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SOLVENT EXTRACTION AND SEPARATION OF COPPER AND ZINC FROM A PICKLING SOLUTION

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Abstract

Solvent extraction studies of copper and zinc have been carried out using Versatic 10 acid and Cyanex 272 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. It was observed that copper was almost completely extracted into the organic phase comprising of 30% Versatic 10 acid at the equilibrium pH of 5.0 using the phase ratio of 1:1 whereas, zinc extraction was noticed at above pH 5.0. On the other hand the pH0.5 values were 3.5 and 4.6 for zinc and copper respectively with 20% Cyanex 272. The difference in pH0.5 value of 1.10 indicated the possible separation of Zn and Cu. By McCabe Thiele diagram number of stages required for the counter current extraction of copper and zinc has been determined for both the solvents. The stripping study showed that 1 mol/L H2SO4 was sufficient to strip metal ions in a single contact from each of the extractant.

Introduction

Brass tends to build up a black coating on the surface called tarnish which is essentially a type of corrosion that is caused by exposure to the air. Therefore, cleaning of the surface becomes increasingly necessary. The cleaning process involves removal of rust and oxide impurities by dipping the material in dilute sulphuric acid solution, which is usually reused several times before its disposal as a waste. As a result the waste pickle liquor is loaded up with pollutant materials such as copper, zinc, chromium etc. Due to its environmentally hazardous nature it can not be disposed off without pretreatment. Recovery of these metals is coincident with the goals of waste management strategy since they could provide some economical benefits and solve the pollution problem too. To obtain valuable end-products like copper powder, copper oxide, zinc oxide and copper/zinc salt from such streams solvent extraction is considered an ideal technique which has been applied extensively.

Several workers carried out numerous investigations for the extraction and separation of different metals such as copper, zinc etc. 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 depend upon pH and temperature had no effect on the extraction of metal. 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. The extraction behaviour of Cyanex 301, Cyanex 302 and their binary mixture with Aliquat 336 towards Cu, Zn, Co, Fe, Mn and Ni was studied by Tait (1992 a,b) and observed that extraction of copper and zinc was quantitative with Cyanex 301 and Cyanex 301/Aliquat 336 in the pH region of Cyanex 301 whereas Cyanex 302/Aliquat 336 can be used as a potential solvent mixture for copper/zinc separation. 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. He observed that upto 97-98% Cu was extracted with negligible co-extraction of Zn, Fe, Cd and Co. A process for the metal extraction using organophosphorous or carboxylic acid as extractant in the acidic range was patented by Preston et al. (1985a). The synergistic effect between extractant and non chelating aldehyde oxime has enabled extraction to take place at lower pH. 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 b). The relative order of extraction with increasing pH found to be Fe(III) < Cu < Zn < Ni < Co < Mn < Ca < Mg. 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. In the present work separation and extraction of copper and zinc from a model brass pickle liquor were investigated by using Versatic 10 acid and Cyanex 272.

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 nickel 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 and Cyanex 272[bis-(2,4,4-trimethylpentyl)-phosphinic acid] 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 H2SO4 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 H2SO4, 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** *Effect of pH* During extraction of metals using acidic extractants, H+ ions are released causing the decrease in pH which subsequently lowers extraction of metals in several instances. So the extraction process is greatly affected by pH. The effect of pH on the extraction of copper and zinc was investigated in the pH range 2-7 using the phase ratio of 1:1. It was observed that extraction of metals increased with pH and copper was 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 (Fig.1) which was almost completely(~99%) extracted into the organic phase at pH 7.0. The different extraction pH for copper and zinc with Versatic 10 acid shows the possible separation of the two metals. A plot of log D vs. pH (Fig.2) gave a straight line in both the cases with a slope of about 2 indicating that 2 mole of H+ ion were exchanged with each metal ions.

