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Extraction and separation of Zn and Ca from solution using thiophosphinic extractant

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Abstract : In view of the increasing importance of waste processing and recycling to meet the stringent environmental regulations and to conserve natural resources, solvent extraction studies have been carried out for the separation of zinc and calcium from the sulphate leach solution of the sludge of a rayon plant. The leach solution contains calcium which is required to be removed before recycling in the spinning bath because it will precipitate as gypsum and forms a scale in the bath with the increase in concentration. Different process parameters such as effect of equilibration time on extraction, separation of metals, stripping of the loaded zinc etc. with synthetic solution have been studied using thiophosphinic extractants viz. Cyanex 272, Cyanex 302 and Cyanex 301 modified with isodecanol and diluted in kerosene. Cyanex 302 has been found to be a suitable reagent for the selective extraction of zinc at pH 3.0-4.5 in 120 seconds leaving all calcium in the raffinate. Both Cyanex 272 and Cyanex 302 form complex $[R_2Zn.3RH]_{org}$ during the extraction of zinc from aqueous solutions. The stage analysis of zinc extraction with 5% Cyanex 302 revealed that zinc is effectively extracted in one stage at an organic to aqueous ratio of 1 at a controlled pH of 3.75-4.0 from the aqueous solution containing 4 g/L zinc. Under the optimised condition, total zinc was extracted from the purified leach liquor solution at pH 4.0 and O/A ratio 1 with Cyanex 302. The loaded zinc can be stripped in one stage with sulphuric acid.

Key Words : *Zinc recovery, rayon sludge, solvent extraction.*

INTRODUCTION

Solvent extraction is a technique for the hydrometallurgical processing of different complex leach solutions. It is used for the selective extraction and purification of different metals such as copper, nickel, cobalt, zinc, uranium, tungsten etc. from the aqueous leach solutions and effluents generated in various processing industries. The process is more effective for the purification and recovery of metals from complex and dilute solutions. The purified solution is used to recover metal or salt by electrolysis or crystallization respectively. The quality of the metal obtained by solvent extraction is also of high purity as compared to the existing conventional processes. Different organic extractants such as anionic, cationic, solvating and mixed organic are used for the selective extraction of metals from different types of solutions, leaving other constituents in the aqueous raffinate. Sometimes impurities are extracted to purify the solution depending on the nature of the constituents present in the solution.

The solvent extraction process has been extensively studied for the extraction of zinc from sulphate leach solution using different extractants such as alkyl carboxylic phosphoric and phosphonic acids.[1-9] Di-(2ethylhexyl) phosphoric acid (DEHPA = RH) is the most widely used solvent for extraction and separation of the common transition metals from sulphate solutions.[1-5, 10-14] The extraction is pH dependent and the separation of different metals could

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be achieved by precise control of the pH of the solution.[15] The order of extraction[10] of some of the metals is: $Fe^{3+} > Zn^{3+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+} > Mg^{2+} > Ca^{2+}$. DEHPA forms $Zn(R)_2$ complex with zinc[16] in the pH range 1-2 during extraction. It finds commercial application during production of zinc by Espindesa (Zincex) Process.[16-17] The process was further modified[18] where zinc is recovered with DEHPA from the sulphuric acid leach solution of secondaries such as Waelz oxides, galvanizing ashes and electric arc furnace dust. A process is in commercial application for zinc production (12.5 MT/day) using DEHPA from secondary sources such as zinc ash and flux, brass ash, die casting etc.[19, 20] DEHPA has also been employed for extraction of zinc from the effluent of a rayon plant[21] and leached solution of zinc plant residue.[4] The loaded zinc is stripped with sulphuric acid. The stripped solution could be used to produce metal by electrowinning (EW).

The phosphinic acid based reagents viz. bis(2,4,4-trimethylpentyl) phosphinic acid [Cyanex 272], bis(2,4,4-trimethylpentyl) dithiophosphinic acid [Cyanex301] and bis(2,4,4-trimethylpentyl) monothiophosphinic acid [Cyanex302] have also been employed for the extraction of zinc from sulphate leach solutions[6-8, 22]. The Cyanex272 and its monothio and dithio analogues extractants[7] were used during the extraction and separation of zinc from sulphate solutions containing calcium [1 g/L Zn^{++} at pH 1 to 2].

The behaviour of the Cyanex 302 was compared with DEHPA and Cyanex 272[22] during zinc extraction. The zinc is extracted from the most acidic pH by means of Cyanex 302. The overall zinc extraction order was found to be Cyanex 302 >= DEHPA > Cyanex 272. Different carboxylic acids viz. n-hexanoic acid and n-pentanol etc. have been studied for zinc(II) extraction from the aqueous solution but all not considered to be efficient extractants[9]. The n-hexanoic acid alone (5-10 vol%) was found to extract zinc only in the pH 3.5-4.5 range. The extraction above 4.5 pH causes the formation of precipitate which was avoided with the addition of pentanol in n-hexanoic acid.

