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High-Pressure Oxidative Leaching and Iodide Leaching Followed by Selective Precipitation for Recovery of Base and Precious Metals from Waste Printed Circuit Boards Ash

Altansukh Batnasan [1,*], Kazutoshi Haga [1], Hsin-Hsiung Huang [2] and Atsushi Shibayama [1,*]

[1] Graduate School of International Resource Sciences, Akita University, 1-1 Tegata-Gakuen machi, Akita 010-8502, Japan; khaga@gipc.akita-u.ac.jp

[2] Department of Metallurgy and Materials Engineering, Montana Technological University, 1300 West Park Street, Butte, MT 59701, USA; hhuang@mtech.edu

* Correspondence: altansux@gipc.akita-u.ac.jp or altansukh.b2008@gmail.com (A.B.); sibayama@gipc.akita-u.ac.jp (A.S.); Tel.: +81-18-889-3296 (A.B.); +81-18-889-3051 (A.S.)

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Abstract: This paper deals with the recovery of gold from waste printed circuit boards (WPCBs) ash by high-pressure oxidative leaching (HPOL) pre-treatment and iodide leaching followed by reduction precipitation. Base metals present in WPCB ash were removed via HPOL using a diluted sulfuric acid solution at elevated temperatures. Effects of potassium iodide concentration, hydrogen peroxide concentration, sulfuric acid concentration, leaching temperature, and leaching time on gold extraction from pure gold chips with KI–H_2O_2–H_2SO_4 were investigated. The applicability of the optimized iodide leaching process for the extraction of gold from the leach residue obtained after HPOL were examined at different pulp densities ranging from 50 g/t to 200 g/t. Results show that the removal efficiency was 99% for Cu, 95.7% for Zn, 91% for Ni, 87.3% for Al, 82% for Co, and 70% for Fe under defined conditions. Under the optimal conditions, the percentage of gold extraction from the gold chips and the residue of WPCBs was 99% and 95%, respectively. About 99% of the gold was selectively precipitated from the pregnant leach solution by sequential precipitation with sodium hydroxide and L-ascorbic acid. Finally, more than 93% of gold recovery was achieved from WPCB ash by overall combined processes.

Keywords: waste printed circuit board; gold; iodide; iodine; ascorbic acid; leaching; precipitation

1. Introduction

Hydrometallurgical processing is often used to produce metals from complex ores, concentrates, mine tailings, and secondary sources containing metals, termed as raw materials that are difficult to treat by conventional mineral processing and pyrometallurgical methods [1–3]. The leaching process is an essential step in hydrometallurgical processing and can extract metals from raw materials containing metals using a solvent. A key challenge in the leaching process is to meet selective extraction of a metal of interest from raw material avoiding some issues associated with the further processing of the pregnant leach solution [4,5].

Printed circuit boards (PCBs) are the essential building block in the majority of electric and electronic equipment (EEE) and account for 3–6% of the total constitution of EEE [6,7]. Various kinds of metals involving precious metals (Au, Ag, and Pd), base metals (Cu, Fe, Al, Ni, and Co), and toxic metals (Hg, Pb, Cr and Cd), and different types of plastic materials including non-flame retardant and flame retardant polymers are used in manufacturing of PCBs in different ratios depending on

the products [8,9]. It means that waste printed circuit boards (WPCBs) generated from discarded electric and electronic equipment (EEE) can be considered as a secondary source for metals. Because the proportion of valuable metals (Au, Ag, Pd, Pt, Cu, Ni, Co, Zn, and Al) is several times higher than those in their primary ore minerals [8–11], the recovery of valuable metals from WPCBs is the real challenge to maintain their supply chains and reduce the environmental consequences of metal mining. Therefore, over the years a variety of methods such as mechanical, hydrometallurgical, bio-metallurgical, and pyrometallurgical technologies have been used to recover valuable metals from WPCBs [12–14]. Among them, highly selective separation methods, such as hydrometallurgical processes, are more suitable due to the diverse and complex characteristics of the waste [2,15]. The recovery of precious metals from WPCBs has been extensively investigated because of their high economic values compared to other metals [16].

Cyanide leaching has been employed for over a century in gold extraction industries all over the world [17,18]. Nonetheless, in gold hydrometallurgy, a great deal of research has been conducted on the replacement of cyanide with alternative reagents such as thiosulfate, thiourea, and halides due to the environmental and human health risks associated with cyanide toxicity [19–22]. Among them, an iodine–iodide solution is a highly selective and efficient leaching agent for the recovery of gold from gold ores and WPCBs [21,23–25]. Several decades ago, the first patented process by Homick et al. (1976) used an iodine–iodide solution and a reducing agent (hydrazine) to recover gold from PCBs [26]. Subsequently, numerous studies have been devoted to developing the iodine–iodide leaching process for the recovery of gold from gold chips, gold ores, and WPCBs [27–29]. Nevertheless, the main obstacles of the leaching process are high reagent consumptions, higher reagent costs, and the complex chemistry of gold leaching in iodide solution. For the last several decades, few authors have studied the dissolution of gold in iodide solution with several oxidants namely hypochlorite, oxygen, and hydrogen peroxide, respectively to reduce iodine consumption [30–32]. Although several studies have focused on the dissolution of gold in iodine–iodide and iodide solutions with different oxidants, much less attention has paid to recover gold from pregnant leach solution (PLS) resulted from leaching [33–35]. Therefore, extensive studies on the process optimization, the dissolution mechanism of gold in iodide solution, and gold recovery from PLS are necessary.

In this study, gold recovery from the WPCBs ash by a two-step leaching process involving HPOL and iodide leaching followed by reductive precipitation was investigated. The removal of base metals from the WPCBs ash by high-pressure oxidative leaching was examined at different temperatures ranging from 100 °C to 180 °C. The dissolution behavior of gold from gold chips in iodide solutions with hydrogen peroxide and sulfuric acid was studied aiming to optimize the leaching process. Various experimental parameters such as iodide concentration, hydrogen peroxide concentration, sulfuric acid concentration, leaching time, pulp density, and leaching temperature were optimized. The feasibility of extracting gold from the leach residue obtained from HPOL was evaluated at the defined $KI–H_2O_2–H_2SO_4$ leaching conditions under different pulp densities. The gold recovery from the pregnant leach solution via sequential precipitation using sodium hydroxide and ascorbic acid was also discussed.

