Ammonium thiosulfate leaching of gold from electronic printed circuit boards – effect of solution copper concentration

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Abstract

This study investigates the effect of ammonium thiosulfate on the leaching of gold from the contacts of unpopulated cut electronic printed circuit boards (PCBs). Studies in the literature show ammonium thiosulfate to be a viable option in comparison to the commonly used but hazardous cyanide leaching route. However, the simultaneous dissolution of Cu interferes with the Au leaching reaction, often limiting the extraction to moderate levels. To optimize the system, an ammonium-thiosulfate system containing 0.5M ammonia, 0.5M ammonium thiosulfate, and Cu(II) sulfate at varying concentrations was studied as an alternative hydrometallurgical option for the recovery of gold from PCB. Tests were done with unpopulated standardized model PCBs (cut to 15 x 30mm pieces). Gold extraction of 47.3% was achieved after a 24-hour leaching experiment with a 0.02M copper background concentration. Further experiments focused using different initial background Cu concentrations (0M – 0.1M) to determine its effect on both gold and copper extractions. An initial Cu concentration of 0.045M resulted in the highest gold extraction, with 93.7% extraction after 6 hours of leaching. Further analysis of the data shows that the kinetic rate of gold leaching is correlated in a first-order dependence with the actual copper concentration in the solution, which increases with the concomitant dissolution of copper and gold from the PCBs. A lower threshold of 0.017M and an upper threshold of 0.15M copper in solution were determined, in between which gold extraction shows this first-order rate increase. The upper threshold is potentially linked to the onset of copper precipitation, which blinds the metal surfaces, slowing further leaching. The findings of this study suggest that in an industrial recovery operation of gold from waste PCB using the thiosulfate method, copper concentrations need to be carefully monitored, and the process should preferably operate with uncut or coarsely cut untreated boards to minimize exposure to copper circuits.

Keywords

leaching, gold, copper, printed circuit boards, thiosulfate

Introduction

Due to rapid advancements in electronic technology and its applications, there is an increase in the demand for new products resulting in an increasingly shorter life span of older models with much of this being disposed of as waste. The technology industry has been estimated to generate 53.6 million metric tonnes of waste electrical and electronic equipment (WEEE) globally per year (Forti et al., 2020). Consequently, the environmental burden due to this 'ecological baggage' has also increased alarmingly causing unsafe and improper waste management (Schwarzer et al., 2005). Printed circuit boards (PCB) make up an estimated 6% of the overall WEEE burden. There are a variety of recycling opportunities to lessen the waste burden; these especially target gold on PCB due to its relatively high value.

PCB contain a large variety of precious and base metals. Base metals, such as copper and tin are found underneath the protective coatings of the board, and precious metals, such as gold and silver are present on the surface of the board. On PCBs, gold is typically found in high concentrations, with some studies reporting figures as high as 903 g/t (Petter et al., 2014), while typical primary gold ores contain only between 10 to 90 g/t (Jeffrey et al., 2003; Arslan and Sayiner, 2018). Although there is a trend to use less precious metal in the manufacturing of PCBs, the waste stream still outmatches primary ores, of which the grades are decreasing, the mineralogy has become more complex, and which are much more difficult to mine.

There are many challenges to the processing of PCBs. Some of these challenges include their complexity and heterogeneity. Industrially, metal recovery of e-waste is carried out mainly via pyrometallurgical routes (Cui and Anderson, 2016), mostly by using PCBs as co-feed to a copper smelter. Although these routes do have disadvantages, mainly stemming from the large energy requirements for processing and the shipping of collected WEEE over long distances, the precious metals can be recovered separately from the produced copper through the processing of anode slimes from electrorefining. The overall recovery of gold through this route from the original feed is unclear as there will be gold losses to flue dust, slag, or incorporation into the cathode copper product.

Active research in the past 20 years has been carried out to find direct hydrometallurgical routes as a viable alternative for operation at a small scale. Hydrometallurgy is perceived to have a lower environmental impact and is easier to manage (Cui and Zhang, 2008). The ammonium thiosulfate system is one such hydrometallurgical option. The system is non-toxic as opposed to its competitor, the cyanide system, and has been shown to extract gold at much faster rates in the processing of primary ores (Sullivan and Kohl, 1997; Aylmore and Muir, 2001; Jeffrey et al., 2001).

