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SOLVENT EXTRACTION OF COPPER AND ZINC FROM A PICKLING SOLUTION USING VERSATIC 10 ACID, CYANEX 272 AND LIX 984N

S.K. Sahu, M.K. Sinha, P. Meshram, B.D. Pandey, V. Kumar

CSIR-National Metallurgical Laboratory (CSIR-NML), Jamshedpur, INDIA

Abstract

Solvent extraction studies of copper and zinc have been carried out using Versatic 10 acid, Cyanex 272 and LIX 984N separately from a model brass pickle liquor. 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 acid free solution increased with increase in pH and their $pH_{0.5}$ values were found to be 4.0 and 5.6, 3.5 and 4.6, and 2.5 and 5.5 with Versatic 10 acid, Cyanex 272 and LIX 984N, respectively. Versatic 10 acid and LIX 984N shows 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 in a single contact from each of the extractant.

Keywords: *solvent extraction, brass pickle liquor wastes, copper, zinc, extraction isotherm*

Introduction

Copper and zinc are the major components of effluent/waste streams of some metallurgical/plating industries. In view of this, the selective extraction and separation of these metals from their mixed solution is of great interest in hydrometallurgical processes due to the possibility of recovering the metal values as well as reducing the environmental pollution problems. A number of investigations carried out for the extraction and separation of copper and zinc for the processing of sulphate solutions of various low grade materials or wastes, such as brass ash, converter slag and complex ores using different organic extractants. The separation of copper and zinc from leach solution of a complex sulphide ore was studied by Kumar et al. (1989) and Pandey et al. (1986). The results show that LIX 64N selectively extracted copper from a copper- zinc solution. The raffinate containing zinc was purified and the metal was produce by EW. Kumar et al. (1997) compared the efficiency of LIX 84 and LIX 64N for the separation of copper and zinc from a solution containing impurities like iron and manganese, LIX 84 showed greater selectivity for copper/zinc separation compared to LIX 64N. Similarly, Reddy and Priya (2004, 2005) developed a process for separation of Cu (II), Ni (II) and Zn (II) using LIX 84I and observed that metal extraction was dependent on pH, and no effect was observed with variation in temperature. Effect of LIX 984N on extraction of copper and zinc was studied by many investigators (Miguel et. al., 1997, Qing-ming et. al., 2008, Lazarova et. al., 2005, Le et. al., 2011). Copper and zinc separation from bioleaching solution was carried out by Zhuo-yue et al. (2005) using LIX 984 and D2EHPA and various parameters for extraction were optimized. The separation of divalent metal ions from a synthetic solution containing Zn, Cu, Ni, Co, and Mg with D2EHPA was studied by Cheng (2000). The extraction order found to be $Zn^{2+}>Ca^{2+}>Mn^{2+}>Cu^{2+}>Co^{2+}>Ni^{2+}>Mg^{2+}$ which showed possible separation of copper from zinc. Sole and Hiskey (1995) reported the extractive nature of Cyanex 272, Cyanex 302 and Cyanex 301 towards extraction of copper and also studied the nature of extracted species in all the cases. The pH at which extraction of each metal takes place, decreases in the order: Cyanex 272 > Cyanex 302 > Cyanex 301. The trend for metal extraction using Cyanex 272 was found to be Fe < Zn < Cu < Co < Ni. Konglo et al. (2003) studied the cobalt and zinc recovery from copper sulphate solution by selective extraction of copper by LIX 984 followed by extraction of cobalt and zinc by D2EHPA. Separation of copper and zinc from Hudson Bay mining and smelting discharge was studied by Owusu (1999) using LIX 622 which reported ~97–98% Cu was extracted with negligible co-extraction of Zn, Fe, Cd and Co. Dukov and Guy (1982) investigated the extraction of copper and zinc by using LIX 34 and Versatic 911 acid and their mixtures and observed that no synergism was found when Versatic acid was added. Zinc and copper can also be extracted from sulphate media by carboxylic acids (Preston et al. 1985) in the relative order of Fe (III) < Cu < Zn < Ni < Co < Mn < Ca < Mg with increasing pH. Copper and zinc recovery from spent copper pickle liquor was studied by Mahmoud et al. (2001) using Acorga 5640 for selective extraction of copper followed by recovery of chromium and zinc by precipitation.

The present study emphasizes on the possibility of extraction and separation of copper and zinc from a model brass pickle liquor by solvent extraction process using Versatic 10 acid, Cyanex 272 and LIX 984N.