2. Materials and Methods

2.1. Materials

Waste printed circuit boards (WPCBs) ash received from the company (Dowa Metals and Mining Co., Ltd., Akita, Japan) and commercially available pure gold chips (99.99%, $10 \times 10 \times 1$ mm^3 in size, AUE02CB) purchased from the chemical company (Kojunda Chemical Laboratory, Co. Ltd., Sakado, Japan) were used as starting materials in this study. The WPCBs ash was crushed and ground to pass through a 100 μm (140 mesh) sieve using a jaw crusher (Pulverisette 1, Fritsch, Fritsch GmbH & Co. KG, Idar-Oberstein, Germany) and a grinder (HERZOG, HP-M 100, Maschinenfabrik GmbH & Co. KG, Osnabrück, Germany).

The pure gold chips were first flattened and then cut into small pieces ($2 \times 2 \times 1$ mm^3) and were used in iodide leaching to optimize the process.

The chemical composition of the WPCBs ash sample was analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES, SPS-5510, Seiko Instruments Inc., Tokyo, Japan) and X-ray fluorescence (XRF, ZSX Primus II, Rigaku Corporation, Tokyo, Japan). The results obtained are presented in Table 1.

Table 1. The chemical composition of the waste printed circuit boards (WPCBs) ash sample.

Main Metals and Non-Metal in WPCBs Ash, wt. %											
Au	Ag	Pd	Cu	Zn	Ni	Al	Co	Fe	Pb	Sn	Si
0.03	0.04	0.02	20.7	1.6	0.7	4.5	0.02	2.5	1.7	3.55	17.5

The particle size distribution of the sample of WPCBs ash was characterized using a particle size analyzer (Microtrac, MT3300EXII, Nikkiso Group, Osaka, Japan) (Figure 1). The main components in the sample identified using X-ray diffractometer (XRD, RINT-2200/PC, Rigaku, Tokyo, Japan) were of copper oxide (CuO), quartz (SiO_2), aluminum oxide (Al_2O_3), and tin oxide (SnO_2), as shown in Figure 2.
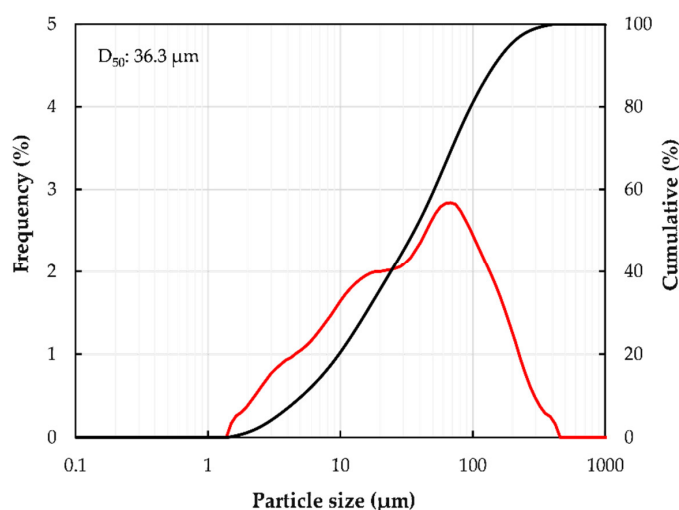
Figure 1. Particle size distribution of waste printed circuit boards (WPCBs) ash.
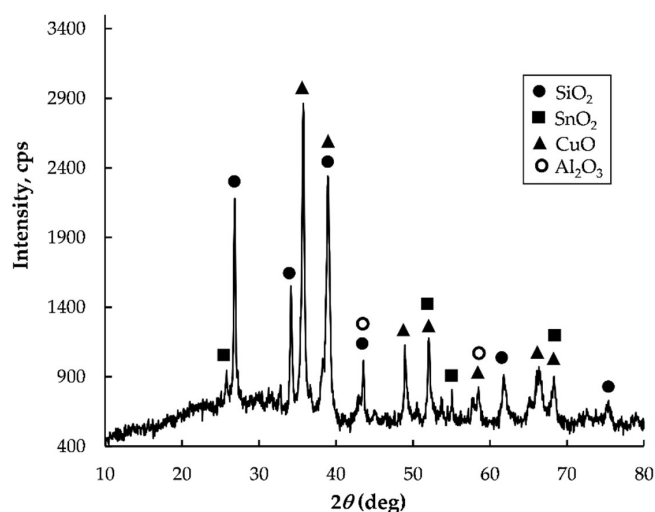
Figure 2. X-ray diffraction pattern of WPCBs ash.

Sulfuric acid (H_2SO_4), potassium iodide (KI), iodine (I), hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), and L-ascorbic acid, L-AA ($C_6H_8O_6$) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All the chemical reagents were analytical grade and used as received. Distilled water was used to prepare all aqueous solutions: 1 M H_2SO_4, 1 M H_2O_2, 18-72 mM KI, 0.1 M NaOH, and 0.1 M L-AA. Chemical composition and constituents of the WPCB ash sample, solid residues from leaching, and precipitates were characterized using XRD, XRF, and field emission-scanning electron microscope combined with energy dispersive x-ray spectroscopy (FE/SEM-EDS), JSM-7800F (JEOL, Tokyo, Japan). Concentrations of metals in the aqueous phases from leaching and precipitation were determined using ICP-OES (Seiko Instruments Inc., Tokyo, Japan). The changes of pH and oxidation-reduction potential (ORP) of the solutions through leaching and precipitation of metals under different media were examined by pH/ORP meter (Laqua, D-74, Horiba, Ltd., Kyoto, Japan). A vacuum pump (Buchi, V-700, BUCHI Labortechnik AG, Flawil, Switzerland) and a mini centrifuge (Cat. Number C0302, Argos Technologies, Inc., Elgin, IL, USA) were used to separate solids from liquid phases after leaching and precipitation experiments.

2.2. Leaching Experiments

The process optimization, separation, and extraction of the base and precious metals from the WPCBs ash via a two-step leaching procedure involving high pressure oxidative leaching (HPOL) and iodide leaching are described in this section.

2.2.1. Optimization of Iodide Leaching

Gold leaching experiments were carried out according to the following procedure: a certain amount of small pieces ($2 \times 2 \times 1$ mm^3) of pure gold chips was inserted in a constant volume (10 mL) of an aqueous solution consisting of a mixture of iodide, hydrogen peroxide, and sulfuric acid (KI–H_2O_2–H_2SO_4) into a lidded 30 mL Teflon beaker, and placed in a glass vessel containing water onto a hot plate. In order to optimize the gold leaching in the system, various relevant variables, which are iodide concentration (18–72 mM KI), H_2SO_4 concentration (0–100 mM), H_2O_2 concentration (5–30 mM), leaching temperature (20–80 °C), and leaching time (2–12 h), were investigated under various intervals at stirring speed of 550 rpm.

