Recovery of Precious and Base Metals from Waste Printed Circuit Boards Using a Sequential Leaching Procedure

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This paper considers the issue of recycling of waste printed circuit boards (WPCBs) containing precious and base metals in appreciable amounts. High-pressure oxidative leaching (HPOL) with dilute sulfuric acid resulted in removal of a significant amount of base metals from a WPCB ash sample obtained by incineration at 800°C. The parameters investigated in the precious metal leaching from WPCB residue after HPOL included the sulfuric acid concentration, thiourea concentration, oxidant concentration, leaching temperature, and leaching time. Recovery of gold, silver, and palladium of 100%, 81%, and 13% from the WPCB residue sample was achieved by thiourea leaching under optimized conditions. The results show that the efficiency of precious metal dissolution from the WPCB sample using thiourea solution depended strongly on the concentration of both thiourea and oxidant.

INTRODUCTION

In recent years, the quantity of discarded electronics such as computers, mobile phones, tablets, and televisions has increased enormously due to the rapid increase in economic growth and production of electronics, as well as the short lifespan of most electronics devices.[1,2] Several researchers have characterized the composition of printed circuit boards, which are essential components of most electronic devices, reporting that printed circuit boards from mobile phones are composed of 63 wt.% metals, including precious metals (gold, silver, platinum, and palladium), base metals (copper, aluminum, iron, zinc, cobalt, and nickel), toxic metals (arsenic, mercury, and chromium), 24 wt.% ceramics, and 13 wt.% polymers.[3,4] It can be inferred that waste printed circuit boards (WPCBs) are an important source of raw materials such as metals, plastics, and ceramics. A number of studies have described the status of electronic waste management and recycling in many countries.[4–6] Various metallurgical approaches, including pyrometallurgy, hydrometallurgy and bio-hydrometallurgy, for recovery of precious and base metals from their ores, concentrates, and raw materials such as WPCBs have been discussed in previous studies.[7–10] Among these methods,

hydrometallurgical processes enable selective recovery of precious metals from resources using aqueous chemistry based on a variety of lixiviants including cyanide, aqua regia, thiosulfate, thiourea, and halogens. Due to the potential environmental, wildlife, and human health risks associated with use of cyanide in gold and silver recovery processes in mining industries, cyanidation processes cannot be employed in many countries in the world. Such risks can occur due to release of cyanide ions from exposed cyanide-bearing solutions stored behind tailings dams under various environmental conditions including mist, ingestion, and adsorption as well as inhalation of dust.[11,12] Therefore, many studies have attempted to identify alternative reagents to cyanide for use in hydrometallurgical processes for recovery of precious metals.[7–10,13–16] Thiourea is an effective reagent for recovery of gold and silver from their primary and secondary resources due to its lower toxicity and faster complexing ability with these metals under appropriate oxidation conditions compared with cyanide. Therefore, the kinetics of gold dissolution in acidic thiourea solutions in presence of a variety of oxidants, namely hydrogen peroxide, iron(III) sulfate, formamidine disulfide, oxygen, sodium peroxide, and manganese dioxide, has been studied by numerous authors.[17–19] However,

commercial application of thiourea in gold recovery processing has been hindered due to the higher consumption of reagents and complexity of the leaching system when treating various ores/concentrates and different recycled materials. Also, the presence of impurities in these raw materials represents a major obstacle to selective leaching of precious metals and increases reagent consumption because of their complexation with thiourea.

Therefore, optimization of various parameters in thiourea leaching processes for recovery of precious metals from WPCBs remains a challenging task. In the work presented herein, a sequential hydrometallurgical approach consisting of high-pressure oxidative leaching (HPOL) and thiourea leaching for recovery of base and precious metals from a WPCB ash sample is discussed.

