Investigating early-stage process flow and reactor sequencing to maximise gold extraction in the thiosulphate leaching of waste printed circuit boards

M.G. Gonte[1], T. Moyo-Mahlangu[1], and J. Petersen[2]

[1]Pennsylvania State University, Pennsylvania, USA
[2]University of Cape Town, Cape Town, South Africa

A conventional leaching sequence when using the thiosulphate system to leach gold (Au) from waste printed circuit boards involves physical pre-treatment, followed by base metal extraction, ending with Au leaching. Despite this convention, it is expected that efficiency of Au extraction will be affected by the sequence in which metals are leached, with the possibility of reducing Au losses and increasing extraction when the sequence is changed. In this study, four leaching sequences were investigated to evaluate Au extraction, Au loss and base metal (BM) co-extraction from PCBs. Sequences A and B involved Au leaching of cut (A) and shredded (B) PCBs using 0.5 M ammonium thiosulphate $(NH_4)_2S_2O_3$) in the presence of 0.04 M copper sulphate ($CuSO_4$) and 1 M ammonia (NH_3), at a solid/liquid ratio of 100 g/L at 25°C. In sequences C and D, BMs were extracted from cut (C) and shredded (D) PCBs prior to Au leaching. 4 M of NH_3 solutions were used to leach BM at 67 g/L solid/liquid ratio, while the subsequent Au leach was done in solution conditions similar to those used in sequences A and B. The results showed that sequence A had the highest Au extraction of 97% accompanied by 28% and 97% co-extraction of Cu & Ni, respectively. Sequence B, C, and D each achieved an overall Au extraction of 69%, 61% and 47%, respectively. This study recommends Sequence A (with minimal size reduction) to leach Au alongside Ni, prior to copper leaching.

Keywords: Waste electrical and electronic equipment, e-waste, printed circuit boards, ammonium thiosulphate leaching, gold extraction, reactor sequences (order/flow of the leaching processes)

INTRODUCTION

According to the UN's Global Electronic waste (E-waste) Monitor 2020, a record 53.6 million metric tons (Mt) of waste electronic and electrical equipment (WEEE) was generated worldwide in 2019, an increase of 21% in just five years (Forti *et al*., 2020). The analysis also projects that by 2030, the amount of e-waste will globally reach 74.7 Mt, nearly doubling in just 16 years (Forti *et al*., 2020). This makes e-waste the fastest-growing waste stream in the world, driven mostly by rising electric and electronic equipment use and consumption, short life cycles, and limited repair options. The increasing volume and high content of both hazardous and valuable materials contained within e-waste, presents an ongoing environmental challenge as well as a business opportunity (Widmer *et al*., 2005). Examples of harmful material include heavy metals and plastics for instance the brominated organic flame retardants (BFRs) (Hossain *et al*., 2015). E-waste contains 3–5% waste PCBs (Cui and Anderson, 2016; Kaya, 2019). These are essential structures in electronic gadgets and the key component of the WEEE recycling process. While the metal traces and planes for the circuitry are typically made of Copper (Cu), the common dielectric material used for PCBs is a flame-resistant composite of woven fiberglass fabric and epoxy resin known as FR-4 (Cadence®, 2023; Chirume, 2019).

Waste PCBs also constitute high value metallic elements such as gold (Au), palladium (Pd), and hazardous elements like lead (Pb) and arsenic (As) as well as other metals such as nickel (Ni), copper (Cu), aluminium (Al), iron (Fe), and zinc (Zn) (Jeon *et al.*, 2020; Moyo *et al.*, 2020; Petter *et al.*, 2013). Au is typically found as the outermost layer (Jeon *et al.*, 2020; Moyo *et al.*, 2020; Petter *et al.*, 2013). Akcil *et al.*, (2015), Jeon *et al.*, (2020), Mishra *et al.*, (2021), further elaborate that the concentrations of precious metals (PMs), especially Au, Ag and Pd, are much higher in waste PCBs than in their respective primary resources. Therefore, although managing the environmental risks of e-waste disposal is important, the economic driver for developing metal recovery methodologies from waste PCBs is the high content of both base metals (BMs) and PMs. In developed countries the more successful recycling of these metals uses integrated pyrometallurgical and hydrometallurgical technologies. These hybrid technologies require a significant capital injection and the installation of gas scrubbers which prevent the emission of toxic flue gases. The extraction of Au through the hydrometallurgical route emerges as more viable and can accommodate the fluctuating waste volumes (Lydall *et al.*, 2017) and unstable supply of feedstock materials. Hydrometallurgical processes also carry the advantage of high selectivity (Kasper and Veit, 2018). Post-collection, sorting and dismantling of e-waste streams, PCB recycling can be classed into stages i.e., pre-treatment, extraction, and recovery. In the context of hydrometallurgical processing, pre-treatment involves processes to 'liberate' the metal, extraction refers to leaching processes, recovery refers to purification and conversion of metal ions to their metallic form or salts.

Physical Pre-treatment of the waste PCBs

Depending on the subsequent treatment procedure, physical pre-treatment mainly involves size reduction and/or upgrading of PCB through implementation of techniques such as grinding, shredding, and electrostatic separation (Cui and Anderson, 2016). In the conventional recycling process, waste PCBs undergo mechanical and physical processes to partially pre-separate BMs and other materials. This pre-treatment is associated with losses of Au (Kasper and Veit, 2018). In this study, it was desired for part of the experiments to use large pieces of PCBs with minimal pretreatment to minimise losses linked to this stage, while the other experiments employed a shredding technology proposed by Prestele, (2020), to liberate the metals. The large PCB pieces were cut to (3×2) cm for the purposes of compatibility with available reactor sizes.

Ammoniacal leaching of Cu

Several studies, mostly at laboratory scale and using different types of lixiviants, have been done on Cu and other BMs extraction without a focus on Au leaching from waste PCBs (Chirume, 2019; Ficeriová *et al.*, 2011; Koyama *et al.*, 2006; Vijayaram *et al.*, 2013). Alkaline ammoniacal lixiviants have several advantages over acidic leaching. For example, their systems are less prone to corrosion problems lixiviants (Ficeriová *et al.*, 2011; Koyama *et al.*, 2006; Radmehr *et al.*, 2013; Vijayaram *et al.*, 2013). Rudnik *et al.*, (2016) also showed that alkaline ammonia–ammonium salt solutions exhibit an advantage in the leaching of polymetallic materials such as PCBs, especially since dissolution of Cu is autocatalytic as shown in the Equations 1 and 2:

$$Cu(NH_3)_4^{2+} + Cu \rightarrow 2\ Cu(NH_3)_4^{+} \tag{1}$$

$$2\ Cu(NH_3)_4^{+} + 4\ NH_4^{+} + 2\ OH^{-} + \frac{1}{2}\ O_2 \rightarrow 2\ Cu(NH_3)_4^{2+} + 3H_2O \tag{2}$$

This characteristic enhances its dissolution compared to other co-extracted metals (Rudnik *et al.*, 2016). Co-dissolving metals include Ni and Zn which are also soluble in ammoniacal solutions, but the rate of their dissolution is determined by oxygen transport to the metal surface (Rudnik *et al.*, 2016). Ammoniacal systems have been studied with recoveries of above 90% for Cu (Bari *et al.*, 2009; Koyama *et al.*, 2006; Rudnik *et al.*, 2016). Ni on the other hand was shown to be impacted by choice of ammoniacal salt. Ammonium sulfate ($(NH_4)_2SO_4)$) was able to extract 70% more Ni compared to $(NH_4)_2CO_3$, under the same conditions at an overall recovery of 80% (Rudnik *et al.*, 2016). This would be a good attribute if the goal is to remove BMs prior to PM leaching to minimise their interference. Chirume, (2019) and Rudnik *et al.*, (2016), agree that a system with ammonium sulfate has the highest Cu recovery despite carbonate salts proving to be a better buffer than sulfate.