After iodide leaching, undissolved pure gold species were separated from the liquor solution by filtration and dried into a drying oven at 80 °C for 24 h. The efficiency of gold extraction was calculated by weighing the amount of gold undissolved and comparing the weight loss of gold to the initial gold weight used in a leaching experiment. The liquor solution was analyzed by ICP-OES (Seiko Instruments Inc., Tokyo, Japan) for determination of gold concentration.

2.2.2. High Pressure Oxidative Leaching

Leaching experiments were carried out in an autoclave equipped with a 200 mL Teflon vessel (Nitto High Voltage Co., Ltd., Tsukuba, Japan), impeller, inlet, and outlet gas pipes, pressure gauge and temperature sensor, and electrical heating system (Figure S1). An amount of 10 g of a powder sample of WPCBs ash was firstly mixed with 100 mL, 1 M H_2SO_4 solution into a vessel, and placed the prepared slurry into the autoclave. Then, the autoclave system was heated up to the selected temperature (100–180 °C) and set to an impeller speed of 750 rpm. After that, pure oxygen gas was injected to the slurry into the vessel by adjusting the total pressure (P_{tot}) of 2 MPa using a pressure gauge and held for 30 min. The total pressure (P_{tot}) includes a partial pressure of oxygen gas (P_{ox}) and vapor pressure (P_v) into the vessel in the autoclave. After the leaching experiment, the autoclave was cooled down up to room temperature, and the slurry from the leaching was filtered using a membrane filter (Toyo Roshi Kaisha, Ltd., Tokyo, Japan) by a vacuum pump. The composition of leachate and solid residue generated from HPOL were analyzed by various techniques to estimate the extraction efficiency of metals.

2.2.3. Iodide Leaching for Extraction of Gold from WPCBs Ash

The leach residue of WPCBs ash obtained from HPOL was used as a sample to extract precious metals especially gold via iodide leaching. The leaching experiments were conducted at varying pulp densities ranging from 50 g/L to 200 g/L under the optimized conditions explained in Section 2.2.1 (72 mM KI, 20 mM H_2SO_4, 15 mM H_2O_2, stirring speed of 550 rpm, at 60 °C for 8 h). After completing the leaching period, solid and liquid phases were separated using the filtration with the membrane filter. The solid residue was analyzed by XRD and XRF, respectively. The concentrations of metals in a pregnant leach solution were determined by ICP-OES. The efficiencies of metals dissolution in the iodide solution and accompanying metals remained in the residue were calculated by mass balance.

2.3. Evaluation of Effectiveness of Iodide Leaching

The extraction of precious and base metals from the residue of WPCBs ash via iodide (KI–H_2O_2–H_2SO_4) leaching was evaluated with the comparison of iodine–iodide (I–KI–H_2O) leaching. The experiments were carried out using 20 mM H_2SO_4, 15 mM H_2O_2 in the iodide solution, and 0.08 mM I_2 in the iodine–iodide solution under the same condition of KI concentration (72 mM), pulp density of 50 g/L, temperature (60 °C), leaching time (8 h), and stirring speed (550 rpm).

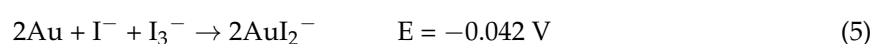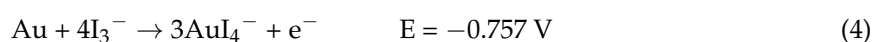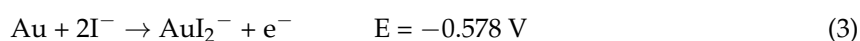### 2.4. Precipitation of Gold from Pregnant Leach Solution

The precipitation experiments were conducted in 20 mL of plastic tube at room temperature (25 °C) at a stirring speed of 550 rpm for 10 min. Firstly, minor amounts of metal impurities in the pregnant leach solution were selectively removed by precipitation under the alkaline conditions using a 0.1 M NaOH solution. Then, gold that remained in the resulting alkaline solution was reduced into its elemental form in acidic conditions using 0.1 M L-AA, which is known as vitamin C as a dietary supplement. After the precipitation experiment, a colloidal solution centrifuged at 9200 rpm for 5 min and the precipitate obtained was washed with 5 mL distilled water and then dried at 80 °C for 24 h. The precipitates were characterized by SEM-EDS. To determine the efficiency of metal precipitation, the supernatant solution from the centrifugation was analyzed by ICP-OES.

3. Results and Discussion

3.1. Optimization of Iodide Leaching

To properly and better optimize the iodide leaching process, pure gold chips dissolved in a mixture composed of potassium iodide, hydrogen peroxide, and sulfuric acid (KI–H_2O_2–H_2SO_4), preventing an interference effect of accompanying metals existing in WPCBs on gold extraction.

The generation of iodine species via oxidation of iodide with hydrogen peroxide in acidic media and the dissolution of gold in the solution are represented by the following Equations (1)–(5) [27–31,36,37]:

$$2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O \qquad E = 1.143 \text{ V} \tag{1}$$

$$I_2 + I^- \rightarrow I_3^- \qquad K = 713 \tag{2}$$

$$Au + 2I^- \rightarrow AuI_2^- + e^- \qquad E = -0.578 \text{ V} \tag{3}$$

$$Au + 4I_3^- \rightarrow 3AuI_4^- + e^- \qquad E = -0.757 \text{ V} \tag{4}$$

$$2Au + I^- + I_3^- \rightarrow 2AuI_2^- \qquad E = -0.042 \text{ V} \tag{5}$$

Leaching parameters such as potassium iodide concentration, hydrogen peroxide concentration, sulfuric acid concentration, leaching temperature, and leaching time that affect the dissolution of gold in the KI–H_2O_2–H_2SO_4 system were investigated, and results obtained are summarized in the following sections.

