Destruction of Cyanide and Removal of Copper from Waste Printed Circuit Boards Leach Solution Using Electro-Generated Hypochlorite Followed by Magnetite Adsorption

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Received: 10 August 2019; Accepted: 28 August 2019; Published: 2 September 2019

Abstract: The removal of the cyanide and copper (Cu) from the waste printed circuit boards (WPCBs) cyanide leach solution through the alkaline chlorination using electro-generated hypochlorite (NaOCl) followed by magnetite (Fe₃O₄) adsorption is investigated. The efficiency of the destruction of cyanide and precipitation of Cu was increased with increasing the concentration of free available chlorine in NaOCl. More than 99% of free cyanide and 76% of Cu were removed under the following conditions: concentration of chlorine in electro-generated NaOCl, 5.2 g/L; volume ratio of NaOCl/leach solution, 1; pH, ~9.8; ambient temperature for 12 h. Then, magnetite adsorption for selective removal of remaining Cu (50.5 mg/L) was selected and more than 99% of copper ion was successfully removed with dosage 10g/100mL, shaking speed 150 rpm within 30 min. The results revealed that the alkaline chlorination using electro-generated NaOCl followed by magnetite adsorption could completely remove the cyanide and Cu, remaining Au in the final solution.

Keywords: destruction of cyanide; copper removal; alkaline chlorination; electro-generated hypochlorite; magnetite adsorption; waste printed circuit boards (WPCBs)

1. Introduction

According to the World Gold Council, the gold (Au) usage in printed circuit boards (PCBs) was estimated to have increased by 5–7% year over year [1]. The content of Au in each electronic equipment varies substantially, from 3 to 440 g/t [2–4] with 130 kg of copper (Cu), 3.5 kg of silver (Ag), and 0.14 kg of palladium (Pd) [5,6]. One ton of E-waste is contained more than 40 times higher than the average Au ore (1–10 g/t) [7,8]. Since natural resources are gradually being exhausted, sustainable society with the recycling of secondary resources should be pursued. Hydrometallurgical recycling processes have been developed to recover gold using cyanide, aqua regia, thiourea, thiosulfate, and halide methods [9–11]. For over a century, cyanidation has dominated despite its toxicity, in the mining industry due to advantages such as lower cost and lesser dosage requirement, besides operation in alkaline solution [12], such that subsequent destruction can be followed for safety and environment. In some cases of gold cyanide leaching process, other metals are also dissolved. Among them, copper dissolution is generally undesirable during the cyanidation because it can consume cyanide and dissolved oxygen, retard Au dissolution rates, interfere with subsequent recovery processes, and contaminate the final product [13].
Robbins [13] and Dai et al. [14] have extensively reviewed to remove and recycle copper and cyanide from the gold cyanide leach solutions. The processes were divided into two categories, i) copper cyanide destruction technologies (Alkaline chlorination, SO$_2$/air process, hydrogen peroxide, Caro’s acid, electrochemical oxidation, biodegradation, ultrasonic, and photolysis), and ii) copper cyanide recovery technologies (acidification, volatilization, reneutralization, sulfidization, acidification, recycling and thickening, direct electrowinning, adsorption over activated carbon, use of ion exchange resins, solvent extraction, poly-chelating polymers, and membrane technologies).

Alkaline chlorination is a well-established and commercially-practiced technology in the many gold mining industries. Among them, an electro-generated chlorine method, which generates chlorine electrically, has advantages such as re-generating chlorine simply and establishing circulation process [2]. During the alkaline chlorination, free and weak metal-cyanide complexes (weak acid dissociable cyanide, WAD), which are bound to copper, cadmium, and nickel, are oxidized to cyanate (CNO$^-$) and subsequently to carbon dioxide and nitrogen gas [15–17]. During the cyanide destruction, the liberated metal ions generally form hydroxide precipitate under the alkaline conditions [18]; thus, the destruction of cyanide and the removal of metal ions could be achieved at the same time. However, since 4% of copper has still remained in the solution in spite of using high concentration of chlorine gas and calcium hypochlorite (65% free available chlorine, Ca(OCl)$_2$), further Cu removal process is required to produce high purity gold [19].