Ammonium thiosulphate leaching of Au

A conventional method used for the recovery of Au from Au ores, is cyanide leaching. However, cyanide application in e-waste has drawbacks that render it difficult to manage despite the high extraction capacity, especially in the context of extracting Au from waste PCBs with a high Cu concentration. Akcil *et al.*, (2015), Kasper and Veit, (2018) and Tripathi *et al.*, (2012) reported that cyanide is not only toxic, and an environmental risk, but the subsequent wastewater generated is also difficult to process. The increasing environmental pressure on the use of cyanide and its limited selectivity is what motivated the ongoing research into non-cyanide alternatives. Amongst a variety of lixiviants, ammonium thiosulfate ($S_2O_3^{2-}$) shows potential because it is less toxic, highly selective, and cheaper (Akcil *et al.*, 2015). The dissolution of Au occurs through the formation of soluble auro-thiosulfate complexes that include $Au(S_2O_3)_2^{3-}$ and $Au(S_2O_3)^-$ via equation (3) (Kasper and Veit, 2018).

$$Au + 5S_2O_3^{2-} + Cu(NH_3)_4^{2+} \rightarrow Au(S_2O_3)_2^{3-} + 4NH_3 + Cu(S_2O_3)_3^{5-} \qquad (3)$$

The ammonia-thiosulfate system chemistry is very complex because of the simultaneous presence of complexing ligands such as ammonia and thiosulfate, the Cu (II)-Cu(I) redox pair and the oxidative decomposition reactions of thiosulfate (Aylmore and Muir, 2001; Zipperian *et al.*, 1988). Thiosulfate is a metastable anion that requires alkaline and near neutral media for the stability and solubility of the complexes (Aylmore and Muir, 2001; Zipperian *et al.*, 1988). Moreso, adequate concentrations of ammonia, ammonium thiosulfate, Cu and gaseous O_2 are what enable efficient extraction of the Au (Kasper and Veit, 2018; Tripathi *et al.*, 2012). The presence of Cu in the form of cupric (Cu^{2+}) ions alongside ammonia form a copper tetramine complex $[Cu(NH_3)_4]^{2+}$, a beneficial catalyst for Au dissolution but also facilitates thiosulfate decomposition especially at excessive Cu concentrations (Aylmore and Muir, 2001; Breuer and Jeffrey, 2000)

Reactor Sequencing in the Thiosulfate Leaching of waste PCBs

Effect of size reduction and reactor sequencing

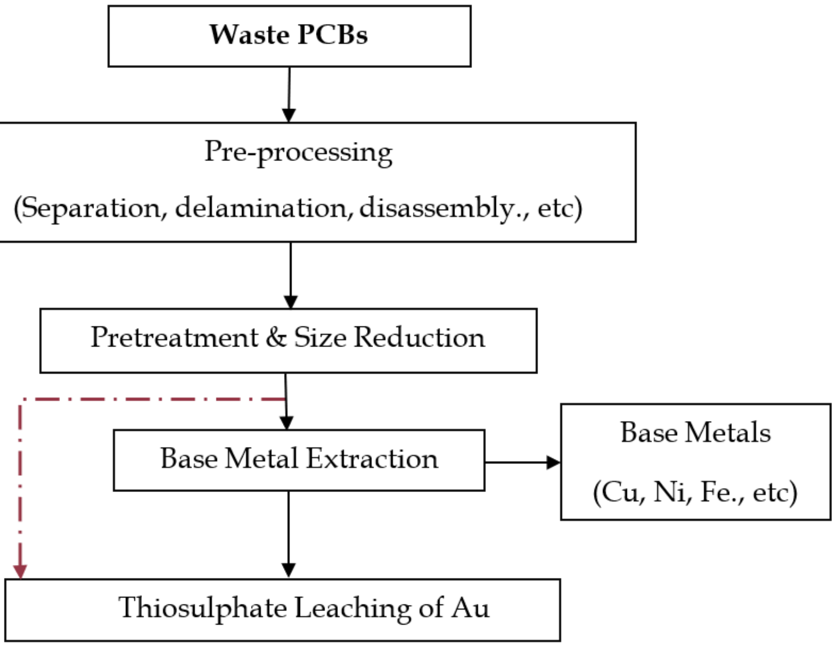

Figure 1. Conventional processing sequence for extraction of Au from PCBs. (The dotted line presents the unconventional route applied in this study).

In conventional PCB processing sequences (Figure 1), size reduction is done primarily to expose the inner layers of Cu which would otherwise be inaccessible to leaching agents. The size reduction steps involve shredding and (sometimes) grinding the PCBs to fine particles (Albertyn, 2017; Ficeriová *et al.*, 2011; Gámez *et al.*, 2019; Petter *et al.*, 2013; Tanisali *et a*l., 2021). This process step is typically associated with significant Au losses through dust and Au-bearing particle entrainment in other streams (Kasper and Veit, 2018; Kaya, 2019). After a BM leaching step, Gámez *et al.*, (2019) reported 5% losses of Au in the Cu leaching stage, despite the 81% Au extraction obtained in the second step targeted at Au leaching. Despite attaining substantial recoveries of Cu due to the pre-treatment processes, Tanisali *et al.*, (2021) and Albertyn, (2017) also achieved Au extractions of 59% and 78.5%, respectively, which meant that significant Au was lost. Beyond the challenges of Au losses from this physical treatment step, PCBs treated this way are also not ideal for thiosulfate leaching as a first step, owing to the highly liberated Cu which will dissolve preferentially to the targeted Au. Without prior BM leaching, Petter *et al.*, (2013) and Tripathi *et al.*, (2012), achieved only 2% and 35 % Au extraction after directly leaching crushed (Petter *et al.*, 2013) and shredded (Tripathi *et al.*, 2012) PCBs in thiosulfate. This further supports the idea that mechanical processing results in significant Au losses. Additionally, excessive concentrations of Cu facilitates the degradation of ammonia and thiosulfate ions by its conversion to tetrathionate and other polythionates. Aylmore and Muir, (2001) and Zipperian *et al.*, (1988) demonstrated this phenomenon via (Equation 4);

$$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \rightarrow 2Cu(S_2O_3)_3^{5-} + S_4O_6^{2-} + 8NH_3 \qquad (4)$$

