Processing of a Waste Stream for Separation and Recovery of Copper and Zinc

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Abstract

Solvent extraction studies of copper and zinc have been carried out using Cyanex 272 and LIX 984N separately from a model waste stream of brass pickling. Various parameters for the extraction and separation of copper and zinc such as effect of pH, extractant concentration, phase ratio etc. have been optimized. The results show that extraction of copper and zinc from solution after acid extraction increased with increase in pH and their $pH_{0.5}$ values were found to be 3.5 and 4.6, and 2.5 and 5.5 with Cyanex 272 and LIX 984N, respectively; LIX 984N showed greater selectivity for copper compared to zinc. By McCabe Thiele diagram number of stages required for the counter current extraction of copper and zinc has been determined for each of the solvents. The stripping study showed that 1 mol/L H_2SO_4 was sufficient to strip metal ions from both the extractants. An attempt was made to prepare high value products such as copper powder and zinc oxide from the loaded or stripped solution which could be imminently suitable for various P/M and other applications.

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1. Introduction

Hydrometallurgical processing of waste streams generated at metal working industries is generally practiced to separate and recover base metals such as copper and zinc to ensure resource recycling and pollution minimisation. A number of studies have been reported for the solvent extraction and separation of copper and zinc from the sulphate solutions of various low grade materials or wastes, such as brass ash, converter slag and complex ores using different organic extractants. Comprehensive studies have been made on oxime based extractants viz. LIX 984N for the extraction of copper and othe metal ions from various media. The solvent extraction of the cations such as Cu(II), Fe(III), Ga(III), Ni(II), Co(II), In(II), Zn(II) and Pb(II) with LIX 984N has been explained by Miguel et al.[1]. It was observed that both monomer and dimer forms of LIX 984N played an important role in extraction equilibria. Konglo et al. [2] studied the separation of cobalt, zinc and copper from sulphate solution by selective extraction of copper with LIX 984 followed by extraction of cobalt and zinc with D2EHPA. Qing-ming et al. [3] reported extraction of copper from synthetic bioleaching solution using 10% LIX 984N. Lazarova et al. [4] discussed extraction behaviour of LIX 984N in nitrate media, and recently Le et al. [5] reported recovery of copper from waste PCBs from nitrate solutions. Copper and zinc separation from bioleaching solution was carried out by Zhuo-yue et al. [6] using LIX 984 and D2EHPA and various parameters for extraction were optimized. Also, organophosphorous reagent, Cyanex 272 has received considerable attention of researchers since quite some time for its ability to extract transition metal ions. Sole and Hiskey [7,8] reported the behaviour of Cyanex 272, Cyanex 302 and Cyanex 301 for the extraction of copper, zinc and other metal ions. The trend for metal extraction using Cyanex 272 was found to be Fe < Zn < Cu < Co < Ni. Cao et al. [9] reported the extraction and separation of Cu and Zn using Cyanex 272. The extraction of Zn(II) with Cyanex 272 in kerosene from aqueous sulphate, chloride and nitrate media was investigated by Ali et al. [10]. Devi et al. [11,12,13] reported the extraction and separation of Zn and Mn from sulphate solutions using sodium salt of D2EHPA, PC 88A and Cyanex 272, and optimized various parameters for extraction including the effect of different sodium salts. Morais et al. [14] described the Cu/Zn separation from the leach liquor generated from the zinc residue using organohosphorous extractants such as D2EHPA, IONQUEST 801 and Cyanex 272 and the chelating reagents particularly LIX 63, LIX 984N and LIX 612N-LV.

This paper presents and discusses results for separating copper and zinc available together in spent brass pickle liquor with Cyanex 272 and LIX 984N separately.

2. Experimental Procedure

Typical brass pickle liquor generated at a copper/brass industries contain 45.1 g/L H2SO4, 25 g/L Zn, 35 g/L Cu(II), 1.1 g/L Cr(III), 0.2 g/L Fe(Total), 0.01 g/L nickel and total sulphate 134.75 g/L. In order to study the recovery of acid and metal values a model solution containing 45 g/L H2SO4, 30 g/L Zn(II) and 35 g/L Cu(II) was prepared. The basic extractants TEHA (tris (2-ethylhexyl) amine) was used to recover sulphuric acid from the model pickle liquor solution. From the acid removed spent pickle liquor, solvent extraction of copper and zinc was studied using Cyanex 272 [bis-(2,4,4-trimethylpentyl)-phosphinic acid] and LIX 984N (1:1 mixture of 5-nonyl salicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime) as extractants in kerosene. Isodecanol was used as the phase modifier with Cyanex 272 and TEHA. All solvent extraction / stripping experiments were carried out by shaking equal volumes of model pickle liquor and desired extractant of known concentration except for the McCabe Thiele plot construction in a separating funnel for 15 min. which was found to be sufficient to reach equilibrium. The pH of the aqueous solution was adjusted to the desired value by adding dilute H_2SO_4 or NaOH before equilibrium. After the phase disengagement the aqueous and organic phases were separated. Metal ion concentration in the aqueous phase was analysed by Atomic Absorption Spectrophotometer (Model: ElementAs AAS4141). Metal contents of the organic phases were determined by mass balance. Stripping of metal ions from the loaded organic phase was carried out with dilute sulfuric acid.