The gold-thiosulfate complex is formed via two reactions in the ammonium thiosulfate system as per Equations [1] and [2]. Initially, the gold-ammonia complex is formed on the gold surface [1] with cupric acting as the oxidant, before converting into the gold-thiosulfate complex [2]. The overall dissolution reaction of gold in an ammonium thiosulfate solution in the presence of cupric ions is represented in Equation [3] (Xia et al., 2003).

$$\begin{aligned} &Cu(NH_3)_4^{2+} + Au + 3S_2O_3^{2-} \rightarrow \\ &Au(NH_3)_2^{+} + Cu(S_2O_3)_3^{5-} + 2NH_3 \end{aligned} \qquad [1]$$

$$Au(NH_3)_2^{+} + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + 2NH_3 \qquad [2]$$

$$\begin{aligned} &Au + Cu(NH_3)_4^{2+} + 5S_2O_3^{2-} \rightarrow \\ &Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 4NH_3 \end{aligned} \qquad [3]$$

The heterogeneous redox reaction between oxygen and copper is shown in Equation [4] (Fleming et al., 2003). Here the cupric ion (Cu^{2+}) concentration eventually reaches steady state and at this point the rate of reduction of the cupric ions through gold dissolution is matched by the rate of oxidation of the cuprous (Cu^{+}) ions by oxygen. Thus, the cuprous ions serve as a redox catalyst in the leaching process and are not consumed.

$$\begin{aligned} &4Cu(S_2O_3)_3^{5-} + O_2 + 16NH_3 + 2H_2O \rightarrow \\ &4Cu(NH_3)_4^{2+} + 12S_2O_3^{2-} + 4OH^{-} \end{aligned} \qquad [4]$$

The overall redox reaction forming the gold-thiosulfate complex is shown in Equation [5]. The cupric-amine complex and the ammonia within the system are recycled and therefore need not appear in the overall Equation [5] (Xia et al., 2003).

$$4Au + 8S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 4Au(S_2O_3)_2{}^{3-} + 4OH^{-} \qquad [5]$$

However, cupric is also known to interfere in this reaction by slowly catalysing the oxidation of thiosulfate to higher oxidation products, such as tetrathionate as per Equation [6], thus effectively destroying the leaching reagent (Fleming et al., 2003):

$$2\,S_2O_3^{2-} + \ 2\,Cu(NH_3)_4^{2+} \rightarrow S_4O_6{}^{2-} + 2\,Cu(NH_3)_2^{+} + 4\,NH_3 \qquad [6]$$

The leaching of high-grade gold ore by ammoniacal solutions of ammonium thiosulfate was investigated by Abruzzese et al. (1995). They found the dissolution was favourable at ambient temperature, moderate copper concentration (0.1M) at elevated concentrations of $(NH_4)_2S_2O_3$ (2M) and NH_3 (4M). The system has also been used for the leaching of gold from waste cell phone PCBs (Ha et al., 2014; Tripathy et al., 2012). In these studies, initial copper concentrations were varied, being from 0 to 0.048M, with increasing initial Cu concentrations resulting in an increased initial rate of leaching, but in all cases the Au extraction eventually levelled around 30%. Substantially better gold dissolution was achieved by leaching from whole boards compared to shredded boards, postulated to be due to the interference of copper, which preferentially dissolved from the shredded material.

A more systematic study of the effect of the Cu concentration on Au extraction as it increases in the course of PCB leaching remains outstanding. In the present study, the role of copper in the thiosulfate leaching of gold was investigated further with the custom-made cut PCBs.

Materials and methods

Materials

Printed circuit boards are complex and heterogeneous and require thorough analysis before being incorporated into experiments. A considerable drawback of studies with waste PCBs is that the gold grade is highly variable from board to board, and it is therefore nearly impossible to determine a consistent head grade for leaching experiments. It was therefore decided to conduct all experiments with a consistent design of the boards of the same composition, dimension and framework, manufactured from the same type of materials, thus ensuring that accurate comparison and reproducibility of the experiments could be accomplished. The PCBs used in all experiments were manufactured custom-made by Trax Interconnect (Pty) Ltd., based in Cape Town, South Africa. The dimension of the boards was 142 x 105 x 1.55 mm. Figure 1 shows both the top-side and the bottom-side of the model board. For the purposes of this paper, only unpopulated boards, as in Figure 1, were used. The single boards were cut into 15 x 30 mm pieces using a bandsaw, to allow a defined and uniform geometry and surface. All pieces of one PCB were used in each leaching trial to ensure a consistent feed throughout.