Thus, it seems logical that a sequence that starts with Au leaching in thiosulfate systems avoids any intensive size reduction. Such an approach will minimise material losses, and curb challenges in reagent consumption among other process chemistry-related factors. Despite this view, there is no consensus in literature on whether processing PCBs without size reduction and BM leaching will result in higher Au extractions. Without size reduction and no prior BM leaching and under similar leaching conditions, Ha *et al.*, (2010) and Kasper and Veit, (2018) achieved 90% and 75% Au extraction, respectively, while Ficeriová *et al.*, (2011) reported a lower Au extraction of 16%, despite applying a higher thiosulphate concentration. On the other hand, Tripathi *et al.*, (2012) achieved Au extraction of 78% under the same leaching conditions as Ha *et al.*, (2010) and Kasper and Veit, (2018). This showed a decline in Au extraction to Ha *et al.*, (2010) but a slight increase to Kasper and Veit, (2018). A trade-off must be made between pre-processing waste PCBs to unlock Cu and avoiding size reduction to improve Au extraction which primarily sits on the external layers. Another solution could be to extract Au before shredding and grinding, after which Cu can be rapidly extracted from shredded and waste PCB to improve the overall extraction efficiency (Maharaj *et al.*, (under review)). In this study, four reactor sequences were evaluated based on the extent of Au extraction, Cu and Ni co-extraction and, associated Au losses in the ammonium thiosulfate leaching of PCBs. This was achieved by tracking Au losses in each sequence for each process step, calculating overall Au extraction over a fixed period across all the reactor sequences, tracking the co-dissolution of base metals in the Au leach steps. Since Au mainly exists on the surface layer of PCBs, it is hypothesised that its extraction before any aggressive size reduction and BM extraction (red dotted line in Figure 1) will minimise Au loss thereby increasing its overall extraction.

MATERIALS AND METHODS

Custom-tailored PCBs

The PCBs (Figure 2) that were used in all tests in this research were made to order by Trax Interconnect (Pty) Ltd in Cape Town, South Africa. This ensured homogeneity across all tests, allowing for effective comparison of results. Each PCB is a four-layered FR-4 (fibreglass with epoxy resin) core board, weighing approximately 52 g. Each of the four layers comprise a laminate of FR-4 inner core sandwiched by two copper foils that are 17 µm in thickness with dimensions of (142 × 102 × 1.63) mm. The inner layers connect to the outer layers with the pre-preg (uncured FR-4 resin) which cures when the layers are combined. The inner copper layers represent the copper inaccessible to leach agents without size reduction to liberate the materials or any other forms of delamination.

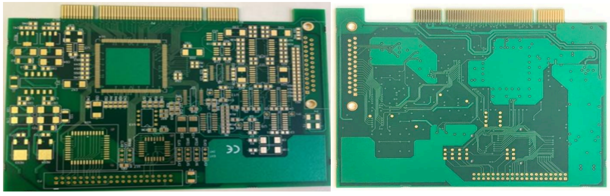

Figure 1. Custom made PCB left - top side of the PCB; right - bottom side of the same PCB.

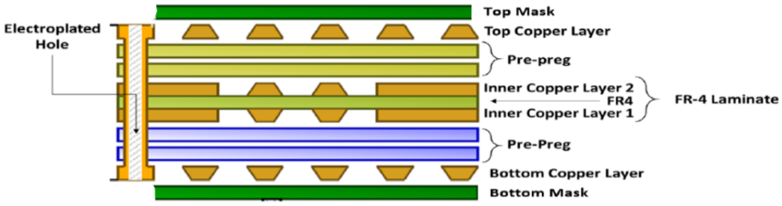

Figure 3. Cross-sectionals schematic of the PCB adapted from Moyo et al.*, 2020.*

Au is found as a Au-Ni alloy on the vias, the upper and lower surfaces of the board as well as the connectors on the sides, and can be seen as the shiny metallic surfaces on the otherwise green board shown in Figure 2. Vias are electroplated holes as shown in Figure 3, connecting the Cu layers in a PCB. Chirume, (2019), presented an analysis of the Cu distribution of the PCB, with 69% being indicated to be in the inner layers (in accessible to leach agents without liberation) and 31% to be on the surface, accessible to leach agents upon removal of the top mask.

Head grade analysis

Table I gives the average PCB head grade which was determined via a procedure outlined in (Gonte, 2023). The tests done on four different samples were reproducible within an average of ±6.9% margin of error.

Table I. Average head grade of PCBs

Metal analysed	**Au**	**Cu**	**Ni**
(mg/PCB)	**4.01**	**10400**	**146**
Wt./wt. %	**0.0080**	**20.8**	**0.292**

Table I shows that the Au content for the PCB samples is appreciable and stands at 4.01 mg for each board weighing approximately 52 g. This translates to 80 g Au/ton PCB which is significantly higher than an average of 5-15 g/ton found in average natural ores, as reported in literature (Forti *et al.*, 2020; Gámez *et al.*, 2019; Kasper and Veit, 2018; Kaya, 2019). The analysis also indicates that Cu is the most abundant metal at 20.8%.

Au leaching in an Ammonium Thiosulphate Leaching System per Sequence

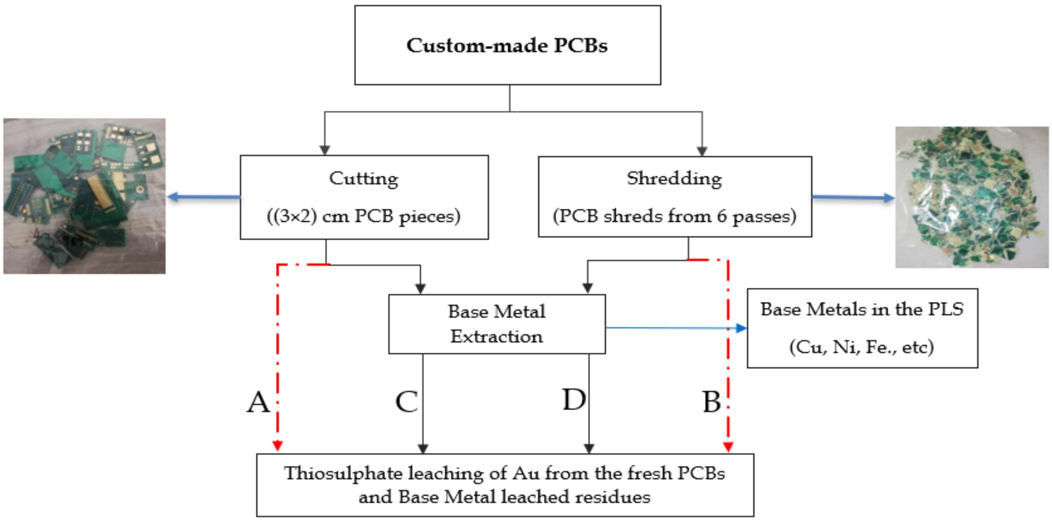

Figure 4. Schematic of the reactor sequencing approaches investigated in this report. The red dotted lines (from far left to far right) present the unconventional sequence (A) and (B) respectively while the other two solid lines (left to right) present sequence (C) and (D).