3.1.1. Effect of Potassium Iodide Concentration and Hydrogen Peroxide Concentration

The gold extraction was examined under different concentrations of KI (18–72 mM) and H_2O_2 (5–30 mM) in dilute aqueous solutions of H_2SO_4 (40 mM). The leaching experiments were performed at 40 °C, 550 rpm for 2 h. The effects of KI and H_2O_2 concentrations on gold extraction from the gold chips were exhibited in Figure 3. Results showed that gold extraction greatly varied with variations in the concentration of KI and H_2O_2, respectively. At 18 mM KI concentration, gold extraction decreased greatly from 84.2 mg/L to 0.2 mg/L as H_2O_2 concentration increases from 5 to 30 mM. Whereas at KI concentrations of 48 mM and 72 mM, rapid increases in the gold concentration from 113.3 mg/L to 180.7 mg/L and 166.5 mg/L to 279 mg/L were observed with the addition of 5–10 mM and 5–15 mM H_2O_2, respectively. When the H_2O_2 concentration increased further up to 30 mM, the extraction of gold decreased to 34.2 mg/L and 112.8 mg/L, respectively. It appears quite clearly in Figure 3 that the maximum gold concentrations of 84.2 mg/L, 180.7 mg/L, and 279 mg/L were achieved after 2 h leaching at 40 °C in KI–H_2O_2–H_2SO_4 solutions composed of 18 mM KI, 40 mM H_2SO_4, and 5 mM H_2O_2; 48 mM KI, 40 mM H_2SO_4, and 10 mM H_2O_2; and 72 mM KI, 40 mM H_2SO_4, and 15 mM H_2O_2, respectively. It implies that the highest gold extraction achieved with KI–H_2O_2 molar ratios within the range of 4:1–5:1. As the molar ratio of KI–H_2O_2 was less than 3:1, the gold extraction was decreased. Results indicate that the appropriate molar amounts of KI and H_2O_2 in the leaching mixture is the most important to generate a suitable amount of tri-iodine species (I_3^-) that promotes the gold extraction from the gold sample. It suggests that the deficient amounts of H_2O_2 (5–10 mM) lead to produce insufficient concentrations of I_3^-; on the contrary, the excessive amounts of H_2O_2 (30 mM) result in the formation of solid iodine ($I_{2(s)}$) under oxidizing conditions as indicated by Equation (6):

$$2I^-_{(aq)} + H_2O_{2(aq)} + H^+_{(aq)} \rightarrow I_{2(s)} + 2H_2O_{(l)} \qquad \text{(high oxidation condition)} \qquad (6)$$
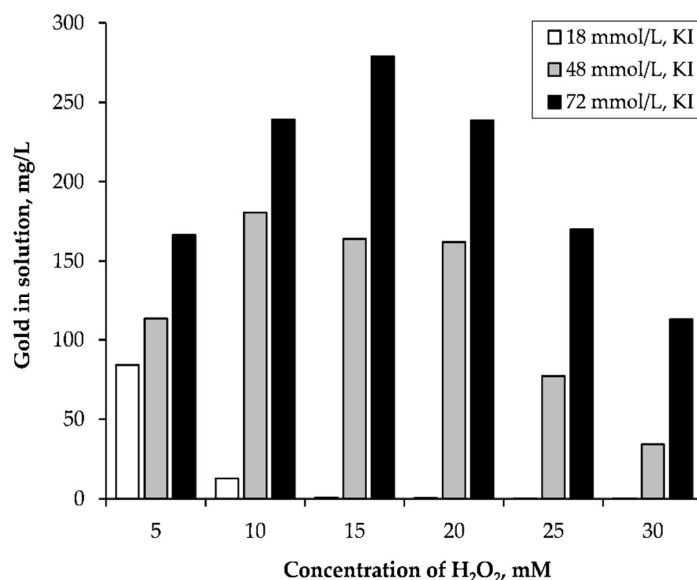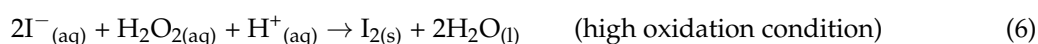
Figure 3. Gold extraction as functions of KI and H_2O_2 concentrations in the KI–H_2O_2–H_2SO_4 solution.

As a result, 72 mM KI and 15 mM H_2O_2 were selected as the suitable molar amount (5:1) between KI and H_2O_2 for the subsequent experiments.

3.1.2. Effect of Sulfuric Acid Concentration

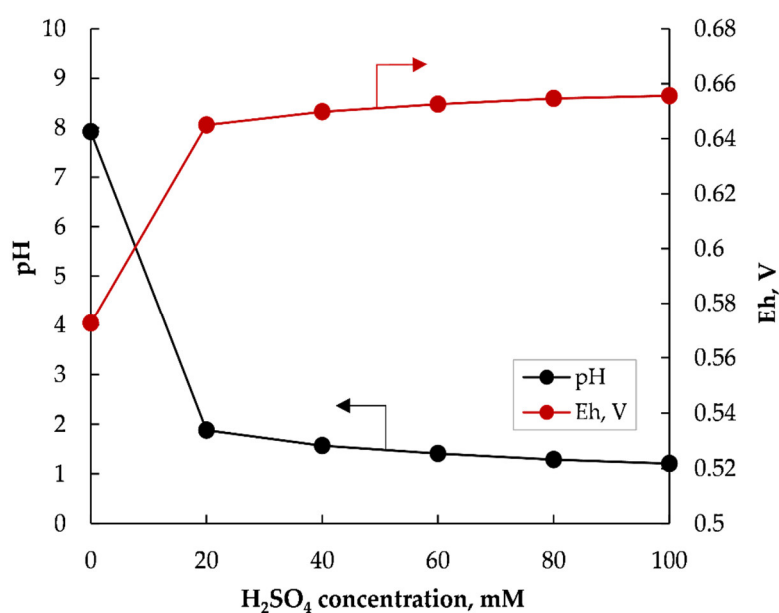Figure 4 shows the effect of sulfuric acid concentration on the gold extraction from pure gold chips. The concentration of H_2SO_4 in the leaching solution consisting of 72 mM KI and 15 mM H_2O_2

was varied between 0 (without H_2SO_4) and 100 mM. Other experimental parameters were fixed as described above.
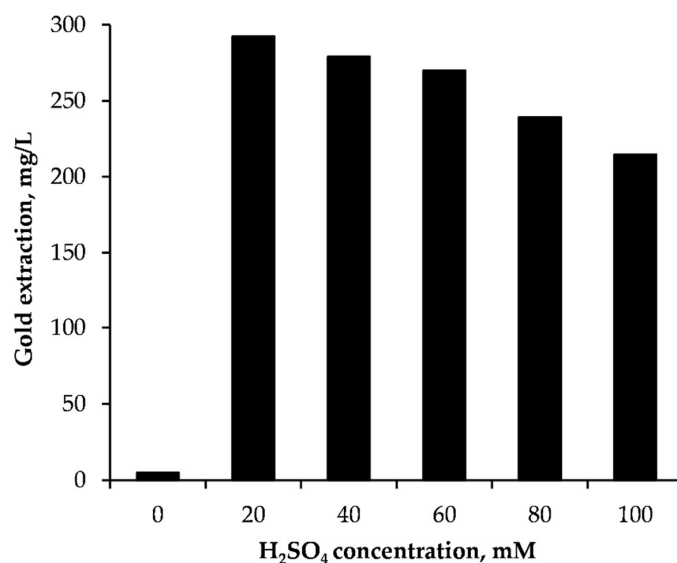
Figure 4. Gold extraction as a function of H_2SO_4 concentration in the $KI–H_2O_2–H_2SO_4$ solution.

