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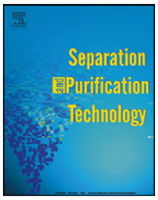

Recovery of copper from zinc leaching liquor using ACORGA M5640

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ABSTRACT

The present paper describes the solvent extraction and separation of Cu(II) from a leaching liquor obtained by the direct atmospheric leaching of a zinc concentrate with an oxidative mixture of $Fe_2(SO_4)_3$ (0.4 M) and H_2SO_4 (0.5 M) in the presence of O_2 at 353 K. The obtained solution, containing 1.35 g L^{-1} Cu(II), 5 mg L^{-1} In(III), 41 g L^{-1} Fe {20% Fe(III), 80% Fe(II)}, and 34 g L^{-1} Zn(II), was extracted with 25% (v/v) solution of ACORGA M5640 (modified with 12.5% (v/v) isodecanol). Quantitative (>98%) and selective transfer of Cu(II) in to the organic phase was achieved in pH range of 1.3–1.5 (A/O = 1). The presence of isodecanol in the extractant solution helped in obtaining complete stripping of copper. Three stages of extraction at an A/O ratio of 5 concentrated the initial metal content $\{Cu(II)_{\text{initial-aqueous}} = 1.35\ g\ L^{-1}\}$ in the organic phase $\{Cu(II)_{\text{after extraction, in LO}} = 6.6\ g\ L^{-1}\}$. This extraction was selective over Zn(II), Fe(II), Fe(III), and In(III). The loaded organic phase was scrubbed with 20 g L^{-1} H_2SO_4 followed by the stripping of Cu(II) with 25 g L^{-1} of Cu^{2+} in 180 g L^{-1} of H_2SO_4 (A/O = 1, two stages).

Introduction

Solvent extraction and recovery of copper from secondary sector and other waste streams is considered as economically and environmentally beneficial [1]. The oxidative pressure leaching or the direct atmospheric leaching of sulphidic concentrates, coupled with the solvent extraction, would cut short the emission of greenhouse gases and is also estimated to be more economical compared to the conventional roasting–leaching–electrowinning processing route. The potential of SX has yet to be fully realized for the parallel recovery of copper from the metallurgical solutions of zinc, cobalt and nickel processing industries. Zinc production from these leaching liquors has to be processed through a number of metal separation steps, e.g. the oxidation of Fe(II), precipitation of the resulting Fe(III) into jarosite/goethite/hematite slurry, cementation of Cu(II), and the solvent extraction of Zn(II). The precipitation and to some extent the cementation parts of the purification process pose two significant problems. Metal contents of value are lost and the solid wastes generated require special landfills for their disposal.

Solvent extraction has the potential to recover pure copper from the zinc leaching solutions. Selective Cu(II) extractants are frequently available in the market. Various hydroxyoximes are known for their selective nature toward Cu(II). Amongst them, the ketoximes and the aldoximes are reported to be useful for the extraction of Cu(II) from the acidic leach solutions [2]. At times, the mixture of ketoximes and aldoximes offers desired advantages in the terms of better extraction kinetics, and easier stripping. COGNIS and CYTEC sell several such oximes under the brand name of LIX and ACORGA, respectively. Though both of these brands share more or less comparable industrial applications, LIX reagents have been more thoroughly investigated [3–6]. LIX 84 and 84-I have been reported for the recovery of Cu(II) at different levels, including the secondary processing [3,5]. LIX 622 has also been suggested for the recovery of Cu(II) from acidic sulphate solutions [7]. Amongst the ACORGA reagents, M5640 is one of the most widely used Cu(II) extractants on commercial levels [8,9]. It is a strong Cu(II) extractant with the presence of a fatty ester to modify stripping characteristics. ACORGA M5640 has been used for the extraction of Cu(II) from both the sulphate and nitrate mediums [8–13]. This reagent is known for its Cu(II) selective nature, more specifically with respect to Fe(III) [8,9], and it seems suitable vis-à-vis the objectives undertaken herein.