EXPERIMENTAL PROCEDURES

Materials

A sample of WPCB ash (< 106 μm in size) for this study was received from DOWA Metals & Mining Company, Japan. Incineration was carried out in a furnace equipped with gas cleaning systems to remove organics and volatiles. The WPCB ash (starting sample) after incineration and solid residues from leaching experiments were analyzed using x-ray diffraction (XRD) analysis (RINT-2200/PC Rigaku) and x-ray fluorescence (XRF) spectroscopy (ZSX Primus II, Rigaku). All leached solutions were analyzed to determine the concentrations of metals using inductively coupled plasma optical emission spectrometry (ICP-OES, SPS-5500; Seiko Instruments Inc.). Reagent-grade chemicals were used in this study, viz. sulfuric acid (H_2SO_4), iron(III) sulfate [$Fe_2(SO_4)_3$], and thiourea [$SC(NH_2)_2$]. Distilled water was used to prepare all solutions. The pH and oxidation–reduction potential (ORP) of the solutions were measured by pH/ORP meter (Laqua, D-74). Changes of temperature and agitation speed were controlled by a multiposition digital stirring hotplate (HSH-6D, AS ONE Corporation).

Methods

High-Pressure Oxidative Leaching

The WPCB ash sample obtained after incineration was dissolved in 1 M H_2SO_4 solution in an autoclave under high-pressure oxidation conditions as determined previously.[20] The autoclave used was equipped with a reaction vessel (Nitto Koatsu-Japan), impeller, inlet and outlet gas pipes, pressure and temperature sensors, and electrical heating system. In this study, slurry was prepared using the ash sample with 1 M H_2SO_4 solution then transferred to the vessel. The vessel was placed into the autoclave and the inlet valves were closed, then the experiment was performed at 120°C at speed of 750 rpm for 30 min under pressure (P_{total}) of 2 MPa, including the partial pressure of oxygen

(P_{O2}) gas and the vapor pressure (P_v) in the system controlled via the oxygen gas flow. After the experiment, the slurry was cooled down to 25°C followed by filtration.

Thiourea Leaching

The next stage of this work was dissolution of precious metals from the WPCB solid residue after HPOL using acidic thiourea solution. Leaching experiments were conducted in sealed bottles while varying conditions including the H_2SO_4 concentration (from 0.5 M to 4 M), thiourea concentration (from 0.25 g/L to 20 g/L), oxidant concentration (from 0 g/L to 7.5 g/L), leaching temperature (from 25°C to 80°C), and leaching time (from 1 h to 10 h). For all experiments, the pulp density and agitation speed were fixed at 50 g/L and 500 rpm, respectively.

RESULTS AND DISCUSSION

High-Pressure Oxidative Leaching

The chemical content of the samples obtained after incineration and HPOL is presented in Supplementary Table SI, revealing recovery of copper (Cu), zinc (Zn), aluminum (Al), nickel (Ni), cobalt (Co), manganese (Mn), and iron (Fe) from the pulverized WPCB ash sample of 99.3%, 96%, 81.6%, 82.7%, 84%, 71.4%, and 63.2%, respectively. The significant amount of base metals (Cu, Zn, Al, Ni, Co, and Fe) reacted with H_2SO_4 solution, and gold (Au), silver (Ag), palladium (Pd), lead (Pb), and silicon dioxide (SiO_2) remained in the solid residue due to the HPOL conditions in the autoclave and soluble/insoluble nature of these metals in dilute H_2SO_4 solution. The most abundant compounds identified by XRD analysis of the ash sample after incineration were Cu and Si, followed by Pb and Sn, whereas the strongest XRD peaks from the residue sample after HPOL corresponded to Si and Pb, respectively (Supplementary Fig. S1).