Materials and Methods

A typical brass pickle liquor generated at a copper/brass industry in India contained 45.1 g/L H_2SO_4, 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 Ni and total sulphate 134.75 g/L. In order to study the recovery of acid and metal values, a model synthetic solution containing 45 g/L H_2SO_4, 30 g/L Zn (II) and 35 g/L Cu (II) was prepared. The basic extractants TEHA (tris (2-ethylhexyl) amine) was used to study the extraction of sulphuric acid. Versatic 10 acid, 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) were used for the extractive separation of copper and zinc from acid free pickle liquor. Isodecanol was used as the phase modifier (with Cyanex 272 and TEHA), and kerosene was used as the diluent in the solvent extraction studies.

All solvent extraction/stripping experiments were carried out by shaking equal volume of synthetic pickle liquor and desired extractant of known concentration (except for the McCabe Thiele 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 (AAS). Acid concentrations in the aqueous phase were estimated by titration method. 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.

Results and Discussion

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 using the phase ratio of 1:1. It was observed that almost total acid content was extracted into the organic phase in a single contact. It was also noticed that no copper and zinc was co-extracted into the organic phase which may be due to the less affinity of TEHA towards copper and zinc as sulphate. However, presence of chloride in the system may show the extraction of copper and zinc as the metal chloro-complexes by amine based extractants. 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.

Solvent extraction of copper and zinc using Versatic 10 acid, Cyanex 272 and LIX 984N

Effect of pH

Acidity of the aqueous solution strongly affects the efficiency of the metal extraction. In order to study the influence of pH, experiments were carried out within the equilibrium pH range from 2–7. It can be observed in figures 1, 2 that extraction of copper and zinc increased with rise in pH, wherein copper was almost completely extracted into the organic phase comprising of 30% Versatic 10 acid at the equilibrium pH of 5.1. Whereas, zinc extraction was noticed only at pH above 5.0 and completely extracted into the organic phase at pH 7.0 using the phase ratio of 1:1. It was observed that zinc extracted at lower pH value than copper with Cyanex 272. Extraction of zinc increased from 14–88% with increase in equilibrium pH range from 3–4 whereas, it was 12–87% for copper in the equilibrium pH range of 4–5.5 with 20% Cyanex 272. The $pH_{0.5}$ values for zinc and copper was found to be 3.5 and 4.6 respectively. The difference in $pH_{0.5}$ values of 1.10 indicates the possibility of separation of both the metals.

On the other hand, $pH_{0.5}$ values for copper and zinc observed to be 2.5 and 5.5 with 30% LIX 984N, which shows the greater selectivity for copper than zinc as like other oxime based extractants. The different pH for extraction of copper and zinc with LIX 984N and Versatic 10 acid shows the possibility for better separation of the two metals. LIX 984N and Versatic 10 acid shows similar behaviour towards zinc extraction. The plot of logD vs. equilibrium pH gave a straight line in each cases with a slope of about 2 indicating that 2 mole of H^+ ion were exchanged with 1 mole of the each extracted metal species.

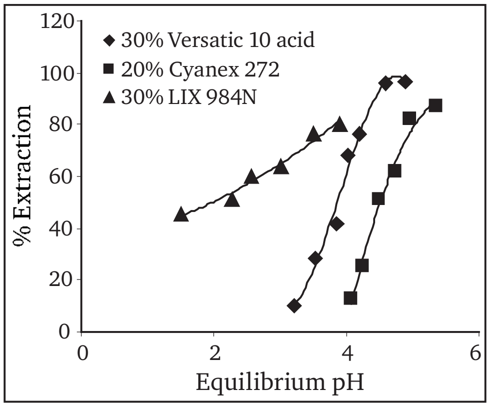

Fig. 1. Effect of pH on the extraction of copper

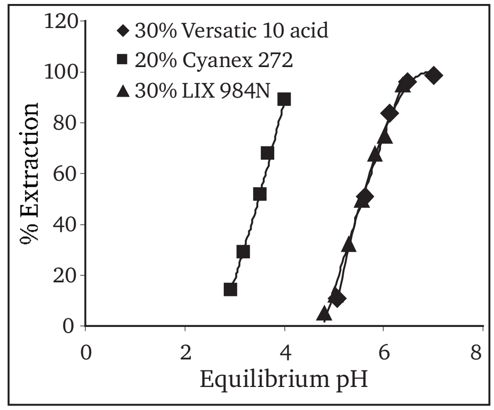

Fig. 2. Effect of pH on the extraction of zinc

[Aq. Phase: 35g/L Cu, 30 g/L Zn, Org. phase: 30% Versatic 10 acid, 20% Cyanex 272 and 30% LIX 984N in kerosene. Phase ratio=1:1, Equilibrium time= 15 min.]

