Comparison of various extractants for recovery of Copper from Sarcheshmeh Chalcopyrite concentrate Ammonia/Ammonium Carbonate Leaching

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Abstract

Solvent extraction of copper from the copper leach solution obtained from the ammoniacal carbonate leaching of the Sarcheshmeh copper concentrate was carried out, and the performance of CP-150, LIX984N, and Kelex100 as well as the effects of different parameters involved were investigated. According to the results obtained, the extraction kinetics of all the three extractants was fast. High concentrations (7.5%, V/V) of CP-150 and Kelex100 were required to completely extract copper, while only 1% of LIX984N was sufficient. Addition of hexane to the diluent decreased the capability of CP-150 to extract copper, while it showed less effects on LIX984N and Kelex100. A desirable stripping of copper from the loaded organic phase could be obtained using H₂SO₄ solution.

Keywords: Copper, Ammoniacal Carbonate Leaching, Kelex 100, LIX984N, CP-150.

1. Introduction

The Sarcheshmeh copper mine is located in the Kerman Province, Iran. The Sarcheshmeh copper complex involves production units of the mine itself, concentrator, smelter, refinery, foundries, and leaching with the capacity of 160,000 tons/year of chalcopyrite concentrate. Various leaching and bioleaching processes for the Sarcheshmeh copper concentrate have been studied [1-3]. The main disadvantages of these processes are their slow kinetics and low copper recovery.

Use of ammonia as an attractive alternative is favorable due to its high complexation characteristics with copper, low toxicity, low cost, and ease of regeneration by evaporation. Furthermore, the major waste components of the ores such as Fe₂O₃, SiO₂, CaO, and MgO are insoluble in ammoniacal solutions, which allow a selective copper extraction [4, 5]. Radmehr et al. have reviewed the applications of ammonia leaching in copper industry, and reported the advantages and disadvantages of this method [6].

Ammoniacal leaching of the Sarcheshmeh chalcopyrite concentrate has been studied by Nabizadeh et al. [7]. According to their results, about 70% of copper was effectively extracted at 60 °C; the ammonia/ammonium carbonate concentrations were 5 M NH₃ + 0.3 M (NH₄)₂CO₃, the agitation speed was 1000 rpm, the solid to liquid ratio was 1:20 g/mL, the oxygen flow rate was 1 L/min, the leaching time was 240 min, and 80% of the passing size was finer than 42 μm.

In order to recover copper from ammoniacal solutions, different methods including precipitation and cementation [8, 9], solvent extraction [10-13], and selective electro-winning [14] have been used.

Solvent extraction is very attractive since it has many advantages like ease of operation, low energy requirement, and ability to handle a wide range of feed concentration [10, 11]. Extraction of copper from ammoniacal leach liquors has been investigated by several investigators, and different extractants have been tested (Table 1).
Hydroxyoximes such as LIX973N, LIX26, LIX84-I, LIX54, and LIX984N are now widely used as extractants for copper solvent extraction in hydrometallurgy. Some of these extractants show a strong extraction of copper from acidic solutions [23]. These extractants also present a high quality for copper in ammoniacal solutions (Table 1).

