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EXPERIMENTAL AND THEORETICAL STUDIES OF SOLVENT EXTRACTION OF COPPER (II) WITH Di-(2-ETHYLHEXYL) PHOSPHORIC ACID

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The preferential extraction of copper from a multicomponent feed is achieved by using kerosene solution of di-(2-ethylhexyl) phosphoric acid. The extraction of metal has been found to be influenced by both distribution constant and dissociation constant of the metal species involved. The theoretical predictions were confirmed experimentally by employing multistage extraction unit.

Key words: Electrical neutrality, Dissociation constant, Separation factor.

Introduction

Solvent extraction is a well established and most important process for separation, purification and concentration of metalions from the aqueous solution of low grade ores. Extraction of metals with acidic extractant release hydrogen ions resulting in decrease in pH. This give rise to the formation of non-extractable metal species and also causes protonation [3] of the extractant in the aqueous phase.

In this study extractant is initially loaded with metal ions and then brought in contact with an aqueous phase containing two metal ions. The system will be in stoichiometric deficiency of anions in relation to the cations present. On dissociation of metal-extractant complex (excess metal) in the aqueous phase, the three metal ions (two from the aqueous phase and one from the organic phase) will complete for the available anions. The metal ions with higher dissociation constant (instability constant) will react preferentially with the anions forming a soluble salt in the aqueous phase releasing charged metal ions. These charged ions will readily be extracted thus causing an enrichment of the extract phase with desired metal ions of high distribution constant and low dissociation constant.

Moreover, this extractant will release negligible quantity of hydrogen ions in the aqueous phase and consequently pH of the aqueous phase will remain high to favour the maximum extraction since equilibrium pH value [3] has the fundamental importance for optimum extraction.

If this principle is extended to multistage counter current operation then the product of high purity can be obtained without using scrubbing stages [4].

The present paper deals with the recovery of copper from a multicomponent feed to study the effect of excess metal in the system. Furthermore, the validity of this concept has been verified on a vertical multistage mixer-settler.

Theory of multi-stage solvent extraction process. Consider a final stage of a counter-current multistage mixer-settler in which a fresh aqeuous feed containing metal ions contacts with the metal loaded extract phase. The amount of total metal ions present in the system exceeds the Stoichiometric amount of anions. The condition of electrical neutrality in the aqueous phase at working pH of 4.9 requires that the metal ions be equal to the anions in the aqueous phase. Thus, any excess metal must remains in its undissociated form in the organic phase because of its very high distribution constant compared to metal species present in the aqueous phase. A number of workers [5-7] have reported that metal in the aqueous phase is only in its dissociated form and undissociated species are extracted into the organic phase. This is another way of describing very high distribution constant for the species.

Now consider a situation when an extractant loaded with a metal Z^{n+} is brought into contact with a fresh aqueous feed of metals M^{n+} and N^{n+}. The extraction mechanism at equilibrium as described in Fig. 1, may be involved.

The electrical neutrality involved may be described by the following equation:-

$$[M^{n+}] + [N^{n+}] + [H^{+}] + [Z^{n+}] = [OH^{-}] + [R^{n-}] + 2[A^{n-}] \quad .....(1)$$

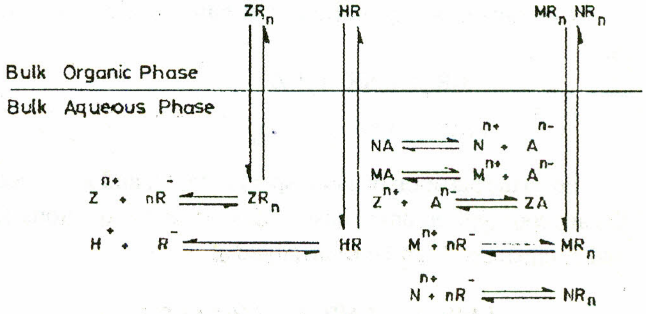

Fig. 1. Reaction mechanism of metal extraction for multi-component system.