The reactor sequencing strategies, summarised in Figure 4, were examined with the goal of choosing one that yields the maximum Au extraction during the thiosulphate leaching stage.

A. Sequence A- unconventional sequence where the PCBs were cut (3 cm x 2 cm) and then subjected to the Au leaching stage.
B. Sequence B- Similar to sequence (A) except in this instance the PCBs were shredded (in 6 passes) instead of being cut.
C. Sequence C- conventional sequence where the PCBs were cut (3 cm x 2 cm) and underwent BM extraction prior to the Au leaching.
D. Sequence D- Similar to sequence (C) except in this instance the PCBs were shredded (in 6 passes) instead of being cut.

Cu leaching tests

For sequences C and D, pre-treatment was followed by Cu leaching in $(NH_4)_2SO_4$ solutions. This was carried out in a bottle roller using a solution mixture of 2 M $(NH_4)_2SO_4$, 4 M NH_3 solution and 100 ppm $CuSO_4$ $5H_2O$ at a pH of 10.5. The roller was kept at 250 rpm and 25°C with 0.1 L/min of compressed air bubbled into each reactor to ensure that the reaction system had enough dissolved oxygen. 5 ml leachate samples were extracted and filtered through a 0.2 µm syringe-driven membrane filters. These were analysed for Au, Cu, and Ni using a microwave plasma atomic emission spectroscopy (MP-AES). After a 72-hour runtime, leached PCB residues (product of interest) were washed using de-ionised water and dried in open air for 24 hours and kept for the subsequent stage of Au leaching.

Thiosulphate leaching of Au from the fresh PCBs and Cu leach residues

Leaching was carried out on pretreated PCB samples from sequence A and B as well as residue from sequence C and D from the Cu leaching stage. A bottle roller and a solution mixture of 1 M NH_3, 0.5 M $(NH_4)_2S_2O_3$ and 40 mM $CuSO_4$. $5H_2O$ were used. pH remained around 10.4 and a solid/liquid concentration of 100 g/l was maintained, for all systems. The roller (Figure 5) was kept at 300 rpm and 25 °C. 0.1 L/min of compressed air was bubbled into each reactor to ensure that the reaction system had enough dissolved oxygen. 5 mL leachate samples were extracted and filtered through a 0.2 µm syringe-driven membrane filters and their pH determined. These were analysed for Au, Cu, and Ni using an MP-AES. After a runtime of 24 hours the solution was filtered off using a Buchner funnel. The PCB residues were dried in an oven and the final PCB mass was measured. These leached residues were preserved for mass balance analysis and calculations.

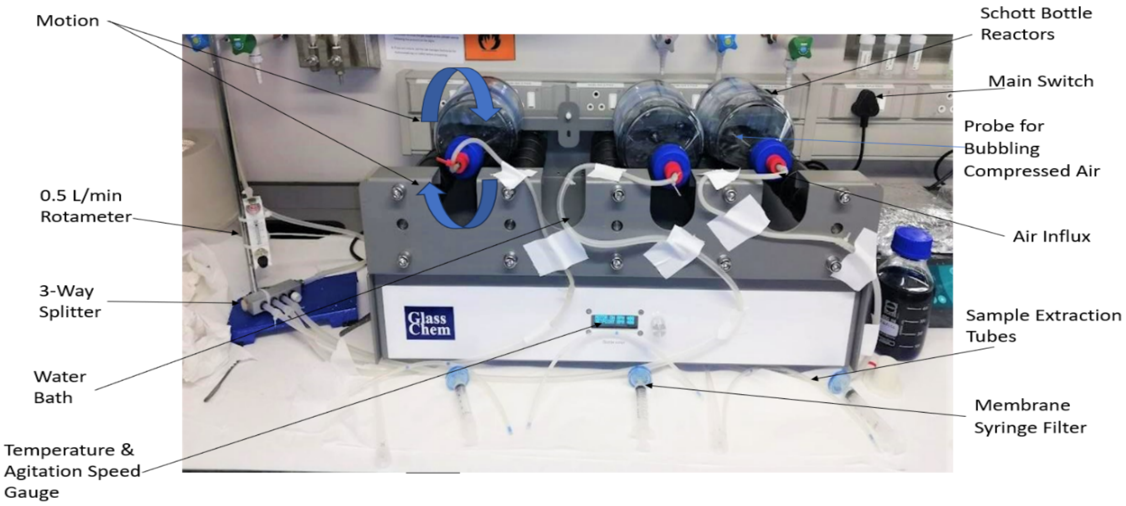

Figure 5. Three parallel Schott bottle reactors, with identical leaching conditions, that were used in the leaching reaction involving the bottle roller.

RESULTS AND DISCUSSION

Table II. Material losses incurred

	Cut PCBs (3cm x 2cm pieces)	**PCB shreds (**after 6 cycles)
Mass loss (g)	3.74	7.1
Mass retained (wt.%)	92.8	86

Table II shows each pre-treatment method and the material losses experienced. The material losses for cut PCBs were 7.2% while those of shredded PCBs were approximately twice as much, at 14%. Material losses during pretreatment represents potential loss of valuable metal. This loss of valuable metal has been linked to Au losses as previously discussed by Birich, (2020), and Kaya, (2019) who reported an approximated 35% loss of Au. Au tends to chip away from the PCBs during shredding and ends up in the dust (Birich, 2020). Beyond valuable metal losses, size reduction generates fine particles which present a safety and health hazard from airborne dust particles in plant operations as reported by Kaya, (2019) and Tuncuk *et al.*, (2012).

Base Metal Extraction Test Results

In the ammonium sulfate-based Cu leaching stage, small flakes of metal were observed, 24 hours into the experiments. These were analysed in a separate study (Mokoena and Tshabalala, 2023) and found to be the Au-Ni alloy plating described to be the outer most metal layer in the previous section. After 72 hours residence time, all the Au on the PCBs had completely flaked off and was visible at the bottom of each reactor as shown in Figure 6. The Au flakes were filtered using a vacuum filter and 0.2 µm filter paper and dried in open air (Figure 6 (c)) The residual PCBs from the base metal leach step were leached together with the dried Au flakes in thiosulphate solutions.