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Medium</th>
<th>Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIX973 N</td>
<td>Ammoniacal carbonate</td>
<td>Organic phase: 2.5-20%, V/V; Temperature: 20-60 ºC; Ammonium carbonate: 10-100 g/L</td>
<td>[11]</td>
</tr>
<tr>
<td>LIX84</td>
<td>Ammoniacal carbonate</td>
<td>Organic phase: 40%, V/V; Temperature: 20 ºC; Ammonium sulfate: 90 g/L</td>
<td>[12]</td>
</tr>
<tr>
<td>LIX973 N</td>
<td>Ammoniacal carbonate</td>
<td>Organic phase: 5%, V/V; Temperature: 25 ºC; Ammonium carbonate: 10 g/L</td>
<td>[13]</td>
</tr>
<tr>
<td>LIX26</td>
<td>Ammoniacal carbonate</td>
<td>Organic phase: 5%, V/V; Temperature: 20 ºC; Ammonium sulfate: 0.5 mol/L</td>
<td>[15]</td>
</tr>
<tr>
<td>LIX84I</td>
<td>Ammoniacal carbonate</td>
<td>Organic phase: 0.09 kmol/m³; Temperature: 20 ºC; Ammonium sulfate: 0.2 mol/L</td>
<td>[16]</td>
</tr>
<tr>
<td>β-diketone (LIX54)</td>
<td>Ammoniacal chloride</td>
<td>Organic phase: 20%, V/V; Temperature: 20 ºC; Ammonium chloride: 2 mol/L</td>
<td>[17]</td>
</tr>
<tr>
<td>β-diketone (LIX54)</td>
<td>Ammoniacal chloride</td>
<td>Organic phase: 20%, V/V; Temperature: 20 ºC; Ammonium chloride: 2 mol/L</td>
<td>[18]</td>
</tr>
<tr>
<td>β-diketone (LIX54)</td>
<td>Ammoniacal chloride</td>
<td>Organic phase: 1 mol/L; Temperature: 20 ºC; Ammonium chloride: 3 mol/L</td>
<td>[4]</td>
</tr>
<tr>
<td>β-diketone (LIX54)</td>
<td>Ammoniacal chloride</td>
<td>Organic phase: 0.2 mol/L; Temperature: 20 ºC; Ammonium chloride: 1 mol/L</td>
<td>[19]</td>
</tr>
<tr>
<td>LIX84I, LIX984N, LIX54-100</td>
<td>Ammoniacal carbonate</td>
<td>Organic phase: 10%, V/V; Temperature: 20 ºC; Ammonium sulfate: Unknown</td>
<td>[20]</td>
</tr>
<tr>
<td>β-diketone (LIX54)</td>
<td>Ammoniacal carbonate</td>
<td>Organic phase: 0.6 mol/L; Temperature: 20 ºC; Ammonium chloride: 2 mol/L</td>
<td>[21]</td>
</tr>
<tr>
<td>LIX54, cinnamate, β-diketone (LIX54)</td>
<td>Ammoniacal carbonate</td>
<td>Organic phase: 20%, V/V; Temperature: 25 ºC; Ammonium carbonate: 14.6 g/L</td>
<td>[22]</td>
</tr>
</tbody>
</table>

Using CP-150, Kelex100, and LIX984N as the extractants. The effects of different parameters such as the extractant concentration, contact time, diluent type, initial pH in the aqueous phase, and phase ratio were investigated.

### 2. Materials and methods

Ammoniacal carbonate leach solution was prepared according to Nabizadeh et al. [7]. Chalcopyrite concentrate was obtained from the Sarcheshmeh copper complex, Kerman, Iran. The main copper mineral was chalcopyrite, and the Cu grade was 25%. Ammonia solution (25%), ammonium carbonate, and sulfuric acid were provided from Merck (Germany). Commercial grade Kelex100 (7-(4-ethyl-1-methylocty)-8-hydroxyquinoline), as an extractant, was obtained from Nanjing Odyssey Chemical Industrial Company (China), while the other commercial extractants LIX984N (a mixture of LIX84I, 2-hydroxy-5-nonylacetophenone oxime, LIX860, 5-nonylsalicylaldoxime), and CP-150 (5-nonyl salicylaldoxime) as well as commercial rissole (mixture of rissole 8401, 8411, and kerosene) as a diluent were provided from the Sarcheshmeh Copper Complex. Analytical grade kerosene and n-hexane was obtained from Fluka (Germany). Copper extraction/stripping experiments were carried out using 100-mL beakers, a magnet, and a
magnetic stirrer (700 rpm) at different aqueous to organic phase ratios. Then the solution obtained from the solvent extraction process stayed in the separating funnel for settling. All the extraction and stripping experiments were carried out at the ambient temperature (25 °C). The samples were analyzed using atomic absorption spectroscopy (AAS), Perkin-Elmer 2100. The ammonia content was determined by the Nessler’s reagent spectroscopy method. The FT-IR spectra for pure extractants and loaded organic phases were obtained on a BRUKER FT-IR EQUINOX 55 instrument spectrometer in KBr disks. All samples were studied in the wavelength range of 400-4000 cm⁻¹. Also the results obtained were analyzed by the OPUS spectroscopy software.