In the aqueous phase, total metal ions equal to the stoichiometric amount of anions will dissociate and remaining will stay in its undissociated form in the organic phase. Furthermore, the metal ions with low distribution and high dissociation contants will shift to the aqueous phase whereas the metal ions with high distribution and low dissociation constants will be extracted into organic phase. The extractant in the equeous phase is considered to be monomer [8,9] and present in a negligible quantity, therefore, it may be neglected in the equation (1). The concentration of H^+ and OH are not significant compared to the remaining terms at the working pH of 4.9

Hence:

$$[M^{n+}] + [N^{n+}] + [Z^{n+}] = 2\,[A^{n-}] \quad ....(2)$$

Now the total cations present in the aqueous phase must be equal to the total anions, any excess cations will be extracted into the organic phase to maintain electrical neutrality [2] of the system. If there is an excess amount of anions present, then more cations will dissociate and extraction will not be favoured.

The partition constant of these metals may be expressed as:-

$$P_M = \frac{[MR_n]_o}{[MR_n]_a} \quad ....(3)$$

$$P_N = \frac{[NR_n]_o}{[NR_n]_a} \quad ....(4)$$

$$P_Z = \frac{[ZR_n]_o}{[ZR_n]_a} \quad ....(5)$$

The reaction takes place in the aqueous phase and the ionization equilibrium for these competing species may be presented as:-

$$(M^{n+})_a + (N^{n+})_a + 2\,(ZR_n)_a \rightleftharpoons (MR_n)_a + (NR_n)_a + 2(Z^{n+})_a ....(6)$$

The ionization equilibrium constant K for equation (6) is:-

$$K = \frac{[MR_n]_a\,[NR_n]_a\,[Z^{n+}]_a^2}{[M^{n+}]_a\;[N^{n+}]_a\;[ZR_n]_a^2} \quad ....(7)$$

From the partition of metal species M, N, and Z between the aqueous and organic phase as described by equations 3,4 and 5, equation 7 can be re-arranged as :-

$$K = \frac{[MR_n]_o}{[M^{n+}]_a P_M}\;\frac{[NR_n]_o}{[N^{n+}]_a P_N}\;\frac{[Z^{n+}]_a^2\,P_Z^2}{[ZR_n]_a^2} \quad ....(8)$$

Defining distribution constant (D) as the ratio of metal ions in the organic phase to the metal ions in the aqueous phase produces:

$$\frac{P_M \cdot P_N \cdot K}{P_Z^2} = \frac{D_M \cdot D_N}{D_Z^2} \quad ....(9)$$

A complex reaction occurs among the metal species M,N, and Z. Each metal species competes with one another in order to get extracted in the organic phase.

If the total cations (M+N+Z) in the system (organic + aqueous) are in excess of the stoichiometric value of A^{n-} then all the metal species in the aqueous phase and metal species in the extract phase on dissociation in the aqueous phase will conete to stay in the dissociated form but only the metal species with lower distribution constant and higher dissociation constant will be favoured and hence other metal species will be extracted in the organic phase and remain there in the undissociated form.

Defining overall separation factor (α) as the ratio of the distribution constants of competing species, the equation 9 may be simplified to:-

$$\alpha = \frac{P_M\,P_N\,K}{P_Z^2} \quad ....(10)$$

In order to achieve the necessary high value for the extraction of a desired metal species M, the value of P_Z and P_N must be low compared to the value of P_M and the value of K should be as high as possible. If these conditions are not met satisfactorily, then metal Z and N may be favoured and metal M will not be able to replace them in the organic phase.

The maximum benefit from this development may be achieved by employing multistage counter-current contact of the organic and aqueous phases. The metal Z^{n+} in the organic phase will completely be exchanged with the metal M^{n+} from the aqueous phase during the operation. This is analogous to a reflux action in an extractive distillation process.