Thiourea Leaching for Recovery of Precious Metals

Effect of Sulfuric Acid Concentration

Leaching tests were conducted using different concentrations of H_2SO_4 ranging from 0.25 M to 4 M at the following selected conditions: thiourea concentration of 1.25 g/L, no extra oxidant, pulp density of 50 g/L, agitation speed of 500 rpm, temperature of 25°C, and 2 h. As shown in Fig. 1, with increasing H_2SO_4 concentration in the investigated range from 0.25 M to 1 M, the efficiency of Au dissolution increased up to 17.3%, whereas the Ag dissolution decreased from 49.5% to 45.5%. Further increase of the acid concentration to 4 M led to decrease in the efficiency of Au and Ag dissolution to 12.5% and 2.3%, respectively. The maximum Au and Ag dissolution of 17.3% and 49.5% were achieved at 1 M and 0.25 M H_2SO_4 solution with
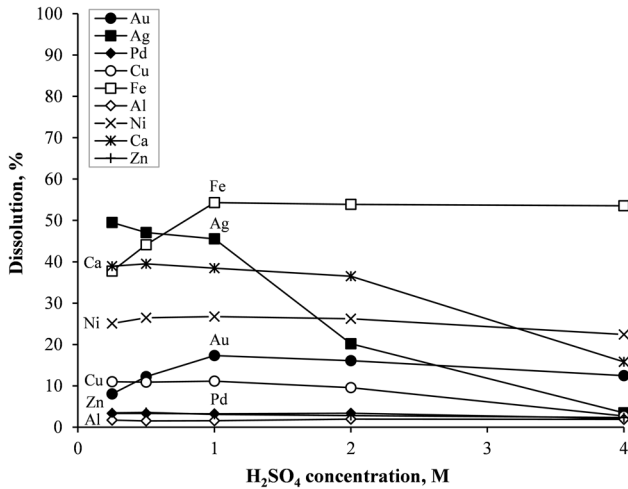
Fig. 1. Dissolution of metals in thiourea solution as function of sulfuric acid concentration.

Fig. 2. Dissolution of precious metals in thiourea solution as function of oxidant concentration.

thiourea, respectively. Palladium exhibited relatively low dissolution efficiency (2.1% to 3.5%) in the thiourea solutions. The trends for the dissolution of Cu, Fe, and Ni were the same as for the leaching of gold in the thiourea solution, while the dissolution results for Al, Ca, and Zn were identical to those for Ag (Fig. 1). It is assumed that the lower dissolution efficiency of metals in the thiourea solutions can be attributed to decomposition of thiourea and the stability of metal complexes formed with thiourea; For instance, the stability constant (log β_2) of $[Au(CS(NH_2)_2)_2]^+$, $[Ag(CS(NH_2)_2)_2]^+$, and $[Cu(CS(NH_2)_2)_2]^{2+}$ are 23.3, 11.7 (15.0), and 11.1, in decreasing order.[21–23] It was observed that dissolution of base metals from the residue sample in thiourea solutions with different concentrations of H_2SO_4 showed no reverse effect on the leaching of precious metals, hence their dissolution in the thiourea solutions under the different conditions were not considered further in these studies.

Effect of Oxidant Concentration

The dissolution of precious metals from the residue sample in acidic thiourea solutions with different concentrations of oxidant [$Fe_2(SO_4)_3$] from 0 g/L to 7.5 g/L was also investigated, using the same values of the other leaching parameters as in the previous studies. Figure 2 shows a plot of the dissolution of precious metals versus the oxidant concentration in thiourea leaching. Increasing the oxidant concentration to 5 g/L resulted in an increase in the dissolution of Au and Pd, but a rapid decrease in Ag dissolution. The equations for dissolution of gold, silver, and palladium in acidic thiourea solutions in presence of Fe^{3+} ions can be generally described as follows:[17,19,21,24]
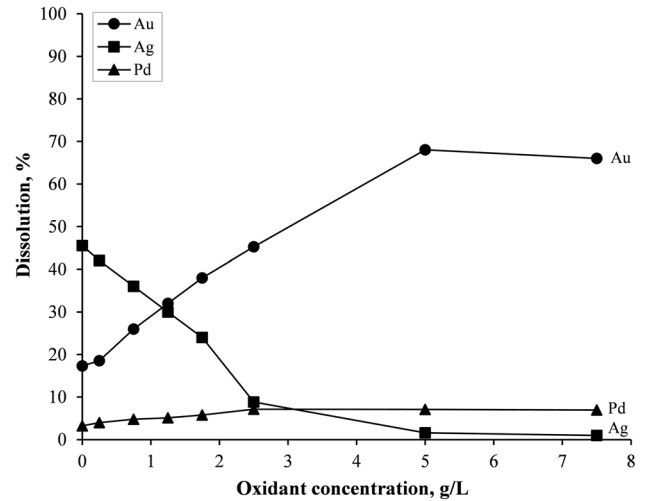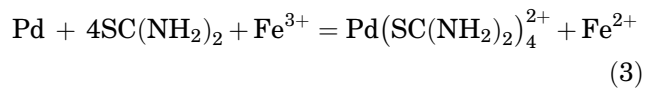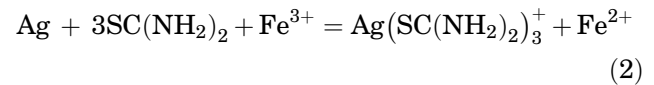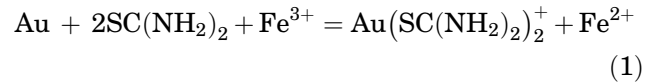
$$Au + 2SC(NH_2)_2 + Fe^{3+} = Au\big(SC(NH_2)_2\big)_2^+ + Fe^{2+} \tag{1}$$