The process has also been used for the extraction of zinc from effluents containing different impurities. The extractant, Cyanex302[23, 24] has been used for the selective extraction of zinc from low-pH sulphate solution leaving calcium in the raffinate. A process was reported by Reinhardt et al.[21] for the recovery of zinc from rayon industry rinse water and other zinc containing effluents containing 0.1-1 g/L Zn along with sodium sulphate and surface active agents at pH 1.5-2.0. Zinc is extracted from the effluent with DEHPA in kerosene. At an effluent pH of 2, more than 95% of the zinc is extracted in two stages and is stripped with sulphuric acid. A plant was built in 1975 at Svenska Rayon AB in Valberg, Sweden based on the developed process. Recently, a plant has also been installed for the production of zinc by Skorpion Zinc, Nambia using D2EHPA[25].

In textile industries, a waste sludge containing zinc (5.12 to 18.9%) along with calcium and iron as impurities is generated during the manufacture of rayon yarn from wood pulp or cotton linters.[26] Almost total zinc is leached in sulphuric acid leaving calcium as gypsum.[26] Due to the low solubility of calcium in water, the solution also contains calcium as impurity. The calcium is required to be removed before recycling in the spinning bath because it will precipitate as gypsum and forms a scale in the bath with the increase in concentration. In the present paper solvent extraction studies have been made for the recovery of zinc from the solution obtained after leaching the rayon plant sludge in sulphuric acid. Different extractants viz. Cyanex 272, Cyanex 302 and Cyanex 301 were studied with respect to their characteristics for the selective extraction and separation of zinc and calcium, effect of equilibration time on extraction, loading capacity, pH of the solution etc. based on the studies a scheme has been proposed to recover zinc from rayon waste sludge.

MATERIALS AND METHODS

The solution similar to one obtained after leaching of the National rayon and Baroda rayon sludge in sulphuric acid was used for the extraction and separation of zinc from the impurities, particularly calcium. Initially the synthetic solution containing the metals in the required proportion was prepared from their respective sulphate salts. Aqueous solutions were made using distilled water. The chemical reagents such as sulphuric acid, sodium hydroxide used for the experiments were of laboratory reagent (L.R.) grade. The extractants Cyanex 272, Cyanex 302 and Cyanex 301 were supplied by Cyanamid Canada, Inc., and were used without further purification.

The extractants have the following structures:

O || R_2 P-OH	S || R_2 P-OH	S || R_2 P-SH
(Cyanex 272)	(Cyanex 302)	(Cyanex 301)

Where, R = C_8H_{17}

All other chemicals were reagent grade quality. The analyses of the samples were carried out by the conventional EDTA-titration method, atomic absorption spectrophotometer and inductively coupled plasma spectrophotometer.

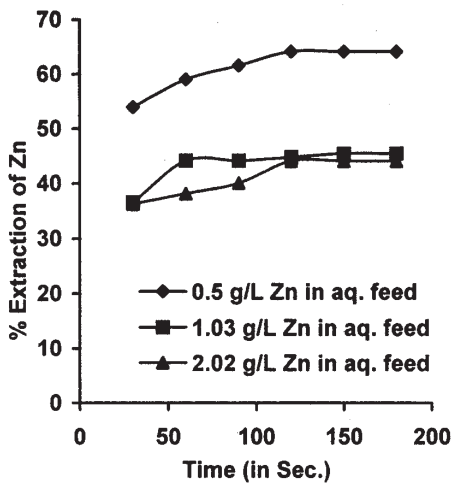
Solvent extraction experiments were carried out in a mangnetically stirred conical flask at room temperature. The organic and aqueous phases were mixed and then separated in a separating funnel. The pH of the solution was adjusted with the addition of sodium hydroxide or sulphuric acid solution. The aqueous raffinate was analysed to know the extraction of metal by organic extractant. Sometimes stripped solution was also analysed to check the material balance. Satisfactory material balance was obtained.

RESULTS AND DISCUSSION

The solution obtained after leaching the rayon sludge in sulphuric acid contains calcium and iron as major impurities. The iron is removed from the solution by oxidation and pH adjustment. The clarified leach solution contains calcium, which is required to be removed before recycling the solution to the spinning bath or recovery of zinc as metal or salt. The solvent extraction process has been employed for the selective extraction of zinc using thiophosphinic organic extractants. Initially the different parameters viz. equilibration time on extraction and stripping, effect of O/A ratio etc. were studied using the synthetically prepared solution. The results of the studies are given below.

Effect of equilibration time

The effect of equilibration time on the extraction of zinc(II) was studied using 5% Cyanex 302 and 1% isodecanol in kerosene at different times from 30 to 180 seconds , while maintaining the O/A ratio 1:1 at room temperature. The results presented in Fig. 1 indicate that the extraction of metal increased with an increase in time from 30 seconds to 120 seconds from the aqueous solutions containing 0.51, 1.03 and 2.02 g/L Zn. Subsequent increases in time have no improvement in the extraction of zinc. The percentage extraction increased from 44.05% to 64.11% with decrease in the metal content in the aqueous feed solutions from 2.02 to 0.51g/L Zn. This is due to the availability of more active sites in the organic phase with low metal content. The prolonged mixing time has no adverse effect on the extraction or phase separation. In all subsequent experiments five minutes mixing time was used as it gives the maximum extraction of metal in the organic phase.