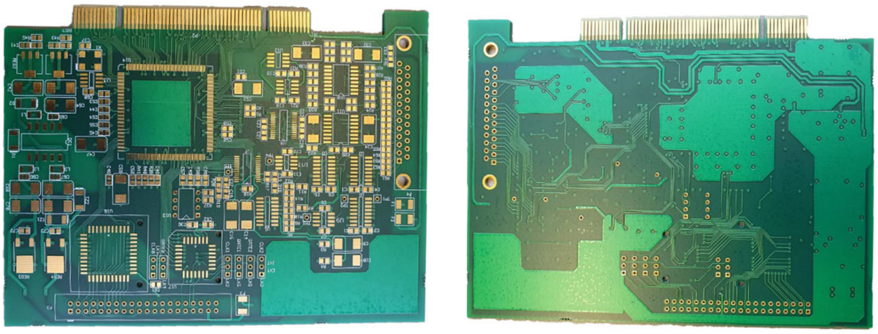

(a)
(b)

Figure 1—(a) Top-side of the PCB (b) Bottom-side of the PCB

The PCBs are comprised of four distinct layers, which aid in the function of the board. The average weight per board was 52.24 g (Prestele, 2020). The four layers constitute the unpopulated PCB with an outer layer on the top and bottom of the PCB covered by the solder mask. The solder mask is a combination of solvents and polymers that make up the ink mask, which has the typical green colour shown in Figure 1. On the inside of the solder mask layer lies a copper layer. A large amount of the copper is found within the inner PCB layers whilst the remaining copper is within the top and bottom layers, as per Table I.

The gold-coloured areas in Figure 1 indicate the layers of gold and nickel that have been plated onto the board as contacts. These contacts are copper not covered by the solder mask which is electroplated with nickel and the nickel is subsequently electroplated with gold in the manufacturing process. The contacts are thus exposed to allow any interaction between the gold and the leach solution.

The mass of gold on the board was quantified utilizing the thickness of the gold plating on the board as well as the area of the gold-plated contacts on the top and bottom layers. The gold plating thickness was 0.07 µm as provided by the manufacturer. Incorporating the gold density, in addition to the gold area and thickness, produced the mass of gold for a single board. Table II contains both the area and mass of gold on the top and bottom outer layers.

The mass of gold was thus determined as 4.22 mg per board, which was taken as the initial gold concentration of the samples (this value was verified through acid digestion of the PCB followed by ICP). The mass of copper present on a single board was determined to be 11.77 g (Table I).

Apparatus

The equipment utilized in the leaching and dissolution experimentation consisted of a set of 3 jacketed 1L batch stirred tank reactors (BSTR) for the PCB leaching experiments (Figure 2). Each BSTR was fitted with an overhead stirrer running a 2-blade metal stirrer at 400 rpm for agitation. Temperature (25 °C) was controlled by circulating water between the reactor jacket and a water bath. In addition, air as an oxidant was bubbled through the reactor at a rate of 70 mL/min, monitored by the flow meter shown on the right of Figure 2b).

Table I

Copper distribution in mass between each layer of a single PCB

	Cu mass (g)	Cu distribution (%)
Outer top layer	1.29	11
Inner top layer	2.94	25
Inner bottom layer	5.19	44
Outer bottom layer	2.11	18
Coating	0.24	2
Total	11.77	100

Table II

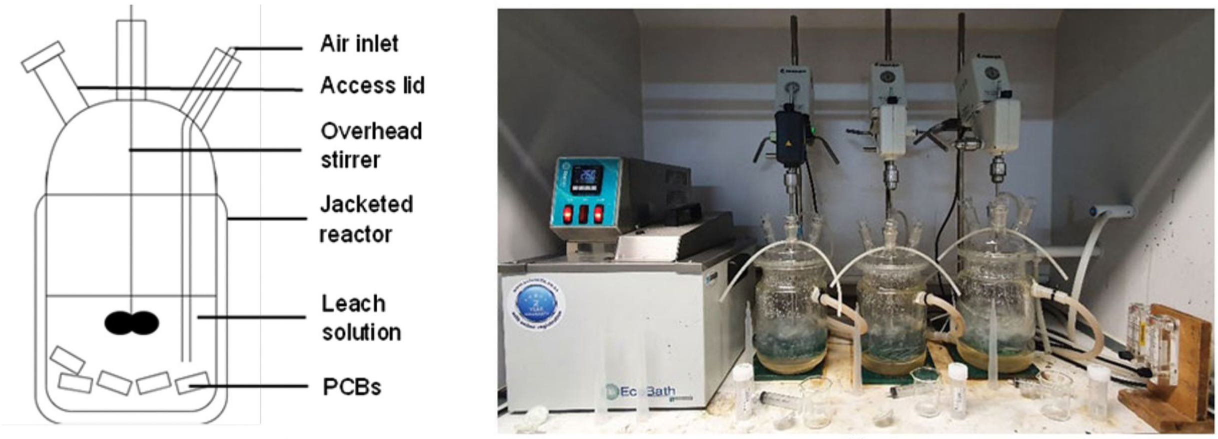
Gold distribution in area and mass on the top and bottom layer of a single PCB