This theory was verified experimentally by studying the extraction of copper from a single component feed and from a solution of copper and nickel feed on a multistage vertical mixer-settler.

Experimental

An experimental programme was devised to test the validity of the theoretical aspects developed by studying steady state distribution of metal ions on a multistage counter-current extraction unit.

Preparation of solution and equilibrium distribution data were obtained at 25° ± 1°, as described previously [1].

Copper, nickel and calcium concentrations in the aqueous phase were determined by Atomic Absorption Spectrophotometer.

Multistage extraction. A vertical multistage mixer settler [10] modified for present work [11] was employed for the multistage counter-current extraction. The contactor consisted of six stages superimposed on one another with alternative position of mixers and settlers forming a rectangular vertical tower as shown in Fig. 2. The mixer and settler compartments were facilitated with sampling ports. The DEHPA solution and the aqueous solution of copper and nickel were pumped into the bottom and the top of mixing compartments respectively. The flow of light and heavy phase within the unit was achieved by difference in their densities and gravity. The mixing of the two phases was achieved by a flat bladed turbine type impellers attached to two common stainless steel shafts driven by variable speed motors. The extractant phase leaving the top settling compartment was stirpped with hydrochloric acid to recover metal contents. Raffinate was fed to the extractant treatment section to extract calcium ions in the organic phase. The organic phase was recycled in the contactor for the recovery of the desired metal.

The mixer-settler was run for four hrs. continuosly and then samples from final extract and raffinate phases were drawn at set intervals of 10 min. and analysed to ensure steady state conditions. Once steady state was achieved, then samples were drawn from each mixing and settling compartments for final analysis.

Results and Discussion

Results in Table1 on the distribution of copper, nickel and calcium with varying concentration of chloride ions in the aqueous phase confirm that the overall distribution constant depends on the amount of total metal and total anions present in the system. The amount of chloride ions in the system varies from 2.324 g dm^{-3} - 11.635 g dm^{-3} and distribution constants for copper and nickel vary from 25.32 - 1.02 and 0.21 - 0.006 respectively, whilst the same for calcium varies from 2.15 - 0.49. These results show that as the concentration of chloride ions in the aqueous phase increases, the total metal concentration (copper, nickel and calcium) does not increase in proportion. Hence the transfer of metal ions to the organic phase reduces, thereby reduces the overall distribution constant of the metals. From these results, it is also evident that the extraction of nickel and calcium is markedly less favourable as compared to the extraction of copper. This also shows that the dissociation constants of nickel and calcium are much higher than copper and therefore these metal ions stay in the aqueous phase, whereas copper having higher distribution constants and lower dissociation constant replace calsium in the organic phase. This trend is also evident in Table 2, 3 and 4.

Furthermore, Table 2 and 3 give the pH values of the feed and of the equilibrated aqueous phase at various copper and nickel concentrations. It is obvious from the results that the increase in final pH is affected by the hydrolyses [1,13] of the metal species in the aqueous phase.