3. Results and Discussion

3.1 Removal of acid from the pickle liquor

In order to remove/recover acid from the pickle liquor the model solution containing 45 g/L H_2SO_4, 30 g/L Zn(II) and 35 g/L Cu(II) was treated with 40%(v/v) TEHA as an extractant. The result of acid extraction with TEHA is reported elsewhere. During acid recovery no copper or zinc was co-extracted into the organic phase which may be due to the less affinity of TEHA towards copper and zinc as sulphate. The acid depleted solution containing 35 g/L Cu and 30 g/L Zn was used for further experiments to separate and recover copper and zinc.

3.2 Solvent extraction of copper and zinc using Cyanex 272 and LIX 984N

3.2.1 Effect of pH

The extraction of metals (M^{2+}) using acidic extractants [RH] in dimeric form takes place by the exchange of H^+ ion of the organic phase. Hence, the pH of the extraction system decreases which consequently affects the metal extraction.

$$M^{2+}{}_{aq} + [RH]_{2\,org} \Leftrightarrow [MR_2]_{org} + 2H^+{}_{aq} \qquad (1)$$

Therefore, the effect of aqueous phase acidity on the extraction process should be controlled to ensure maximum metal recovery. The effect of equilibrium pH on the extraction of copper and zinc was investigated using 20% (v/v) Cyanex 272 and 30% (v/v) LIX 984N in kerosene. As can be seen from Fig.1 extraction of copper and zinc increased with the rise in equilibrium pH. The $pH_{0.5}$ values for zinc and copper were found to be 3.5 and 4.6 respectively with 20% Cyanex 272 and those with 30% LIX 984N were found to be 2.5 for copper and 5.5 for zinc. The $pH_{0.5}$ values of Cu and Zn with these extractants indicate that Cyanex 272 is selective for Zn, whereas LIX 984N is selective for Cu. The differences in $pH_{0.5}$ values for metal ions with a particular extractant clearly indicate the potential of separating metal ions during counter-current extraction. The $|pH_{0.5}(Cu)-pH_{0.5}(Zn)|$ with LIX 984N (3) is greater than that with Cyanex 272 (1.1) which further infers that LIX 984N may serve as a better extractant for the separation of Cu and Zn. The plot of logD vs. equilibrium pH gave a straight line in each case with a slope of about 2 indicating that 2 mole of H^+ ion were exchanged with 1 mole of Cu and Zn extracted with LIX 984N or Cyanex 272.

3.2.2 Effect of extractant concentration

To study the effect of extractant concentration on the separation of copper and zinc, the concentration of Cyanex 272 and LIX 984N was varied within the range 10-50%(v/v), the corresponding concentration of the extractants being 0.15-1.6 and 0.34-1.68M respectively. The experimental results showed an increase in extraction of copper from 26-92% with Cyanex 272 and from 20-84% with LIX 984N at the equilibrium pH of 4.6 and 2.5 respectively. Whereas zinc extraction increased from

13-94% with Cyanex 272 and 20-77% with LIX 984N at the equilibrium pH of 3.5 and 5.5 respectively. The plot of logD vs. log [Extractant] had slope of about 2 (Fig.2) indicating that two molecules of extractants participated in the extraction process to form copper and zinc complexes in the organic phase.

