RECOVERY OF VALUABLE METALS FROM ELECTRONIC WASTE USING A NOVEL AMMONIA-BASED HYDROMETALLURGICAL PROCESS

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RECOVERY OF VALUABLE METALS FROM ELECTRONIC WASTE USING A NOVEL AMMONIA-BASED HYDROMETALLURGICAL PROCESS

DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By

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2023

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ABSTRACT OF DISSERTATION

RECOVERY OF VALUABLE METALS FROM ELECTRONIC WASTE USING A NOVEL AMMONIA-BASED HYDROMETALLURGICAL PROCESS

The growing quantity of waste electrical and electronic equipment (WEEE), also known as electronic waste (E-waste), has been an area of growing public concern. The abundance of valuable metals contained in waste printed circuit boards (WPCBs) has made it a promising secondary resource, especially for Cu and Au. Although the recovery of metals from WPCBs via hydrometallurgical routes has been studied extensively over the past 20 years, most of the research has been limited in the laboratory. In current hydrometallurgical processes, strong acids and expensive oxidizers are often used to ensure a high recovery of metals without considering the sustainability aspects of the environment and economics. To improve upon current hydrometallurgical offerings, the current study seeks to develop an energy-saving, environmentally friendly, economic and sustainable process to efficiently recover the valuable metals from real-world end-of-life WPCBs. The new contributions presented in this study are 1) design and evaluation of a comprehensive hydrometallurgical flowsheet; 2) employment of real end-of-life PCBs as feed materials in an investigation on Cu-NH$_3$ leaching kinetics; 3) further application of kinetic model on a counter flow process simulation; and 4) evaluation of the influences by co-existing metals in Au-S$_2$O$_3$ leaching and recommendation for favorable leaching conditions.

A novel processing flowsheet was developed in the presented study, using ammonia-based hydrometallurgical methods to recover Cu and Au from WPCB materials. The proposed process includes a preliminary physical process for metal enrichment and material characterization, and multiple chemical processes for Cu and Au extraction. The chemical processes consisted of two major parts, the extraction of Cu by ammoniacal sulfate solution and the extraction of Au by oxidative thiosulfate leaching. The materials studied in the physical process were a mixture of general WPCBs, obtained from various sources, to provide a broader application using the developed physical method. Waste RAM chips, with a relative higher content of Cu and Au, were used specifically in the
chemical processes. SEM-EDS results on the feed materials proved the existence of Au-Ni-Cu interlayers, which could hypothetically reduce the efficiency of Au recovery in leaching.

The investigation on physical beneficiation by different size and density fractions revealed that sufficient metal liberation providing an effective metal concentration occurred at a particle size less than 2 mm and specific gravity (S.G.) over 2.67. Further investigation on thermogravimetric properties provided additional information on the thermal processing that were useful for analytical methods and, although not implemented here, a pretreatment for hydrometallurgical processing.

In Cu-ammoniacal leaching process, an in-depth study on the kinetic characteristics was conducted under an anaerobic environment. In comparison to the conventional ammoniacal leaching with assistance of oxygen, where Cu was oxidized all the way to Cu(II), the anaerobic ammoniacal leaching allowed partial oxidation of Cu to Cu(I). The anaerobic ammoniacal leaching was designed under assumption of a potentially coupled leaching-electrowinning circuit, to produce Cu from a leaching solution replenished of Cu(I) and depleted in Cu(II). A feasible kinetic model was obtained using real end-of-life RAM chips, by assessing the effect of stirring rate, particle size, Cu(II) concentration, and temperature. Results on the kinetic study revealed that particle size and initial Cu(II) concentration were the two most important factors affecting the leach efficiency. Cu recovery of 96% was achieved using 40 g/L Cu(II) as initial oxidizer concentration, 1.2 mm as top particle size, under ambient temperature. Kinetic models which approximate changing reactant concentration and mixed diffusion mechanism showed a reasonable fitting of the leach data, with average R² of 0.97 and 0.96, respectively. The estimated activation energy was 4 kcal/mol, indicating that the anaerobic Cu-ammoniacal leaching was governed by diffusion-controlled mechanism. Furthermore, the kinetic data was adopted in modeling of a counter-current leaching circuit to optimize the leaching performance and to promote the EW current efficiency.

Dissolution behavior of Au in oxidative thiosulfate leaching system using Cu(II)-NH₃ as the catalyst was studied. Under influences by the co-existing metals, the co-extraction of Ni was found to have an inverse impact on the Au recovery, as a result of chemical interactions within the Au-Ni-Cu interlayer. Decopperization as a pretreatment
was found necessary, especially when using complex PCB materials, to removal the pre-existing Cu and prevent Au deposition during leaching. Investigation on leaching parameters indicated the importance of the initial Cu(II) concentration, the controlled aeration, and the suitable range of thiosulfate-to-ammonia ratio on achieving a satisfactory Au recovery up to 98%. Suggested by the leaching result, a maintained solution Eh value around 0.15 V was favorable to the Au leaching by preventing the formation of sulfur species.

KEYWORDS: E-waste recycling, waste printed circuit boards, mineral processing and extractive metallurgy, copper ammoniacal leaching, gold thiosulfate leaching, kinetic modeling.

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TABLE OF CONTENTS

ACKNOWLEDGEMENT ........................................................................................................ iii

LIST OF TABLES .................................................................................................................. viii

LIST OF FIGURES ................................................................................................................ x

CHAPTER 1.  INTRODUCTION .............................................................................................. 1
  1.1  Background and Current Research Opportunities ..................................................... 1
  1.2  Overview .................................................................................................................... 3

CHAPTER 2.  LITERATURE REVIEW .................................................................................. 5
  2.1  E-waste and Waste Printed Circuit Boards (WPCBs) .................................................. 5
  2.1.1  Recycling methods for WPCBs ........................................................................... 9
  2.1.2  Comparison among pyrometallurgy, hydrometallurgy, and electrochemical recovery (ER) ......................................................................................................................... 13
  2.1.3  Recovery of Cu and Au from WPCBs by hydrometallurgical process ...... 16
  2.2  Ammonia-based Hydrometallurgical Process .......................................................... 20
  2.2.1  Chemistry in ammoniacal system ......................................................................... 21
  2.2.2  Historic development of the ammoniacal process in mining .............................. 25
  2.2.3  Cu extraction in ammoniacal solution .................................................................. 27
  2.2.4  Cu recovery by coupled leaching-EW circuit ...................................................... 32
  2.2.5  Purification and recovery of Cu from ammoniacal leaching solution .......... 35
  2.2.6  Au extraction in ammonia-thiosulfate system ...................................................... 36
  2.2.7  Recovery of Au from thiosulfate leaching solution ............................................. 40
  2.3  Proposed Flowsheet and Research Objectives ......................................................... 40

CHAPTER 3.  MATERIAL CHARACTERIZATION AND PHYSICAL PROCESSING .......... 46
  3.1  Introduction .............................................................................................................. 47
  3.2  Materials and Methods .......................................................................................... 52
  3.2.1  Materials ............................................................................................................ 52
3.2.2 Size reduction .................................................................................................................. 52
3.2.3 Density separation .......................................................................................................... 53
3.2.4 Assaying .......................................................................................................................... 55
3.2.5 Characterization ............................................................................................................. 56

3.3 Results and Discussions .................................................................................................... 57

3.3.1 Particle size distribution ............................................................................................... 57
3.3.2 Elemental distribution in different size fractions .......................................................... 60
3.3.3 Elemental distribution in various density fractions (size -5 mm) ................................. 63
3.3.4 Elemental distribution in different density fractions (size -2 mm) ................................. 66
3.3.5 Effect of surfactant in finer-particle-size density separation (size -2 mm)................. 68
3.3.6 SEM-EDS characterization of WPCBs by density fractions ....................................... 69
3.3.7 Thermogravimetric properties of general PCBs ......................................................... 72

3.4 Conclusions ...................................................................................................................... 75

CHAPTER 4. KINETIC CHARACTERISTICS OF CU LEACHING FROM WASTE RAM CHIPS IN A Cu(II)-NH₃-SO₄ SYSTEM ............................................................................. 77

4.1 Introduction ....................................................................................................................... 79

4.2 Materials and Methodologies ......................................................................................... 82

4.2.1 Waste RAM chips ....................................................................................................... 82
4.2.2 Leaching experiments ................................................................................................. 83
4.2.3 Chemical assay and analytical methods ...................................................................... 86

4.3 Results and Discussions ................................................................................................. 87

4.3.1 Element composition in waste chips .......................................................................... 87
4.3.2 Effect of leaching parameters (stirring rate, particle size, Cu(II) concentration and temperature) ........................................................................................................ 89
4.3.3 Eh, pH and Cu oxidation state in leaching ................................................................. 92
4.3.4 Ammonia evaporation in leaching ............................................................................. 95
4.3.5 Kinetic modeling for Cu ammoniacal leaching system ............................................ 96

4.4 Conclusions ...................................................................................................................... 105
CHAPTER 5. MODEL DEVELOPMENT AND PROCESS SIMULATION OF CU AMMONIACAL LEACHING ................................................................. 107

5.1 Introduction ...................................................................................... 107

5.2 The Diffusion-controlled Models .......................................................... 111

5.2.1 Model 1 - Mixed diffusion-controlled model (Dickinson & Heal, 1999a). 112
5.2.2 Model 2 - Changing concentration diffusion-controlled model (Zhuravlev et al., 1948) ........................................................................ 113
5.2.3 Model 3 - Constant concentration diffusion model (Jander, 1927) ........ 113

5.3 Applications of Selected Kinetic Models in Process Simulation ................. 115

5.3.1 Example 1 – Batch (semi counter-current) leaching simulation ............ 115
5.3.2 Example 2 – CSTR counter-current leaching circuit ............................ 119

CHAPTER 6. DISSOLUTION BEHAVIOR OF AU FROM WASTE RAM CHIPS USING OXIDATIVE AMMONIACAL THIOSULFATE LEACHING .......... 127

6.1 Introduction ...................................................................................... 128

6.2 Materials and Methods ........................................................................ 135

6.2.1 Materials and pretreatment ............................................................... 135
6.2.2 Leaching experiment ........................................................................ 137
6.2.3 Analytical and characterization methods ............................................ 138

6.2.3.1 Solid assay .................................................................................. 138
6.2.3.2 ICP-OES analysis ....................................................................... 138
6.2.3.3 SEM-EDS characterization ........................................................... 139

6.3 Results and Discussions ....................................................................... 139

6.3.1 Effect of decopperization ................................................................ 139

6.3.2 Ammoniacal thiosulfate leaching ...................................................... 142

6.3.2.1 Effect of Cu(II) concentration and aeration .................................... 142
6.3.2.2 Effect of ammonium thiosulfate to ammonium hydroxide concentrations (AT/AH ratio) ........................................................................ 146
6.3.2.3 Effect of particle size .................................................................... 148
6.3.2.4 Effect of temperature ................................................................... 149
6.3.3 Solution Eh/pH and the characterization of solids ................................. 151
6.3.3.1  Eh and pH in leaching solution .................................................. 151
6.3.3.2  SEM images of original Au-fingers .................................................. 155
6.3.3.3  SEM images of treated Au-fingers .................................................. 157

6.4  Conclusions ............................................................................................. 160

CHAPTER 7.  CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK
.................................................................................................................. 162

  7.1  New Contributions .................................................................................. 162

  7.2  Conclusions ............................................................................................ 162

  7.3  Recommendations for Future Work ....................................................... 165

REFERENCES ................................................................................................ 167

VITA ................................................................................................................. 183
LIST OF TABLES

Table 1.1. Considered processes and proposed studied fields in fulfill the research gaps of the proposed process. ........................................................................................................ 3

Table 2.1. Contents of major metals in PCBs. Adapted from (Cui & Anderson, 2016; Ning et al., 2017). ......................................................................................................................... 8

Table 2.2. Comparison of different metallurgy treatments. Adapted from (Z. Li et al., 2019; Mitovski et al., 2014). ........................................................................................................... 15

Table 2.3. Alternative lixiviants and recovery % of Au from WEEE. Adapted from (Sethurajan et al., 2019). ....................................................................................................................... 19

Table 2.4. Physical properties of ammonia. Adapted from (Meng & Han, 1996). ........ 22

Table 2.5. Diffusivities of various metal-amine species in ammoniacal solution at 25°C. Adapted from (Meng & Han, 1996). .......................................................... 24

Table 2.6. Thermodynamic data of various metal-ammine species. Adapted from (Meng & Han, 1996). ....................................................................................................................... 25

Table 3.1. Summary of relevant studies with particular focus on physical processing and characterization (since 2011). ........................................................................................................ 51

Table 3.2 Fitting parameters of GGS and RR models. ........................................... 60

Table 3.3. Summary of TGA results at a temperature range of 25-1000 °C, under nitrogen and oxygen. .............................................................................................................. 75

Table 4.1 Summary of critical parameters/conditions in bench-scale Cu leaching. .... 85

Table 4.2. Contents of main elements in waste RAM chips. ........................................ 87

Table 4.3. Correlation coefficient ($R^2$) of Cu extraction in 3 evaluated models under different particle sizes ($d_p$) (data corresponds to Figure 4.16, Figure 4.18 and Figure 4.20). ............................................................................................... 101

Table 4.4. Correlation coefficient ($R^2$) of Cu extraction in 3 evaluated models under different initial Cu(II) concentrations ($c(Cu^{2+})$) (data corresponds to Figure 4.17, Figure 4.19 and Figure 4.21). ............................................................................................... 101

Table 5.1 Linear equations and assumptions of three suggested kinetic models. .... 110

Table 5.2 Summary of adopted diffusion-controlled models. ................................. 114

Table 5.3. Input parameters for process simulation using the adopted model. .... 116
Table 5.4. Calculated $\alpha$ in each leaching tank using the adopted model. .................. 117

Table 5.5. Sum of error minimization between model-fitted k values and calculated k values. .................................................................................................................................................................................. 121

Table 5.6. Input parameters for process simulation using the justified model. ............. 124

Table 5.7. Calculated $\alpha$ in each leaching tank by the justified model. ..................... 124

Table 6.1. Elemental assay of original Au-fingers (AF) as stamped and decopperized Au-fingers (AF) after Cu pre-leach. ................................................................................................................................. 136

Table 6.2. Leaching parameters in Au-Cu(II)-NH$_3$ thiosulfate system. ....................... 137
LIST OF FIGURES

Figure 2.1. Material compositions and recovery values in E-waste. Adapted from (Z. Li et al., 2019) and (Golev & Corder, 2017). ................................................................. 7

Figure 2.2. General flowchart for the pyrometallurgical process of E-waste recycling. Adapted from (Ebin & Isik, 2016). ................................................................. 10

Figure 2.3. The general process for the hydrometallurgical recycling of WPCBs. Adapted from (H. Li et al., 2018). ................................................................. 12

Figure 2.4. Normalized impact factor of each component in comparison among the ER, pyro, and hydro method. Adapted from (Z. Li et al., 2019). ........................................ 14

Figure 2.5. Cu recoveries from PCBs by various lixiviants including acid leaching (Choi et al., 2004; Havlik et al., 2010; Kinoshita et al., 2003; Oh et al., 2003), ammoniacal leaching (Bari et al., 2009; Koyama, Tanaka, & Lee, 2006; Oishi, Koyama, Alam, et al., 2007; Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b; Xiao et al., 2013a), and bioleaching (Choi et al., 2004; Ilyas et al., 2007; Xiang et al., 2010; Yang et al., 2009). 17

Figure 2.6. Au recoveries Au from WPCBs by various alternative lixiviants including acid leaching (Sethurajan et al., 2019), thiosulfate leaching (Camelino et al., 2015; Ficeriová et al., 2011; Oh et al., 2003; Petter et al., 2014), and thiourea leaching (Birloaga & Vegliò, 2016; J. Li et al., 2012). ................................................................. 18

Figure 2.7. Change of total vapor pressure (kPa) of aqueous NH₃ solution with different concentrations (%wt.) under various temperatures. Adapted from (Meng & Han, 1996). 23

Figure 2.8. Eh-pH diagram for Cu-NH₃-H₂O system (constructed by HSC 9.0: Cu conc.=0.63M, NH₃ conc.=6M, T=25°C). ...................................................... 29

Figure 2.9. Schematic illustration of electrochemical dissolution of Cu in oxidative ammoniacal solution. Adapted from (Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b). ................................................................. 31

Figure 2.10. Schematic illustration of the coupled leaching-EW circuit in Cu(II)-NH₃-SO₄ system (adapted from (Oishi, Koyama, Konishi, et al., 2007; Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b)). ................................................................. 34

Figure 2.11. Schematic illustration of reaction mechanism in Cu-ammoniacal leaching system. ........................................................................................................ 35

Figure 2.12. Schematical extrapolation of Au leaching mechanism in Cu(II)-NH₃ catalyzed thiosulfate system. Adapted from (Xu et al., 2017). ........................................ 38
Figure 2.13. Simplified route of thiosulfate degradation (left route: reductive degradation; right route: oxidative degradation; greyer color: more reductive product; bluer color: more oxidative product). Adapted from (Xu et al., 2017). ................................................................. 39

Figure 2.14. Conceptual flowsheet incorporating Cu-ammoniacal and Au-thiosulfate systems............................................................................................................................................. 43

Figure 3.1. Contents of metals in different types of waste PCBs. Adapted from (Pant et al., 2012). .................................................................................................................................................. 48

Figure 3.2. Values of metals in unit of USD per gram of waste PCBs. Adapted from (Hsu et al., 2019). .............................................................................................................................................. 49

Figure 3.3. Coarse shred of general circuit boards: (a) bulk; (b) hand-sorted by metal occurrence.................................................................................................................................................. 52

Figure 3.4. Representation of preliminary shredding and sizing of circuit boards........ 53

Figure 3.5. Two-stage, three-fraction density separation for general circuit boards (size -5 mm).................................................................................................................................................. 54

Figure 3.6. Four-stage, five-fraction density separation for general circuit boards (size -2 mm).................................................................................................................................................. 55

Figure 3.7. Mass distribution (%wt.) of shredded general circuit boards (size -9.5 mm). 58

Figure 3.8. (a) GGS model of shredded circuit boards; and (b) RR model of shredded circuit boards.............................................................................................................................................. 60

Figure 3.9. Elemental concentration (ppm) in different size fractions (size -9.5 mm)..... 62

Figure 3.10. Elemental distribution (%) in different size fractions (size -9.5 mm). ....... 62

Figure 3.11. Cu and Au distribution (%) in different size fractions (size -9.5 mm). ....... 63

Figure 3.12. Mass distribution (%wt.) in different density fractions (size -5 mm). ....... 64

Figure 3.13. Elemental concentration (ppm) in different density fractions (size -5 mm). 65

Figure 3.14. Elemental distribution in different density fractions (size -5 mm). ........... 65

Figure 3.15. Distribution (%) and enrichment ratio (ER) of Cu and Au in different density fractions (size -5 mm). .................................................................................................................. 66

Figure 3.16. Mass distribution (%wt.) in different density fractions (size -2 mm). ........ 67

Figure 3.17. Elemental concentration (ppm) in different density fraction (size -2 mm). 67

Figure 3.18. Elemental distribution in different density fractions (size -2 mm). ......... 68
Figure 3.19. Distribution (%) and enrichment ratio (ER) of Cu and Au in different density fractions (size -2 mm). .......................................................... 68

Figure 3.20. Effect of utilizing 2 mg/L nonylphenol ethoxylate as the surfactant in density separation (size -2 mm). .......................................................... 69

Figure 3.21. SEM-EDS characterization of WPCBs with elemental mapping (S.G. <1.48): (a) SEM image; (b) overlayed elemental mapping; (c) EDS spectrum. ................. 71

Figure 3.22. SEM-EDS characterization of WPCBs with elemental mapping (S.G. 1.68 to 1.96): (a) SEM image; (b) overlayed elemental mapping; (c) EDS spectrum. ................. 71

Figure 3.23. SEM-EDS characterization of WPCBs with elemental mapping (S.G. >2.67): (a) SEM image; (b) overlayed elemental mapping; (c) EDS spectrum. ................. 71

Figure 3.24. SEM elemental mapping of Au and Ni in different density fractions: (a) S.G. 1.68 to 1.96; (b) S.G. >2.67. .......................................................... 72

Figure 3.25. Thermo-gravimetry (weight %) and the first derivate (FD) of general PCBs under oxygen and nitrogen atmosphere. ............................................... 73

Figure 4.1. Schematic illustration of the coupled leaching-EW circuit in Cu(II)-NH$_3$-SO$_4$ system. Adapted from references (Oishi, Koyama, Konishi, et al., 2007; Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b). .......................................................... 81

Figure 4.2. The appearance of waste chips (a) before and (b) after coarse shredding (top size achieved as -3.4mm). .......................................................... 83

Figure 4.3. Leaching apparatus used in bench-scale Cu ammoniacal leaching............ 84

Figure 4.4. Elemental concentration (mg/kg) in Au-finger and non-finger portions of waste RAM chips. .......................................................... 88

Figure 4.5. Elemental distribution (%) in Au-finger and non-finger portions of waste RAM chips. .......................................................... 88

Figure 4.6. Effect of stirring rate (rpm) on Cu recovery in ammoniacal leaching. (S/L ratio: 50 g/L, (NH$_3$)$_2$SO$_4$: 1M, NH$_4$OH: 4M, Cu(II): 40 g/L, Particle size: -2mm, Temp. 18°C) .......................................................... 89

Figure 4.7. Effect of particle size (diameter, mm) on Cu recovery in ammoniacal leaching. (S/L ratio: 50 g/L, (NH$_3$)$_2$SO$_4$: 1M, NH$_4$OH: 4M, Cu(II): 40 g/L, Stirring: 750 rpm Temp. 18°C) .......................................................... 90

Figure 4.8. Effect of initial Cu(II) concentration (g/L) on Cu recovery in ammoniacal leaching. (S/L ratio: 50 g/L, (NH$_3$)$_2$SO$_4$: 1M, NH$_4$OH: 4M, Particle size: -2mm, Stirring:750 rpm, Temp. 18°C) .......................................................... 91
Figure 4.9. Effect of temperature (°C) on Cu recovery in ammoniacal leaching. (S/L ratio: 50 g/L, (NH₃)₂SO₄: 1M, NH₄OH: 4M, Cu(II): 40 g/L, Particle size: -2mm, Stirring: 750 rpm) .............................................................. 92

Figure 4.10. Ratio of ∆Cu(II)/∆Cu(I) concentrations during leaching (initial Cu(II): 10, 20, 30, 40 g/L, S/L ratio: 50 g/L, (NH₃)₂SO₄: 1M, NH₄OH: 4M, Particle size: -2mm, Stirring: 750 rpm, Temp. 18°C). ................................................................. 93

Figure 4.11. Ratio of Cu(II)/Cu(I) concentrations and the calculated potential during leaching (initial Cu(II): 10, 20, 30, 40 g/L, S/L ratio: 50 g/L, (NH₃)₂SO₄: 1M, NH₄OH: 4M, Particle size: -2mm, Stirring: 750 rpm, Temp. 18°C). ............................................................................. 95

Figure 4.12. Solution pH and Eh (mV vs SHE) during leaching (initial Cu(II): 10, 20, 30, 40 g/L, S/L ratio: 50 g/L, (NH₃)₂SO₄: 1M, NH₄OH: 4M, Particle size: -2mm, Stirring: 750 rpm, Temp. 18°C). ............................................................................. 95

Figure 4.13. Effect of temperature (°C) on NH₃ evaporation rate in leaching. (S/L ratio: 50 g/L, (NH₃)₂SO₄: 1M, NH₄OH: 4M, Cu(II): 40 g/L, Particle size: -2mm, Stirring: 750 rpm) .............................................................. 96

Figure 4.14. Effect of initial Cu concentration (g/L) on NH₃ evaporation rate in leaching. (S/L ratio: 50 g/L, (NH₃)₂SO₄: 1M, NH₄OH: 4M, Particle size: -2mm, Stirring: 750 rpm, Temp. 18°C) .............................................................. 96

Figure 4.15. Schematic illustration of reaction mechanism in Cu-ammoniacal leaching system. ....................................................................................................................................................... 97

Figure 4.16. Plot of $1 + 2a - 3 - a23$ vs time under various particle sizes (diameter, mm), data corresponding to Figure 4.7 .......................................................................................................................... 99

Figure 4.17. Plot of $1 + 2a - 3 - a23$ vs time under various initial Cu(II) concentration (g/L), data corresponding to Figure 4.8 ...................................................................................................................................... 99

Figure 4.18. Plot of $(1 - a - 13 - 1)2$ vs time under various particle sizes (diameter, mm), data corresponding to Figure 4.7 ...................................................................................................................................... 100

Figure 4.19. Plot of $(1 - a - 13 - 1)2$ vs time under various initial Cu(II) concentration (g/L), data corresponding to Figure 4.8 ...................................................................................................................................... 100

Figure 4.20. Plot of $13ln1 - a + 1 - a - 13 - 1$ vs time under various particle sizes (diameter, mm), data corresponding to Figure 4.7 ...................................................................................................................................... 100

Figure 4.21. Plot of $13ln1 - a + 1 - a - 13 - 1$ vs time under various initial Cu(II) concentration (g/L), data corresponding to Figure 4.8 ...................................................................................................................................... 100

Figure 4.22. Plot of $13ln1 - a + 1 - a - 13 - 1$ vs time under various temperatures (°C), data corresponding to Figure 4.9 ...................................................................................................................................... 102
Figure 4.23. Arrhenius plot for Cu ammoniacal leaching, data corresponding to Figure 4.22.  .................................................................................................................. 102

Figure 4.24. Plot of $\log \frac{d\alpha}{dt} (1 - \alpha + 1 - 13 - 1) \ln 1 - \alpha + 1 + 1 - 13 - 1$ vs $\log \left( \frac{R^2}{mm} \right)$ for the estimation of reaction order. ................................................................................................. 103

Figure 4.25. Plot of $\log \frac{d\alpha}{dt} (1 - \alpha + 1 - 13 - 1) \ln 1 - \alpha + 1 + 1 - 13 - 1$ vs $\log \left( \frac{Cu^{2+}}{mol/L} \right)$ for the estimation of reaction order. ................................................................................................. 103

Figure 4.26. The goodness of model prediction (Cu: concentration of initial Cu(II), $d_p$: diameter of particles, black dotted line: $y = x$, red dotted line: linear regression of dataset, data corresponding to Figure 4.7 and Figure 4.8). .................................................................................. 104

Figure 5.1. Schematic illustration of shrinking-core model with approximation of both diffusion-controlled and changing-concentration mechanism........................................... 112

Figure 5.2. Predicted reaction fraction (a) in each leaching stage under various initial Cu(II) concentrations by the adopted model ................................................................. 115

Figure 5.3. Out-of-tank Cu(II) concentration (g/L) estimated by the adopted model. ... 117

Figure 5.4. Flowchart of kinetic modeling and simulation of batch leaching circuit in ammoniacal system ............................................................................................................. 118

Figure 5.5. Plot of Zhuravlev’s linear expression $(1 - \alpha + 1 - 13 - 1)^2$ vs time under various initial Cu(II) concentration (g/L), data corresponding to Figure 4.8 .................. 120

Figure 5.6. Out-of-tank Cu(II) concentration (g/L) estimated by the justified model. ... 122

Figure 5.7. Predicted reaction fraction (a) in each leaching stage under various initial Cu(II) concentrations by the justified model ................................................................. 123

Figure 5.8. The accumulated reacted fraction (a) in the CCL circuit, predicted by the justified model. ................................................................................................................. 123

Figure 5.9. Flowchart of kinetic modeling and simulation of CCL leaching circuit in ammoniacal system ............................................................................................................. 126

Figure 6.1. Schematic extrapolation of Au leaching mechanism in Cu(II)-NH$_3$ catalyzed thiosulfate system. Adapted from (Xu et al., 2017) .................................................... 131

Figure 6.2. Simplified route of thiosulfate degradation (left route: reductive degradation; right route: oxidative degradation; greyer color: more reductive product; bluer color: more oxidative product). Adapted from (Xu et al., 2017). .................................................... 133

Figure 6.3. Flowchart of feed preparation, leaching process, and sample characterization in this study ................................................................................................................. 136
Figure 6.16. SEM images and elemental mapping of as-shredded RAM chips with Au-fingers and boards. ........................................................................................................................................ 155

Figure 6.17. SEM images and elemental mapping of as-shredded RAM chips (Au-fingers only). ........................................................................................................................................ 155

Figure 6.18. SEM images and elemental mapping of as-shredded RAM chips (Au-fingers with the scratched surface). .................................................................................................. 156

Figure 6.19. SEM images and elemental mapping of Au leaching residues (High Au %R, data corresponding to Figure 6.8, 50mM Cu, 120 mL/min aeration). ............................... 158

Figure 6.20. SEM images and elemental mapping of Au leaching residues (Low Au %R, data corresponding to Figure 6.6, 50mM Cu, 0 mL/min aeration). ........................................ 158

Figure 6.21. EDS average weight% of leaching residues (High Au %R and Low Au %R, data corresponding to Figure 6.6 and Figure 6.8, using 50mM Cu, 0.5M/0.5M AT/AH ratio, under 120 and 0 mL/min aeration rates, respectively). ............................................ 160
CHAPTER 1. INTRODUCTION

1.1 Background and Current Research Opportunities

Rapid growth and technological innovations have resulted in large amounts of waste electric and electronic equipment (WEEE) (Lu & Xu, 2016). Among those, waste printed circuit boards (WPCBs) are considered the most valuable stream due to the significant contained value of metals, especially Cu and Au, found in WPCBs (Behnamfard et al., 2013). To date, there has been extensive research carried out in the field of recovering metals from WPCBs via hydrometallurgical processing.

The conventional hydrometallurgical processes to recover Cu and Au involves the use of strong and corrosive chemicals, such as sulfuric acid, aqua regia, and hydrogen peroxide. This raises serious environmental concerns, as well as high energy input and costly chemical usage. In comparison to the conventional acid system, ammoniacal systems were found to be more favorable, owing to its high selectivity towards desired metals. Since Cu is able to exist in the solution as stable Cu-NH₃ complexes in the presence of NH₃. It is therefore possible to selectively extract Cu using ammoniacal solution, while leaving the unwanted impurities (Fe and Al) out of the product stream. Another merit of ammoniacal solution is the complexation of NH₃ ions in aqueous allows Cu ions to be stabilized as Cu(I)-ammmine, making the downstream Cu electrowinning less costly.

Recovery of Cu by ammoniacal leaching has been well-studied in the mining industry. The work done by a group of researchers provided an initial exploration of Cu recovery in leaching, solvent extraction, and Cu electrowinning process, using multiple ammonia salts (Alam et al., 2007; Koyama, Tanaka, & Lee, 2006; Oishi et al., 2008b; Oishi, Koyama, Alam, et al., 2007; Oishi, Koyama, Konishi, et al., 2007). In Cu ammoniacal leaching, Cu was partially oxidized to Cu(I) by Cu(II) as the oxidizer, and electrodeposited primarily from Cu(I), which significantly saved the energy consumed in the electrowinning (EW) circuit. However, to our knowledge, this flowsheet has not yet been successfully scaled and applied in industry. The research gaps existing in Cu(I) ammoniacal leaching include 1) the difficulties of oxidizer control and Cu(II) regeneration; 2) the inevitable loss of NH₃ due to evaporation; 3) the balance between minimizing Cu(II) and maximizing Cu(I) in pregnant leaching solution entering EW circuit; 4) a non-standard
leaching-EW circuit design to prevent NH$_3$ loss and Cu(I) oxidation during transportation; and 5) the demand of kinetic modeling for the further application of counter-current leaching circuit.

In terms of Au recovery, cyanidation has been used to extract Au from primary ores and secondary resources for decades (O. Sitando et al., 2018). However, due to the increasingly restrictive environmental regulations and the detrimental impact caused by cyanidation contamination, extensive studies have been conducted to investigate alternative reagents to recover Au from e-waste (Sethurajan et al., 2019). Thiosulfate leaching has proven to be an efficient, economic, and greener method to recover Au amongst the above-mentioned alternatives (Camelino et al., 2015; Ficeriová et al., 2011; Oh et al., 2003; Petter et al., 2014). Au thiosulfate leaching is commonly operated under alkaline conditions using NH$_4$OH as a pH conditioner and Cu(II)-ammine as a catalyst to enhance Au extraction. However, due to the metastability of thiosulfate, Au thiosulfate leaching is a highly unstable system. There were multiple routes of thiosulfate decomposition, which is difficult to eliminate and can pose threats to Au recovery. Moreover, in a complicated multi-metal matrix like WPCBs, the impact of co-existing metals on Au extraction in thiosulfate system is yet to know.

To fulfill the identified research gaps in the literature and overcome the hypothesized obstacles hindering the commercialization of the proposed process, the study fields detailed in Table 1.1 were investigated.
Table 1.1. Considered processes and proposed studied fields in fulfill the research gaps of the proposed process.

<table>
<thead>
<tr>
<th>Considered Process</th>
<th>Study Fields</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical Processing</td>
<td>• Metal beneficiation by both size and density fractions</td>
</tr>
<tr>
<td></td>
<td>Cu Ammoniacal Leaching</td>
</tr>
<tr>
<td></td>
<td>• Controlling the oxidizer and NH\textsubscript{3} evaporations</td>
</tr>
<tr>
<td></td>
<td>• Optimizing the leaching performance by varying the affecting parameters</td>
</tr>
<tr>
<td></td>
<td>• Understanding the leaching mechanism by kinetic modeling</td>
</tr>
<tr>
<td>Cu Leaching Kinetics</td>
<td>• Developing an applicable kinetic model</td>
</tr>
<tr>
<td></td>
<td>• Applying the developed model for counter-current leaching circuit design</td>
</tr>
<tr>
<td>Au Thiosulfate Leaching</td>
<td>• Identifying the impact of co-existing metals</td>
</tr>
<tr>
<td></td>
<td>• Investigating the interplay between oxidizers</td>
</tr>
<tr>
<td></td>
<td>• Studying the key processing parameters</td>
</tr>
<tr>
<td></td>
<td>• Revealing the precipitation of Au by sulfur/metal sulfides</td>
</tr>
</tbody>
</table>

1.2 Overview

The dissertation is organized into seven chapters. Chapter one provides background information and the organizational details for the dissertation. In the second chapter (Chapter two), a thorough literature review on WPCBs and their recycling methods are presented. Additional review on the hydrometallurgical recovery of Cu and Au from WPCBs in ammoniacal systems is provided including theoretical principles of ammoniacal leaching and thiosulfate leaching.

Chapter three focuses on a detailed study of the physical properties of the material. Particle size distribution of shredded WPCBs, thermogravimetric properties, and metal occurrences are presented. The metal enrichment by size and density fractions was studied. A density-based pre-treatment was proposed to prepare suitable feed for the downstream hydrometallurgical processes.
Using a feed material (waste RAM chips) enriched in Cu and Au which was relatively homogeneous form, Chapters four to six present findings from chemical processes in Cu ammoniacal and Au thiosulfate systems. Chapter four evaluates the leaching kinetics and reveals the reaction mechanism under proposed anaerobic Cu ammoniacal leaching system. In this chapter, the investigated parameters and their effects on the leaching rate are presented and discussed. Moreover, by examining a few kinetic models with reasonable approximations, a general expression of kinetic model is provided. Chapter five further extends the application of kinetic studies to the flowsheet simulation for the optimization and demonstration purposes. Following the studies on Cu leaching, Chapter six validates the feasibility of Au recovery from waste chips in a Cu(II)-ammine catalyzed thiosulfate system. This chapter also reveals the investigation on the effect of oxidizers, complexing agents, and the influence of other metals. Of specific interest are several interesting observations on Au recovery trends under various conditions.

Lastly, Chapter seven summarizes the new contributions and the most important findings in this study. Recommendations for future work are also provided at the end to prompt the wide application of this proposed flowsheet, as well as to the prospects in a broader aspect of E-waste recycling.
CHAPTER 2. LITERATURE REVIEW

2.1 E-waste and Waste Printed Circuit Boards (WPCBs)

With the increasing development and growing demand in advanced technology and electrical industries, electrical and electronic equipment items (EEE) have become an essential part of human society (Ning et al., 2017). These electrical and electronic devices include mobile phones, music players, computers, tablets, and so on. During the last two decades, the consumption of electrical goods per capita has increased significantly, because of the lower costs and faster generation of new products. At the same time, the average lifetime of electrical items keeps decreasing (Ogunseitan, 2013). As a result, waste electrical and electronic equipment (WEEE), or E-waste, has been generated in significant quantities (H. Wang et al., 2017). The generated E-waste can be categorized into temperature exchange equipment, screens and monitors, lamps, large equipment, small equipment, and small IT, according to the Global E-waste Monitor 2020 (Forti et al., 2020). The yearly growth of E-waste generation per inhabitant was estimated to be 6.8 kg by the year 2021 (Baldé et al., 2017). Meanwhile, it was predicted that by the year 2021, the annual amount of E-waste will reach 52.2 million metric tons (Baldé et al., 2017).