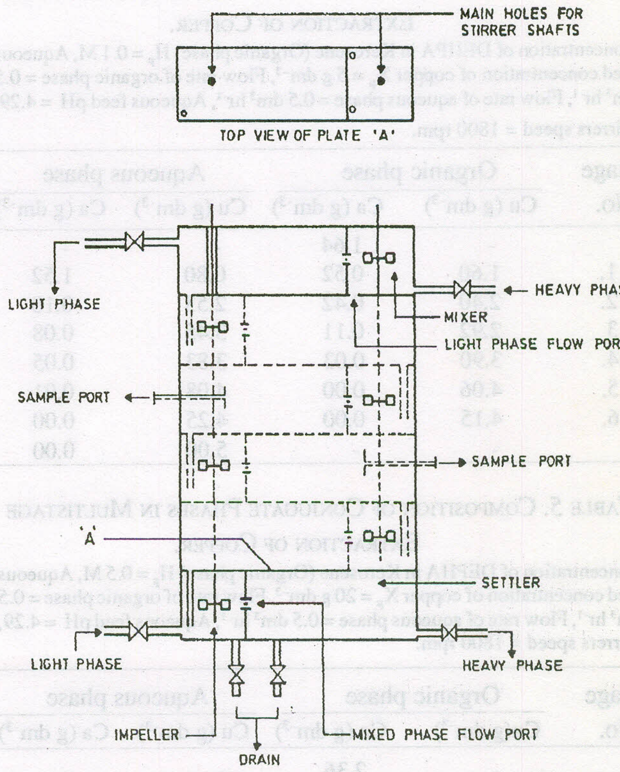

Fig. 2. Internal arrangement of vertical mixer settler.

TABLE 1. EQUILIBRIUM DISTRIBUTION OF METAL IONS SPECIES (DEHPA = 0.1 M; FEED pH = 4.29).

	Aqueous phase					Organic phase			Distribution constant, D		
No.	Equlib. pH	Cl_2 (g dm^{-3})	Cu (g dm^{-3})	Ni (g dm^{-3})	Ca (g dm^{-3})	Cu (g dm^{-3})	Ni (g dm^{-3})	Ca (g dm^{-3})	Cu	Ni	Ca
1.	5.84	2.324	0.038	0.825	0.520	0.962	0.175	1.120	25.32	0.210	2.15
2.	5.15	4.656	0.280	1.883	0.710	1.720	0.117	0.930	6.14	0.060	1.31
3.	4.42	6.979	0.880	2.905	0.860	2.120	0.095	0.780	2.41	0.030	0.91
4.	4.18	9.310	1.620	3.956	1.035	2.380	0.044	0.605	1.47	0.010	0.58
5.	4.09	11.635	2.480	0.970	1.104	2.520	0.030	0.536	1.02	0.006	0.49

Table 2. Equilibrium Distribution of Metal Ions Species (DEHPA = 0.1 M; Copper = 1.0 g/1, Nickel = 1.0 g/1).

Feed	Aqueous phase				Organic phase			Distribution constant, D		
pH	Equilibrium pH	Cu (g dm^{-3})	Ni (g dm^{-3})	Ca (g dm^{-3})	Cu (g dm^{-3})	Ni (g dm^{-3})	Ca (g dm^{-3})	Cu	Ni	Ca
4.29	5.84	0.038	0.825	0.52	0.962	0.175	1.12	25.32	0.210	2.15
3.40	5.78	0.053	0.916	0.61	0.947	0.084	1.03	17.87	0.092	1.69
2.50	5.45	0.095	0.939	0.68	0.905	0.058	0.96	9.52	0.062	1.41
2.00	4.15	0.121	0.980	0.84	0.879	0.019	0.80	7.26	0.019	0.95

Table 3. Equilibrium Distribution of Metal Ions Species (DEHPA = 0.5 M; Copper = 5 g/1, Nickel = 5 g/1).

Feed	Aqueous phase				Organic phase			Distribution constant, D		
pH	Equilibrium	Cu (g dm^{-3})	Ni (g dm^{-3})	Ca (g dm^{-3})	Cu (g dm^{-3})	Ni (g dm^{-3})	Ca (g dm^{-3})	Cu	Ni	Ca
4.29	2.37	3.950	4.97	1.208	1.050	0.03	1.152	0.270	0.006	0.954
3.40	2.33	4.000	5.00	1.270	1.000	-	1.090	0.250	-	0.858
2.50	2.19	4.246	5.00	1.312	0.754	-	1.048	0.178	-	0.799
2.00	2.08	4.520	5.00	1.350	0.480	-	1.010	0.106	-	0.748

Table 4. Composition of Conjugate Phases in Multistage Extraction of Copper.