	Area (m^2)	Au mass (mg)	Gold distribution (%)
Top layer	2.33×10^{-3}	3.15	74.8
Bottom layer	7.87×10^{-4}	1.06	25.2
Total	3.12×10^{-3}	4.22	100

PCB leaching experiments

In the leaching experiments, ammonia and ammonium thiosulfate were used and copper(II) sulfate pentahydrate was added in small amounts to catalyse the reaction. A standard solution consisting of 0.5M ammonium thiosulfate, 0.5M ammonia, and 0.02M copper(II) sulfate pentahydrate was prepared for an initial 24-hour leaching experiment. All chemicals were supplied by Merck. The concentration of the added copper(II) sulfate pentahydrate was varied between 0.008M and 0.1M in later experiments, as reflected in Table III. Furthermore, 500 mL of the lixiviant solution was used in each reactor.

Sampling of 6 mL leachate through a 0.2 µm nylon syringe filter occurred at 15-minute intervals for the first hour, 30-minute intervals in the second hour and every hour up until the 6-hour mark. The reactors were left to run overnight with samples taken



a) b)

Figure 2—a) Schematic of the batch stirred tank reactor (BSTR); b) Reactor set-up with a heating water bath, 3 BSTRS and air supply

Table III

Lixiviants and conditions for ammonia-ammonium thiosulfate leaching

Lixiviants/Conditions	Units	Values
$(NH_4)_2S_2O_3$ concentration	M	0.5
$CuSO_4.5H_2O$ concentration	M	0.008/ 0.02/ 0.045/ 0.1
NH_3 concentration	M	0.5
pH	–	9–10
Temperature	°C	25
Time	Hours (h)	6/24
Stirring speed	rpm	400
Volume	mL	500
Compressed air flowrate	L/min	0.07
Solid to liquid ratio	–	1:10

again every hour from the 21-hour mark up until 24 hours. The solution samples were further diluted at a 1:1 ratio using a fresh solution of 0.5M ammonium thiosulfate and 0.5M ammonia before being refrigerated until analysis. Refrigeration was found to be essential to stabilize the solution over sufficiently long periods prior to analysis. To ensure a constant 500 mL volume in the reactor, 6 mL of the initial standard solution consisting of ammonium thiosulfate, ammonia, and copper(II) sulfate pentahydrate was added back into the reactor at each sampling time. The pH was determined at the start and the end of the 24-hour experiment. Solutions samples were then analysed for both gold and copper using inductively coupled plasma atomic emission spectroscopy (ICP-AES). At the end of each leach experiment the solutions were filtered using a 0.2 µm micro filter to recover any residues. Experimental gold extractions and recoveries were determined based on the initial gold and copper on the board, in relation to the extracted metal in the pregnant leaching solution.

The 6-hour experiments followed a similar procedure to the 24-hour experiment. Four tests were run at the various copper concentrations shown in Table III. Sampling occurred at the same intervals as the 24-hour experiment up until 6 hours, at which point the experiment was complete. In both the 24-hour and 6-hour experiments, one board, cut into 15 x 30 mm pieces, was leached in each reactor, resulting in a solid to liquid ratio of approximately 1:10. The blade of the overhead stirrer was immersed into the solution allowing for it to be slightly above the cut PCB pieces whilst at the same time allowing continuous mixing of the solution. However, the PCB board pieces itself were not brought into suspension by this. Once the experiment was completed, the solution and PCB were separated via a vacuum filter using a compressor, a Buchner funnel, and filter paper. The mass of the residual PCB pieces was recorded once they were completed dried.

