were left on a separatory funnel to separate the aqueous and organic phases. In all the solvent extraction experiments, the phase ratio of the two phases was fixed at unity. Finally, adequate amount of NaOH was added to the raffinate to recover nickel hydroxides. The percentages of extraction (%E), reduction (%R), and precipitation (%P) were defined by Eqs (1), (2), and (3).

$$\%E = \frac{x_s - x_{aq}}{x_s} \times 100 \tag{1}$$

$$\%R = \frac{k^*_{aq} - k^{**}_{aq}}{k^*_{aq}} \times 100 \tag{2}$$

$$\%P = \frac{q_i - q_{ii}}{q_i} \times 100 \tag{3}$$

where x_s and x_{aq} are the mass of the metal ions in the solution before and after extraction, respectively. Moreover, k^*_{aq} and k^{**}_{aq} are the mass of the metal ions in the solution before and after reduction. In addition, q_i and q_{ii} are the mass of the metal ions in the solution before and after precipitation.

3. Results and discussion

3.1. Recovery of Au(III) and Pd(II) from the leaching solutions of PCBs

In our recent work (Nguyen and Lee, 2023), a process was reported for the recovery of gold metal powder and Pd(II) compounds from the leaching solutions of PCBs. In this process, both Au(III) and Pd(II) were recovered at the same time from the leaching solutions through cementation with copper metal powder. Following the cementation reaction, the residues (cemented copper) were gathered to recover gold and palladium. The recovery process for gold and palladium in cemented copper involves three key steps: Firstly, the cemented copper containing Au, Pd, and Cu metals are dissolved using a 5 M HCl solution with 8% NaClO as an oxidizing agent. Secondly, Au(III) is extracted using Cyanex 272. Lastly, the Pd(II) present in the raffinate is then separated from Cu(II) through oxidative precipitation, using a mixture of $NaClO_3$ and NH_4Cl.

Table 2 lists the composition of the filtrate after the cementation of the leaching solution with copper metal. Because the reduction potential of Fe(III) to Fe(II) is higher than that of Cu(II) to copper metal (see Table 3), Fe(III) would be reduced to Fe(II) during the cementation of Au(III) and Pd(II) with copper metal. Therefore, the concentration of Fe(II) in the filtrate after cementation of Au(III) and Pd(II) was measured by titration with $KMnO_4$ and is represented in Table 2. The ratio of Fe(II) to the total iron ion was about 0.17. Since copper metal is employed as a cementation agent and the demand for nickel compound is increasing, it is desirable to recover Cu(II) and Ni(II) present in the filtrate after the recovery of Au(III) and Pd(II) from the leaching solutions of PCBs. In this study, the filtrate with the same composition as Table 2 was employed to recover Cu(II) and Ni(II).

Table 2. The concentrations of the metal ions in the filtrate after the separation of Au(III) and Pd(II) by cementation of copper metal

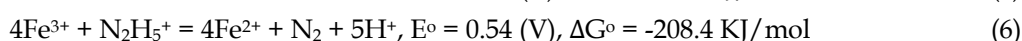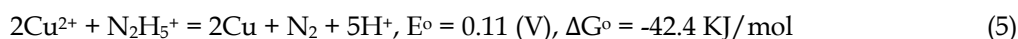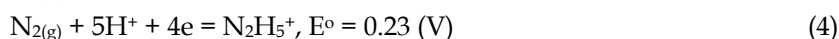| Ions	Au(III)	Pd(II)	Al(III)	Cu(II)	Fe(III)	Fe(II)	Na(I)	Ni(II)	Zn(II)	Sn(II)
g/L	ND	ND	0.53	17.9	0.10	0.02	1.35	0.64	6.43	0.08

*ND: Not detected

Table 3. Standard reduction potentials (E^o) of the metal ions in the filtrate at 25°C (Bard et al., 2017)

Half reactions	E^o(V)
$Fe^{3+}_{(aq)} + e^- = Fe^{2+}_{(aq)}$	+0.77
$Cu^{2+}_{(aq)} + 2e^- = Cu^0_{(s)}$	+0.34
$Sn^{4+}_{(aq)} + 2e^- = Sn^{2+}_{(aq)}$	+0.15
$Sn^{2+}_{(aq)} + 2e^- = Sn^0_{(s)}$	-0.13
$Ni^{2+}_{(aq)} + 2e^- = Ni^0_{(s)}$	-0.25
$Fe^{2+}_{(aq)} + 2e^- = Fe^0_{(s)}$	-0.44
$Zn^{2+}_{(aq)} + 2e^- = Zn_{(s)}$	-0.76
$Al^{3+}_{(aq)} + 3e^- = Al^0_{(s)}$	-1.66
$Na^+_{(aq)} + e^- = Na^0_{(s)}$	-2.71