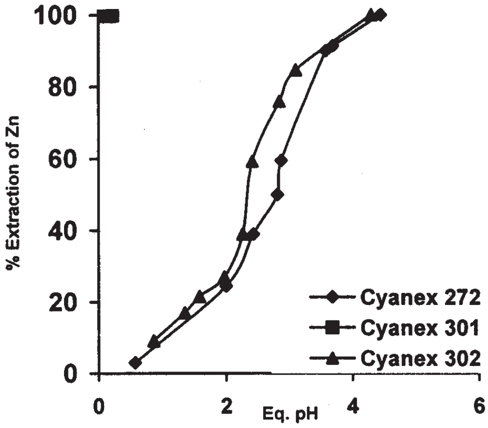
[Organic : Aqueous = 1, Temperature = Room temp. (25-30^{0}C), Eq. pH=2]

Fig. 1. Effect of equilibration time on the extraction of zinc from different concentration solutions using 5% Cyanex 302.

Extraction of zinc with different extractants

Initially different extractants such as Cyanex 272, Cyanex 301 and Cyanex 302 modified with isodecanol and diluted in kerosene have been studied for the extraction of zinc from the solution containing 2g/L Zn at different pH range at an organic to aqueous ratio of 1. The results presented in Fig. 2 show the increase in the percentage extraction of metal with a rise in equilibrium pH of the aqueous solution. The solvent 5% Cyanex 301 and 1.0% isodecanol diluted in kerosene completely extracted zinc below pH 0.22. On comparing the extraction behavior of zinc with Cyanex 272 and Cyanex 302, it was found that the extraction of zinc with Cyanex 302 takes place at a relatively lower pH than Cyanex 272. The pH for 50% extraction of zinc is 2.34 and 2.81 for Cyanex 302 and Cyanex 272 respectively (Fig. 2). The complete extraction takes place at about pH 4.4 with both extractants. The studies indicate that the thiophosphinic acids, Cyanex 302 and 301 are stronger extractants than their oxy-acid analogue, Cyanex 272. Cyanex 301 extracts zinc effectively from highly acidic solutions in comparison to the other two extractants as it forms a strong complex of zinc[7]. It will also require a high acid concentration (>300 g/L H_2SO_4) for metal stripping from the loaded solvent, which is not desirable for electrolysis.

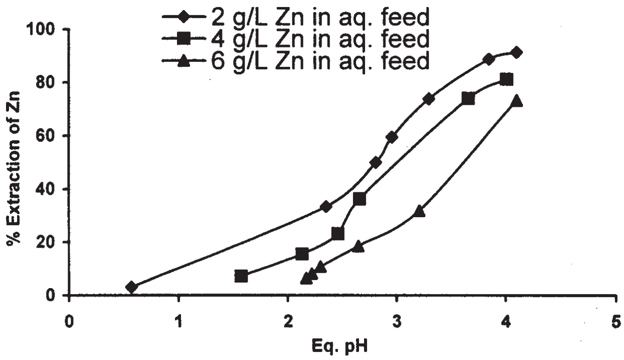
Effect of concentration of metal ions on the zinc extraction with Cyanex 272



[Organic = 5% Cyanex + 1% isodecanol in kerosene (v/v), Aq. feed = 2 g/L zinc in sulphate solution, Organic : Aqueous = 1, Temperature = Room temp. (25-30^{0}C). Eq. pH=2]

Fig. 2. Extraction of zinc with different extractants at varying pH

The concentration of metal ions in the aqueous solution plays an important role on the extraction of metal and formation of the complex in the organic phase. The studies have been carried out for the extraction of zinc from solutions containing 2.0, 4.0 and 6.0 g/L Zn at different pH using the organic extractant, Cyanex 272. The results given in Fig. 3 for the extraction of zinc with 5% Cyanex 272 and 1% isodecanol in kerosene indicate the increase in the extraction of zinc with increase in the equilibrium pH of the solution for different aqueous feed solutions. The percentage extraction increases to even 91.39% at pH 4.1 from the aqueous feed solution containing 2.0 g/L Zn. The percentage extraction decreases to 81% and 73% for the aqueous feed solution containing 4.0 g/L and 6.0 g/L Zn. The pH required for the 50% extraction increases from 2.81 to 3.6 with increase in the zinc content in the aqueous feed solution from 2.0 g/L to 6.0 g/L (Fig. 3) as the metal extraction increases with increase in equilibrium pH of the solution and it also requires pH adjustment with base, similar to one reported by Rickelton and Boyle[7]. The distribution ratio of zinc extraction also increased due to increase in zinc extraction with increase in the pH of the solution.



[Organic = 5% Cyanex 272 + 1% isodecanol in kerosene (v/v), Organic : Aqueous = 1, Temperature = Room temp. (25-30^{0}C), Eq. pH=2]

Fig. 3. Effect of concentration of metal ions on the Extraction of zinc with Cyanex 272.