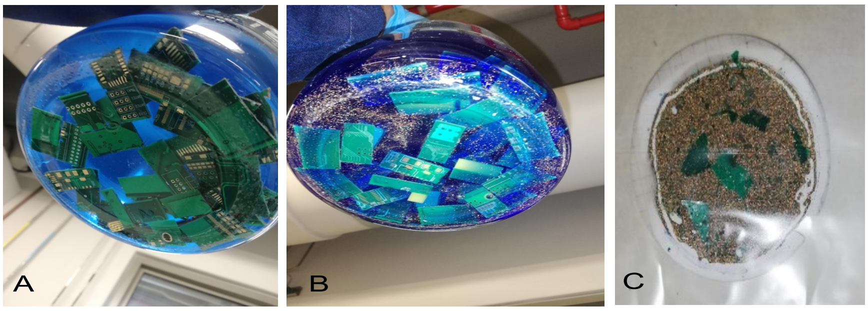

Figure 6. Part (a) The bottom of the reactor just before leaching experiment and part (b) the bottom of the same reactor 72 hours later (c) The flakes after filtration.

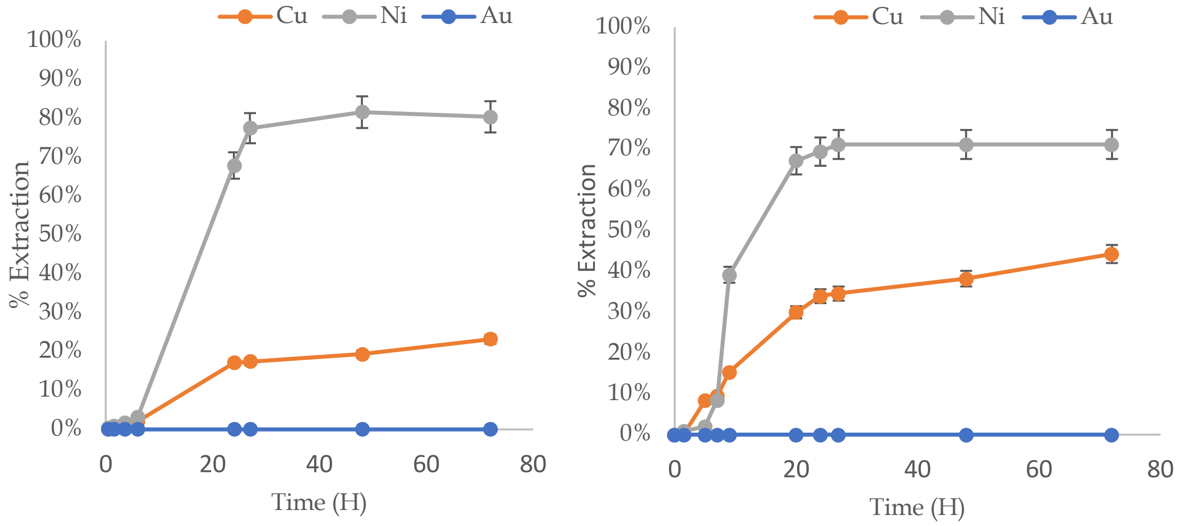

Figure 7. (a) BM extraction for sequence C-cut PCBs.   (b) BM extraction for sequence D-Shredded PCBs.

Figure 7 (a) and (b), show the metal extraction results for sequences C and D (cut and shredded), respectively, during Cu leaching using ammonium sulphate. For both cut and shredded PCBs, Ni had the highest extraction, with at least 67% Ni extracted within the first 24 hours. 34% of the Cu was extracted from the shredded PCBs after 24 hours of leaching, compared to 17% from the cut PCBs, suggesting that the shredded PCBs had faster leach kinetics. After 72 hours of leaching in the base metal leach stage, 71% and 80% Ni, and 44% and 23% Cu was extracted from shredded and cut PCBs, respectively, with no evidence of Au co-extraction. The extent of Ni extraction was 9% higher for cut PCBs than shredded PCBs. This is likely due to the losses that were encountered during the shredding process given that at least 7 g of the board was lost (Table II). As was previously indicated, Birich, (2020) demonstrated that when PCBs are shredded, Au tends to chip away, translating to loss. Kasper and Veit, (2018) also noted that most of the Au loss presumably occurs during size reduction. Since Ni is present in PCBs as a Au-Ni alloy, Figure *it is plausible to think it would be lost alongside the Au.*
Table

Compared to shredded PCBs, the Cu concentration in cut PCBs is about twice as high. This is due to shredding, which increases surface areas thereby improving leaching kinetics as well as increasing the liberation of the inner copper layers which were otherwise not accessible to leach agents. Figure 7 (b), indicates that the total Cu extracted from PCBs that were shredded was 44%, which exceeded the total Cu deemed to be accessible, by 13% as previously discussed (Figure 3). Ni had overall higher extraction than Cu in Figure 7 (a) and (b), because of its location of the PCB surfaces. Furthermore, the standard reduction potential for Cu^{2+} is +0.34 V, and for Ni^{2+}, it is -0.26 V. This means Ni has a higher propensity to lose electrons to form cations, hence dissolves more readily than Cu.

Au Extraction Test Results

The summarised percentage Au extractions for sequences A through D is shown in Figure 8.

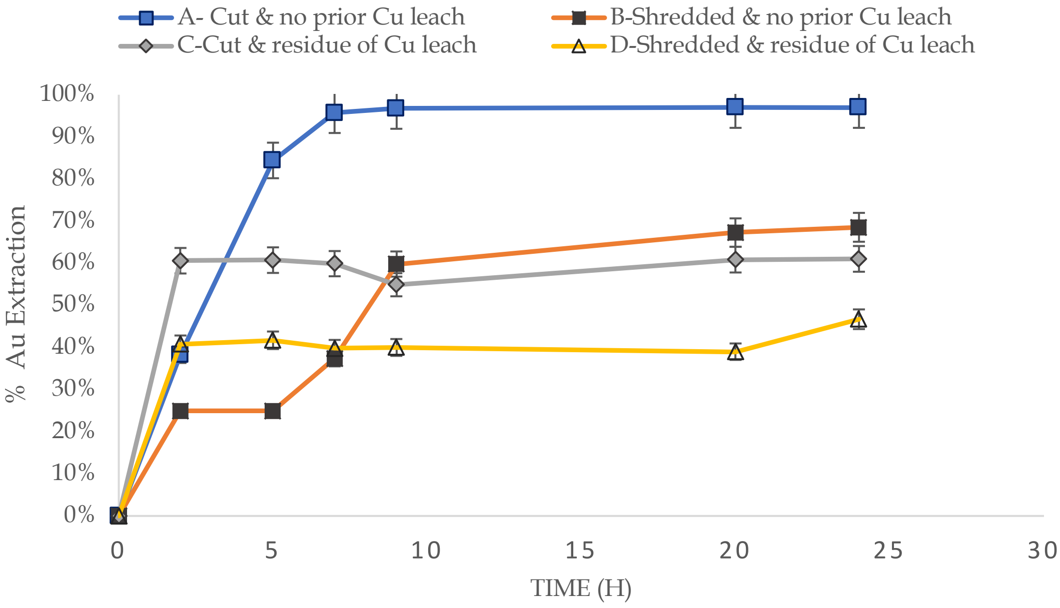

Figure 8. Au extracted from four reactor sequences: PCBs without a previous Cu leaching step and PCB residues from Cu leaching.