Effect of extractant concentration

To study the effect of extractant concentration on the extraction of copper and zinc, the concentration of Versatic 10 acid, Cyanex 272 and LIX 984N were varied within the range 10–50% (v/v), the corresponding concentration of the extractants being 0.52–2.6, 0.15–1.6 and 0.34–1.68M respectively. The experimental results showed an increase in extraction of copper from 33–99% with Versatic 10 acid, 26–92% with Cyanex 272 and 20–84% with LIX 984N at the equilibrium pH of 4.0, 4.6 and 2.5 respectively. Whereas, zinc extraction increased from 15–89% with Versatic 10 acid, 13–94% with Cyanex 272 and 20–77% with LIX 984N at the equilibrium pH of 5.5, 3.5 and 5.5 respectively, using the equal volumes of aqueous and organic phases. In order to establish the number of mole of extractants participating in the extraction system, a plot of logD vs. log [Extractant] was made for each case (fig.3, 4). A slope of about 2 was obtained which indicated that two molecules of extractants participated in the extraction process to form copper and zinc complex species in the organic phase. The existence of di-solvated metal complex in the organic phase was reported in the earlier investigations (Sastre et al., 1990, Sole and Hiskey, 1992 and 1995, Miguel et al., 1997, Pouillon and Doyle, 1988).

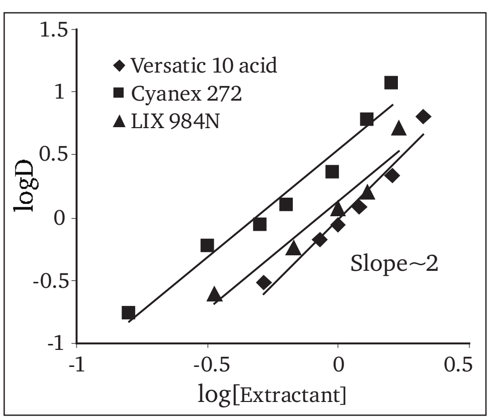

Fig. 3. Effect of extractant concentration on the extraction of copper

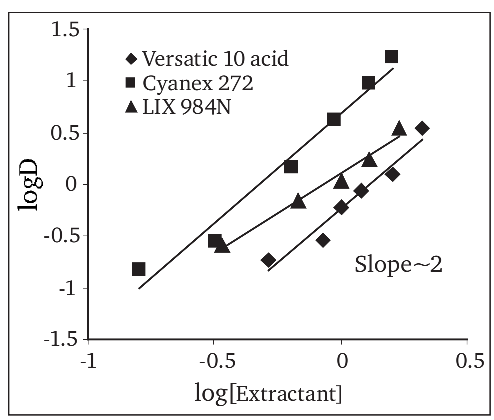

Fig. 4. Effect of extractant concentration on the extraction of zinc

[Aq. Phase: 35g/L Cu, 30 g/L Zn, Org. phase: Different concentration of Versatic 10 acid, Cyanex 272 and LIX 984N in kerosene. Phase ratio=1:1, Equilibrium time= 15 min.]

Thus, the extraction equilibrium of copper and zinc (M^{2+}) with Versatic 10 acid, Cyanex 272 and LIX 984N (HA) in kerosene can be expressed by a general equation as,

$$M^{2+}_{aq.} + 2HA_{org.} \Leftrightarrow [MA_2]_{org.} + 2H^{+}_{aq.}. \quad (1)$$

Effect of phase ratio variation

In order to determine the extraction capacity of 30% Versatic 10 acid, 20% Cyanex 272 and 30% LIX 984N separately, the extraction of copper and zinc from brass pickle liquor was studied at different phase ratios within 1:5 to 5:1. McCabe Thiele plot (Extraction isotherm) constructed to determine the theoretical number of stages for complete extraction of copper and zinc (fig. 5, 6), using the data of phase ratio variation. The extraction isotherm for copper with Versatic 10 acid illustrated quantitative extraction in 4-stages at phase ratio of 1.12 : 1 and equilibrium pH of 4.0; whereas, Cyanex 272 and LIX 984N required 2 and 3-stages at the phase ratios of 1.75:1 and 2:1 and at the equilibrium pH of 4.6 and 2.5 respectively. McCabe Thiele plot for complete extraction of zinc suggested that a total 3-stages were required at the phase ratio of 1.9:1 and 2:1 and equilibrium pH of 5.5 with Versatic 10 acid and LIX 984N respectively. With Cyanex 272, 2-stages were only required to achieve quantitative extraction of zinc at the phase ratio of 1.7 : 1 and equilibrium pH of 3.5.