3.2. Separation of Cu(II) from the filtrate after recovery of Au(III) and Pd(II)

According to Table 2, the filtrate after recovery of Au(III) and Pd(II) contained Cu(II), Ni(II), Al(III), Fe(III), Fe(II), Zn(II), Sn(II) and Na(I). Among these metal ions, the concentration of Cu(II) was the highest. Since there is much difference in the reduction potential between Cu(II) and other metal ions except Fe(III), chemical reduction was tried to separate Cu(II) from the filtrate. Among several chemical reductants, hydrazine has two nucleophilic nitrogen atoms and thus has high electron-donating ability. The nitrogen atoms in hydrazine have lone electron pair and thus hydrazine would be protonated in acidic solution and exists as $N_2H_5^+$ (Kim et al., 2008). The reduction reaction of a mixture of nitrogen gas and hydrogen ion into $N_2H_5^+$ and the simultaneous reduction reactions of Cu(II) and Fe(III) by $N_2H_5^+$ can be represented as Eqs. (5) and (6).

$$N_{2(g)} + 5H^+ + 4e = N_2H_5^+, E^o = 0.23 \text{ (V)} \tag{4}$$

$$2Cu^{2+} + N_2H_5^+ = 2Cu + N_2 + 5H^+, E^o = 0.11 \text{ (V)}, \Delta G^o = -42.4 \text{ KJ/mol} \tag{5}$$

$$4Fe^{3+} + N_2H_5^+ = 4Fe^{2+} + N_2 + 5H^+, E^o = 0.54 \text{ (V)}, \Delta G^o = -208.4 \text{ KJ/mol} \tag{6}$$

The molar ratio of hydrazine to Cu(II) is of importance in chemical reduction. Eqs. (5) and (6) show that at least one mole of hydrazine is required to reduce two moles of Cu(II) and four moles of Fe(III). Therefore, reduction experiments were done by varying the molar ratio of hydrazine to Cu(II) from 1 to 10. The reduction experiments were carried out for 30 mins at 20°C with a stirring speed of 500 rpm. Fig. 1 show that the reduction percentage of Cu(II) increased significantly from 36% to 99.7% when the molar ratio of hydrazine to Cu(II) increased from 1 to 8, and was constant with the further increase of the molar ratio to 10. In these experimental ranges, the reduction percentage of other metal ions except iron ion was nearly zero. Therefore, a molar ratio of 8 for the hydrazine to Cu(II) was selected in further experiments.
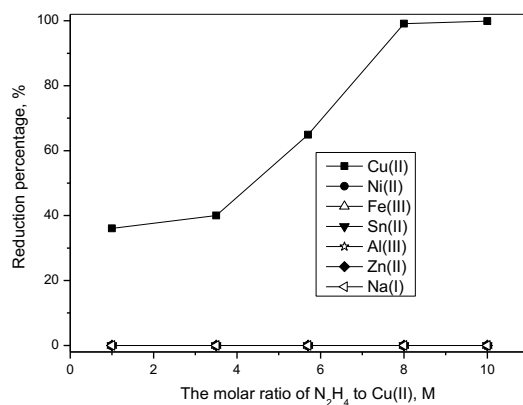
Fig. 1. Effect of molar ratio of hydrazine to Cu(II) on the reduction of the metal ions in the filtrate. (Temperature: 20°C, reaction time: 30 min, and stirring speed: 500 rpm)

To investigate the effect of reaction temperature, experiments were done by varying temperature from 20 to 80°C for 30 mins at a stirring speed of 500 rpm and the molar ratio of hydrazine to Cu(II) was fixed at 8. Fig. 2 shows that Cu(II) was completely reduced in the temperature range between 20 and 60°C. However, at 80°C, the reduction percentage of Cu(II) decreased significantly to 43%. This might be ascribed to the decomposition of hydrazine into hydrogen and nitrogen gas at high temperature, resulting in a decrease in the effective concentration of hydrazine which can act as a reducing agent. As a result, reaction temperature of 20°C was selected as an optimum temperature. Besides iron ions, the reduction percentage of other metal ions was negligible.
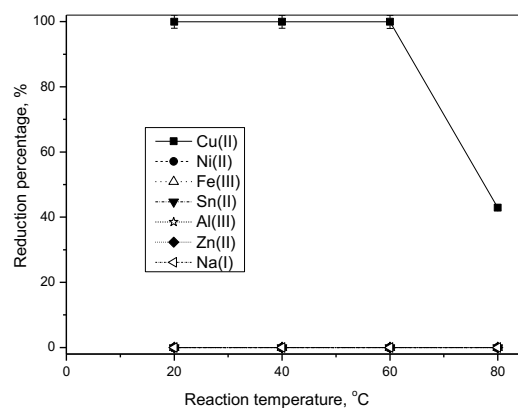