ACORGA M5640, being a very strong Cu(II) extractant, normally offers stripping of up to around 95% of total extracted metal ion. Recovery of Cu(II) from ACORGA M5640 phase loaded with small concentration of the metal ion has not been reported. In this paper, the objective of the research is to explore ACROGA M5640 extractant for the recovery of small concentration of Cu(II) from the leaching solution of a zinc concentrate. ACORGA M5640 has not earlier been reported for the recovery of copper from dilute solutions because it was not possible to strip the extracted metal beyond a particular concentration. The authors have attempted to extract around 1.2 g L^{-1} Cu(II) by keeping a high A/O ratio so as to pre-

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concentrate the metal ion in the organic phase followed by its quantitative stripping. The selectivity of ACORGA M5640 for copper extraction with respect to some generally associated metals, such as indium, iron and zinc, has also been studied. The procedure has been extended to recover pure Cu(II) from a direct atmospheric leachate of zinc concentrate sample from Somicor, Portugal. Several parameters, including the effect of the equilibrium pH, extractant concentration, and modifier, on the extraction or stripping were investigated for achieving quantitative extraction and quantitative stripping of Cu(II). Extraction and stripping isotherms have been drawn to identify experimental conditions for upgrading of a synthetic spent cell electrolyte. The regeneration capacity of the proposed extraction–stripping system has been checked. The proposed procedure for the recovery of copper can also be employed for the utilization of other copper bearing low grade ores and waste materials.

Experimental

Reagents and equipment

ACORGA M5640 and ESCAID 110 (200–248 °C fraction hydrocarbon fluid with 99.5% aliphatic content) were received from Cytec Netherlands and ExxonMobil Spain, respectively. The active substance of ACORGA M5640 was 5-nonylsalicylaldoxime. A fatty ester, 2,4,4-trimethyl 1,3-pentanediol di-isobutyrate, was present as a modifier. Isodecanol, a 99% pure product from Riedel-de Haën, Germany, was used as a second modifier. All the other chemicals were of Analytical Reagent grade from Merck, UK. The working solutions of the metal ions were prepared by dissolving their suitable salts, namely, $CuSO_4{\cdot}5H_2O$, $ZnSO_4{\cdot}7H_2O$, $In_2(SO_4)_3$ and $Fe_2(SO_4)_3$, in the dilute sulfuric acid, and making up the required volume with deionized water. The pH values were measured with a Metrohm 827 pH lab pH meter using Metrohm 6.0228.010 glass electrode.

Solvent extraction procedure

The aqueous and the organic phases, contained in 250 mL separating funnels were contacted (150 rpm) in an orbital shaker ($T = 298 \pm 1$ K) for 10 min to ensure the maximum mass transfer. Further increase in the contact time of the two phases did not change the results. Wherever necessary, the pH of the aqueous phase was adjusted by adding suitable volumes of NaOH or H_2SO_4 solution. After the separation of the equilibrated phases, the metal concentration in the aqueous phase was determined by the AAS (AAnalyst 200, Perkin Elmer). The metal concentration in the organic phase was computed by the mass balance considering that the volumes of aqueous and organic phases did not change during the equilibration. The stripping of the loaded organic phase was carried out ($t = 15$ min) at 298 ± 1 K by using a synthetic spent electrolyte solution of 25 g L^{-1} Cu(II) in 180 g L^{-1} H_2SO_4 (A/O = 1) as the reagent.

Additional experimental details, wherever required, have been given along with the related results and discussion.

Leaching of the zinc concentrate

The oxidative leaching of a sample of zinc concentrate, mined from the Neves-Corvo mine, Portugal, was carried out with a mixture of 0.40 M $Fe_2(SO_4)_3$ and 0.50 M H_2SO_4 (S/L ratio = 100 g in 1 L) in a five-necked round bottom reactor (1 L, 13 cm diameter) fitted with an agitating (450 rpm) single round paddle impeller. The reaction temperature was maintained at 353 ± 3 K. Throughout the course of the experiment, oxygen gas was sparged in to the reaction vessel (60 L/h) to maintain ferric form of the oxidant. Under these conditions, the dissolution of Zn(II) took place according to the following equation

$$ZnS + Fe_2(SO_4)_3 \Rightarrow ZnSO_4 + 2FeSO_4 + S^0 \tag{1}$$

Twelve hours of the leaching reaction yielded 85 and 50% recovery of Zn(II) and Cu(II), respectively. Final total concentrations of Fe (total) and In(III) were 42 g L^{-1} {80% Fe(II), 20% Fe(III)} and 6 mg L^{-1}, respectively.