Results and discussion

Gold and copper extraction over 24 hours

Figure 3 depicts the gold extraction over 24 hours for PCB dissolution using the ammonia-ammonium thiosulfate system in the presence of 0.5M ammonia and ammonium thiosulfate and 0.02M background copper(II) sulfate. Additional conditions were stated in Table III. There was an increase in extraction up to 47.9% at 6 hours after an initial delay. Further sampling at 21 hours suggests that the concentrations exhibited only a slight increase and thereafter started to decrease. The experiment reached a maximum amount of gold in solution at 52% at 21 hours, indicating that only half of the gold had been extracted from the PCB. Between 6 and 21 hours, there was a slower increase in gold extraction and at 24 hours the gold in solution had declined to an equivalent of 47% extraction. Analysis of the residue confirmed approximately 50% of the gold had dissolved.

The dissolution rate of the PCB leaching experiment during the rapid phase between 4 and 6 hours was 0.77 mg/h. Additional copper leached from the PCB is likely to have hindered the gold leaching process as copper is known to compete with gold in forming a thiosulfate complex (Ha et al., 2014). The decline in the concentration after 21 hours of leaching was unexpected and is thought to be due to thiosulfate decomposition within the system, therefore hindering gold from staying in solution. This is in line

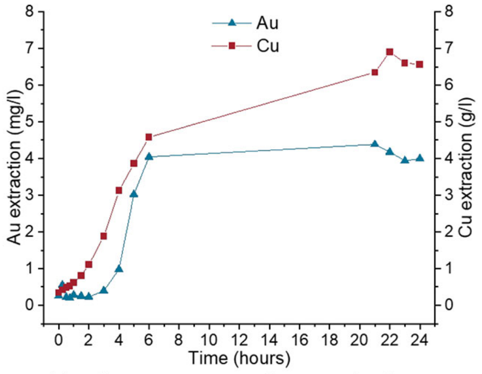


Figure 3—Gold and copper extraction from PCB leaching over 24 hours

with observations made by Senanayake (2004) and Birich (2020), who found that over time gold losses increase due to the oxidation of thiosulfate into polythionates.

Figure 3 also shows the dissolution of copper in parallel with that of gold expressed in terms of measured solution concentrations. This clearly indicates that copper is released much more rapidly than gold and at much higher concentrations. The rapid leaching of copper, especially in the early stages of the experiment, may explain the initial delay in gold extraction. Furthermore, the PCBs contained other metals such as nickel and zinc, which also compete with gold ions for complexation with the thiosulfate ion. It was also noted that around 21 hours, the PCB experiment appeared to have attained its highest gold extraction. The increase in gold extraction between 6 and 21 hours for the PCB leaching experiment were 47.9% to 52%, respectively. Although the maximum extraction was at 21 hours, the increase between 6 and 21 hours was marginal and this experiment could have been terminated at 6 hours. The trend for the PCB leach curve could also indicate that a higher peak might have been reached between 6 and 21 hours. Nonetheless, it was assumed that maximum gold extraction in solution was achieved after 6 hours at the conditions of 0.5M NH_3, 0.5M $(NH_4)_2S_2O_3$, and 0.02M background $CuSO_4.5H_2O$.

The decline in extractions after 21 hours may be due to the consumption of thiosulfate as well as the loss of ammonia in the solution. Consumption of thiosulfate is attributed to the ion being meta-stable in addition to potentially becoming oxidized to tetrathionate by cupric (Equation [6]). Both Molleman and Dreisinger (2002) and Xu et al. (2017) reported that thiosulfate consumption was a cause for lower gold extractions over time. Loss of ammonia due to evaporation and complexation with cupric in solution could also be a contributor to low gold extractions, as this disrupts the ratio of thiosulfate to ammonia, thereby inhibiting the regeneration of the cuprous ion and causing a decrease in pH due to a shift of the ammonium/ammonia buffer in solution (Equation (7), Xia et al., 2003).

$$NH_4^+ = NH_3 + H^+ \qquad [7]$$

Indeed, the pH of the solution decreased from the initial 9.51 to 9.16 for PCB leaching over 24 hours. Thus, it is possible that low gold extractions can be attributed to ammonia loss in the PCB leaching experiment.

