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Two-stage countercurrent solvent extraction of copper from cuprous chloride solution: Cu(II) loading coupled with Cu(I) oxidation by oxygen and iron scrubbing

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ABSTRACT

This study was conducted as part of the development of a novel process for copper recovery from copper sulfide concentrates by chloride leaching, simultaneous cuprous oxidation and cupric solvent extraction to transfer copper to a conventional sulfate electrowinning circuit and hematite precipitation to reject iron. Four LIX reagents (LIX84-I, LIX612N-LV, XI-04003 and LIX984N) were used as extractants while kerosene was used as a diluent. Copper was effectively extracted into LIX reagent organic solution from chloride solution. However, iron co-extraction exceeded 0.5 g/L. Two-stage countercurrent solvent extraction is proposed to reduce iron extraction. In the first stage, copper-loaded organic solution was pre-scrubbed by contacting with the cuprous and ferrous chloride pregnant leach solution. The extent of iron removal increased from 78 to 91 to 95% with decreasing pH from 1.0 to 0.5 to 0.0 while the extent of copper removal increased from 1 to 17 to 36%. Although more iron was removed at a pH below 0.5, copper was removed to an unacceptable level. Therefore, it is recommended that pH should be controlled around 1.0 to remove the bulk of the loaded iron while avoiding excessive copper stripping. In the second solvent extraction stage, copper is loaded into the organic solution by simultaneous cuprous oxidation by oxygen and cupric extraction. After two-stage counter current solvent extraction, the organic solution was further scrubbed by contacting with copper sulfate (4 g/L Cu) and sulfuric acid (15 g/L) solution. The iron extraction was reduced to a satisfactory level at an A/O ratio of 1/40 to 1/20 while the copper extraction practically did not change. The Cu/Fe ratio in the copper-loaded organic solution can meet the industrial requirement.

1. Introduction

Ferric and/or cupric chloride leaching processes have been extensively studied to treat sulfide concentrates of copper, lead and zinc (Dutrizac, 1992; Peters, 1977). Chloride leaching has several advantages over sulfate systems: (1) supporting high metal solubility, (2) enhanced redox behavior, (3) increased rates of leaching and (4) the formation of predominantly elemental sulfur. In a chloride system, both cuprous and cupric ions are stabilized through complexation with chloride ions. Copper can be efficiently extracted into chloride solution from chalcopyrite concentrates and a copper extraction of 99% can be reached at a temperature below 100 °C using a two-stage countercurrent chloride leach circuit (Lu and Dreisinger, 2013a,b). Compared to the conventional sulfate system, one challenge for the chloride system is to produce high quality copper since some impurities such as silver are not removed efficiently from chloride solution and dendritic copper cathodes are produced by electrowinning from chloride solution. The high surface area dendrites are difficult to wash to remove surface contamination.

Generally there are four processes to recover copper from chloride solution: (1) the precipitation of CuCl at lower temperature and reduction to Cu in the UBC-Cominco and the Cymet processes (Dutrizac, 1992; Peters, 1977), (2) the direct electrowinning of Cu from chloride solution (Moyes et al., 2000), (3) the precipitation of Cu_2O and reduction to Cu with hydrogen (Hyvarinen and Hamalainen, 2005) and (4) the solvent extraction of copper into a sulfate system from a chloride system and electrowinning of copper from sulfate media (Demarthe et al., 1976; Liddicoat and Dreisinger, 2007). The first two methods may result in impure copper (such as contamination with silver) while the third one is generally suitable for leach solution containing a small amount of iron and other impurities. The fourth one can generate high purity copper since the impurities are separated from copper by solvent extraction.

With the use of solvent extraction to transfer copper to a conventional sulfate electrowinning circuit from a chloride leaching system, the advantages of the chloride leaching system can be well utilized. The transfer of copper from a Cu(I) chloride solution to a Cu(II) sulfate solution requires extraction with a hydroxyoxime extractant (HR) as is used normally in the processing of sulfate-based copper leach solutions. The solvent extraction process for copper recovery involves simultaneous cuprous oxidation by oxygen and cupric solvent extraction:

$$4CuCl + 4HR(org) + O_2 = 2CuR_2(org) + 2CuCl_2 + 2H_2O. \quad (1)$$

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Half of the copper in aqueous solution is extracted into organic solution. Conveniently, the remaining copper as cupric chloride in the raffinate from solvent extraction serves as a leaching agent upon recycle.

Four LIX extractants (LIX84-I, LIX612N-LV, XI-04003 and LIX984N) from BASF were tested since they have a high selectivity for copper over iron. LIX84-I is formulated with a C9 ketoxime. LIX984N is a 50:50 mixture of LIX860N-I (C9 aldoxime) with LIX84-I. XI-04003 is formulated with a C12 aldoxime and LIX612N-LV is formulated with a C9 aldoxime. Both are formulated with a ketone as a modifier to the same degree of modification. If properly formulated, they should give identical performance within the limits of error of the experiment.