In the present study, alkaline chlorination using electro-generated NaOCl and reagent-grade NaOCl followed by magnetite adsorption was investigated to decompose cyanide and to remove copper ions from the waste printed circuit boards (WPCBs) cyanide leach liquor for purifying the leach solution. The effects of experimental factors on the precipitation of Cu and destruction of cyanide examined are: concentration of free available chlorine, pH, and contact time. The precipitation behavior of copper ions was also compared using electro-generated NaOCl and a reagent-grade NaOCl solution. After the precipitation of Cu, the residual Cu in the solution was further removed by adsorption on magnetite powders. The adsorption behavior of Cu was investigating while studying the effect of contact time, and temperature.

2. Materials and Methods

2.1. Materials

Leach solution was obtained from a small-business recycling company in Korea, and metal concentrations were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Model: JY-38 plus, Jobin Yvon Ltd. (Horiba Korea, Anyang, Korea) and given in Table 1. The concentrations of Au and Cu are 60.9 and 421 mg/L, respectively, and those of other metals are relatively low. The reagent grade NaOCl (9–11%, Daejung chemical & metals Co., Ltd., Siheung, Korea) and Magnetite (Fe$_3$O$_4$, 95%, Sigma-Aldrich Inc., Darmstadt, Germany) were used in this study.

| Elements | Au  | Ag  | Cu  | Ni  | Fe  | Sn  | Zn  | Pb  | Free Cyanide |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|--------------|
| mg/L     | 60.90 | 0.08 | 421.00 | 1.80 | 0.10 | 0.06 | 0.41 | 0.07 | 105.00       |

2.2. Methods

NaOCl was generated from the high strength sodium hypochlorite generator (Danam-ene, Co., Ltd., Paju, Korea) by the following reactions.

At the anode:

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \tag{1}
\]

At the cathode:

\[
2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \tag{2}
\]
In the bulk:

\[ \text{Cl}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{HClO} + \text{Cl}^- + \text{H}_3\text{O}^+ \]  \hspace{1cm} (3)

\[ \text{HClO} + \text{H}_2\text{O} \leftrightarrow \text{ClO}^- + \text{H}_3\text{O}^+ \]  \hspace{1cm} (4)

During generation of chlorine, the concentration of \(\text{OCl}^-\) increases by re-circulating solution as shown in Table 2. A known volume of the leached solution (of WPCBs) was placed in a 200 mL Erlenmeyer flask and a desired concentration of solution of electro-generated or reagent-grade NaOCl was added with the volume ratios (NaOCl/leach solution) of 1. The flasks after capping with rubber stoppers were placed and experiments were conducted at pre-determined temperature for 12 h. After the tests were completed, the solution was filtered with 5A-110 mm filter paper. The filter cake was dried and then analyzed by X-ray diffractometer (XRD, D/Max 2200PC, Rigaku Corporation, Tokyo, Japan), X-ray photoelectron spectrometer (XPS, AXIS Nova, Kratos Analytical Ltd., Manchester, UK), Fourier transform infrared spectrometer (FT-IR, Nicolet 5700, Thermo Fisher Scientific Ltd., Waltham, MA, USA), transmission electron microscope (TEM, JEM-ARM200F, JEOL Ltd., Tokyo, Japan) and scanning electron microscopy-energy dispersive X-ray spectrooscope (SEM-EDS, JSM-6308LA instrument, JEOL Ltd., Tokyo, Japan). The mudline test was measured using measuring cylinder 250 mL with the volume ratios (NaOCl/leach solution) of 1. The concentration of metals was measured with ICP-AES after dilution using 0.1 vol% HCl solution. To confirm the concentration of free cyanide, the colorimetric method was used by UV-Vis spectrophotometer (HS-3300, HUMAS. Co., Ltd., Daejeon, Korea). The following steps of pretreatment were required to measure the absorbance of the solution [20]:

1. add mixture of phenolphthalein and ethyl alcohol (0.5 W/V%).
2. add acetic acid until the red color of the solution disappears.
3. add phosphate-buffer and chloramine-T and waiting for 5 min.
4. add pyridine and waiting for 30 min and then measure the wavelength.

| Sample | Initial | 1 Cycle | 2 Cycle | 3 Cycle | 4 Cycle | 5 Cycle |
|--------|---------|---------|---------|---------|---------|---------|
| Time [min] | 5 | 20 | 30 | 40 | 50 | 60 |
| Chlorine conc. [g/L] | 1.600 | 3.368 | 4.224 | 5.215 | 5.250 | 5.252 |

The chlorine concentration (\(C_{Cl}\)) was measured by titration method using thiosulfate solution with a mixture of acetic acid and potassium iodide as an indicator; the concentration can be calculated as:

\[ C_{Cl} = \frac{V_a \cdot C_a}{V_b} \cdot M_{Cl} \]  \hspace{1cm} (5)

where \(V_a\) and \(V_b\) are the volumes of the sodium thiosulfate and the sample, respectively, \(C_a\) is the concentration of thiosulfate and \(M\) is molar atomic mass of chlorine.

3. Results and Discussion

As shown in Table 1, the other metal concentrations are low except Cu and Au, thus, the behavior of Au and Cu were discussed below in this study. The precipitation of Cu and the destruction of cyanide from WPCBs leach solution were investigated under the following conditions: ambient temperature, NaOCl/Leach solution ratio of 1, total volume 200 mL, free available chlorine concentration range from
0.52 to 130 g/L using electro-generated or reagent-grade NaOCl without agitation for 12 h. As shown in Figure 1a, the removal efficiencies of Cu increased gradually from 10.3% to 76% with increasing the chlorine concentration of electro-generated NaOCl. All gold ions remained in the solution whereas the destruction efficiency of free cyanide is 46.7% with 0.52 g/L of chlorine concentration. The free cyanide was decomposed and remained at the range of about 0.12 to 0.15 mg/L irrespective of the pH or the type of NaOCl. However, the removal efficiencies of Cu were 76% ± 2.5% in the test with electro-generated NaOCl and 83% ± 2.5% using reagent-grade NaOCl without adjusting the pH and 81% ± 1.5% with adjusting the pH. Even the pH was adjusted from 11.4 to 9.8, Cu removal efficiency was slightly decreased within standard error range. However, the color of precipitated Cu and destruction of free cyanide were given as follows.

\[
2Cu(CN)_3^{2-} + 7ClO^- + 2OH^- + H_2O \rightarrow 2Cu(OH)_2\downarrow + 6CNO^- + 7Cl^- \tag{6}
\]
\[
2CNO^- + 3ClO^- + H_2O \rightarrow N_2\uparrow + 3Cl^- + 2HCO_3^- \tag{7}
\]

To determine the effect of higher concentration of chlorine than electro-generated NaOCl, the removal efficiencies of Cu and free cyanide was investigated with reagent-grade NaOCl, because the chlorine concentration was limited through by the electrolysis method as shown in Table 2. All the experimental conditions were the same as the experiments excluding the concentration of chlorine. As shown in Figure 1b, the free cyanide was removed at 99% or more under all conditions. On the other hand, as the concentration of chlorine increased, the removal efficiency of Cu increased from 83% to 93%. The most of concentration of chlorine was adequate for destructing the free cyanide but the removal efficiency of Cu could not be increased dramatically despite using a high concentration of chlorine.