Gold and copper extraction over 6 hours

A further set of experiments investigated the effect of background copper(II) sulfate concentration on gold extraction in the PCB leaching experiment. Four different background copper concentrations (0.008M, 0.02M, 0.045M, and 0.1 M) were introduced into the system and the leaching experiment was conducted over 6 hours. Additionally, a 0M background copper concentration test was introduced to determine the effect on the gold extraction rate with the copper catalyst being extracted from the PCB material only. The results are demonstrated in Figure 4.

The lowest extraction after 6 hours was achieved in the 0M copper experiment. It was clear that an initial amount of copper in the solution was necessary to initiate the gold dissolution reaction via the formation of the Cu(II) amine complexes. With the absence of background copper in the solution, the gold oxidation reaction needed to be facilitated through the direct reduction of oxygen, which has poor kinetics, whereas in the presence of copper the cupric/cuprous couple can act as a redox mediator. In the system without initial copper there will be a lag until sufficient copper has dissolved from the PCB to allow the cupric/cuprous couple to become active and act as the redox mediator. This was confirmed by the low gold extraction of a mere 1.66% after 6 hours for the 0M background copper experiment (Table IV). Gold extraction was found to increase up to 93.7% after 6 hours with the addition of 0.045M background copper. This value was much higher than the 25% gold extraction at 0.04M background copper in the copper leaching experiments conducted by Tripathy et al. (2012) in 0.1M ammonium thiosulfate after 6 hours. The authors attributed the low extraction value of 25% to the slow agitation rate of 250 rpm used in their investigation. Although a higher agitation rate was used in the present study (400 rpm), their study used shredded material, which was easier to suspend. The lower gold extraction reported by these researchers may need to be attributed to the lower thiosulfate background or stronger interference from copper dissolving from the material.

It is interesting to note that gold dissolution appears to reach an equilibrium at the 0.1M and 0M background copper concentrations after 6 hours, whereas the other reactions are continuing. A background copper concentration of 0.1M was expected to have a similar gold extraction to 0.045M, similar to the results reported in Abruzzese et al. (1995) at ambient temperature and 4M NH3; however, this was not demonstrated by the present experiments. Therefore, it can be said that at very high background copper concentrations, the gold extraction becomes independent of, or even impeded by the copper concentration in the context of PCB leaching. These results were consistent with those reported by Ha et al. (2010) who found that after 2 hours at concentrations higher

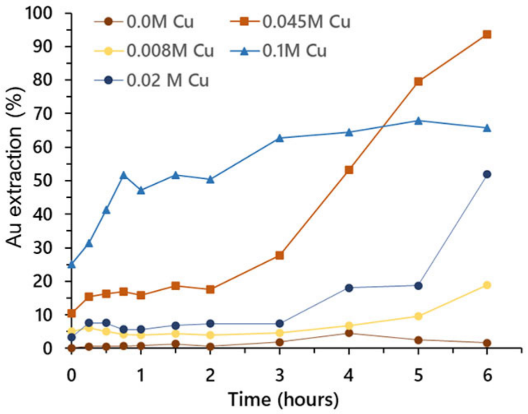


Figure 4—Gold extraction from PCB leaching at various initial copper concentrations (0M, 0.008M, 0.02M, 0.045M, and 0.1M)

Table IV

Gold extraction rates determined for the rapid leaching phase in each of the leach experiments as well as the average copper concentration in solution during these phases

Initial Cu concentration (M)	Au average extraction rate (%/h)	Average Cu concentration (M)
0.008	6.0	0.036
0.02	13.4	0.065
0.045	25.9	0.113
0.1	35.7	0.137
24-hour leach	15.4	0.073

than 0.015M background copper, the ultimate leaching of gold remained around 30% gold extraction. There was a significant difference in gold extraction between 0.02M and 0.045M copper from the start of the experiment up to 2 hours. After 2 hours, gold extraction in the 0.045M copper experiment occurred at a much faster rate than in the 0.02M copper experiment. This was similar to the results reported by Tripathi et al. (2012), where the gold extraction increased at a faster rate from 10% to 30% after 8 hours. Even lower gold extractions were observed for the 0.008M copper experiment due to the limited amount of copper in the system in comparison to the other experiments.

