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Recovery of Copper(II) and Silver(I) from Nitrate Leaching Solution of Industrial Dust via Solvent Extraction with LIX63

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Abstract: A nitrate leachate containing Cu(II), Ag(I), Ni(II), Mg(II), and Al(III) was obtained during the leaching of industrial dust, which arises during the pyrometallurgy of spent camera modules. To separate and recover Cu(II) and Ag(I) from the leaching solution, solvent extraction experiments using 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX63) were conducted. LIX63 was found to selectively extract Cu(II) and Ag(I) over other metal ions (Ni(II), Mg(II), and Al(III)) at low nitric acid concentrations. The extraction efficiency of Cu(II) was more affected than that of Ag(I) by the acidity of the feed solution and the LIX63 concentration in the organic phase. Cu(II) and Ag(I) were simultaneously extracted using 2 mol/L LIX63. Cu(II) was separated from the loaded LIX63 via stripping with 4 mol/L HNO₃, whereas Ag(I) was recovered via stripping with 0.1 mol/L thiourea after the removal of Cu(II). McCabe–Thiele diagrams for the extraction and stripping of Cu(II) and Ag(I) were constructed. The complete extraction of Cu(II) and Ag(I) was confirmed via counter-current extraction. Moreover, stripping simulation tests confirmed that higher than 99.99% of Cu(II) and 99.2% of Ag(I) were stripped. The purities of Cu(II) and Ag(I) in the recovered solution were 95.2% and 99.993%, respectively. A process flow chart for the recovery of Cu(II) and Ag(I) from the nitrate leachate of the target industrial dust was also provided.

Keywords: silver; copper; nitric acid; LIX63; separation; industrial dust

1. Introduction

Copper (Cu(II)) and silver (Ag(I)) are essential elements that are widely used in daily life. In the industry, Cu(II) is used in the manufacture of electrical materials and telecommunication devices and in the construction, power generation, transportation, petroleum refining, and electroplating industries [1–4]. Ag(I) has been employed in the production of brazing alloys, electrical and electronic products, photographic paper and film, catalysts, and other systems [5–7]. Cu(II) and Ag(I) are reported to be two common co-existing valuable metals in industrial waste [8]. From economic and environmental perspectives, the recovery of Cu(II) and Ag(I) from industrial waste is particularly important.

Hydrometallurgical methods have been widely used for the recovery/extraction of Cu(II) and Ag(I) from various solutions. The results of studies on the extraction separation of Cu(II)/Ag(I) from various resources are summarized in Tables 1 and 2. The extraction of Cu(II) has been investigated using chelating extractants such as LIX84-IC, LIX622N, LIX860N, LIX984N, LIX54, and LIX63 + Versatic10 + TBP [9–15], as well as acidic and solvating extractants such as D2EHPA, Cyanex 272, Cyanex 301, Cyanex 302, Cyanex 921, and Cyanex 923 from various media [16–20]. When Cyanex 301 is used as an extractant, the stripping of Cu(II) is reported to be highly difficult and aqua regia is required as a strippant [21]. LIX984 is added to Cyanex 301 to improve the efficiency of stripping Cu(II) from Cyanex 301 systems [17]. It has been proven that the chelating extractant
is the most effective among these extractants for Cu(II) extraction and is widely used commercially [22].

