Iranian Journal of Chemical Engineering
Vol. 8, No. 3 (Summer), 2011, IAChE

Solvent Extraction of Zinc from Acidic Solution Obtained from Cold Purification Filter Cake of Angouran Mine Concentrate Using D2EHPA

A.A. Balesini, H. Razavizadeh, A. Zakeri*
Islamic Azad University of Miyaneh Branch, Miyaneh, Iran
Department of Materials and Metallurgy Engineering, Iran University of Science and Technology, Tehran, Iran

Abstract
Filter cakes obtained in the conventional acid leaching of zinc concentrate are considered a major secondary source for zinc. Solvent extraction may be utilized for the selective separation of zinc from other elements in hydrometallurgical processing of such resources. In the present work, extraction of zinc from the solution obtained from sulfuric acid leaching of cold purification filter cake of Angouran concentrate were performed by using D2EHPA as the extractant. The effects of extractant concentration diluted in Kerosene, solution pH and phase ratio (O:A) were investigated and their optimized values were obtained to be 40 vol.%, 2.5-3 and 4:1, respectively. Under these conditions, 98.8% of Zn could be extracted.

Keywords: *Zinc Hydrometallurgy, Purification, Filter Cake, D2EHPA*

1- Introduction

Approximately 30% of global zinc production arises from recycled zinc. With increasing awareness of secondary zinc materials as a valuable resource and stricter environmental legislation that restricts dumping of these hazardous materials, interest in their recycling has increased [1]. Zinc bearing materials such as zinc dusts, zinc oxide, smelting slags, etc, which is dissolved in sulfuric acid, can be refined by suitable solvent extraction processes [2]. Numerous studies have been performed in this regard, using di-2ethylhexyl phosphoric acid (D2EHPA) as the extractant because this extractant is selective for zinc over most the species deleterious to EW (Cu, Cd, Co, Ni, and the halides) and is readily stripped by acid concentrations typical of the spent tankhouse electrolyte (~180 g/L H_2SO_4) [1-6].

For example, Cox *et. al.* [7] have investigated the extraction of Zn, Cd, Pb and Cu from waste streams in the zinc-lead industry. This research shows that, Zn is extracted stronger than Cd in lower pH, and

∗ Corresponding author: A.Balesini@m-iau.ac.ir

stripping of metals from D2EHPA, by using only 2M H_2SO_4, is easy. Owusu [8] has investigated selective extraction of Zn from Zn-Cd-Co-Ni sulphate solution by D2EHPA and TBP. Martin *et. al.* [9] have suggested a method for electrolytic production of zinc with acidic solution-solvent extraction by D2EHPA and di-2 ethylhexyl phosphonic acid-electrowinning process from secondary zinc raw materials.

Also, Zincex processes have the ability to treat primary and/or secondary zinc materials. In this processes solvent extraction is the key step used to concentrate and purify the zinc solution, so a solution of di-2ethylhexyl phosphoric acid (D2EHPA) as extractant reagent in Kerosene base is used as the organic phase. In recent years, the reactive system Zn/H_2SO_4/D2EHPA has been investigated by many workers, and various diluents have been used, but models of reaction are different. For Kerosene, the overall reaction to extract the zinc is suggested, according to the reaction 1 [4, 10-11]:

$$2(R-H)_{org} + (Zn^{2+})_{aq} \leftrightarrow (R_2Zn)_{org} + 2(H^+)_{aq} \quad (1)$$

2- Experimental

In this research, cold purification filter cake from conventional hydrometallurgical treatment of Angouran mine concentrate was selected and leached in a sulfuric acid solution. The resulting feed solution contained Zn, residual Cd and Ni, and were subjected to a series of systematic SX trials for zinc extraction ($[Zn^{2+}]$ =25 g/L, $[Ni^{2+}]$ =1.5 g/L and $[Cd^{2+}]$ <20 mg/L). In a typical run, about 100-500 mL of the leach solution was mixed with the appropriate volume of the organic phase for 5 minutes. Ammonia (12.5 vol.%) and Na_2SO_4 (0.1 mol/L) solutions were used for controlling and keeping pH constant, respectively. WTW type indicator and HW type electrode were used for pH measuring. Perkin-Elmer AA300 was used for analyzing samples with the AAS method.