Extraction and separation of zinc and calcium

Further, studies have been carried out for the extraction and separation of zinc from the aqueous feed solution containing calcium (2.13 g/L Zn and 0.118 g/L Ca). The results given in Table-1 indicate that calcium is also extracted along with zinc when 5% Cyanex 272 and 1% isodecanol diluted in kerosene is used. The extraction of calcium was found to increase from 11.86% to 23.72% with an increase in the equilibrium pH of the aqueous solution from 2.16 to 4.21. Similar results have been reported for calcium extraction.[7] The extracted calcium in the organic phase is stripped with sulphuric acid. It will precipitate as gypsum when its concentration increases with the recycling of the stripping solution in the bath. The studies carried out from the aqueous solution containing 0.87 g/L Zn and 0.22 g/L Ca with 5% Cyanex 302 and 1% isodecanol in kerosene indicated selective extraction of zinc leaving all the calcium in the aqueous raffinate. The stripped solution obtained is free from the calcium, and could be recycled in the spinning bath of the rayon plant. Thus Cyanex 302 is the selective reagent for the purification of solution containing calcium. The subsequent studies have been carried out with Cyanex 302.

Table-1. Extraction and separation of Zn/Ca using different solvent

Organic : 5 % Cyanex 272 and 1% isodecanol in kerosene (v/v)
5 % Cyanex 302 and 1% isodecanol in kerosene (v/v)

Aqueous feed : (A) 2.13 g/L Zn and 0.118 g/L Ca, (B) 0.87 g/L Zn & 0.22 g/L Ca,

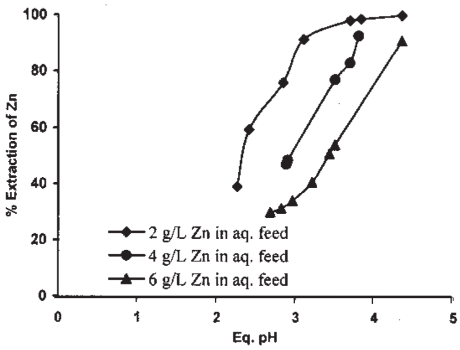
Org : Aq. : 1:1, Time : 5 minutes, Temperature : Room Temperature (25-30^{0}C)

Eq. pH is adjusted by adding pellets of NaOH and Conc. H_2SO_4

Sl. No.	% Extraction					
	A with Cyanex 272			B with Cyanex 302		
	Eq. pH	Zn	Ca	Eq. pH	Zn	Ca
1.	2.16	17.84	11.86	1.83	45.97	Nil
2.	2.67	56.61	12.45	1.90	53.44	Nil
3.	2.76	60.32	13.29	2.00	65.51	Nil
4.	2.99	69.62	15.22	2.13	77.47	Nil
5.	3.58	93.66	17.50	2.32	80.45	Nil
6.	4.21	99.71	23.72	2.92	96.5	Nil

Effect of concentration of metal ions on the zinc extraction with Cyanex 302

Initially, the effect of the concentration of zinc in aqueous solutions has been studied on metal extraction at different pH using 5% Cyanex 302 and 1% isodecanol in kerosene at organic to aqueous ratio 1. The results presented in Fig. 4 indicate an increase in metal extraction with a rise in the pH of the aqueous solutions. The extraction of zinc increased from 39% to 99.9% with rise in pH from 2.26 to 4.35 for the aqueous feed solution containing 2.0 g/L Zn. Further increases in the concentration of zinc in the solution from 2.0 g/L to 6.0 g/L, cause the extraction to drop from 99.90% to 90.90% at pH 4.35. The higher pH from 2.4 to 3.4 is required for 50% extraction for the solution containing 2.0 g/L to 6.0 g/L Zn, as the extraction efficiency improves with rise in pH of the solution[24]. The solvent also extracted total zinc from the purified leach liquor (1.93 g/L Zn and 0.086 g/L Fe) of rayon sludge at 4.0 pH and O/A ratio 1.

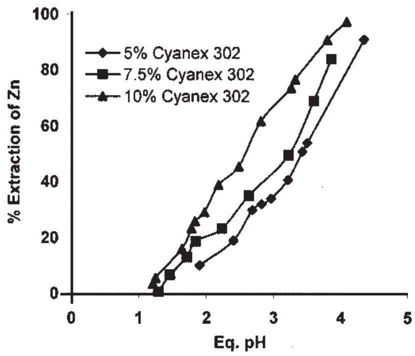


[Organic = 5% Cyanex 302 + 1% isodecanol in kerosene (v/v), Aq. feed = 2 , 4 and 6g/L zinc in sulphate solution, Organic : Aqueous = 1, Temperature = Room temp. (25-30^{0}C), Mixing time = 5 minutes]

Fig. 4. Effect of concentration of metal ions on the zinc extraction with Cyanex 302.

Effect of the concentration of Cyanex 302 on the extraction of zinc

As the concentration of organic extractant[24] plays an important role on the formation of complexes in the organic phase and the phase separation of the aqueous and organic phases during extraction of metals, studies have been carried out by varying the concentration of Cyanex 302 and phase modifier isodecanol diluted in kerosene. The results presented in Fig. 5 indicate an increase in zinc extraction from 90.90% (pH = 4.35) to 97.47% (pH = 4.09) from the aqueous feed solution containing 6.0 g/L Zn with increase in the extractant concentration from 5.0% to 10.0% Cyanex 302. The pH required for 50% extraction is 3.40, 3.30 and 2.50 for the different concentrations of the extractnts viz. 5%, 7.5% and 10.0%, respectively. There was no problem in the phase separation during the studies under the experimental condition mentioned above with rise in the organic extractants.