3. Results and discussion

3.1. Effect of extractant concentration

Extraction of copper was performed using various solvents diluted in kerosene. Various concentrations of CP-150, LIX984N, and Kelex100 were tested and compared. The results obtained are presented in Figure 1.

As indicated, the kinetics of copper extraction using CP-150, Kelex100, and LIX984N was fast, and 100% of Cu was extracted within 1 min.

3.2. Kinetics of copper extraction

The effect of contact time on copper extraction from ammoniacal leach liquor was studied (Figure 2).

3.3. Effect of diluent type

The effect of diluent type on copper extraction from ammoniacal leach solution was studied using an organic phase of 7.5% (V/V) CP-150, LIX984N, and Kelex100 in kerosene, hexane, and their 50-50% mixture (Figure 3).

According to Figure 3, the best results were obtained using kerosene or rissole. CP-150 was more sensitive to the diluent type compared to the other two. The hexane addition reduced the copper extraction. The first reason is that in extraction through the cation exchange mechanism, the diluents having the least dielectric constant (e.g. kerosene) lead to the best extractions. This is because such diluents do not favor polymerization of the extractant in the organic phase through hydrogen bridges [24]. The dielectric constants for kerosene and hexane were 1.8 and 2, respectively. Secondly, according to Bishop et al. [25], 10 to 20% aromatic range gives a higher extraction and the fastest break times. The major components of kerosene are branched and straight-chain alkanes and naphthenes (cycloalkanes), which normally account for at least 70% by volume. Aromatic hydrocarbons in this boiling range such as alkylbenzenes (single ring) and alkynaphthalenes (double ring) do not normally exceed 25% by volume of kerosene. Addition of hexane to kerosene decreases the aromaticity of the diluent, and, therefore, the extraction of copper.
3.4. Effect of aqueous pH

The effect of pH on copper extraction was determined using the organic phase of 7.5% (V/V) extractant in rissole diluent. The aqueous pH was adjusted to 10-13. The results obtained for the three extractants were similar, and one CP-150 is shown in Figure 4. As indicated, the extraction percentage of copper decreases slightly with increase in the initial pH.

Some researchers have reported a decrease in copper extraction from ammoniacal solution at pH values beyond 8 [19, 25]. Hu et al. [19] have mentioned that this phenomenon should mainly result from the formation of copper complexes. Rao et al. [25] have proposed that copper ammine complexes are non-extractable; however, He et al. believed that the formation of these complexes only restrained the extraction of copper because copper extraction could be promoted by increasing the extractant concentration.

3.5. Ammonia co-extraction

The ammonia co-extraction was measured and determined to be less than 0.04 mole NH₃ per mole Cu. Similar phenomena were also observed by Fu et al. [4], Hu et al. [14], and Flett et al. [26, 27]. According to Hu et al. [14], oxime molecules (HA) hardly extract ammonia in the absence of copper ion, whereas a very small quantity of ammonia can be extracted by coordinating with copper extracts into the organic phase. In their work, the average number of ammonia per copper extract was 0.053 [17]. Flett et al. [26] found that the copper loaded organic phase could extract a small amount of ammonia when LIX54 was used as the extractant (0.012-0.026 mol NH₃ per mol Cu).