As expected, no Au was extracted during the BM leaching step, the total Au extracted was based on the initial head grade, however co-extraction of Ni and Cu was normalised against the recalculated head grade, after the total mass of Ni and Cu extracted during the prior Cu leaching stage was subtracted. After the first two hours, 61% and 41% Au was extracted in Sequences C and D, respectively, which points to faster Au leaching rates. By contrast, in Sequences A and B only 38 and 25 % were extracted, respectively. After a residence time of 24 hours, sequence A had the maximum Au extraction of 97% followed by B with 69%, and C and D with 61% and 47%, respectively. Sequences B and D showed low overall extraction owing to the Au lost during shredding as previously discussed in Table II. The faster Au extraction observed in sequences C and D can be attributed to the Au particles now being available as flakes. The flakes present a larger surface area compared to the Au-Ni which is still plated on the PCB as is the case in sequences A and B. Considering the faster initial leaching kinetics, it therefore makes sense that this reactor sequence equilibrated quicker than sequence A and B. The low Au leaching extractions observed in sequences C and D are discussed in the next sections.

Reactor Sequencing A vs Reactor Sequencing C

Figure 9 (a) and (b), show the graphs for coextraction of Au, Cu and Ni of Sequence A and C, respectively in the $S_2O_3^{2-}$ leach. **Error! Reference source not found.**The boards that were processed through sequence C were found to have the least amount of co-extracted Cu and Ni. Only 7% of the overall 19% remaining Ni was co-extracted. In Sequence A, a total of 97% Ni was coextracted. With regards to Cu, the total Cu extracted in sequence A was 28%, which was more than double the total extracted during Sequence C. In sequence C, only 12% of the overall remaining 72% Cu was extracted. In sequence A, in the first two hours, Au leached 1.6 times higher than Ni, but both metals reached equilibrium after eight hours and a maximum of 97% of each metal was extracted. Cu was the least metal extracted, with a maximum extraction of 28% attained after 24 hours.

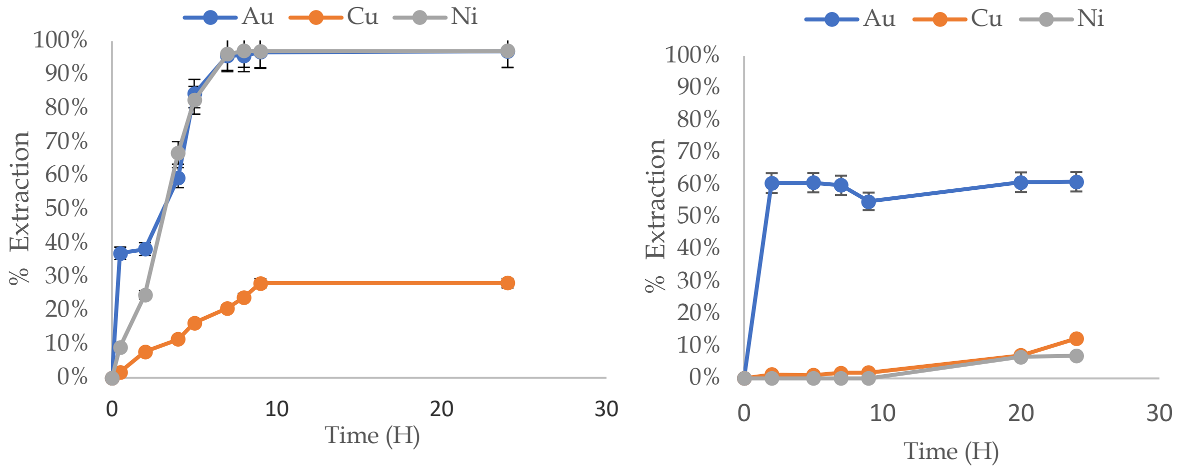

Figure 9. Reactor Sequence A, cut and no prior Cu leach PCBs & (b) Reactor Sequence C, cut and PCB residue of Cu leach, respectively.

The differences in the extent of Au extractions are likely to be a result of Cu concentration in the leach solution. The pH of the system remained at 10.4 and thus, it is unlikely that the poor Au dissolution could have been related to the precipitation of Cu as CuO and Cu_2O and CuS (Aylmore and Muir, 2001; Breuer and Jeffrey, 2000)

Figure 9 a) and b) show that a Cu concentration of 28% is not detrimental, in fact, it aids the Au leaching reaction compared to a lower concentration of 12%. This is due to the stabilisation of the cuprous ion in form of $Cu(NH_3)_4^{2+}$ which allows for the Cu(II)/Cu(I) redox couple to play a catalytic role in Au leaching. This is clearly illustrated in the Pourbaix diagram for the $Cu\text{-}NH_3\text{-}S_2O_3^{2-}$ system by Aylmore and Muir, (2001), and Zipperian *et al.*, (1988). As shown in Figure 9 b) most Cu had already been extracted during the previous step of BM extraction. Hence in the leach there was relatively less elemental Cu exposed to aid the autocatalytic reaction. This means that there was less Cu to form $Cu(NH_3)_2^+$ ions which are converted by O_2 to $Cu(NH_3)_4^{2+}$, which catalyses the Au leaching reaction. In the case of Ni (Figure 9 (a)), a significant amount of it had been extracted during the previous Cu leaching cycle as shown in Figure 7 (a).

Reactor Sequencing B vs Reactor Sequencing D

Figure 10 (a) and (b) focus on the different graphs for the coextraction of Au, Cu, and Ni from Sequences B and D, respectively. Figure 10 displays a pattern similar to Figure 9, except sequences B and D extracted less Au overall. The PCBs that were processed through sequence D had the least amount of co-extraction of Cu and Ni overall, as demonstrated by the curves in Figure 10 (b). In contrast to Sequence B, where a total of 83% Ni was coextracted, a small amount of Ni was leached reaching a maximum extraction of 4%. With regards to Cu, the overall percentage extracted during Sequence B was two times higher than the total amount extracted in Sequence D.

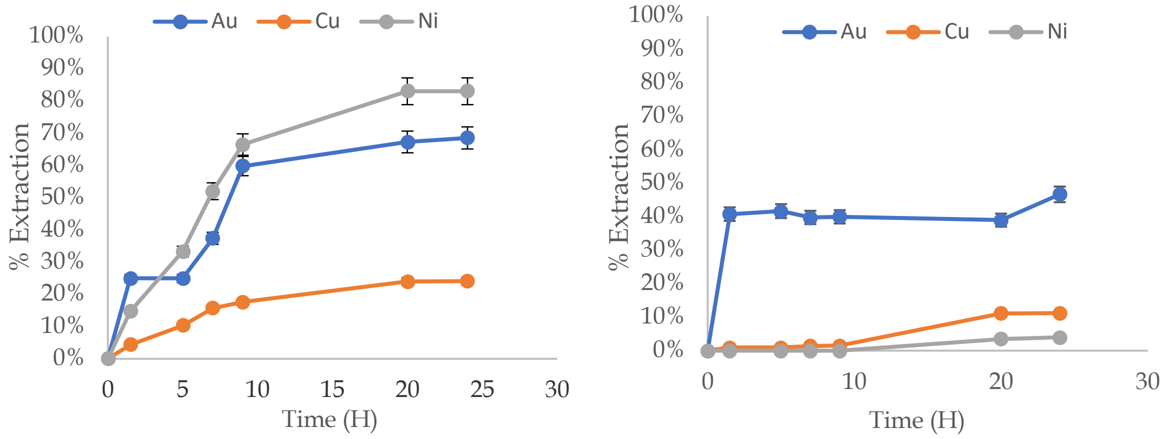

Figure 10. (a) Reactor Sequence B, Shredded and no prior Cu leach PCBs & (b) Reactor Sequence D, Shredded and PCB residue of Cu leach, respectively.