[Organic = 5% Cyanex 302 + 1% isodecanol in kerosene (v/v), Aq. feed = 6g/L zinc in sulphate solution, Organic : Aqueous = 1, Temperature = Room temp. (25-30^{0}C), Mixing time = 5 minutes]

Fig. 5. Effect of concentration of Cyanex 302 on the extraction of zinc.

Chemistry of solvent extraction

The extraction of zinc from the aqueous solution depends on the formation of complexes in the organic phase which depends on the concentration of the metal ions in the aqueous solution, concentration of the organic extractants, impurities etc. Two mechanisms as given below have been proposed to confirm the formation of the complex during the extraction.

Mechanism-A

When the solvent extracts a metal by replacing the hydrogen atoms of the solvent molecules, R_2Zn is the only extracting species and metal ions in the aqueous phase predominantly exist as Zn^{2+}, the equation can be represented as:[2, 24]

$$Zn^{2+}_{aq} + 2[RH]_{org} <\quad> R_2Zn_{org} + 2H^{+}_{aq} \qquad [1]$$

The equilibrium constant (K) may be expressed as:

$$K = [(R_2Zn)_{org}(H^+)^2_{aq}] / [(Zn^{2+})aq\ (RH)^2_{org}] \qquad [2]$$

$$\log [D] = \log K + 2\ pH + 2\log [(RH)] \qquad [3]$$

where distribution ratio D = $(R_2Zn)_{org}/(Zn^{2+})_{aq}$

At low acid concentration (H^+) in the aqueous phase, it will result in a high equilibrium proportion of the zinc in the organic phase (as R_2Zn). A high acid concentration will have the opposite effect, i.e. the stripping of metal takes place from the organic phase.

Mechanism-B

The neutral form of the extractant (Cyanex 272) exists as monomers in the organic phase whereas the acidic form exists as dimers.[27] Thus, the acidic as well as the neutral form of the extractant take part in the extraction process of metal ions. Assuming that $[R_2Zn.3RH]_{org}$ is the only extracting species in the organic phase and metal ions in the aqueous phase predominantly exist as Zn^{2+}, the distribution ratio [D] can be calculated by the expression as given below.

$$Zn^{2+}_{aq} + 2[(RH)_2]_{org} + [R^-]_{org} \longleftrightarrow [R_2Zn.3RH]_{org} + H^+_{aq} \qquad [4]$$

For which equilibrium constant may be written :

$$K = [(R_2Zn.3RH)_{org}\ (H^+)_{aq}]/[(Zn^{2+})_{aq}\ \{(RH)_2\}^2_{org}.\ (R^-)] \qquad [5]$$

$$\log D = \log K + pH + \log [R^-] + 2\log[(RH)_2] \qquad [6]$$

Both the mechanisms have been considered for the extraction of zinc from aqueous feed solutions over a wide pH range of extraction with Cyanex 272 and Cyanex 302. The results (Fig. 3&4) are plotted log D vs pH of the solutions in Fig. 6 and 7.

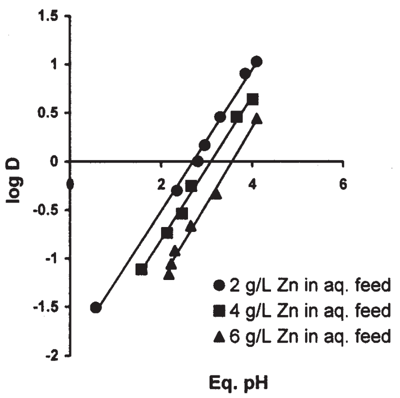


Fig. 6. Distribution ratio during extraction of zinc with Cyanex 272 at different pH.

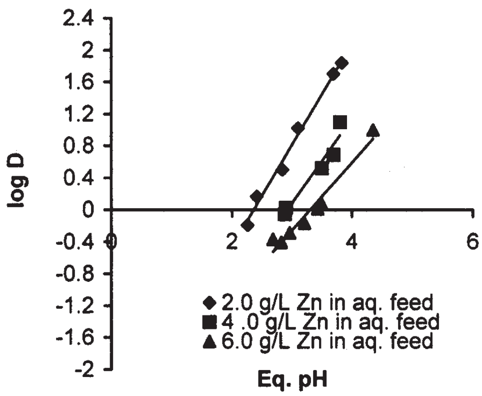


Fig. 7. Distribution ratio during extraction of zinc with Cyanex 302 at different pH.

The slope analysis (Table-2) supports mechanism-B for the formation of the complex as $[R_2Zn.3RH]_{org}$ in the organic phase for both Cyanex 272 and Cyanex 302 under the experimental conditions similar to those used by Devi et. al.[27] for zinc extraction from the sulphate solution.

Table 2. Slope analysis during extraction of zinc using different organic solvent.