Analysing the effect of copper concentration on the gold leaching rate

Given the gold extraction results from Figure 4, there possibly is a threshold background copper concentration required for the reaction to proceed. Concentrations below this threshold result in sluggish kinetics, and thus minimal gold recovery. At the same time, there may be an upper threshold beyond which excessive thiosulfate degradation takes place. The previous study (Ha et al. , 2010) found that at background copper concentrations between 0.032M and 0.048M similar gold extractions of around 30% - 35% after 8 hours of leaching were achieved. They noted that at 0.005M, gold extraction was excessively slow, attaining below 5% gold extraction with a 0.2M thiosulfate concentration. The same study also confirmed that at a background copper concentration above 0.015M, no enhancing effect on gold extraction was observed. This was attributed to high cupric-ammonia complex concentrations causing higher losses of thiosulfate through its degradation into tetrathionate.

However, none of these studies measured the actual copper concentration in the solution, considering that in a cupric ammonia solution a considerable amount of metallic copper is dissolved simultaneously to Au from the PCB as per Equation [8]:

$$Cu + Cu(NH_3)_4^{2+} \rightarrow 2\,Cu(NH_3)_2^{+} \qquad [8]$$

In this sense, Figure 5 shows the total copper concentration accumulating in the solution as leaching progresses over the 6 hours at the different initial copper concentrations. In all experiments, this concentration increases steadily, quite independent of the gold leaching shown in Figure 4. In all experiments the total copper concentration increases 2- to 3-fold for the 6 hours. It must also be understood that the molar concentration levels of copper in solution (0.005M to 0.22M) exceed the maximum molar concentration of gold in the present case (0.043mM) by 2–4 orders of magnitude and therefore entirely dominate the system.

Comparing Figures 4 and 5 allows one to draw some conclusions about the effect of copper solution concentration on the kinetics of gold extraction. It appears that a rapid increase in the dissolution of copper is linked to a certain background concentration of copper in solution. Thus, for example, the onset of more rapid leaching in the 0.02M experiment after 3 hours coincides with a copper concentration of 0.04M.

A possible correlation between gold leaching kinetics and actual copper concentration in solution was therefore investigated further, as illustrated in Figure 6. Here the phases during which gold leached most rapidly in the course of the various experiments were analysed by linear regression in order to determine an average leaching kinetic rate in each case. The results are shown in Table IV.

Also included in Table IV are the average copper concentrations determined in each experiment during the rapid leach phase. This analysis was also done for the rapid leach phase in the 24-hour experiment between 3 and 6 hours (Figure 3). From this data, the correlation between Au leaching rate and copper concentration is plotted in Figure 7.

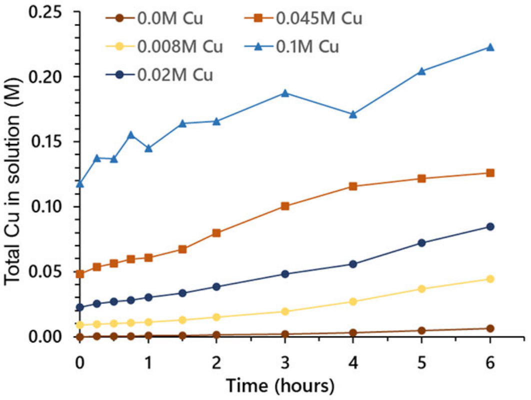


Figure 5—Total copper in solution from PCB leaching at various initial copper concentrations (0M, 0.008M, 0.02M, 0.045M, and 0.1M)

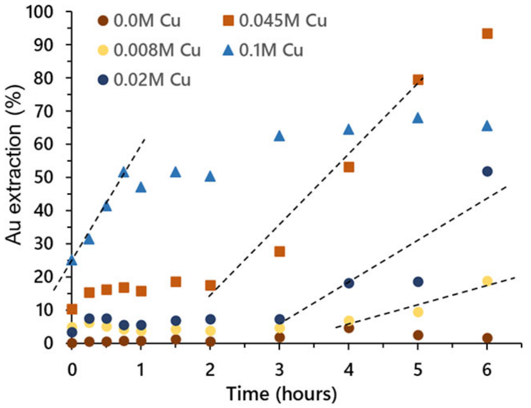


Figure 6—Gold extraction data at various initial copper concentrations (0M, 0.008M, 0.02M, 0.045M, and 0.1M) with the dashed lines marking phases of rapid increases used in the linear regression analysis