Fig. 2. Effect of reaction temperature on the reduction of the metal ions in the filtrate when the molar ratio of hydrazine to Cu(II) was fixed at 8. (Reaction time: 30 min, and stirring speed: 500 rpm)
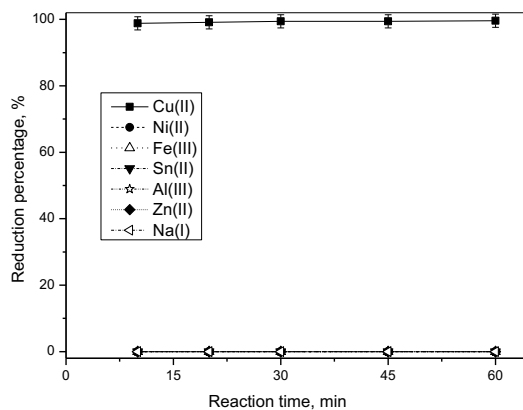

Fig. 3. Effect of reaction time on the reduction of the metal ions in the filtrate when the molar ratio of hydrazine to Cu(II) was fixed at 8. (Temperature: 20°C and stirring speed: 500 rpm)

In order to investigate the effect of reaction time on the reduction of Cu(II), reduction experiments were conducted by varying the reaction time from 10 to 60 mins. The experiments were done at 20°C and at a stirring speed of 500 rpm by fixing the molar ratio of hydrazine to Cu(II) at 8. Fig. 3 shows that the reduction percentage of Cu(II) increased slightly from 98.8% to 99.9% after 20 min, and there was little change in the reduction percentage of Cu(II) as the reaction time increased to 60 min. The percentage of reduction for metal ions (Ni, Sn, Al, Zn, and Na) other than iron was close to zero under identical conditions. These findings indicate that it is possible to selectively recover Cu(II) from the filtrate using hydrazine under the following conditions: a temperature of 20°C, a stirring speed of 500 rpm, and a molar ratio of 8 for hydrazine to Cu(II), a reaction time of 20 min.

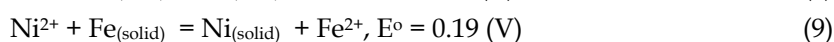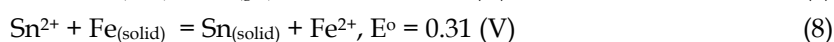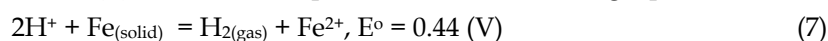### 3.3. Separation of Ni(II) from the filtrate after separation of Cu(II)

Table 4 displays the concentration of the metal ions present in the filtrate after chemical reduction of Cu(II) by hydrazine at the optimum condition. During the chemical reduction of Cu(II) by hydrazine, all the Fe(III) ion was reduced to Fe(II). The pH of this filtrate was 1.03 and the concentration of Ni(II) was 647.6 mg/L.

Table 4. The concentrations of the metal ions in the filtrate after separation of Cu(II) by chemical reduction with hydrazine

Ions	Ni(II)	Sn(II)	Fe(II)	Al(III)	Zn(II)	Na(I)
mg/L	647.6	81.5	112.2	535.6	6489.4	1356.7

Considering the demand for nickel sulfate for the manufacture of electrode materials for lithium-ion batteries, it is necessary to recover the Ni(II) in the filtrate. Several methods such as ion exchange (Lin et al., 2008), precipitation (Nguyen, T.T.H. and Lee, 2023), cementation (Choi et al., 2021), and adsorption (Li et al., 2019) have been employed to recover Ni(II) from acidic solution. Considering the composition of the filtrate and the nature of the metal ions, cementation and precipitation would be more effective in separating Ni(II) from the filtrate than adsorption and ion exchange. Therefore, cementation and precipitation were tried to separate Ni(II) from the filtrate after recovering Cu(II).