**Table 1.** Summary of some studies on the extraction of Cu(II) using various extractants.

| Extractant          | Media          | Diluent | Remark                                                                 | Ref. |
|---------------------|----------------|---------|------------------------------------------------------------------------|------|
| LIX 84, LIX 973N    | H₂SO₄          | kerosene| 1. The extraction behavior of the two extractants for copper(II) was compared. | [9]  |
|                     |                |         | 2. A copper(II) extraction of 95–99% was achieved via three extraction stages with LIX 84 and two extraction stages with LIX 973N. |      |
| LIX 84I, LIX 622N   | H₂SO₄          | kerosene| 1. Cu(II) extractions of 98.64% and 99.95% were obtained using LIX 84I and LIX 622N, respectively. | [10] |
|                     |                |         | 2. Stripping was conducted by using 2 mol/L H₂SO₄.                      |      |
| LIX84-I, LIX612N-LV, XI-04003, LIX984N | HCl       | kerosene| 1. The copper loading capacity order for four extractants was LIX984N > LIX612N-LV and XI04003 > LIX84-I. | [11] |
|                     |                |         | 2. At a pH of <0.5, copper extraction efficiency increased quickly with increasing pH, while at a pH value above 0.5, it increased only slightly with increasing pH. |      |
| LIX 84-I, LIX 984N, LIX54-100 | Ammonia | Escaid110 | Extraction efficiency was much higher for systems using hydroxy reagents than that using β-diketone oximes. | [12] |
| LIX-54, cinnamate, β diketone | Ammoniacal carbonate | Arol-light | 1. Solvents cinnamate and a mixture of β-diketone were suitable alternatives to LIX 54. | [13] |
|                     |                |         | 2. About 97.3%, 99.7%, and 99.6% of copper(II) can be extracted using LIX 54, cinnamate, and β-diketone, respectively. |      |
|                     |                |         | 3. Stripping was conducted by using 2 mol/L H₂SO₄.                      |      |
| LIX860N-I           | HCl            | kerosene| 1. Fe(III) and Pb(II) were co-extracted with Cu(II) at pH 2.            | [14] |
|                     |                |         | 2. Stripping was conducted using 1.5 mol/L H₂SO₄.                       |      |
| LIX63 + Versatic10; LIX63 + Versatic10 + TBP | HCl       | Shellsol D70 | 1. Using a Versatic 10/LIX63/TBP system, 95% of Cu(II) and 12% of Ni(II), Zn(II), Co(II), and Cl(I) were extracted. | [15] |
|                     |                |         | 2. At pH 3–3.5, impurities of Ni(II), Zn(II), Co(II), and Cl(I) were stripped, and Cu(II) was transferred to a sulfate solution. |      |
|                     |                |         | 3. Cu(II) was recovered by electrowinning.                              |      |
|                     |                |         | 4. The Versatic 10/LIX63 system was used to separate Cu(II) from Fe(III) in strong chloride solutions. |      |
| D2EHPA              | Acetate buffer | kerosene| 1. Acetate ions greatly improved the Cu(II) extraction efficiency.     | [16] |
|                     |                |         | 2. At an initial pH value of 4.44, acetate ion concentration was 0.18 mol/L, and the single stage extraction efficiency was >99.5%. |      |
| Cyanex 301, LIX 984N | H₂SO₄          | kerosene| 1. The extraction equilibria of Cu(II) with Cyanex 301, LIX 984N, and their mixtures were investigated. | [17] |
|                     |                |         | 2. Stripping efficiency was improved by the addition of LIX 984N to Cyanex 301. |      |
Table 1. Cont.

| Extractant     | Media               | Diluent | Remark                                                                 | Ref.   |
|----------------|---------------------|---------|------------------------------------------------------------------------|--------|
| Cyanex 302     | H₂SO₄/              | kerosene| 1. Cyanex 302 was a potential extractant for the extraction of copper(II) from aqueous solutions. 2. The endothermic nature of the extraction process for the three studied systems was in the order: chloride > nitrate > sulfate media. | [18]   |
|                | HCl/HNO₃            |         |                                                                        |        |
| Cyanex 272, Na-Cyanex 272 | H₂SO₄ | kerosene| 1. The solvent extraction of Cu(II) with Na-Cyanex 272 was more efficient than that with Cyanex 272 | [19]   |
| Cyanex 921     | HCl                 | kerosene| 1. Cu(II) extraction was quantitative using 0.5 mol/L Cyanex 921 and 5 mol/L HCl. 2. By using using 0.2 mol/L H₂SO₄ or 0.5 mol/L HCl, 99.7% Cu(II) was recovered from the loaded organic phase. | [20]   |
| Cyanex 923     | HCl                 | kerosene| 1. The extraction mechanism was investigated.                          | [21]   |

In the case of Ag(I), the applicability of calix(4)arene amide derivatives [23], ketonic derivatives of calixarenes [24], Cyanex 272, Cyanex 302, Cyanex 301 [25], N,N-diethyl-2,7-dihexyl-3,6-diazaoctanoic acid, 1,5-bis[2-(2′-carboxypentadecyloxy)phenoxy]-3-oxapentane [26], bis-triazin-bi-pyridine (BTBP) [27], trioctlyphosphate oxide (TOPO) [28], and 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX63) [29,30] for the extraction of Ag(I) has been investigated. From a chloride-leaching solution of anode slimes containing Cu(II), Ag(I), and Au(II), Cu(II) was recovered by extraction with LIX63, followed by stripping with HCl, whereas Ag(I) was recovered via extraction with Alamine 336, followed by stripping with an NH₄SCN solution [31]. Although Cu(II) and Ag(I) were simultaneously extracted using Cyanex 301, their stripping from the loaded Cyanex 301 was difficult. The efficient stripping of Cu(II) and Ag(I) was possible only by using aqua regia [31].