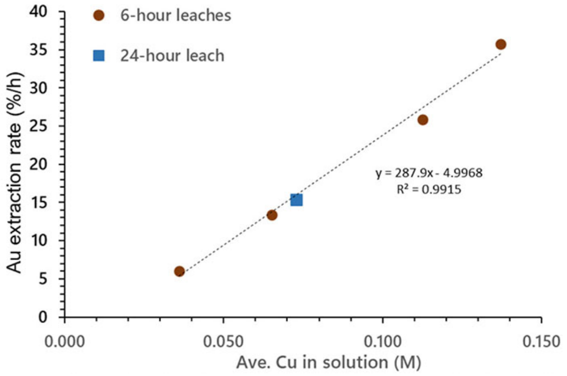


Figure 7—Gold average extraction rates plotted again average copper concentration in the leach solution for the rapid leach phases in various 6-hour leach experiments as well as the initial 24-hour run

The data suggests a linear correlation of the Au extraction rate to the copper concentration within the context of the present experiment (1 PCB with 4.22 mg of gold in 0.5 L of a solution 0.5M in $(NH_4)_2S_2O_3$ and 0.5M in NH_3), i.e., the reaction is first order with respect to Cu(II) in solution.

It is now of interest to evaluate this result in the context of the leaching thresholds mentioned earlier. Taking the linear correlation shown in Figure 4, the line would intersect the x-axis at a copper concentration of 0.017M, i.e., gold leaching would become inhibited at concentrations below this level. This is plausible when looking at the 0M and 0.008M gold and copper curves in Figures 4 and 5, respectively. Gold leaching accelerates for the 0.008M curve only once the copper concentration in solution exceeds 0.02M after about 3.5 hours, but the 0M copper curve stays well below this threshold throughout, and consequently gold leaching never accelerates in this experiment.

However, there also appears to be a maximum threshold beyond which gold leaching becomes inhibited. This is evident in both the 0.1M copper curve beyond the first hour, where the copper concentration exceeds 0.15M, and in the 24-hour leach experiment, where inhibition can be observed during the overnight period (between 6 and 21 hours) and the copper concentration exceeds 0.12M (Figure 6). Copper ions form strong complexes with both ammonia and the thiosulfate ion as was shown in Equations [1] to [3]. As Senanayake (2004) has shown, the $Cu(NH_3)_4^{2+}$ complex strongly prevails in the region pH 8-10 over other complexes at high ratios of ammonia to copper(II) concentrations (10^5) and mixed NH_3 and OH-complexes at lower excess ratios.

With an increasing Cu(II) concentration in solution, an increasing shift away from the dominance of $Cu(NH_3)_4^{2+}$ occurs, which is the complex that drives Equations [1] to [3]. Likewise, the stability regions also of the $Au\text{-}NH_3$ and $Au\text{-}S_2O_3$ complexes are shifted, resulting in decreased availability of total ammonia. In the current experiments the total initial ammonia/ammonium concentration was 1.5M and thus only around 10 times higher than the observed upper threshold copper concentration of 0.15M. Nonetheless, the abrupt cessation of gold leaching at the upper threshold points to a sudden onset of other mechanisms inhibiting the reaction, such as precipitation of CuS on the surface of the PCB, thus restricting further gold leaching. This is supported by the erratic nature of the copper in solution curve for the 0.1M copper experiment in Figure 6, once the 0.15M threshold has been exceeded.

Conclusions

This study investigated the ammonium-thiosulfate system for the leaching of gold from PCB. It was found that the ammonium-thiosulfate system was promising for PCB leaching experiments, which achieved gold extractions of as much as 93.7% using 0.045M background copper.

However, the $Cu\text{-}NH_3\text{-}S_2O_3$-system is also conducive to the leaching of copper directly from PCBs in parallel with gold, thus resulting in a continued increase of the background copper concentration. Closer analysis of the data has shown that the rate of gold dissolution is in fact increased with copper concentrations in a first-order dependence up to 0.15M, but that once this threshold is exceeded, both gold and copper dissolution become more inhibited and erratic. This inhibition is likely caused by the onset of copper precipitation on the surface of the PCB rather than the gradual decomposition of thiosulfate.

In summary, the ammonium-thiosulfate system can be effective in removing gold from PCBs in solution, providing that the background concentration of copper is carefully managed to stay well below the potential inhibition threshold. In the ideal case, this should occur with the copper on the board minimally exposed during gold leaching, i.e., the feed should be boards that have been de-populated but not been size reduced, or it should be done on boards/residues where the copper has already been completely leached before thiosulfate leaching.

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