The standard reduction potential of the metal ions in Table 3 indicate that iron, zinc and aluminum can be employed for the cementation of Ni(II) from the filtrate. Aluminum metal can be passivated during initial oxidation, which would hinder the cementation of Ni(II). In this work, iron powder was employed for the cementation on the basis of the price. When iron powder is added to the filtrate, the reduction of hydrogen ion, Sn(II) and Ni(II) can occur as represented in the following equations.

$$2H^+ + Fe_{(solid)} = H_{2(gas)} + Fe^{2+}, E^o = 0.44 \text{ (V)} \tag{7}$$

$$Sn^{2+} + Fe_{(solid)} = Sn_{(solid)} + Fe^{2+}, E^o = 0.31 \text{ (V)} \tag{8}$$

$$Ni^{2+} + Fe_{(solid)} = Ni_{(solid)} + Fe^{2+}, E^o = 0.19 \text{ (V)} \tag{9}$$

The cementation experiments were done at 20°C for 30 mins with a stirring speed of 500 rpm, and the molar ratio of iron powder to Ni(II) was fixed at 20. The cementation percentages of Ni(II) and Sn(II) were 99% and 95%, respectively, while the cementation of Zn(II) and Al(III) did not occur. Since the reduced tin and nickel metals coexist on the surface of the iron powder, it is necessary to treat the cemented nickel to recover pure nickel. In this case, it is necessary to separate nickel from iron and tin present in the cemented iron. Therefore, cementation of Ni(II) by iron powder was not effective in terms of nickel recovery due to the coexistence of iron and tin.

Table 5 lists the solubility products of metal oxalates at 25°C. There is some difference in the solubility products of the oxalates between Ni(II)/Zn(II) and other metal ions. By utilizing this difference in the solubility of metal oxalates, it might be possible to separate Ni(II) from the filtrate by precipitation with sodium oxalate. The precipitation reactions of Ni(II) and Zn(II) by sodium oxalate are represented in the following equations (Nguyen, and Lee, 2023; Moon et al., 2021).
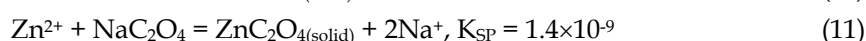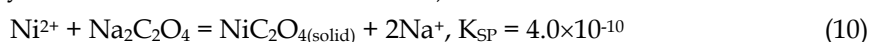
$$Ni^{2+} + Na_2C_2O_4 = NiC_2O_{4(solid)} + 2Na^+, K_{SP} = 4.0 \times 10^{-10} \tag{10}$$

$$Zn^{2+} + NaC_2O_4 = ZnC_2O_{4(solid)} + 2Na^+, K_{SP} = 1.4 \times 10^{-9} \tag{11}$$

Table 5. The solubility products of some metal oxalates at 25°C (Speight, 2005; Verma et al., 2019; Haynes, 2014).

Compounds	K_{sp}
$NiC_2O_4 \cdot 2H_2O$	4.0×10^{-10}
SnC_2O_4	1.4×10^{-8}
$FeC_2O_4 \cdot H_2O$	3.2×10^{-7}
ZnC_2O_4	1.4×10^{-9}
$Al_2(C_2O_4)_3$	5.2×10^{-5}
$Na_2C_2O_4$	8.7×10^{13}

In precipitation, the molar ratio of the reactants is of importance. Therefore, precipitation experiments were done by varying the molar ratio of sodium oxalate to Ni(II) from 1 to 20 at 20°C for 30 mins and a stirring speed of 500 rpm. Fig. 4 illustrates that the precipitation percentage of Ni(II) and Zn(II) increased from 22% to 94% and 4% to 32% as the molar ratio of sodium oxalate to Ni(II) increased to 20. In these experimental ranges, the precipitation percentage of other metal ions (Fe, Sn, Al, Na) was nearly zero. Therefore, the molar ratio of 20 for sodium oxalate to Ni(II) was selected for further experiments.
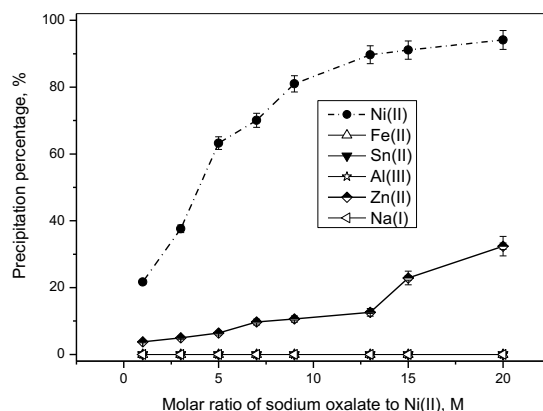

Fig. 4. Effect of molar ratio of sodium oxalate to Ni(II) on the precipitation of the metal ions after separation of Cu(II). (Temperature: 20°C, reaction time: 30 min, and stirring speed: 500 rpm)

According to Table 5, there is not much difference in the solubility products of oxalates between Sn(II) and Ni(II)/Zn(II). However, no Sn(II) oxalates were precipitated in our experimental conditions. In general, precipitation occurs through two steps, nucleation and growth. The critical radius of spherical nuclei during nucleation depends on the degree of super-saturation. The concentrations of Ni(II), Zn(II) and Sn(II) in the filtrate were 0.64, 6.43 and 0.08 g/L, respectively. Since the concentration of Sn(II) is the least among the three metal ions, its super-saturation degree would be the least. In this situation, the critical radius of Sn(II) would be the largest so that nucleation of Sn(II) is difficult to occur. This might be responsible for no precipitation of Sn(II) oxalates.