Table 2. Summary of some studies on the extraction of Ag(I) using various extractants.

| Extractant                  | Media        | Diluent | Remark                                                                 | Ref. |
|-----------------------------|--------------|---------|------------------------------------------------------------------------|------|
| Cyanex 272                  | HNO₃         | kerosene| 1. Extraction mechanisms were investigated.                            | [25] |
| Cyanex 302                  | HNO₃         | kerosene|                                                                        |      |
| Cyanex 301                  | HNO₃         | kerosene|                                                                        |      |
| ketonic derivatives of calixarenes | HNO₃ | HCl     | 1. Tetrameric ketone facilitated selective extraction of Ag(I) over Pd(II) using ~1 mol/L HNO₃. 2. It effectively removed traces of Ag(I) from a large excess of Pd(II). | [26] |
| Bis-triazin-bi-pyridine (BTBP) | HNO₃       | /       | 1. The side group of the ligand affected the distribution of Ag(I). 2. CyMe4-BTBP is a more efficient extractant for Ag(I) compared to C2-BTBP. | [27] |
| Trioctyl Phosphine oxide (TOPO) | HNO₃       | kerosene| 1. TOPO selectively extracted Ag(I) over Al using 0.1 mol/L HNO₃ solution. 2. The selective stripping of Ag(I) was successful using a 0.1 mol/L thiourea solution. 3. TOPO was regenerated by stripping of co-loaded Al(III) using 3 mol/L HNO₃. | [28] |
| LIX63                       | HNO₃         | kerosene| 1. Ag(I) extraction followed a solvating extraction mechanism, when the concentration of HNO₃ was higher than 0.1 mol/L. | [29] |
Table 2. Cont.

| Extractant | Media | Diluent | Remark | Ref. |
|------------|-------|---------|--------|------|
| LIX63      | HNO₃  | kerosene| 1. The selective extraction of Ag(I) over Zn(II) was achieved by using LIX63, when the HNO₃ concentration was 0.001–1 mol/L. 2. The stripping of Ag(I) was conducted by using 5 mol/L HNO₃. [30] |
| LIX 63, Alamine 336; Cyanex 301 | HCl | kerosene | 1. Cu(II) was recovered by extraction with LIX 63 and stripping with an HCl solution, while Ag(I) was recovered by extraction with Alamine 336 followed by stripping with NH₄SCN solution. 2. Cu(II) and Ag(I) were simultaneously extracted by Cyanex 301. 3. Stripping from Cyanex 301 was achieved using diluted aqua regia. [31] |
| LIX63      | HNO₃  | kerosene| 1. LIX63 exhibited selectivity for the extraction of Cu(II) and Ag(I) over Ni(II), Mg(II), and Al(III) at low concentrations of HNO₃. 2. Cu(II) was selectively stripped over Ag(I) from the loaded LIX63 using 4 mol/L HNO₃. 3. After the removal of Cu(II), Ag(I) was stripped from the loaded LIX63 using 0.1 mol/L thiourea. Present study |

Herein, a simple and efficient process was developed for recovering Cu(II) and Ag(I) from a nitrate-leaching solution of industrial dust that arises during the pyrometallurgy of spent camera modules. In the proposed process, LIX63 was employed as an extractant to simultaneously extract Cu(II) and Ag(I). Several parameters that affect the extraction and stripping efficiencies, such as the acidity of the solution, concentration of the extractant, species and concentration of the strippant, and volume ratio of the aqueous to organic phases, were investigated. Moreover, the feasibility of the proposed process was verified by performing a batch simulation of counter-current extraction and stripping experiments.

2. Materials and Methods

2.1. Leaching Procedure

The industrial dust composed of Cu(II), Ag(I), Ni(II), Mg(II), Al(III), Si (II), and C, which arose during the pyrometallurgy of spent camera modules, was used. It was leached using 1 mol/L of nitric acid at 70 °C for 2 h. The pulp density used for leaching was 10 g/L. The leaching solution contained 0.003 mol/L Ag(I), 0.02 mol/L Cu(II), 0.007 mol/L Ni(II), 0.001 mol/L Mg(II), and 0.003 mol/L Al(III).