Organic : 5% Cyanex 302 and isodecanol in kerosene (v/v)
5% Cyanex 272 and isodecanol in kerosene (v/v)

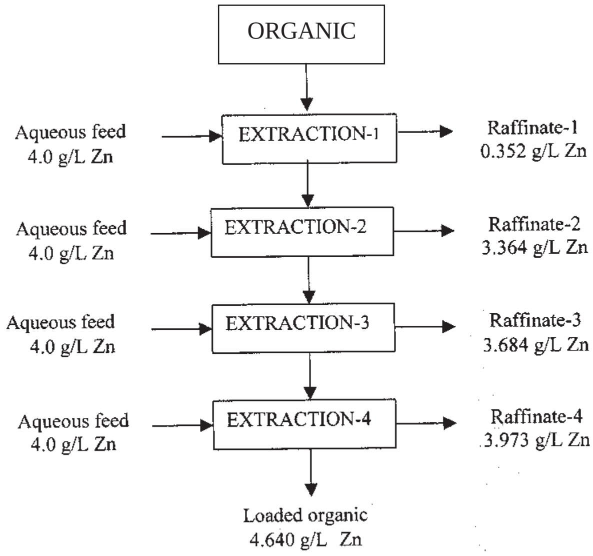
Aqueous feed : 2, 4 and 6 g/L Zn in aq. feed

Org.:Aq. : 1:1, Time : 5 minutes, Temperature : Room Temp. (25-30^{0}C)

Sl. No.	Aq. feed containing Zn (g/L)	Slope analysis for different solvent	
		Cyanex 272	Cyanex 302
1.	2	0.77	0.94
2.	4	0.78	0.90
3.	6	0.80	0.85

Loading capacity of the solvent

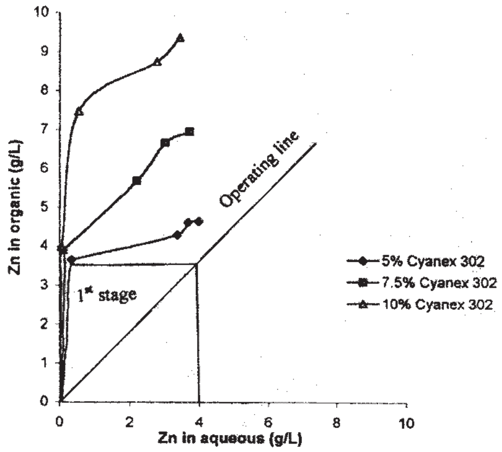
The loading capacity of the solvent has also been determined by using the same organic extractant each time with fresh aqueous feed solution while maintaining a pH constant. The organic extractant, Cyanex 302 of 5.0%, 7.5% and 10.0% modified with isodecanol and diluted in kerosene, was contacted with aqueous feed solution containing 4.0 g/L Zn at organic to aqueous ratio of 1 at room temperature. The extraction of zinc in different cross-current extractions is presented in Fig. 8 for 5.0% Cyanex. The results show the metal present in the aqueous raffinate at different stages of extraction. Subsequently, the calculation has been made for the metals present in the organic phase based on the raffinate analysis. The results presented in Fig. 9 show the loading of zinc in the organic phase. The loading capacities of 4.64, 6.94 and 9.36 g/



[Organic = Aqueous = 1, Temperature = Room temp. (25-30^{0}C), Mixing time = 5 minutes]

Fig. 8. Cross-current extraction of zinc using 5% Cyanex 302 and 1% isodecanol in kerosene.

L Zn were obtained for 5.0%, 7.5% and 10.0% Cyanex 302 respectively. The extraction isotherm has been made by plotting concentration of zinc in the organic phase against the concentration of zinc in the aqueous phase for different concentrations of the extractants (Fig. 9). A operating line drawn at an organic to aqueous ratio of 1 shows the complete extraction of zinc in one stage from aqueous feed solution containing 4.0 g/L Zn using 5% Cyanex 302 and 1% isodecanol in kerosene. The higher concentration of the extractant could be used for the selective extraction of zinc from the concentrated zinc aqueous solution under the controlled pH.



[Organic = 5% Cyanex 302 + 1% isodecanol in kerosene (v/v), Aq. feed = 4 g/L zinc in sulphate solution, Organic : Aqueous = 1, Temperature = Room temp. (25-30^{0}C), Mixing time = 5 minutes)

Fig. 9. Loading capacity and isotherm for the extraction of zinc with Cyanex 302.

Stripping studies

In the hyrometallurgical processing of zinc, the metal is obtained by electrowinning from acidic solution of sulphuric acid. Even the chloride leach solutions are converted to sulphate system before metal production as in the case of Zincex process[28, 29]. As reported in the literature, Cyanex 302 diluted in kerosene is stable with 200 g/L sulphuric acid during stripping even for 500 h at 30^{o}C[24]. The studies for zinc stripping were carried out from the loaded organic obtained after extracting zinc in optimised conditions from the sulphate leach solution (1.93 g/L Zn, 0.086 g/L Fe) of rayon sludge. The loaded organic contains 1.9 g/L Zn and 0.079 g/L Fe. Stripping of metals from the loaded Cyanex 302 was carried out using different concentration of sulphuric acid at an A/O ratio of 1 after scrubbing with water to remove any entrapped aqueous feed solution. The results depicted in Fig. 10 indicate that total zinc containing 1.9 g/L is stripped with 0.25% H_2SO_4 solution at room temperature. The stage requirement for the stripping of the loaded organic will be one stage as total zinc is stripped even with dilute sulphuric acid of 0.5%. However, iron present to the extent of 0.079 g/L in the organic phase is partially stripped. The stripping of iron increased from 46.8% to 54.4% with increase in acid concentration from 0.25% to 0.50% H_2SO_4. Further increase in acidity up to 5% H_2SO_4 has no effect on the stripping of iron. This may require sufficiently high acidity to regenerate the solvent for recycling. In order to control iron extraction a part of the solvent will be bled-off for stripping with strong acid.