The effect of temperature on the precipitation of Ni(II) by sodium oxalate was investigated by varying temperature from 20 to 80°C for 30 mins with a stirring speed of 500 rpm. In these experiments, the molar ratio of sodium oxalate to Ni(II) was fixed at 20. Fig. 5 shows that the precipitation percentage of Ni(II) and Zn(II) increased from 94% and 35% to 99% and 99% as the temperature increased to 80°C. The precipitation percentage of Al(III), Sn(II), Fe(II), and Na(I) was negligible at 80°C. Our data indicates that reaction temperature has a remarkable effect on the precipitation of Zn(II) compared to that of Ni(II). The difference in the precipitation percentage between Ni(II) and Zn(II) became smaller as temperature increased, indicating that lower temperature would be favorable in separating Ni(II) from the filtrate. Therefore, further experiments will be performed at 20°C.

Fig. 6 shows the effect of reaction time on the precipitation of Ni(II) and Zn(II) at 20°C and at a stirring speed of 500 rpm. The experiments were done by varying reaction time from 10 to 60 mins and the molar ratio of sodium oxalate to Ni(II) was fixed at 20. The precipitation percentage of Ni(II) and Zn(II) increased from 77% to 99% and 13% to 38%, respectively when the reaction time increased to 60 mins. The precipitation percentage of other metal ions (Fe, Al, Sn and Na) was negligible at these

conditions. Therefore, most of Ni(II) and some amount of Zn(II) were co-precipitated from the filtrate by using sodium oxalate at the following conditions: 20°C for 60 mins with a stirring speed of 500 rpm and a molar ratio of 20 for sodium oxalate to Ni(II). The mixed precipitates of NiC_2O_4 and ZnC_2O_4 from the precipitation reaction with sodium oxalate were gathered and then dissolved to recover the nickel.
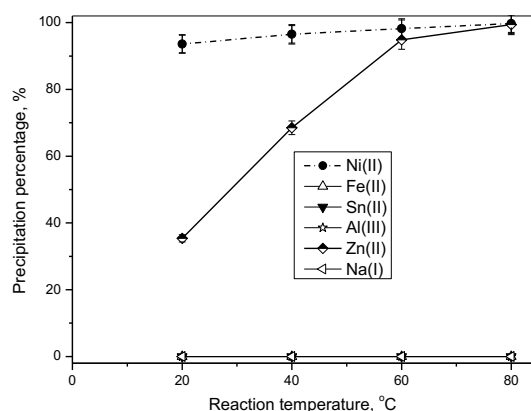

Fig. 5. Effect of reaction temperature on the precipitation of the metal ions after separation of Cu(II) when the molar ratio of sodium oxalate to Ni(II) was fixed at 20. (Temperature: 20°C, reaction time: 30 min, and stirring speed: 500 rpm)
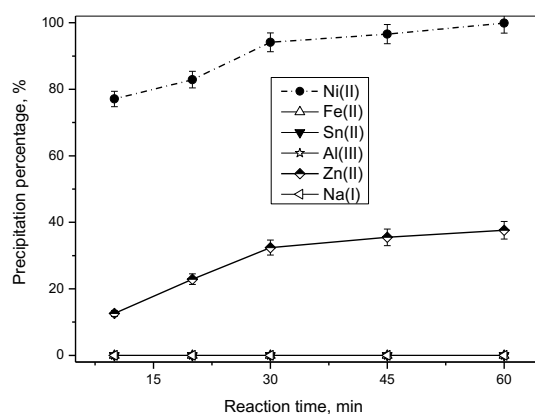

Fig. 6. Effect of reaction time on the precipitation of the metal ions after separation of Cu(II) when the molar ratio of sodium oxalate to Ni(II) was fixed at 20. (Temperature: 20°C, and stirring speed: 500 rpm)