3.6. Loading capacity

The loading capacity of the extractants was determined using an organic solution of 7.5% (V/V) at 20 °C and 10 min but various A/O phase ratios (1:1 to 1:10). The experimental results showed that the loading capacity of CP-150, LIX984N, and Kelex100 was 6.7, 14.5, and 27 g/L, respectively.
3.7. Extraction isotherm
An extraction isotherm defines the maximum amount of copper that can be removed from PLS for each organic to aqueous volumetric ratio (A/O). In order to determine the number of stages for a given phase ratio for all the three extractants, the copper loading isotherms were obtained using ammoniacal solution as aqueous phase. Figure 5 shows the extraction isotherms for CP-150, Kelex100, and LIX984N.

Figure 5. McCabe-Thiele plot for copper extraction from ammoniacal leach solution using (a) CP-150, (b) kelex100, and (c) LIX984N, \([\text{CP-150}]_{\text{org}} = [\text{Kelex100}]_{\text{org}} = [\text{LIX984N}]_{\text{org}} = 7.5\% \text{ (V/V)}\) in rissole.
The McCabe-Thiele diagrams for CP-150, Kelex100, and LIX984N (Figure 7) revealed that the quantitative copper extraction could be achieved in two counter-current stages at an A/O ratio of 1:1, where the copper extraction of CP-150, Kelex100, and LIX984N in a single stage was 99.6%, 99.96%, and 100%, respectively.

### 3.8. Copper extraction mechanism

Since CP-150, Kelex100, and LIX984N are weak acid chelating agents, they extract copper via a cation exchange mechanism (the extractants are denoted by HA):

$$\text{Cu}^{2+} (\text{aq}) + n\text{HA}_{(\text{org})} \leftrightarrow \text{CuA}_2^{-} (\text{org}) + 2\text{H}^+ (\text{aq})$$

(3)

The equilibrium constant, $K_{\text{cu}}$, of the reaction is obtained as below:

$$K_{\text{cu}} = \frac{[\text{CuA}_2^{-} (\text{org})][\text{H}^+]^2 (\text{aq})}{[\text{Cu}^{2+}] (\text{aq})[\text{HA}]^n (\text{org})}$$

(4)

$$K_{\text{cu}} = D_{\text{cu}} [\text{H}^+]^2 (\text{aq}) / [\text{HA}]^n (\text{org})$$

(5)

where,

$$D_{\text{cu}} = \frac{[\text{CuA}_2^{-} (\text{org})][\text{H}^+]^2 (\text{aq})}{[\text{Cu}^{2+}] (\text{aq})}$$

(6)

Taking logarithm of Eq. (1) and rearranging it, Eq. (3) is obtained as:

$$\log D_{\text{cu}} = n \log [\text{HA}] (\text{org}) + \log K_{\text{cu}} + 2pH$$

(7)

In order to determine the stoichiometric of the extracted species, the slope analysis method was used. In this work, the aqueous solutions containing 0.37 M Cu$^{2+}$ and 0.27 M total ammonia at an initial pH of 11 were mixed with CP-150, Kelex100, and LIX984N of different concentrations at an A/O ratio of 1/1.

According to Figure 6, the slope of the straight line was found to be near 2 for the three extractants, indicating that the number of extractant molecules involving in the extracted species was 2.

Based on this stoichiometric relation, the copper extraction reaction with CP-150, Kelex100, and LIX984N could be expressed as below:

$$\text{Cu}_{(\text{aq})}^{2+} + 2\text{HA}_{(\text{org})} \leftrightarrow \text{CuA}_2^{-} (\text{org}) + 2\text{H}^+ (\text{aq})$$

(8)