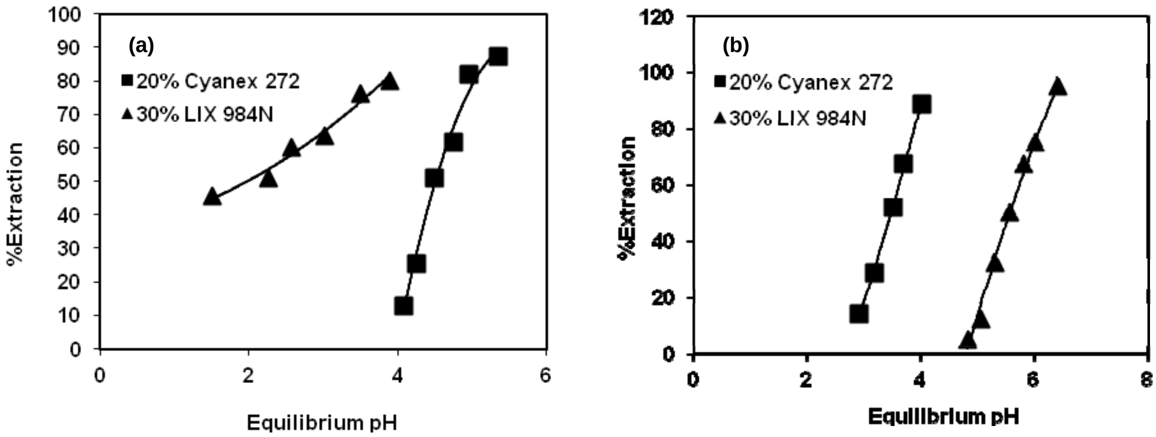

Fig.1: Effect of pH on the extraction of copper (a) and zinc (b).
[Aq. Phase: 35g/L Cu, 30 g/L Zn, Org. phase: 20% Cyanex 272 and 30% LIX 984N in kerosene. Phase ratio=1:1.]

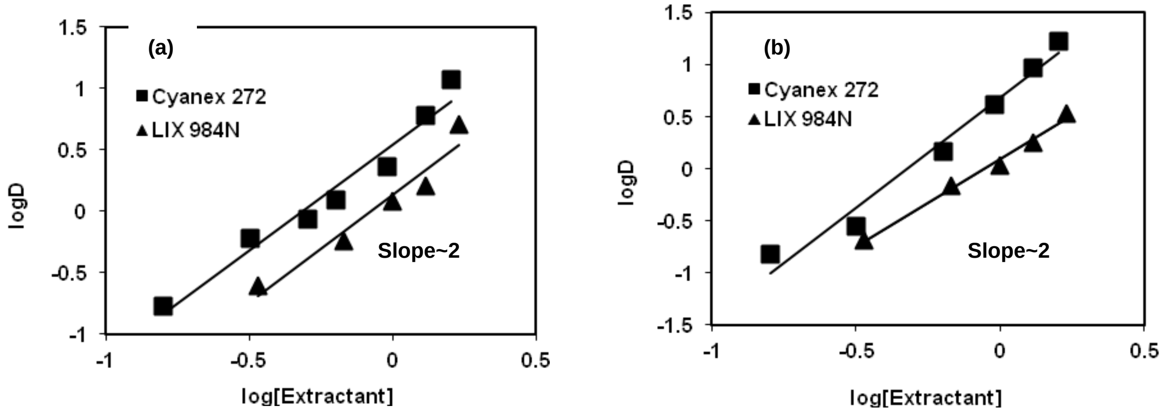

Fig.2: Effect of extractant concentration on the extraction of copper (a) and zinc (b).
[Aq. Phase: 35g/L Cu, 30 g/L Zn, Org. phase: Different concentration of Cyanex 272 and LIX 984N in kerosene. Phase ratio=1:1.]

3.2.3 Effect of phase ratio variation

When extraction of Cu and Zn with Cyanex 272 or LIX 984N at different phase ratio (O/A=1:5 to 5:1) was carried out, it was found that extraction of Cu and Zn increased with increase in phase ratio for both the extractants. The loading capacity of Cyanex 272 was found to be 34.32 g/L for Cu and 29.35 g/L for Zn, and that of LIX 984N was found to be 31.8 g/L for Cu and 22.9 g/L for Zn. In order to find out the number of counter-current stages required for complete extraction of Cu and Zn, McCabe Thiele diagram (Fig.3) was made using data obtained from phase ratio variation. The extraction isotherm for copper with Cyanex 272 illustrated complete extraction in 3-stages at phase ratio of 1.75:1 and equilibrium pH of 4.6, whereas, 2 stages were required at the phase ratios of 2:1 with LIX 984N at the equilibrium pH of 2.5 respectively. McCabe Thiele plot for complete extraction of zinc suggested that a total of 3-stages were required at the phase ratio of 2:1 and equilibrium pH of 5.5 with LIX 984N. On the other hand, with Cyanex 272, 2-stages were required to achieve complete extraction of zinc at the phase ratio of 1.7:1 and equilibrium pH of 3.5.