The pH of the leaching solution was observed to be 0.5. It was raised to 1.4 by slow addition of 5 M NaOH solution. Finally the leaching solution had the following composition: 1.35 g L^{-1} Cu(II), 5 mg L^{-1} In(III), 41 g L^{-1} Fe (total), and 34 g L^{-1} Zn(II).

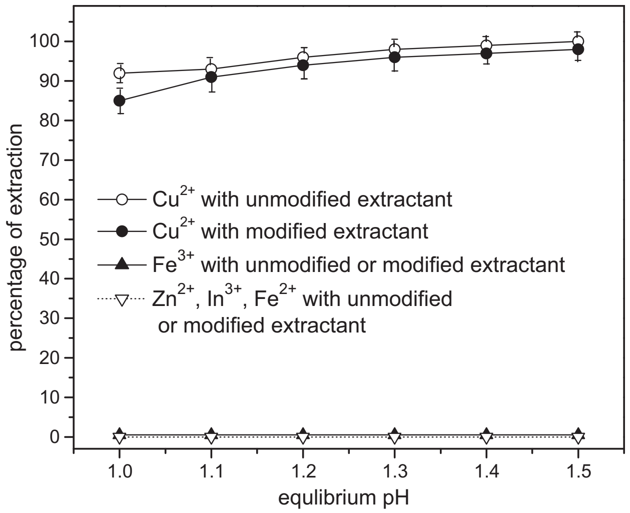

Fig. 1. Extraction of Cu(II) (0.5–2.0 g L^{-1}), Zn(II) (15–40 g L^{-1}), In(III) (1–50 mg L^{-1}), Fe(III) (1.0–40 g L^{-1}), and Fe(II) (1.0–40 g L^{-1}) in unmodified and modified (with 12.5% (v/v) isodecanol) 25% (v/v) ACORGA M5640 (A/O = 1, $T = 298$ K, $t = 10$ min).

Results and discussion

Cu(II) extraction with 25% (v/v) ACORGA M5640 (ESCAID 110) as a function of equilibrium pH

Fig. 1 shows the extraction behaviour of Cu(II) with 25% extractant solution (A/O = 1). Apparently, the cation exchange mechanism governs the extraction of Cu(II) in 5-nonylsalicylaldoxime. The quantitative extraction (≥96%) was achieved at pH values higher than 1.3. The plotted effect of equilibrium pH on the extraction of Cu(II) is valid for initial metal concentration of 0.50, 0.75, 1.0, 1.3, 1.5, 1.7, 2.0 g L^{-1} Cu. Evidently, more or less similar distribution pattern was observed. The extraction of Zn(II), In(III), Fe(III), and Fe(II) in the extractant solution has also been investigated under identical experimental conditions. A negligible extraction (<0.001%, no detection) of these metal ions was observed over the entire investigated range of the aqueous phase pH in the following metal ion concentration ranges, Zn(II): 15–40 g L^{-1}, In(III): 1–50 mg L^{-1}, Fe(III): 1–40 g L^{-1}, and Fe(II): 1–40 g L^{-1}.

ACORGA M5640 extractant is a salicylaldoxime derivative and forms Copper complexes in a *trans* structure. The extractant's functional group is fairly acidic to form stable chelates with copper even at low pH values. This chelating complex is formed at a very fast kinetics. In case of iron and indium, the steric hindrance is large enough to avoid the formation of any complex with ACORGA extractant. In the particular case of Zn(II), a high concentration of sulphate in zinc leaching liquor means that $Zn(SO_4)_2^{2-}$ is the dominant species, whereas free Zn^{2+} ions are practically non-existent. The anionic Zn(II) sulphate species have high degree of hydration