Results indicate that the absence of H_2SO_4 in the leaching solution results in lower gold extraction (5 mg/L), whereas the presence of H_2SO_4 leads to a positive effect on the gold extraction. At 20 mM H_2SO_4 concentration, gold extraction increased significantly to a maximum of 292 mg/L Au. Whereas an increase in H_2SO_4 concentration further up to 100 mM resulted in a decrease in Au concentration to 214.6 mg/L. It suggests that the efficiency of the gold extraction depends on the molar ratio of the reactants in the leaching solution. It is estimated that the molar ratios of $KI–H_2O_2–H_2SO_4$ in the solutions were in the range between 5:1:0 and 5:1:7. The maximum gold extraction of 292 mg/L was achieved at the molar ratio between $KI–H_2O_2–H_2SO_4$ of 5:1:1. The decrease in gold extraction might be explained by the formation of a precipitate of iodine ($I_{2(s)}$) due to the presence of 40–100 mM H_2SO_4, at which the values of pH and Eh of solutions did not change obviously, whereas these values changed drastically with 20 mM H_2SO_4 (Figure 5).


Figure 5. Effect of H_2SO_4 concentration on pH and Eh in the leaching solution.

As a result, the most appropriate sulfuric acid concentration for the extraction of gold was selected as 20 mM for the next experiments.

3.1.3. Effect of Leaching Temperature and Time

The effect of leaching temperature and leaching time on gold extraction from the gold chips were investigated under different temperature ranges from 20 °C to 80 °C and the various times from 0.25 h to 12 h. Other experimental variables such as KI concentration, H_2O_2 concentration, H_2SO_4 concentration, and stirring speed were kept constant explained in the above experiments. The results are summarized in Figure 6. It showed that the extraction of gold rises dramatically with an increase in leaching temperature and time, respectively. At the temperatures of 20 °C and 40 °C, gold extraction grew continuously for a period of leaching time (0.2–12 h), and reached its highest levels of 670 mg/L and 1127 mg/L from 18 mg/L and 30 mg/L, respectively. The maximum extraction of gold was 1137 mg/L at 60 °C after 8 h leaching that was equal to 99% extraction efficiency of gold. Whereas at 80 °C, the most effective extraction of gold had achieved 1064 mg/L for 6 h leaching that was consistent with 92.6% extraction efficiency of gold. Further increase in the temperature and time results in the decrease in the extraction of gold (Figure 6). The results revealed that the gold extraction with the KI–H_2O_2–H_2SO_4 solution is dependent on various leaching parameters such as iodide concentration, hydrogen peroxide concentration, sulfuric acid concentration, leaching temperature, and leaching time, respectively. Consequently, the best conditions for gold leaching in the KI–H_2O_2–H_2SO_4 solution determined were: KI concentration of 72 mM, H_2O_2 concentration of 15 mM, H_2SO_4 concentration of 20 mM, stirring speed of 550 rpm, leaching temperature of 60 °C, and leaching time of 8 h.
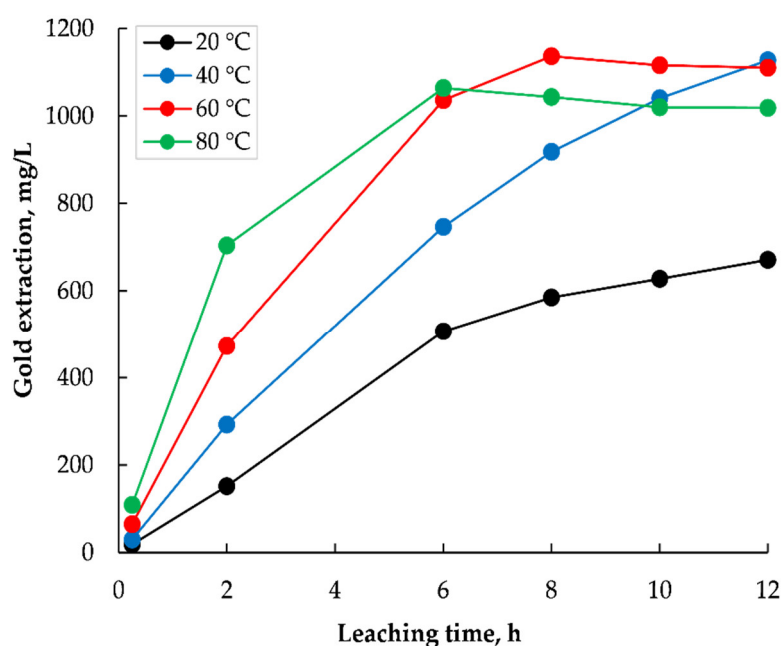
Figure 6. Gold extraction as a function of leaching time under different temperatures.

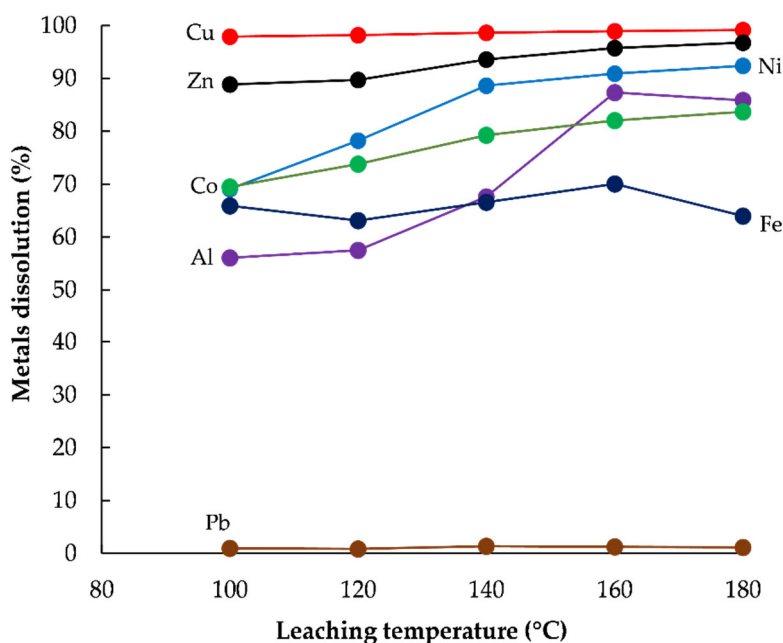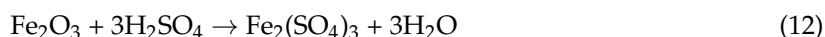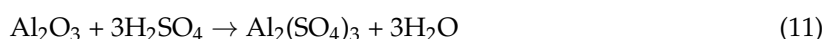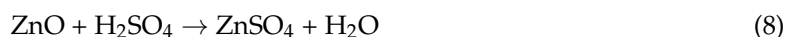### 3.2. Extraction of Base Metals from WPCBs Ash by HPOL

The presence of higher amounts of metal impurities in WPCBs causes adverse effects on precious metals extraction and reagent consumption [30]. To reduce the side effects of metal impurities on gold extraction and iodide consumption, HPOL experiments were carried out at different temperatures.