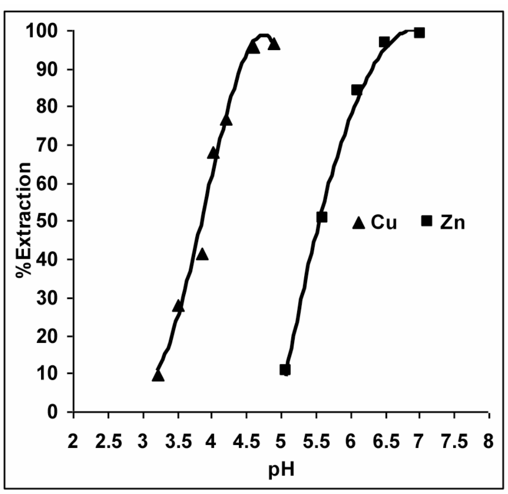

Fig.1: Effect of pH on the solvent extraction of copper and zinc**.** Aq. phase: 35 g/L Cu, 30 g/L Zn, Org. phase: 30 % Versatic 10 acid in kerosene.

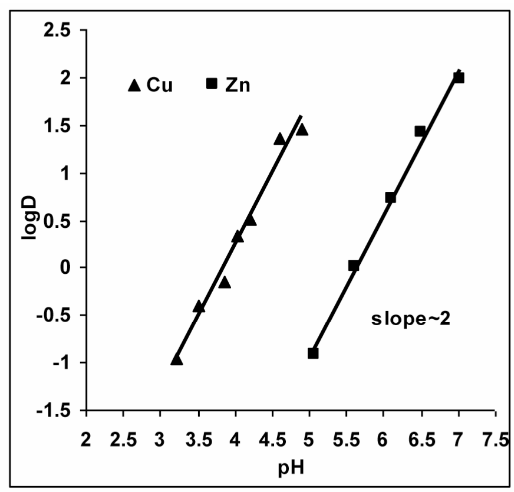

Fig.2: Log D vs. Equilibrium pH

Thus, the extraction equilibrium of copper and zinc (M^{2+}) with Versatic 10 acid (HA) in kerosene can be expressed as,

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

The equilibrium constant K_{ex} can be given as:

$$K_{ex} = \frac{[MA_2][[H^+]^2}{[M^{2+}][HA]^2} \quad (2)$$

Equation (2) can be rewritten as

$$\text{Log } D_M = \log K_{ex} + 2(\log[HA] + pH) \quad (3)$$

$$D_M = \frac{[MA_2]}{[M^{2+}]} \quad (4)$$

, where D_M is the distribution ratio

For the further experiments equilibrium pH 4.0 and 5.6 were chosen to extract copper and zinc respectively from the model solution.

Effect of extractant concentration

To study the effect of extractant concentration on extraction of copper and zinc, the concentration of Versatic 10 acid was varied in the range 10-50% (v/v) corresponding to 0.52- 2.6M in kerosene. The experimental results show that extraction of copper and zinc increases with increase in extractant concentration (Fig.3). As can be seen copper extraction increases from 33-99 % at the equilibrium pH of 4.0 whereas, extraction of zinc increases from 15-89% at the equilibrium pH of 5.6 using the phase ratio of 1. The plots of log D vs. log [Versatic 10 acid] are straight lines with the slope of ~2 for both copper and zinc, indicating the association of 2 mole of extractant in the extracted metal species (Fig.4), which validates the equation (3).

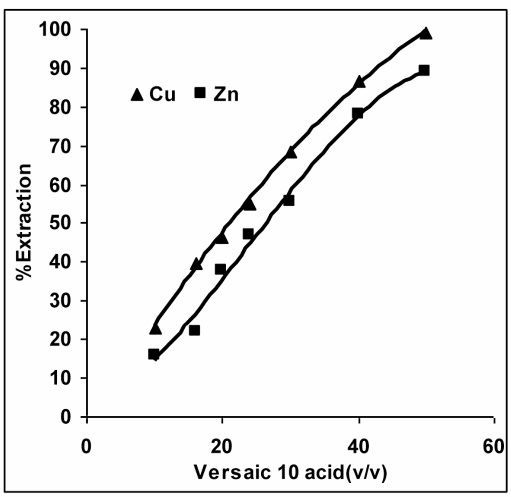

Fig.3: Effect of extractant concentration on the solvent extraction of copper and zinc**.** Aq. phase: 35 g/L Cu and 30 g/L Zn, Org.phase: Different conc.of Versatic 10 acid in kerosene.