Au extraction was 1.6 times higher than that of Ni in the first 1.5 hours of Sequence B. Ni and Au were extracted to a maximum of 83% and 69%, respectively, while only a maximum of 24% Cu extraction was achieved. In sequence D, only 14% of the remaining 29% Ni from the Cu pre-leach was extracted. An additional 11% of Cu Figure was also extracted from the Cu pre-leach. Only 47% of the Au was extracted in total in sequence D. Overall Cu and Ni extraction discrepancies in sequences B and D were mostly owing to the fact that the majority of the Cu had already been removed (Figure 7 (b)). As was previously discussed, the differences between the Au extraction in sequences B and D can be explained by the different Cu concentration in both systems. Sequence B had a higher Cu concentration in solution than sequence D. This resulted in less Au oxidation since there was less production of the cupric ammine catalyst, which facilitates Au oxidation as was previously mentioned. In addition to this, a significant quantity of Au and Ni was presumably lost during shredding as previously discussed.

Selection of the Optimal Reactor Sequencing in an Ammonium Thiosulphate Leaching System that Maximises the amount of Au Extracted from PCBs

Sequence A was selected as the best route since it had the highest overall Au extraction of 97%. These findings differ from those of Ficeriová *et al.*, (2011), who reported 16% extraction under similar conditions without a BM pre-leach. However, results from the current study are an improvement over those of Kasper and Veit, (2018), who under similar conditions only extracted a maximum of 79% Au from PCBs that did not undergo size reduction and BM pre-extraction. The use of depopulated PCBs in this paper sets it apart from their studies as it eliminated possible interference from other ions such as Zn and Sn ions which are typically found in solder materials. 97% Ni was also co-dissolved with Au in sequence A, since the Au exists as a Au-Ni alloy on the external layers of the PCB. However, in Sequence A, 28% Cu was co-extracted, and which might not be favourable for downstream processes.

On the other hand, sequence B has drawbacks such as significant Au losses. Upon inferring this to large scale operations, an excess Cu concentration in solution, during Au leaching, results in larger losses of thiosulphate ions by its degradation to tetrathionate and other polythionates (Aylmore and Muir, 2001). As a result, there is less thiosulphate available for complexation with the Au (Equation 3) leading to a lower extraction of Au from shredded PCBs. BMs are removed in significant quantities during the prior leaching stage of sequences C and D, which is advantageous for downstream processes. However, for sequence D, this comes at a significant Au loss of 53%. For the PCBs processed through sequence C, 35% Au was not extracted. A subsequent investigation confirmed that no Au dissolved during BM leaching, however the flaking of Au particles will require the incorporation of a filtration step prior to Au leaching.

CONCLUSION AND RECOMMENDATIONS

Sequence A, of cut PCBs without any prior Cu leach step, was selected and recommended as the best route, as it stood out as having the maximum Au extraction. However, compared to Sequences C&D, it had a higher percentage of Cu and Ni co-extraction. The results showed that through this sequence, 28% of Cu and 97% Ni were coextracted along with the highest Au extraction of 97%. This co-extraction extent may not be favourable, especially for downstream processes. On the other hand, other sequences have the fundamental drawback of considerable Au losses owing to size reduction and insufficient Cu ions for the formation of the cuprous catalyst. Sequence D suffered severe Au loss, as high as 53%, while Sequence B suffered a total of 26% Au lost. A prior Cu leaching step in sequence C and D, lowers the elemental Cu concentration in solution, responsible for the autocatalytic Au dissolution reaction, which ultimately results in the less dissolution of Au. No Au was leached during Cu leaching reaffirming that it is inert and simply peels off during the Cu leaching step.

A few measures could be implemented to improve the extraction of Au from waste PCBs. The optimisation of Cu ion concentration on the thiosulphate leaching of Au from PCBs should be investigated. The optimised process can then be applied on real waste PCBs to evaluate the practicality of the selected sequence on actual waste PCBs.

ACKNOWLEDGEMENTS

This research was supported through the following grants: 1) German African Innovation Incentive Awards (GAIIA) 2019; 2) Council for Scientific and Industrial Research (CSIR), South Africa under Grant Number CSIR/BEI/WRUI/2019/026; and 3) the South African National Research Foundation (NRF) through the Community of Practice ‘Waste to Value’ under grant UID 128149. Ms Gonte received a scholarship associated with the NRF SARChI Chair in Mineral Beneficiation (Grant UID 64829). The NRF accepts no liability for the findings presented in this paper.

REFERENCES

Akcil, A., Erust, C., Gahan, C.S., Ozgun, M., Sahin, M. & Tuncuk, A. 2015. Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixiviants – A review. *Waste Management.* 45:258-271. DOI:https://doi.org/10.1016/j.wasman.2015.01.017.

Albertyn, P.W. 2017. Ammonium Thiosulphate Leaching of Gold from Printed Circuit Board Waste. Stellenbosch University. [13 September 2022].

Aylmore, M.G. & Muir, D.M. 2001. Thiosulfate leaching of gold—A review. *Minerals Engineering.* 14(2):135-174. DOI:https://doi.org/10.1016/S0892-6875(00)00172-2.

Bari, M., Begum, N., Hamaludin, S.B. & Kamarudin, H. 2009. Selective leaching for the recovery of copper from PCB, proceedings of the Malaysian Metallurgical Conference ‘09, 1-1.12 2009. *Kuala Perlis.*1-4.

Birich, A. 2020. Early Stage Gold Recovery from Printed Circuit Boards via Thiosulfate Leaching. RWTH Aachen University.

Breuer, P.L. & Jeffrey, M.I. 2000. Thiosulfate leaching kinetics of gold in the presence of copper and ammonia. *Minerals Engineering.* 13(10):1071-1081. DOI:https://doi.org/10.1016/S0892-6875(00)00091-1.

Cadence®, C.P.S. 2023. *An Introduction to Printed Circuit Boards*. Cadence Design Systems. Available: https://www.cadence.com/en_US/home/tools/pcb-design-and-analysis.html [2023].

Chirume, B.H. 2019. *Investigation of a hydrometallurgical process route to recover metals from waste printed circuit boards.* Faculty of Engineering and the Built Environment.