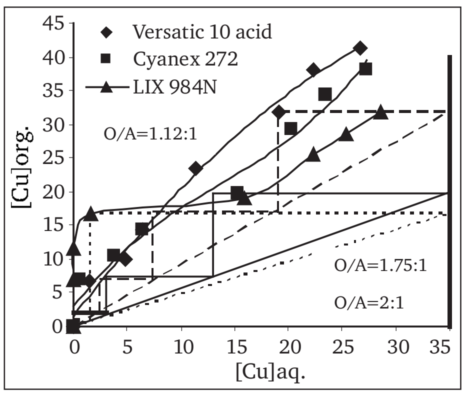

Fig. 5. McCabe Thiele plot for the extraction of copper

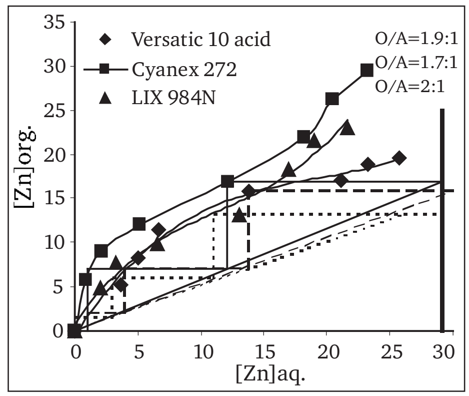

Fig. 6. McCabe Thiele plot for the extraction of zinc

[Aq. Phase: 35g/L Cu, 30 g/L Zn, Org. phase: 30% Versatic 10 acid, 20% Cyanex 272 and 30% LIX 984N in kerosene. Equilibrium time= 15 min.]

Effect of temperature

Effect of temperature on the extraction of copper and zinc from brass pickle liquor was studied in the range of 30–60 °C. Temperature effect for copper extraction was studied with both LIX 984N and Versatic 10 acid, whereas effect of temperature on the extraction efficiency of zinc was studied only with Cyanex 272, keeping the selective extraction of metal vis-à-vis solvent in consideration. It was observed that extraction of metal ions increases with temperature. The plots of logD vs. $1/T\times10^3$ give a straight line with a negative slope values (fig. 7). Thus, change in enthalpy of the extraction processes, ΔH can be obtained from the slope of logD vs. 1/T using the Van't Hoff equation:

$$\frac{\Delta \log D}{\Delta\ 1/T} = -\frac{\Delta H}{2.303RT} + C. \quad (2)$$

Table 1

Thermodynamic functions for the extraction for the extraction of copper and zinc

Temp K	Versatic 10 acid $(Cu)_{ext.}$			Cyanex 272 $(Zn)_{ext.}$			LIX 984N $(Cu)_{ext.}$		
	ΔG $\frac{kJ}{mol}$	ΔS $\frac{kJ}{mol\cdot K}$	ΔH $\frac{kJ}{mol}$	ΔG $\frac{kJ}{mol}$	ΔS $\frac{kJ}{mol\cdot K}$	ΔH $\frac{kJ}{mol}$	ΔG $\frac{kJ}{mol}$	ΔS $\frac{kJ}{mol\cdot K}$	ΔH $\frac{kJ}{mol}$
303	-1.409	0.244	75.61	-0.232	0.172	52.00	-0.464	0.102	30.63
313	–2.471	0.233		–1.054	0.169		–1.438	0.102	
323	–4.844	0.219		–2.950	0.170		–2.659	0.103	
333	–8.225	0.202		–5.387	0.158		–3.507	0.102	

Positive values of ΔH indicated the extraction to be endothermic in nature in each of the cases. Further the free energy ΔG and entropy ΔS (table 1) were calculated from the following equations:

$$\Delta G = -2.303\,RT\log D \qquad (3)$$

$$\text{and}\ \ \Delta S = \frac{\Delta H - \Delta G}{T}. \qquad (4)$$

The negative free energy value in each case shows that copper and zinc extraction using these extractants are thermodynamically favourable. The positive ΔS values indicated that metal ions being transferred from a highly ordered state to more disordered state.