Without appropriate disposal, E-waste is considered hazardous because of the composition of toxic metals and organic plastics (Ogunseitan, 2013). The potential hazardous toxins contained in E-waste can lead to the pollution of soil and groundwater in the vicinity and cause an irreparable impact on the environment (Hadi et al., 2013). According to the U.S. Environmental Protection Agency (EPA), more than 80% of E-waste traditionally reports to landfills (Hadi et al., 2013). Globally, only 17.4% of generated E-waste is properly recycled, and the recycled quantity of E-waste is much lower in developing countries, compared to developed regions (Forti et al., 2020). The rest of unrecycled WPCBs, accounting for 80-85%, is destinated in the landfill conventionally. Therefore, the disposal and recycling of E-waste have raised significant concerns.

Recent studies on Circular Economy (CE) show the major challenges in E-waste recycling (Jawahir & Bradley, 2016; Reuter et al., 2019). Recovery of E-waste, processing of recovered E-waste, and purifying techniques applied to convert the waste to its useful forms are essential in order to reach the sustainable goal of CE (Reck & Graedel, 2012).
The major driving force for E-waste recycling is the contained value of metals in E-waste (Reck & Graedel, 2012). As indicated in Figure 2.1, metal fractions dominate 60% of E-waste by weight, and many of them are valuable elements, such as Cu, Au, and Ag (Z. Li et al., 2019). Despite the varied sources of E-waste, the average grade of valuable metals, including Cu, Au, and Ag, in E-waste is considerably higher than those in conventional ore deposits (Z. Li et al., 2019). Due to the declining metal grade in conventional mining, E-waste can thereby be considered a promising secondary source for metals, in contrast to primary metal resources from mines. Additionally, the recovery of contained metals from E-waste, also known as urban mining, could potentially become more efficient and profitable compared to conventional mining, if the appropriate processing techniques and flowsheet are employed.

Among the material compositions contained in E-waste, printed circuit boards (PCBs) play an important role in electrically connecting and mechanically supporting other components in electronic equipment. Therefore, they constitute an integral component of many electronic devices (B. Ghosh et al., 2015). In total E-waste, PCBs account for 4% to 7% by weight (H. Li et al., 2018). Although the weighted fraction of PCBs in total E-waste is not noticeable, the estimated value of recovery metals from PCBs can reach up to USD 3 billion in China, and the total value of E-waste materials can be equal to USD 56 billion globally, by the year of 2014 (H. Li et al., 2018). As shown in Figure 2.1, contained metal values in PCBs range from 26% up to 81% in screens, monitors and small electronic equipment, (Golev & Corder, 2017). The enrichment of precious metals in PCBs has become the driving force for the recycling of waste PCBs (WPCBs) as the secondary resource for metal recovery (Golev & Corder, 2017).

The basic structure of PCBs is a copper-clad laminate containing epoxy resin and metallic portions, including base and precious metals (B. Ghosh et al., 2015). It has been widely acknowledged that PCBs consist of about 30% metallic fraction and about 70% non-metallic fraction by weight (Ning et al., 2017). As shown in Table 2.1, the metal contents vary among different circuit board materials. For instance, the weight percentage of Cu in PCBs range from 18% to 34%. Typically, the content of Cu in PCBs is 10% to 30% by weight (Oishi, Koyama, Alam, et al., 2007). The primary challenge in characterizing PCBs is the heterogeneity in morphology and the diversity in elemental
distribution (Ning et al., 2017). Homogenization of feed materials by proper size reduction or physical enrichment is highly recommended because the higher homogeneity assures accuracy in material characterization and favors the subsequent treatment process.

Figure 2.1. Material compositions and recovery values in E-waste. Adapted from (Z. Li et al., 2019) and (Golev & Corder, 2017).
Table 2.1. Contents of major metals in PCBs. Adapted from (Cui & Anderson, 2016; Ning et al., 2017).

<table>
<thead>
<tr>
<th>Metal Contents</th>
<th>Computer PCBs</th>
<th>Printer PCBs</th>
<th>Mobile PCBs</th>
<th>PCBs with CPU</th>
<th>Unspecified general PCBs</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[1]*</td>
<td>[2]*</td>
<td>[3]*</td>
<td>[4]*</td>
<td>[5]*</td>
<td></td>
</tr>
<tr>
<td>Cu (wt.%)</td>
<td>19.60</td>
<td>19.19</td>
<td>32.50</td>
<td>31.95</td>
<td>31.77</td>
<td>33.87</td>
</tr>
<tr>
<td>Al (wt.%)</td>
<td>2.34</td>
<td>4.01</td>
<td>3.73</td>
<td>11.11</td>
<td>10.54</td>
<td>2.57</td>
</tr>
<tr>
<td>Pb (wt.%)</td>
<td>0.30</td>
<td>0.39</td>
<td>0.00</td>
<td>--</td>
<td>4.92</td>
<td>4.96</td>
</tr>
<tr>
<td>Fe (wt.%)</td>
<td>--</td>
<td>1.13</td>
<td>1.42</td>
<td>1.94</td>
<td>13.77</td>
<td>1.03</td>
</tr>
<tr>
<td>Ni (wt.%)</td>
<td>--</td>
<td>0.17</td>
<td>0.34</td>
<td>2.71</td>
<td>1.96</td>
<td>0.13</td>
</tr>
<tr>
<td>Zn (wt.%)</td>
<td>0.01</td>
<td>0.84</td>
<td>0.64</td>
<td>1.19</td>
<td>2.23</td>
<td>0.94</td>
</tr>
<tr>
<td>Sn (wt.%)</td>
<td>0.17</td>
<td>0.69</td>
<td>0.96</td>
<td>1.78</td>
<td>6.98</td>
<td>0.15</td>
</tr>
<tr>
<td>Au (ppm)</td>
<td>--</td>
<td>130.25</td>
<td>40.00</td>
<td>--</td>
<td>369.00</td>
<td>6.61</td>
</tr>
<tr>
<td>Ag (ppm)</td>
<td>34.00</td>
<td>704.31</td>
<td>3100.00</td>
<td>3400.00</td>
<td>689.00</td>
<td>398.00</td>
</tr>
</tbody>
</table>

*Adapted from references [1] (Xing & Zhang, 2013); [2] (Behnamfard et al., 2013); [3] (Silvas et al., 2015); [4] (Calgaro et al., 2015); [5] (Birloaga et al., 2013); [6] (Evangelopoulos et al., 2015); [7] (Fogarasi et al., 2014).
2.1.1 Recycling methods for WPCBs

Current methods for the recycling of waste PCBs (WPCBs) can be divided into three major types: direct treatments, primitive recycling techniques, and advanced recycling techniques based on recovery efficiency, as reported by Ning et al (Ning et al., 2017). The direct treatments of WPCBs include landfill and incineration. The primitive recycling techniques include pyrometallurgy, hydrometallurgy, and bio-hydrometallurgy. The advanced recycling techniques cover most of the mechanical/physical separation, such as density separation, magnetic separation, and electronic conductivity separation.

Disposal of WPCBs by landfill has the widest application worldwide due to its simplicity. However, if not treated properly, the land for WPCBs disposal may turn into liability and cannot be utilized for other purposes. Furthermore, the heavy metal contamination by WPCBs in landfill sites results in the pollution of the atmosphere, soil, and groundwater in adjacent regions (Ning et al., 2017). In fact, evidence found in the literatures showed that the leaching of heavy metals takes place in an acidic leaching environment when mixing the E-waste with municipal solid waste (Hadi et al., 2013).

Another type of direct treatment is incineration. Incineration of WPCBs is a combustion process that removes most of its non-metallic fraction (NMF) at temperatures above 1200°C, and it reduces 70% of WPCBs by weight. The release of toxic emissions, including heavy metals, fly ash, dioxins and other greenhouses gaseous into the atmosphere, attracts considerable concerns about air pollution (Oguchi et al., 2013; Tange & Drohmann, 2005). Incineration of WPCBs is also categorized as part of the pyrometallurgy treatment by researchers (H. Wang et al., 2017).

Pyrometallurgical processing is a widely used method in treating WPCBs, whose basic principle is to decompose the WPCBs under an inert atmosphere (Ning et al., 2017; H. Wang et al., 2017). Typical pyrometallurgical treatments include pyrolysis, plasma, and molten salts (H. Wang et al., 2017). As depicted by Figure 2.2, general pyrometallurgical processes start with sorting and size reduction. The collected particles, properly sized, then undergo the physical process where the ferromagnetic fraction is separated. The non-ferromagnetic metals, blended with Cu scrap, are then fed to a smelter or converter, wherein the impurities are separated, and impure Cu is produced. This thermo-process is
followed by electro-refining (ER) to recover precious metals and to upgrade the Cu product (Z. Li et al., 2019). During the thermo-process of Cu, elements sharing similar thermodynamic behaviors tend to deposit together, and need to be reprocessed in alloy form (Reck & Graedel, 2012).

![General flowchart for the pyrometallurgical process of E-waste recycling. Adapted from (Ebin & Isik, 2016).](image)

Figure 2.2. General flowchart for the pyrometallurgical process of E-waste recycling. Adapted from (Ebin & Isik, 2016).

The Metal Wheel, reported by Reck and Graedel, provides a visual illustration of metal interactions and grouping in typical metallurgical processes (Reck & Graedel, 2012). Take a Cu converter as an example, wherein Cu is processed as a primary metal, and precious metals, such as Au and Ag, remain in the dominant Cu metal phase and can be
recovered by electro-refining as anode slimes and recovered separately. However, some other valuable metals, particularly in the case of E-waste, for instance, Ni, Pb, and Zn, behave as alloying metals and remain in the Cu metal phase (Nakajima et al., 2011). The removal of these alloying metals is difficult, and it cannot be achieved efficiently (Reck & Graedel, 2012). This inevitable circumstance not only causes a decrease in product quality but also results in the loss of valuable metals in thermo-processes. Further, Fe and Al as the most predominant metals by mass, are not easily recoverable with pyro processing and must be segregated prior to treatment. On the contrary, Fe, and Al, as the most concerning impurities, are not recovered in the thermo-process with Cu, which is beneficial to the process. Several toxic elements, including Cd and Hg, are emitted to the gas phase during the thermo-process, which without proper flue gas treatment are environmentally dangerous.

The current industrial norm for the recycling of E-waste is the utilization of smelting (Sum, 1991). However, these trends continue to change and evolve. There are three currently operating smelters in the United States, and they are all processing Cu ores, rather than treating WPCBs (reported by USGS) (USGS Open-File Report 03-075, 2002). A successful industrial application of pyrometallurgical treatment for E-waste recycling is Umicore, in Belgium. The Umicore Hoboken plant processing flowsheet demonstrates an integrated smelter with hydrometallurgical treatment to recover a wide range of metals (Vanbellen, 2010). This integrated flowsheet shows the segregated separation of Cu, Ni, Pb, and Sn, in addition to precious metals and other elements of interest. According to the reported flowsheet, the Hoboken refinery complex is comprised of 2 main pyrometallurgical streams focusing on Cu and Pb, in conjunction with 3 refining streams of Ni, Cu, and Pb (Vanbellen, 2010). The other elements are recovered as byproducts of these primary refining steps due to lower quantities. These byproducts include precious metals. A key consideration of smelting operations is the carbon and air emission inherent to such processes. To meet air emission standards and for economic viability, integrated smelting processes are capital intensive.

Besides pyrometallurgy, hydrometallurgy has become a popular research topic on the recycling of WPCBs, due to its lower capital cost and lower potential environmental impact (Cui & Anderson, 2016). The hydrometallurgical processes used in recycling
WPCBs can be divided into pre-treatment, leaching/extraction of metals, further purification of metals from leachate, and recovery of metals as final products in solid forms (H. Li et al., 2018). A general flowsheet of the hydrometallurgical process for the treatment of WPCBs is depicted in Figure 2.3.

In order to take the first step of dissolving metals from WPCBs in solutions, leaching/extraction of metals using various acids (e.g. H$_2$SO$_4$, HNO$_3$, aqua regia, and HClO$_4$) with oxidants (e.g. H$_2$O$_2$, O$_2$, Fe$^{3+}$, and Cl$_2$) is well established and extensively studied (Cui & Anderson, 2016). It has also been published that Cu in WPCBs can be recovered by ammoniacal leaching, followed by a complete hydrometallurgical processing route in the alkaline ammoniacal system (Alam et al., 2007; Oishi et al., 2008b; Oishi, Koyama, Alam, et al., 2007; Oishi, Koyama, Konishi, et al., 2007). For the recovery of precious metals, particularly Au, reagents including thiourea, thiosulfate, halide, and aqua regia, have been used as alternatives to cyanide (Cui & Anderson, 2016). Among these leaching reagents, thiosulfate is regarded as the most promising owing to its lesser
environmental impact, higher extraction selectivity, lower corrosivity in solution, and lower reagent cost (Xu et al., 2017).

2.1.2 Comparison among pyrometallurgy, hydrometallurgy, and electrochemical recovery (ER)

Li et al. have done work on the Life Cycle Assessment (LCA) of E-wastes, in terms of comparing environmental impacts by the three most commonly used recycling methods, i.e., pyrometallurgical, hydrometallurgical, and electrochemical recovery methods. Adapted from the work by Li et al., Figure 2.4 identifies the major source of the environmental impact for different processes, by analyzing the normalized percentage contribution of each component among all three processes. By this means, various environmental impacts that stand out in each recycling method can easily be visualized as a percentage contribution. For instance, pyrometallurgical processes have the highest contribution to environmental impact in terms of global warming because of carbon dioxide emissions. In the hydrometallurgical processes, ozone and fossil fuel depletion are the two biggest contributors to environmental impacts (H. Li et al., 2018). This is mainly due to the utilization of hydrogen peroxide as an oxidizer and sulfuric acid as a leaching reagent. Also, the use of sulfuric acid in the hydrometallurgical process is a significant factor, contributing to acidification and respiratory effects in LCA (Z. Li et al., 2019). The environmental impact of electrochemical recovery (ER) is relatively mild, compared to pyro and hydro processes. In the ER processes, the highest environmental impact is ozone depletion due to the use of hydrochloric acid. The second biggest issue in ER process is the consumption of power and electricity, which constitutes 5 - 40% of the environmental impact (Z. Li et al., 2019).
Additionally, the consumption of major chemical reagents used in pyrometallurgy, hydrometallurgy, and electrochemical recovery treatment of E-waste recycling was assessed and summarized by Li et al. (Z. Li et al., 2019). According to the life cycle inventory (LCI), to make USD 1000 profit from each process, the consumption of each input and output was assessed. Electricity and enriched air are the two biggest input consumptions, and the release of CO\textsubscript{2} and other gasses is the biggest output consumption in pyrometallurgical processes (Z. Li et al., 2019). The inputs of hydrogen peroxide and sulfuric acid are the top two consumptions, which are 226 kg and 165 kg, respectively, in hydrometallurgical processes (Z. Li et al., 2019). In electrochemical recovery, acid and water consumptions are the top concerns. The summary of the pros and cons of using these three processes is shown in Table 2.2, in terms of capital and operation expenses, energy input, reagent usage, gas emissions, waste management, etc.
Table 2.2. Comparison of different metallurgy treatments. Adapted from (Z. Li et al., 2019; Mitovski et al., 2014).

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantage</th>
<th>Limitation</th>
</tr>
</thead>
</table>
| Pyrometallurgy      | • Higher reaction rates  
                     • Easier separation of valuable and waste                                | • More energy requirement  
                     • Low recovery rate, non-metals cannot be recycled  
                     • Iron and aluminum are difficult to recover  
                     • Large capital investment  
                     • Higher emissions of hazardous gas, dioxin and dust                   |
| Hydrometallurgy     | • More accurate and predictable  
                     • Better pollution control  
                     • Less energy intensive  
                     • More environmentally friendly                                          | • Slow and time-consuming  
                     • Require finer size in pre-processing  
                     • Require more chemicals that can make the process more toxic           |
| Electrochemical     | • Fewer chemicals involved  
                     • Higher efficiency  
                     • Lower investment and operation cost                                      | • Less practical applications |
| Recovery            |                                                                          |                                                                          |

In general, the pyrometallurgical process, using high temperatures, allows a high reaction rate of metal separation, but it also causes environmental issues because of hazardous emissions (Ebin & Isik, 2016; Z. Li et al., 2019). Also, the alloying of metals due to their similarity in chemical properties when undergoing a high-temperature process increases the complexity of the pyrometallurgical process. In comparison to the pyrometallurgical process, the hydrometallurgical process is more economical and environmentally friendly (H. Li et al., 2018). However, despite the reduced energy demand, the toxicity and acidification of reagents used in the hydrometallurgical process cannot be neglected (Z. Li et al., 2019). Meanwhile, electrochemical recovery has the merits of low chemical consumption, enhanced operating control, and less energy input (B. Ghosh et al., 2015). Therefore, a novel hydrometallurgical process, in combination with electrochemical recovery, is proposed in this study in order to achieve a high metal recovery as well as to reduce environmental impact.
2.1.3 Recovery of Cu and Au from WPCBs by hydrometallurgical process

The high content of valuable metals, such as Cu and Au, in WPCBs, has made it a candidate for secondary resources (Syed, 2012). Recovery of these metals from WPCBs could potentially become more efficient and profitable compared to conventional mining if the appropriate processing techniques and flowsheet are employed.

Figure 2.5 summarizes select literature on Cu recoveries from PCBs using various lixiviants, including acids, bases, and biological processes. Metal extraction in acidic solutions is the most widely used and is well-established by researchers (Cui & Anderson, 2016). In acid leaching, strong acids, such as H₂SO₄, HNO₃, HCl+HNO₃ (aqua regia), and HClO₄, are typically utilized with the assistance of oxidizing reagents, such as H₂O₂, O₂, Fe³⁺ and Cl₂ (Cui & Anderson, 2016). In practice, acid leaching systems are easier to operate, considering the downstream SX and EW processes. However, strong oxidizing reagents are not only costly but also inefficient because of the lack of selectivity to target metals.

Bioleaching has been studied adequately using a variety of bacteria strains (Brandl et al., 1999; Choi et al., 2004; Ilyas et al., 2007, 2010; Yang et al., 2009). Bacteria, such as Acidithiobacillus Ferrooxidans, were used to extract Cu in acidic conditions (Yang et al., 2009). Some of them show higher Cu recovery, and some of them show less. However, the problems associated with bioleaching methods are the difficulty to control bacteria activity, and the slow kinetics reaching reaction equilibrium (Xiang et al., 2010).

In addition to acid leaching and bioleaching, ammoniacal leaching, specifically targeting basic metals, has been well acknowledged and regarded as a promising hydrometallurgical process for metal recovery from WPCBs (Alam et al., 2007; Oishi et al., 2008b; Oishi, Koyama, Alam, et al., 2007; Oishi, Koyama, Konishi, et al., 2007). As indicated by Figure 2.5, the ammoniacal process shows reasonable performance in Cu recovery, and it seems a favorable method owing to its low capital expense (CapEx) and operational expense (OpEx), high recovery efficiency, and lower environmental impact (Oishi, Koyama, Konishi, et al., 2007). Particularly in comparison to acidic leaching involving corrosive acids and H₂O₂, ammoniacal leaching has the following advantages (Radmehr et al., 2012):
1) Higher selectivity towards basic metals (i.e. Cu, Ni, Co, Zn, etc.);
2) Lower dissolvability of potential contaminants (i.e. Fe, Al, Ca, Si, etc.);
3) Lower power requirement and reagent consumption;
4) Reduction of corrosion potential compared to acid treatment;
5) Less harmful byproducts generated.

Figure 2.5. Cu recoveries from PCBs by various lixiviants including acid leaching (Choi et al., 2004; Havlik et al., 2010; Kinoshita et al., 2003; Oh et al., 2003), ammoniacal leaching (Bari et al., 2009; Koyama, Tanaka, & Lee, 2006; Oishi, Koyama, Alam, et al., 2007; Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b; Xiao et al., 2013a), and bioleaching (Choi et al., 2004; Ilyas et al., 2007; Xiang et al., 2010; Yang et al., 2009).

For Au recovery, cyanidation has been used to extract Au from primary ores and secondary resources for decades (O. Sitando et al., 2018). However, due to the increasingly restrictive environmental regulations, and the detrimental impact caused by cyanidation contamination, extensive studies have been done to investigate other reagents, such as thiourea, thiosulfate, thiocyanate, and glycine, as potential alternatives to cyanide (Barbosa-Filho & Monhemius, 1994; Eksteen & Oraby, 2015; Sethurajan et al., 2019; Xu et al., 2017). Figure 2.6 summarized some of the literature utilizing alternative reagents to recover Au from e-waste (adapted from (Sethurajan et al., 2019)). Acid methods, such as...
chloride leaching and aqua regia digestion, use highly corrosive chemicals that pose threats to the environment. Due to the extreme nobility/inactivity of Au, hydrogen peroxide ($\text{H}_2\text{O}_2$) is usually employed in acid leaching as a strong oxidant to improve Au extraction. However, because of the toxicity of the chemicals used, the oxidative acid method for Au extraction is not recommended. In comparison to acids, thiourea and thiosulfate have become more promising alternatives to recovering Au. However, in thiourea leaching, sulfuric acid is applied alongside $\text{Fe}^{2+}$ as an oxidant, which still poses threats to the environment (Birloaga & Vegliò, 2016; J. Li et al., 2012). Thiosulfate leaching is commonly operated under alkaline conditions, using $\text{NH}_4\text{OH}$ as a pH conditioner and $\text{Cu}^{2+}$ as an oxidant to enhance the Au recovery. It has been proven to be an efficient, economic, and greener method to recover Au amongst the above-mentioned alternatives (Camelino et al., 2015; Ficeriová et al., 2011; Oh et al., 2003; Petter et al., 2014).

Figure 2.6. Au recoveries Au from WPCBs by various alternative lixiviants including acid leaching (Sethurajan et al., 2019), thiosulfate leaching (Camelino et al., 2015; Ficeriová et al., 2011; Oh et al., 2003; Petter et al., 2014), and thiourea leaching (Birloaga & Vegliò, 2016; J. Li et al., 2012).
Table 2.3. Alternative lixiviants and recovery % of Au from WEEE. Adapted from (Sethurajan et al., 2019).

<table>
<thead>
<tr>
<th>Method</th>
<th>Lixiviants</th>
<th>Au Recovery %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromide</td>
<td>Acidic NaBr + H₂O₂</td>
<td>98.00</td>
<td>(Kogan, 2006)</td>
</tr>
<tr>
<td>Aqua Regia</td>
<td>HCl + HNO₃</td>
<td>97.00</td>
<td>(Park &amp; Fray, 2009)</td>
</tr>
<tr>
<td>Chloride</td>
<td>HCl + H₂O₂</td>
<td>30.00</td>
<td>(Imre-Lucaci et al., 2017)</td>
</tr>
<tr>
<td>Chloride</td>
<td>NaClO₃</td>
<td>93.00</td>
<td>(Lu et al., 2017)</td>
</tr>
<tr>
<td>Iodide</td>
<td>KI + I₂</td>
<td>99.00</td>
<td>(Serpe et al., 2015)</td>
</tr>
<tr>
<td>Iodide</td>
<td>Iodine/iodide</td>
<td>98.00</td>
<td>(Xiu et al., 2015)</td>
</tr>
<tr>
<td>Thiourea</td>
<td>Thiourea + Fe(III)</td>
<td>90.00</td>
<td>(J. Li et al., 2012)</td>
</tr>
<tr>
<td>Thiourea</td>
<td>Thiourea + Fe(III) + H₂SO₄</td>
<td>84.00</td>
<td>(Behnamfard et al., 2013)</td>
</tr>
<tr>
<td>Thiourea</td>
<td>Thiourea + Fe(III) + H₂SO₄</td>
<td>90.00</td>
<td>(Birloaga &amp; Vegliò, 2016)</td>
</tr>
<tr>
<td>Lime Sulfur</td>
<td>Lime Sulfur Synthetic Solution + Na₂S₂O₃-CuSO₄-NH₄OH</td>
<td>92.00</td>
<td>(J. Li &amp; Huang, 2010)</td>
</tr>
<tr>
<td>Synthetic Solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>(NH₄)₂S₂O₃ + CuSO₄ + NH₄OH</td>
<td>95.00</td>
<td>(Oh et al., 2003)</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>(NH₄)₂S₂O₃ + CuSO₄·5H₂O + NH₃</td>
<td>98.00</td>
<td>(Ficeriová et al., 2011)</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>Na₂S₂O₃ + NH₄OH + Cu²⁺</td>
<td>15.00</td>
<td>(Petter et al., 2014)</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>(NH₄)₂S₂O₃ + Cu²⁺</td>
<td>70.00</td>
<td>(Camelino et al., 2015)</td>
</tr>
</tbody>
</table>

Successful commercialization of thiosulfate leaching of Au was performed at the Newmont Mining Corporation and Barrick Gold Corporation for the processing of carbonaceous gold ores (Bhakta & Arthur, 2002; Fleming et al., 2003). To improve the efficiency of Au leaching, Cu(II) is employed as an essential catalyst, and ammonia is
required to stabilize the ionic species in the thiosulfate solution. Over the last 10 years, numerous research has been done to leach Au in Cu(II) catalyzed ammoniacal thiosulfate solution (Dong et al., 2019; Ha et al., 2014; Kasper & Veit, 2018; Tripathi et al., 2012; J. Wang et al., 2019).

Using a leaching condition of 0.2M (NH₄)₂S₂O₃, 25mM CuSO₄, and 1.5M NH₃, 80.5% of Au extraction was achieved from an oxide Au concentrate, as reported by Dong et al (Dong et al., 2019). Using a similar lixiviant containing 0.1M (NH₄)₂S₂O₃, 40 mM CuSO₄, at pH of 10-10.5, Tripathi et al. reported a Au extraction of 56.7% from secondary resources (Tripathi et al., 2012). The recovery of Au in secondary resources was generally low due to the complexity of feed materials and interference from the co-existing metals (Jeon et al., 2018).

Based on the information given in Figure 2.5 and Figure 2.6, an ammonia-based hydrometallurgical process shows a reasonable performance for the extraction of Cu in NH₃-SO₄ solution and the extraction of Au in NH₃-S₂O₃ solution. Besides the merits of cheaper process costs, high recovery efficiency, and lower environmental impact (Oishi, Koyama, Konishi, et al., 2007), the combined process of Cu ammoniacal leaching and Au thiosulfate leaching has the following advantages:

1) Higher selectivities towards target metals (Cu and Au);
2) Lower power consumption and less equipment corrosion;
3) Greener process compared to acid leaching and cyanidation;
4) Ease of integration of Cu and Au circuits due to the similar chemistry;
5) Saved reagent usage and simplified material transition between circuits.

2.2 Ammonia-based Hydrometallurgical Process

This section provides the theoretical principles and fundamental background of the proposed Cu and Au processing methods, based on a literature review of related techniques. The chemistry in Cu-NH₃-SO₄-H₂O system and Au-NH₃-S₂O₃-H₂O system was studied and the following purification/recovery methods were discussed. Current research on proposed Cu and Au processes was summarized and reviewed. Scoping work and
preliminary experiments were planned and introduced in the aspect of addressing the research gaps within current processes and the proposed flowsheet.

2.2.1 Chemistry in ammoniacal system

\( \text{NH}_3 \) is highly soluble in water that can easily dissolve in the aqueous phase as \( \text{NH}_4\text{OH} \) under room temperature. At the standard condition, the amount of \( \text{NH}_3 \) in the saturated solution can reach as high as 30% wt. As \( \text{NH}_3 \) is dissolved in water, it forms an alkaline solution by \( \text{NH}_4\text{OH} \) is a strong alkaline with pH above 12 in 28 – 30% \( \text{NH}_4\text{OH} \). The dissolution of \( \text{NH}_3 \) gas in water and the formation of aqueous ammonia \( \text{NH}_4\text{OH} \) are expressed as Eqs. (2.1) and (2.2). Other physical properties of ammonia, such as the melting/boiling points, density, viscosity, etc., were given in Table 2.4. \( \text{NH}_3 \) has a high vapor pressure, which increases with temperature (Meng & Han, 1996). The relation between the vapor pressure of \( \text{NH}_3 \) and various temperatures is shown in Figure 2.7.

\[
\begin{align*}
\text{NH}_3(g) + \text{H}_2\text{O} & \leftrightarrow \text{NH}_3(\text{aq}) \quad (2.1) \\
\text{NH}_3(\text{aq}) + \text{H}_2\text{O} & \leftrightarrow \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad (2.2)
\end{align*}
\]
Table 2.4. Physical properties of ammonia. Adapted from (Meng & Han, 1996).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>-77.74 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>-33.42 °C</td>
</tr>
<tr>
<td>ΔH (fusion at melting pt)</td>
<td>5662 J/mole</td>
</tr>
<tr>
<td>ΔH (vaporization at boiling pt)</td>
<td>23370 J/mole</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>132.9 °C</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>11.379 MPa</td>
</tr>
<tr>
<td>Dielectric constant (liquid at -60 ± 10°C)</td>
<td>26.7</td>
</tr>
<tr>
<td>Density (liquid at -70°C)</td>
<td>0.7253 g/cm³</td>
</tr>
<tr>
<td>Density (liquid at -30°C)</td>
<td>0.6777 g/cm³</td>
</tr>
<tr>
<td>ΔH⁰, 25°C</td>
<td>-46.23 kJ/mole</td>
</tr>
<tr>
<td>ΔG⁰, 25°C</td>
<td>-16.65 kJ/mole</td>
</tr>
<tr>
<td>logK</td>
<td>2.9144</td>
</tr>
<tr>
<td>Entropy, S⁰, 25°C</td>
<td>192.67 J/deg.mole</td>
</tr>
<tr>
<td>Heat capacity, C⁰_p, 25°C</td>
<td>35.69 J/deg.mole</td>
</tr>
<tr>
<td>Viscosity (liquid at 25°C)</td>
<td>0.00135 poise</td>
</tr>
<tr>
<td>Vapor pressure (liquid at -20°C)</td>
<td>190.22 kPa</td>
</tr>
<tr>
<td>Vapor pressure (liquid at 0°C)</td>
<td>429.94 kPa</td>
</tr>
<tr>
<td>Vapor pressure (liquid at 20°C)</td>
<td>857.05 kPa</td>
</tr>
</tbody>
</table>
Figure 2.7. Change of total vapor pressure (kPa) of aqueous NH₃ solution with different concentrations (%wt.) under various temperatures. Adapted from (Meng & Han, 1996).

NH₃ is well known as a complexing ligand for transition metals, such as Cu, Ni, Co, Zn, Ag, Au, etc., and can form soluble complexes with these metals under alkaline conditions. This unique chemical property makes NH₃ a widely used reagent in hydrometallurgical processes in the history of mining. Besides the soluble species listed above, a distinguishing advantage of the ammonia leaching system is that the major contaminants in most of the primary resources, i.e. Al and Fe, are not as soluble as the more valuable metals in ammonia solution. In an ammonia-based hydrometallurgical process, ammonium hydroxide (NH₄OH) or gaseous NH₃ is used to provide NH₃ complex and maintain the leaching solution in highly alkaline conditions. Ammonium salts, such as (NH₃)₂SO₄, (NH₃)₂CO₃, and NH₄Cl, are needed, alongside aqueous ammonia (NH₃ or NH₄OH), as the complexing agent, as well as to provide the anions for electron-neutralism in solution. The dissolution of metals from the mineral matrix, or substrate (malachite, chrysocolla, etc.), by ammonia/ammonium salts takes place due to the formation of soluble metal-ammine compounds under alkaline conditions (Bingöl et al., 2005; Künkül et al., 1994; W. Liu et al., 2010). The diffusivities of some transition metals complexed with NH₃ in different anion systems are listed in Table 2.5.

Generally, there are two types of ammoniacal leaching, oxidative and reductive leaching reactions. Either an oxidant or reductant is requested in ammoniacal leaching to
extract metals from the mineral matrix, with electron transportation involved in the Redox reaction. Typically, in oxidative NH₃ leaching, oxygen is used as the oxidant to oxidize sulfide and release metals (Cu, Ni, Co, Zn, and Fe) from the mineral matrix (Conejeros et al., 2020; M. K. Ghosh et al., 2003a; Karimov et al., 2020; Williamson et al., 2021; Yin et al., 2018). In the case of metal extraction from E-waste, pure metals are oxidized by oxygen and dissolved in ammoniacal solutions, where the stable metal-amine compounds are formed. In reductive NH₃ leaching, CO gas, or a mixture of CO/CO₂ gases, is used as a reducing agent, when extracting metals/minerals from a highly oxidative form, such as zinc ferrite (C. Wang et al., 2020), nickel/cobalt laterite (Caron, 1950; Chen et al., 2010; Ma et al., 2013), and ocean manganese nodules (Han et al., 1974). To enhance the leaching efficiency in ammonia/ammonium salt, elevated temperature and pressure are sometimes employed (Caron, 1950; Chase, 1980; Forward & Mackiw, 1953; Kuhn et al., 1974).

Table 2.5. Diffusivities of various metal-amine species in ammoniacal solution at 25°C. Adapted from (Meng & Han, 1996).

<table>
<thead>
<tr>
<th>Species</th>
<th>Chloride</th>
<th>Nitrate</th>
<th>Sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(NH₃)₂⁺</td>
<td>1.95</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Cu(NH₃)₄²⁺</td>
<td>1.39</td>
<td>1.3</td>
<td>0.93</td>
</tr>
<tr>
<td>Co(NH₃)₄²⁺</td>
<td>1.37</td>
<td>1.32</td>
<td>0.97</td>
</tr>
<tr>
<td>Ni(NH₃)₆²⁺</td>
<td>1.19</td>
<td>1.2</td>
<td>0.89</td>
</tr>
<tr>
<td>Zn(NH₃)₄²⁺</td>
<td>1.35</td>
<td>1.3</td>
<td>0.9</td>
</tr>
</tbody>
</table>

In addition to extracting base metals, i.e. Cu, Ni, Co, Zn, etc., NH₃ is widely used in the leaching of precious metals, i.e. Ag and Au. In precious metal extraction, NH₃ acts as the catalyst, without involving in the formation of the final product, but facilitating the leaching process as an intermediate step. For example, in ammoniacal-thiosulfate leaching, Cu(II) sulfate and thiosulfate solution are used as the oxidizer and leaching reagent, respectively. In this reacting mechanism, NH₃ is involved as an intermediate step to stabilize the dissolved Au and the reacted Cu(I)/Cu(II) as metal-ammine compounds. The
thermodynamic data of possible species formed during the leaching process are given in Table 2.6.

Table 2.6. Thermodynamic data of various metal-ammine species. Adapted from (Meng & Han, 1996).