In order to recover pure nickel compounds from the co-precipitates of Ni(II) and Zn(II), the co-precipitates were first dissolved by using HCl solution. When the co-precipitates were dissolved in 0.5 M HCl solution at 20°C and at a pulp density of 1 g/L, the co-precipitates were completely dissolved and the concentrations of Ni(II) and Zn(II) were 140 and 793.7 mg/L, respectively and solution pH was 1.3. The precipitation pH values of Ni(II) and Zn(II) hydroxides are similar. Therefore, solvent extraction was employed to separate the Ni(II) and Zn(II) from the HCl solution. According to the reported extraction data of Ni(II) and Zn(II), Cyanex 272 could selectively extract Zn(II) over Ni(II) when solution pH is maintained between 1 to 3 (Bari et al., 2009). Therefore, Cyanex 272 was employed to remove the Zn(II) in the HCl solution containing Ni(II) by solvent extraction. Extraction experiments were performed by varying the concentration of Cyanex 272 from 0.5 M to 3.0 M at room temperature, with a shaking time of 30 mins and unity volume ratio of organic to aqueous phase. Fig. 7 illustrates the effect of Cyanex 272 concentration on the extraction percentage of Zn(II) and Ni(II). As the concentration of Cyanex 272 increased from 0.5 M to 2.5 M, the extraction percentage of Zn(II) increased significantly from 7% to 86%. However, further increase of Cyanex 272 concentration to 3.0 M did not result in any additional improvement in Zn(II) extraction and its extraction percentage remained constant at 86%. Notably, in the entire range of Cyanex 272 concentrations tested, the extraction percentage of Ni(II) remained near zero. This demonstrates the high selectivity of Cyanex 272 for Zn(II) over Ni(II) under

these conditions. Based on these results, a Cyanex 272 concentration of 2.5 M was selected as optimal for the separation of Zn(II) from Ni(II). To achieve complete removal of Zn(II) from the HCl solution, five stages of cross-current extraction were performed using 2.5 M Cyanex 272.
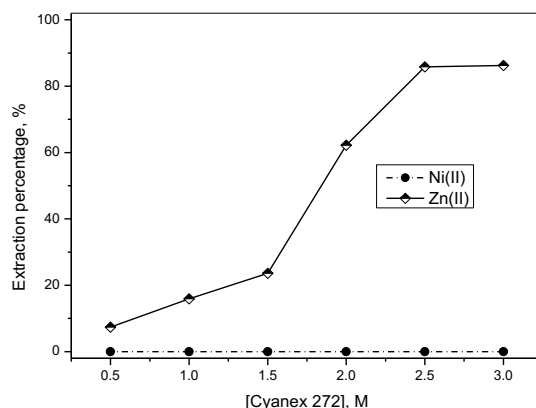

Fig. 7. Effect of Cyanex 272 concentration on the separation of Ni(II) and Zn(II) by solvent extraction at unity phase ratio. (reaction time: 30 min, O/A = 1:1)

Table 6 shows the composition of the raffinate and the extraction percentage of Zn(II) at each stage during a five-stage cross-current extraction. After five stages of cross-extraction with Cyanex 272, Zn(II) ions were completely removed from the solution. Although there was a small decrease in the concentration of Ni(II) in the raffinate after the fifth stage, pure Ni(II) solution was obtained. In order to recover nickel hydroxide from the raffinate, the pH of the raffinate was increased to 9.5 by adding NaOH solution. Most of Ni(II) was precipitated after 60 mins at 20°C. The purity of nickel in the hydroxide precipitates was determined by dissolving the precipitates with aqua regia solution and then the concentration of the metal ions present in the resulting solution was measured by ICP-OES. According to ICP-OES results, the concentration of Ni(II) and Zn(II) in the solution was 140 and 0.2 mg/L, inidcating that the purity of the nickel in the precipitates was approximately 99.8%.

Table 6. The change in the concentration of the metal ions and the extraction percentage of Zn(II) during five stages of cross-current extraction with 2.5 M Cyanex 272.

Stages	Ni(II), mg/L	Zn(II), mg/L	Extraction percentage of Zn(II), %
1	141.7	33.7	74.5
2	141.6	5.67	83.2
3	140.1	0.4	92.3
4	138.5	0.02	96.6
5	137.0	ND	Completeness

3.4. A proposed process for the recovery of Au(III), Pd(II), Cu(II) and Ni(II) from the leaching solutions of PCBs

Fig. 8 illustrates a proposed process for the recovery of noble metal ions like Au(III), Pd(II), Cu(II) together with Ni(II) from the leaching solutions of PCBs. The process involves several steps, including cementation, leaching, solvent extraction, chemical reduction, and precipitation.