2.2. Materials

AgNO₃ (99.8%; Daejung), Cu(NO₃)₂·2H₂O (99%; Daejung), Ni(NO₃)₂·6H₂O (97%; Junsei), Mg(NO₃)₂·6H₂O (99%; Junsei), and Al(NO₃)₃·9H₂O (98%; Daejung) were used to prepare the leaching solution. The concentrations of metals Ag(I), Cu(II), Ni(II), Mg(II), and Al(III) were fixed at 0.003, 0.02, 0.007, 0.001, and 0.003 mol/L, respectively, to maintain a composition identical to that of the leaching solution. HNO₃ (60%; Daejung) was used to adjust the acidity of the solution. Thiourea (98%; Junsei), HNO₃ (60%; Daejung), Na₂S₂O₃·5H₂O (99.5%; Samchun), NH₄NO₃ (99%; Daejung), (NH₄)₂SO₄ (99%; Daejung), and CH₃COONH₄ (97%; Daejung) were used to prepare the strippant solution. The feed and strippant solutions were prepared by dissolving the required quantity of reagents in the desired volume of distilled water.

Extractant 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX63) was purchased from Cognis and used without further purification. Kerosene (90% distillation at 265 °C; Daejung) was used as a diluent.
2.3. Solvent Extraction and Stripping

In batch simulation extraction experiments, equal volumes (20 mL) of aqueous and organic phases were mixed in a sealed bottle (100 mL) and shaken for 30 min using a wrist-action shaker (Model 75, Burrell, Pittsburgh, PA, USA) at ambient temperature (24 ± 1 °C). The shaking speed was 200 rpm. The aqueous solution was collected, after the two phases were well-separated in ~5 min using a separation funnel. Stripping was performed through the same procedure by mixing the loaded organic phase and the strippant solution. Subsequently, the concentration of metal ions in the aqueous phase was measured through inductively coupled plasma optical emission spectrometry (Optima 8300, PerkinElmer, Waltham, MA, USA). The concentration of metal ions in the organic phase was determined by using a mass balance.

3. Results and Discussions

3.1. Effect of the HNO₃ Concentration on the Extraction of Metal Ions

Metal ions were extracted from the synthetic leaching solution by using LIX63 and varying the concentration of HNO₃ from 0.001 to 3 mol/L. The concentrations of metals Ag(I), Cu(II), Ni(II), Mg(II), and Al(III) were fixed at 0.003, 0.02, 0.007, 0.001, and 0.003 mol/L, respectively. The concentration of LIX63 was maintained at 0.5 mol/L. The aqueous-to-organic phase (A/O) ratio was fixed at 1:1.

Figure 1 shows the effect of the HNO₃ concentration in the feed solution on the extraction percentages of metal ions. LIX63 selectively extracted Cu(II) and Ag(I) over other metal ions (Ni(II), Mg(II), and Al(III)) at low HNO₃ concentrations. The extraction percentage of Cu(II) decreased with an increase in the HNO₃ concentration, whereas that of Ag(I) first decreased with an increase in the HNO₃ concentration to 0.1 mol/L and then increased with a further increase in the HNO₃ concentration to 1 mol/L. The extraction efficiency was slightly changed by increasing the HNO₃ concentration from 1 to 3 mol/L. These results agree well with those of a previous study [29]. At a low acid concentration ([HNO₃] < 0.1 mol/L), the extraction of Cu(II) and Ag(I) can be explained by the typical cationic exchange theory, whereas at a higher acid solution ([HNO₃] > 0.1 mol/L), the extraction of Ag(I) followed the solvating extraction mechanism [29]. The reaction equations for Cu(II) and Ag(I) can be represented as follows [12,29]:

\[
[\text{Ag}^+]_{\text{aq}} + [\text{NO}_3]_{\text{aq}} + [\text{H}_2\text{R}]_{\text{org}} = [\text{Ag}(\text{H}_2\text{R})\text{NO}_3]_{\text{org}} \quad ([\text{HNO}_3] > 0.1 \text{ mol/L}) \quad (1)
\]

\[
2[\text{Ag}^+]_{\text{aq}} + [\text{H}_2\text{R}]_{\text{org}} = [\text{Ag}_2\text{R}]_{\text{org}} + 2\text{H}^+ \quad ([\text{HNO}_3] < 0.1 \text{ mol/L}) \quad (2)
\]

\[
[\text{Cu}^+]_{\text{aq}} + [\text{H}_2\text{R}]_{\text{org}} = [\text{CuR}]_{\text{org}} + 2\text{H}^+ \quad (3)
\]

where H₂R denotes LIX63.