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G^0_f$, kJ/mol</th>
<th>Species</th>
<th>$\Delta G^0_f$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag(NH}_3\text{)}^+$</td>
<td>31.658</td>
<td>$\text{NH}_3$</td>
<td>-26.633</td>
</tr>
<tr>
<td>$\text{Ag(NH}_3\text{)}_2^+$</td>
<td>-17.253</td>
<td>$\text{NH}_4^+$</td>
<td>-79.439</td>
</tr>
<tr>
<td>$\text{Au(NH}_3\text{)}_2^+$</td>
<td>-41.353</td>
<td>$\text{Ni(NH}_3\text{)}^2+$</td>
<td>-87.814</td>
</tr>
<tr>
<td>$\text{Au(NH}_3\text{)}_4^{3+}$</td>
<td>64.489</td>
<td>$\text{Ni(NH}_3\text{)}_2^{2+}$</td>
<td>-126.842</td>
</tr>
<tr>
<td>$\text{Cu(NH}_3\text{)}^+$</td>
<td>-10.469</td>
<td>$\text{Ni(NH}_3\text{)}_3^{2+}$</td>
<td>-162.981</td>
</tr>
<tr>
<td>$\text{Cu(NH}_3\text{)}_2^+$</td>
<td>-65.285</td>
<td>$\text{Ni(NH}_3\text{)}_4^{2+}$</td>
<td>-196.022</td>
</tr>
<tr>
<td>$\text{Cu(NH}_3\text{)}_2^{2+}$</td>
<td>15.578</td>
<td>$\text{Ni(NH}_3\text{)}_5^{2+}$</td>
<td>-22.647</td>
</tr>
<tr>
<td>$\text{Cu(NH}_3\text{)}_2^{2+}$</td>
<td>-30.486</td>
<td>$\text{Ni(NH}_3\text{)}_6^{2+}$</td>
<td>-252.931</td>
</tr>
<tr>
<td>$\text{Cu(NH}_3\text{)}_3^{2+}$</td>
<td>-73.199</td>
<td>$\text{Co(NH}_3\text{)}^{2+}$</td>
<td>-92.546</td>
</tr>
<tr>
<td>$\text{Cu(NH}_3\text{)}_4^{2+}$</td>
<td>-111.39</td>
<td>$\text{Co(NH}_3\text{)}_2^{2+}$</td>
<td>-127.722</td>
</tr>
<tr>
<td>$\text{Zn(NH}_3\text{)}^{2+}$</td>
<td>-186.6</td>
<td>$\text{Co(NH}_3\text{)}_3^{2+}$</td>
<td>-159.548</td>
</tr>
<tr>
<td>$\text{Zn(NH}_3\text{)}_2^{2+}$</td>
<td>-226.299</td>
<td>$\text{Co(NH}_3\text{)}_4^{2+}$</td>
<td>-189.698</td>
</tr>
<tr>
<td>$\text{Zn(NH}_3\text{)}_3^{2+}$</td>
<td>-266.415</td>
<td>$\text{Co(NH}_3\text{)}_5^{2+}$</td>
<td>-220.352</td>
</tr>
<tr>
<td>$\text{Zn(NH}_3\text{)}_4^{2+}$</td>
<td>-304.648</td>
<td>$\text{Co(NH}_3\text{)}_6^{2+}$</td>
<td>-162.898</td>
</tr>
</tbody>
</table>

2.2.2 Historic development of the ammoniacal process in mining

The metallurgical processes involving ammonia and ammonium salts was first reported in 1916 (Greenawalt, 1912; Newton & Wilson, 1942). The pioneering application of the ammonia process was adopted for copper extraction from high-grade copper ores in two processing plants, by Kennecott in Alaska and Calumet and Hecla in Northern Michigan, respectively (Grauman, 1978; Moffit, 1916). As the mining industry
continuously develops, the ore deposit has become more and more complex. Thus, the application of the ammonia process has transferred from readily dissolved copper oxide towards more refractory sulfide ores. Elevated temperature and pressure were often adopted to convert sulfide to oxide, in which case the copper extraction was facilitated.

Ammonia leaching employing high temperature and pressure was invented by Sherritt Gordon in 1947 (Forward & Mackiw, 1953). In the Sherritt Gordon process, recovery of multiple elements, including copper, nickel, and cobalt from flotation concentrates of sulfide minerals was achieved under 105 °C and 0.8 MPa due to their increased solubility in a direct ammonia environment with the assistance of high temperature and enhanced air pressure. Conversely, iron from the sulfide matrix was left in the residues and successfully separated from the valuable metals. The dissolved elements were then recovered by precipitation as hydroxides and the excessive ammonia in leachate was recycled by evaporation at boiling temperature. Successful commercialization of the Sherritt Gordon process was constructed at Fort Saskatchewan, Alberta, Canada, in 1954 (Forward & Mackiw, 1955; Mackiw et al., 1958).

Another process employing ammonia leaching with increased temperature was the Arbiter process, first innovated in a pilot plant in Arizona, in 1970 (Kuhn et al., 1974). Copper and nickel, from the concentrate of chalcopyrite, were recovered in an environment of ammonia and oxygen at temperatures of 70-80 °C. Target metals were dissolved in the solution as metal-ammine sulfate complex while iron was left in the residues as iron hydroxide. This process was later scaled up in commercial operation in Anaconda with a copper production of 91 tons per day. The downstream purification of leached copper used LIX65N as an extractant in solvent extraction. After stripping by sulfuric acid, the enriched electrolyte was then fed to electrowinning to produce high-purity copper cathodes. Although ammonia was recycled by evaporation to some extent, the process was considered less applicable from the technical and economic points of view due to the inefficient utilization of ammonia and sulfate (Radmehr et al., 2012).

Aiming at extracting copper, nickel, and cobalt from flotation concentrate, another process used ammoniacal process was developed by INCO of Copper Cliff, Ontario, Canada (Chase, 1980). The concentrate was previously treated by oxide roasting and reductive quenching, then followed by leaching in ammonia solution. Rather than using
direct ammonia, this process applied ammonia-ammonium carbonate as leaching solution. The reaction between metal-bearing minerals and ammoniacal lixiviant resulted in a pregnant solution containing soluble metal-ammine carbonate complexes.

More recently, Taguchi method was developed for Meskani Mine copper ore in Iran, to investigate the affecting factors in column leaching using ammoniacal solutions (Radmehr et al., 2012). Various parameters, including ammonia concentration, flow rate, particle size, and retention times, were studied. The results of Taguchi’s research revealed the importance of ammonia concentration and particle size to achieve leaching recovery of copper up to 80.6%.

Besides the recovery of copper, the ammonia process is also widely used in the extraction of other base metals, such as nickel, cobalt, and zinc. The Caron process, invented in 1924, was adapted preliminarily to extract nickel and cobalt from low-grade laterite ores, using ammonia-ammonium carbonate solution (Caron, 1950). The laterite ore was pre-treated by roasting in a reductive atmosphere and then leached in a solution mixed with ammonia and ammonium carbonate. The commercialization of the Caron process was adopted worldwide, in Cuba, Philippines, and Australia (Moskalyk & Alfantazi, 2002). Recently, a review on zinc extraction by ammonium carbonate also called the “Schnabel process” was reported by Harvey (Harvey, 2006). The Schnabel process can be dated back to 1880 (Schnabel, 1880). In general, the zinc-bearing feed was roasted in an air-enriched environment, and the roasted feed was leached using an ammonia/ammonium carbonate solution. Later, the pregnant leaching solution (PLS) is purified using cementation and precipitation methods. Dissolved contaminants in PLS are displaced with metallic zinc, and iron was precipitated by air oxidation. Further, zinc from the purified solution is precipitated by steam heating and calcinated to zinc oxide as the final product. After heating, NH₃ and CO₂ are also able to be recycled (Harvey, 2006).

2.2.3 Cu extraction in ammoniacal solution

In Cu-NH₃-H₂O system, the dominant species consist of NH₃, NH₄⁺, H⁺, Cu²⁺, Cu⁺, Cu(OH)₃⁻, Cu(OH)₄²⁻, Cu₂(OH)₂²⁺, and the corresponding Cu species complexed with NH₃ ions. The soluble Cu-ammine species composite various ligancy with NH₃ (from 1 to 4)
and two different oxidation states of Cu (Cu$^{2+}$ and Cu$^+$): Cu(NH$_3$)$^+$, Cu(NH$_3$)$_2^+$, Cu(NH$_3$)$^{2+}$, Cu(NH$_3$)$_2^{2+}$, Cu(NH$_3$)$_3^{2+}$ and Cu(NH$_3$)$_4^{2+}$ (Konishi, 2007). To demonstrate the principles of ammoniacal leaching, via the existence of stable Cu-amine complexes, an Eh-pH diagram of Cu-NH$_3$-H$_2$O system was constructed using HSC 9.0, as shown in Figure 2.8. The conditions applied for the construction of the Eh-pH diagram were under Cu concentration of 0.63M, NH$_3$ concentration of 6M (1M of (NH$_3$)$_2$SO$_4$ and 4M of NH$_4$OH), the temperature of 25°C, and pH range from 0 to 14, across the water stability region. It is noticed that the stability regions of discussed Cu-amine species under this condition were different than in other literature, where Cu(NH$_3$)$_2^+$ stabilizes at pH 7-12 and Cu(NH$_3$)$_4^{2+}$ stabilizes at pH 8-11, from Eh -0.3 V (vs SHE) or higher (Konishi, 2007). However, according to the constructed Eh-pH diagram shown in Figure 2.8, the stable Cu-amine species, i.e. Cu(NH$_3$)$_2^+$ and Cu(NH$_3$)$_4^{2+}$, are able to remain in ionic forms in a wide range of pH, from 7 to 14. It was noted that the pH range for the stability regions of Cu(NH$_3$)$_2^+$ and Cu(NH$_3$)$_4^{2+}$ were wider, in comparison to the Eh-pH diagram reported by Koyama et al., where Cu(NH$_3$)$_2^+$ was stabilized at pH 7-12 and Cu(NH$_3$)$_4^{2+}$ at pH 8-11 (Koyama, Tanaka, & Lee, 2006). The variety of pH range was likely due to the different software used for constructing the diagram (i.e. differences in thermodynamic database, default settings on activity, etc.), and the different input concentrations for the Cu-NH$_3$ species. Additionally, the stability regions depend significantly on the potential. Despite the differences in pH in the reported Eh-pH diagrams, there is similarity that the stability region of Cu(NH$_3$)$_4^{2+}$ is located above the stability region of Cu(NH$_3$)$_2^+$ in these diagrams. Accordingly, it is possible that the higher oxidation species, Cu(NH$_3$)$_4^{2+}$, can serve as an oxidant, and the lower oxidation species, Cu(NH$_3$)$_2^+$, can act as a reductant, during Cu ammoniacal leaching. The relationship of the potential between these two species can be written as:

$$E_h = 0.074 - 0.1182 \log[\text{NH}_3] + 0.0591 \log \frac{[\text{Cu(NH}_3)_4^{2+}]}{[\text{Cu(NH}_3)_2^+]}$$ (2.3)

Additionally, the more positive oxidation-reduction potential (ORP) of Cu(NH$_3$)$_4^{2+}$/Cu$^0$, compared to the ORP of Cu(NH$_3$)$_2^+$/Cu$^0$, indicates that Cu(NH$_3$)$_4^{2+}$ can serve as an oxidant to oxidize Cu$^0$ to Cu(NH$_3$)$_2^+$ in the presence of NH$_4^+$ (Koyama, Tanaka,
& Lee, 2006; Radmehr et al., 2013). This can be illustrated by the following equations (Oishi, Koyama, Konishi, et al., 2007):

\[
\begin{align*}
\text{Cu(NH}_3\text{)_4}^{2+} + e^- &= \text{Cu(NH}_3\text{)_2}^+ + 2\text{NH}_3 \quad E_0 = 0.10 \text{ V vs SHE} \\
\text{Cu(NH}_3\text{)_2}^+ + e^- &= \text{Cu} + 2\text{NH}_3 \quad E_0 = -0.10 \text{ V vs SHE} \\
\text{Cu(NH}_3\text{)_4}^{2+} + \text{Cu} &= 2\text{Cu(NH}_3\text{)_2}^+ \quad E_{\text{net}} = 0.20 \text{ V vs SHE}
\end{align*}
\]

Figure 2.8. Eh-pH diagram for Cu-NH\textsubscript{3}-H\textsubscript{2}O system (constructed by HSC 9.0: Cu conc.=0.63M, NH\textsubscript{3} conc.=6M, T=25°C).

In Cu ammoniacal leaching using oxygen as an oxidant, there are two main reactions involved. First, Cu is oxidized by oxygen and forms CuO. CuO complexes with NH\textsubscript{3} in the solution and forms soluble species of \text{Cu(NH}_3\text{)_4}^{2+}. On the other hand, oxygen was consumed and OH\textsuperscript{-} was released, which increases the pH of the solution. The half-cell reactions and the general reaction can be written as:

\[
\text{Cu} + \frac{1}{2} \text{O}_2 = \text{CuO}
\]
\[ \text{CuO} + 4\text{NH}_3 + \text{H}_2\text{O} = \text{Cu(NH}_3)_4^{2+} + 2\text{OH}^- \]  
(2.8)

\[ \text{Cu} + \frac{1}{2} \text{O}_2 + 4\text{NH}_3 + \text{H}_2\text{O} = \text{Cu(NH}_3)_4^{2+} + 2\text{OH}^- \]  
(2.9)

It was found that in studying the kinetics of Cu dissolution in ammoniacal solution, the total concentration of oxidizer (oxygen), and ammonia, play an important role in determining the reaction rate, as expressed below (Radmehr et al., 2012):

\[
\text{Rate} = \frac{2AD_{\text{O}_2} [O_2] (K_{\text{NH}_4^+} [\text{NH}_4^+] + K_{\text{NH}_3} [\text{NH}_3])}{8D_{\text{O}_2} [O_2] + \delta (K_{\text{NH}_4^+} [\text{NH}_4^+] + K_{\text{NH}_3} [\text{NH}_3])}
\]

(2.10)

It was proven from the literature that Cu can be effectively leached from electronic scrap in ammoniacal solution by various ammonium salts (Konishi, 2007; H. Li et al., 2018; Radmehr et al., 2012, 2013; Rudnik et al., 2016; Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b). A schematic illustration of Cu leaching from waste PCBs in an oxygen-involved system is shown in Figure 2.9. The leaching mechanism can be divided into the following steps: 1) diffusion of oxidizer and ammonia ions from the bulk solution to the surface of metallic copper through the boundary layer; 2) chemical reaction takes place on the surface of metallic copper; 3) diffusion of formed Cu-ammine species from the surface of copper to the bulk solution.

**Aerobic Ammoniacal Solution**

\[
\text{Anodic}
\]

\[
\text{Cu} + 4\text{NH}_3 \rightarrow \text{Cu(NH}_3)_4^{2+} + 2e^- \]

\[
\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- \]

\[
\text{Nernst's Boundary Layer}
\]

\[
\text{C}_\text{u}
\]

**Cathodic**

\[
\text{NH}_3
\]

\[
\text{O}_2
\]

\[
\text{OH}^- \]

**Board Substrate**

*Other metals: Ni, Zn, Al, Fe, Au. etc.*

**Waste PCBs**
Sun et al. investigated the recovery of Cu from e-waste using ammoniacal lixiviant, under controlled aeration to facilitate the leaching efficiency (Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b). By this means, more than 90% Cu recovery was achieved within 3 hours of leaching. However, a potential concern of using air to continuously oxidize Cu is that Cu(II) becomes the predominant ion in the pregnant leaching solution (PLS). This in the further electrowinning process could raise the energy consumption by reducing Cu from Cu(II) to Cu(0). Moreover, a counter-reaction of oxygen evolution will most likely occur at the anode. Therefore, in considering the downstream EW circuit, continuous oxidation of leached Cu from Cu(I) to Cu(II) is not recommended due to losses in the current efficiency in EW circuit.

To solve this problem, some researchers applied similar leaching principles while using Cu(II) as the only oxidizer, rather than using oxygen as a traditional oxidizer in Cu ammoniacal leaching. As reported by Koyama et al., the leaching of Cu was done using unpopulated circuit boards as a feed source, ammoniacal solution as lixiviant, Cu(NH$_3$)$_4^{2+}$ as the oxidizer, under the elimination of oxygen by N$_2$ gas covering in a glove box (Koyama, Tanaka, & Lee, 2006). In this way, as Cu(NH$_3$)$_4^{2+}$ being the only oxidizer, Cu$^0$ is predominantly extracted as Cu(NH$_3$)$_2^{+}$ and stabilizes in the ammoniacal solution. Without the facilitation of continuous aeration, it took 4 hours to reach 80% Cu recovery using a similar ammoniacal lixiviant as Sun et al., reported in the work done by Koyama et al. (Koyama, Tanaka, & Lee, 2006). But the merit of using this way is the energy consumption in the subsequent electrowinning process was significantly reduced by depositing Cu from Cu(I) on the cathode and regenerating Cu(II) on the anode.

In comparison to the traditional Cu EW from Cu$^{2+}$ to Cu$^0$, the energy requirement is significantly reduced in Cu EW from Cu(NH$_3$)$_2^{+}$ to Cu$^0$ in ammoniacal solution. The reduced energy consumption is indicated by the lower net potential of Cu(NH$_3$)$_4^{+}$/Cu in ammoniacal Cu system, in contrast to that of Cu$^{2+}$/Cu in acidic Cu system, is shown in Eq. (2.11) and (2.12) (Koyama, Tanaka, & Lee, 2006).
The preliminary work investigating this process under an oxygen-excluded environment, covering leaching, solvent extraction, and electro-winning of Cu in the ammoniacal systems, was reported (Alam et al., 2007; Koyama, Tanaka, Miyasaka, et al., 2006; Oishi et al., 2008b; Oishi, Koyama, Alam, et al., 2007; Oishi, Koyama, Konishi, et al., 2007). However, in the reported study, unpopulated circuit boards were used, which left the need to evaluate real-world feed sources using end-of-life waste boards (Koyama, Tanaka, & Lee, 2006). Although a preliminary leaching kinetic study has been performed, kinetic models have not been proposed under a systematic design of experiments. From the literature, a gap exists in fitting traditional kinetics models under typical leaching variables (i.e. particle sizes, stirring rates, oxidizer concentrations, temperatures, etc.). Determining the effect of these variables on the kinetics is needed, to predict the outcome of Cu leaching which directly affects further circuit board processing. To address the gaps identified in the literature, the following outcomes and variables were considered in the presented study:

1) Evaluation of Cu ammoniacal leaching using populated end-of-life PCBs;
2) Design of experiments for kinetic modeling, considering initial Cu(II) concentrations, particle sizes, stirring rates, and temperatures as primary experimental factors;
3) The goodness of fit of various kinetic models;
4) Insights into the feasibility of leaching PCBs in an ammoniacal system.

2.2.4 Cu recovery by coupled leaching-EW circuit

As mentioned previously, EW of Cu(0) from Cu(I) on the cathode, with Cu(II) simultaneously regenerated from Cu(I) on the anode, significantly improves the current efficiency. To achieve the ideal Cu(I) concentration for EW, it is crucial to consume the
Cu(II) in leaching, as far as possible, prior to EW. As such, a coupled circuit consisting of Cu leaching and electrowinning was designed. An illustration of this concept is depicted in Figure 2.10. In the leaching circuit of the designed system (on the left), the dissolution of Cu from PCBs can be divided into two steps: 1) the oxidation of Cu(0) to Cu(I) by Cu(NH$_3$)$_4^{2+}$ ions in the solution; and 2) the formation of stable Cu(NH$_3$)$_2^+$ species by complexation of leached Cu(I) and NH$_3$. In the EW circuit (on the right), high-purity Cu plate is produced in the cathodic compartment. Simultaneously, in the anodic compartment, Cu(I)) is oxidized to Cu(II) and recycled to the leaching vessel to continuously serve as the oxidant (Oishi, Koyama, Konishi, et al., 2007). The anode and cathode compartments are separated by a diaphragm (indicated by the dashed line in the EW cell) to prevent Cu(II) from being reduced on the cathode via backwash. In this manner, not only the energy consumption in Cu EW will be significantly lowered, but the oxidizer in Cu leaching will also be greatly reutilized.

As the circuit operates and consumes Cu(II) in leaching, a Cu(I)-rich and Cu(II)-lean leachate solution is fed to EW to maximize current efficiency. Thus, a predictable model is needed to simulate the composition of the leaching solution reporting to EW. This work seeks to develop such models by performing batch-leaching experiments in an anaerobic atmosphere to approximate the desired system. For this reason, the initial Cu(II) concentration is considered the predominant factor that affects the efficiency of the coupled leaching-EW circuit.
Figure 2.10. Schematic illustration of the coupled leaching-EW circuit in Cu(II)-NH$_3$-SO$_4$ system (adapted from Oishi, Koyama, Konishi, et al., 2007; Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b)).

Regarding the leaching kinetics and the components of Cu(II)/Cu(I), shrinking core models were considered to describe the consumption of Cu(II) and leaching mechanisms in an ammoniacal system. Generally, there are 5 rate-limiting steps in the leaching reaction, where the slowest among these 5 steps is the rate-controlling step. These steps are:

1) The diffusion of oxidizer Cu(II)-amine from the bulk solution to the interface of a non-reactive product layer;
2) Penetrating of Cu(II)-amine through the product layer terminating at the reaction interface, i.e. the surface of Cu(0);
3) Chemical reaction occurs at the interface where Cu(0) is oxidized to Cu(I);
4) Leached Cu(I) ions complex with NH$_3$ to form stable ionic species and penetrate through the product layer;
5) Diffusion of Cu(I)-amine complex from the interface of the product layer to the bulk solution.
As the reaction continues, the unreacted core of a particle shrinks inward. Around that particle, the concentration of Cu(II) and Cu(I) in the bulk solution keeps changing and decreases with time (assuming a finite reactant), resulting in the change of reaction rate accordingly.

![Figure 2.11. Schematic illustration of reaction mechanism in Cu-ammoniacal leaching system.](image)

2.2.5 Purification and recovery of Cu from ammoniacal leaching solution

Solvent extraction has been widely used in hydrometallurgy, to purify and upgrade the pregnant leaching solution (PLS). Common commercial extractants used to extract Cu\(^{2+}\) from the ammoniacal system include, but are not limited to, LIX63, LIX64N, LIX54, LIX984, P204, P50, and so on. The general expression of extraction equilibrium between Cu\(^{2+}\) and extractant is:

\[
\text{Cu}^{2+}(\text{aq}) + 2\text{HR}(\text{org}) \leftrightarrow \text{CuR}_2(\text{org}) + 2\text{H}^+(\text{aq}) \quad (2.13)
\]

Particularly in Cu-ammoniacal system, where high pH allows the release of free NH\(_3\) ions, Cu-ammine complex becomes the dominant species involved in the reaction. During solvent extraction, ammonia was co-extracted with Cu ions from the aqueous phase to the organic phase in the form of [Cu(NH\(_3\))\(_m^{2+}\)]R\(_2\)(org), as indicated by Eqs. (2.14) and (2.15):

\[
\text{Cu}^{2+}(\text{aq}) + m\text{NH}_3(\text{aq}) \leftrightarrow [\text{Cu(NH}_3)_m^{2+}]\text{R}_2(\text{org}) \quad (2.14)
\]
\[
[Cu(NH_3)_{m}^{2+}] (aq) + 2HR(\text{org}) \leftrightarrow [Cu(NH_3)_{m}^{2+}]R_2(\text{org}) + 2H^+(aq)
\] (2.15)

where HR(\text{org}) is the extractant in the organic phase; CuR_2(\text{org}) is the extracted Cu chelated with solvent to the organic phase; \([Cu(NH_3)_{m}^{2+}] (aq)\) is the Cu-ammine complex in the aqueous phase; and \([Cu(NH_3)_{m}^{2+}]R_2(\text{org})\) is the Cu-ammine complex extracted by the chelation from solvent in the organic phase.

It has been reported that the LIX series (LIX 84, LIX984N and LIX84IC) has been used to extract Cu in acidic environment with a satisfactory extraction rate (> 99%) (H. Li et al., 2018). Whilst LIX26 was adopted by Oishi et al. to purify Cu(I) leaching solution by extraction divalent impurities, such as Zn, Pb, Mn, Ni and Fe, from oxygen-excluded ammonia system (Alam et al., 2007; H. Li et al., 2018).

2.2.6 Au extraction in ammonia-thiosulfate system

Thiosulfate solution has become a promising alternative to cyanide for the extraction of Au from WPCBs owing to its high selectivity, low toxicity and less corrosivity to the equipment (H. Li et al., 2018; Xu et al., 2017). Thiosulfate leaching is normally operated at a pH range from 9 to 10.5, since it is readily decomposed in acidic conditions (H. Li et al., 2018). Au dissolution in thiosulfate system could be extremely slow without the assistance of the catalyst. To facilitate Au leaching, Cu^{2+} and NH_3 are commonly employed as catalyst, in the form of Cu(NH_3)_4^{2+}. The overall expressions of Au thiosulfate leaching under Cu(II)-ammine catalyzed condition are represented by Eqs. (2.16) and (2.17) (Xu et al., 2017):

\[
Au(NH_3)_2^+ + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + 2NH_3
\] (2.16)

\[
Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e^- \rightarrow Cu(S_2O_3)_3^{5-} + 4NH_3
\] (2.17)

Molleman et al. studied the Pourbaix diagram of gold-ammonia-thiosulfate leaching system (Au-S_2O_3-H_2O system) and modified the diagram by comparing different values of reported Gibbs free energy of the S_2O_3^{2-} species (Molleman & Dreisinger, 2002). The updated Eh-pH diagram of Au-NH_3-S_2O_3-H_2O system showed that Au-NH_3 complex (i.e.
Au(NH$_3$)$_2^+$ appears next to the stability region of the gold-thiosulfate complex (Au(S$_2$O$_3$)$_2^{3-}$) (Molleman & Dreisinger, 2002). The gold-thiosulfate complex is more stable under pH 9, whereas the Au-NH$_3$ complex is dominant at a pH higher than 9. This result proved the possibility of leaching Au in thiosulfate solution, with the facilitation of Cu-NH$_3$ catalyst, by manipulating the pH.

The chemistry of Au extraction in the Cu(II)-NH$_3$-S$_2$O$_3$ system is well established (Senanayake, 2004, 2005a, 2005b; Xu et al., 2017). The mechanism of Au thiosulfate leaching in Cu(II)-NH$_3$-S$_2$O$_3$ system is shown in Figure 6.1 (Nie et al., 2019). The reactions involved in Au dissolution in Cu ammoniacal thiosulfate system are described in Eqs. (2.18) to (2.21). As shown in Figure 2.12, in Cu(II)-catalyzed ammoniacal thiosulfate system, Au dissolution occurs in the anodic reaction as Au$^0$ is oxidized to Au$^+$ by Cu(II) and complexes with NH$_3$ to form stable Au-amine compound (Eqs. (2.18) and (2.19)). In the presence of S$_2$O$_3^{2-}$, ionic Au further complexes with S$_2$O$_3^{2-}$ due to the higher affinity between Au$^+$ and S$_2$O$_3^{2-}$ (Eq.(2.20)). In the cathodic reaction, Cu(II)-amine complex is reduced to Cu(I) and forms Cu(I)-thiosulfate compound (Eq.(2.21)).

In the thiosulfate leaching of Au, the formation of Au-thiosulfate complex proceeds via the catalytic oxidation reaction, with Cu(NH$_3$)$_4^{2+}$ acting as the primary oxidant/catalyst. This process can be divided into two steps: 1) the oxidation of Au$^0$ to Au$^+$ in the form of Au(NH$_3$)$_2^+$ under the oxidative environment provided by the presence of Cu(NH$_3$)$_4^{2+}$, which is also a product of the previous Cu ammoniacal leaching process; and 2) the Au(NH$_3$)$_2^+$ reaction with the S$_2$O$_3^{2-}$ ion in the solution and forms stable Au(S$_2$O$_3$)$_2^{3-}$ species (Grosse et al., 2003).
Figure 2.12. Schematical extrapolation of Au leaching mechanism in Cu(II)-NH₃ catalyzed thiosulfate system. Adapted from (Xu et al., 2017).

\[
\begin{align*}
Au & \rightarrow Au^+ + e^- \quad (2.18) \\
Au^+ + 2NH_3 & \rightarrow Au(NH_3)_2^+ \quad (2.19) \\
Au(NH_3)_2^+ + 2S_2O_3^{2-} & \rightarrow Au(S_2O_3)_2^{3-} + 2NH_3 \quad (2.20) \\
Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e^- & \rightarrow Cu(S_2O_3)_3^{5-} + 4NH_3 \quad (2.21)
\end{align*}
\]

Although the leached Au⁺ is soluble as Au(S₂O₃)₂³⁻, the thiosulfate ligand has low stability under typical leaching conditions and tends to decompose through time. Xu et al. did an extensive review on the degradation of thiosulfate compounds. They proposed a simplified degradation route of thiosulfate compounds, as shown in Figure 2.13 (Xu et al., 2017). The reactions and thermodynamic data involved in thiosulfate decomposition were given in Eqs. (2.22) to (2.25) (Xu et al., 2017). As thiosulfate reacts with O₂ and OH⁻ in the leaching solution, it further decomposes into polythionates/polysulfide compounds,
such as $S_4O_6^{2-}$, $S_3O_6^{2-}$, $SO_3^{2-}$ and $SO_4^{2-}$. Moreover, thiosulfate self-decomposes into $S^0$ and $S^2^-$ (as expressed by Eqs. (2.26) and (2.27)). The self-decomposition of thiosulfate eventually forms elemental sulfur and Cu sulfide, which then deposit on the surface of Au. This phenomenon prohibits the further access of lixiviant to Au. Meanwhile, the generated sulfide during thiosulfate self-decomposition recaptures the leached Au-thiosulfate complex and causes the re-precipitation of Au sulfide. This phenomenon not only hinders the gold recovery but also leads to the loss of leached Au in the leachate (pregnant leaching solution).

The formation of elemental sulfur and metal sulfides on the surface of Au is referred to as the passivation reaction which inhibits further Au dissolution in thiosulfate leaching. Using surface-enhanced Raman scattering spectroscopy (SERS), Jeffrey et al. were able to confirm the formation of polymeric sulfur and Au$_2$S in Cu(II)-NH$_3$-S$_2$O$_3$ solution (Jeffrey et al., 2008). However, there was rare literature discussing the mechanism of this passivation phenomenon and the solutions to this problem remained unsolved.

![Figure 2.13. Simplified route of thiosulfate degradation (left route: reductive degradation; right route: oxidative degradation; greyer color: more reductive product; bluer color: more oxidative product). Adapted from (Xu et al., 2017).](image)

$$4S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 2S_4O_6^{2-} + 4OH^- \quad \Delta G^0 = -106.7 \text{ kJ/mol} \quad (2.22)$$

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \quad \Delta G^0 = -183.4 \text{ kJ/mol} \quad (2.23)$$

$$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \quad \Delta G^0 = -330.2 \text{ kJ/mol} \quad (2.24)$$

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \quad \Delta G^0 = -516.4 \text{ kJ/mol} \quad (2.25)$$
\[
S_2O_3^{2-} \rightarrow SO_3^{2-} + S \quad \Delta G^0 = 45.7 \text{ kJ/mol} \quad (2.26)
\]
\[
S_2O_3^{2-} + 2e \rightarrow SO_3^{2-} + S^{2-} \quad \Delta G^0 = 137.6 \text{ kJ/mol} \quad (2.27)
\]

2.2.7 Recovery of Au from thiosulfate leaching solution

Au recovery is commonly achieved by cementation using the Merrill-Crowe process in cyanide solution. But in Au thiosulfate solution, the cementation mechanism is different. Karavasteva studied Au cementation in thiosulfate-ammonia solution on different cementing reagents, including Zn, Al, Cu, Mg and Fe (Karavasteva, 2010). His research indicates that Au is preferably deposited on copper, with a fast cementation rate in comparison to other chosen cementing reagents. The Au cementation rate decreases in order Cu > Zn > Mg > Fe. A porous layer of Au was formed on Cu. Hiskey and Lee reported the cementation kinetics of Au thiosulfate solution on a Cu rotating disc electrode (RDE) (Hiskey & Lee, 2003). Their findings show the Au cementation on Cu followed first-order kinetics initially and was further enhanced under a rotating disc geometry. The morphology of Au deposition on the Cu surface was Cu-Au alloy and transferred to Cu₃Au alloy when heated. The later research by Choo et al. shows that Au cementation on a Cu substrate is enhanced in the presence of ammonia and Cu (both metallic Cu and dissolved Cu) (Choo & Jeffrey, 2004).

2.3 Proposed Flowsheet and Research Objectives

In summary, the specific research gaps identified in the literature review and the engineering challenges this dissertation seeks to address are:

1) Need for a comprehensive flowsheet recover Cu and Au from waste PCB materials from the as-received wastes to valuable products (Cu cathode and Au cemented alloys);
2) An thorough understanding of PCB material’s physical properties with regards to preparing a suitable feed for chemical processing;
3) Employment of real-world waste materials and modified circuit design for a simplified leaching system;
4) A feasible kinetic model with satisfactory goodness of fit to provide a reasonable explanation in reaction mechanisms;
5) A preliminary leaching model to explore leaching process design;
6) Exploration of Au thiosulfate leaching using complex waste materials, and the interaction among existing metals (Cu, Ni, Au and S);
7) Determine leaching conditions favorable for Au recovery by minimizing the impact by other elements.

To fulfill the research opportunities mentioned above, and to provide insights in Cu and Au recovery in ammoniacal/thiosulfate systems, an integrated hydrometallurgical process was proposed as a greener, energy-efficient method to recover Cu and Au from WPCBs. The overall concept of process development satisfied the following goals:

1) Environmentally friendly operation
2) Reduced chemical consumption and energy input
3) Minimized capital and operational costs
4) Optimized process performance
5) Integrated processing flowsheet for both Cu and Au
6) Regeneration and re-utilization of reagents

In the presented study, a coupled Cu leaching-EW circuit was proposed adopting (NH₃)₂SO₄ and NH₄OH solution. In this process, Cu²⁺ is added in leaching as the oxidant to leach Cu⁰ in PCBs as Cu⁺. The leached Cu⁺ is then transferred to EW circuit and deposited on the cathode. Meanwhile, Cu²⁺ is regenerated on the anode. The employment of coupled leaching-EW circuit in ammoniacal systems has the merits of 1) largely decreasing energy input in electro-chemical reaction by depositing Cu from Cu⁺; and 2) significantly reducing reagent consumption by regenerating Cu²⁺ and recirculating it back to leaching to continuously act as an oxidant.

Following Cu ammoniacal leaching, an Au recovery circuit by thiosulfate leaching is proposed. The non-selectivity of Au in the previous Cu leaching circuit allows the further recovery of Au in the subsequent thiosulfate leaching circuit. Moreover, the remaining
Cu(II) and NH$_3$ act as the catalyst and the complexing agent in Au-thiosulfate system. This integrated ammoniacal/thiosulfate processing circuit is innovative and beneficial in the aspect of combining Cu and Au processes under similar chemical solutions. As both Cu and Au processes are operated under alkaline conditions, no extensive rinsing or pH conditioning is required to treat the residues from Cu-ammoniacal leaching when transferring the materials to Au leaching. By taking advantage of the similarity in the chemistry of Cu and Au processes, significant savings in energy input and reagent consumption can be achieved. In addition, there is little research combining the recovery of Cu in ammoniacal system and the recovery of Au in ammoniacal thiosulfate system.

The overall flowsheet of proposed processes is depicted in Figure 2.14. This flowsheet shows a two-stage shredding, followed by a density-based physical processing. In Cu ammoniacal processing circuit, the counter-current leaching consists of 4-stage continuous flow reactors (CFR), followed by an electrowinning tank. The Cu process is operated in an oxygen-eliminated environment, under inert gas covering. As discussed, Cu is extracted in the leaching solution as Cu$^+$, and later transferred to EW, where a high-purity Cu cathode is produced. At the same time, Cu$^{2+}$ is regenerated in the EW and recirculated back to leaching. The outstanding innovation of this flowsheet is the self-regeneration of Cu(II) as its own oxidizer in the circuit. The Au thiosulfate circuit is operated in a similar counter-current manner. Transfer between the two processes can be accomplished by a belt filter. Complete washing and drying of solid residues from Cu process are unnecessary owing to the similarity of the lixivants. Furthermore, Cu and NH$_3$ remained in solution act as the catalysts for Au leaching. High purity of Au is further recovered from thiosulfate solution via cementation on Cu powder. This was chosen for simplicity and to lower the inventory costs of keeping significant quantities of dissolved Au in solution. The resulting flowsheet is feasible at the pilot plant level and the commercial scale.
Figure 2.14. Conceptual flowsheet incorporating Cu-ammoniacal and Au-thiosulfate systems.
In general, the whole flowsheet can be further divided into three major fields, i.e. the physical processing circuit, the Cu recovery circuit, and the Au recovery circuit. To validate the proposed flowsheet, each study field composes its own chapter in this dissertation, with specific purposes to achieve. The objectives of these proposed research areas are summarized below:

1) Physical processing – The purpose is to understand the nature of PCBs and provide adequate knowledge in determining the suitable feed for leaching. Primary size reduction was conducted to determine the liberation by size fraction and the effect on subsequent density separation efficiency.

2) Cu ammoniacal leaching – This chapter seeks to gain knowledge of Cu leaching behavior by studying the effect of various parameters on the leaching recovery and leaching rate. The objectives of this chapter include: 1) the design of experiments and methodologies for the specific leaching system; 2) determining the optimized condition for Cu(I) and Cu(II) composition in the leaching solution; 3) studying the effect of temperature on both leaching rate and ammonia evaporation rate; 4) obtaining the activated energy in order to decide the suitable expression for modeling; 5) evaluating three most reasonable kinetic models and determining the most suitable one in our case by the goodness of fitting using batch experiment data; 6) understanding the leaching mechanism by best fitting kinetic model.