One of the advantages of this process is that most of these steps can be carried out at room temperature, which helps to reduce energy consumption. This process enables the recovery of pure metal powders and compounds of the metal ions from the leaching solutions of PCBs. The process involved first the separation of Au(III) and Pd(II) from the leaching solution by cementation using copper powder. Other metal ions including Fe(III), Fe(II), Sn(II), Al(III), Ni(II), Cu(II), Zn(II), and Na(I) were left in the filtrate. Gold metal and palladium compounds with extra high purity were recovered from the cemented Cu, which had been reported in the previous work (Nguyen et al., 2023). Copper

ions in the filtrate after cementation were recovered through chemical reduction with hydrazine. Then chemical precipitation with sodium oxalate resulted in co-precipitates of Ni(II) and Zn(II). After dissolving these co-precipitates of Ni(II) and Zn(II) with dilute HCl solution, the Zn(II) can be removed by solvent extraction with Cyanex 272, leaving Ni(II) in the raffinate. By this process, the metals or compounds of Au, Pd(II), Cu and Ni(II) with purity higher than 99% can be recovered from the leaching solution of PCBs.

Table 7 compares the method and efficiency for the recovery of Cu(II) and Ni(II) from the leaching solutions of PCBs between the work reported in the literature and this work. The recovery percentage of both metal ions by solvent extraction with naphthol and dimethylglyoxime (Souza et al., 2018) was the same obtained in this work. However, compared to the process reported in the literature, pure copper metal and nickel hydroxide can be easily recovered by the process proposed in this work.
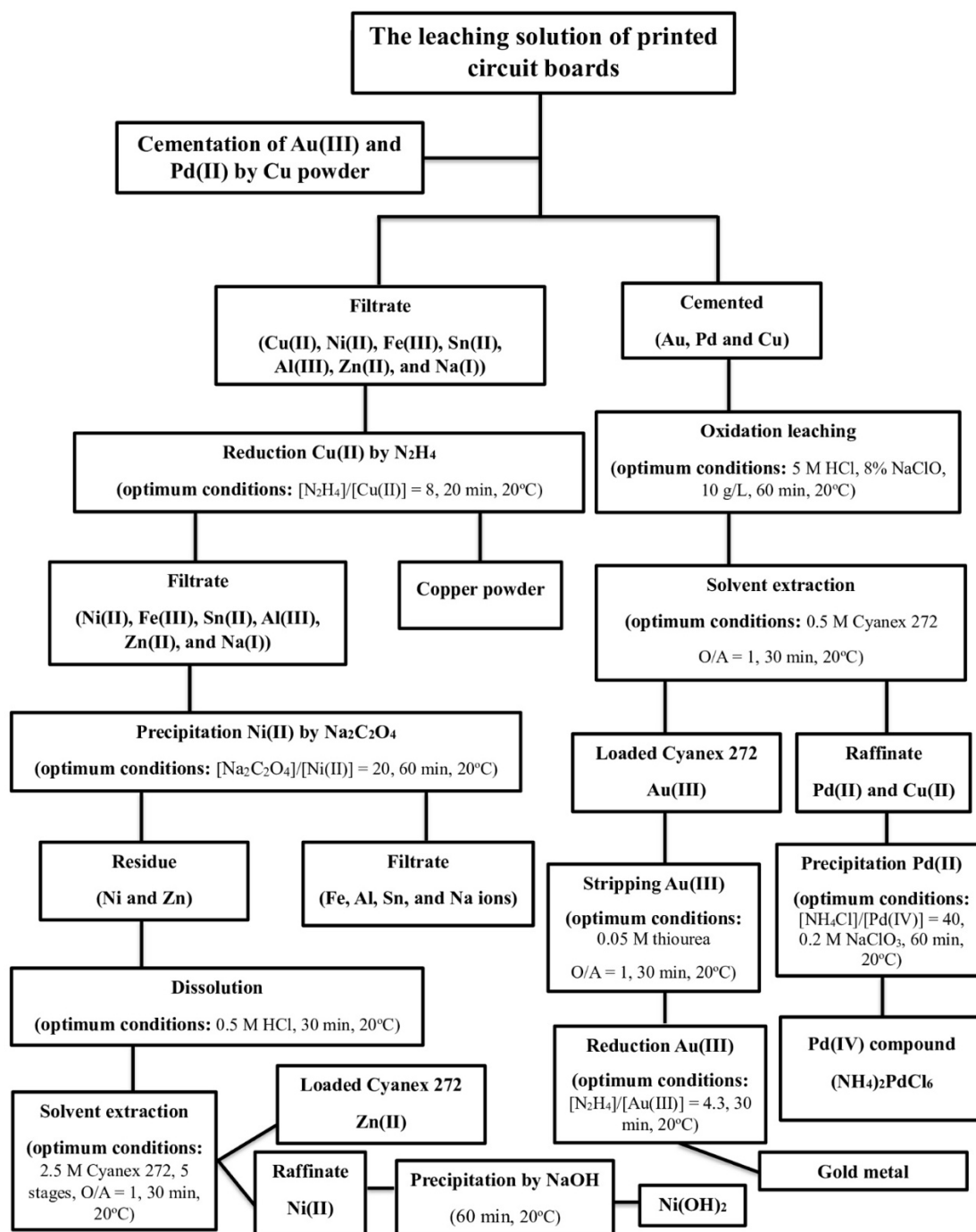