Four concentrations of 10, 20, 30, and 40 vol.% of D2EHPA diluted in Kerosene were chosen for determining optimum extractant concentration. Extraction percentage vs. equilibrium pH for O:A=1 was plotted for determining optimum pH. Extraction isotherm was plotted by using O:A ratios of 4:1, 2:1, 1:1, 1:2, 1:5, and 1:10. These experiments were carried out at 40±2°C using a thermostatic reaction bath.

3- Results and discussion

3.1- Effect of D2EHPA concentration on Zn extraction

In these experiments, a high concentration of zinc in solution caused a high pH mixture of aqueous and organic phases to convert to gelling condition, and the tests continuation was stopped. So, a synthetic solution was used for this part of the experiments with: $[Zn^{2+}]$ = 5 g/L, $[Ni^{2+}]$ = 1.5 g/L and $[Cd^{2+}]$ <20 mg/L.

Figure 1 and Table 1 shows the effect of D2EHPA concentration from 10 to 40 vol.% on Zn, Cd and Ni extraction.

It is observed that increasing D2EHPA concentration from 10 to 40 vol.% caused pH_{50}^{Zn} to decrease from 1.4 to 0.7. On the other hand, $pH_{50}^{(Cd-Zn)}$ increased from 1.0 to

1.2 and $pH_{50}^{(Ni-Zn)}$ increased from 2.2 to 2.5. Therefore, by increasing D2EHPA concentration up to 40 vol.%, zinc extraction was shifted to lower pH values and it changed the difference of pH_{50}^{Zn} with pH_{50}^{Cd} and pH_{50}^{Ni} to high possible contents. Hence, selective separation of Zn using 40 vol.% D2EHPA was better than other concentrations.

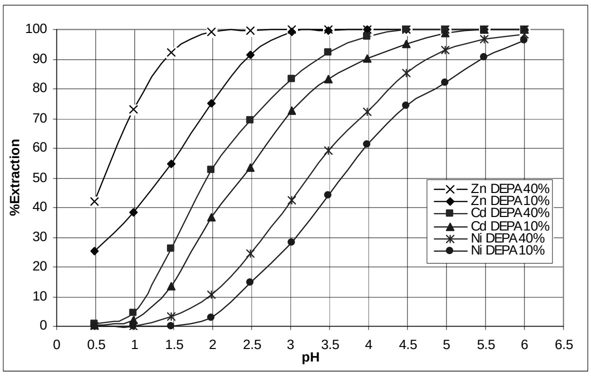

Figure 1. Extraction of metals in synthetic solution by different concentration of D2EHPA (in 10 and 40(vol. %)), O: A=1, T=40±2°C and feed solution: $[Zn^{2+}]$ = 5 g/L, $[Ni^{2+}]$ = 1.5 g/L and $[Cd^{2+}]$ <20 mg/L

3.2- Effect of pH on Zn extraction

After determination of the D2EHPA concentration, diluted in Kerosene (40 vol.%), using a synthetic solution, the optimum pH of Zn extraction was determined in acidic solution obtained from cold purification filter cake.

Figure 2 shows the extent of Zn extraction as a function of equilibrium pH. It is observed that at 2.5<pH<3, Zn could be extracted from the solution with little contamination from the other metals. These results corresponded to the Owusu [8] research, in which Zn was extracted at pH<3.

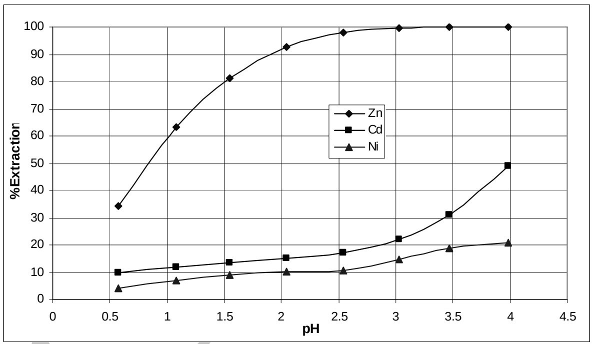

Figure 2. Extraction of metals as a function of equilibrium pH [D2EHPA] = 40 vol. %, O: A=1 and feed solution: $[Zn^{2+}]$ = 25g/L, $[Ni^{2+}]$ = 1.5g/L and $[Cd^{2+}]$ < 20mg/L

On the other hand, according to reaction (1), if one mole of Zn^{2+} ion is extracted by D2EHPA, two moles of H^+ ion are relieved into the aqueous phase. Therefore, the slope of curve $LogD_{Zn}$ vs. pH is near 2. Figure 3 shows that the slope of $LogD_{Zn}$ vs. pH for zinc extraction, according to Fig 2, is equal to 1.9. Therefore, the Zn extraction model by D2EHPA can be suggested in R_2Zn complexes.