The pH of the WPCBs leach liquor was 10.3, and the initial pH of the electro-generated NaOCl and the reagent-grade NaOCl was 9.8 and 11.4, respectively, at the same concentration (5.2 g/L). The pH of the electro-generated NaOCl was fixed to the generated state as 9.8 and the pH of the reagent-grade NaOCl was controlled to investigate the behavior of Cu precipitation. As shown in Figure 2, the most of the free cyanide was decomposed and remained in the range of about 0.12 to 0.15 mg/L irrespective of the pH or the type of NaOCl. However, the removal efficiencies of Cu were 76% ± 2.5% in the test with electro-generated NaOCl and 83% ± 2.5% using reagent-grade NaOCl without adjusting the pH and 81% ± 1.5% with adjusting the pH. Even the pH was adjusted from 11.4 to 9.8, Cu removal efficiency was slightly decreased within standard error range. However, the color of precipitated Cu and sedimentation rate during the precipitation of Cu were quite different with electro-generated NaOCl and reagent-grade NaOCl. Therefore, the effects of contact time and mudline test were examined to identify the settling velocity during the precipitation of Cu. As mentioned above, 14.7 mg/L of Cu was remained after reaction with 130 g/L of reagent-grade NaOCl despite much high concentration.
The chlorine concentration of both was fixed at 5.2 g/L and the volume ratio 1 (NaOCl/leach solution), ambient temperature, without agitation for 24 h.

Figure 2. Removal efficiency of Cu, Au, and free cyanide with electro-generated NaOCl and reagent-grade NaOCl (initial pH, 9.8, 11.4; temperature, 298 K; time, 12 h without agitation; total volume, 200 mL with NaOCl/leach solution ratio 1; electro-generated and reagent-grade NaOCl chlorine concentration 5.2 g/L).

As shown in Figure 3a, the removal efficiency of Cu using electro-generated NaOCl was about 53% which was much higher than that of using reagent-grade NaOCl at the beginning of the reaction (before 1 h). On the other hand, after 1 h, the removal efficiency of Cu increased rapidly to 56% using reagent-grade NaOCl, showing a similar to that of using electro-generated NaOCl. In both cases, the precipitation efficiency of Cu increased with increasing contact time. The equilibrium was reached after 12 h and the removal efficiencies were 76% and 83%, respectively. Moreover, the mudline tests were performed to examine settling velocity of the precipitate. As shown in Figure 3b, in the case of using electro-generated NaOCl, the mudline decreased rapidly with contact time and then remained about 1 cm after 150 min, whereas the mudline decreased gradually with contact time in the case of using reagent-grade NaOCl. It can cause problems in the separation of the solution and precipitate during filtration.

Figure 3. Behavior of copper precipitation used electro-generated NaOCl and reagent-grade NaOCl with contact time (a) copper precipitation efficiency, (b) mudline change (initial pH, 9.8–11.4; temperature, 298 K; time, 24, 35 h without agitation; total volume, 200 mL with NaOCl/leach solution ratio 1; chlorine concentration 5.2 g/L).
The XPS analysis was performed to examine the transformation of the oxidation state of Cu precipitate. Biesinger [21] has reported the two ways of confirming suspected CuO or Cu(OH)$_2$ as follow:

(i) Peak-shape and main peak to shake-up peak separation is quite different for CuO and Cu(OH)$_2$.

(ii) O 1 s spectra must show the presence or absence of hydroxyl group or lattice oxide peak.

Results presented in Table 3 and Figure 4 and, Figure 5 clearly reflect difference in spectrum for valence state of precipitated Cu. The XPS spectra detected the peaks (peak 2) at the binding energies of 950.7 eV (reagent-grade NaOCl) and 951.2 eV (electro-generated NaOCl) which can be attributed to the Cu$^{1/2}$. The peaks (peak 5) at the binding energies of 930.3 eV(reagent-grade NaOCl) and 932.0 eV (electro-generated NaOCl) can be attributed to the Cu$^{2p3/2}$ position of CuO and Cu(OH)$_2$, respectively [21,22]. Additionally, it has been reported that the dominant peak at ~530 eV is attributed to lattice oxygen in a metal oxide, such as CuO or Cu$_2$O, and the oxygen components in the hydroxyl group of the Cu(OH)$_2$ structure is appear higher binding energy than lattice oxygen region [23]. Although the pH of the solution after reaction using electro-generated NaOCl and reagent-grade NaOCl was 9.4 and 9.3, respectively, the different between precipitated Cu species in the XPS characteristic results verify the structure of CuO and Cu(OH)$_2$.