The extraction percentages of Ni(II), Mg(II), and Al(III) in all the extraction experiments were ~0%. Further experiments were performed using a 0.001 mol/L HNO₃ solution.
The metal ion concentrations were the same as those in the leaching solution (stated in Section 2.1). The concentration of HNO$_3$ in the feed solution was maintained at 0.001 mol/L. The metal ion concentrations were the same as those in the leaching solution. The HNO$_3$ concentration in the feed solution was maintained at 0.001 mol/L. The metal ion concentrations were the same as those in the leaching solution (stated in Section 2.1).

Figure 2 shows that the extraction percentages of Cu(II) and Ag(I) increased with an increase in the LIX63 concentration from 0.5 to 2 mol/L. No variation in the extraction percentages of Ni(II), Mg(II), and Al(III) was observed; their extraction percentages were ~0%. (The data are not presented in the figure for brevity) The LIX63 concentration did not affect the extraction percentages of Ni(II), Mg(II), and Al(III), whereas higher than 90% of Cu(II) and Ag(I) were extracted when the LIX63 concentration exceeded 2 mol/L. This suggests the possibility of the simultaneous separation of Cu(II) and Ag(I) from the leaching solution.

Figure 1. Effect of HNO$_3$ concentration on metal extraction.

3.2. Effect of the LIX63 Concentration on the Extraction of Cu and Ag

The effects of the extractant (LIX63) concentration on the extraction of Cu(II) and Ag(I) were investigated by varying the LIX63 concentration in the organic phase from 0.5 to 2 mol/L. The HNO$_3$ concentration in the feed solution was maintained at 0.001 mol/L. The metal ion concentrations were the same as those in the leaching solution (stated in Section 2.1).

Figure 2 suggests that the extraction percentages of Cu(II) and Ag(I) were ~0%. (The data are not presented in the figure for brevity) The LIX63 concentration did not affect the extraction percentages of Ni(II), Mg(II), and Al(III), whereas higher than 90% of Cu(II) and Ag(I) were extracted when the LIX63 concentration exceeded 2 mol/L. This suggests the possibility of the simultaneous separation of Cu(II) and Ag(I) from the leaching solution.

Figure 2. Effect of the LIX63 concentration on the extraction of metals.
3.3. Effect of the A/O Ratio on the Extraction of Cu(II) and Ag(I)

The effect of the aqueous-to-organic phase ratio (A/O) on the quantitative extraction of Cu(II) and Ag(I) was investigated by varying the A/O ratio from 1:5 to 2:1. The concentrations of Cu(II), Ag(I), Ni(II), Mg(II), and Al(III) were the same as those in the leaching solution list presented in the experimental section. The concentration of HNO₃ in the feed solution and that of LIX63 in the organic phase were fixed at 0.001 and 2 mol/L, respectively.

The results indicated that the extraction percentage of Cu(II) increased from 58% to 99% as the A/O ratio decreased from 2:1 to 1:5. However, the extraction percentage of Ag(I) was higher than 90% for all the studied A/O ratios. Ni(II), Mg(II), and Al(III) were not extracted in any of these experiments. The results for the extraction of Cu(II) and Ag(I) are represented as the McCabe–Thiele diagrams in Figures 3 and 4, respectively. Figure 3 indicates that two stages were needed for the quantitative extraction of Cu(II) from a 0.001 mol/L HNO₃ solution using 2 mol/L LIX63 at an A/O ratio of 1:2. Figure 4 suggests that the quantitative extraction of Ag(I) was achievable under the conditions identical to those used for the quantitative extraction of Cu(II).

Based on the obtained results, a two-stage counter-current batch simulation test was performed at an A/O ratio of 1:2 and using 2 mol/L LIX63. The test results indicated that after the two-stage counter-current extraction, neither Cu(II) nor Ag(I) was detected in the raffinate, indicating that higher than 99.99% of Cu(II) and Ag(I) were co-extracted from the feed solution by using LIX63. The concentrations of Ni(II), Mg(II), and Al(III) after extraction were the same as those before extraction.