Concentration of DEHPA in Kerosene (Organic phase) $H_F = 0.1$ M, Aqueous feed concentration of copper $X_F = 5$ g dm^{-3}, Flow rate of organic phase = 0.5 dm^3 hr^{-1}, Flow rate of aqueous phase = 0.5 dm^3 hr^{-1}, Aqueous feed pH = 4.29, Stirrers speed = 1800 rpm.

Stage	Organic phase		Aqueous phase	
No.	Cu (g dm^{-3})	Ca (g dm^{-3})	Cu (g dm^{-3})	Ca (g dm^{-3})
	-	1.64	-	-
1.	1.60	0.52	0.80	1.52
2.	2.40	0.42	2.53	0.10
3	2.92	0.11	3.45	0.08
4.	3.90	0.03	3.83	0.05
5.	4.06	0.00	4.08	0.01
6.	4.15	0.00	4.25	0.00
	-	-	5.00	0.00

Table 5. Composition of Conjugate Phases in Multistage Extraction of Copper.

Concentration of DEPHA in Kerosene (Organic phase) $H_F = 0.5$ M, Aqueous feed concentration of copper $X_F = 20$ g dm^{-3}, Flow rate of organic phase = 0.5 dm^3 hr^{-1}, Flow rate of aqueous phase = 0.5 dm^3 hr^{-1}, Aqueous feed pH = 4.29, Stirrers speed = 1800 rpm.

Stage	Organic phase		Aqueous phase	
No.	Cu(g dm^{-3})	Ca (g dm^{-3})	Cu (g dm^{-3})	Ca (g dm^{-3})
	-	2.36	-	-
1.	9.24	0.58	3.51	2.300
2.	11.20	0.40	13.00	0.135
3	12.01	0.13	15.00	0.080
4.	13.24	0.02	15.85	0.011
5.	15.05	0.00	17.16	0.000
6.	15.72	0.00	19.00	0.000
	-	-	20.00	0.000

Table 6. Composition of Conjugate Phases in Multistage Extraction of Copper.

(Concentration of DEHPA in Kerosene (Organic phase) $H_F = 0.5$ M, Aqueous feed concentration of copper $X_F = 20$ g dm^{-3} ,Nickel $X_F = 20$ g dm^{-3} , Flow rate of organic phase = 0.5 dm^3 hr^{-1}, Flow rate of aqueous phase = 0.5 dm^3 hr^{-1}. Aqueous feed pH = 4.29, Stirrers speed = 1800 rpm.)

Stage	Organic phase			Aqueous phase		
No.	Cu (g dm^{-3})	Ni (g dm^{-3})	Ca (g dm^{-3})	Cu (g dm^{-3})	Ni (g dm^{-3})	Ca (g dm^{-3})
	0.00	0.00	2.360	-	-	-
1.	9.20	3.05	0.680	3.14	18.000	2.310
2.	13.95	3.50	0.240	12.34	1.360	0.200
3	14.59	3.11	0.175	17.09	18.800	0.065
4.	15.29	0.89	0.045	17.73	18.910	0.040
5.	16.49	0.82	0.000	18.43	19.760	0.010
6.	16.86	0.00	0.000	19.63	20.000	-
	-	-	-	20.00	20.000	-

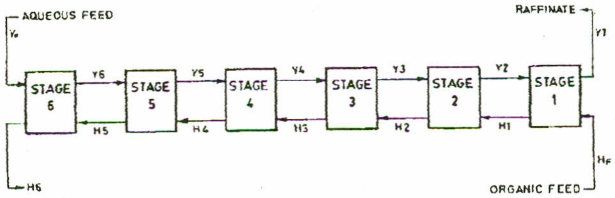

Fig. 3. Flow diagram of mixer-settler extractor.

Table 2 and 3 also give the values of the distribution constants of copper nickel, and calcium. In this case, the total metal in the system remains the same but the anion concentration is varied by the addition of hydrochloric acid. As expected, the overall distribution constant for the metal species decreases as the anions concentration increases and this supports the theoretical analysis presented earlier.