Table 3. Position of components in precipitated Cu species X-ray photoelectron spectrometer (XPS) spectrum. (Unit: eV).

| Compound                  | Cu Peak1 | Cu Peak2 | Cu Peak3 | Cu Peak4 | Cu Peak5 | O     |
|---------------------------|----------|----------|----------|----------|----------|-------|
| Reagent-grade NaOCl       | 958.6    | 950.7    | 940.6    | 937.5    | 930.3    | 526.4 |
| Electro-generated NaOCl   | 959.6    | 951.2    | 940.5    | -        | 932.0    | 528.8 |

Figure 4. XPS spectra of the precipitated Cu (a) by reagent-grade hypochlorite and (b) by electro-generated hypochlorite.

The morphological structure of the precipitated Cu using electro-generated NaOCl and reagent-grade NaOCl were examined by TEM images as well as selected area electron diffraction (SAED) analysis. Figure 6a,b shows that TEM images of the precipitated Cu using electro-generated NaOCl, and it can be seen that precipitates have aggregated to form relatively regular morphologies with uniform diameters of 20 nm. The SAED pattern (inset of Figure 5b) further confirms that the precipitates are amorphous [22]. The TEM images of the precipitated Cu using reagent-grade NaOCl are also shown in Figure 5c,d. The morphological structure shows that smaller nanoparticles were formed together with the nanoellipsoids. The SAED pattern shows apparent diffraction ring and spots (inset of Figure 5d), indicating that the precipitates are of polycrystalline structure [23]. The different particle size was proved that sedimentation rate was quite faster using electro-generated NaOCl than using reagent-grade NaOCl. Hence, the use of electro-generated NaOCl improves the separation efficiency of precipitated Cu.
Consequently, the noble metal ions could be reduced and adsorbed as elemental metal on the surface from magnetite, where ferrous oxidizes into ferric ions in the texture, to the noble metal ions [24,25]. Magnetite powder was selected to adsorb copper ions over gold ions. Magnetite (Fe₃O₄) consists of Fe²⁺ and Fe³⁺O₄²⁻, so, when noble metal ions approach the surface of magnetite, electron moves from magnetite, where ferrous oxidizes into ferric ions in the texture, to the noble metal ions [24,25]. Consequently, the noble metal ions could be reduced and adsorbed as elemental metal on the surface.

Even though 93% of Cu and more than 99% of cyanide were removed from the leach solution using reagent-grade NaOCl (130 g/L), still 14.7 mg/L Cu and 0.13 mg/L CN⁻ were left out in the leach solution after the reaction. Therefore, further removal of Cu was considered essential, which was performed by adsorption process with the electro-generated NaOCl treated leach solution.

As mentioned above most of the free cyanide from the leach liquor of the WPCBs was removed by using electro-generated NaOCl at room temperature, although the removal ratio of Cu was 76%. Magnetite powder was selected to adsorb copper ions over gold ions. Magnetite (Fe₃O₄) consists of Fe²⁺ and Fe³⁺O₄²⁻, so, when noble metal ions approach the surface of magnetite, electron moves from magnetite, where ferrous oxidizes into ferric ions in the texture, to the noble metal ions [24,25]. Consequently, the noble metal ions could be reduced and adsorbed as elemental metal on the surface.

Figure 5. The surface element analysis of the precipitated Cu after reaction with reagent-grade hypochlorite (RGH) and electro-generated hypochlorite (EGH) using XPS.