Effect of Temperature

High pressure oxidative leaching as a pretreatment for recycling of base metals from the WPCBs ash was conducted at different temperatures ranging from 100 to 180 °C using a laboratory-scale

autoclave under conditions of fixed sulfuric acid concentration (1 M), pulp density (10 g/t), agitation speed (750 rpm), total pressure (2 MPa), and leaching time (30 min). Figure 7 shows the extraction percentage of base metals from the WPCBs ash under the conditions. Results showed that the maximum extraction of Cu (99%), Zn (95.7%), Ni (91%), Al (87.3%), Co (82%), and Fe (70%), which are main base metals in the pulverized WPCBs ash, were achieved in 1 M H_2SO_4 at 160 °C, while only 1.3% of Pb was dissolved. The reaction between metal oxides and a dilute acid is often quite slow because the oxidant (H^+, SO_4^{2-}) is not enough to oxidize the metal. However, it is possible to take place the progress of the reaction in the presence of oxygen that acts as an oxidizing agent. The dissolution of base metals with dilute sulfuric acid in the presence of oxygen is, hence, represented as follows [38,39]:

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \tag{7}$$

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \tag{8}$$

$$CoO + H_2SO_4 \rightarrow CoSO_4 + H_2O \tag{9}$$

$$NiO + H_2SO_4 \rightarrow NiSO_4 + H_2O \tag{10}$$

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O \tag{11}$$

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O \tag{12}$$

Figure 7. Extraction percentage of base metals as a function of temperature. (Conditions: 1 M H_2SO_4, 100–180 °C, 10 g/t pulp density, 750 rpm stirring speed, 2 MPa pressure for 30 min leaching).

It can be seen that precious metals (Au, Ag, and Pd) and tin (Sn) in the WPCBs ash were not dissolved in 1 M H_2SO_4 under the high pressure oxidation conditions due to their extremely slow leaching kinetics. It may require strong H_2SO_4 and longer leaching time to extract these metals.

The chemical composition of the leachate and the solid residue resulted from HPOL with 1 M H_2SO_4 are presented in Table 2.

Table 2. The chemical composition of the leachate and the solid residue of the WPCBs ash after high-pressure oxidative leaching (HPOL).

Sample	Au	Ag	Pd	Cu	Zn	Ni	Al	Co	Fe	Pb	Sn	Si
Leachate, (g/L)	0	0	0	22.0	1.6	0.06	3.4	0.02	1.7	0.01	0	0
Leach residue, (wt. %)	0.06	0.21	0.02	0.23	0.07	0.04	0.48	0.004	0.7	1.67	7.7	24.4

It shows that the concentration of precious metals in the leach residue was higher than that in the WPCBs ash. It is worth noting that the residue is a potential source of precious metals. On the other hand, the leachate contained the proper amount of base metals for recovery. It suggests that HPOL could be used to concentrate base metals in the leachate and precious metals in the leach residue, separately. Therefore, the leach residue obtained by HPOL was used to recover precious metals by iodide leaching in a further study.

The intensities of diffraction peaks corresponding to the copper phases in the residue became rather low compared to those from the initial WPCBs ash sample (Figure S2).

3.3. Extraction of Precious Metals from Leach Residue via Iodide Leaching

Effect of Pulp Density

The leach residue of WPCBs ash obtained from HPOL was dissolved in a mixture of $KI–H_2O_2–H_2SO_4$ under the selected conditions described in the previous section (Section 3.1). Figure 8 shows the percentage of metals extracted from the leach residue of WPCBs under the different pulp densities of 50 g/t, 100 g/t, and 200 g/t at the optimum conditions. The results show that an increase in the pulp density leads to a decrease in the percentage extraction of metals from the leach residue. It means that the extraction of metals had similar tendencies under the conditions.
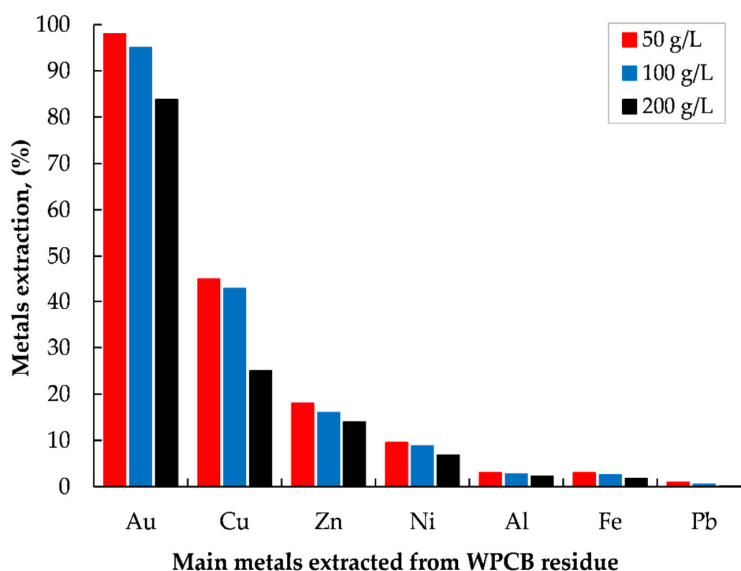
**Figure 8.** The percentage extraction of metals as a function of pulp density.

It is observed that gold and copper are preferentially extracted from the residue via $KI–H_2O_2–H_2SO_4$ leaching. The percentage extraction of gold and copper decreased from 98% to 84% and from 45% to 25%, respectively, with an increase in the pulp density, whereas the percentages of both silver and palladium extraction were lower than 1%. However, the percentage extraction of metals at high pulp density reduced obviously than that in lower pulp densities, and the concentrations of metals in pregnant leach solutions increase with an increase in pulp density, as shown in Table 3.

Table 3. Concentration of metals in the pregnant leach solutions after leaching, mg/L.