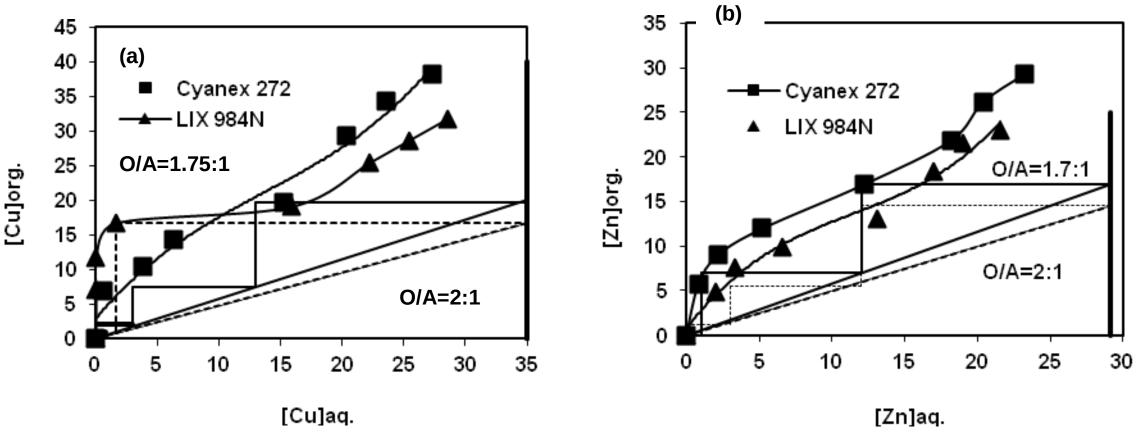

Fig.3: McCabe Thiele plot for the extraction of copper (a) and zinc (b).
[Aq. Phase: 35g/L Cu, 30 g/L Zn, Org. phase: 20% Cyanex 272 and 30% LIX 984N in kerosene.]

3.2.4 Stripping of metal ions from the loaded organic phase

A study on the stripping of copper and zinc values from the loaded Cyanex 272 and LIX 984N was carried out at equal phase ratio with different concentrations of sulphuric acid in the range of 0.25-1.5M. The results of first stage stripping are given in table-1. The experimental data show that even 0.25M H_2SO_4 is very effective in case of stripping of copper and zinc from the loaded Cyanex 272. However, quantitative amount of copper and zinc can be stripped off by 0.5M H_2SO_4 concentration. Whilst copper and zinc stripping from the loaded LIX 984N is found to be ~80% with 1M H_2SO_4 which increased to almost ~99% for both copper and zinc with 1.5M H_2SO_4 in a single stage. The stripped metals can be recovered as salts by evaporation-crystallisation or metal cathodes or powder by electrowinning. The electrowinning of copper from the purified solution produced copper powders of >99.9% purity with dendritic morphology. ZnO from the sulphate solutions was produced by hydrothermal synthesis under autoclave. The copper powder and ZnO obtained as above can be used for P/M and other applications.

Title-1: Stripping of metal ions from the loaded solvents.
Cyanex 272: 34.22 g/L Cu, 29.35 g/L Zn, LIX 984N: 31.8 g/L Cu, 22.9 g/L Zn.

H_2SO_4(M)	% Stripping of metal ions from the loaded solvents in single contact			
	Cyanex 272		LIX 984N	
	Cu	Zn	Cu	Zn
0.25	87	92	40	33
0.50	100	100	65	54
1.00	100	100	80	75
1.50	100	100	99	99

4. Conclusions

Extraction and separation of copper and zinc from a model brass pickle liquor has been carried out using Cyanex 272 and LIX 984N in kerosene. Extraction isotherms of Cu and Zn with increasing equilibrium pH are reported with each extractants. Cyanex 272 has greater selectivity for Zinc at lower pH than Copper, whereas LIX 984N shows higher selectivity towards Copper. The percentage extraction of both metals increased with increase in concentration of Cyanex 272 and LIX 984N. From the McCabe Thiele diagram, it is observed that almost complete extraction of copper and zinc requires three and two extraction stages, respectively with 20% Cyanex 272 at the phase ratio of 1.75:1 and 1.7:1. Whereas, 30% LIX 984N requires two and three counter-current stages at the phase ratio of 2:1 for complete extraction of copper and zinc at an equilibrium pH of 2.5 and 5.5, respectively. Stripping of metal ions from the loaded organic phases was also carried out using different concentration of sulphuric acid. Metal loaded solvent and stripped metal solution can be utilized for their recovery as metal salt, metal powder or other value added products such as oxides.

5. Acknowledgements

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