3) Kinetic modeling and simulation – To provide an in-depth understanding of the three kinetic models examined in the previous chapter. The later justified kinetic models were adapted in order to extend their uses to industrial leaching applications. The selected models were further programmed in a mass-balanced flowsheet to 1) represent the material flows and stream conditions of the multi-stage leaching process; 2) evaluate the leaching performance under a given condition; and 3) simulate the Cu(II)/Cu(I) behavior in the leaching circuit.

4) Au thiosulfate leaching – Due to the complicity of Au leaching in Cu-NH\textsubscript{3}-S\textsubscript{2}O\textsubscript{3} system, the following need to be understood to enable the process: 1) the importance of controlled aeration on Cu(II) regeneration and Au recovery; 2)
the effect of key processing parameters to optimize the leaching performance; 3) influence/interaction of other co-existing elements from both solid and liquid phases; 4) understand the possible causes for low Au recovery observed during the reaction.
CHAPTER 3. MATERIAL CHARACTERIZATION AND PHYSICAL PROCESSING

Abstract:

Due to the rapid development of electronic devices and their shortened lifespans, waste electrical and electronic equipment (WEEE), or E-waste, is regarded as one of the most fast-growing wastes. Among the categories of E-waste, waste printed circuit boards (WPCBs) are considered the most complex waste materials, owing to their various constituents, such as plastics, capacitors, wiring, and metal plating. To date, a variety of processing technologies have been developed and studied. However, due to the heterogeneous nature of WPCBs, thorough studies on both material characterization and physical separation were needed to provide a better understanding of material handling as well as to prepare a suitable feedstock prior to the downstream chemical process. In the present study, integrated size and density separations were performed to understand the liberation of contained metals, particularly Cu and Au, from the plastic substrates. The separation performance was evaluated by the elemental concentration, distribution and enrichment ratio of valuable metals in different size and density fractions. Further, SEM-EDS on the density separation products was carried out to characterize the surface morphology, elemental mapping and quantified elemental contents. Moreover, thermogravimetric properties of waste PCBs were investigated by TGA to understand the effect of temperature on volatile and combustible fractions during the thermal processing.

Keywords: E-waste; size distribution; density separation; copper; gold; liberation; metal enrichment; SEM-EDS characterization.
3.1 Introduction

With the continuous improvement in advanced technologies, electrical and electronic equipment (EEE), such as mobile phones, portable music players, computers, and tablets, has become an essential part of human society (Forti et al., 2020; Ning et al., 2017). During the last two decades, the consumption of electrical devices per capita has increased significantly, with an estimated annual growth of 6.8 kg per inhabitant by 2021. Due to increasing demand for new products, the average lifetime of electrical items continues to decrease (Baldé et al., 2017; B. Ghosh et al., 2015; H. Wang et al., 2017). As a result of improper disposal, electronic waste (E-waste) is considered hazardous material as it contains toxic metals and organic plastics which pose threats to the environment (Ogunseitan, 2013). The improper disposal of E-waste also caused the extensive loss of valuable metals (Kumar et al., 2018). Recent studies on circular economy revealed the essence of developing processing and purifying techniques to recover E-waste and turn it into useful forms (Jawahir & Bradley, 2016; Reck & Graedel, 2012; Reuter et al., 2019). Despite the varied sources of E-waste, the average grade of valuable metals in E-waste, such as Cu, Au and Ag, is high and valuable to recycle (Z. Li et al., 2019).

As an integral component of electronic devices, printed circuit boards (PCBs) account for 4 to 7% by weight of E-waste (B. Ghosh et al., 2015; H. Li et al., 2018). The basic structure of PCBs is a copper-clad laminate containing epoxy resin and metallic interlayers (B. Ghosh et al., 2015). The metal fraction in PCBs is approximately 30% by weight, while the rest of PCBs consist of non-metallic fraction (Ning et al., 2017). By estimation, the metal content in PCBs, account for 40% by value of E-waste, is worth $150 million (US dollars) in 2014 (Golev & Corder, 2017). The abundance of valuable metals in PCBs has made it a trading commodity and a secondary source for metals (Golev & Corder, 2017). Typical metals in waste PCBs include basic metals (Cu, Al, Pb, Fe, Zn, Ni, Sn), precious metals (Au, Ag, Pd, Ta), and heavy hazardous metals (Cd, Hg, As, Se), as summarized in Figure 3.1 (Debnath et al., 2018; Hsu et al., 2019; Pant et al., 2012). For copper, the weight percentage ranges between 7% and 22% in PCBs (Pant et al., 2012). Cu is also regarded as most valuable among base metals found in waste PCBs, as shown in Figure 3.2. For precious metals, Au contains the most significant value referencing $41/g of PCBs compared to Ag which is $0.53/g of PCBs (Hsu et al., 2019).
Figure 3.1. Contents of metals in different types of waste PCBs. Adapted from (Pant et al., 2012).
Studies into the characterization and physical processing of E-Waste are not new with numerous studies performed to recover valuable metals from WPCBs using a variety of processing techniques (Awasthi et al., 2019; Bauer, 2020). These techniques can be categorized into mechanical/physical separation (Bizzo et al., 2014; Tatarians et al., 2018; Veit et al., 2014; Zhao et al., 2017; Zhu et al., 2020, 2021) and chemical separation (Castro & Martins, 2009; Kinoshita et al., 2003; Oh et al., 2003; Tuncuk et al., 2012). Mechanical/physical separation usually starts with size reduction, with further separation utilizing physical properties, such as density, electrostatic, and conductivity (Ning et al., 2017). Chemical separation can be divided into pyrometallurgical treatment (Fujita et al., 2014; Jie et al., 2008; Quan et al., 2010), hydrometallurgical treatment (Eng et al., 2016; Kumari et al., 2016; Sethurajan et al., 2019; Tunsu & Retegan, 2016), and bio-metallurgical process (İşildar et al., 2019; Natarajan & Ting, 2014; Pant et al., 2012; Xiang et al., 2010).

Due to the simplicity of mechanical/physical process, it is often utilized as a pre-treatment step prior to chemical processes. Preliminary physical process as a pre-treatment step has the merits of maximizing metallic fraction entering the chemical processes while
leaving non-metallic fraction behind, homogenizing complex materials to provide a suitable feed for downstream process, and reducing the energy consumed by unnecessary size reduction (Ning et al., 2017; Otsuki et al., 2020; Sarvar et al., 2015).

To date, extensive studies on WPCBs recycling by physical processing as a preliminary enrichment method using size, density, electrostatic or conductivity properties, have been performed with valuable insights for the purpose of beneficiation (Duan et al., 2009; Estrada-Ruiz et al., 2016; Eswaraiah et al., 2008; J. Li et al., 2007; J. Li & Xu, 2010; Tan et al., 2011; Zhou et al., 2016). Additional studies reported successful physical processing methods and include additional characterization (Bizzo et al., 2014; Fujita et al., 2014; Guo et al., 2011; Nekouei et al., 2018; Ogunniyi et al., 2009; Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015a; Yamane et al., 2011). A summary of recent studies on physical processing and characterization of WPCBs is provided in Table 3.1. To compare, the physical properties and characterization features investigated in this study are listed at the end of table. As shown in Table 3.1, none of these studies have investigated the specific range of particle sizes, densities, and elemental assay, combined with the characterizations by thermogravimetric analysis (TGA) and SEM-EDS, as performed in this work. In general, the highlights of this study include:

1) Thoroughly characterizing a general type of WPCBs by studying different sizes, densities, by SEM-EDS;
2) Evaluating by particle size and density the separation performance by elemental assay;
3) Identifying the need of surfactant on finer particles for effective density separation;
4) Providing information surface elemental mapping via SEM-EDS for several select particle densities;
5) Investigating thermal-reaction zones and possible reactants/products by TGA.
Table 3.1. Summary of relevant studies with particular focus on physical processing and characterization (since 2011).

<table>
<thead>
<tr>
<th>Type of Study</th>
<th>Particle Size (mm)</th>
<th>Separation Methods</th>
<th>Elemental Assay</th>
<th>Thermo-gravimetry</th>
<th>Spectrum Characterization</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical Processing</td>
<td>-2.8</td>
<td>Air table</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>(Zhou et al., 2016)</td>
</tr>
<tr>
<td></td>
<td>-0.25</td>
<td>Flotation (Superficial air)</td>
<td>N/A</td>
<td>N/A</td>
<td>SEM-EDS (Al, Si, Sn, Pb)</td>
<td>(Estrada-Ruiz et al., 2016)</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>SEM-EDS (Cu, Al)</td>
<td>(Gonçalves &amp; Otsuki, 2019)</td>
</tr>
<tr>
<td></td>
<td>-4, -2</td>
<td>Magnetic and electrostatic</td>
<td>Ag, Au, Al, Cu, Fe, Ni, Pb, Zn, Sn</td>
<td>N/A</td>
<td>N/A</td>
<td>(Yamane et al., 2011)</td>
</tr>
<tr>
<td></td>
<td>-4</td>
<td>Density (S.G. 2.89)</td>
<td>Au, Ag, Cu, Fe, Ni, Pb, Zn, Sn</td>
<td>GCV*</td>
<td>N/A</td>
<td>(Bizzo et al., 2014)</td>
</tr>
<tr>
<td></td>
<td>+1.68, +0.59-1.68, -0.59</td>
<td>Wet jigging, flotation</td>
<td>Cu, Au</td>
<td>N/A</td>
<td>N/A</td>
<td>(Fujita et al., 2014)</td>
</tr>
<tr>
<td>Physical Processing and Characterization</td>
<td>-4</td>
<td>N/A</td>
<td>N/A</td>
<td>TGA- DSC*</td>
<td>SEM-EDS (Al, Pb, Zn, Cu, Au, Fe, Si, etc.)</td>
<td>(Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015a)</td>
</tr>
<tr>
<td></td>
<td>-0.8, -0.45</td>
<td>Density (S.G. 2.82)</td>
<td>Ag, Au, Al, Cu, Fe, Ni, Pb, Sn, Ti, Zn</td>
<td>N/A</td>
<td>SEM-EDS FTIR XRD&amp;XRF</td>
<td>(Nekouei et al., 2018)</td>
</tr>
<tr>
<td></td>
<td>-9, -5, -2</td>
<td>Density (S.G. 1.45 to 2.67)</td>
<td>Au, Al, Cu, Fe, Ni, Pb, Zn, Ta</td>
<td>TGA*</td>
<td>SEM-EDS (Al, Zn, Cu, Fe, This Study Si, Ni, Au)</td>
<td>(This Study)</td>
</tr>
</tbody>
</table>

*GCV: gross calorific value; DTA: differential thermal analysis; TGA: thermo-gravimetric analysis; DSC: differential scanning calorimetry.
3.2 Materials and Methods

3.2.1 Materials

The WPCBs used in this study were highly heterogeneous, consisting of various components, including but not limited to bare metals, alloy coatings, capacitors, resistors, epoxy laminates, fiberglass, etc. obtained from a wide variety of sources. These broader sources were an assortment of motherboards, RAM cards, graphics cards and power supplies extracted from end-of-life computers. The constituents were either friable or closely associated with each other. Further investigations of physical processing by multi-stage shredding and density separation were carried out to gain a deeper knowledge of the elemental distribution in a range of sizes and densities. The WPCBs after primary size reduction are shown in Figure 3.3 (a) and (b). Figure 3.3 (a) shows the appearance of the PCBs as shredded and (b) shows the hand-sorted constitutes in shredded PCBs by their occurrence for visual comparison. It can be seen that Cu mainly exist as either Cu laminate, or tangled Cu wires, while Au mainly presents as strip-shape Au fingers.

![Figure 3.3](image1.jpg)

(a) (b)

Figure 3.3. Coarse shred of general circuit boards: (a) bulk; (b) hand-sorted by metal occurrence.

3.2.2 Size reduction

Preliminary size reduction of 8 kg of general circuit boards was accomplished using stomp shears, band saws, and other rudimentary methods, to size the boards to feed into a
shredder (Ameri-Shred AMS-300 HD hard drive shredder). The schematic procedure of preliminary size reduction is presented in Figure 3.4. The resulting material was then screened to remove fractions smaller than 9.5 mm while the >9.5 mm (+3/8’’) materials were further shredded in a Retch SM 300 knife mill. To evaluate the particle size distribution (PSD), the resulting weight percentage (%wt.) of each size fraction was fitted into two commonly used size distribution models, the Gates-Gaudin-Schuhmann Model (GGS) and Rosin-Rammler Model (RR), and will be described later.

![Figure 3.4. Representation of preliminary shredding and sizing of circuit boards.](image)

3.2.3 Density separation

Following size reduction, a preliminary 2-stage density separation was performed. The waste circuit boards shredded to -9.5 mm were further reduced to a top size of -5 mm. Subsequently, a 2-stage density separation was performed as depicted in Figure 3.5. A follow-up experiment was performed with a top size of -2 mm and then processed into
additional density fractions, as shown in Figure 3.6. This was performed to evaluate the effect of additional size reduction on liberation.

Lithium metatungstate (LMT), an inorganic salt heavy liquid with a specific density of 2.95 g/cm³, was used to prepare dense media with a certain specific gravity (S.G.) to separate the shredded circuit boards. In 2-stage density separation, S.G. of 1.45 and 1.96 were used, while in 4-stage separation, additional S.G. of 1.45, 1.68, 1.96 and 2.67 were used. The choice of these specific gravities was to intentionally separate the heavier elements such as Cu, Ni, Fe, Zn and Au, the lighter elements such as Ca, Mg and Al, and the plastics such as epoxy resins and laminated boards. In addition, for density separation using finer top size (-2mm), a surfactant was employed to reduce the high surface tension of fine-shred circuit boards. The surfactant used to wet the ground circuit board was a nonionic surfactant, nonylphenol ethoxylate, supplied from Huntsman Petrochemical Co. The concentration of surfactant used in the density separation (top size -2mm) was 2 mg/L. After the multi-stage density separations, the materials from various density fractions were weighed and assayed to determine the metal content in the samples.

![Diagram](image)

Figure 3.5. Two-stage, three-fraction density separation for general circuit boards (size -5 mm).
3.2.4 Assaying

To determine the quantity of metals contained in various samples, a procedure of chemical assaying was developed for solid PCBs. The assaying procedure can be divided into three main steps, size reduction, roasting and acid digestion. The solid samples were each pulverized by an analytical mill (Cole-Parmer Analytical Mill 4301-00) to -30 mesh (600 µm). Following size reduction, roasting is utilized to remove the organic and volatile components from PCBs that are insoluble in the subsequent acid digestion. For reliable assaying, the sample should be completely dissolved into a liquid phase prior to ICP-OES elemental analysis.

In roasting, approximately 10 g of solid WPCB sample was weighed and placed in a tared ceramic crucible and roasted in a muffle furnace at 460 °C for 10 hours. 460 °C was chosen to avoid the sintering and agglomeration of metal and alloys during the roasting process. After 10 hours, the crucible was cooled to room temperature in a desiccator and re-weighed to determine the residual mass.

The roasted samples were then homogenized manually using a motor and pestle. Representative 0.5 g of samples were taken for acid digestion. The weighed samples were...
placed in a 50 mL PFA (perfluoralkoxy) digestion tube. Hydrofluoric acid (HF) and aqua regia (molar ratio of HCl:HNO₃ = 3:1) were used as the digesting reagents. Firstly, 20 mL of aqua regia was added to a digestion tube wherein it reacted with the metals. Then, 20 mL of HF was added to dissolve silica, fiberglass, or other insolubles. The digestion was conducted in a hot block at 145 °F (63 °C) for 5 hours until the liquid was evaporated completely. The final digested residues were then prepared in 5% HNO₃ matrix and 5% HCl matrix for ICP-OES analysis. The final solutions were topped off to a total volume of 20 mL with deionized (DI) water to maintain volumetric consistency.

ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry), manufactured by Spectro Arcos, was used for elemental analysis. The liquid samples were prepared in two acid matrixes for the following analysis: 1) 5% HNO₃ matrix for base metals, rare earth elements (REEs) and Ag; 2) 5% HCl matrix for other precious metals, i.e. Au, Pt and Pd.

To compare the separation performance by different sizes or densities, the results of element concentrations were plotted in ppm, versus the size or density fractions. Distribution % of elements in the processed WPCBs, on a whole mass basis, was calculated using Eq. (3.1). Moreover, the enrichment ratio (ER) was calculated using Eq. (3.2), to provide a clear comparison among the separation methods.

\[
Distribution (\%) = \left( \frac{C_{\text{fraction}} \times c_{\text{fraction}}}{F \times f} \right) \times 100
\]  

(3.1)

\[
Enrichment \text{ } Ratio = \frac{c_{\text{fraction}}}{f}
\]  

(3.2)

where \( C_{\text{fraction}} \) is the mass (g) of the product in each fraction, \( c_{\text{fraction}} \) is the element concentration (ppm) in the fraction after size or density separation, \( F \) is the mass (g) of the feed, and \( f \) is element concentration (ppm) in the feed.

3.2.5 Characterization

Representative samples from different densities fractions were characterized using Energy Dispersive x-ray Spectroscopy (EDS, X-Max detector, Oxford Instruments, Abingdon, UK) in a Scanning Electron Microscope (SEM, Quanta 250, ThermoFisher
Scientific formerly FEI, Hillsboro, OR, USA). The detector used on SEM was an Everhart-Thornley detector (ETD), equipped with an adjusted bias to optimize signal intensity while minimizing charging effects in the image. For each sample, multiple fields of view were scanned automatically at high magnification using incident electrons with 30 keV energy and appropriate beam currents to balance signal intensity and spectrum accuracy. An accelerating voltage of 30 kV (at a working distance of 10 mm on the SEM) was used to excite x-rays from all potentially present elements, and to maximize the amount of x-rays generated so as to accumulate lots of counts in each field-of-view. Automation of the acquisition over a large area, EDS spectra analysis and maps generation were achieved using Oxford Instruments’ AZtec 6.0 software with TruMap algorithm.

Thermogravimetric Analysis (TGA) was conducted using a LECO TGA701 to analyze the thermo-chemistry properties of the PCBs. To prepare representative samples, 50 g of PCBs was ground to <600 microns to provide sufficient quantity for replicate analyses. For each set of experiments, 0.2 g of ground sample, with 5 replicates, were added to ceramic crucibles. The temperature was ramped from 25°C to 1000 °C, with a ramp rate of 5 °C/min. At each increment, the temperature was held for 5 minutes to allow a full reaction of materials. The process was carried out under nitrogen and oxygen atmospheres, respectively. The initial weight of materials and the weight loss according to temperature rise were measured, and the thermo-gravimetry (TG, weight %) was calculated by the following equation:

$$TG(\%) = (1 - \frac{Weight_{loss}}{Weight_{initial}}) \times 100$$

(3.3)

where Weight\textit{loss} and Weight\textit{initial} are the weight loss according to temperature change and initial weight of the material in grams.

3.3 Results and Discussions

3.3.1 Particle size distribution

To understand the propensity of generating coarse and fine particles during the size reduction process, particle size distribution (PSD) of shredded WPCBs was studied and the results were fitted into two PSD models. Under the shredding and screening procedure
described in the Materials and Methods, WPCBs were shredded to a top size of 9.5 mm and screened into 5 different particle size ranges (i.e. -9.5 +4.8, -4.8 +2.4, -2.4 +1.0, -1.0 +0.6 and -0.6 mm). Each size fraction was weighed with the data reported in Figure 3.7. A representative sample of the shredded material was then assayed to get the elemental concentration in each size fraction.

![Mass distribution (%wt.) of shredded general circuit boards (size -9.5 mm).](image)

Figure 3.7. Mass distribution (%wt.) of shredded general circuit boards (size -9.5 mm).

Two popular PSD models were assessed, and the results are shown in Figure 3.8. The Gate-Gaudin-Schuhmann (GGS) (Schuhmann Jr, 1960) and the Rosin-Rammler (RR) (Rosin, 1933) models have been used to describe PSD in granular materials for many years in material processing. GGS model was developed in the metalliferous mining industry and described with a size parameter (k) and a distribution parameter (m) (Schuhmann Jr, 1960). The RR model was widely used to evaluate coal fragmentation at first but had also been broadly applied in many other processing industries. The RR size parameter (R) corresponds to the geometric mean particle size, and the shape parameter (b) defines the spread of sizes (Rosin, 1933). The fitting accuracy of these models depends on the material nature and the chosen sizes.

The GGS model predicts the cumulative percent passing distribution:

\[ Y = 100 \left( \frac{x}{k} \right)^m \]  

(3.4)
where \( Y \) is the cumulative oversize mass, in wt.\%; \( x \) is the particle size, in mm; \( k \) is the size parameter; and \( m \) is the distribution parameter. The values of \( k \) and \( m \) can be determined by linear regression:

\[
\log Y = m \log x + k
\]  

(3.5)

The Rosin-Rammler model is typically used to predict the % retained. The modified equation to predict the % finer is:

\[
Y = 100 \times 100 \exp \left\{ -\left( \frac{x}{R} \right)^b \right\}
\]  

(3.6)

where \( \frac{1}{R} \) is the Rosin-Rammler geometric mean diameter, in mm; \( b \) is the Rosin-Rammler skewness parameter or distribution parameter (dimensionless). In the above equation, a smaller \( R \) indicates a larger average particle size and a larger \( b \) means a wider spread in particle size distribution (PSD) (Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015a).

The GGS and RR models were compared with the experimental PSD data using the least-squares method to find the fitting parameters, and the model presenting the most agreeing statistical values was selected. The least-squares procedure was obtained considering a nonlinear optimization method, and the sum of squared residual (SSR) was minimized using SOLVER in Excel, the function of SSR was established as:

\[
RRS = \sum_{i=1}^{n} \left( P_{i,\text{measured}} - P_{i,\text{predicted}} \right)^2
\]  

(3.7)

where \( P_{i,\text{measured}} \) and \( P_{i,\text{predicted}} \) represent experimental and model cumulative passing material, respectively. The obtained values of independent variables and SSR of the fitted model were summarized in Table 3.2. The fitted GGS model and RR model were shown in Figure 3.8 (a) and (b), respectively. The particle size distribution is shown to fit the GGS model which is better aligned to fine particle distributions (Colorado-Arango et al., 2021).
Table 3.2 Fitting parameters of GGS and RR models.

<table>
<thead>
<tr>
<th>PSD Model</th>
<th>Expression</th>
<th>Variables</th>
<th>SSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGS</td>
<td>$F(x_i) = 100 \left( \frac{x_i}{k} \right)^m$</td>
<td>$k=4.79; m=0.94$</td>
<td>14.67</td>
</tr>
<tr>
<td>RR</td>
<td>$F(x_i) = 100 \left( 1 - \exp \left( - \frac{x_i}{R} \right)^b \right)$</td>
<td>$R=2.57; b=1.48$</td>
<td>144.45</td>
</tr>
</tbody>
</table>

Figure 3.8. (a) GGS model of shredded circuit boards; and (b) RR model of shredded circuit boards.

Results of the particle size distribution show a better fit using the GGS model, indicating a tendency of generating a greater portion of fines during the shredding process. This result was well aligned with the fact that fines/dust were visually observed during the shredding of PCBs, possibly produced from the organic substrate in the PCBs. In addition, the metallic fractions were more difficult to shred due to the malleability of metal and metal alloys. Tangled wires and fibers from shredded PCBs also tended to agglomerate together during the screening process. The visual observation was further justified by SEM images, with elemental mapping, and the results were discussed in the later sections.

3.3.2 Elemental distribution in different size fractions

To determine the proclivity for the segregation of valuable metals by size during the liberation process, various size distributions were assayed. The results were plotted in
elemental concentrations (ppm) and distribution (%) of elemental concentrations in each size fraction, as shown in Figure 3.9 and Figure 3.10, respectively. The distribution of Cu and Au associated with different sizes is shown in Figure 3.11. In Figure 3.9, Cu concentrations varied from 322,623 ppm (32.26%wt.) to 383,648 ppm (38.36%wt.) in the coarsest (+4.8mm) and finest (-0.6mm) size fractions, respectively. The low variability of Cu content between each size fraction indicates that there is minimal liberation regardless of particle size. Similarly for other metals, such as Al, Fe, Ni and Pb, the highest concentration occurred in the finest size fraction, but the differences in metal concentrations by size fractions were not distinguishing. Au was found most concentrated in -1.0+0.6mm fractions, while Zn and Ta, were found more concentrated in the intermediate fractions, i.e. -4.8+2.4mm for Zn and -2.4+1.0mm for Ta, respectively.

The cumulative elemental distribution, as shown in Figure 3.10, indicates little relativity of element liberation by different sizes, which led to similar results as seen in Figure 3.9. These results also seem consistent with visual observations that the small fractions are composed of friable materials, while coarse materials consisted of malleable metals and alloys. Observations during the grinding process seemed to show that the malleable metals, such as Al and Cu, tended to agglomerate together, and were less susceptible to size reduction, making further size reduction difficult once these metals are liberated from the circuit boards. On the other hand, the board-type material (plastic/fiber portion) was more easily comminuted into fine particles. As a result, the finer size fraction contained more plastic.

Distribution % and enrichment ratio (ER) of Au and Cu in different size fractions presented in Figure 3.11 reveal that the correlations of both distribution and enrichment were discrete by size. Over half of the Cu (58%) was found in coarse size (+4.8mm), occurring as metallic Cu in wires/laminates which were difficult to be further shredded. However, the enrichment ratio of Cu showed similar numbers with an average of 1.1, indicating there was no preference for Cu enrichment in a certain size fraction. Approximately half of the Au (48%) was found in finer size fractions (-4.8+2.4mm), while the other half was relatively evenly distributed in other size fractions. The enrichment ratio of Au showed less correlation in sizes, with the highest ER of 3.21 in -1.0+0.6mm and the lowest ER of 0.25 in +4.8mm size fraction.
Figure 3.9. Elemental concentration (ppm) in different size fractions (size -9.5 mm).

Figure 3.10. Elemental distribution (%) in different size fractions (size -9.5 mm).
3.3.3 Elemental distribution in various density fractions (size -5 mm)

The WPCBs were further shredded to a top size of -5 mm to perform a 2-stage density separation, as depicted in Figure 3.5. This test was performed to provide insight in metal distribution by density rather than size. The propensity of the mass partition to the heavy fraction is indicative of the metal contents. The results of elemental concentration and distribution in various density fractions were shown in Figure 3.13 and Figure 3.14. The distribution % and enrichment ratio (ER) of Cu and Au in density fractions was shown in Figure 3.15.

It can be seen from Figure 3.13 that the concentration of Cu was enriched in the dense fraction with 508,079 ppm (50.8% Cu) in the densest fraction (1.96 sink) and 167,365 ppm (16.74% Cu) reporting to intermediate density (1.45 sink x 1.96 float). Only a small portion of Cu reported to the light fraction (1.45 float). Similarly, as shown in Figure 3.14, Cu content (%wt.) was enriched as the specific gravity increased. About 79% of Cu reported to the densest fraction (S.G. 1.96 sink). However, over 20% of Cu remained in the lightest and intermediate density fraction (S.G. 1.45 float and 1.45 sink x 1.96 float). This suggests that, under the given feed size (-5 mm), the separation of Cu by density is inefficient due to poor metal liberation at this level of liberation. Although each of the other metals showed
a general trend of increasing metal content with density, the middle fractions still contained significant quantities of valuable metals.

Further, as shown in Figure 3.15, the distribution of Au in 1.45 and 1.96 S.G. did not show good separation, with 43% in S.G. 1.45 sink x 1.96 float and 55% in S.G. 1.96 sink, respectively. Although the enrichment ratio of Cu showed an improving trend by increasing the density, the enrichment ratio of Au did not follow the same trend. There was little noticeable enhancement of ER for Au from density fraction of 1.45 sink x 1.96 float to 1.96 sink. With significant amounts of metals remaining in the light and intermediate density fractions, it is indicated that additional size reduction may be needed to improve metal liberation by density. To this end, further size reductions were performed and results were shown in the subsequent section.

Figure 3.12. Mass distribution (%wt.) in different density fractions (size -5 mm).
Figure 3.13. Elemental concentration (ppm) in different density fractions (size -5 mm).

Figure 3.14. Elemental distribution in different density fractions (size -5 mm).
Figure 3.15. Distribution (%) and enrichment ratio (ER) of Cu and Au in different density fractions (size -5 mm).

3.3.4 Elemental distribution in different density fractions (size -2 mm)

The results presented in Figure 3.16 show that about one-fourth of the mass reported to the lightest fraction. To further interpret the processing implications, elemental concentration and distribution % of the -2 mm material were shown in Figure 3.17 and Figure 3.18. The results indicate an improvement in Cu liberation at -2 mm vs. -5 mm, as evidenced in the Cu concentrations in the heavy fractions (66.16%wt.). Except for Al, all the elements assayed, including Au, Cu, Fe, Ni, Pb, Zn and Ta, were significantly concentrated in the densest fraction (2.57 sink). Al was found to be mostly concentrated in density fraction of 1.96 sink x 2.67 float, while least concentrated in 2.67 sink. This result suggests a possible cut point of separating Al from other metals at a density fraction of 2.67 float.

In comparison to density separation with a -5 mm top size (Figure 3.14), where only 79% of Cu reported to dense fraction, 93% of Cu reported to 2.67 sink fraction in the density separation with top size of -2 mm (Figure 3.18). Notable improvements in the distribution of Cu ad Au, are shown in Figure 3.19. Over 81% of Au and 93% of Cu were reported to S.G. 2.67 sink, respectively. If combining the amount of Au and Cu in S.G. 1.96 sink x 2.67 float and S.G. 2.67 sink, over 88% and 95% of Au and Cu, respectively,
were reported in S.G. 1.96 sink. Significant increase in enrichment ratio for Cu and Au in the densest fraction were found, as high as 3.5 for Cu and 3.0 for Au, respectively. By evaluating both the distribution % and the enrichment ratio of Cu and Au among different separation methods, i.e. size separation, coarse-shred density separation and fine-shred density separation, it is apparent that the density separation using -2mm top size yielded the best beneficiation efficiency.

Figure 3.16. Mass distribution (%wt.) in different density fractions (size -2 mm).

Figure 3.17. Elemental concentration (ppm) in different density fraction (size -2 mm).
3.3.5 Effect of surfactant in finer-particle-size density separation (size -2 mm)

As a supplement to the previous section, it was discovered that with finer particle size, the effect of particle wetting became pronounced. As the particle size used in the density process reduced to -2 mm, surface tension interacting with the circuit boards started to play an important role in float-sink testing. Observations showed that heavy elements,
such as Au and Cu, may still report to the lighter fraction even fully liberated. This is because the surface of PCBs materials is highly hydrophobic, thus as the particle size decreased, the fines, regardless of density, tended to float to the top of a liquid phase. Thus, when performing the density separation at a finer size (-2 mm), PCBs were prewetted before density separation using a nonionic surfactant. The cumulative recovery (%) of Cu and Au in a range of specific densities (1, 1.48, 1.96, 2.67 g/cm³) with and without the surfactant are presented in Figure 3.20. With surfactant, the Cu and Au recovery in the densest fraction (S.G. 2.67) were 93% and 81%, respectively. By improving wetting, entrainment of both Cu and Au to the light fractions was reduced, as more of each metal reported to the heavier density fraction. This may be a significant factor in the hydrometallurgical treatment of finely ground WPCBs.

![Figure 3.20. Effect of utilizing 2 mg/L nonylphenol ethoxylate as the surfactant in density separation (size -2 mm).](image)

3.3.6 SEM-EDS characterization of WPCBs by density fractions

To characterize the distribution of metals and plastics fractions in different densities, SEM was utilized with an EDS spectrum to quantify the element content. Samples from three density fractions obtained from the previous density separation using a top size of -2 mm and three density fractions (the lighter fraction (S.G. <1.48), the intermediate fraction (S.G. from 1.68 to 1.96), and the heaviest fraction (S.G. >2.67)) were analyzed. The samples were mounted on an aluminum stage with a conductive carbon platform, shown
as the square edges (in Al mapping) in all the SEM results (Figure 3.21, Figure 3.22 and Figure 3.23). In general, SEM images show there was a higher portion of finer debris in the lighter fraction (S.G. <1.48). This is due to the abundance of plastics and suspected organic compounds generated from shredding. In contrast, the heavier fraction (S.G. >2.67) contains significantly higher metal contents. Since metals are malleable rather than friable, it leads to the proclivity for larger particles observed in the denser fraction.

In the lightest and intermediate fractions (S.G. <1.48, shown in Figure 3.21 and S.G. 1.68 to 1.96, shown in Figure 3.22), O, Si, and C are often associated with each other, attributing to the Si-O in fiberglass and carbon-associated binders/plastics, which appear to report to the lighter fractions. The lack of metals indicated in Figure 3.21 agrees well with the chemical assays shown in Figure 3.17 and Figure 3.18. Due to the liberation of metallic portions, the heaviest density fraction (S.G. >2.67, Figure 3.23) has the highest metal concentration, as well as larger particle size. The metals Cu, Fe, and Zn were largely enriched in the dense fraction. This result is also confirmed by ICP analysis (as compared to Figure 3.17 and Figure 3.18 showing the elemental assay).

In terms of Cu contents in the three density fractions, enhancement of Cu was visually observed in SEM images in denser fractions. The occurrences of Cu show both laminar and wire forms. The EDS spectrums indicate that the estimated Cu contents increased from 0.3%wt. in the lighter fraction, to 3.7%wt. in intermediate fraction, and then further enriched up to 11%wt. in the heavier fraction. Other base metals, Fe and Ni, were also found to be more concentrated in the densest fraction, accounting for 3.9%wt. and 2.4%wt., respectively.

In addition, Au was found more evenly distributed in the densest fraction. Visual enrichment of Au was observed in the denser fraction, compared to that in the intermediate fractions, as shown in Figure 3.24. It is worth mentioning that a small amount of Au in the 2.67 sink fraction was found to be associated with Ni, indicating the possibility of Au-Ni inter-plating in PCBs. In general, the results of elemental distribution by EDS fraction were well aligned with the previous findings given by the chemical assay.
Figure 3.21. SEM-EDS characterization of WPCBs with elemental mapping (S.G. <1.48): (a) SEM image; (b) overlayed elemental mapping; (c) EDS spectrum.

Figure 3.22. SEM-EDS characterization of WPCBs with elemental mapping (S.G. 1.68 to 1.96): (a) SEM image; (b) overlayed elemental mapping; (c) EDS spectrum.

Figure 3.23. SEM-EDS characterization of WPCBs with elemental mapping (S.G. >2.67): (a) SEM image; (b) overlayed elemental mapping; (c) EDS spectrum.
3.3.7 Thermogravimetric properties of general PCBs

To provide additional insights into the processing of WPCBs, the thermalgravimetric analysis was performed on samples under oxygen and nitrogen cover gasses. The results are shown in Figure 3.25. The change in mass stabilized at temperatures above 600 °C, corresponding to a final mass of 80.24% of the original under nitrogen and 74.29% under oxygen, respectively. It can be seen from the TGA results for both N$_2$ and O$_2$ that there exist 4 distinct kinetic stages (region A to D): region A with temperature ranging from 25-270 °C; region B from 270-410 °C; region C from 410-570 °C; and last region D from 570-1000 °C. The kinetics regions (A to D) are summarized in Table 3.3 with similar observations referenced from the literature studying the thermal decomposition of PCB materials (Evangelopoulos et al., 2015; Grause et al., 2008; Kim et al., 2015).
As shown in Table 3.3, the first region A corresponds to the evaporation of water and slow decomposition of carbon, released as carbon dioxide or volatile organic compounds (VOCs). In region A, there was a slight difference between the % wt. loss in N\textsubscript{2} and O\textsubscript{2}, attributed to evaporation of water and VOCs under N\textsubscript{2} and in the O\textsubscript{2} cover gas potential CO\textsubscript{2} creation in addition to water and VOC evaporation.