$$Ag + 3SC(NH_2)_2 + Fe^{3+} = Ag\big(SC(NH_2)_2\big)_3^+ + Fe^{2+} \tag{2}$$

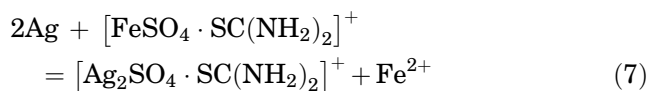$$Pd + 4SC(NH_2)_2 + Fe^{3+} = Pd\big(SC(NH_2)_2\big)_4^{2+} + Fe^{2+} \tag{3}$$

Further increase of the oxidant concentration in the thiourea solution adversely affected the efficiency of the leaching of the precious metals due to oxidation of thiourea to form a stable ferric sulfate complex and formamidine disulfide, which rapidly decomposes to thiourea, cyanamide, and elemental sulfur as follows:[19,21]

$$Fe^{3+} + SO_4^{2-} + SC(NH_2)_2 = \big[FeSO_4 \cdot SC(NH_2)_2\big]^+ \tag{4}$$

$$2SC(NH_2)_2 + 2Fe^{3+} = (SCN_2H_3)_2 + 2Fe^{2+} + 2H^+ \tag{5}$$

$$(SCN_2H_3)_2 = SC(NH_2)_2 + NH_2CN + S \tag{6}$$
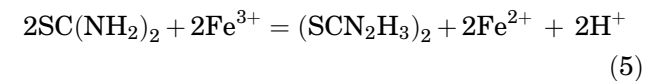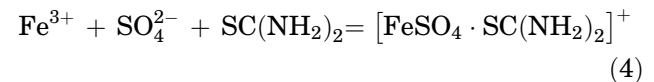
The maximum dissolution of Au and Pd was found to be 68% and 7.1%, respectively, when the oxidant concentration was 5 g/L, whereas the Ag dissolution was 1.6%. It was observed that the trends with respect to silver dissolution in aqueous thiourea solutions in presence of H_2SO_4 (0.25 M to 4 M) and $Fe_2(SO_4)_3$ oxidant (0 g/L to 7.5 g/L) exhibited quite similar profiles (Figs. 1 and 2). This observation is

probably related to formation of an insoluble silver–thiourea complex and silver sulfide (Ag_2S) under the oxidation conditions based on Eqs. 4–6:[19,25]

$$2Ag + \left[FeSO_4 \cdot SC(NH_2)_2\right]^+$$
$$= \left[Ag_2SO_4 \cdot SC(NH_2)_2\right]^+ + Fe^{2+} \tag{7}$$

$$2Ag + S = Ag_2S \tag{8}$$

Formation of metal–thiourea complexes can be attributed to the variations in the pH and redox potential (Eh) of the thiourea solutions with the addition of oxidant, as shown in Supplementary Fig. S2. It can be seen from Figs. 2 and S2 that the high redox potential and acidity of the solution led to an increase of the Au and Pd leaching, in contrast to a decrease in the leaching of Ag. It appears that optimization of the oxidant concentration during the thiourea leaching process is the main challenge to avoid thiourea loss/oxidation, because the dissolution of precious metals was strongly dependent on the oxidant concentration.