Fig. 8. Hydrometallurgical process scheme for the recovery of Au(III), Pd(II), Cu(II) and Ni(II) from the leaching solutions of printed circuit boards

Table 7. Comparison of the recovery of Cu(II) and Ni(II) from the leaching solution of PCBs between the reported work and this work

		Conditions	Recovery percentage, %
Literature work	Recovery Cu(II) and Ni(II) by Dowex M 4195 resin (Ajiboye et al., 2019)	pH = 2, 0.5 g Dowex M 4195 for 180 mins	94.09% Cu 53.4% Ni
	Copper sulfide precipitation (Sethurajan and Hullebusch, 2019)	$[Na_2S \cdot 9H_2O]/[Cu] = 1:3$, pH = 1-2, $[Fe^{3+}] < 100$ ppm	98% Cu 5% Fe
	Recovery Cu(II) and Ni(II) by solvent extraction (Suza et al., 2018)	pH = 6, 3.5 mmol/kg 1-(2-pyridylazo)-2-naphthol, 6 sequential steps	99.9% Cu
		pH = 9, 5 mmol/kg dimethylglyoxime	99.9% Ni
Our work (leach solution: Au(III), Pd(II), Cu(II), Ni(II), etc)	Separation of Au(III) and Pd(II) by copper powder (Nguyen and Lee, 20203)	[Cu powder]/[Au(III) + Pd(II)] = 25, 60 min at 20°C	99.9% Au, Pd and Cu
	Recovery Cu(II) by chemical reduction	$[N_2H_4]/[Cu] = 8$, 20 min at 20°C	99.9% Cu
	Recovery Ni(II) precipitation	(i) Oxalate precipitation — $[Na_2C_2O_4]/[Ni] = 20$, 60 min at 20°C	99% NiC_2O_4 38% ZnC_2O_4
		(ii) Dissolution — 0.5 M HCl, 30 min at 20°C	99.9% Ni and Zn
		(iii) remove Zn(II) by solvent extraction — 2.5 M Cyanex 272, 5 stages, O/A = 1 for separation Zn(II)	99.9% Zn (II)
		(iv) Ni(II) hydroxide precipitation — 60 min at 20°C	99.9% $Ni(OH)_2$

4. Conclusions

Leaching solutions of printed circuit boards contain noble metal ions (Au(III), Pd(II) and Cu(II)) together with base metal ions such as Al(III), Fe(III), Ni(II), Sn(II), and Zn(II). The gold and palladium metal ions can be separated from the leaching solutions by cementation with copper metal. Then the filtrate contained Al(III), Cu(II), Fe(III), Fe(II), Ni(II), Sn(II) and Zn(II). In order to recover Cu(II) and Ni(II) from the filtrate, separation experiments were done. First, the Cu(II) was separated from the filtrate by chemical reduction with hydrazine. Most of the Cu(II) was separated as copper metal at the following conditions: a temperature of 20°C, a stirring speed of 500 rpm, and a molar ratio of 8 for the hydrazine to Cu(II), and a reaction time of 20 mins. The purity of the copper metal was nearly 99.9%. Oxalate precipitation were tried to separate Ni(II) from the filtrate after chemical reduction of Cu(II). Ni(II) and Zn(II) were co-precipitated by sodium oxalate. Most of Ni(II) and 38% of Zn(II) were co-precipitated at the following conditions: 20°C for 60 mins at a stirring speed of 500 rpm and a molar ratio of 20 for sodium oxalate to Ni(II). After dissolving the co-precipitates of Ni(II) and Zn(II) oxalates in 0.5 M HCl solutions at a pulp density of 1 g/L, the Zn(II) in the solution was completely removed by a five-stage of cross-current extraction with 2.5 M Cyanex 272. Pure nickel hydroxides were recovered from the raffinate by precipitation with NaOH. The purity of copper metals and $Ni(OH)_2$ was 99.9% and 99.8%, which was measured by dissolving them in aqua regia solution. A process was proposed to recover noble metal ions and Ni(II) from the leaching solutions of PCBs.

Acknowledgments

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