### 3.9. FT-IR studies

The FT-IR spectra for the pure extractants and copper-loaded organic phases containing 7.5% (V/V) extractant in rissole were obtained and compared (Figure 7). For all of the three pure extractants, the peak for O-H bond could be observed at the wavelength of 3400 cm$^{-1}$. During the extraction process, presence of NH$_3$ breaks the O-H bond, and the peak disappears in the spectrum of the organic phase. An appropriate mixing of aqueous and organic phases could be concluded by vanishing the mentioned peak. The peak at 1624 cm$^{-1}$ (related to the C=N-H bond in the oxime structure) disappeared after the N-Cu bond formation during the extraction process. According to the FT-IR spectra, the stable chelate of Cu with the extractant molecule formed. The proposed chemical structure for the copper extract is shown in Figure 8.
Figure 7. FT-IR spectra for pure extractant and loaded organic phase; (a) CP-150, (b) Kelex100, and (c) LIX984N.
3.10. Copper striping
3.10.1. Effect of sulfuric acid concentration
The copper in the loaded organic phases with 7.5% HA (V/V) was stripped with different concentrations of H₂SO₄ solution at a 1/1 phase ratio for 10 min; then the solutions were settled and separated by gravity. The experimental results are given in Figure 9.

Figure 9. Effect of concentration of H₂SO₄ solution on copper extraction from loaded organic phase; O/A ratio, 1/1; temperature, 25°C; and contact time, 10 min.
As shown, the stripping efficiency increases by increasing the acid concentration. While a high copper stripping of 85% from LIX984N can be obtained using 1 M H₂SO₄ solution, only 80% of copper was recovered from Kelex100 using 6 M H₂SO₄ solution.

The extraction mechanism of copper from ammoniacal leach solution is cation exchange. Thus in the stripping process, the reaction is reversed by adding concentrated acid. During the stripping process, the hydrogen ions displace the metal ions from the organic phase.

4. Conclusions
A comparative study of various organic solvents for extraction of copper from the copper leach solution obtained from the ammoniacal carbonate leaching of the Sarcheshmeh copper concentrate was carried out, and the performance of CP-150, LIX984N, and Kelex100 was evaluated. The results obtained showed that the extraction kinetics was fast for all the three extractants. The copper extraction efficiency was improved with increase in the concentration of extractant. A higher concentration (7.5%) of CP-150 and Kelex100 was required for a complete extraction of copper compared with 1% LIX984N. The slope analysis suggested that the copper chelated a copper:reagent mole ratio of 1:2. Increasing the diluent aromaticity by hexane addition decreased the extraction of copper. A desirable stripping of copper from the loaded organic phase could be obtained using H₂SO₄ solution. While the high copper stripping of 85% from LIX984N could be obtained using 1 M H₂SO₄ solution, only 80% of copper was recovered from Kelex100 using 6 M H₂SO₄ solution.

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References


مقایسه عملکرد استخراج کننده‌های مختلف برای استخراج مس از محلول حاصل از لیچینگ آمونیاکی کنسانتره کالکوپیری بی‌سروچمته

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چکیده:
در این پژوهش، استخراج مس از محلول حاصل از لیچینگ آمونیاکی کنسانتره کالکوپیریتی مجتمع مس سرچشمه سرچشمه مطالعه شد و عملکرد استخراج کننده‌های CP-150، LIX984N و Kelex100 مورد بررسی قرار گرفت. بر اساس نتایج، سینتیک استخراج مس توسط همه استخراج کننده‌های مورد استفاده سریع بود. در حالی که برای استخراج کامل مس، غلظت بالای 5/1 درصد حجمی از استخراج کننده‌های CP-150 و Kelex100 مورد نیاز بود، تنه‌اکننده غلظت 7 درصد از LIX984N کفایت کرد. افزودن هگزا ن به رقیق کننده سبب کاهش قدرت استخراج CP-150 در حالت که این کننده بر قدرت استخراج LIX984N و Kelex100 ناچیز بود اثری نداشت. استریپ مس از فاز آبی باردار با استفاده از محلول اسید سولفوریک انجام شد.

کلمات کلیدی: مس، لیچینگ آمونیاکی، CP-150، LIX984N، Kelex100