The second region B represents the pyrolysis of brominated compounds with a steeper slope. In region B (270-410 °C), the %wt. losses under both N\textsubscript{2} and O\textsubscript{2} increased significantly. As indicated in Figure 3.25, there were two noticeable weight loss subregions in region B, from 270-370 °C and 370-410 °C. According to Kim et al., the weight loss from temperature 270-370 °C is mainly assigned to the pyrolysis and decomposition of paper laminates and tetrabromo bisphenol A (TBBA) (Kim et al., 2015). And as reported by Li et al., the remarkable weight loss at a temperature above 370 °C was resulted from the pyrolysis and decomposition of the phenol compounds, epoxy resins (ERs) and brominated epoxy resins (BERs) (J. Li et al., 2010). In comparing the weight losses under N\textsubscript{2} and O\textsubscript{2}, there is no noticeable difference at temperatures of 270-370 °C. This suggests that O\textsubscript{2} might not participate significantly in the pyrolysis of TBBA at 270-370 °C, provides a possible reason for this. According to the research by Grause et al., there was no additional oxygen supply required during the decomposition of TBBA (Grause et al.,

Figure 3.25. Thermo-gravimetry (weight %) and the first derivate (FD) of general PCBs under oxygen and nitrogen atmosphere.
2008). As the temperature reached above 370 ºC, the weight loss under O₂ started surpassing the weight loss under N₂.

The third region C after 410 ºC is the degradation of phenolic, specifically phenolic aromatic compounds. In region C (410-570 ºC), under both N₂ and O₂ conditions, the rates of weight changes were slower compared to the rate of weight loss in region B. The cumulative % wt. losses in this temperature range were 19.56% in N₂ and 25.7% in O₂, respectively. After 410 ºC, the weight change started to reach the steady-state in N₂ while the weight loss was still going on in O₂. The higher weight loss under an oxygen environment at a high temperature over 410 ºC is likely a result of the combustion of polymers and organic compounds in PCBs. Similar results of higher weight loss under oxygen than under an inert gas atmosphere were observed in the literature (Diaz et al., 2018; Jin et al., 2011; Ortuño et al., 2013, 2014).

The last region D, with no noticeable weight change after 570 ºC, is the stabilization zone of the thermo-reaction. At temperature above 410 ºC, the bonding of long-chain-hydrocarbon starts to crack, alongside the decomposition of high-carbon polymers, causing the emission of H₂, CO, CO₂, and CH₄ in the presence of oxygen (Diaz et al., 2018; Ortuño et al., 2014). Other than the evolution of carbon and hydrogen, bromophenol compounds also decompose during oxidative combustion, releasing HBr and Br₂ (Jin et al., 2011). Accordingly, the difference between weight losses (6.14%) under N₂ and O₂ mainly accounted for the gas emissions during oxidative combustion.
Table 3.3. Summary of TGA results at a temperature range of 25-1000 °C, under nitrogen and oxygen.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Temperature (°C)</th>
<th>Type of Reaction</th>
<th>Major Compounds</th>
<th>%Wt. Loss (N₂)</th>
<th>%Wt. Loss (O₂)</th>
<th>Similar Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25-270</td>
<td>Evaporation of moisture and volatile organics</td>
<td>H₂O and VOCs</td>
<td>1.40</td>
<td>2.25</td>
<td>(Kim et al., 2015)</td>
</tr>
<tr>
<td>B</td>
<td>270-410</td>
<td>Pyrolysis of brominated resins</td>
<td>TBBA and ERs/BERs</td>
<td>13.40</td>
<td>17.17</td>
<td>(J. Li et al., 2010)</td>
</tr>
<tr>
<td>C</td>
<td>410-570</td>
<td>Decomposition and combustion of polymers</td>
<td>Polymer resins</td>
<td>4.76</td>
<td>6.28</td>
<td>(Ortuño et al., 2014)</td>
</tr>
<tr>
<td>D</td>
<td>&gt;570</td>
<td>Stabilization</td>
<td>Ash of general PCBs</td>
<td>0.20</td>
<td>0.01</td>
<td>(Grause et al., 2008)</td>
</tr>
</tbody>
</table>

3.4 Conclusions

In conclusion, this work suggests that there is a critical size to promote metal liberated from PCBs. The observed trend indicates that particle size and liberation are directly related. Further, it was observed that as the top size of processed PCB materials decreased, the surface energy effects of the particles became important leading to the use of a surfactant. In terms of particle sizes, -9mm, -5mm and -2mm were utilized with the -2mm sizes showing the greatest metallic separation from plastics and fibers with greater enrichment in the denser fractions. A majority of the metals analyzed, including Au, Cu, Fe, Zn, Pb, Ni and Ta, were congregated to the heavier fractions (S.G. >2.67), while the Al was concentrated in the lighter fraction (S.G. <2.67).

Further characterization using SEM-EDS agreed with the results from assaying. The results showed that the metal particles were liberated from plastic debris and provided additional evidence that density separation of WPCBs under 2 mm particle size favors the enrichment of metallic portions in the densest fraction (S.G. >2.67) while leaving fiber glasses and organic debris in the lighter fraction (S.G. <1.48).
Thermogravimetric analysis with temperature increments to 1000 °C resulted in total weight losses of 19.76% under a N₂ atmosphere and 25.71% under O₂ environment, respectively. Suspected volatile organic compounds evaporated at a temperature range of 25-270 °C. Suspected brominated phenol compounds were observed to be decomposed at temperatures of 270-410 °C, which further formed volatile compounds under N₂ and O₂. Combustion of PCBs under oxygen environment at high temperature range (410-570 °C) yielded a difference of 6.14% wt. weight loss compared to N₂ environment, assigned for the production of off-gasses such as CO, CO₂, HBr and Br₂. Thermo-reaction of PCBs was stabilized after 570 °C with little weight loss.

For future perspectives, this study provides important information in terms of physical processing and material characterization that are essential for the subsequent chemical processing of WPCBs. With the primary investigation of physical properties, i.e. size, density, surface morphology and temperature, the later hydrometallurgical process can be significantly enhanced by optimizing the physical beneficiation of proper feed materials, based on the results given in the presented study.
CHAPTER 4. KINETIC CHARACTERISTICS OF CU LEACHING FROM WASTE RAM CHIPS IN A CU(II)-NH₃-SO₄ SYSTEM

Abstract:

Leaching of Cu in ammoniacal solutions has proved to be an efficient method to recover Cu. This method has been utilized to recover Cu from waste printed circuit boards (WPCBs) by many researchers over the last two decades. This study investigated cupric ammoniacal leaching system under anaerobic conditions and Cu(II)-amine (Cu(NH₃)₄²⁺) was used to leach Cu as Cu(NH₃)₂⁺ or Cu(NH₃)₃⁺. These conditions were selected to explore a potential leaching circuit coupled with EW for the regeneration of the oxidizer. To understand the leaching mechanism and Cu leaching behavior in this particular system, a set of experiments was designed and conducted. In this study, end of life waste RAM chips were used as feed sources and Cu(II)-ammoniacal solution was used as the lixiviant. The effects of various processing parameters on the Cu recovery and the leaching rate were evaluated such as particle sizes, stirring rates, initial Cu(II) concentrations and temperatures. It was found that the particle size and initial Cu(II) concentration were the two most important factors in Cu leaching. Using a particle top size of 1.2 mm of particle size and 40 g/L of initial Cu(II) concentration, a maximum Cu recovery value of 96% was achieved.

The leaching kinetics and reaction mechanism were further investigated. Three potential kinetic models selected for variable diffusion mechanisms and changing concentration approximation were examined via the goodness of fit adopting the batch experiment data. It was found that both Zhuravlev’s changing-concentration model and Dickinson’s mixed diffusion model yielded acceptable fit, although Dickinson’s model was slightly better within the studied range of variables. The activation energy of Cu ammoniacal leaching was calculated as 4 kcal/mol, which indicated that this reaction was diffusion controlled. Furthermore, a general expression of the kinetic model was proposed in this study. The proposed expression, based on the assumption of a mixed diffusion-controlled kinetics, revealed that among the variables tested, initial concentration of the oxidizer (c[Cu²⁺]) and the particle size (1/R²), were the two most important affecting
factors with reaction orders of 1.6738 and 0.8151, respectively. With the validated accuracy of prediction, this model appears to be applicable in the future scaleup of this process.

**Keywords:** circuit boards, recycling, copper leaching, ammoniacal solution, kinetic modeling, diffusion-controlled
4.1 Introduction

Waste printed circuit boards (WPCBs), as a major constituent of electronic waste, contain approximately of 30% metallics and 70% non-metallics by weight (Ning et al., 2017). The abundance of Cu content in WPCBs, varying from 10 to 30%, has made WPCBs a promising secondary resource (Golev & Corder, 2017; Oishi, Koyama, Alam, et al., 2007). Recycling of Cu from WPCBs, has attracted increasing attention during the last two decades (Z. Li et al., 2019; Mitovski et al., 2014). Ammoniacal process, employing a mixture of ammonium salts ((NH$_3$)$_2$SO$_4$, (NH$_3$)$_2$CO$_3$ and NH$_4$Cl) and ammonium hydroxide (NH$_4$OH), has shown satisfying performance for Cu recovery, as reported in the literature (Konishi, 2007; H. Li et al., 2018; Radmehr et al., 2012, 2013; Rudnik et al., 2016; Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b). The merits of using ammoniacal system to extract Cu from WPCBs are: 1) higher selectivity towards Cu and other base metals, such as Zn, Ni, Co, etc.; 2) lower solubilities for common contaminants in WPCBs, such as Fe and Al; 3) lower corrosivity to the equipment used in the process; and 4) less harmful byproducts and wastes generated, in comparison to acid systems.

To date, extensive research has been conducted to explore Cu leaching in ammoniacal solutions (Bari et al., 2009; Koyama, Tanaka, & Lee, 2006; Oishi, Koyama, Alam, et al., 2007; Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b; Xiao et al., 2013b). The concept of leaching Cu as Cu(I)-ammine under an oxygen-eliminated environment was also studied preliminarily by Oishi et al (Alam et al., 2007; Oishi et al., 2008a; Oishi, Koyama, Alam, et al., 2007; Oishi, Koyama, Konishi, et al., 2007). In the subsequent electrowinning, it is proposed that a significant amount of energy could be saved by depositing Cu from Cu(I)-ammine compounds (Oishi et al., 2008b). The theoretical principles supporting the feasibility of this system were previously reported by Koyama et al (Koyama, Tanaka, & Lee, 2006). Accordingly, the higher oxidation-reduction potential (ORP) of Cu(NH$_3$)$_4^{2+}$/Cu$^0$, in comparison to the ORP of Cu(NH$_3$)$_2^{2+}$/Cu$^0$, indicates the capability of Cu(NH$_3$)$_4^{2+}$ to oxidize Cu$^0$ as Cu(NH$_3$)$_2^{2+}$ in the presence of NH$_4^+$ (Koyama, Tanaka, & Lee, 2006; Radmehr et al., 2013). The oxidation of Cu$^0$ by Cu(NH$_3$)$_4^{2+}$ and the formation of stable Cu(NH$_3$)$_2^{2+}$ complex are illustrated by Eqs. (4.1) and (4.2) (Oishi, Koyama, Konishi, et al., 2007). In the proposed system, the leached Cu(NH$_3$)$_2^{2+}$ is then subject to the electrowinning circuit where Cu$^0$ is deposited on
the cathode. The reported net potential ($E_{\text{net}}$) of Cu(NH$_3$)$_4^{2+}$/Cu$^0$ in ammoniacal system is 0.20 V (as given in Eq. (4.3)), which is much lower than that of Cu$^{2+}$/Cu$^0$ in acidic Cu system (0.89 V) (Koyama, Tanaka, & Lee, 2006). Electrochemically, the reduced net potential indicates a significant decrease in energy consumption, when depositing Cu from Cu(NH$_3$)$_4^{2+}$, as opposed to traditional Cu electrowinning from Cu$^{2+}$.

Anodic reaction:
$$\text{Cu(NH}_3\text{)}_4^{2+} + e^- = \text{Cu(NH}_3\text{)}_2^{2+} + 2\text{NH}_3 \quad E_0 = 0.10 \text{ V vs SHE} \quad (4.1)$$

Cathodic reaction:
$$\text{Cu(NH}_3\text{)}_2^{2+} + e^- = \text{Cu} + 2\text{NH}_3 \quad E_0 = -0.10 \text{ V vs SHE} \quad (4.2)$$

Net reaction:
$$\text{Cu} + \text{Cu(NH}_3\text{)}_4^{2+} = 2\text{Cu(NH}_3\text{)}_2^{2+} \quad E_{\text{net}} = 0.20 \text{ V vs SHE} \quad (4.3)$$

An outstanding concern related to this system is replenished Cu(I) in leaching, while depleting the Cu(II) as much as possible for the subsequent electrowinning. In considering this specific condition, direct electrowinning of Cu from Cu(I) was proposed with a coupled Cu leaching-ew circuit integrating Cu leaching using Cu(II) as an oxidizer and direct electrowinning from leached Cu(I). A schematic illustration of the integrated circuit is depicted in Figure 4.1 (adapted from references (Oishi, Koyama, Konishi, et al., 2007; Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b)). As a Cu(I)-rich and Cu(II)-lean solution being the critical prerequisite to maximize the current efficiency in Cu EW, it is essential to develop a predictable model in order to simulate the behavior of Cu(I) and Cu(II) during leaching.
The shrinking-core model (SCM) has been regarded as the most widely used kinetic model in many hydrometallurgical processes (M. Free, 2013). Within the existing literature, the SCM under surface chemical reaction controlled, film diffusion controlled, and product layer diffusion controlled were adopted and evaluated in different ammoniacal systems (Baba et al., 2014; Bingöl et al., 2005; W. Liu et al., 2010; Z. X. Liu et al., 2014). Most of these studies focused on the ammoniacal leaching of Cu and base metals from primary ores. It was found that the dissolution kinetics of target metals (Cu and Zu) in refractory sulfide ores were mainly chemical reaction controlled, when using elevated temperature and pressure in leaching to break the mineral structure (Baba et al., 2014; M. K. Ghosh et al., 2002, 2003b). Only a few studies focused on ammoniacal leaching of Cu from secondary resources (Oluokun & Otunniyi, 2020; Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b). It was reported by Oluokun and Otunniyi (2020) that, when adopting H$_2$O$_2$ as a strong oxidizer, the dissolution kinetics of Cu in WPCB dust followed the chemical reaction and mixed reaction-diffusion controlled mechanism (Oluokun & Otunniyi, 2020). Sun et al.
characterized the leaching kinetics of Cu in ICT waste using ammoniacal carbonate medium under aeration (Z. Sun, Xiao, Sietsma, Agterhuis, Visser, et al., 2015b). An early kinetic stage where O₂ was slowly diffused from the bulk solution to the reaction interface was revealed. The leaching kinetics of Cu in ammoniacal solution oxidized by the dissolved O₂ was found to be mass transport-controlled.

However, the above-mentioned studies only evaluated ammoniacal leaching under oxidative conditions utilizing oxygen. For a specific system under an anaerobic conditions, where the oxidizer was strictly controlled as Cu(II) only, the development of a feasible kinetic model is needed. Plus, the treatment of real-world complex PCB waste may pose a significant effect on the leaching kinetics. This work seeks to address the gaps in literature, namely, evaluating suitable kinetic models for the leaching of populated circuit boards utilizing Cu(II) as an oxidizer to provide a deeper understanding of the reaction mechanism. To accomplish these objectives this work considers the following:

1) Evaluation of Cu ammoniacal leaching using real-world end-of-life PCBs under anaerobic conditions;
2) Design of experiments for kinetic modeling, considering initial Cu(II) concentrations, particle sizes, stirring rates, and temperatures as primary experimental factors;
3) Examination of various kinetic models by the goodness of fit;
4) Determination of an applicable kinetic model using batch experiment data;
5) Explanation of leaching mechanism and prediction of leaching behavior based on the fitted kinetic models;
6) Development of a general expression for the kinetic model feasible in future industrial scaleups.

4.2 Materials and Methodologies

4.2.1 Waste RAM chips

Waste RAM chips used in this study were obtained from the University of Kentucky Recycling Service. These PCBs were selected due to the higher Cu and Au content in a
relatively homogeneous form. As shown in Figure 4.2, waste chips can be divided into two fractions, by their appearance. The edge of the chips (golden yellow color), referred to as “Au-finger”, accounts for 9.8 %wt. The remainder of the chips (blue or green color), referred to as “non-finger”, accounts for 90.2 %wt.. The Au-finger was concentrated in Au content, so this fraction was stamped from the whole chips and used as the feed material in Au leaching experiments. The majority of Cu occurs in the non-finger fraction, appearing on the surface and within the laminates. In Cu leaching, the whole chips were used as the feed material.

Size reduction of waste chips was achieved by a knife mill (Retch SM 300), with different sizes of interchangeable screens. The particle size was reduced to -3.4, -2.0 and -1.2 mm by the shredder via multiple passes. For further chemical assaying purposes, an analytical mill (Cole Parmer Analytical Mill 4301-00) was used to further pulverize the shredded chips to -600 μm.

![Figure 4.2](image)

Figure 4.2. The appearance of waste chips (a) before and (b) after coarse shredding (top size achieved as -3.4mm).

4.2.2 Leaching experiments

A leaching apparatus, equipped with heating and stirring mantle, a three-neck round bottom vessel, and a pH/Eh/Temperature probe, was utilized for Cu ammoniacal leaching as shown in Figure 4.3. The reaction vessel was connected to an air-tight sampling port, a
gas purging port, and a condenser with outlet to a gas scrubber. The air-tight sampling port was attached with syringes to take liquid samples during leaching while preventing oxidation of Cu(I) in liquid by contacting air. The NH₃ gas scrubber was filled with a known amount of H₂SO₄, to capture the evaporated NH₃, and the amount of NH₃ evaporation was determined by the pH shift of the prefilled H₂SO₄ solution. The solution Eh, pH and temperature during leaching process were monitored by a multi-functional pH/ORP/ATC (Automatic Temperature Compensation) probe (Mettler-Toledo InPro 3100i).

Figure 4.3. Leaching apparatus used in bench-scale Cu ammoniacal leaching.

The leaching experiments were carried out using shredded waste chips in ammoniacal solution with a solid/liquid ratio of 50 g/L under atmospheric pressure for 8 hours. The total volume used in each leaching test consisted of 25 g of solids and 500 mL of liquid. Elevating pressures were not considered in this study as the leaching reactor was open to a gas scrubber, in order to track the evaporation of NH₃. According to existing literatures studying Cu ammoniacal leaching, lixiviant compositing (NH₄)₂SO₄ ranging from 0.3M to 2M, and NH₄OH ranging from 4M to 6M was sufficient to achieve a satisfying Cu recovery (Koyama, Tanaka, & Lee, 2006; Z. Sun, Xiao, Sietsma, Agterhuis,
In this work, a composition of ammoniacal solution consisting of 1 M \((\text{NH}_4)_2\text{SO}_4\) and 4 M \(\text{NH}_4\text{OH}\) was employed. 1 M of \((\text{NH}_4)_2\text{SO}_4\) was chosen to supply sufficient \(\text{SO}_4^{2-}\) as the anions to stabilize the leached Cu-amine species, and 4 M \(\text{NH}_4\text{OH}\) was chosen to provide excessive \(\text{NH}_3\) ions in the solution as complexing agent, as well as to condition the pH at a range from 9-11. In the ammoniacal lixiviant, initial Cu(II) was made up to various concentrations by dissolving \(\text{CuSO}_4\cdot5\text{H}_2\text{O}\), to serve as the oxidizer in facilitating the Cu recovery. All the experiments were run under argon covering gas to expel the existing oxygen in the system and control the initial concentration Cu(II) as the only oxidizer. The amount of initial Cu(II) added in the beginning of leaching were 10, 20, 30 and 40 g/L. Other experimental parameters include particle sizes (1.2, 2.0, and 3.4 mm), stirring rate (450, 600, and 750 rpm using magnetic stirrer), and temperature (18, 25, 35, 45, 55, and 65 °C). In addition, the influences of elevating temperatures and decreasing Cu concentration on the rate of \(\text{NH}_3\) evaporation were evaluated. The conditions of bench-scale Cu ammoniacal leaching experiment were summarized in Table 4.1.

Table 4.1 Summary of critical parameters/conditions in bench-scale Cu leaching.

<table>
<thead>
<tr>
<th>Leaching agent</th>
<th>Sampling time</th>
<th>Particle size</th>
<th>Cu(II) Conc.</th>
<th>S/L ratio</th>
<th>Temp.</th>
<th>Agitation</th>
<th>Ar flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol/L</td>
<td>min</td>
<td>mm</td>
<td>g/L</td>
<td>g/L</td>
<td>°C</td>
<td>rpm</td>
<td>L/min</td>
</tr>
<tr>
<td>1M ((\text{NH}_4)_2\text{SO}_4) and 4M (\text{NH}_4\text{OH})</td>
<td>15, 30, 60, 120, 240, 480</td>
<td>1.2, 2.0, 3.4</td>
<td>10, 20, 30, 40</td>
<td>50</td>
<td>18, 25, 35, 45, 55, 65</td>
<td>450, 600, 750</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Samples were taken at 0, 15, 30, 60, 120, 240 and 480 minutes of leaching time. All the samples were filtered immediately to stop any further leaching reaction. The filtered liquid samples were prepared for ICP analysis to determine the elemental concentrations. Solid residues after leaching were rinsed and dried in an oven at 65°C. The leaching residues were later subject to a chemical digestion procedure to determine the metal contents remaining in the solid phase. De-ionized water was used in all processes.
chemicals used in the assay, sample preparation, and leaching experiments were reagent grade.

4.2.3 Chemical assay and analytical methods

Due to the formation of precipitation when transferring the liquid samples from alkaline condition (in leaching test) to acidic condition (in sample matrix required for ICP), a sample preparation procedure was developed to stabilize the species in liquid samples. Liquid samples (1 mL) were first acidified by 1 mL of concentrated HNO₃ to stabilize the metal species as nitrates. The acidified sample was then oxidized by 1 mL of concentrated H₂O₂ to stabilize the Cu ions as Cu(II)-nitrate compound. Lastly, the stabilized liquid samples were topped off to 10 mL total volume (10X dilution) by de-ionized water.

Solid samples, feed RAM chips and leaching residues were subject to a chemical assay process to determine metal contents and perform a precise calculation. The solids were pulverized by an analytical mill, roasted in a muffle furnace, and then digested in HF and aqua regia on a hot block. The elemental concentration in digested solution was analyzed by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry). The instrument utilized was a Thermo Scientific iCAP 6500 Duo, dual view ICP-OES. The concentration of total Cu was determined by ICP-OES. The concentration of Cu(II) in the solution was measured by a UV/Vis-spectrophotometry, at a wavelength of 630 nm. A sampling port attached with syringes were used to prevent contact of air and oxidation of Cu(I) outside of leaching vessel. The concentration of Cu(I) was calculated by subtracting the Cu(II) amount from the total Cu.

Because of the heterogeneity of the feed source, Cu recovery was calculated by taking into account the Cu content in both liquid phase and solid residues, as expressed by Eq. (4.4):

\[
Cu\ Recovery\ (%) = \frac{[Cu]_{solution} \times V_{solution}}{[Cu]_{solution} \times V_{solution} + [Cu]_{residue} \times m_{residue}}
\]  

(4.4)

where [Cu]solution is the concentration of total ionic Cu leached in solution (including Cu(II) and Cu(I)), in mg/L; Vsolution is the volume of solution, in liters; [Cu]residue is the
remaining Cu concentration in leaching residues, in mg/kg; and the \( m_{\text{residue}} \) is the mass of the leaching residues, in kilograms.

4.3 Results and Discussions

4.3.1 Element composition in waste chips

The obtained waste chips were shredded to -2 mm and used as feed material for Cu ammoniacal leaching. The shredded chips were further pulverized to -20 mesh and homogenized for chemical assay. The metal contents in waste chips determined by assay are shown in Table 4.2. Copper was the highest by mass metal, accounting for 309,691 ppm (~30.97%wt.). There was also 15,256 ppm (~1.53%wt.) of Ni and 693 ppm of Au found in the security chips. The contents of the main containments, Fe, Al, and Pb, were 18,066 ppm (~1.81%wt.), 8,629 ppm and 2,584 ppm, respectively. The chips also contained 1,224 ppm of Co and 6,448 ppm of Sn.

Table 4.2. Contents of main elements in waste RAM chips.

<table>
<thead>
<tr>
<th>Al</th>
<th>Au</th>
<th>Bi</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Ga</th>
<th>Ge</th>
<th>Mg</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Sb</th>
<th>Sn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>%wt.</td>
<td>%wt.</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>%wt.</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>8,629</td>
<td>693</td>
<td>308</td>
<td>1,224</td>
<td>447</td>
<td>30.97</td>
<td>1.81</td>
<td>102</td>
<td>116</td>
<td>472</td>
<td>775</td>
<td>1.53</td>
<td>2,584</td>
<td>695</td>
<td>6,448</td>
<td>338</td>
</tr>
</tbody>
</table>

The concentration and distribution of elements in Au-finger and non-finger are shown in Figure 4.4 and Figure 4.5, respectively. As indicated in Figure 4.5, 62% of Au occurred in the Au-finger while 38% of Au was lost in the non-finger. For Cu, 88% was distributed to the non-finger fraction, while another 12% of Cu existed in the Au-finger. For the following Cu leaching experiment, the whole chips were shredded and used as the feed material.
Figure 4.4. Elemental concentration (mg/kg) in Au-finger and non-finger portions of waste RAM chips.

Figure 4.5. Elemental distribution (%) in Au-finger and non-finger portions of waste RAM chips.
4.3.2 Effect of leaching parameters (stirring rate, particle size, Cu(II) concentration and temperature)

Leaching experiments using shredded RAM chips were carried out to investigate the parameters of significance. A fixed amount of 25 g feed RAM chips, 500 mL lixiviant composed of 1M \((\text{NH}_3)_2\text{SO}_4\) and 4M \(\text{NH}_4\text{OH}\), and consistent Argon cover gas at 0.1 L/min were adopted in all the leaching tests. The effect of stirring rate, at 450, 600, and 750 rpm, on Cu recovery is shown in Figure 4.6. As the three curves from variation of the stirring rate appear nearly identical, it seems that this variable in these ranges have little to no noticeable effect on Cu leaching. The average Cu recovery was 86% for these stirring speeds.

![Figure 4.6](image)

Figure 4.6. Effect of stirring rate (rpm) on Cu recovery in ammoniacal leaching. (S/L ratio: 50 g/L, \((\text{NH}_3)_2\text{SO}_4\): 1M, \(\text{NH}_4\text{OH}\): 4M, Cu(II): 40 g/L, Particle size: -2mm, Temp. 18°C)

To study the effect of liberation and the impact on leaching efficiency, waste chips were shredded to a the top size of 3.4, 2.0, and 1.2 mm, respectively. The effect of particle size is shown in Figure 4.7. As indicated in Figure 4.7, Cu recovery increased from 77% to 86%, and 93%, as the particle size decreased from 3.4 to 2.0, and 1.2 mm, respectively. As the particle size decreased, the surface area of the chips exposed to the lixiviant increased, causing a faster dissolution of Cu(0) into the solution.
In an anerobic environment, the initial input of oxidizer, Cu(II), was believed to have the most significant effect on the Cu leaching for both recovery % and leaching rate. Based on the estimation of an amount of Cu(0) existing in feed (equivalent to 15.5 g/L at 100% recovery), initial Cu(II) concentrations were chosen as 10, 20, 30, and 40 g/L. Results shown in Figure 4.8 demonstrate that in a range of 10 to 30 g/L, Cu(II) plays an important role during leaching. Further increasing the initial Cu(II) concentration from 30 to 40 g/L slightly enhanced the Cu recovery from 84% to 86%. As the Cu(II) concentration increased, the rate of reaction also increased, indicated by the steepness at the beginning of leaching curves (within the first 2 hours). To maintain the optimum performance of Cu(II) oxidation, 40 g/L as the initial concentration was used in the subsequent tests.
The effect of temperature was also studied. Due to the high vapor pressure of NH$_3$, the evaporation of NH$_3$ from solution (NH$_4$OH) to gaseous phase (NH$_3$) is increased at a higher temperature. Therefore, the temperature range selected was from 18 °C (natural temperature of lixiviant solution) up to 65°C. As revealed in Figure 4.9, elevated temperatures resulted in an increased Cu recovery, as well as an enhanced leaching rate. According to the difference in Cu recovery and initial kinetics, the temperature influence can be divided into two ranges, a lower temperature zone from 18 to 35°C, and a higher temperature zone from 45 to 65°C. At lower temperatures, the average Cu recovery was 88% while at higher temperatures, an average recovery of 93% was achieved.
4.3.3 Eh, pH and Cu oxidation state in leaching

To show the oxidizer influence and potential thermodynamics during leaching, pH, Eh and Cu oxidation states in solution were measured. The ratio of $\Delta \text{Cu(II)}$ to $\Delta \text{Cu(I)}$ was plotted in Figure 4.10. For leaching experiments varying initial Cu(II) concentrations, the ratio of $\text{Cu(II)}/\text{Cu(I)}$ ratio were plotted in both as a ratio of $\text{Cu(II)}/\text{Cu(I)}$ and logarithm form in Figure 4.11, and the corresponding solution pH and Eh were shown in Figure 4.12. The data shown in Figure 4.11 and Figure 4.12 corresponds to the leaching tests shown in Figure 4.8.

For the predominant leaching reaction depicted in Eq.(4.7), there was a stoichiometry relationship between the reactant (Cu$^{2+}$) and the product (Cu$^{+}$), i.e. $\frac{\Delta \text{Cu}^{2+}}{\Delta \text{Cu}^{+}} = 0.5$. The results of $\Delta \text{Cu(II)}/\Delta \text{Cu(I)}$ ratio, presented in Figure 4.10, showed approximate parity to 0.5 (the dashed line), although there was still some experimental error showing under higher concentration (above 20 g/L) and later leaching time (after 2 hrs). The experimental error is likely resulted from two different ranges of accuracy when comparing data obtained from different analytical instruments, i.e. ICP-OES (accuracy of measurement in 0.1 ppm level).
for total Cu and UV/vis spectrophotometry (accuracy of measurement in 0.1 g/L level) for Cu(II).

![Figure 4.10. Ratio of ΔCu(II)/ΔCu(I) concentrations during leaching (initial Cu(II): 10, 20, 30, 40 g/L, S/L ratio: 50 g/L, (NH\textsubscript{3})\textsubscript{2}SO\textsubscript{4}: 1M, NH\textsubscript{4}OH: 4M, Particle size: -2mm, Stirring: 750 rpm, Temp. 18°C).](image)

As shown in Figure 4.11, the Cu(II)/Cu(I) ratio gradually decreased during leaching, indicating the depleting of Cu(II) and the enriching of Cu(I) simultaneously. In the first 60 min of leaching, the rate of Cu(II)/Cu(I) change was largely affected by the initial concentration of Cu(II). This observation was well-aligned with the leaching kinetics presented in Figure 4.8. After 60 min, the redox potential stabilized at -70 mV (vs SHE) using 40 g/L initial Cu(II) concentration, although the reaction was still ongoing at a lower rate. In log-scale, the change of Cu(II)/Cu(I) couple showed a flatter trend after 60 min, while leaching was continuing. This was reflected in the change of potential (Eh, mV vs SHE) during leaching, as shown in Figure 4.12, which depended significantly on the Cu(II)/Cu(I) redox couple. According to the Nernst equation shown in Eq. (4.4), under fixed NH\textsubscript{3} concentration, the change of solution Eh was largely governed by the logarithm of Cu(II) to Cu(I) ratios (Meng & Han, 1996). A comparison of calculated potential by Eq. (4.4) versus the measured potential by probe was provided in Figure 4.11 and Figure 4.12. Consistent with the flatter shape of calculated Eh after 60 min, the measured Eh seemed to reach the plateau around the same time. Although the comparison was for illustration purpose, it is noted that the theoretically calculated Eh was in general higher than the
measured value, with a roughly 50-100 mV difference. The difference between the theoretical and empirical values may be the result of a complex mixed potential by the existence of other components in the waste circuit boards, and the concentrations of other ligands presented in the lixiviant, such as $\text{SO}_4^{2-}$.

$$E_h = 0.074 - 0.118 \log[\text{NH}_3] + 0.059 \log\left(\frac{\text{Cu}(\text{NH}_3)_4^{2+}}{\text{Cu}(\text{NH}_3)_2^{2+}}\right)$$ (4.5)

For solution pH, the starting pH values in lixiviants containing different concentrations of Cu(II) varied from 10 to 10.5. As indicated by Figure 4.12, solution pH was lower in the lixiviant containing higher initial Cu(II) concentration. It was anticipated that in concentrated Cu(II) solution, there were more NH$_3$ complexed with Cu(II) to form Cu(II)-amine species, while leaving less free NH$_3$ unbonded in solution. As the free NH$_3$ in solution decreased, the dissolution of NH$_3$ in water (shown in Eq. (4.6)) was depressed, thus lessening (or lowering) the OH$^-$ generated in this reaction. In the work reported by Koyama et al. (2006), Cu was leached mainly in the form of Cu(NH$_3$)$_2^+$, as referred in Eq. (4.7). Stoichiometrically, there should be no significant change of free NH$_3$ in solution when leaching Cu as Cu(NH$_3$)$_2^+$ (Koyama, Tanaka, & Lee, 2006). However, the more recent findings by Velásquez-Yévenes et al. revealed that the leached Cu(I) predominantly exists as Cu(NH$_3$)$_3^+$ at the pH range from 9.4 to 10.2, while Cu(II) at the same pH range mainly exists as Cu(NH$_3$)$_4^{2+}$ (Velásquez-Yévenes & Ram, 2022). This means that, in addition to the primary reaction in Cu-ammoniacaial leaching shown in Eq. (4.7), a side reaction of Cu(NH$_3$)$_2^+$ complexing one more mole of free NH$_3$ would likely occur (Eq. (4.8)). Similarly, the decrease of free NH$_3$ in the solution caused by the complexation with additional NH$_3$ further resulted in a decreasing trend of solution pH as leaching proceeded. Plus, as the leaching was performed under Ar purging, and the outlet of the system was open to the atmosphere, the loss of NH$_3$ by evaporation cannot be eliminated completely. This also resulted in a decrease in solution pH over time.

$$\text{NH}_3 + H_2O \leftrightarrow \text{NH}_4^+ + OH^-$$ (4.6)

$$\text{Cu}(\text{NH}_3)_4^{2+} + \text{Cu} = 2\text{Cu}(\text{NH}_3)_2^{2+}$$ (4.7)

$$\text{Cu}(\text{NH}_3)_2^{2+} + \text{NH}_3 = \text{Cu}(\text{NH}_3)_3^+$$ (4.8)
4.3.4 Ammonia evaporation in leaching

As discussed in the previous section, NH$_3$ evaporated during leaching and was captured by a gas scrubber, which was filled with 100 mL of 1M H$_2$SO$_4$ to calculate the NH$_3$ evaporation rate. The rate of NH$_3$ evaporation was measured in the unit of millimoles of NH$_3$ evaporated per liter of leaching volume per minute of leaching duration. The amount of dissolved NH$_3$ in H$_2$SO$_4$ was determined by the pH shift in H$_2$SO$_4$ solution at the beginning and end of the leaching process. As depicted by Eq. (4.9), 1 mole of NH$_4$OH consumes 1 mole of H$^+$ in H$_2$SO$_4$. The amount of H$^+$ consumed in Eq. (4.10) resulted in the pH drift as described below:

$$\text{H}_2\text{SO}_4 + 2\text{NH}_4\text{OH} \rightarrow 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{SO}_4$$

(4.9)

$$\text{pH} = - \log_{10}[\text{H}^+] \quad [\text{H}^+] = 10^{-\text{pH}}$$

(4.10)

The result of NH$_3$ evaporation under different temperatures and initial Cu(II) concentrations are shown in Figure 4.13 and Figure 4.14, respectively. Expectedly, NH$_3$ evaporation rate was higher in the high-temperature zone (45-65°C) than that in the low-temperature zone (18-35°C).
Interestingly, it was observed that the initial Cu(II) concentration, or the total amount of Cu ions in solution, also affected the NH$_3$ evaporation more significantly than the temperature. Under a consistent argon cover gas, starting with 10 g/L Cu(II), there was more NH$_3$ escaping from the leaching vessel due to fewer available Cu ions to complex with NH$_3$. Consequently, there were more free NH$_3$ ions existing in the solution in forms of NH$_4$OH, which more readily evaporated under Ar gas purging. Conversely, with the 40 g/L starting Cu concentration, more NH$_3$ was complexed with Cu ions decreasing free NH$_3$, thus resulting in a lower NH$_3$ evaporation rate.