Effect of Thiourea Concentration

To study the effect of the thiourea concentration on the dissolution of precious metals from the residue sample, leaching experiments were conducted using 1.25 g/L to 20 g/L thiourea under the constant optimized conditions based on the studies described above. The dissolution efficiency of the precious metals increased drastically with increase of the thiourea concentration from 1.25 g/L to 12.5 g/L, then remained nearly unchanged on further increase of the thiourea concentration up to 20 g/L, as illustrated in Fig. 3. The maximum dissolution efficiency of 91%, 81%, and 11.9% for Au, Ag, and Pd was achieved at thiourea concentration of 12.5 g/L due to the appropriate thiourea/$Fe_2(SO_4)_3$ molar ratio under this condition. Use of appropriate concentrations of thiourea and formamidine disulfide results in an increase in the leaching of precious metals, which can be expressed as follows:[17–19,21,26]
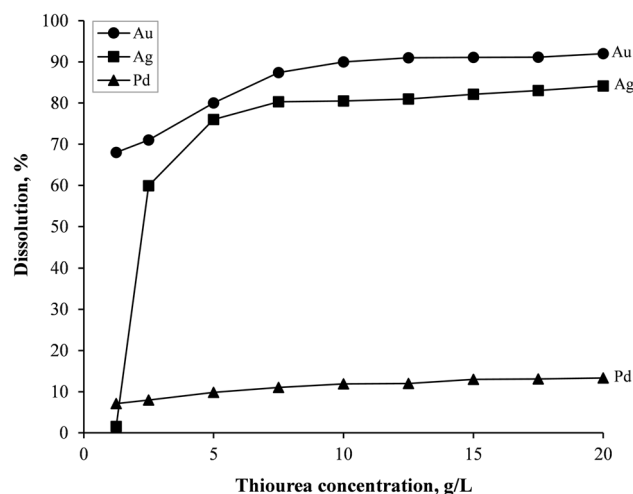
$$2Au + 2SC(NH_2)_2 + (SCN_2H_3)_2 + 2H^+$$
$$= 2Au\left[SC(NH_2)_2\right]_2^+ \tag{9}$$

$$2Ag + 2SC(NH_2)_2 + 2(SCN_2H_3)_2 + 4H^+$$
$$= 2Ag\left[SC(NH_2)_2\right]_3^+ \tag{10}$$

$$Ag_2S + 6SC(NH_2)_2 + 2H^+ = 2Ag\left[SC(NH_2)_2\right]_3^+ + H_2S \tag{11}$$

$$2Pd + 4SC(NH_2)_2 + 2(SCN_2H_3)_2 + 4H^+$$
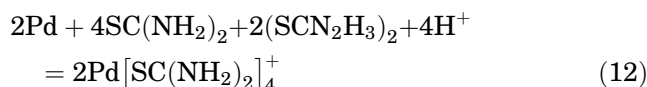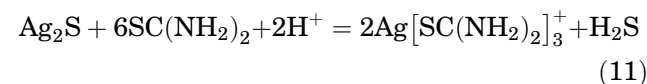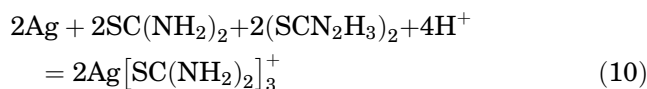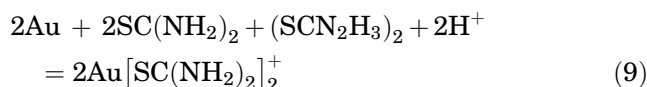$$= 2Pd\left[SC(NH_2)_2\right]_4^+ \tag{12}$$

Fig. 3. Dissolution of precious metals in acidic solution as function of thiourea concentration.