Figure 3. McCabe–Thiele plot for Cu(II) extraction using 2 mol/L LIX63.
3.4. Selection of a Strippant for the Stripping of Cu(II) and Ag(I) from the Loaded LIX63

The experiments for stripping Cu(II) and Ag(I) from the loaded LIX63 were performed using various strippant solutions such as Na$_2$S$_2$O$_3$, NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, CH$_3$COONH$_4$, HNO$_3$, and thiourea solutions. These solutions have been found to be effective for stripping of Ag(I) from LIX63 [29]. A synthetic leaching solution with 0.001 mol/L HNO$_3$ was used as a feed solution. The loaded organic phase was prepared by contacting the feed solution and 2 mol/L LIX63 at an A/O ratio of 1:2. In the stripping experiments, the obtained loaded LIX63 was in contact with each strippant solution at an A/O ratio of 1:1.

The experiment results indicated that NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, and CH$_3$COONH$_4$ failed to strip Cu(II) or Ag(I) from the loaded LIX63 (Table 3). Although Na$_2$S$_2$O$_3$ could be used to strip Cu(II) and Ag(I), its low selectivity limited its use in this process.

Table 3. Stripping of Cu(II) and Ag(I) from the loaded LIX63 with various strippants.

| Strippants            | Stripping Percentage (%) |
|-----------------------|--------------------------|
|                       | Cu(II)       | Ag(I)       |
| 1 mol/L Na$_2$S$_2$O$_3$ (pH 4.7) | 63.89       | 98.90       |
| 1 mol/L NH$_4$NO$_3$ (pH 4.6)   | 0.6         | 0.8         |
| 1 mol/L (NH$_4$)$_2$SO$_4$ (pH 5.1) | 2.1         | 6.7         |
| 0.5 mol/L CH$_3$COONH$_4$ (pH 7.1) | 0           | 0           |

The results of stripping with HNO$_3$ and thiourea solutions are presented in Figures 5 and 6, respectively. As shown in Figure 5, the stripping of Cu(II) over Ag(I) was possible at HNO$_3$ concentrations of <4 mol/L. When thiourea was used (Figure 6), no selectivity in stripping Ag(I) over Cu(II) was observed because of the lower concentration of Ag(I) than that of Cu(II) in the loaded LIX 63. However, the results in Figure 6 indicated that the quantitative stripping of Ag(I) from the loaded LIX63 was possible.
Accordingly, 4 mol/L HNO₃ was used as a strippant in the stripping experiments. Thus, in the subsequent stripping experiments, the separation of Cu(II) and Ag(I) from the loaded LIX63 was performed to remove Cu(II) first by using 4 mol/L HNO₃ solution, followed by the stripping of Ag(I) by using 0.1 mol/L thiourea.

3.5. Effects of the A/O Ratio on the Stripping of Cu(II) and Ag(I)

The effects of the A/O ratio on the stripping of Cu(II) and Ag(I) from the loaded LIX63 using 4 mol/L HNO₃ were investigated by varying the A/O ratio from 1:2 to 3:1. A two-stage counter-current extraction process at an A/O ratio of 1:2 was performed to prepare the loaded LIX63. A synthetic leaching solution with 0.001 mol/L HNO₃ was used as a feed solution, and 2 mol/L LIX63 was used as an extractant. The concentrations of Cu(II) and Ag(I) in the loaded LIX63 were 1 × 10⁻² and 1.5 × 10⁻³ mol/L, respectively. Accordingly, 4 mol/L HNO₃ was used as a strippant in the stripping experiments.

![Figure 5](image1.png)

**Figure 5.** Stripping percentages of Cu(II) and Ag(I) at various HNO₃ concentrations.

![Figure 6](image2.png)

**Figure 6.** Stripping percentages of Cu(II) and Ag(I) at various thiourea concentrations.
The results (Figure 7) indicated that the stripping percentage of Cu(II) increased sharply with an increase in the A/O ratio from 1:2 to 2:1 whereas that of Ag(I) increased slightly. The complete stripping of Cu(II) was achieved, when the A/O ratio exceeded 2:1. Over this A/O ratio range, the stripping percentage of Ag(I) was lower than 10%. Thus, in the subsequent stripping experiments, selective stripping of Cu(II) was performed by using 4 mol/L HNO$_3$ and an A/O ratio of 2:1 in one stage. Moreover, 10% of Ag(I) was co-stripped, indicating that the purity of Cu(II) in the stripping solution was 95.2%. The removal of Ag(I) from the stripping solution by cementation with a copper sheet is a potential method of increasing the purity of Cu(II) in the stripping solution.