4.3.5 Kinetic modeling for Cu ammoniacal leaching system

For simplicity, the shredded Cu-containing chips may be viewed as spherical particles. In addition, considering the occurrence of Cu within board laminations and the solid-liquid interaction between metallic Cu and Cu(II)-bearing solution, shrinking-core, alongside diffusion-controlled model, were taken into account to describe the reaction mechanism in such a system. In considering shrinking core models, 5 rate-limiting steps can be considered consisting of: 1) diffusion of oxidizer Cu(II)-amine from the bulk solution to the interface of non-reactive product layer; 2) penetration of Cu(II)-amine
through the non-reactive layer terminating at the reaction surface of Cu(0); 3) chemical reaction at the interface where Cu(0) was oxidized to Cu(I); 4) the leached Cu(I) complexed with NH₃ to form soluble Cu(I)-amine compound and penetrated through the product layer to the interface; 5) diffusion of Cu(I)-amine complex from the interface to the bulk solution, with the slowest among these 5 steps is considered the rate-controlling step. A schematic illustration of these 5 rate-limiting steps is provided in Figure 4.15.

![Schematic illustration of reaction mechanism in Cu-ammoniacal leaching system.](image)

Figure 4.15. Schematic illustration of reaction mechanism in Cu-ammoniacal leaching system.

Considering the Cu-NH₃ leaching system, several commonly used kinetic models were evaluated for goodness of fit using the experimental data from different particle sizes and initial Cu(II) concentrations. These models considered film diffusion, product layer diffusion, surface reaction and semi-empirical models (Dickinson & Heal, 1999a; Levenspiel, 1998; W. Liu et al., 2010; Zhuravlev et al., 1948). However, most of them were not suitable for this specific Cu-ammoniacal leaching system due to poor data/model fit. Conversely, the three models presented in the following discussion, based on seemingly plausible assumptions of shrinking-core and diffusion-controlled mechanism, showed a better data correlation with R² over 0.8. The linear expressions of the considered models were given in Eq.(4.11) to (4.13):

Model 1) SCM under product layer diffusion (Levenspiel, 1998)

\[ 1 + 2(1 - \alpha) - 3(1 - \alpha)^3 = k_1 t \]  

(4.11)
where \( k_1 = \frac{6bDC_0}{C_Br_0^2} \); \( \alpha \) is the reacted fraction of Cu; \( D \) is the diffusion coefficient, \( \text{m}^2/\text{s} \); \( C_0 \) is the concentration of fluid outside the particle, \( \text{mol/L} \); \( C_B \) is the apparent concentration of solid reactant, \( \text{mol/L} \); \( r_0 \) is the initial outside radius of the particles (Levenspiel, 1998).

Model 2) Changing \( C_0 \) concentration model (Zhuravlev et al., 1948)

\[
((1 - \alpha)^{-\frac{1}{3}} - 1)^2 = k_2 t
\]

(4.12)

where \( k_2 = DV_mC_0 \); \( \alpha \) is the reacted fraction of Cu; \( D \) is the diffusion coefficient, \( \text{m}^2/\text{s} \); \( V_m \) is the volume of product formed from 1 mole of the slowest penetrating component; \( C_0 \) is the initial concentration of reactant, \( \text{mol/L} \), and the change in concentration is based on \( C_0 \times (1 - \alpha) \) (Zhuravlev et al., 1948).

Model 3) Mixed diffusion control model for spherical particles (Dickinson & Heal, 1999a)

\[
\frac{1}{3} \ln(1 - \alpha) + (1 - \alpha)^{\frac{1}{3}} - 1 = k_3 t
\]

(4.13)

where \( k_3 = 4\pi DV_mC_0 \); \( \alpha \) is the reacted fraction of Cu; \( D \) is the diffusion coefficient, \( \text{m}^2/\text{s} \); \( V_m \) is the volume of product formed from 1 mole of the slowest penetrating component; \( C_0 \) is the concentration of penetrating species at the surface, \( \text{mol/L} \) (Dickinson & Heal, 1999a).

To determine goodness of fit, the Cu recoveries, in \%, obtained from the batch leaching experiments, with regard to different particle sizes and changing Cu(II) concentrations, were converted to the reacted fraction, \( \alpha \) (which ranges from 0-1, 0 being unreacted, and 1 being fully reacted). The left term containing \( \alpha \), in each model, was plotted versus reaction time. The linear regressions from kinetic models 1) to 3) are shown in Figure 4.16 to Figure 4.21. The slopes of each linear line, \( k \), are the rate constants varied by the considered variables.

As can be seen in Figure 4.16 and Figure 4.17, the fitting of Model 1), the shrinking-core model under diffusion control, did not well align with the experimental data from different sizes and Cu(II) concentrations, with \( R^2 \). Moreover, the data from different concentrations showed a certain curved trend, meaning that there were likely some other factors not well accounted for in this model.
Figure 4.16. Plot of $1 + 2(1 - \alpha) - 3(1 - \alpha)^{2/3}$ vs time under various particle sizes (diameter, mm), data corresponding to Figure 4.7.

Figure 4.17. Plot of $1 + 2(1 - \alpha) - 3(1 - \alpha)^{2/3}$ vs time under various initial Cu(II) concentration (g/L), data corresponding to Figure 4.8.

The regression of Model 2 with the changing $C_0$ bulk concentration, is shown in Figure 4.18 and Figure 4.19. The result indicates an improvement of fit with $R^2$ of above 0.99 for both sizes and initial concentrations. Since the Cu(II) concentration was considered the most important factor in leaching, it was not beyond reason that when considering the changing concentration in bulk solution, the correlation between the predicted model and experimental data show improved fit. However, the data fitting for the smallest particle size, 1.2 mm, is of some concern and should not be neglected.
In comparison to Models 1) and 2), Model 3) had the best fit for both various sizes and Cu(II) concentrations, as indicated by Figure 4.20 and Figure 4.21. In particular, the fitting on smaller particle sizes was greatly improved. The resulting regression coefficient was above 0.99 for various sizes and above 0.98 for different Cu(II) concentrations. For these reasons, Model 3) was adopted for further data analysis and kinetic modeling.
Table 4.3. Correlation coefficient (R^2) of Cu extraction in 3 evaluated models under different particle sizes (d_p) (data corresponds to Figure 4.16, Figure 4.18 and Figure 4.20).

<table>
<thead>
<tr>
<th>d_p (mm)</th>
<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>0.9104</td>
<td>0.9675</td>
<td>0.9928</td>
</tr>
<tr>
<td>2.0</td>
<td>0.8861</td>
<td>0.9924</td>
<td>0.9792</td>
</tr>
<tr>
<td>3.4</td>
<td>0.9274</td>
<td>0.9961</td>
<td>0.9877</td>
</tr>
</tbody>
</table>

Table 4.4. Correlation coefficient (R^2) of Cu extraction in 3 evaluated models under different initial Cu(II) concentrations (c(Cu^{2+})) (data corresponds to Figure 4.17, Figure 4.19 and Figure 4.21).

<table>
<thead>
<tr>
<th>c(Cu^{2+}) (g/L)</th>
<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.8163</td>
<td>0.8585</td>
<td>0.8484</td>
</tr>
<tr>
<td>20</td>
<td>0.9380</td>
<td>0.9908</td>
<td>0.9820</td>
</tr>
<tr>
<td>30</td>
<td>0.9192</td>
<td>0.9905</td>
<td>0.9825</td>
</tr>
<tr>
<td>40</td>
<td>0.8861</td>
<td>0.9924</td>
<td>0.9792</td>
</tr>
</tbody>
</table>

The relationship between reaction rate and temperature can be described by Arrhenius Equation (Eq. (4.14)) (Laidler, 1984). Model 3 as the best-fitted model was chosen to fit with varying temperature data and the corresponding rate constant (k_T) was plotted in Figure 4.22, according to Arrhenius Equation. The activation energy (E_a) can be evaluated from the Arrhenius plot by taking the natural logarithm of the rate constant (ln(k_T/h^1)) versus the inverse of temperature (T^{-1/K^1}), as shown in Figure 4.23. The slope resulting in Figure 4.23 is \(-E_a/R\), where R is the gas constant of 8.314 J·K^{-1}·mol^{-1}. Extrapolating from plot Figure 4.22 and Figure 4.23, the activation energy (E_a) in Cu-NH_3 leaching system was 4 kcal/mol, which suggested that this leaching reaction was mainly mass transport controlled.
\[ K = Ae^{-\frac{E_a}{RT}} \]  

(4.14)

To further determine the dependency of reaction order regarding various particle sizes and initial Cu(II) concentrations, within the studied range, the logarithm of apparent rate constants obtained from Figure 4.20 and Figure 4.21 was taken and plotted vs \( \log \left( \frac{R^2}{mm} \right) \) and \( \log [c(Cu^{2+})/(mol/L)] \), as shown in Figure 4.24 and Figure 4.25, respectively. The estimated reaction order under different sizes \( \frac{1}{R^2} \) was 0.8151 (Figure 4.24), while the reaction order under different Cu(II) concentrations \( c(Cu^{2+}) \) was 1.6738 (Figure 4.25).
Consequently, the general expression of the kinetic model for Cu ammoniacal leaching can be attained by combining the terms for the reaction orders and activation energy. The yielded kinetic model, under the studied range, can be written as Eq. (4.15):

\[
\left(\frac{1}{3}\ln(1 - \alpha) + (1 - \alpha)^{-\frac{1}{3}} - 1\right) = 0.1159 \times (c[Cu^{2+}])^{1.6738} \times \left(\frac{1}{R^2}\right)^{0.8151} \times \exp\left(-\frac{1.9683}{T}\right) \times t
\]

where \(\alpha\) is the reacted fraction (from 0 to 1), \(c(Cu^{2+})\) is the initial oxidizer concentration in mol/L, \(R\) is the radius of particles in mm, \(T\) is the leaching temperature in K, and \(t\) is the residence time of leaching in an hour. The empirical constant of 0.1159 was obtained by fitting the experimental data within the studied range of leaching conditions.

As revealed by the expression of Eq. (4.15) under diffusion-controlled mechanism, the 
Cu(II) concentration was regarded as the most influencing factor with a reaction order higher than 1.67. The particle size, indicated by the radius \(R\) of a spherical shape, showed a nearly equal importance on affecting the leaching rate, with a reduced order of -1.63. The minus value indicated the inverse impact of particle size on leaching rate (i.e. the rate increases as the particle size reduces). The increase in temperature resulted in a slight acceleration of leaching kinetics, with a relatively lower activation energy of 4 kcal/mol.
Under higher concentration of Cu(II), the kinetics was predominantly governed by the diffusion of Cu species in solution.

To evaluate the goodness of the proposed kinetic model, Cu recoveries under studied parameters were calculated by the general expression in Eq. (4.15) and plotted as a comparison to actual data obtained from experiments, as shown in Figure 4.26. The black dot line is the line of “y = x” and the red dot line is the line of linear regression using all the data presented in Figure 4.26. Ideally, if all the predicted data is identical to the actual experimental data, the linear regression should have a slope of 1, i.e. the two dot lines overlay with each other. As can be seen, using the proposed model, the linear regression, with an expression of $y = 1.0133x$ ($R^2 > 0.99$), almost overlayed the ideal “y = x” line. The comparison between data obtained from the model and data obtained from the experiment reveals that the proposed model has done a good prediction under the studied conditions.

![Figure 4.26. The goodness of model prediction (Cu: concentration of initial Cu(II), dp: diameter of particles, black dotted line: y = x, red dotted line: linear regression of dataset, data corresponding to Figure 4.7 and Figure 4.8).](image-url)
4.4 Conclusions

An energy-saving, environmentally friendly process for Cu extraction from waste RAM chips with high efficiency and with the potential of oxidizer regeneration was proposed and investigated. In this process, the ammoniacal solution was used as lixiviant and Cu(II) as the oxidizer, Cu from waste PCBs was leached as Cu(I) which benefits the current efficiency in subsequent Cu electrowinning. To provide an in-depth understanding of the most important parameters, the leaching kinetics, and the Cu oxidation state, the leaching mechanism was evaluated and kinetic modeling was executed.

Experiments of Cu leaching utilizing shredded waste chips in ammoniacal solutions were carried out under argon cover gas. The optimum Cu recovery of 96% occurred under the condition using 50 g/L S/L ratio, 1.2 mm particle size, 750 rpm stirring rate, 8 hours residence time at room temperature (18°C), using 1M ammonium sulfate and 4M ammonium hydroxide as lixiviant and 40 g/L initial Cu(II) concentration as the oxidizer. Both higher temperature and decreasing Cu concentrations were found to have an impact on NH₃ evaporation during leaching.

The reaction rate was examined under various parameters. The result indicates that particle size and initial Cu(II) concentration have the most significant impact on kinetics. From the result of kinetic modeling, both Zhuravlev’s changing concentration model and Dickinson’s mixed diffusion model show almost identical goodness of fit. In considering the actual leaching mechanism, it appears that the change of concentration during leaching has a significant effect on the leaching rate. The goodness of fit in Dickinson’s model may be coincidental because the change in stirring rate does not affect the leaching kinetics, leading to the conclusion that the boundary layer diffusion mechanism in Dickinson’s model may be coincidental in describing data/model fit.

Moreover, the activation energy was calculated to be 4 kcal/mol by the Arrhenius equation, which further confirms that this reaction is dominantly mass transport controlled. The general expression of Cu leaching in ammoniacal system was established within the studied range of variables. The reaction order regarding Cu(II) concentration and 1/R² were 1.6738 and 0.8151, respectively. As such, initial Cu(II) concentration was found to be the most important factor influencing Cu leaching rate. Finally, the comparison between the
dataset predicted by the model and the experimental data further proved the feasibility of the proposed model expression.
5.1 Introduction

Studies of the fundamental aspects of shrinking-core models, developed by Levenspiel, have undergone a revival in the last 30 years (Liddell, 2005). Many researchers adapted and extended the earlier models to situations more complex with an emphasis on mineral leaching reactions (Baba et al., 2014; Beckstead & Miller, 1977; Bingöl et al., 2005; M. L. Free, 2021; Künkül et al., 1994; Z. X. Liu et al., 2014). For generations, the shrinking-core model (SCM) has been presented in hydrometallurgy as the most widely used kinetic model (M. Free, 2013).

It was noted in previously reported literatures that two outstanding concerns exist regarding the originally developed SCM (Liddell, 2005). First, the basis of the SCM was restricted to a gas-solid reaction, as stated by Levenspiel in his book. Although SCM managed to fit in many of the solid-liquid reactions, there were some cases where it failed to illustrate the leaching mechanism. In fact, researchers found that the SCM can only predict the leaching processes accurately when applied under circumstances where the concentration of fluid reactant is very low. This explicitly caused the failure of adopting the most widely used SCM model to describe the Cu ammoniacal leaching data in a highly concentrated system.

The second remarkable defect is the approximation of the pseudo-steady state (PSS) made in this model. The physical meaning of PSS assumes that the movement of the interface between the unreacted solids and the product is slow enough than the diffusion rate of species through the porous shell, thus allowing the concentration profile across the shell to be determined from a steady-state aspect (Liddell, 2005). As such, the motion of the interface can be solved by equating the mass flux to the rate of disappearance of the reacting solid. The resulted expression is given as:

$$\frac{t}{\tau} = 1 - 3 \left( \frac{R_c}{R_p} \right)^2 + 2 \left( \frac{R_c}{R_p} \right)^3$$  \hspace{1cm} (5.1)
where \( \tau \) is the time required to achieve complete reaction; \( R_c \) is the radius of unreacted core; \( R_p \) is the initial radius of the spherical particle. However, one problem associated with the PSS assumption in the differential mass balance is that the effective diffusivity \( D \) and the porosity \( \varepsilon \) are assumed constant in SCM. Although the model is greatly simplified by this assumption and becomes much accessible for entry-level students to take advantage of it, the valid range of its application is constrained to the situation where the fluid reactant’s concentration is very low. In 1968, Wen proposed a valid range by the following equation (Wen, 1968):

\[
\frac{\varepsilon C_{A,0}}{a C_{s,0}} < 0.1
\]

(5.2)

where \( a \) is the stoichiometric coefficient for the liquid reactant, \( C_{A,0} \) is the bulk concentration of the liquid reactant, and \( C_{s,0} \) is the initial concentration of the solid reactant. Around the same time, Luss further introduced the Nusselt number for mass balanced and identified the upper and lower limit of Levenspiel’s model, as shown below (Luss, 1968):

\[
0 < \delta < \frac{1}{2} \left( \frac{1}{N u} + 1 \right) \frac{C_A}{\rho_s}
\]

(5.3)

where \( N u = \frac{kR_p}{D} \) and \( \rho_s \) is the molar density of the solid reactant. It was observed by Luss’s work that SCM tends to fail as the conversion exceeds 0.3 or 0.4, and the error \( \delta \) increases as leaching progresses under constant \( C_A \) assumption.

In summary, it was concluded that the SCM yields an acceptable accuracy in fluid-solid reactions where the concentration of reactant may be relatively high. However, the error is small at lower concentrations. This raised concerns in this study that we are using Cu leaching in an extremely high concentration (approximately from 40-80 g/L Cu) and the change in diffusivity could not be neglected.

Therefore, in this chapter, the author seeks to explore additional kinetic models that could serve as a tool to apply the experimental data, as well as to further develop a justified method in the application of industrial-scale process simulation. Several kinetic models, besides the SCM, were examined and only a few of them showed a goodness of data fitting and acceptable validity in the later process simulation (Dickinson & Heal, 1999b; Jander, 1927; Zhuravlev et al., 1948). The models selected and the reasons for their consideration were listed below:
1) Dickinson’s model – this was the model used in the last chapter with the best data fitting of batch leaching experiments.

2) Zhuravlev’s model – this model showed an acceptable data fitting; it was a better fit than Dickinson’s model in higher concentrations; it also composed an interchangeable rate constant term that allowed the transfer of constants into a constant concentration model.

3) Jander’s model – the rate constant is same as Zhuravlev’s model, but Jander’s model assumes a constant concentration.

The results of leaching experiments presented in Chapter 4 indicated that the mechanism of Cu ammoniacal leaching was diffusion controlled. The initial Cu concentrations and the particle sizes were found to be the two most significant affecting factors in leaching reaction. Because of the high initial input and the continuous change of Cu concentration in the leaching system, the varying Cu concentration was believed to have the most significant effect on the leaching rate. Although the mixed diffusion model showed a good prediction in general, the changing concentration model was found to be more accurate specifically under higher concentrations. Moreover, to extend the application of this model obtained from batch reactors to a real-world counter-current leaching (CCL) circuit, operated by continuously stirring tank reactors (CSTR), a justified model with interchangeable rate constant is needed. In this chapter, there were three diffusion-controlled models being adopted and further applied in the conceptual scaleup process simulations, as listed below:

1) Mixed diffusion-controlled model (Dickinson & Heal, 1999a);
2) Changing concentration diffusion-controlled model (Zhuravlev et al., 1948);
3) Constant concentration diffusion model (Jander, 1927).

The linear equations, basic assumptions, and the rate constant of these three models were summarized in Table 5.1.
Table 5.1 Linear equations and assumptions of three suggested kinetic models.

<table>
<thead>
<tr>
<th>Equations</th>
<th>Assumptions</th>
<th>Rate constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1 - \alpha)^{-\frac{1}{3}} + \frac{1}{3} \ln(1 - \alpha) - 1 = k_d t$</td>
<td>Diffusion-controlled at interface and across product layer</td>
<td>$k_d = 4\pi D V_m C_0$</td>
<td>(Dickinson &amp; Heal, 1999a)</td>
</tr>
<tr>
<td>$\left((1 - \alpha)^{-\frac{1}{3}} - 1\right)^2 = k_z' t$</td>
<td>Diffusion-controlled with changing concentration</td>
<td>$k_z' = \frac{2D V_m C_0}{r_0^2}$</td>
<td>(Zhuravlev et al., 1948)</td>
</tr>
<tr>
<td>$\left(1 - (1 - \alpha)^{\frac{1}{3}}\right)^2 = k_j' t$</td>
<td>Diffusion-controlled with constant concentration</td>
<td>$k_j' = \frac{2D V_m C_0}{r_0^2}$</td>
<td>(Jander, 1927)</td>
</tr>
</tbody>
</table>
5.2 The Diffusion-controlled Models

As introduced, in our system, we are seeking to find a kinetic model, based on the diffusion-controlled mechanism, to better describe the liquid-solid reaction under higher and changing reactant concentration. In the previous studied Cu leaching, we found that the reaction is diffusion controlled and the two most significant factors were the particle size of feed solid and the concentration of oxidizer in solution. Also, the leaching reaction took place in a solid-liquid system. Therefore, considering the Cu particles in WPCBs dissolving in a solution consisting of various ions and multiple valent states, a basic model was drawn, showing the leaching mechanism and interaction between the solid, the liquid, and the intermediate product layer phase. The basic assumption in this model, differing from Levenspiel’s original SCM, were the inconsistency of time dependence of molarity for reactant A \( \left( \frac{dN_A}{dt} \right) \), as it moved through a distance:

\[
- \frac{dN_A}{dt} = 4\pi r^2 Q_A \neq \text{constant} \tag{5.4}
\]

A schematic drawing of the basic model showing the concept of multi-layer diffusion and a change of concentration in both external layer (bulk) and product layer was shown in Figure 5.1. A few other kinetic models, with approximations that may satisfy this concept were discussed in detail in the next section.

As illustrated schematically in Figure 5.1, the spherical particle A refers to the Cu particles in WPCBs reacted during leaching, with an original radius of \( R \) (\( r_0 \)). Solution B refers to the leaching solution containing similar chemical compositions and various initial concentrations of Cu-amine ions. The Cu(II)-amine complex in leaching solution diffuses from the bulk solution B and contact with the particle A, meanwhile travels inward through a distance of diffusion \( r \) (\( x \)), at time \( t \). The reacted fraction of particle A, also known as leaching recovery, is referred to as \( \alpha \). To the opposite, the un-reacted fraction is referred to as \( (1 - \alpha) \).
Figure 5.1. Schematical illustration of shrinking-core model with approximation of both diffusion-controlled and changing-concentration mechanism.

Since the SCM failed to describe the system with a low goodness of data fitting and incorrect approximation, we now consider other diffusion-controlled models that are believed to better illustrate the solid-liquid reaction under approximations of changing concentration, and/or diffusion in the bulk and across the product layer. The theoretical principles of diffusion-controlled kinetic models are based on a chemical process carried out by instantaneous surface nucleation (Dickinson & Heal, 1999a).

5.2.1 Model 1 - Mixed diffusion-controlled model (Dickinson & Heal, 1999a)

Proposed by Dickinson et al., a model assuming the rate of reaction is affected by both the interface transfer and the diffusion across the product layer (Dickinson & Heal, 1999a).

\[
\frac{dx}{dt} = \frac{D V_m C_0 4 \pi r^2}{x} = \frac{k_d r^2}{x}
\]  (5.5)
\[ k_d = 4\pi D V_m C_0 \]  \hfill (5.6)

The linear expression of Dickinson’s mixed diffusion model can be described as:

\[
(1 - \alpha)^{-\frac{1}{3}} - 1 + \frac{1}{3} \ln(1 - \alpha) = k_d t \]  \hfill (5.7)

where \( k_d = 4\pi D V_m C_0 \); \( D \) is the diffusion coefficient (slowest transport); \( V_m \) is the volume of product AB formed from 1 mole of the slowest penetrating component, and \( C_0 \) is the concentration of penetrating species at the surface (Dickinson & Heal, 1999a).

### 5.2.2 Model 2 - Changing concentration diffusion-controlled model (Zhuravlev et al., 1948)

Regarding to a reaction where the concentration of reactant varies over time, Zhuravlev et al. proposed a diffusion-controlled model assuming the concentration of one reactant, \( C_0 \) is not a constant, but a factor of reactant activity varying with \( (1 - \alpha) \) (Zhuravlev et al., 1948). As such, the change of concentration \( C_0 \) is proportional to \( (1 - \alpha) \), and the instant concentration at time \( t \) is \( C_0(1 - \alpha) \).

\[
\frac{dx}{dt} = \frac{D V_m C_0 (1 - \alpha)}{x} = \frac{k_x (1 - \alpha)}{x} \]  \hfill (5.8)

\[
k_x = D V_m C_0 \]  \hfill (5.9)

The final expression of Zhuravlev’s changing concentration model can be given as:

\[
\left( (1 - \alpha)^{-\frac{1}{3}} - 1 \right)^2 = k_x' t \]  \hfill (5.10)

where \( k_x' = \frac{2k_x}{r_0^2} = \frac{2D V_m C_0}{r_0^2} \); \( r_0 \) is the original radius of spherical particle A.

### 5.2.3 Model 3 - Constant concentration diffusion model (Jander, 1927)

Considering constant concentration but a three-dimensional diffusion around the reacted particle, Jander proposed a diffusion-controlled model where the time dependence of the gradual buildup of the layer can be described by the parabolic law. In his model, the rate constant varied inversely with the diffusion distance \( x \), as indicated by:

\[
x^2 = 2D V_m C_0 t = k_j t \]  \hfill (5.11)

\[
2 \frac{xdx}{dt} = k_j \quad \text{or} \quad \frac{dx}{dt} = \frac{k_j}{2x} = \frac{D V_m C_0}{x} \]  \hfill (5.12)
For above mechanism, the final expression can be given as:

\[
\left( 1 - (1 - \alpha)^{\frac{1}{3}} \right)^2 = k_j' t
\]

(5.13)

where \( k_j' = \frac{k_j}{r_0^2} = \frac{2DV_mC_0}{r_0^2} \).

It was noted that the rate constant \( k_z' \) and \( k_j' \) were written in an interchangeable form, i.e. \( k_z' = k_j' \). This allows us to solve the constants (D, \( V_m \), \( C_0 \), \( r_0 \)) in the changing-concentration model fitted by the previous batch experiment data, and apply the constants to the constant-concentration model that are suitable in a certain industrial performance. The summary of these three models, the rate constant, and their suitability of applications were given in Table 5.2.

Table 5.2 Summary of adopted diffusion-controlled models.

<table>
<thead>
<tr>
<th>Linear expression</th>
<th>Rate constant</th>
<th>Application</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (1 - \alpha)^{-\frac{1}{3}} + \frac{1}{3} \ln(1 - \alpha) - 1 = k_d t )</td>
<td>( k_d = 4\pi DV_mC_0 )</td>
<td>Diffusion through bulk and product layer</td>
<td>D, ( V_m ), ( C_0 )</td>
</tr>
<tr>
<td>( \left( (1 - \alpha)^{-\frac{1}{3}} - 1 \right)^2 = k_z' t )</td>
<td>( k_z' = \frac{2DV_mC_0}{r_0^2} )</td>
<td>Changing concentration</td>
<td>D, ( V_m ), ( C_0 ), ( r_0 )</td>
</tr>
<tr>
<td>( \left( 1 - (1 - \alpha)^{\frac{1}{3}} \right)^2 = k_j' t )</td>
<td>( k_j' = \frac{2DV_mC_0}{r_0^2} )</td>
<td>Constant concentration; three-dimensional diffusion</td>
<td>D, ( V_m ), ( C_0 ), ( r_0 )</td>
</tr>
</tbody>
</table>

In general, the experimental data was adopted to solve the interchangeable rate constant \( k \), by applying the changing-concentration model. The solved coefficients were then employed in the constant-concentration model. These coefficients were interchangeable between the two models, with error minimization using Excel Solver. The resulted reacted fraction (\( \alpha \)) by constant-concentration model was further applied in a mass-balanced program.
5.3 Applications of Selected Kinetic Models in Process Simulation

5.3.1 Example 1 – Batch (semi counter-current) leaching simulation

Concluded from the previous leaching experiment (Chapter 4), Dickinson’s model with the assumption of a mixed diffusion control mechanism showed the best goodness of fit in the experimental data. Therefore, this model was used in the batch leaching circuit simulation under different initial Cu(II) concentrations. The estimated reacted fraction ($\alpha$) by this model was then input in a simulation program for mass balance.

In the application of a batch (semi-counter-current) leaching circuit discussed in this section, we adopted the fitted Dickinson’s diffusion model:

$$\left(1 - \alpha\right)^{\frac{1}{3}} + \frac{1}{3}\ln(1 - \alpha) - 1 = 4\pi D V_m C_0 t$$

And we approximated the circuit performance by solving the reacted fraction $\alpha$. The predicted recovery under various initial Cu(II) concentrations were plotted in Figure 5.2.

![Figure 5.2](image)

**Figure 5.2.** Predicted reaction fraction ($\alpha$) in each leaching stage under various initial Cu(II) concentrations by the adopted model.

In our first example, a flowsheet simulating a multi-stage batch leaching circuit was designed. A 4-stage leaching circuit with solution and solid flowing in an opposite direction was employed. The residence time in each leaching tank was approximated as 2 hours. Other processing inputs for the simulation were listed in Table 5.3. The incoming flowrate of solid Cu(0) in the feed WPCBs was 1 t/h. In the lixiviant, the replenished solution
returned from EW was used, assuming a starting Cu(II) concentration of 35 g/L, and a residual Cu(I) concentration of 5 g/L.

Table 5.3. Input parameters for process simulation using the adopted model.

<table>
<thead>
<tr>
<th>Input</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate coefficient (constant)</td>
<td>$k_d$</td>
<td>0.042</td>
<td>Unitless</td>
</tr>
<tr>
<td>Feed particle size</td>
<td>$R$</td>
<td>1</td>
<td>mm</td>
</tr>
<tr>
<td>Leaching temperature</td>
<td>$T$</td>
<td>20</td>
<td>°C</td>
</tr>
<tr>
<td>Initial Cu(II) concentration in solution</td>
<td>Cu(II)</td>
<td>35</td>
<td>g/L</td>
</tr>
<tr>
<td>Initial Cu(I) concentration in solution</td>
<td>Cu(I)</td>
<td>5</td>
<td>g/L</td>
</tr>
<tr>
<td>Initial Cu(0) concentration in feed</td>
<td>Cu(0)</td>
<td>30</td>
<td>%wt.</td>
</tr>
<tr>
<td>Lixiviant flow rate</td>
<td>$Q_{\text{lix}}$</td>
<td>1200</td>
<td>L/min</td>
</tr>
<tr>
<td>Mass flow of feed</td>
<td>$Q_{\text{feed}}$</td>
<td>3.33</td>
<td>Metric ton/h</td>
</tr>
<tr>
<td>Mass flow of Cu(0)</td>
<td>$Q_{\text{Cu}(0)}$</td>
<td>1</td>
<td>Metric ton/h</td>
</tr>
</tbody>
</table>

Given by the Dickinson’s model:

$$(1 - \alpha)^{\frac{1}{3}} + \frac{1}{3} \ln(1 - \alpha) - 1 = k_d t$$

where $k_d = 0.1159 \times (c[Cu^{2+}])^{1.6738} \times \left(\frac{1}{R^2}\right)^{0.8151} \times \exp\left(-\frac{1.9683}{T}\right)$, as developed by fitting the empirical data from Chapter 4. The solved $k$ value under 35 g/L of initial Cu(II) concentration was 0.0424. The corresponding cumulative recovery $\alpha$ was calculated using Excel solver, and the results were shown in Table 5.4.
Table 5.4. Calculated $\alpha$ in each leaching tank using the adopted model.

<table>
<thead>
<tr>
<th>Tank #</th>
<th>Time (hr)</th>
<th>$[\text{Cu}^{2+}]_{\text{out}}$ (g/L)</th>
<th>Cumulative $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tank 1</td>
<td>2</td>
<td>21.97</td>
<td>0.69</td>
</tr>
<tr>
<td>Tank 2</td>
<td>4</td>
<td>32.42</td>
<td>0.80</td>
</tr>
<tr>
<td>Tank 3</td>
<td>6</td>
<td>34.09</td>
<td>0.85</td>
</tr>
<tr>
<td>Tank 4</td>
<td>8</td>
<td>34.85</td>
<td>0.89</td>
</tr>
</tbody>
</table>

The result of calculated recoveries ($\alpha$) was further programmed HSC SIM software for the purposes of process simulation and mass balance. The obtained flowsheet, with visualized chemical composition in each leaching stage, was shown in Figure 5.4. As the leaching process started with 1 t/h of Cu(0) in solid feed, and 35 g/L of Cu(II) in lixiviant with 5 g/L residual Cu(I) left from EW return, the pregnant leaching solution (PLS) coming out from the last stage of leaching Tank 1 contains 32 g/L of Cu(I) and 22 g/L of Cu(II) entering the EW. In the leaching residues coming out at the bottom of Tank 4, 0.1 t/h of remaining Cu is transferred to the next Au leaching circuit. Visually indicated in Figure 5.3, the corresponding concentration of Cu(II) leaving for the EW circuit was not that satisfying, as the ideal PLS is in a Cu(II)-depleted and Cu(I)-enriched condition.

Figure 5.3. Out-of-tank Cu(II) concentration (g/L) estimated by the adopted model.
Figure 5.4. Flowchart of kinetic modeling and simulation of batch leaching circuit in ammoniacal system.
5.3.2 Example 2 – CSTR counter-current leaching circuit

Although the results presented in Figure 5.4 showed a good visualization of Cu flow, the final Cu(II) concentration and Cu recovery were not ideal with residual amount of 21.97 g/L Cu(II) entering the EW and almost 11% of Cu unreacted in WPCBs leaving for next Au recovery. To optimize the circuit performance and resolve the above problems, the flowsheet was modified with CSTR and CCL concept.

A distinguish assumption in CSTR is that the concentration in each individual leaching tank was held constant as reactions going on. In CCL circuit, consisting of 4 CSTR leaching tanks, the concentration existing each tank was different, thus varying the performance of Cu leaching in the upcoming leaching tank. In other words, the predicted models, assuming a constant concentration mechanism, differed from tank to tank with a different starting C₀. The differed starting C₀ by tanks therefore resulted in a differed rate constant to the kinetic model.

In short, to take the application of developed model to the next level of scaleup in a continuous stirring tank reactor (CSTR) counter-current leaching (CCL) circuit, the following approximations need to be met:

1) The concentration in the circuit was constant, due to the constantly stirring and ideal mass transfer in tanks.
2) To adopt the model (with assumption of changing concentration) to constant concentration CCL circuit, D (diffusivity) of reactant under a given leaching condition needs to be solved and transferable to the constant concentration model.
3) As the concentration of reactant is constant, i.e. sufficient regeneration of reactant, the depletion of reactant is minimized inside the reactors and the leaching rate can thus be optimized in a CSTR CCL circuit.

Considering Zhuravlev’s changing concentration model, we have:

\[ \left( (1 - \alpha)^{-\frac{1}{3}} - 1 \right)^2 = \frac{2DV_mC_0}{r_0^2} t = k_z' t \]

As for constant concentration, C₀ is held constant in the expression of rate constant k. But to transfer the constant concentration on the occasion of CCL circuit where the Cu
concentration coming out of each stage of leaching tank was changed according to the reacted fraction $\alpha$ in the tank. The physical definition of reaction expression $k$ in the CCL circuit is depicted as:

$$k_{rxn} = \frac{1 - \alpha_{out}}{1 - \alpha_{in}}$$

Since the concentration $C_0$ in each leaching stage is varied due to the variation of reacted fraction $\alpha$ in each tank, the rate constant becomes:

$$k_x' = \frac{2DV_mC_0}{r_0^2} = b \times C_0$$

where $b$ is the model-conversion constant written as $b = \frac{2DV_m}{r_0^2}$; $C_0$ is the initial Cu concentration coming in the reaction tank, in g/L.

Referring back to the fitting of Zhuravlev’s model using batch experimental data under various Cu(II) concentrations, as presented in Figure 5.5. The model-conversion constant b in linear relationship of rate constant k (as indicated by the slopes in Figure 5.5) across four different concentrations (10, 20, 30, 40 g/L) can be obtained. As shown in Table 5.5, by minimizing the sum of error between fitted k values and predicted k values applying Excel Solver, solved value for constant $b$ is 0.002882.

![Figure 5.5. Plot of Zhuravlev’s linear expression $((1 - \alpha)^{\frac{1}{2}} - 1)^2$ vs time under various initial Cu(II) concentration (g/L), data corresponding to Figure 4.8.](image-url)
Table 5.5. Sum of error minimization between model-fitted $k$ values and calculated $k$ values.