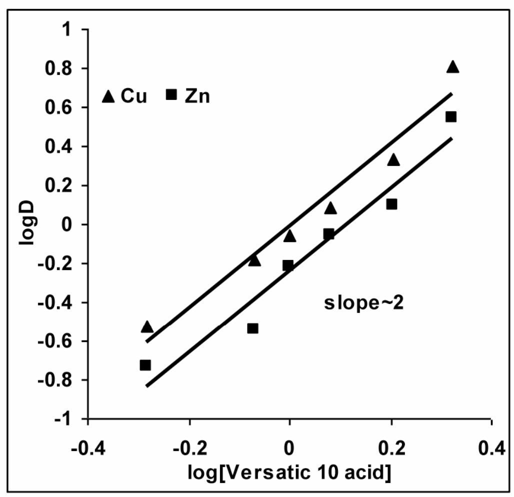

Fig.4: Log D vs. [Versatic 10 acid]

Effect of phase ratio variation

In order to determine the extraction capacity of 30% Versatic 10 acid, the extraction of copper and zinc from sulphate solution at different O/A ratio was studied at the equilibrium pH of 4.0 and 5.6 respectively. The percentage extraction of copper increased from 18 to 96% whereas, zinc extraction increased from 13% to a maximum of 87% with the increase in phase ratio from 0.2 to 5. Number of counter-current stages required for complete metal extraction can be predicted by the use of McCabe Thiele diagram. Extraction isotherm for copper indicates that a total of four stages are required for complete extraction of copper whereas, complete extraction of zinc could be achieved in three stages using the phase ratio of 1.12:1 and 1.9:1 respectively (Fig.5 and Fig.6).

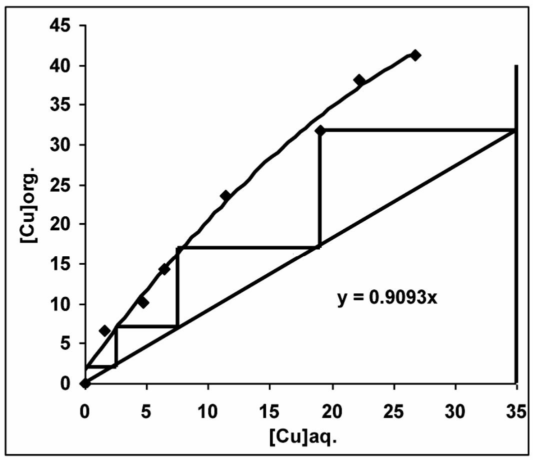

Fig.5: McCabe -Thiele Plot for the extraction of copper with Versatic acid. Aq. phase: 35 g/L Cu and 30 g/L Zn, Org. Phase: 30 % Versatic 10 acid in kerosene.

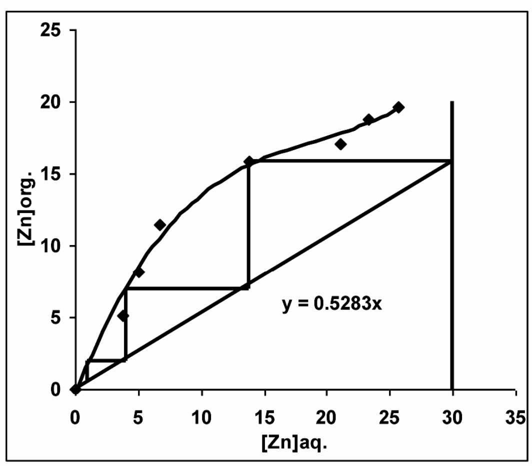

Fig.6: McCabe -Thiele Plot for the extraction of zinc with Versatic acid. Aq. phase: 30 g/L Zn, Org. Phase: 30 % Versatic 10 acid in kerosene.