Cui, H. & Anderson, C. 2016. Literature Review of the Hydrometallurgical Recycling of Printed Circuit Boards (PCBs). *Journal of Advanced Chemical Engineering.* 6:11. DOI:10.4172/2090-4568.1000142.

Ficeriová, J., Baláž, P. & Gock, E. 2011. Leaching of gold, silver and accompanying metals from circuit boards (PCBs) waste. *Acta Montanistica Slovaca.* 16.

Forti, V., Baldé, C., Kuehr, R. & Bel, G. 2020. *The Global E-waste Monitor 2020. Quantities, flows, and the circular economy potential.*

Gámez, S., Garcés, K., De La Torre, E. & Guevara, A. 2019. Precious metals recovery from waste printed circuit boards using thiosulfate leaching and ion exchange resin. *Hydrometallurgy.* 186. DOI:10.1016/j.hydromet.2019.03.004.

Gonte, M. 2023. ETD: Investigating Early-Stage Process Flow and Reactor Sequencing to Maximise Gold Extraction ln the Thiosulphate Leaching of Waste Printed Circuit Boards. Available: http://hdl.handle.net/11427/39436.

Hossain, M.S., Al-Hamadani, S. & Rahman, M.T. 2015. E-waste: A Challenge for Sustainable Development. *J Health Pollut.* 5(9):3-11. DOI:10.5696/2156-9614-5-9.3.

Jeon, S., Tabelin, C.B., Park, I., Nagata, Y., Ito, M. & Hiroyoshi, N. 2020. Ammonium thiosulfate extraction of gold from printed circuit boards (PCBs) of end-of-life mobile phones and its recovery from pregnant leach solution by cementation. *Hydrometallurgy.* 191:105214. DOI:https://doi.org/10.1016/j.hydromet.2019.105214.

Kasper, A. & Veit, H. 2018. Gold recovery from printed circuit boards of mobile phones scraps using a leaching solution alternative to cyanide. *Brazilian Journal of Chemical Engineering.* 35:931-942. DOI:10.1590/0104-6632.20180353s20170291.

Kaya, M. 2019. *Electronic Waste and Printed Circuit Board Recycling Technologies.* 1. Springer ChamDOI:https://doi.org/10.1007/978-3-030-26593-9.

Koyama, K., Tanaka, M. & Lee, J.-c. 2006. Copper Leaching Behavior from Waste Printed Circuit Board in Ammoniacal Alkaline Solution. *MATERIALS TRANSACTIONS.* 47(7):1788-1792. DOI:10.2320/matertrans.47.1788.

Maharaj, D., Moyo, T. & Petersen, J. (under review). Ammonium thiosulfate leaching of gold from electronic printed circuit boards – effect of solution copper concentration' *submitted to SAIMM Journal.*1-12.

Mishra, G., Jha, R., Rao, M., Meshram, A. & Singh, K. 2021. Recovery of Silver from Waste Printed Circuit Boards (WPCBs) through Hydrometallurgical Route: A Review. *Environmental Challenges.* 4:100073. DOI:10.1016/j.envc.2021.100073.

Mokoena , K. & Tshabalala, N. 2023. Evaluation of process steps towards metal recovery from printed circuit boards. University of Cape Town.

Moyo, T., Chirume, B.H. & Petersen, J. 2020. Assessing alternative pre-treatment methods to promote metal recovery in the leaching of printed circuit boards. *Resources, conservation and recycling.* 152:104545. DOI:10.1016/j.resconrec.2019.104545.

Petter, P., Veit, H. & Bernardes, A. 2013. Evaluation of gold and silver leaching from printed circuit board of cellphones. *Waste management (New York, N.Y.).* 34. DOI:10.1016/j.wasman.2013.10.032.

Prestele, M.P. 2020. Assessment of a Shredding Technology of Waste Printed Circuit Boards in preparation for Ammonia-based Copper leaching. Available: http://hdl.handle.net/11427/32969.

Radmehr, V., Koleini, S.M.J., Khalesi, M.R. & Tavakoli Mohammadi, M.R. 2013. Ammonia Leaching: A New Approach of Copper Industry in Hydrometallurgical Processes. *Journal of The Institution of Engineers (India): Series D.* 94:95-104. DOI:10.1007/s40033-013-0029-x.

Rudnik, E., Pierzynka, M. & Handzlik, P. 2016. Ammoniacal leaching and recovery of copper from alloyed low-grade e-waste. *Journal of Material Cycles and Waste Management.* 18(2):318-328. DOI:10.1007/s10163-014-0335-x.

Tanisali, E., Özer, M. & Burat, F. 2021. Precious Metals Recovery from Waste Printed Circuit Boards by Gravity Separation and Leaching. *Mineral Processing and Extractive Metallurgy Review.* 42(1):24-37. DOI:10.1080/08827508.2020.1795849.

Tripathi, A., Kumar, M., Sau, D., Agrawal, A., Chakravarty, S. & Mankhand, T. 2012. Leaching of Gold from the Waste Mobile Phone Printed Circuit Boards (PCBs) with Ammonium Thiosulphate. *International Journal of Metallurgical Engineering.* 1:17-21. DOI:10.5923/j.ijmee.20120102.02.

Tuncuk, A., Stazi, V., Akcil, A., Yazici, E.Y. & Deveci, H. 2012. Aqueous metal recovery techniques from e-scrap: Hydrometallurgy in recycling. *Minerals Engineering.* 25(1):28-37. DOI:https://doi.org/10.1016/j.mineng.2011.09.019.

Vijayaram, R., Nesakumar, D. & Chandramohan, K. 2013. Copper extraction from the discarded printed circuit board by leaching. *Research Journal of Engineering Sciences.* 2:11-14

Widmer, R., Oswald-Krapf, H., Sinha-Khetriwal, D., Schnellmann, M. & Böni, H. 2005. Global perspectives on e-waste. *Environmental Impact Assessment Review.* 25(5):436-458. DOI:https://doi.org/10.1016/j.eiar.2005.04.001.

Zipperian, D., Raghavan, S. & Wilson, J.P. 1988. Gold and silver extraction by ammoniacal thiosulfate leaching from a rhyolite ore. *Hydrometallurgy.* 19(3):361-375. DOI:https://doi.org/10.1016/0304-386X(88)90041-2.

Thandazile Moyo-Mahlangu

Assistant Professor of Energy and Mineral Engineering
The Pennsylvania State University, USA

Thandazile is an Assistant Professor of energy and mineral engineering at the Pennsylvania State University. She teaches into the Mining and Mineral Process Engineering Program and the Energy and Sustainability Program. Her research focus is primarily in hydrometallurgy, working on metal extraction and recovery from primary minerals and secondary materials. Some of her current work takes a process mineralogical approach in the evaluation and design of flow sheets for extracting lithium and REE from clay minerals. Her other research is on flow sheet evaluation for Li-ion battery recycling processes, the leaching of chalcopyrite in novel lixiviants and some non-technical work on developing metrics for assessing sustainability in the development of selected critical minerals.