Table 1. Value of pH50 and ΔpH50 of Zn, Cd and Ni extraction by different concentration of D2EHPA (in 10 and 40(vol. %)), O: A=1, T=40±2°C and feed solution: [Zn2+] = 5 g/L, [Ni2+] = 1.5 g/L and [Cd2+] <20 mg/L

D2EHPA (%)	pH_{50}^{Zn}	pH_{50}^{Cd}	pH_{50}^{Ni}	$\Delta pH_{50}^{(Cd-Zn)}$	$\Delta pH_{50}^{(Ni-Zn)}$
10	1.4	2.4	3.6	1.0	2.2
20	1.2	2.2	3.6	1.0	2.4
30	1.0	2.0	3.4	1.0	2.4
40	0.7	1.9	3.2	1.2	2.5

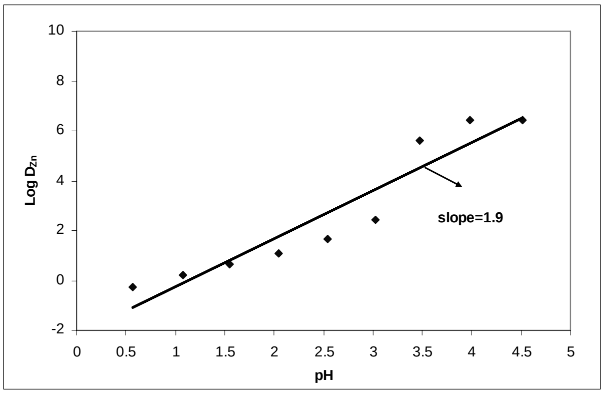

Figure 3. $LogD_{Zn}$ vs. pH in Zn extraction using [D2EHPA] = 40 vol. %, O: A=1 and feed solution: $[Zn^{2+}]$ = 25g/L, $[Ni^{2+}]$ = 1.5g/L and $[Cd^{2+}]$ < 20mg/L

3.3- Effect of O:A ratio on Zn extraction

Figure 4 shows zinc distribution isotherm for different O:A ratios. In Table 2, as the experimental results show, the extraction percentage of zinc for O:A=4:1 was equal to 98.8, and for a ratio of 1:10 it reduced to 25.6. At the same time, the distribution coefficient of zinc (D_{Zn}) was decreased from 31 to 3.4, and it was found that $\beta_{Zn/Ni}$ (separation factor of zinc from Ni) and $\beta_{Zn/Cd}$ were reduced from 6200 to 16 and from 115.5 to 9.2, respectively.

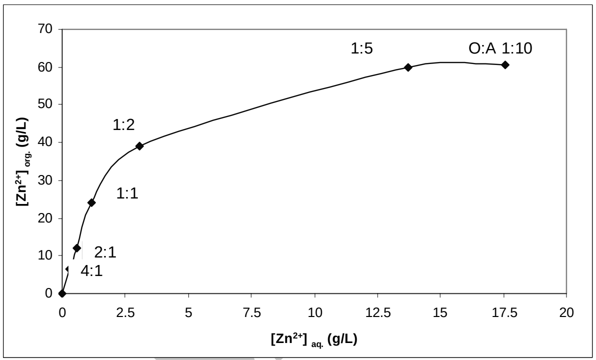

Figure 4. Distribution isotherm for extraction of Zn at pH = 2.5-3 and [D2EHPA] = 40 vol.%, from feed solution: $[Zn^{2+}]$ = 25g/L, $[Ni^{2+}]$ = 1.5g/L and $[Cd^{2+}]$ < 20mg/L

Table .2 Extraction percentage, distribution coefficient and separation factor of Zn, Ni and Cd in different phase ratio at pH=2.5-3, [D2EHPA] = 40 vol.%, from feed solution: $[Zn^{2+}]$ = 25g/L, $[Ni^{2+}]$ = 1.5g/L and $[Cd^{2+}]$ < 20mg/L