Solvent extraction of copper and zinc using Cyanex 272

Acidic form of the extractant alkyl phosphate Cyanex 272 often exists in the dimer form (Tait, 1993). Hence, the metal extraction using Cyanex 272 (HA) can be expressed by the following reactions:

$$M^{2+}_{aq} + 2(HA)_{2\,org} \Leftrightarrow MA_2 \bullet 2HA_{org} + 2H^{+}_{aq} \quad (5)$$

The equilibrium constant K_{ex} can be given by

$$K_{ex} = \frac{[MA_2 \bullet 2HA][[H^{+}]^2}{[M^{2+}][(HA)_2]^2} \quad (6)$$

Equation (6) can be rewritten as

$$\text{Log}\, D_M = \log K_{ex} + 2(\log[(HA)_2] + \text{pH}) \quad (7)$$

$$D_M = \frac{[MA_2 \bullet 2HA]}{[M^{2+}]} \quad (8)$$

Effect of pH

The extraction of copper and zinc was studied over the pH range 2-5.5 by using equal volumes of aqueous and organic (20% v/v Cyanex 272) phases. The percentage extraction of metals increases with increases in the equilibrium pH of the aqueous phase (Fig.7). It was observed that zinc extracted at lower pH value than copper and their respective $pH_{0.5}$ values are 3.5 and 4.6. The difference in $pH_{0.5}$ values of 1.10 indicates the possibility of separation of copper and zinc. The plots of log D vs. equilibrium pH (Fig.8) show straight lines with slope ~2 indicating the exchange of 2 mole of H^+ ion with 1 mole of the metal ion extracted.

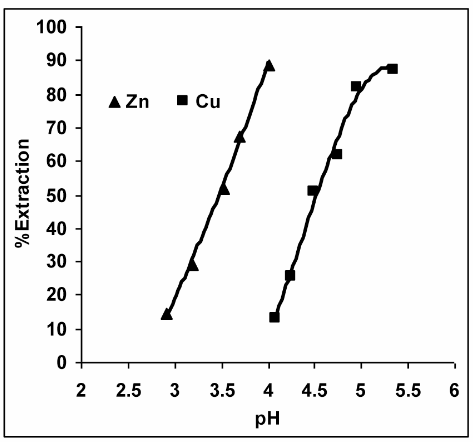

Fig.7: Effect of pH on the solvent extraction of copper and zinc**.** Aq. phase: 30 g/L Zn, 35 g/L Cu, Org. Phase: 20 % Cyanex 272 in kerosene.

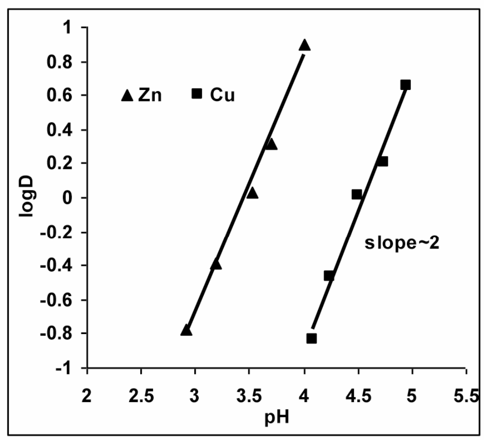

Fig.8: Log D vs. Equilibrium pH

Effect of extractant concentration

The effect of extractant concentration on the extraction of zinc and copper was studied in the range 5-50% (v/v) Cyanex 272, the corresponding concentration being 0.15-1.6M at the equilibrium pH of 3.5 and 4.6 respectively(Fig.9). It was observed that the percentage extraction of zinc and copper increased with increase in extractant concentration. Zinc extraction increased