<table>
<thead>
<tr>
<th>Cu(II) conc. (g/L)</th>
<th>$k$ (experimental)</th>
<th>$k$ (calculated)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.1153</td>
<td>0.1153</td>
<td>0.0000</td>
</tr>
<tr>
<td>30</td>
<td>0.0907</td>
<td>0.0865</td>
<td>0.0042</td>
</tr>
<tr>
<td>20</td>
<td>0.0298</td>
<td>0.0576</td>
<td>0.0278</td>
</tr>
<tr>
<td>10</td>
<td>0.0095</td>
<td>0.0288</td>
<td>0.0193</td>
</tr>
<tr>
<td>Constant $b$</td>
<td>0.002882</td>
<td>Sum of Error</td>
<td>0.0514</td>
</tr>
</tbody>
</table>

Correspondingly, a justified model for leaching under constant concentration, was developed by adopting the interchangeable $k$ value from Zhuravlev’s changing-concentration model into Jander’s constant-concentration model (Jander, 1927):

$$\left(1 - (1 - \alpha)^{\frac{1}{3}}\right)^2 = \frac{2DmC_0}{r_0^2}t = k_j't$$

By substituting the solved value for $b$ as 0.002882, the justified model is expressed as:

$$t = \left(\frac{1 - (1 - \alpha)^{\frac{1}{3}}}{0.002882C_0}\right)^2$$

The form for reacted fraction $\alpha$ can be solved mathematically:

$$\alpha = ((k_j't)^3 + 6(k_j't)^2 + 9k_j't)^{\frac{1}{3}} - 3k_j't$$

where $k_j' = 0.002882 \times C_0$.

To further demonstrate the concept of CCL in CSTR reactors, experimental data was adopted and plotted into the justified model. The resulted Cu concentration (g/L) after each stage of leaching estimated by the justified model is shown in Figure 5.6. As shown, when started with approximately 35 g/L Cu(II) and 5 g/L Cu(I) from the EW return, the stabilized final Cu(II) concentration when reaching steady-state in the CSTR was about 32 g/L. Likewise, after each stage of leaching, the final concentration of Cu(II) gradually decreased, eventually to about 4 g/L when leaving the leaching circuit for EW. Indicated by this trend, there should be a change on the rate constant $k$, corresponding to the change
of Cu(II) concentration. In other words, the predicted model is changed from a higher concentration to a lower concentration one when transferring from tank to tank.

Figure 5.6. Out-of-tank Cu(II) concentration (g/L) estimated by the justified model.

In the CCL circuit, starting from Tank 1, the solid is the most intact and the lixiviant is the most depleted in the oxidizer, and vice versa. In this case, the predicted value for reacted fraction α in Tank 1 undergoes the constant concentration model where the initial reactant concentration is 4 g/L, as shown in Figure 5.7 (blue curve). Note that the retention time in Tank 1 is 1.6 hours as sufficient to achieve the same recovery as in the next leaching tank. Subsequently, in Tank 2, the started concentration felt in the orange curve, under an in-tank concentration of 16 g/L. Similarly, in Tank 4, which is the beginner tank with highest concentration of Cu(II) and the last tank with most diluted Cu(0) in solid, the predicted model therefore fits in the later retention time of yellow curve. In fact, the operation manner in CCL circuit resulted in a “zig-zag” shape of leaching curve, where the α corresponds to two different times when the solid changes tanks which have two different concentrations, as shown in Figure 5.8.
Figure 5.7. Predicted reaction fraction (a) in each leaching stage under various initial Cu(II) concentrations by the justified model.

Figure 5.8. The accumulated reacted fraction (a) in the CCL circuit, predicted by the justified model.

Applying the following input parameters (as listed in Table 5.6) for a CCL circuit using CSTR, accumulative reacted fraction α was obtained and listed in Table 5.7. Note that a significant change in the inputs is the rate coefficient, now held as a variable differed by concentrations from tank to tank. The radius of fee particles is 1 mm (top size of 2 mm), and the reaction takes place under ambient temperature. The starting lixiviant, composing 35 g/L Cu(II) and 5 g/L Cu(I), enters the CCL circuit at Tank 4, at a flow rate of 500 L/min. The pulp density is 10%. The solid phase, containing 30%wt. of Cu(0), flows through the circuit from Tank 1 at a mass flowrate of 3.33 t/h for total solid, and 1 t/h for Cu(0),
respectively. The estimated reaction fraction \( \alpha \) listed in Table 5.7, showed a depleting trending for Cu(II) from Tank 4 (most concentrated) to Tank 1 (most depleted). The cumulative \( \alpha \) at the end of leaching was 0.97 (97% Cu recovery).

Table 5.6. Input parameters for process simulation using the justified model.

<table>
<thead>
<tr>
<th>Input</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate coefficient (variable)</td>
<td>( k' )</td>
<td>0.002882×( C_0 )</td>
<td>Unitless</td>
</tr>
<tr>
<td>Feed particle size</td>
<td>( R )</td>
<td>1</td>
<td>mm</td>
</tr>
<tr>
<td>Leaching temperature</td>
<td>( T )</td>
<td>20</td>
<td>°C</td>
</tr>
<tr>
<td>Initial Cu(II) concentration in solution</td>
<td>( \text{Cu(II)} )</td>
<td>35</td>
<td>g/L</td>
</tr>
<tr>
<td>Initial Cu(I) concentration in solution</td>
<td>( \text{Cu(I)} )</td>
<td>5</td>
<td>g/L</td>
</tr>
<tr>
<td>Initial Cu(0) concentration in feed</td>
<td>( \text{Cu(0)} )</td>
<td>30</td>
<td>%wt.</td>
</tr>
<tr>
<td>Lixiviant flow rate</td>
<td>( Q_{\text{lix}} )</td>
<td>500</td>
<td>L/min</td>
</tr>
<tr>
<td>Mass flow of feed</td>
<td>( Q_{\text{feed}} )</td>
<td>3.33</td>
<td>t/h</td>
</tr>
<tr>
<td>Mass flow of Cu(0)</td>
<td>( Q_{\text{Cu(0)}} )</td>
<td>1</td>
<td>t/h</td>
</tr>
</tbody>
</table>

Table 5.7. Calculated \( \alpha \) in each leaching tank by the justified model.

<table>
<thead>
<tr>
<th>Tank #</th>
<th>Time (hr)</th>
<th>([\text{Cu}^{2+}]_{\text{out}}) (g/L)</th>
<th>Cumulative ( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tank 1</td>
<td>1.6</td>
<td>3.88</td>
<td>0.35</td>
</tr>
<tr>
<td>Tank 2</td>
<td>3.2</td>
<td>15.53</td>
<td>0.66</td>
</tr>
<tr>
<td>Tank 3</td>
<td>4.8</td>
<td>25.73</td>
<td>0.84</td>
</tr>
<tr>
<td>Tank 4</td>
<td>6.4</td>
<td>31.84</td>
<td>0.93</td>
</tr>
</tbody>
</table>

The estimated \( \alpha \) were then programmed in a mass-balanced flowsheet drawn in Excel, as shown in Figure 5.9. As presented, the fresh lixiviant composing about 40 g/L Cu(II) and 5 g/L Cu(I) enters the leaching circuit from Tank 4. The waste PCBs, containing
30% wt. of Cu(0), is fed into the circuit from Tank 1, with 0 fraction reacted. The reacted solids in Tank 1 are then transferred to Tank 2, where the Cu(II) concentration is higher. By the time the materials reached Tank 4, the remaining Cu(0) is already very low. As it hits the highest Cu(II) concentration of 32 g/L, the residual Cu(0) is readily extracted in such concentrated solution, improving the total recovery from 89% in batch leaching circuit to 93% in CCL circuit. At the end, the PLS. consisting of 4 g/L of Cu(II) and 36 g/L of Cu(I), enters the EW, where the current efficiency is benefited from the Cu(II)-depleted and Cu(I)-enriched solution.

In summary, by comparing between the leaching performances illustrated in Example 1 (batch leaching) and Example 2 (counter-current leaching), it can be concluded that the CCL circuit design allows the optimization of the process operation by 1) maximizing the leaching recovery; 2) efficiently consuming the oxidizer to promote EW current efficiency; and 3) greatly shortening the residence time. The optimization of this circuit is beyond the scope of this work.
Figure 5.9. Flowchart of kinetic modeling and simulation of CCL leaching circuit in ammoniacal system.
CHAPTER 6. DISSOLUTION BEHAVIOR OF AU FROM WASTE RAM CHIPS USING OXIDATIVE AMMONIACAL THIOSULFATE LEACHING

Abstract:

Thiosulfate is a promising method as an alternative to cyanidation for Au leaching, as cyanide is considered a toxic and dangerous substance. This study seeks to understand the recovery of Au from waste RAM chips using a Cu(II)-NH$_3$-S$_2$O$_3$ solution, by varying the affecting parameters. The investigated parameters include the Cu(II) concentration and the regeneration of Cu(II) by various aeration rates, the thiosulfate to ammonia concentration ratios, particle sizes, and temperatures. The characterization of waste chips by SEM-EDS showed the existence of Au-Ni-Cu interlayers. The association of Au with Ni and Cu resulted in the reduction of Au during the leaching process by cementation reaction. It was found that the pre-removal of existing Cu prior to Au thiosulfate leaching was important. In addition, the recovery of Ni was found to be reversible to the Au recovery. The further SEM results on the leaching residues identified the passivation layer by elemental sulfur and metal sulfides formed during leaching, as the main cause of decreased Au recovery. Most interestingly, this study reveals the observations on the leaching recoveries of Au and Ni, and the cementation of Au on Cu simultaneously.

Keywords: waste chips, thiosulfate leaching, Au recovery, Ni recovery, decopperization, passivation, copper sulfides
6.1 Introduction

Rapid growth in technological innovation has resulted in large amounts of waste printed circuit boards (WPCBs) (Lu & Xu, 2016). The significant content of Au in WPCBs, has made it a valuable waste stream (Behnamfard et al., 2013). Therefore, WPCBs has become a promising candidate as a secondary resource for the recovery of Au (Syed, 2012).

For decades, cyanidation has been used to recover Au from primary ores and secondary resources (O. Sitando et al., 2018). However, due to the increasingly restrictive environmental regulations, and the detrimental impact caused by cyanidation contamination, extensive studies have been performed to investigate other reagents, such as thiourea, thiosulfate, thiocyanate, and glycine, as potential alternatives to cyanide (Barbosa-Filho & Monhemius, 1994; Eksteen & Oraby, 2015; Sethurajan et al., 2019; Xu et al., 2017). In comparison to acids, thiosulfate has been proven to be an efficient, economic, and greener method to recover Au amongst the above-mentioned alternatives (Camelino et al., 2015; Ficeriová et al., 2011; Oh et al., 2003; Petter et al., 2014). More specifically, thiosulfate was chosen for the leaching of Au from WEEE due to the benefit of its high selectivity towards Au, while eliminating the co-extraction of other contaminants (such as Fe and Al). Thiosulfate leaching is commonly applied in alkaline conditions, using NH₄OH as a pH conditioner and Cu²⁺ as an oxidant to enhance the Au recovery. In addition, it was reported that Cu can be leached in ammoniacal solution (Koyama, Tanaka, & Lee, 2006). As such, a potential pretreatment of Cu removal could be achieved prior to Au thiosulfate leaching under similar alkaline conditions with synergistic effect between these two lixiviants. To improve the efficiency of Au leaching in thiosulfate system, Cu(II) is employed as an essential catalyst, and ammonia is required to stabilize the ionic species in the thiosulfate solution. Cu(II)-catalyzed ammoniacal thiosulfate leaching has been used in recovering Au WPCB materials over the last 10 years (Camelino et al., 2015; Ficeriová et al., 2011; Ha et al., 2014; Kasper & Veit, 2018; Murali et al., 2022; Tripathi et al., 2012). It is worth mentioning that, although similar lixiviants, mainly consisting of thiosulfate, ammonia, and cupric ions, were used for Au leaching, the recovery of Au reported in the literature varied significantly. The main difference contributing to the higher Au recoveries is the adoption of chemical pretreatment prior to Au leaching. According to the results presented by Oh et al., the materials were
preliminarily beneficiated by physical processing, which removed 73% of the plastics (Oh et al., 2003). The enriched metallic fraction was then treated in 2M H₂SO₄ solution with assistance with 0.2M H₂O₂, where other base metals, such as Cu, Ni, Zn, Fe and Al, was further removed (Oh et al., 2003). The subsequent thiosulfate leaching yielded a 95% Au recovery (Oh et al., 2003). Without a chemical pretreatment, Tripathi et al. reported a Au extraction of 78.8% from complete WPCBs, and an Au extraction of 56.7% from granule WPCBs, using lixiviant containing (NH₄)₂S₂O₃, CuSO₄, and NH₄OH, at pH of 10-10.5 (Tripathi et al., 2012). It can be seen that the recovery of Au from WPCBs can be less effective without any chemical pre-treatment, due to the complexity of feed materials and the interference from the co-existing metals (Jeon et al., 2018).

The chemistry of Au extraction in the Cu(II)-NH₃-S₂O₃ system has been studied, but consensus about the exact mechanism remains unsettled (Senanayake, 2004, 2005a, 2005b; Xu et al., 2017). A proposed mechanism of Au thiosulfate leaching in Cu(II)-NH₃-S₂O₃ system is shown in Figure 6.1 (Nie et al., 2019). The reactions involved in Au dissolution in Cu ammoniacal thiosulfate system are described in Eqs. (6.1)-(6.5).

Aerobic Oxidation of Au: As depicted in Figure 6.1, Au thiosulfate leaching is an electrochemical reaction, catalyzed by the Cu-amine complexes in thiosulfate system. In the anodic reaction, Au dissolution occurs as Au⁰ is oxidized to Au⁺ by Cu(II) and complexes with NH₃ to form stable Au-amine compound (Eqs. (6.1) and (6.2)). In the presence of S₂O₃²⁻, leached Au further complexes with S₂O₃²⁻ due to the higher affinity between Au⁺ and S₂O₃²⁻ (Eq. (6.3)). In the cathodic reaction, Cu(II)-amine complex (Cu(S₂O₃)₃⁵⁻) is reduced to Cu(I) and forms Cu(I)-thiosulfate compound (Cu(S₂O₃)₃⁵⁻) (Eq. (6.4)). The overall reaction of Au leaching in Cu(II)-NH₃-S₂O₃ system can be expressed as Eq. (6.5).

In the thiosulfate leaching system, oxygen is involved in the cathodic reaction, to oxidize Cu(I) (Cu(S₂O₃)₃⁵⁻) back to Cu(II) (Cu(NH₃)₄²⁺), as shown in Eq. (6.6). In this case, Cu(NH₃)₄²⁺ is regenerated in the presence of oxygen, and continually acts as the oxidizer to leach Au. With the Cu(NH₃)₄²⁺ regeneration, only a minimum amount of Cu(NH₃)₄²⁺ is consumed, thus Cu(NH₃)₄²⁺ is regarded as the catalyst (Feng & van Deventer, 2007). However, with the assistance of O₂ and a high level of Cu(NH₃)₄²⁺ in the solution, the
decomposition of thiosulfate was enhanced and tetrathionate was formed, as indicated by Eq. (6.7).

Anerobic Oxidation of Au: In the absence of oxygen, Cu(NH$_3$)$_4^{2+}$ mainly acts as the oxidizer to extract Au, being constantly consumed without further regeneration. In an oxygen-excluded system, the decomposition of thiosulfate is low and the limitation of Cu(NH$_3$)$_4^{2+}$-S$_2$O$_3^{2-}$ reaction (Eq. (6.7)) contributed to improved leaching kinetics of Au (Breuer & Jeffrey, 2002). A critical condition of oxygen-eliminated system is that the mix potential of solution needs to be maintained at a high level above 0.19 V, which is still governed by the equilibrium potential of Cu$^{2+}$/Cu$^+$ couple (Feng & van Deventer, 2007). Therefore, to efficiently leach Au with Cu(II) as the oxidizer under an oxygen-eliminated condition, the remaining concentration of Cu(II) needs to be maintained at a certain level to control the solution potential (Feng & van Deventer, 2007). However, an excessive concentration of Cu(II) could also lead to the decomposition of thiosulfate (Breuer & Jeffrey, 2002, 2003). As such, controlled aeration may be needed to partially regenerate the Cu(II) and to maintain the solution Eh at a suitable level.
Figure 6.1. Schematical extrapolation of Au leaching mechanism in Cu(II)-NH$_3$ catalyzed thiosulfate system. Adapted from (Xu et al., 2017).

Anodic reaction:

$$Au \rightarrow Au^+ + e^-$$ \hspace{1cm} (6.1)

$$Au^+ + 2NH_3 \rightarrow Au(NH_3)_2^+$$ \hspace{1cm} (6.2)

$$Au(NH_3)_2^+ + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + 2NH_3$$ \hspace{1cm} (6.3)

Cathodic reaction:

$$Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e^- \rightarrow Cu(S_2O_3)_3^{5-} + 4NH_3$$ \hspace{1cm} (6.4)

Overall reaction:

$$Au + 5S_2O_3^{2-} + Cu(NH_3)_4^{2+}$$ \hspace{1cm} (6.5)

$$\rightarrow Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 4NH_3$$
Cu(II) regeneration (aerobic leaching):

\[
Cu(S_2O_3)_3^{5-} + 4NH_3 + \frac{1}{4}O_2 + \frac{1}{2}H_2O
\rightarrow Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + OH^-
\] (6.6)

Cu(II) promoting decomposition:

\[
2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \rightarrow 2Cu(S_2O_3)_3^{5-} + 8NH_3 + S_4O_6^{2-}
\] (6.7)

Although Au\(^{+}\) can be leached and stabilized in thiosulfate solution as Au(S\(_2\)O\(_3\))\(_2\)^{3-}, the thiosulfate ligand has low stability under typical leaching conditions and tends to decompose with time (Xu et al., 2017). Xu et al. performed a profound review on the degradation of thiosulfate compounds. They proposed a simplified degradation route of thiosulfate compounds shown in Figure 6.2 (adapted from (Xu et al., 2017)). The reactions involved in thiosulfate decomposition were given in Eqs. (6.8) to (6.11) (Xu et al., 2017). As thiosulfate reacts with O\(_2\) and OH\(^-\) in the leaching solution, it further decomposes into polythionates/polysulfide compounds, such as S\(_4\)O\(_6\)^{2-}, S\(_3\)O\(_6\)^{2-}, SO\(_3\)^{2-} and SO\(_4\)^{2-}. Moreover, thiosulfate self-decomposes into S\(^0\) and S\(^2\^-\) (as expressed by Eqs. (6.12) and (6.13)). The self-decomposition of thiosulfate eventually forms elemental sulfur and Cu sulfide, which then deposit on the surface of Au. This phenomenon prohibits the further access of lixiviant to Au. Meanwhile, the generated sulfide during thiosulfate self-decomposition recaptures the leached Au-thiosulfate complex and causes the re-precipitation of Au sulfide. This phenomenon not only hinders the gold recovery, but also leads to the loss of leached Au in the solution.

The formation of elemental sulfur and metal sulfides on the surface of Au is referred to as the passivation reaction which inhibits further Au dissolution in thiosulfate leaching. Using surface-enhanced Raman scattering spectroscopy (SERS), Jeffrey et al. was able to confirm the formation of polymetric sulfur and Au\(_2\)S in Cu(II)-NH\(_3\)-S\(_2\)O\(_3\) solution (Jeffrey et al., 2008). However, there was little literature discussing the mechanism of this passivation phenomenon and the solutions to this problem remained unsolved.
Figure 6.2. Simplified route of thiosulfate degradation (left route: reductive degradation; right route: oxidative degradation; greyer color: more reductive product; bluer color: more oxidative product). Adapted from (Xu et al., 2017).

\[
4S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 2S_4O_6^{2-} + 4OH^- \quad (6.8)
\]

\[
4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \quad (6.9)
\]

\[
2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \quad (6.10)
\]

\[
2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \quad (6.11)
\]

\[
S_2O_3^{2-} \rightarrow SO_3^{2-} + S \quad (6.12)
\]

\[
S_2O_3^{2-} + 2e \rightarrow SO_3^{2-} + S^{2-} \quad (6.13)
\]

So far, the industrial application of Au thiosulfate leaching from e-waste has not been widespread due to residual problems. The first difficulty is the complex chemistry of Cu(II) ammoniacal thiosulfate solution and the interactions between involved species in the solution (Jeffrey et al., 2003; Senanayake, 2005a). To sustain the gold leaching in solution and to stabilize the reacted species to a greater extent, few key parameters must be controlled. Many researchers studied the role of oxygen and Cu(II) as the oxidizer in Au thiosulfate leaching (Breuer & Jeffrey, 2003; Feng & van Deventer, 2007; Jeffrey et al., 2003). As such, the oxidation mechanism is critical to maintain the stability of Cu, Au, and sulfur spices in the system. Meanwhile, balancing the amount of Cu(II) in solution is also critical as the excessive Cu(II) react with thiosulfate, which further leads to the thiosulfate decomposition and Cu sulfide formation (Breuer & Jeffrey, 2002, 2003).

The second barrier to Au thiosulfate leaching is the thiosulfate decomposition. Wan reported that the addition of sulfite ions (SO_3^{2-}) helps to prevent thiosulfate decomposition,
as it self-reacted and generated thiosulfate ions (Wan & LeVier, 2003). However, Breuer discussed that, from an electrochemistry point of view, any addition of sulfite ions will result in the significant reduction of Cu(II) thus inhibiting the Au dissolution rate (Breuer & Jeffrey, 2003). On the other hand, the metastability of thiosulfate can also self-decompose to form elemental sulfur and sulfide ions (Eq. (6.12) and (6.13)). The latter then complexes with Cu to form Cu sulfide precipitates on the surface of Au. This phenomenon is referred to as the passivation on the surface of Au. Some additives, including ammonia, thiourea, EDTA, and EN, were found to be helpful to promote Au dissolution while thiosulfate decomposes during a prolonged leaching time (Nie et al., 2019). Nie et al. studied the role of Cu on Au passivation and identified Cu as the main component of the passivation layer, using combined electrochemical and spectroscopic techniques (Nie et al., 2019). As Cu(II) in the solution is stabilized by the additives, the degree of thiosulfate decomposition and Au passivation was greatly reduced. However, the passivation issue cannot be solved completely as the thiosulfate decomposition is always accompanied by Au dissolution.

The third barrier is the thiosulfate consumption during leaching. In a complex material like PCBs, Au is often associated with other metals such as Cu and Ni. Due to the similarity in their chemical properties, and the affinity to complex with thiosulfate ions, Cu and Ni can also be leached by a thiosulfate solution and consume free thiosulfate ions during leaching. As these metals were leached under the alkaline leaching condition, they take over the available thiosulfate ions and form metal-thiosulfate complexes. When this happens, thiosulfate ions in the solution become less available to Au, thus largely decreasing the stability of Au ions in solution. A such, the stabilization and further extraction of Au was prohibited.

Furthermore, in a heterogeneous matrix such as waste circuit boards, where Au is tightly associated with other metals that may affect the solution chemistry in Au an ammoniacal thiosulfate system. The interference of coexisting Cu and Ni on Au cementation, was studied by Jeon et al., using a PCB type of material (Jeon et al., 2018). It was found that dissolved Au thiosulfate complex preferentially adsorbed and cemented on the surface of Cu. Particularly, when Al is coexisted with Cu, the rate of Au cementation was significantly enhanced.
In summary, the major considerations related to Au thiosulfate leaching using Cu(II)-amine compound as the oxidizer/catalyst are:

1) A suitable amount of Cu(II)-NH$_3$ above the stoichiometric requirement is needed; however, an excessive amount will lead to the thiosulfate decomposition;

2) Aeration, to some degree, regenerates Cu(II)-amine catalyst but has a further impact on the degradation of thiosulfate;

3) In heterogeneous materials such as WPCBs, coextraction of other existing metals can significantly increase the thiosulfate consumption.

Based upon the aforementioned literature, the present study seeks to determine the effects of various parameters on end-of-life RAM chips. Specifically, this study provides understanding the interaction between Au and other dissolvable metals (particularly Ni) in thiosulfate leaching after a copper leaching pretreatment. The Au dissolution time versus recovery were studied by varying decopperization, aeration, initial Cu(II) concentrations, ammonium thiosulfate and ammonium hydroxide concentrations, particle sizes, and temperatures. Additionally, SEM-EDS characterization was performed on pre and post leached materials to better understand the effects of leaching and to assist in explaining the results.

6.2 Materials and Methods

6.2.1 Materials and pretreatment

The feed materials used in this study was waste RAM chips, obtained from the Recycling Services at the University of Kentucky. The edge of RAM chips containing high Au content was stamp-sheared from the RAM chips, as referred to Au-fingers (AF). The main chemical compositions in original Au-fingers (AF) were shown in Table 6.1.

Preliminary size reduction of cut Au-fingers was achieved by a knife mill (Retch SM 300), to a top size of 3.4 mm. Further size reduction to -2 and -1.2 mm was carried out using a laboratory analytical mill (Cole-Parmer Analytical Mill 4301-00). The shredded Au-fingers were then leached in Cu-ammoniacal solution as a pre-step to remove existing
Cu in the RAM chips, prior to Au thiosulfate leaching. The Cu-ammoniacal solution was made from 1M (NH₃)₂SO₄, 4M NH₄OH and 40 g/L Cu²⁺. The lixiviant was chosen based on the previous results on Cu leaching. The residues after Cu pre-leach were then rinsed and dried in a drying oven at 70°C overnight. The decopperized Au fingers were fed to the subsequent Au thiosulfate leaching. The flowchart of feed preparation and leaching experiments was depicted in Figure 6.3.

![Flowchart](image)

Figure 6.3. Flowchart of feed preparation, leaching process, and sample characterization in this study.

<table>
<thead>
<tr>
<th>Feed Materials</th>
<th>Ag (ppm)</th>
<th>Al (ppm)</th>
<th>Au (ppm)</th>
<th>Co (ppm)</th>
<th>Cu (ppm)</th>
<th>Fe (ppm)</th>
<th>Mg (ppm)</th>
<th>Ni (ppm)</th>
<th>Zn (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original AF</td>
<td>93</td>
<td>26,331</td>
<td>6,434</td>
<td>37</td>
<td>290,447</td>
<td>366</td>
<td>930</td>
<td>18,092</td>
<td>66</td>
</tr>
<tr>
<td>Decopperized AF</td>
<td>91</td>
<td>30,197</td>
<td>7,713</td>
<td>41</td>
<td>28,984</td>
<td>697</td>
<td>926</td>
<td>19,163</td>
<td>66</td>
</tr>
</tbody>
</table>

Table 6.1. Elemental assay of original Au-fingers (AF) as stamped and decopperized Au-fingers (AF) after Cu pre-leach.
6.2.2 Leaching experiment

Au thiosulfate leaching tests were carried out using 10 g/L pulp density at constant stirring speed for 4 hours. 10 g/L pulp density was chosen to produce approximately 100 ppm Au solution, if assuming 100% recovery. Leaching tests were ran under alkaline conditions, which equated to about pH 9.6. During leaching, Eh, pH and temperature were monitored by a multi-functional pH/ORP/ATC probe (Mettler-Toledo InPro 3100i). Leachate samples were taken at 0, 15, 30, 60, 120 and 240 min.

In Au thiosulfate leaching, the effects of decopperization, aeration, initial Cu(II) concentrations, ammonium thiosulfate and ammonium hydroxide concentrations, particle sizes, and temperatures were studied and summarized in Table 6.2. The lixiviant consisted of ammonium thiosulfate ((NH₄)₂S₂O₃), ammonium hydroxide (NH₄OH), and additional cupric sulfate pentahydrates (CuSO₄·5H₂O) as the catalyst. Based on the feed assay, 0.25 - 0.75 M of (NH₄)₂S₂O₃, 0.5 - 1.0 M of NH₄OH, and 25 - 75 mM of initial Cu(II) were chosen, to provide excessive reactants and catalyst in the solution.

During leaching tests, continuous aeration was provided by air sparging (21% O₂ and 78% N₂) at controlled rates (0, 60, 120 L/min). In 0 mL/min aeration tests, argon gas was purged into the reactor to expel the existing oxygen in the system. Particle sizes were varied from 3.4-, 2.0-, to 1.2-mm. Temperatures were elevated from 25, 35, 45 to 55°C. All chemicals used in this study were reagent grade. De-ionized water was used in chemical makeup, sample preparation, and all the leaching experiments.

Table 6.2. Leaching parameters in Au-Cu(II)-NH₃ thiosulfate system.

<table>
<thead>
<tr>
<th>Pulp Density</th>
<th>Particle Size</th>
<th>c[Cu²⁺]</th>
<th>c[S₂O₃²⁻]</th>
<th>c[NH₃]</th>
<th>Temperature</th>
<th>Aeration (21%O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/L</td>
<td>mm</td>
<td>mM</td>
<td>M</td>
<td>M</td>
<td>°C</td>
<td>mL/min</td>
</tr>
<tr>
<td>10</td>
<td>3.4, 25</td>
<td>0.25</td>
<td>0.50</td>
<td></td>
<td>25, 35</td>
<td>0 (Ar),</td>
</tr>
<tr>
<td></td>
<td>2.0, 50</td>
<td>0.50</td>
<td>0.75</td>
<td></td>
<td>45, 55</td>
<td>60,</td>
</tr>
<tr>
<td></td>
<td>1.2, 75</td>
<td>0.75</td>
<td>1.00</td>
<td></td>
<td></td>
<td>120</td>
</tr>
</tbody>
</table>
6.2.3 Analytical and characterization methods

6.2.3.1 Solid assay

To determine the concentration of metals contained in the solid phase, solid samples were assayed by an acid digestion method. Representative solid samples were pulverized by an analytical mill (Cole-Parmer Analytical Mill 4301-00) to -30 mesh (600 µm). The pulverized samples were then roasted in the furnace at 580 °C for 8 hours to remove the organic and volatile components. For reliable assaying, the sample should be completely dissolved into a liquid phase prior to ICP-OES elemental analysis. The roasted samples were homogenized by pestle and mortar.

After roasting and homogenizing, a representative 0.5 g of samples were taken for acid digestion. The weighed samples were placed in a 50 mL PFA (perfluoroalkoxy) digestion tube. Hydrofluoric acid (HF) and aqua regia (molar ratio of HCl:HNO₃ = 3:1) were used as the digesting reagents. Firstly, 20 mL of aqua regia and 20 mL of HF were added to dissolve metals and polymers. The digestion was conducted in a hot block at 145°F (63°C) for 5 hours until the liquid was evaporated completely. The final digested samples were further prepared for elemental analysis.

6.2.3.2 ICP-OES analysis

ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry), manufactured by Spectro Arcos, was used for elemental analysis. To eliminate the precipitation of sulfur species during sample preparation when transitioning from alkaline to acid matrix, the following sample preparation process was developed. Solution samples containing Au-thiosulfate complex were oxidized by adding concentrated H₂O₂ to allow fully oxidation of polythionate species to stable into SO₄²⁻ compounds. The oxidized samples were then acidified by adding aqua regia to stabilize Au⁺ with excessive complexing Cl⁻ ions. The prepared samples were further diluted in 5% HNO₃ matrix for ICP-OES analysis.

Due to the heterogeneity of waste RAM chips, solid samples, including feed and residues after each treatment step, were digested and used in the calculation of metal recovery. As expressed in Eq. (6.14), the metal recovery % is calculated by:
\[
Metal \ Recovery \ (\%) = \frac{[Me]_{solution} \times V_{solution}}{[Me]_{solution} \times V_{solution} + [Me]_{solid} \times m_{solid}} \quad (6.14)
\]

where \([Me]_{solution}\) is the metal concentration in liquid phase (mg/L); \(V_{solution}\) is the volume of liquid phase; \([Me]_{solid}\) is the metal concentration in solid phase (mg/kg); and \(m_{solid}\) is the mass of solid phase.

6.2.3.3 SEM-EDS characterization

Three samples were tested, the feed material to Au thiosulfate leaching, the residues after Au leaching with higher Au extraction, and the residues from Au leaching where suspected re-precipitation of Au/Cu sulfides occurred. The residue samples were selected from leaching tests to examine the change of Au/Ni/Cu/S species in the solid phase.

A Scanning Electron Microscope (SEM, Quanta 250, ThermoFisher Scientific formerly FEI, Hillsboro, OR, USA), equipped with Energy Dispersive X-ray Spectroscopy (EDS, X-Max detector, Oxford Instruments, Abingdon, UK) was used. The detector used on SEM was an Ever-hart-Thornley detector (ETD), with adjusted bias to optimize signal intensity while minimizing charging effects in the image. Multiple fields of view in each sample were scanned automatically at high magnification using incident electrons with 30 keV energy and appropriate beam currents to balance signal intensity and spectrum accuracy. An accelerating voltage of 30 kV (at a working distance of 10 mm on the SEM) was used to excite x-rays from all potentially present elements, and to maximize the amount of x-rays generated so as to accumulate lots of counts in each field-of-view. Automation of the acquisition over a large area, EDS spectra analysis and maps generation were achieved using Oxford Instruments’ AZtec 6.0 software with TruMap algorithm.

6.3 Results and Discussions

6.3.1 Effect of decopperization

Due to the large amount of Cu in the Au-fingers and its high solubility in thiosulfate solution, Cu would consume a significant amount of thiosulfate, thus prohibiting the Au dissolution (as described in (6.7)). Also, Cu is known as a cementing agent for Au-thiosulfate species, therefore the presence of Cu surfaces will result in a deposition of
leached Au-thiosulfate (Jeon et al., 2018). As such, the Cu in the shredded Au-fingers was reduced significantly prior to the Au thiosulfate leaching using a Cu-ammoniacal lixiviant containing 1M (NH$_3$)$_2$SO$_4$, 4M NH$_4$OH and 40 g/L Cu$^{2+}$, under air purging at 120 mL/min. Decopperization achieved a maximum of 90% Cu removal. The concentrations of remaining compositions in Au-fingers were listed in Table 6.1 and shown in Figure 6.4. Given a leaching time over 8 hours, with sufficient oxidizer supply, the maximum Cu removal achieved was 90%. It was suspected that the rest of Cu was masked by the Au layer and, thus unable to be extracted by ammoniacal solution.

![Figure 6.4](image)

**Figure 6.4.** Elemental concentration (mg/kg) in Au-fingers before and after decopperization.

The decopperized Au-fingers were used as feed materials in the following Au thiosulfate leaching tests. To examine the effect of decopperization as a feed preparation step, two Au leaching tests were carried out using original Au-fingers and decopperized Au-fingers as feed materials. The results were shown in Figure 6.5. It is clear to see that Au extraction % in thiosulfate solution was largely improved by decopperization. The optimum Au recovery achieved was 88.7%. Conversely, without the pre-removal of Cu, Au leaching was limited. Only 12.7% of Au was leached during 4-hours. Interestingly, the recovery of Ni showed an ongoing increasing trend, and reached 74.1% after 4 hours.

It was observed that, without decopperization, Ni was preferentially leached in the thiosulfate system as indicated by Figure 6.5. According to the metal nobility order of
Cu>Ni>Au, Au is the most noble among Cu and Ni. As such, the minimization of Au extraction was likely due to the lower complexing affinity towards thiosulfate ions. As Cu and Ni were extracted in the solution, the free thiosulfate ions were consumed by Cu and Ni complexation and became less available to Au. Therefore, further extraction of Au was prohibited when there were excessive amount of Cu and Ni existing in the solution and consuming accessible thiosulfate ions. Another possibility of low Au extraction using high Cu material is that the abundant surface area of solid Cu provided much higher opportunity for the leached Au to re-deposit on it. In this case, as soon as the Au was leached, it immediately deposited on any available Cu surface.