Copper can effectively be extracted into organic solution containing the above four LIX reagents from copper chloride solution with minimum transfer of impurities (Lu and Dreisinger, 2013c,d). However, the final iron extraction after the extraction of half of the copper from chloride solution reached an unacceptable level, which can significantly affect copper electrowinning from sulfate media. Therefore the iron extraction must be decreased. A typical ratio of Cu/Fe in a copper-loaded organic phase exceeds 500 in normal solvent extraction practice. The co-loading of iron with copper is a result of Reaction (2) below.

$$4FeCl_2 + 6HR(org) + O_2 = 2FeR_3(org) + 2FeCl_3 + 2HCl + 2H_2O \quad (2)$$

Two-stage countercurrent solvent extraction is proposed to reduce iron extraction. In the first stage, no oxygen is introduced. A copper-loaded organic phase is pre-scrubbed by contacting with pregnant cuprous and ferrous leach solution to remove iron. In the second stage, oxygen is introduced to load copper into the organic solution. The oxidative loading of copper (and iron) is shown in Reactions (1) and (2) and the removal of iron (and possibly some copper) in the countercurrent scrubbing process is shown in the reactions below.

$$FeR_3(org) + CuCl + HCl = FeCl_2 + CuR_2(org) + HR(org) \quad (3)$$

$$CuR_2(org) + 2HCl = CuCl_2 + 2HR(org) \quad (4)$$

After solvent extraction, the copper-loaded organic solution must be washed to remove entrained aqueous solution and especially prevent the transfer of excess chloride to electrowinning. Washing solution can be made by mixing copper sulfate electrolyte and water (Virnig and Fisher, 2003). A typical wash solution composition contains around 15 g/L H_2SO_4 and 3–4 g/L Cu. When the washing solution is contacted with the copper-loaded organic solution, iron can further be scrubbed.

The objective of this study is to find a way to minimize iron extraction during copper solvent extraction and effectively scrub iron from copper-loaded organic solution. This study was necessary for the development of a novel process for copper recovery from chalcopyrite concentrates by chloride leaching, simultaneous cuprous oxidation and cupric solvent extraction to transfer copper to a conventional sulfate electrowinning circuit and hematite precipitation to reject iron.

2. Experimental

2.1. Apparatus

Copper loading was conducted in a 400-mL glass reactor with three glass baffles and a rubber stopper fitted with a sleeve to house an impeller, a gas dispersion tube, a pH probe and other openings (Fig. 1). The reactor was placed in a water bath and the temperature was maintained at 40 ± 0.2 °C. The temperature of pregnant leaching solution can be as high as 90 °C. At a higher temperature, the solvent extraction is faster and the organic solution is less viscous. However the organic reagent degrades rapidly at a temperature above 40 °C. If the solvent extraction is conducted below 40 °C, the leaching solution has to be cooled down at an additional cost. Therefore 40 °C was selected for this study. The titanium stirrer was made of 5-mm diameter rod with a 25-mm diameter 45° pitched blade impeller and was driven via overhead motors.

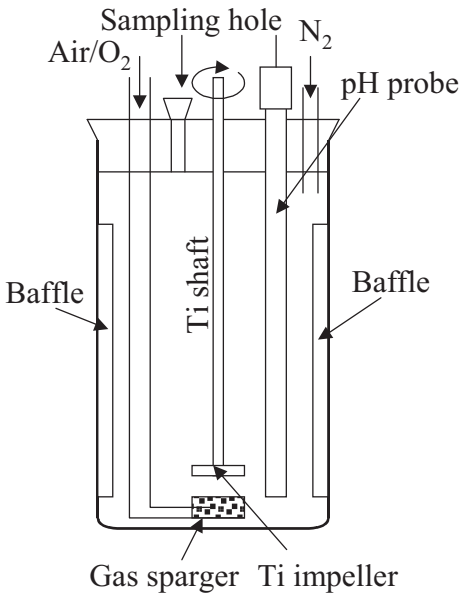

Fig. 1. A schematic diagram of the glass reactor for oxidation–solvent extraction.

Scrubbing loaded organic solution using ferrous and cuprous chloride solution was also conducted in the reactor shown in Fig. 1 under a nitrogen environment without the use of an oxygen gas sparger. Scrubbing loaded organic solution using copper sulfate and sulfuric acid solution was conducted manually in a separatory funnel.

2.2. Experimental procedures

The procedures for copper loading are:

(1) A required amount of organic solution is added into the reactor and it is then purged with nitrogen gas.
(2) The pregnant cuprous and ferrous chloride solution is transferred to the reactor under a nitrogen atmosphere.
(3) The mixture of aqueous and organic solutions is stirred and then air or oxygen is introduced to the reactor.
(4) The pH is monitored and recorded and the sample is taken using a syringe.
(5) The sample is centrifuged to separate aqueous and organic phases.
(6) The organic and aqueous samples are taken for analysis using a pipette.
(7) The final aqueous and organic solutions were separated using a separatory funnel.

The procedures for pre-scrubbing the copper-loaded organic solution using pregnant cuprous and ferrous chloride solution are:

(1) A required amount of the copper-loaded organic solution is added into the reactor and it is then purged with nitrogen gas.
(2) The pregnant cuprous and ferrous solution is transferred to the reactor under a nitrogen atmosphere.
(3) The mixture of aqueous and organic solutions is stirred and the pH is adjusted to a target value by the addition of sulfuric acid solution.
(4) The mixture is transferred to a separatory funnel to separate the aqueous and organic solutions.
(5) The aqueous solution is filtered using Whatman No. 3 filter paper to remove entrained organic solution while the organic