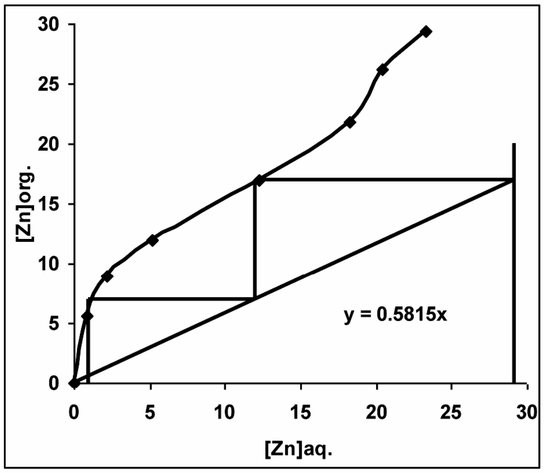

Fig.11: McCabe-Thiele Plot for the extraction of zinc with Cyanex 272. Aq. phase: 30 g/L Zn, Org. Phase: 20 % Cyanex 272 in kerosene.

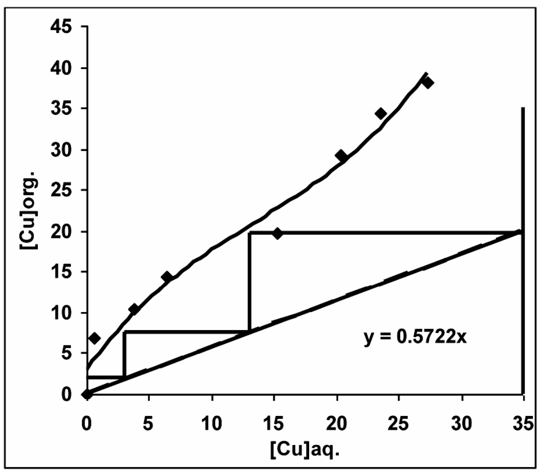

Fig. 12: McCabe -Thiele Plot for the extraction of copper with Cyanex 272. Aq. phase: 35 g/L Cu, Org. Phase: 20 % Cyanex 272 in kerosene.

Stripping of metal ions from the loaded organic phase

Stripping of copper and zinc was performed from the loaded Versatic 10 acid and Cyanex 272 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-1. It was observed that 0.25M H2SO4 stripped 50% and 46% of copper and zinc respectively from the loaded Versatic 10 acid whereas 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 H2SO4 in a single contact at a phase ratio of 1. As regards stripping of acid from the acid loaded TEHA which was carried out with distilled water, it was found that the total acid was stripped in a single contact at a 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-1: Stripping of metal ions from the loaded solvents. Organic phase: 35 g/L Cu and 30 g/L Zn in Versatic 10 acid and Cyanex 272.

H_2SO_4(M)	% Stripping of metal ions from the loaded solvents in single contact			
	Versatic 10 acid		Cyanex 272	
	Cu	Zn	Cu	Zn
0.25	50	46	87	92
0.50	90	91	100	100
1.00	100	100	100	100
1.50	100	100	100	100

Conclusions

The model brass pickle liquor which contains Cu: 35 g/L, Zn: 30 g/L has been treated with Versatic 10 acid and Cyanex 272 in kerosene. It was observed that copper was almost completely extracted into the organic phase comprising of 30% Versatic 10 acid at the equilibrium pH of 5.0 using the phase ratio of 1:1 whereas, zinc extraction was noticed only at pH above 5.0. The McCabe Thiele plot for copper and zinc indicated that 4 counter-current stages were required for complete extraction of copper and 3 counter-current stages for that of zinc at the phase ratios of 1.12:1 and 1.92:1 at the equilibrium pH 4.0 and 5.6 respectively. Solvent extraction of copper and zinc with Cyanex 272 shows the pH0.5 values of 3.5 and 4.6, respectively with 20% Cyanex 272 and difference in pH0.5 values of 1.10 indicates the possibility of separation of zinc and copper. Increasing the concentration of Cyanex 272 from 5 to 50% increased the percentage extraction of both the metals, for copper it increased from 26.13 to 92.15% and for zinc it was 13.11 to 94.39 %. Versatic 10 acid and Cyanex 272 can be used as a extractants for the extraction and separation of copper and zinc from brass pickle liquor. 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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