Element Name	O/A	Concentration (g/L)		Distribution Coefficient (D_M)	% Extraction	Separation Factor ($\beta_{Zn/M}$)
		Aqueous	Organic			
Zn	4:1	0.2	6.2	31.0	98.8	-
	2:1	0.6	13.1	21.8	97.6	-
	1:1	1.2	24.0	20.0	94.9	-
	1:2	3.1	39.2	12.7	86.8	-
	1:5	13.7	60.0	4.4	42.8	-
	1:10	17.6	60.5	3.4	25.6	-
Ni	4:1	1.304	0.007	0.005	6.05	6200.0
	2:1	1.308	0.005	0.004	5.4	5450.0
	1:1	1.315	0.005	0.004	5.1	5000.0
	1:2	1.313	0.004	0.003	4.8	4233.3
	1:5	1.38	0.004	0.003	0.7	1466.7
	1:10	1.344	0.286	0.213	0.2	16.0
Cd	4:1	0.010	0.004	0.4	49.8	77.5
	2:1	0.010	0.005	0.5	38.7	43.6
	1:1	0.017	0.004	0.24	12.8	83.3
	1:2	0.018	0.002	0.11	7.0	115.5
	1:5	0.019	0.002	0.11	1.0	40.0
	1:10	0.019	0.007	0.37	0.5	9.2

Therefore, corresponding to the above results, it was found that O:A=4:1 is a suitable ratio for Zn separation from other impurities.

4- Conclusions

Zinc values of the leach solution obtained from cold purification filter cake of Angouran mine concentrate was selectively extracted via solvent extraction by D2EHPA. Increasing extractant concentration improved the selective separation of zinc. Under the optimum conditions ([D2EHPA] =40 vol.%, equilibrium pH=2.5-3. O:A=4:1) 98.8% of the Zn could be extracted.

References

[1] Cole, P.M. and Sole, K.C., "Solvent Extraction in the Primary and Secondary Processing of Zinc", Proceeding of The Int. Solvent Extraction Cong. (ISEC), Cape Town, South Africa, pp. 863-870 (2002).

[2] Noueira, E.D, Regife, J.M, Martin, S.L. and Nogueira, G.D., "Using Zinc Secondaries Feed an Electrowinning Plant", Zinc Proceeding of The Int. Symposium on Extractive of Zinc, Tokyo, Japan, pp. 736-780 (1985).

[3] Noueira, E.D, Regife, J.M, and Blythe, P.M., "Zincex- The Development of a Secondary Zinc Process", Chemistry and Industry, January, pp.63-67(1980)

[4] Huang, T.C. and Juang R. S. "Kinetics and Mechanism of Zinc Extraction from Sulfate with Di-2-ethylhexyl Phosphoric Acid", J. of Chem. Japan, 19(5), pp-379-386(1986)

[5] Dalton, R.F. and Quan, P.M., "Novel Solvent Extraction Reagents for Recovery of Zinc from Sulphate Leach Solution", Hydrometallurgy, pp-601-611 (1994)

[6] Lorenzo, M. S., Nogueira, D. and Leon, G., European Patent Application.1 258535 A1 (2002)

[7] Cox, M., Flett, D.S. and Gotfryd, L., "The Extraction of Copper, Zinc, Cadmium and Lead from Waste Streams in the Zinc-Lead Industry", Proceeding of The Int. Solvent Extraction Cong. (ISEC), Cape Town, South Africa, pp. 879-883 (2002).

[8] Owusu, G., "Selective extractions of Zn and Cd from Zn-Cd-Co-Ni Sulphate Solution Using Di-2-ethylhexyl Phosphoric Acid Extractant", Hydrometallurgy, 47, pp.205-215 (1998).

[9] Martin, D., Regife, J.M. and Nogueria, E.D., US Pat. 4401531 (1983).

[10] Martin, D., Diaz, G., Garcia, M.A. and Sanchez, F., "Extending Zinc Production Possibilities Through Solvent Extraction Proceeding of The Int. Solvent Extraction Cong. (ISEC), Cape Town, South Africa, pp. 1045-1051 (2002).

[11] Antonelli, D., Veglio, F., Mansur, M.B., Biscaia Junior, E.C. and Slater, M.J., "Zinc Extraction and Stripping with D2EHPA: Further Consideration as a Test System", Proceeding of The Int. Solvent Extraction Cong. (ISEC), Cape Town, South Africa, pp. 1058-1063 (2002).