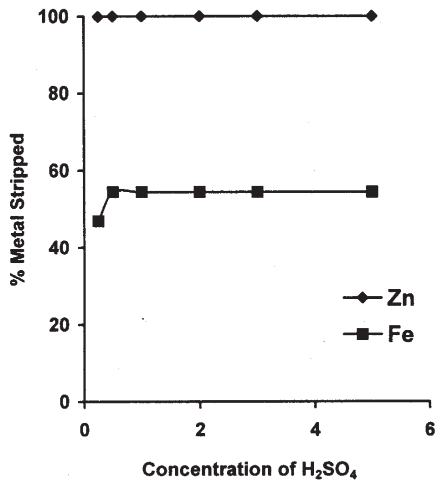


Fig. 10. Stripping studies of Zn/Fe loaded Cyanex 302.

Based on the above studies, a scheme has been proposed for the recovery of zinc from the rayon industry sludge following sulphuric acid leaching, iron precipitation by oxidation and pH adjustment, zinc extraction by solvent extraction and metal production by electrowinning (Fig. 11). The residue and raffinate generated after the recovery of zinc could be disposed safely without affecting environment.

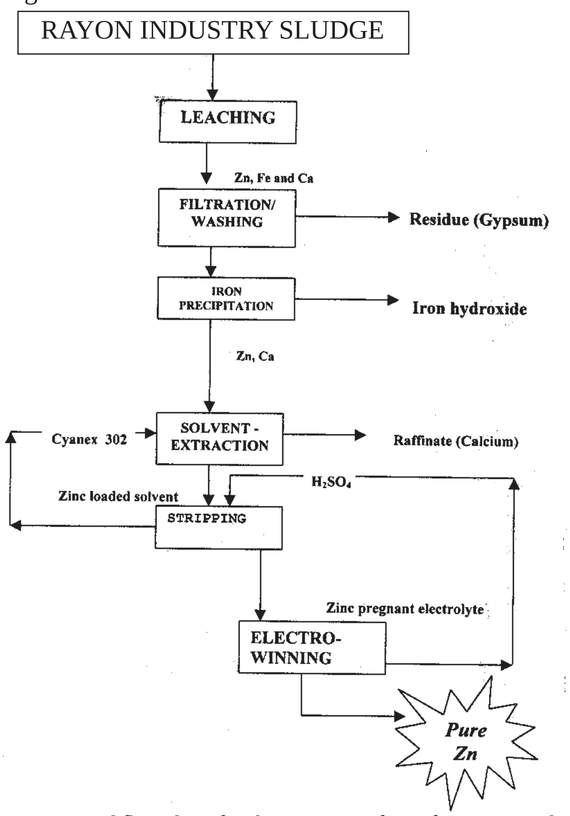


Fig. 11. Proposed flow sheet for the recovery of zinc from Rayon sludge.

CONCLUSION

The following conclusions are drawn from these studies:

- On comparing the thiophosphinic extractants, Cyanex 272, 301 and 302, Cyanex 302 has been found to be suitable reagent for selective extraction of zinc in (3.0-4.5) pH in 120 seconds leaving calcium in the raffinate.
- Both Cyanex 272 and Cyanex 302 form complex $[R_2Zn.3RH]_{org}$ during the extraction of zinc from the aqueous solution.
- The stage analysis of the Cyanex 302 revealed that zinc is effectively extracted in one stage at appropriate organic to aqueous ratio at controlled pH. The loaded zinc can be stripped in one stage only with adjustment of acid concentration.