Figure 6. Transmission electron microscope (TEM) image of (a,b) the precipitated Cu using electro-generated NaOCl and (c,d) using reagent-grade NaOCl. The insets in (b) and (d) are the corresponding selected area electron diffraction (SAED) patterns.
of magnetite. Alorro et al. [24] showed that gold ions adsorbed on magnetite due to higher standard reduction potential of Au than the open circuit potential (OCP) of magnetite, and also observed that small amount of Cu adsorbed even though the standard reduction potential of Cu is lower than OCP of magnetite. Since the standard reduction potential of gold cyanide complex ions decreased to −0.3 V versus SHE from 1.1 V versus SHE in chloride solution [26–28], it was expected that the remaining cyanide ions would prevent Au adsorption on the magnetite, whereas a few amounts of copper ions could be adsorbed due to the pH and difference of solution media [29–32].

The remaining copper ions can have a detrimental effect on the purity of gold in an electrowinning process of gold [33]. Therefore, the adsorption tests were performed using the solution obtained from the experiments of electro-generated NaOCl at room temperature, with residual Cu (50.5 mg/L) and Au (30.4 mg/L) while varying the contact time under the following conditions: initial pH 9.5, adsorption dosage 10 g/100 mL and shaking speed 150 rpm for 8 h.

Figure 7 shows the adsorption behavior of Cu and Au as a function of contact time at 25 °C. More than 99% of Cu was adsorbed on magnetite in 30 min, whereas total Au remained in the solution. These results indicate that Cu was successfully removed from the leach solution at ambient temperature leaving Au in the solution. However, further study would be required to confirm the mechanism.

![Figure 7. Adsorption efficiency of Au, Cu as a function of contact time (initial pH, ~9.5; dosage, 10 g/100 mL; temperature, 25 °C; contact time, 8 h; agitation speed, 150 rpm).](image)

Based on the above results, a process was provided for destruction of cyanide and removal of copper ions, and the flowsheet is presented in Figure 8. Most of the cyanide and 76% of Cu can be removed from the leach solution by using electro-generated NaOCl. The precipitated Cu is generated as a by-product in the process of recovering Au from WPCBs leach liquor. After alkaline chlorination with electro-generated NaOCl, the solution still contains about 50.5 mg/L of Cu and 30.4 mg/L of Au. Thus, it is desired to remove copper ions selectively which was achieved by adsorbing the same over magnetite. Finally, pure Au can be recovered from Cu depleted solution to Au metal by electro-winning [34].
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Figure 8. Flow sheet for the removal of cyanide and copper from WPCBs leach solution using electro-generated NaOCl and magnetite adsorption.

4. Conclusions

The process for the removal of cyanide and Cu from WPCBs leach solution was presented with the alkaline chlorination using electro-generated NaOCl followed by magnetite adsorption. For the alkaline chlorination for removal of copper ion and destruction of free cyanide, electro-generated NaOCl was used with following conditions: the concentration of free available chlorine, 5.2 g/L; initial pH, ~9.8; ambient temperature; the optimized yield was above 99% free cyanide decomposed and 76% Cu precipitated put as Cu(OH)₂. A remained Cu (50.5 mg/L) after alkaline chlorination was successfully adsorbed by using magnetite. The enhanced removal efficiency of Cu was observed to increase to more than 99%, which contributed successfully for purifying leach solution. Therefore, the alkaline chlorination using electro-generated NaOCl followed by magnetite adsorption could effectively eliminate the cyanide and Cu from WPCBs cyanide leach solution with remaining 30.2 mg/L Au in the solution.

Author Contributions: Methodology, M.B. and K.Y.; writing-original draft preparation, M.B. and K.Y.; project administration and funding acquisition, H.L. and S.K.; data curation, M.B. and H.L.; writing-review and editing, providing ideas, M.B., S.K. and K.Y.

Funding: This research was funded by the R&D Center for Valuable Recycling (Global-Top R&BD Program), Ministry of Environment, Republic of Korea, project number 2016002250004.

Conflicts of Interest: The authors declare no conflict of interest.

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