In our study, as Ni was extracted after Au, the Cu surface beneath Ni layer was exposed and became more available for Au precipitation. Under a typical leaching condition at pH from 9-10 and Eh from 0.15 - 0.20 V (vs SHE), Au ions preferentially deposits on the surface of Cu due to the cementation reaction. Furthermore, in a heterogeneous material like PCBs, the presence of Al tends to stimulate Au deposition on Cu (Jeon et al., 2018). This could explain the leaching trends of Ni and Au, where Au extraction was increased at the beginning, but dramatically dropped as soon as Ni was extracted. To prevent the negative impact of surface Cu on Au extraction in thiosulfate system, the decopperization was a critical pretreatment prior to Au leaching.
6.3.2 Ammoniacal thiosulfate leaching

6.3.2.1 Effect of Cu(II) concentration and aeration

Using the decopperized Au-fingers as feed, the effects of oxidizers, i.e. Cu(II) and O₂, were investigated by setting up a 3-by-3 design of experiments. Based on the stoichiometry of Au leaching reactions, the minimum amount of Cu(II) needed was 12.71 millimolar (12.71 mM) based on the feed assay. To provide sufficient Cu(II) as an oxidant while not overdosing and creating an extremely oxidative leaching condition, the initial Cu(II) concentrations were chosen as 25, 50, and 75 mM. To maintain the Cu(II) regeneration and catalyzation during leaching, the aeration rate was chosen as 0 (argon purging), 60, and 120 mL/min. The result of Cu(II) concentrations (25, 50, and 75mM) under 0 (Ar purging), 60, and 120 mL/min aeration, are shown in Figure 6.6 (Ar purging), Figure 6.7 (60 mL/min aeration), and Figure 6.8 (120 mL/min aeration), respectively.
Figure 6.6. Au and Ni extraction (%) using 25, 50, 75 mM Cu(II), under 0 mL/min aeration (Argon purging) (S/L ratio: 10 g/L; particle size: -2 mm; S\textsubscript{2}O\textsubscript{3}: 0.5M; NH\textsubscript{3}: 0.5M; Temp.: 25℃).

Figure 6.7. Au and Ni extraction (%) using 25, 50, 75 mM Cu(II), under 60 mL/min aeration (air purging) (S/L ratio: 10 g/L; particle size: -2 mm; S\textsubscript{2}O\textsubscript{3}: 0.5M; NH\textsubscript{3}: 0.5M; Temp.: 25℃).
Without the additional aeration, the initial input of Cu(II) was controlled as the dominant oxidant in leaching and the regeneration of Cu(I) to Cu(II) during leaching was prevented. The results showed low Au recoveries in all three tests. As discussed previously, an additional amount of 25mM Cu(II) was enough to leach all the Au in solids, stoichiometrically, even after accounting for other leachable metals such as Cu, Ni, and Co. Therefore, it is hypothesised that the lack of Cu(II) oxidizer was not a major cause of low Au recoveries.

As shown in Figure 6.6, Au recoveries increased at the beginning of leaching, and then decreased dramatically once Ni recoveries commenced. This phenomenon occurred in all three tests using different Cu(II) concentration with no aeration. However, as the initial Cu(II) concentration increased from 25 to 75 mM, the impact of Ni on the decrease of Au was delayed from 120 to 240 min of residence time.

As the aeration increased to 60 mL/min (Figure 6.7), leached Au-thiosulfate complex was successfully stabilized in solution for 4 hours using 50 and 75mM Cu(II) as initial oxidant. As indicated in Figure 6.7, 84.5% and 80.3% Au recoveries were achieved using 50 and 75mM Cu(II), respectively, while very little Ni was extracted. However, 25mM of
Cu(II) was not sufficient to maintain the leached Au under 60 mL/min aeration. Similar to the previous result achieved at Cu(II) 25 mM and 60 mL/min aeration, Au recovery reached its optimum in the first hour but then dropped down to 14.8% once Ni was leached in solution. The final Ni extraction reached 87.6% after 4 hours.

The results of Au and Ni extractions using 120 mL/min of aeration were shown in Figure 6.8. The observed leaching trends, and the interaction of Au and Ni extraction, were similar to that using 60 mL/min aeration. Au recovery % was slightly improved to 88.7% and stabilized during 4-hour leaching test, using 50 mM Cu(II) and 120 mL/min aeration.

From the above observations, it appears that Ni extraction was either coincident to or caused by the decrease in Au recovery with the reasons behind this phenomenon remaining unclear. In considering the mechanism of decreasing Au recovery shown in Figure 6.6 to Figure 6.8, it appears that either cementation or precipitation may have occurred to remove Au from leachate solution. It is hypothesized that this may occur in a number of ways. First, the thiosulfate consumption resulting from the extraction of Ni. As Ni was extracted, it competed with Au for the complexation with the thiosulfate ions, thereby causing the leached Au⁺ to loose its complexation with thiosulfate. However, as calculated, the thiosulfate concentration was sufficient even if all the Ni and Au was extracted in solution. It is less likely that the enriched Ni concentration would result in the full depletion of thiosulfate ions during Au leaching.

The second possibility is the cementation of leached Au on the newly exposed Cu surface. In the case of cementation, it has been observed that the Au occurred as a Au-Ni-Cu laminate on the chips. As Ni was leached, a Cu layer was exposed, which led to the cementation of Au on Cu. Although over 90% of Cu in waste chips was removed by decopperization pretreatment, the extraction of Ni exposed residual Cu surfaces. As a result, the leached Au-thiosulfate ions was deposited on the newly exposed Cu surface, via a cementation reaction. This hypothesis was further investigated in the characterization section by examining pre- and post-leaching chips. Nevertheless, the only definitive observation is that Au recovery decreased as Ni extraction increased. This phenomenon was shown specifically in the result showing 100% Au recovery which then dropped to 0% when using 25mM Cu(II) without aeration (black curve in Figure 6.6).
6.3.2.2 Effect of ammonium thiosulfate to ammonium hydroxide concentrations (AT/AH ratio)

Two sets of experiments were carried out to study the effect of the thiosulfate to ammonia ratio (AT/AH ratio). In the first set, NH₃ concentrations varied from 0.5, 0.75, and 1.0M, while the S₂O₃ concentration was held constant at 0.5M this corresponded to AT/AH of 1, 0.67, and 0.5. The results of varying NH₃ concentrations are shown in Figure 6.9. In the second experimental set, S₂O₃ concentrations varied from 0.25, 0.5, and 0.75 M, whilst NH₃ concentration was kept at 0.5M. The AT/AH ratio in the second set corresponded to 0.5, 1, and 1.5. The results of varying the S₂O₃ concentrations are shown in Figure 6.10.

![Figure 6.9](image)

Figure 6.9. Au and Ni extraction (%) using AT/AH ratio of 0.5/0.5, 0.5/0.75, 0.5/1.0 (with fixed thiosulfate concentration of 0.5 M) (S/L ratio: 10 g/L; particle size: -2 mm; Cu(II) 50mM; aeration: 120 mL/min; Temp.: 25℃).
As indicated in Figure 6.9, increasing the NH$_3$ concentration resulted in an increase in the rate of initial Au recovery. At lower NH$_3$ concentrations of 0.5 and 0.75M, Au leaching continued through the duration of experiment whereas higher NH$_3$ concentration of 1.0M (AT/AH ratio of 0.5M/1.0M) resulted in a slight decrease in Au recovery at 180 min, which occurred concurring with an increase in Ni extraction. Nevertheless, under higher NH$_3$ concentration, the detrimental impact of Ni co-extraction on Au recovery was not as significant as previous disclosed (Figure 6.6 to Figure 6.8). It has been discussed in the literature that it is important to maintain the NH$_3$ level in thiosulfate solution for the following reasons: 1) providing sufficient NH$_3$ complexing ligand to stabilize Cu(NH$_3$)$_4^{2+}$ as oxidizer and the intermediate Au(NH$_3$)$_2^+$ specie (Breuer & Jeffrey, 2002); 2) conditioning the solution pH to maintain the Au-thiosulfate species at a stability region (Aylmore & Muir, 2001); 3) preventing the formation of sulfurs and sulfides on the surface of Au, and preventing the Au deposition on Cu by dissolving the exposed Cu surface (Senanayake, 2005a). Accordingly, as the excessively available NH$_3$ being preferentially adsorbed on the surface of Cu, the deposition of Au on Cu was prevented.
In Figure 6.10, when the AT/AH ratio increased to 1.5 (AT/AH of 0.75M/0.5M), it appears the leaching of Ni was possible, which led to the corresponding decrease in Au concentration. It was suspected that, as Au and Ni was leached, the Cu layer beneath was released, which resulted in the cementation of Au on Cu. Thus, a decrease of Au recovery corresponding to the increase of Ni recovery occurred. Interestingly, with excessive amount of thiosulfate and given enough residence time, Au was re-dissolved after 2 hours while Ni extraction started to reach its equilibrium.

It was suggested by these results that a slightly higher concentration of NH$_3$ than S$_2$O$_3$ (i.e. AT/AH ratio from 0.5 to 1) facilitated Au extraction in two ways. First, the excessive amount of NH$_3$ provided sufficient complexing ions to stabilize the leached Au ions (as Au(NH$_3$)$_2$$^{2+}$), thus minimizing the competing impact by Ni extraction. Second, a higher amount of NH$_3$ prevented the deposition of Au on Cu. As reported by other researchers, NH$_3$ not only acts as a complexing ligand to stabilize Cu and Au species in thiosulfate solution Cu(NH$_3$)$_4$$^{2+}$ as oxidizer and the intermediate Au(NH$_3$)$_2$$^{2+}$ specie (Breuer & Jeffrey, 2002), but also acts as a leaching agent to dissolve the exposed Cu surface below the Au layer, therefore preventing the leached Au re-depositing on the Cu surface (Senanayake, 2005a). To understand the validity of the results in view of a potentially heterogeneous system, leaching was repeated under identical conditions yielding largely similar results.

6.3.2.3 Effect of particle size

The effect of particle sizes was studied, and the results are shown in Figure 6.11. Three different particle sizes were used with top sizes of 3.4, 2.0, and 1.2 mm. As indicated by Figure 6.11, both the 3.4- and 2-mm top sizes yielded high Au recoveries of 86.9% and 88.7%, respectively. Using the waste chips tested in this study, since most of Au exist on the surface, the decrease of particle size from -3.4 to -2 mm had no significant effect on leaching kinetics. However, using a finer particle size of 1.2 mm, about 81% of Au was leached first but the precipitation of Au occurred after 2 hours, corresponding to the initiation of Ni extraction. Combining the previous results shown in Figure 6.4 and Figure 6.5, it can be seen that Au thiosulfate leaching was significantly influenced by the co-
existing Ni and Cu in the waste chips. It is hypothesized that, as the chips were further shredded to -1.2 mm, the Ni underlayer was more readily exposed and leached. The fast kinetic of Ni removal led to the accessibility of Cu layer under it, which then caused the rapid Au reprecipitate on Cu surface.

![Graph showing Au and Ni extraction (%) using particle sizes of -3.4, -2.0, and -1.2 mm (S/L ratio: 10 g/L; Cu(II) 50mM; S_2O_3: 0.5M; NH_3: 0.5M; aeration: 120 mL/min; Temp.: 25°C).]

Figure 6.11. Au and Ni extraction (%) using particle sizes of -3.4, -2.0, and -1.2 mm (S/L ratio: 10 g/L; Cu(II) 50mM; S_2O_3: 0.5M; NH_3: 0.5M; aeration: 120 mL/min; Temp.: 25°C).

6.3.2.4 Effect of temperature

As thiosulfate decomposes at a higher temperature, the highest temperature studied in this work was 55 °C. The results of Au thiosulfate leaching under various temperatures are shown in Figure 6.12. Leaching at 25 °C show the highest Au recover, but in the next temperature (35 °C), the initial Au leaching rate were faster in the first 30 min. However, the elevated temperature appeared amenable to Ni extraction, which demonstrated a similar pattern of decreasing Au recovery as discussed previously. At temperatures of 45 and 55 °C, there were little Au recovery in the first 2 hours. Interestingly, as the leaching continued, under higher temperature (35-55 °C), a delayed Au extraction took place after 2 hours while 80% of Ni was already leached. After 3 hours, as Ni extraction reached the
plateau, Au leaching kinetics was enhanced with a steeper slope, represented by the blue, red, and green solid curves from 3-hour to 4-hour leaching time in Figure 6.12.

Figure 6.12. Au and Ni extraction (%) under temperatures of 25, 35, 45, and 55 ℃ (S/L ratio: 10 g/L; particle size: -2 mm; Cu(II) 50mM; S₂O₃⁻: 0.5M; NH₃: 0.5M; aeration: 120 mL/min).

As visually indicated by leaching curves under elevated temperatures (35-55 ℃), there were three regions of Au and Ni reactions in thiosulfate system. In the first hour, it is hypothesized that Au was competing with Ni to be leached and stabilized in solution; from 2- to 3-hour, Ni extraction took over and Au extraction was inhibited; after 3 hours, Ni extraction reached equilibrium and a second attempt of Au extraction was initiated. It was interesting to see that after 3 hours, Au was redissolved in thiosulfate solution while Ni was mostly leached. The later redissolution of Au indicated that the previous drop of Au recovery was not due to the degradation of thiosulfate.

A possible reason to explain this phenomenon is the decrease of NH₃ concentration in solution due to the elevation of temperatures. NH₃ (or NH₄OH) is known to vaporize at higher temperature (Meng & Han, 1996). As the temperature increased, there was less NH₃ presented in the liquid phase. As shown in the leaching mechanism (Figure 6.1), NH₃ provides complexing ligands to Au and form Au(NH₃)₂⁺ as an intermediate product before Au complexes with thiosulfate and stably exists in solution (Xu et al., 2017). Under higher
temperature, with both Ni extraction and NH$_3$ evaporation taking place at the same time, Au loses the competition to Ni on complexing with NH$_3$ ions. Thus, the Au extraction was inhibited at the beginning when Ni extraction was activated.

6.3.3 Solution Eh/pH and the characterization of solids

6.3.3.1 Eh and pH in leaching solution

To understand the conditions in leaching solutions, the pH and Eh were monitored during leaching. In Figure 6.13 (a) and (b), two leaching tests, under 0 and 120 mL/min aeration, with similar pH but different Eh were compared. Whilst in Figure 6.14 (a) and (b), the leaching tests with similar Eh, but different pH, were discussed.

![Figure 6.13](image1.png)

(a)

![Figure 6.14](image2.png)

(b)

Figure 6.13. (a) Au and Ni extraction (%); and (b) pH and Eh (mV vs SHE), in previous leaching tests (Cu(II) 50mM; aeration: 0 and 120 mL/min; data corresponding to Figure 6.6 and Figure 6.8).
Figure 6.14. (a) Au and Ni extraction (%); and (b) pH and Eh (mV vs SHE), in previous leaching tests (AT/AH: 0.5/1 and 0.75/0.5; data corresponding to Figure 6.9 and Figure 6.10).

It can be seen from Figure 6.13 (b) that there was no noticeable difference in the pH because of the same amount of the initial NH$_3$ concentration (0.5M). However, the difference in the Eh was quite remarkable. In leaching test resulted in a higher Au recovery (120 mL/min aeration), Au recovery reached its steady state with little Ni co-extraction. The corresponding Eh decreased as Au was extracted and maintained at around 180 mV (vs SHE). In the leaching test resulted in a lower Au recovery leaching (0 mL/min aeration), the corresponding Eh decreased in the first hour as Au was extracted. However, at 60 minutes, as Ni was leached and Au was suspectedly deposited, Eh declined continuously and dropped to 40 mV (vs SHE) at the end of leaching. According to Feng et al., in an oxygen-eliminated system (anaerobic), the mixed potential of solution largely depended on the redox couple of Cu(II)/Cu(I) (Feng & van Deventer, 2007). A critical condition of an oxygen-eliminated system is that the mix potential of solution needs to be maintained at a high level above 0.19 V, which is still governed by the equilibrium potential of Cu(II)/Cu(I) couple (Feng & van Deventer, 2007). According to the Eh-pH diagram reported by Molleman and Dresingner, as the solution Eh went below -0.1V, reduction of metallic Au0 occurred in their leaching system (Molleman & Dreisinger, 2002). Similarly in our leaching condition, it is essential to keep the Eh at a slightly oxidative environment
to prevent the reduction of Au, by maintaining the redox coupled of Cu(II)/Cu(I) at a higher level.

Without the facilitation of aeration to regenerate the Cu(II) from Cu(I), the Eh was significantly lowered by the composition of Cu(II)/Cu(I) in solution. At low potentials where oxygen was deficient and Cu(II) regeneration was limited, the decomposition of thiosulfate resulted in the formation of Cu sulfide precipitate (Aylmore & Muir, 2001). Consistently, the electrochemistry study by Nie et al. indicated that the reduction of Cu(II) complex in NH$_3$-S$_2$O$_3$ system occurred at a potential of 0.15V, and the black Cu sulfide was formed on the surface of Au after the reduction of Cu(II) complex (Nie et al., 2019).

In Figure 6.14 (a) and (b), with varying ammonia thiosulfate to ammonium hydroxide ratios (AT/AH ratios), the ending Au recoveries were close, but the trends were quite different. In two leaching tests shown in Figure 6.14 (a) and (b), the Eh was similar to each other, around 0.15V. The main difference was the solution pH, due to the different concentrations of NH$_3$ (0.5M and 1.0M). As shown in Figure 6.14 (a), in leaching solution containing higher thiosulfate (AT/AH 0.75/0.5), Au recovery decreased from time 30 – 120 min, while Ni was co-extracted. Correspondingly, in Figure 6.14 (b), there was a declining trend on Eh in the beginning, but increased slightly after 60 min. As a result of higher thiosulfate concentration, the precipitated Au (on Cu surface) was re-leached by available thiosulfate in the solution, following the Ni leaching. There was also a decreasing trend on solution pH, as Ni was leached. The formation of Ni(NH$_3$)$_6$$^{2+}$ consumed a significant amount of NH$_3$ ions, which caused the following reaction to shift left.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad \text{(6.15)}$$

Comparing between Figure 6.13 and Figure 6.14, the results in this work showed the criticality of maintaining the Eh above 0.15V for the purpose of preventing Au precipitation under reductive potential. In Figure 6.13, as Cu(II) was consumed, the solution Eh was lowered to less than 0.15V, and the precipitation of Au occurred. Whereas, as indicated by Figure 6.14, in the presence of sufficient oxidizer, the precipitation of Au might be temporarily depressed, but the leaching of Au continued to proceed after Ni leaching.

An Eh-pH diagram including Cu-NH$_3$-S$_2$O$_3$ species in current leaching system was constructed using HSC 9.0 program. The corresponding concentrations of Cu, NH$_3$, and
$S_2O_3$ were 0.05M, 1.5M and 1M, respectively. The resulted Eh-pH diagram shown in Figure 6.15 indicates that, at current leaching conditions, at a pH ranging from 9-10, there were three possible Cu species across different Eh range from 0 to 0.25V. At lower Eh range around 0V, Cu stably exists at $Cu_2S$, indicating the formation of $Cu_2S$ precipitates when Eh is not maintained. It was also observed by other researchers that the precipitation of Cu sulfides occurred together with the co-precipitation of Au (Jeon et al., 2021), which agreed with the drop of Au at a lower Eh where $Cu_2S$ was formed, as presented in Figure 6.13. At a higher Eh around 0.15V, which is the corresponding Eh when higher Au recoveries were achieved in this study, Cu mainly exists as $Cu(NH_3)_2^+$ and $Cu(NH_3)_4^{2+}$. Since the boundary of stability regions of $Cu(NH_3)_2^+$ and $Cu(NH_3)_4^{2+}$ species are largely depends on the Eh at pH 9-10, it further confirms the important role of maintaining Cu(II)/Cu(I) redox couple by controlled aeration in Au thiosulfate leaching system. In alignment with the result shown in Figure 6.14, at maintained Eh above 0.15V, although the Au recovery was first lowered as Ni was extracted, as there were sufficient oxidizer ($Cu(NH_3)_3^{2+}$) and complexing ions (NH$_3$ and $S_2O_3^{2-}$), Au recovery was re-initiated after Ni extraction.

![Eh-pH diagram of Cu-NH$_3$-S$_2$O$_3$ system](image)

Figure 6.15. Eh-pH diagram of Cu-NH$_3$-S$_2$O$_3$ system ($Cu$: 0.05M; NH$_3$: 1.5M; S$_2$O$_3$: 1M, constructed by HSC 9.0).
6.3.3.2 SEM images of original Au-fingers

The as shredded Au-fingers were analyzed via SEM-DES. Three typical particles were selected being 1) Au-fingers with board substrates (Figure 6.16); 2) the Au-fingers separated from major board substrates (Figure 6.17); and 3) the single Au-finger flake with a scratched surface (Figure 6.18).

Figure 6.16. SEM images and elemental mapping of as-shredded RAM chips with Au-fingers and boards.

Figure 6.17. SEM images and elemental mapping of as-shredded RAM chips (Au-fingers only).
Figure 6.18. SEM images and elemental mapping of as-shredded RAM chips (Au-fingers with the scratched surface).

As shown in Figure 6.16, the Au-fingers were located at the edge of waste chips, sitting on top of board substrates. The most abundant elements in the Au-fingers were Au, Ni, and Fe, while Al was mainly found in the board substrate. The elemental mapping of Au, Ni and Fe indicates their association with each other in the layer of chips/fingers. The better contrast of Au shows that Au was masking on the surface, while Ni and Fe underlayers were located beneath the surface. Cu mainly presented on the surface and the edge due to the shearing of Cu-clad laminates. In the board substrates, Al was found to be the predominant element, as the Al-clad substrate.

As indicated in Figure 6.17, in Au-fingers, Au, Ni, and Cu were found to be well-aligning layered with each other, indicating a Au-Ni-Cu interlayer. In the manufacturing of these chips, Cu is mainly used for conduction purpose as a cheaper material than Ni and Au. Ni above the Cu provides a convenient layer to assist the plating of Au, as it prevents the corrosion of direct contact between Au and Cu. On surface, Au covers the top of chips/fingers as a mask due to its corrosion resistant for electrical contact. Regardless, it was difficult to tell the position of Au-Ni-Cu interlayers, i.e. the order of these elements from top to bottom from these SEM result. To be able to examine that, a Au-finger sample with scratched surface was further analyzed.

Based on the elemental mapping of Cu, Ni, and Au shown in Figure 6.18, it was apparent to see that the shape of Ni mapping coincidently matched the shape of scratches on the Au surface. As such, Ni was likely the next layer below the Au surface layer. Moreover, Cu was only exposed at the sheared edge at the cross-section of the Au-finger flake, as a result of shredding rather than surface abrasion.
The identification of Au-Ni-Cu interlayers further revealed the high possibility of Au re-deposit on Cu during thiosulfate leaching. As Au was successfully leached, the Ni underlayer was exposed and reacted with thiosulfate lixiviant. After the dissolution of the Ni layer, the Cu layer under Ni was further exposed and became available to the leached Au-thiosulfate complex. Electrochemically, \( \text{Au(S}_2\text{O}_3)_2^{3-} \) ions tend to precipitate on the accessible Cu surface via a cementation reaction. Particularly in the presence of Al, the cementation of Au on Cu was greatly promoted (Jeon et al., 2018). The most recent findings by Jeon et al discovered Au deposition in ammoniacal thiosulfate solution was enhanced by increasing Cu concentration up to 50mM. Their SEM-EDS results showed that the deposition of Au occurred together with the deposition of Cu (Jeon et al., 2021). Au deposition in thiosulfate solution and its standard redox potential are shown in Eq. (6.16) (Jeon et al., 2021).

\[
\text{Au(S}_2\text{O}_3)_2^{3-} + e^- \rightarrow \text{Au} + 2\text{S}_2\text{O}_3^{2-} \quad \text{E}^0 = 0.27 \text{ V} \quad (6.16)
\]

From the previous leaching results, there were several conditions that could lead to the deposited Au re-dissolve in solution, given sufficient aeration and Cu(II) supply. These conditions include a higher NH\(_3\) concentration (or lower AT/AH ratio), excessive thiosulfate ions, or mildly elevated temperature.

6.3.3.3 SEM images of treated Au-fingers

Two leaching residues were submitted for SEM-EDS characterization. Figure 6.19 showed the leaching residue from the experiment (50mM Cu(II), 0.5M \( \text{S}_2\text{O}_3 \), 0.5M NH\(_3\), 0 mL/min aeration) with Au recovery reaching steady state over time (88.7% Au recovery, 1.4% of Ni recovery in leaching). Figure 6.20 showed the leaching residue from the experiment (50mM Cu(II), 0.5M \( \text{S}_2\text{O}_3 \), 0.5M NH\(_3\), 120 mL/min aeration) with suspected Au re-precipitation, where Au concentration was first increased to 71% and then decreased to 5% (5.0% Au recovery, 42.2% of Ni recovery in leaching). By comparing Figure 6.19 (80% Au recovery) and Figure 6.20 (0% Au recovery) side by side, it is clear to see that in both residues, elemental mapping of Au, Ni, and Cu were associated with each other, indicating the overlaying Au-Ni-Cu layers. The sulfur mapping showed two distinct patterns in Figure 6.19 and Figure 6.20. In Figure 6.19, as Au leaching reached steady state,
S showed a scatter occurrence, with little correlation with other elements. However, in Figure 6.20, S showed a similar pattern to Au, Ni and Cu.

![Figure 6.19](image1.png)

**Figure 6.19.** SEM images and elemental mapping of Au leaching residues (High Au %R, data corresponding to Figure 6.8, 50mM Cu, 120 mL/min aeration).

![Figure 6.20](image2.png)

**Figure 6.20.** SEM images and elemental mapping of Au leaching residues (Low Au %R, data corresponding to Figure 6.6, 50mM Cu, 0 mL/min aeration).

The changed pattern of S occurrence in different leaching tests proved that there was a precipitation of S species occurred in low Au recovery test. Unfortunately, it was difficult to identify whether the precipitated sulfur species was elemental sulfur, Cu sulfides, Au sulfide, or all of these. Given by the information from SEM-EDS results, the lower Au recovery, especially where Au was leached first and then re-precipitated, was likely due to
the passivation layer formed on the solid surface, by the precipitation of sulfur/sulfide species.

The EDS result on the weight % of concerning elements, i.e. Ni, Cu, Au and S, were shown in Figure 6.21. In the leaching residues with higher Au recovery (Figure 6.8), there were higher content of Ni remain in the solid phase, which was consistent with the observation of low Ni concentration in the solution. On the other hand, in low Au recovery residue (Figure 6.6), since 42.2% recovery of Ni was achieved in leaching, the average weight % of Ni was much lower in residue, only 4.4%wt. The Au contents in these two residues were slightly different, 0.2%wt. in high recovery samples and 0.3%wt. in low recovery sample. The slight increase of Au in the residues indicates that it was likely the formation of Au sulfide that caused the loss of Au during leaching, as referring to the result shown in Figure 6.6. These results of Ni and Au in the solid phase agreed with the observations in the leaching solutions. Moreover, a higher Cu content (5.9%wt.) was detected in low Au recovery residue, indicating a significant amount of Cu/Au sulfide species precipitated in the solid phase during leaching. The content of S showed about 1%wt. increase in low Au recovery residue, attributing to the formation of sulfide species. These results further confirmed the hypothesis that during the leaching, there were a certain amount of sulfur/sulfide species formed. The formation of Cu sulfides and elemental sulfur attributed to the passivation of Au, which further inhibited the leaching of Au. And the formation of Au sulfide possibly attributed to the loss of Au in leaching, as Ni was extracted, and sulfide species started to form. As the EDS only shows the electron on the surface of particles, there was a reason for little Au detected in both samples. Since the surface of Au-finger was masked by the sulfide precipitation, the penetration of the electron beam across the passivation layer to access the surface of Au layer beneath was limited.
Referring back to the previous leaching results and the solution Eh/pH shown in Figure 6.13 (a) and (b), in the absence of O₂, Cu(II) consumption was enhanced by exposing the Cu(0). Meanwhile, the Eh was gradually lowered without the regeneration of Cu(II). As the Eh decreased to below 0.15V, precipitation of Au was observed. Moreover, when solution Eh is low, the reductive degradation of thiosulfate (as shown in Figure 6.2) occurred, which resulted in the formation of sulfur and sulfides (as shown in Eqs. (6.12) and (6.13)). The formation of sulfur/sulfides on the residues was proved by SEM-EDS. These results further confirmed that under a reductive Eh below 0.15V, Au cementation and thiosulfate degradation, together with formation of Cu sulfides, all occurred simultaneously and caused the decrease of Au recovery in leaching.

6.4 Conclusions

Characterization of waste chips by SEM revealed the association of Au-Ni-Cu as the interlayers. Due to the significant amount of Cu existing in waste chips, and the preferential deposition of Au on Cu, a decopperization pretreatment was needed prior to Au leaching. During Au thiosulfate leaching, the co-extraction of Ni resulted in the dramatic decrease in Au recovery, either due to the competition between Ni and Au on S₂O₃ complexation, or the deposition of Au on the newly exposed Cu surface after Ni extraction. Further SEM-EDS characterization on the residues indicated that the conflicting effect of Ni recovery on
Au recovery was mainly due to the passivation of reduced sulfur/sulfide species formed under unfavored leaching conditions.

Controlled aeration was found important in facilitating the initial Au recovery by maintaining the Cu(II)/Cu(I) oxidation-reduction potential (ORP) in leaching solution. By comparing the Eh during different leaching experiments, it was found that a maintained Eh around 0.18 V (vs SHE) was favorable to achieve a satisfying Au recovery during 4 hours of residence time. In a leaching solution containing higher NH$_3$ concentrations (with ammonium thiosulfate to ammonium hydroxide ratio from 0.5 to 1), the limited Ni extraction prohibited the exposure of Cu layer beneath, thus preventing the Au deposition on Cu during leaching. The elevation of temperature significantly slowed down the Au extraction, but enhanced the extraction of Ni.

For future perspectives, the work may focus on exploring the characterization techniques to prove the formation of passivation layer and to identify chemical composition of the passivation layer. Also, in the thiosulfate leaching of waste chips, the effect of Au cementation, and the preferential Ni leaching under certain conditions may be an interesting research area.
CHAPTER 7. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

7.1 New Contributions

In summary, the novel aspects and important achievement of this study include:

1) A comprehensive flowsheet, integrating the enrichment and recovery of Cu and Au from waste PCBs using an ammonia-based system, was proposed and investigated.
2) Physical enrichment by a unique combination of size and density was performed, and the characterization via TGA was evaluated.
3) In the Cu leaching process, anaerobic ammoniacal leaching using Cu(II)-amine as the only oxidizer was investigated. A kinetic study in such a system was conducted and a feasible kinetic model was developed.
4) This study further extended the kinetic modeling to a counter-current leaching circuit design and simulation for the demonstration purpose.
5) In the studied Au thiosulfate system, the existence of Au-Ni-Cu interlayer in waste RAM chips was found to influence the recovery of Au. The inverse impact of Ni extraction on Au recovery was likely due to the exposure of new Cu surface that caused the Au deposition, after the removal of Ni layer. Pre-removal of Cu by decopperization and maintained solution Eh by aeration was helpful to prevent the Au deposition during leaching.
6) In addition, the presented study provided a suitable operating range for the key processing parameters, intended to achieve a reasonable Au recovery under various parameters.

7.2 Conclusions

The conclusions in each chapter were summarized below:

1) Preliminary study on the material characterization and physical processing suggested that the WPCBs can be efficiently liberated at a top size of 2 mm. The following density separation using S.G. 1.48 and 2.67 can further separate the metallic fraction and non-metallic fractions in WPCBs. With assistant of a
surfactant in density separation, the contained metals, including Cu, Au, Ni, Zn, Fe, were enriched in the dense fraction (S.G.>2.67). Whilst, the fiberglass, plastic and other the non-metallic fractions were left in the lighter fraction (S.G.<1.48). This result was further confirmed by the SEM-EDS characterization on different density fractions.

2) Thermogravimetrically, brominated resins and polymers contained in WPCBs decomposed at temperature above 270-410°C. Combustion reaction of WPCBs occurred at higher temperature range from 410-570°C, where off gases such as CO, CO₂, HBr and Br₂ were released. Thermo-reaction of PCBs appeared to reach steady state after 570°C.

3) Results on Cu ammoniacal leaching under anaerobic environment showed a high efficiency of Cu extraction using ammoniacal lixiviant and initial Cu(II) as the oxidizer. Cu recovery of 96% occurred using 1M (NH₃)₂SO₄ and 4M NH₃OH solution, 40 g/L Cu(II) concentration, 1.2 mm particle size, 8 hours residence time at ambient temperature (18°C).

4) Results of leaching kinetics indicated that particle size and initial Cu(II) concentration were the most significant impact on leaching rate. The examined kinetic models suggested that both the changing concentration model and the mixed diffusion model had a goodness of fit to the experimental data. In considering the actual leaching mechanism, it appears that the change of concentration during leaching has a significant effect on the leaching rate. The activation energy was 4 kcal/mol, estimated by the Arrhenius equation, which further explained that this reaction was dominated by mass transport mechanism.

5) Kinetic modeling in Cu leaching showed a feasibility of predicting Cu recovery in an oxygen-eliminated ammoniacal sulfate system. The established model expression for Cu leaching in ammoniacal system revealed that the reaction orders of Cu(II) concentration and 1/R² were 1.6738 and 0.8151, respectively. Within the studied parameters, initial Cu(II) concentration was found to be the most important factor influencing Cu leaching rate, followed by the particle sizes and temperatures.
6) In Au-thiosulfate leaching, the pre-existing Cu in stamped Au-fingers was found to be detrimental to Au recovery as it provided available Cu surface for the deposition of Au in thiosulfate solution. Decopperization to remove Cu prior to Au thiosulfate leaching was deemed needed. Besides Cu, the co-extraction of Ni in leaching was found to have an inverse relationship with Au recovery. The decrease of Au recovery by the increase of Ni recovery was hypothetically attributed to the unique association among Au-Ni-Cu interlayer. In waste chips, Au existed on the surface, covering the Ni layer beneath, while certain amount of Cu was embedded under Ni layer and difficult to remove during decopperization. As Ni recovery increased, the extraction of Ni revealed the new Cu surface and provided available site for Au deposition, thus resulting in a corresponding decrease on Au recovery.

7) A sufficient aeration rate between 60-120 mL/min (equivalent to 0.24-0.48 mL/min per milliliter of lixiviant volume) and initial Cu(II) concentration from 50-75mM were proved critical to maintain the regeneration of oxidizer and an oxidative leaching environment. A maintained solution Eh around 0.15-0.18 V (vs SHE) by aeration and Cu(II) regeneration was found important to prevent the Au deposition and achieve a satisfactory Au recovery.

8) The concentration ratio of thiosulfate to ammonia (AT/AH ratio) from 0.5 to 1 (i.e. AT/AH from 0.5M/1M to 0.5M/0.5M) was helpful to achieve a satisfactory Au recovery, as the excessive NH₃ tended to mask the exposed Cu surface and prevent Au deposition. Higher temperature was found to favor the Ni leaching first, and the Au leaching afterwards. A reasonable Au recovery of 98% was obtained using 50mM Cu(II), 120 L/min aeration rate, 0.5M (NH₃)₂S₂O₃ and 0.75M NH₄OH, 4 hours residence time at room temperature (25°C).

9) SEM-EDS characterization on leaching residues revealed the formation of sulfur species or Cu sulfides under unfavored leaching conditions (at Eh below 0.15 V), which may further result in the co-deposition of Au on the surface of Cu.
7.3 Recommendations for Future Work

The current study investigated the leaching processes of Cu and Au in ammoniacal and thiosulfate solutions using waste PCBs. Although a predictable kinetic model was provided and tested feasible for scaleup simulation, the experiments were limited in lab-scale. It was recommended that additional efforts should be devoted to the following areas:

1) Unlike the existing literatures using pure metals in a similar leaching system, in the presented study, real-world waste PCBs were used as the feed materials to examine the potential effect of co-existing metals. The waste chips employed in this study were highly heterogeneous. In the future industrial application of the proposed flowsheet, it is likely that various feed sources will be involved, thus making the materials even more difficult to handle without any pre-treatment. In the scaleup operation, more attention should be paid on the physical pre-treatment to provide a high-grade material prior to the chemical process.

2) From a processing point of view, additional information on reagent usage and power consumption is required to complete the economic assessment of this flowsheet. Equipment costing and wastewater treatment costs are suggested. In terms of sustainability, it is necessary to conduct a toxicity characteristic leaching procedure (TCLP) test on the final solid waste, to prove the suitability of landfilling.

3) The current study conducted a preliminary simulation on counter-current leaching, but the work was limited on Cu leaching process. The further work may focus on the improvement of developing a comprehensive flowsheet with accessible software. This will also help on preparing for the commercialization for small and medium-sized enterprises, in terms of investment on CapEx and OpEx of the plant.

4) In Au leaching experiments, it was noted that sulfur species was formed under unfavored leaching conditions, which may also cause the co-deposition of Au. However, due to the lack of suitable characterizing methods and techniques, the identification of the sulfur species and the pathway of thiosulfate
decomposition, remained unclear. The future work in this aspect may focus on the utilization of advanced characterization techniques, such as high-performance liquid chromatography (HPLC), to identify the chemical composition of the sulfur layer.
REFERENCES


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