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REFERENCES

1. Bart, H.J.; Marr, R.; Scheks, J. and Koncar, M. (1992) Modelling of solvent extraction equilibria of zinc(II) from sulphate solutions with bis-(2-ethylhexyl)phosphoric acid. Hydrometallurgy, 31, pp. 13-28.
2. Corsi, C.; Gnagnarelli, G.; Slater, M.J. and Veglio, F. (1998) A Study of the kinetics of zinc stripping for the system Zn/H_2SO_4 /D2EHPA/n-heptane in a Hancil constant interface cell and a rotating disc contactor. Hydrometallurgy, 50(2), pp. 125-141.
3. Cote, G. (2000) Hydrometallurgy of strategic metals. Solvent Extr. Ion Exch., 18(4), pp. 703-727.
4. Heng, R.; Lehmann, R. and Garcia, D.J. (1986) In Zinc recovery from hydrometallurgical zinc processing residues by solvent extraction, Proceedings of the Int. Conf. ISEC '86, Munich, FRG, Sept 11-16, 2, pp. 613-624.
5. Huang, T.C. and Juang, R.S. (1986) Kinetics and mechanisms of zinc extraction from sulphate medium with di-(2-ethylhexyl) phosphoric acid. J. Chem. Eng. Jpn., 19(5) pp. 279-285.
6. Rickelton, W.A. and Boyle, R.J. (1988) Solvent extraction with organophosphines - commercial and potential applications. Sep. Sci. Technol., 23, pp. 1227-1250.
7. Rickelton, WA and Boyle, R.J. (1990) The selective recovery of zinc with new thiophosphinic acids. Solvent Extraction and Ion Exchange, 8(6), pp. 783-797.
8. Sole, K.C. and Hiskey, J.B. (1992) Solvent extraction characteristics of thiosubstituted organophosphinic acid extractant. Hydrometallurgy, 30, pp. 345-365.
9. Kopacz, S. (1994) Extraction of zinc(II) ions from sulphate solutions with mixtures of n-hexanoic acid and pentanol in n-decane. Hydrometallurgy, 35, pp. 313-319.
10. Ritcey, G.M. and Ashbrook, AW. (1979) Solvent Extraction: Principles and Applications to Process Metallurgy, Part II. Elsevier Scientific Publishing Co: Amsterdam, pp. 533-541.
11. Roy, D.L. and Sardesai, S.G. (1977) Recovery of zinc from industrial zinc wastes. Chemical Concepts, October, pp. 23-30.
12. Svendsen, H.F.; Schei G. and Osman, M. (1990) Kinetics of extraction of zinc by di(2-ethylhexyl) phosphoric acid in cumene. Hydrometallurgy, 25, pp. 197-212.

13. Ajawin, L.A.; Perez Ortiz, E.S. and Sawistowski, H. (1983) Extraction of zinc by di(2-ethylhexyl) phosphoric acid. Chem. Eng. Res. Des., 61, pp. 62-66.

14. Sato, T.; Kawamura, M. and Ueda, M. (1978) The extraction of divalent manganese, iron, cobalt, nickel, copper and zinc from hydrochloric acid solutions by di(2-ethylhexyl) phosphoric acid. J. Apl. Chem. Biotechnol, 28, pp. 85-94.

15. Preston, J.F. (1983) Solvent extraction of base metals by mixtures of organophosphoric acids and non-chelating oximes. Hydrometallurgy, 10, pp. 187-204.

16. Thorsen, G. (1983) Commercial Processes for Cadmium and Zinc. In Hand Book of Solvent Extraction, Lo T.C., Handson, C., Eds.; John Wiley & Sons: New York, pp. 709-716.

17. Grimm, R. and Kolarik, Z. (1974) J. Inorg. Nucl. Chemistry, 36, pp. 174.

18. Diaz, G.; Martin, D. and Lombera, C. (1994) Zinc recycling through the modified Zincex process. In Recycling of Metals, Proceedings of Second International Conference, Amsterdam, Netherlands, Oct 19-21, ASM International Europe, Belgium, pp. 77-84 .

19. Shah, V. (1998) Solvent extraction in electrowinning of zinc from secondary sources. In Lead & Zinc Recycling Technology & Environment, Proceedings of National Conference, New Delhi, India, Dec 17-18, India Lead Zinc Development Association, New Delhi, India.

20. Koppiker, K.P. (1993) Solvent extraction electrowinning of metals from secondary sources in India-opportunities and challenges. In Hydrotech '93, Proceedings of Conference, pp. India, 29-46.

21. Reinhard, H.; Ottertun, H. and Troeng, T. (1975) Solvent extraction process for the recovery of zinc from weakly acidic effluent. In Appl. Chem. Engg. Treat. Sewage Ind, Liquid. Effluents. Symposium Proceedings, Chem. Engg. Symposium Series No. 41.

22. Caravaca, C.; Cobo, A. and Alguacil, F.J. (1994) Considerations about the recycling of EAF flue dusts as source for the recovery of valuable metals by hydrometallurgical processes. Resources Conservation and Recycling, 10, pp. 35-41.

23. Cyanamid, American Cynamid Company, Technical Brochures, New Jersey, pp.1-8.

24. Caravaca, C. and Alguacil, F.J. (1991) Study of the ZnSO4- Cyanex 302 extraction equilibrium system. Hydrometallurgy, 27, pp. 327-338.

25. Sole, K.C.; Feather, A.M. and Cole, P.M. (2005), Solvent extraction in southern Africa: An update of some recent hydrometallurgical developments, Hydrometallurgy 78, pp. 52-78.

26. Jha, M.K.; Kumar, V.; Maharaj, L. and Singh, R.J. (2004) Studies on leaching and recycling of zinc from rayon waste sludge", Industrial & Engineering Chemistry Research , Pulb. American Chemical Society, Vol.43(5), pp.1284-1295.

27. Devi, N.B.; Nathsarma, K.C. and Chakravortty, V. (1997) Extraction and separation of Mn(II) and Zn(II) from sulphate solutions by sodium salt of Cyanex 272. Hydrometallurgy 1997, 45(1-2), pp. 169-179.

28. Nogueira, E.D.; Regife, J.M. and Arcocha, A.M. (1979) Winning zinc through solvent extraction and electrowinning. Engineering and Mining Journal, 180(10), pp. 92-94.

29. Nogueira, E.D.; Regife, J.M. and Blythe, P.M. (1980) Zincex- the development of a secondary zinc process. Chemistry and Industry, 2, pp. 63-67.