Table 1,2 and 3 indicate that the nickel and calcium have higher dissociation constant and replace copper by an ion exchange process in the aqueous phase. The high concentration of calcium and nickel remaining in the organic phase after an equilibrium stage could be further reduced and the effect of difference in dissociation constant is best exploited by employing a multistage mixer settler. A set of experimental results carried out on a six stage vertical mixer-settler unit is given in Table 4, 5 and 6.

The results given in Table 4, 5 and 6 are tabluted according to Fig.3. The results in Table 4 for multistage extraction of single species (copper) strongly confirm the predictions made by equilibrium studies. The organic phase (0.1 M DEHPA) loaded with 1.64 g dm^{-3} calcium was contacted counter currently in a vertical mixer-settler with the aqueous phase containing 5.0 g dm^{-3} of copper. The contactor was run continuously for 4 hrs at the set conditions. The results indicated a consistent replacement of calcium by coppper as it passes through the stages. In the first equilibrium stage, 1.60 g dm^{-3} copper was extracted in the organic phase nd shifted most of the calcium to the aqueous phase. At the fifth stage all the calcium was transferred to the aqueous phase and the exit flow of organic phase after the sixth stage contained 4.15 g dm^{-3} copper and no calcium.

The results in Table 5 for 0.5 M DEHPA loaded with 2.36 g dm^{-3} calcium and the aqueous feed concentration of 20 g dm^{-3} of copper also indicated the same trend and showed an extraction of 15.72 g dm^{-3} copper.

The results given in Table 6 show a practical situation in which more than one metal ions are present in the system. The extraction of copper from an aqueous solution containing 20 g dm^{-3} copper and 20 g dm^{-3} nickel with 0.5 M DEHPA loaded with 2.36 g dm^{-3} calcium was carried out. The concentration of copper and nickel increases in the organic phase at the initial two stages and both replace calcium. No sooner all the calcium transfers to the aqueous phase than copper starts replacing all the nickel from the organic phase in the later stages of mixer settler due to the difference in their dissociation and distribution constants as discussed in the theory. Furthermore, these results also cofirm the view that employing an excess metal in a mixer-settler contactor will not give an impurity in the final product as long as proper studies has been carried out for the selection of the execess metal.

Burin [12] and Ritcey [4] also applied multistage contactors to remove the impurities from the extract phase by using pure metal solution to scrub extract phase which also highlights the principle of metal exchange. It could have been understood better if it had been explained on the basis of competition of metals to stay in the organic phase depending upon their difference in dissociation and distribution constants.

Conclusions

The overall distribution constant of a metal depends on the amount of total cations and total anions present in the system.

The use of excess metal enhances the pH in favour of extraction of copper and hence the control of pH in a multistage mixer-settler seems unnecessary for this particular system.

In a continuous process, metals with higher dissociation constant present in the extract phase can be used to replace any other metal with lower dissociation constants present in the aqueous phase without contamination of the final products. It also maintains the equilibrium pH in favour of higher extraction.

NOMENCLATURE

A^{n-} = Concentration of anions (chloride in the aqueous phase)
D_i = Distribution constant of metal i
H^+ = Concentration of hydrogen ions in the aqueous phase
H_F = Initial concentration of DEHPA in the organic feed in mixer-settler.
H_R = Concentration of DEHPA in the organic phase
K = Equilibrium constant
PM,PN,PZ = Partition constant of metal M, N and Z, respectively
M, N, Z, = Concentration of metal ions.
MA,NA,ZA = Concentration of undisssociated metal salts in the aque ous phase
MR,NR,ZR = Concentration of undissociated metal salts in the organicphase
R = Concentration of organic anions
X_F = Initial concentration of metal ions in the aqueous feed in the mixer-settler

GREEK LETTERS:

α = Separation factor.

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