These results indicate that the formamidine disulfide $(SCN_2H_3)_2$ produced can be beneficial to the efficiency of leaching of precious metals under precisely optimized leaching conditions. It is noteworthy that, with addition of thiourea, the pH of the leaching medium does not change remarkably, whereas the redox potential in the medium falls from 0.67 V to 0.43 V (Supplementary Fig. S3). The variations of the redox potential with addition of thiourea and oxidant show completely opposite trends, as seen in Figs. S2 and S3, which is probably related to oxidation of thiourea to form a ferric–thiourea complex and formamidine disulfide, respectively.

The experimental procedure described above was also used to determine the optimal values of other parameters, particularly the leaching temperature and leaching time (Supplementary Figs. S4 and S5, respectively). The optimum leaching conditions determined are summarized in Supplementary Table SII.

Assessment of Leaching Behavior of Precious and Base Metals from Different WPCB Samples

WPCB samples obtained after incineration and HPOL were treated with acidic thiourea solutions under nonoptimized and optimized conditions, respectively. The leaching conditions and results for the dissolution of precious and base metals are compared in Supplementary Table SII and Fig. S6, respectively. It can be seen from Fig. S6 that, under nonoptimized leaching conditions, the dissolution efficiencies of Au, Ag, and Pd into the thiourea solution from the WPCB ash sample after incineration were 4.7%, 0.1%, and 2.6%, whereas values of 17.3%, 45.5%, and 3.1%, respectively, were obtained by dissolution from the WPCB residue sample after

HPOL. For base metals, the percentage of leached Cu, Zn, Al, Ni, and Ca was 80.0%, 98.0%, 44.2%, 48.4%, and 64.4% from the ash sample, but 11.1%, 3.1%, 1.5%, 29.7%, and 38.5% from the residue sample, respectively. Under the optimized conditions, the vast majority of gold (100%) and silver (> 81%) were dissolved in the acidic thiourea solution, while the maximum dissolution of Pd was 13%. The leaching efficiencies of base metals except Zn and Ni were slightly higher than when dissolved in thiourea solution under nonoptimized conditions. These results may be related to their complexation with thiourea under nonoptimized and optimized conditions, respectively (Supplementary Fig. S6 and Table SII). Note that sequential application of the two pretreatment processes, viz. incineration and HPOL for removal of impurities, followed by thiourea leaching under the optimized conditions, resulted in a significant increase of the efficiency of leaching of precious metals from the WPCB sample.

The results presented herein indicate that thiourea leaching under the optimized conditions was several times faster and could take place under ambient conditions, compared with the conventional cyanidation process that is carried out under alkaline conditions (pH 9.5 to 12) at temperature between 60°C and 95°C during 24 h in presence of oxygen.[11,19,21] These results suggest that precious metals, especially gold and silver, present in WPCB ash samples can be effectively recovered using such a sequential leaching procedure.

CONCLUSION

A combined hydrometallurgical method consisting of HPOL and thiourea leaching for recovery of precious and base metals from a WPCB ash sample is discussed. The results obtained can be summarized as follows:

- Some base metals present in the WPCB ash sample were effectively extracted via HPOL with dilute H_2SO_4 solution, including recovery of Cu, Zn, Ni, Co, Al, and Fe of 99.3%, 96.0%, 82.7%, 84.0%, 81.6%, and 63.2%, respectively.
- The optimized thiourea leaching process dissolved 100% Au, 81% Ag, and 13% Pd from the WPCB residue sample after HPOL in acidic thiourea solution.
- Higher oxidant concentration played a vital role in leaching of Au and Pd, but had a deleterious effect on Ag leaching in thiourea solution.
- The efficiency of dissolution of precious metals strongly depended on the concentration of both thiourea and oxidant in the leaching medium.

ELECTRONIC SUPPLEMENTARY MATERIAL

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