Pulp Density, g/L	Au	Cu	Zn	Ni	Al	Fe	Pb
50	32.3	17.2	11.5	8.2	29.2	19.0	14.0
100	58.2	34.2	24.7	18.0	64.4	41.2	13.2
200	108	40.7	43.4	26.6	102.8	55.7	9.2

3.4. Evaluation of Effectiveness of Iodide Leaching

Figure 9 presents the results of a quantitative comparison of the effectiveness of the iodide ($KI–H_2O_2–H_2SO_4$) and iodine–iodide ($I_2–KI–H_2O$) leaching for precious and base metals extraction from the leach residue of WPCBs ash under the same leaching conditions.
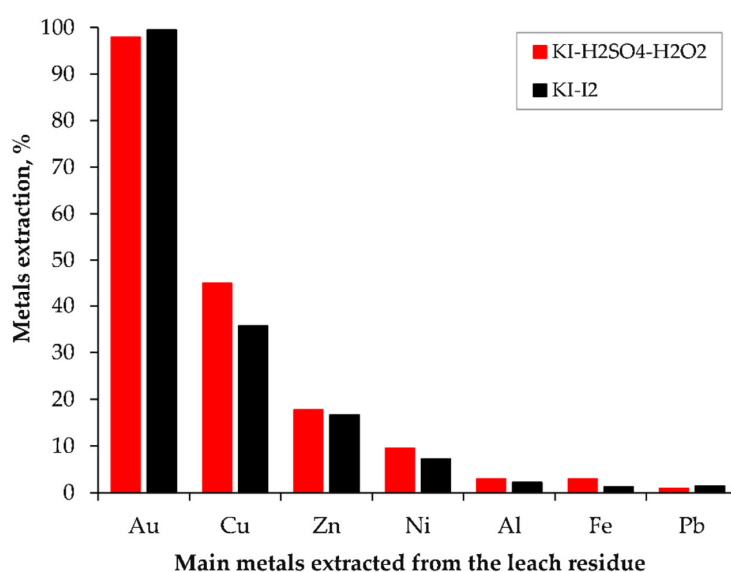
Figure 9. Comparison of the efficiency of metals extraction via iodide leaching and iodine–iodide leaching at pulp density of 50 g/L.

The results show that the extraction of gold and lead by leaching with $KI–I_2–H_2O$ are somewhat higher than those achieved with $KI–H_2O_2–H_2SO_4$. On the contrary, the efficiencies of other metals (Cu, Zn, Ni, Al, and Fe) extraction with $KI–H_2O_2–H_2SO_4$ were slightly higher than that in $KI–I_2–H_2O$ due to the existence of SO_4^- ions in $KI–H_2O_2–H_2SO_4$ leaching system. It was observed that no significant differences resulted in the gold extraction from the sample by both iodide and iodine–iodide leaching. It suggests that iodide leaching is as much an effective method as iodine–iodide leaching for the extraction of gold from samples containing gold and can potentially reduce reagent cost, particularly in iodine consumption.
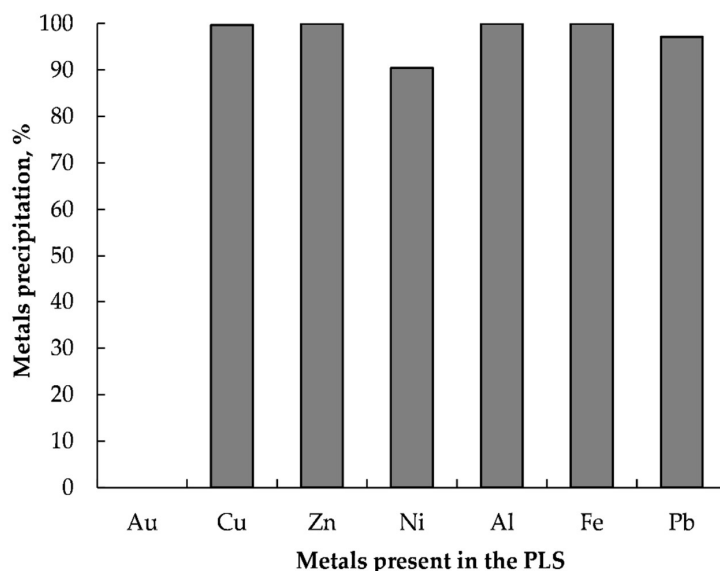
3.5. Recovery of Gold from the Pregnant Leach Solution

The pregnant leach solution (PLS) containing 32.3 mg/L Au and considerable amounts of base metal impurities such as Cu, Zn, Ni, Al, Fe, and Pb was used in the subsequent study (Table 3). The PLS has a pH of 1.9 and Eh of 0.64 V. The recovery of gold from the PLS consists of two steps: (1) removal of metal impurities via precipitation using NaOH; (2) gold recovery from the resulting solution by reductive precipitation using L-AA as a reducing agent. The results of the sequential precipitation are presented in the following sections.

3.5.1. Removal of Metal Impurities from the PLS

Based on the preliminary experimental results [25,40], the pH of the PLS was adjusted up to 9.0 from 1.9 using 0.1 M NaOH at ambient temperature and stirring speed of 500 rpm. The efficiency

of metals precipitation is shown in Figure 10. The results show that the vast majority of Cu (99.6%), Zn (100%), Ni (90.4%), Al (100%), Fe (100%), and Pb (97%) as metal impurities were precipitated from the PLS, whereas gold did not precipitate under the condition. It indicates that most gold (32 mg/L) and trace amounts of Cu (618 µg/L), Ni (665.6 µg/L), and Pb (237.3 µg/L) have remained into the resulting solution which had a pH of 9.0 and Eh of 0.21 V. It implies that this process is efficient in removal of metal impurities from PLS.

Figure 10. Removal of metal impurities from the pregnant leach solution (PLS) by precipitation at pH 9.

3.5.2. Recovery of Gold from the Solution by Reductive Precipitation Using L-AA

Metals remained in the alkaline solution that resulted from the precipitation of base metals with NaOH were recovered by reductive precipitation using a 0.1 M, L-AA solution under conditions that were fixed as the molar ratio between Au and L-AA of 1:1, temperature of 25 °C, stirring speed of 500 rpm and precipitation time for 10 min [25,40]. Figure 11 shows the recovery of metals like Au, Cu, Ni, and Pb from the solution via precipitation with L-AA.
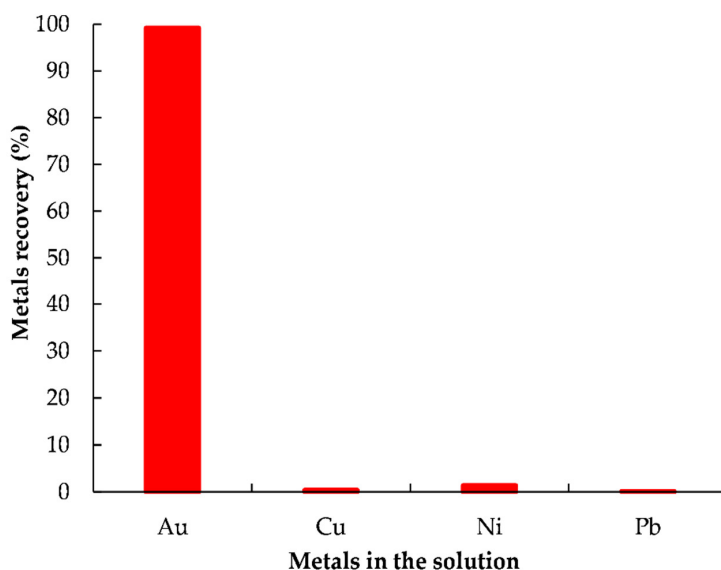
Figure 11. Recovery of metals from the solution by reductive precipitation with L-AA.