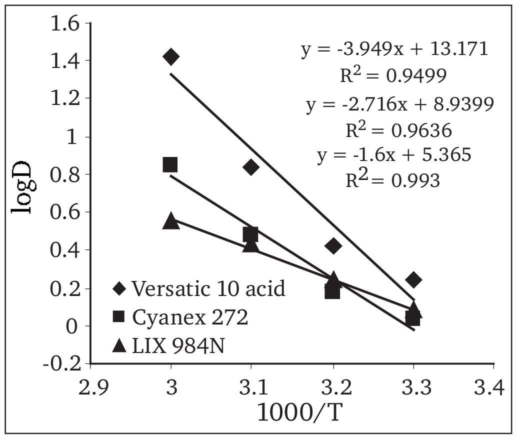

Fig. 7. Effect of temperature on the extraction of copper and zinc
[Aq. Phase: 35g/L Cu, 30 g/L Zn, Org. phase: 30% Versatic 10 acid (for copper), 20% Cyanex 272 (for zinc) and 30% LIX 984N (for copper) in kerosene. Phase ratio=1:1, Equilibrium time= 15 min, Temperature= 30–60°C.]

Stripping of metal ions from the loaded organic phase

Stripping of copper and zinc was performed from the loaded Versatic 10 acid, Cyanex 272 and LIX 984N containing 35 g/L Cu and 30 g/L Zn using various concentration of sulphuric acid (0.25–1.5M) and the result obtained are given in table 2. It was observed that complete stripping of copper and zinc was achieved in a single contact using 1.0M sulphuric acid. Complete stripping of copper and zinc from the loaded Cyanex 272 was achieved using 0.5M H_2SO_4 in a single contact at a phase ratio of 1. Stripping of acid from the acid loaded TEHA was carried out with distilled water and it was found that the total acid was stripped in a single contact at an O/A phase ratio of 1:1. The stripped metals can be recovered as salts by evaporation-crystallisation or metal cathodes powder by electrowinning.

Table 2

Stripping of metal ions from the loaded solvents

[Organic phase: 35 g/L Cu and 30 g/L Zn in Versatic 10 acid, Cyanex 272 and LIX 984N.]

H_2SO_4 (M)	% Stripping of metal ions from the loaded solvents in single contact					
	Versatic 10 acid		Cyanex 272		LIX 984N	
	Cu	Zn	Cu	Zn	Cu	Zn
0.25	50	46	87	92	40	33
0.50	90	91	100	100	65	54
1.00	100	100	100	100	80	75
1.50	100	100	100	100	99	99

Conclusions

The model brass pickle liquor which contains Cu: 35 g/l, Zn: 30 g/l has been treated with Versatic 10 acid, Cyanex 272 and LIX 984N in kerosene. The results show that extraction of copper and zinc from acid free solution increased with increase in pH and their $pH_{0.5}$ values were found to be 4.0 and 5.6, 3.5 and 4.6, and 2.5 and 5.5 with Versatic 10 acid, Cyanex 272 and LIX 984N, respectively. Versatic 10 acid and LIX 984N shows greater selectivity for copper compared to zinc. Increasing the concentration of extractants increased the percentage extraction of both metals and the plot of logD vs. log [Extractant] gave a straight line with the slope of about 2 elucidating that the extracted metal species contained 2 mol of the solvents in each case. It was evident from extraction isotherms that complete extraction of copper and zinc with 30% Versatic 10 acid at the phase ratios of 1.12:1 and 1.92:1 required four and three counter-current stages respectively. The extraction stages required with 20% Cyanex 272 at the phase ratio of 1.75:1 and 1.7:1 were three and two respectively. The 30% LIX 984N required 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. Extraction of copper and zinc was found to be thermodynamically favourable within the temperature range 30–60 °C. Stripping with 1 mol/l H_2SO_4 was sufficient to recover copper and zinc in a single contact from the extractants. Also, metal loaded solvent and stripped metal solution can be utilized for their recovery as salt, metal powder or other value added products. Thus, the present investigation opens up a scope to recover and recycle the metals from the brass pickle liquor in an eco-friendly manner.

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