![Figure 7](image.png)

**Figure 7.** Effects of the A/O ratio on the stripping percentages of Cu(II) and Ag(I) using 4 mol/L HNO$_3$.

### 3.6. Effects of the A/O Ratio on the Stripping of Ag(I) with Thiourea

After the removal of Cu(II) from the loaded LIX63, thiourea was employed for the stripping of Ag(I) from the loaded LIX63. To investigate the effect of the A/O ratio on the stripping of Ag(I), stripping experiments were performed by varying the A/O ratio from 1:2 to 3:1. The loaded LIX63, as discussed in Section 3.5, was employed, and the concentration of Ag(I) in the loaded LIX63 was $1.35 \times 10^{-3}$ mol/L. Accordingly, 0.1 mol/L thiourea was used as a strippant in these stripping experiments.

The results indicated that the stripping percentage of Ag(I) increased from 60% to 97.7% as the A/O ratio increased from 1:2 to 3:1. A McCabe–Thiele diagram for the stripping of Ag(I) was constructed to represent the results (Figure 8). Figure 8 indicates that two counter-current stripping stages were required for the complete stripping of Ag(I) from the loaded LIX63 at an A/O ratio of 1:1. LIX63 can be regenerated after the stripping of Ag(I) using 0.1 mol/L thiourea.

Two-stage counter-current batch simulation stripping experiments were performed to verify the results obtained from the McCabe–Thiele diagram. The loaded LIX63 after the removal of Cu(II) using 4 mol/L HNO$_3$ at an A/O ratio of 2:1 in one stage was used. After the two-stage counter-current stripping using 0.1 mol/L thiourea at an A/O ratio of 1:1, 99.2% of Ag(I) was stripped. The concentration of Ag(I) in the obtained stripping solution was $1.34 \times 10^{-3}$ mol/L. This indicated that the purity of Ag(I) was higher than 99.993% (detection limit: 0.01 mg/L).
Figure 8. McCabe–Thiele plot for the stripping of Ag(I) using 0.1 mol/L thiourea.

Compared to the reported results (Table 1) [31], the purity of Cu(II) in the recovered solution was low (95.2%); however, by using the present process, Cu(II) and Ag(I) can be separated and recovered using a unique extractant (LIX63). Further, when simultaneous extraction of Cu(II) and Ag(I) was achieved by using Cyanex 301, only aqua regia was suitable for their stripping from loaded Cyanex 301 [31]. Thus, the proposed process is advantageous in that the simultaneous extraction of Cu(II) and Ag(I) is achieved by using LIX63 and the stripping of Cu(II) and Ag(I) is achieved by using HNO$_3$ and thiourea solutions, respectively.

4. Conclusions

A solvent-extraction process was developed to recover Cu(II) and Ag(I) from a nitrate leaching solution of industrial dust arising during the pyrometallurgy of spent camera modules. A flow chart for the proposed process is illustrated in Figure 9. From the leaching solution, Cu(II) and Ag(I) were selectively extracted by using LIX63 at an A/O ratio of 1:2 in two stages, leaving Ni(II), Mg(II), and Al(III) in the raffinate. The complete stripping of Cu(II) with a 10% stripping percentage of Ag(I) from the loaded LIX63 was achieved by using 4 mol/L HNO$_3$ at an A/O ratio of 2:1 in one stage. After the removal of Cu(II), Ag(I) from the loaded LIX63 was recovered via stripping by using 0.1 mol/L thiourea at an A/O ratio of 1:1 in two stages. Finally, the feasibility of this process was verified via batch counter-current simulation extraction and stripping experiments. A Cu(II) solution with a 95.2% purity and a Ag(I) solution with a 99.993% purity were obtained. In future, strategies to increase the purity of the obtained Cu(II) solutions can be developed.
Figure 9. Flow chart of the proposed process for the separation of Cu(II) and Ag(I) from a nitrate leaching solution of industrial dust.

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