The result showed that gold recovery of 99.2% was achieved from the solution via the precipitation with L-AA under the conditions, while yields of Cu (0.4%), Ni (1.4%), and Pb (0.1%) as metal impurities in the precipitate were negligible. It was observed that the addition of L-AA results in a reduction of pH of the solution from 9 to 1.8 and an increase of Eh from 0.21 V to 0.64 V. The Eh-pH diagram for gold iodide and ascorbic acid species in the solution was constructed at 25 °C within the pH range from 0 to 14 using STABCAL software (N NBS, Helgeson thermodynamic data source, W32-Stabcal Version 1.0, Montana Technological University (Montana Tech), Butte, MT, United States) as shown in Figure 12.
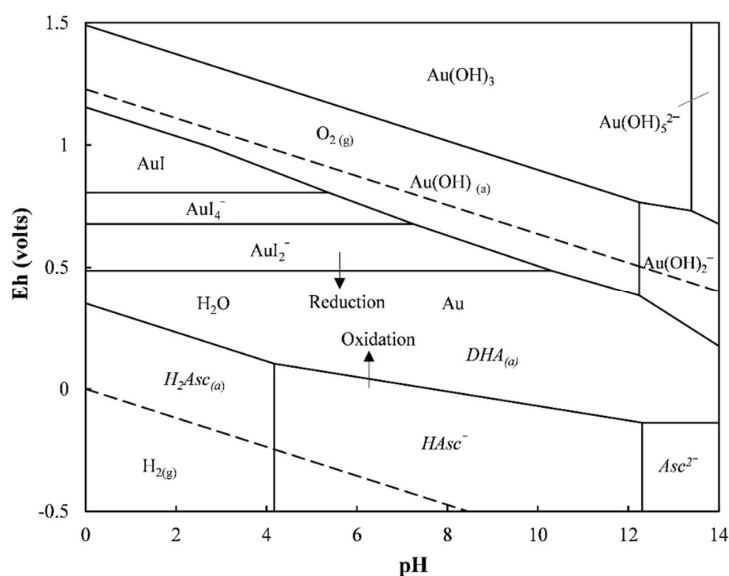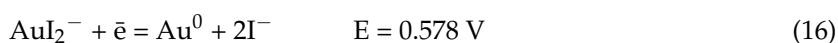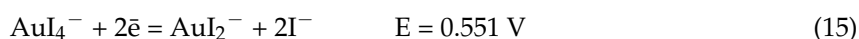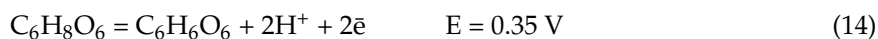

Figure 12. The Eh–pH diagram of gold–iodide and ascorbic acid species in the solution. (Condition: [Au] = 32.3 mg/L, [I] = 0.072 M (72 mM), Eh = −0.5–1.5 volts, *P* = 1 atm at pH 0–14, 25 °C, (NBS, STABCAL software)).

The thermodynamic data for gold iodide and L-AA related species were imported from the references [25,41–43]. Table S1 summarizes the thermodynamic data for individual species in the solution used to construct the Eh–pH diagram. As shown in Figure 12, L-AA/H_2Asc is converted into its oxidized forms such as HAsc$^-$, Asc^{2-}, and DHA at the different pH conditions as indicated by Equation (13) [43–45].

$$H_2Asc \rightleftharpoons HAsc^- \rightleftharpoons Asc^{2-} \rightleftharpoons DHA \tag{13}$$

It implies that DHA-dehydroascorbic acid ($C_6H_6O_6$) is the most stable oxidized product of L-AA in the pH range from 0 to 14.

These findings suggest that colloidal gold can be obtained from gold–iodide solutions by reductive precipitation with L-AA. The mechanism of the reduction of gold iodide complexes via L-AA is generally explained by the Equations (14)–(16) [25,46]:

$$C_6H_8O_6 = C_6H_6O_6 + 2H^+ + 2\bar{e} \qquad E = 0.35 \text{ V} \tag{14}$$

$$AuI_4^- + 2\bar{e} = AuI_2^- + 2I^- \qquad E = 0.551 \text{ V} \tag{15}$$

$$AuI_2^- + \bar{e} = Au^0 + 2I^- \qquad E = 0.578 \text{ V} \tag{16}$$

The colloidal gold as a precipitate formed from the reductive precipitation was analyzed by using FE/SEM-EDS. The SEM result shown in Figure S3 indicates that produced particles do not have a definite shape and size due to the agglomeration of particles formed. The EDS analysis in the area identified a sharp peak corresponding to gold (Figure S4).

4. Conclusions

This study aimed to recover gold from WPCBs ash by hydrometallurgical processes involving HPOL and potassium iodide leaching (KI–H_2O_2–H_2SO_4) followed by sequential precipitation using NaOH and L-AA. The following conclusions can be drawn based on the results obtained from this study:

- The maximum gold extraction of 1137 mg/L (99% extraction efficiency) was achieved from pure gold chips in KI–H_2O_2–H_2SO_4 media under the conditions determined through this study, while the molar ratio of KI–H_2O_2–H_2SO_4 reactants was 5:1:1.
- The most effective extraction of Cu (99%), Zn (95.7%), Ni (91%), Al (87.3%), Co (82%), and Fe (70%) from the WPCBs ash were achieved in 1 M H_2SO_4 solution by HPOL pre-treatment at the defined conditions.
- Over 95% of gold could be extracted from the leach residue from HPOL via iodide leaching under the conditions determined from the leaching of gold chips in the KI–H_2O_2–H_2SO_4 solution.
- Results suggested that iodide leaching is an effective method for the extraction of gold from WPCBs.
- Efficient gold recovery (>99.2%) could be achieved from the PLS by reductive precipitation using L-AA after selectively removed metal impurities via precipitation with NaOH at a pH of 9.

As a result, a multi-stage hydrometallurgical procedure with greater than 93% gold recovery from WPCBs is proposed.

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