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## **RECOVERY OF ZINC(II) FROM ACIDIC SULFATE SOLUTIONS. SIMULATION OF COUNTER-CURRENT EXTRACTION-STRIPPING PROCESS**

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Cyanex 272 and di(2-ethylhexyl)phosphoric acid (DEHPA) were used for extraction of zinc(II) from sulphate solutions. Counter-current extraction-stripping process was simulated. The simulation enabled CYANEX 272 to be selected for the recovery of zinc(II) from acidic sulphate solutions. A higher selectivity of zinc(II) extraction was the main benefit of using CYANEX 272. Technologically significant conclusions could be arrived at only when process solutions with metal contaminants were used for the studies and several extraction-washing-stripping cycles were carried out. The studies of individual extraction and/or stripping using model solutions could be only considered as an initial step and were of a limited technological value.

*Key words: zinc(II) extraction, CYANEX 272, di(2-ethylhexyl)phosphoric acid, counter-current extraction-stripping process simulation*

### INTRODUCTION

Pyrometallurgy of zinc, especially of secondary resources, gives several dust streams of which further pyrometallurgical processing is difficult and very inconvenient. Such wastes could be processed by hydrometallurgical methods (Dutrizac et al. 1998). Zinc could not be directly electrowinned from leach solutions because of the presence of metal contaminants. The contaminants should be separated in an extraction-stripping process. Acidic extractants, especially those containing dialkylphosphoric acid and dialkylphosphinic acid, are convenient for such separation (Gega et al. 1991, Sastre et al. 1984).

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The fundamental technological problems of zinc(II) extraction were discussed in several reviews (Bart, 2000, Jha et al. 2002, Mishonov et al. 2002). In most of the published papers, model feed solutions were used and either single extraction or the stripping stage was studied. Such results were very important for basic studies but they were of a limited value for designing the extraction-stripping process. Such basic studies should be verified using actual process solutions containing metal contaminants. Moreover, the process should be verified in a continuous multistage counter-current extraction-stripping process.

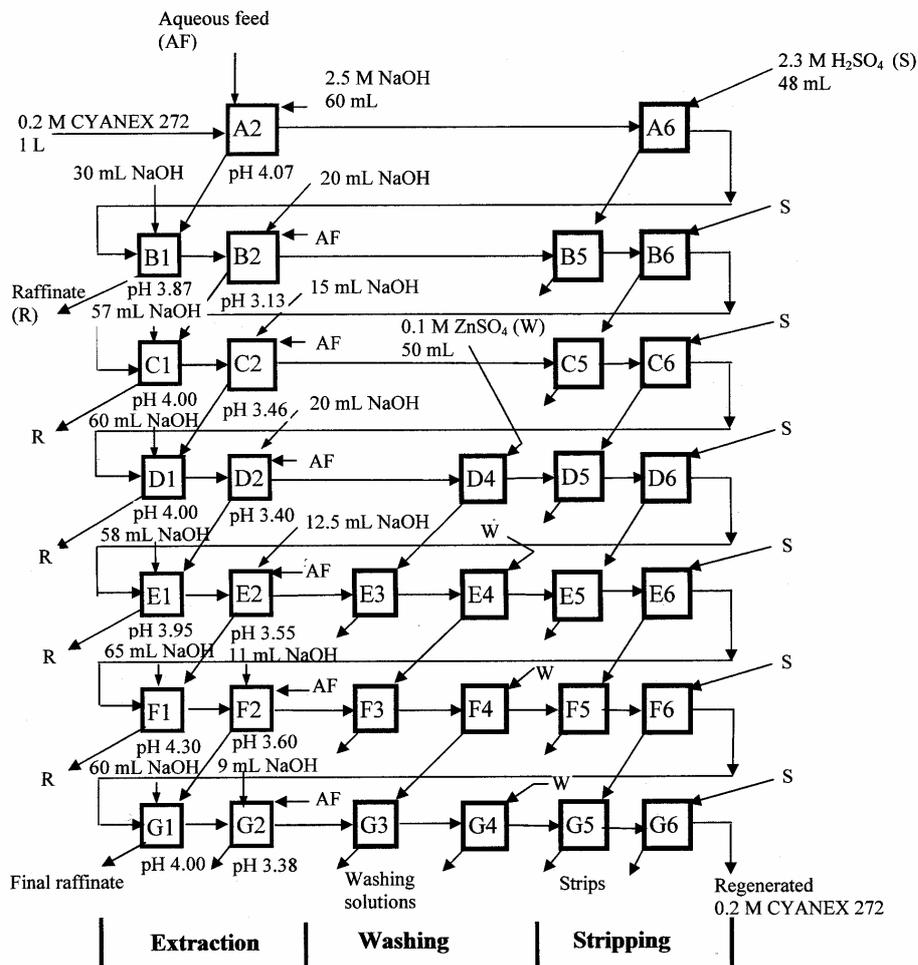


Fig. 1. Simulation of counter-current extraction-stripping process. 0.2 M CYANEX 272 as extractant (99.5 mL of the aqueous feed (AF) used for extraction in each cycle A2-G2, 45 mL of 2.3 M sulfuric acid (S) used for stripping in each cycle A6-G6, different volumes of 2.5 M NaOH (N) used for pH adjustment in each extraction, 50 mL of 0.1 M  $ZnSO_4$  (W) used for washing in each cycle D4-G4)

The aim of this work was to simulate a counter-current extraction-stripping process in a laboratory scale using an actual sulphate process solution containing zinc(II), and contaminated with Cu(II), Cd(II), Na(I), K(I), Mg(II), Ca(II) and As(V). These studies were considered as the first step in the design of the counter-current extraction-stripping step working in a continuous mode.

## EXPERIMENTAL

The aqueous feed was obtained by leaching electric furnace dust obtained from a copper smelter, Glogow, Poland, with sulphuric acid. Silica was removed from the leach solution by changing its pH value with sodium carbonate solution, and precipitation. The feed contained (in g/L): Zn 68.6, K 9.40, Na 4.4, Mg 3.05, Cu 3.4, Cd 0.38, Cl approx. 1 and As 0.053. 0.2 M solutions of CYANEX 272 (Cytec Inc., Canada) and di(2-ethylhexyl)phosphoric acid (DEHPA, SIGMA-Aldrich, Germany) in ESCAID 120 (Esso/Exxon, USA) were used for the extraction.

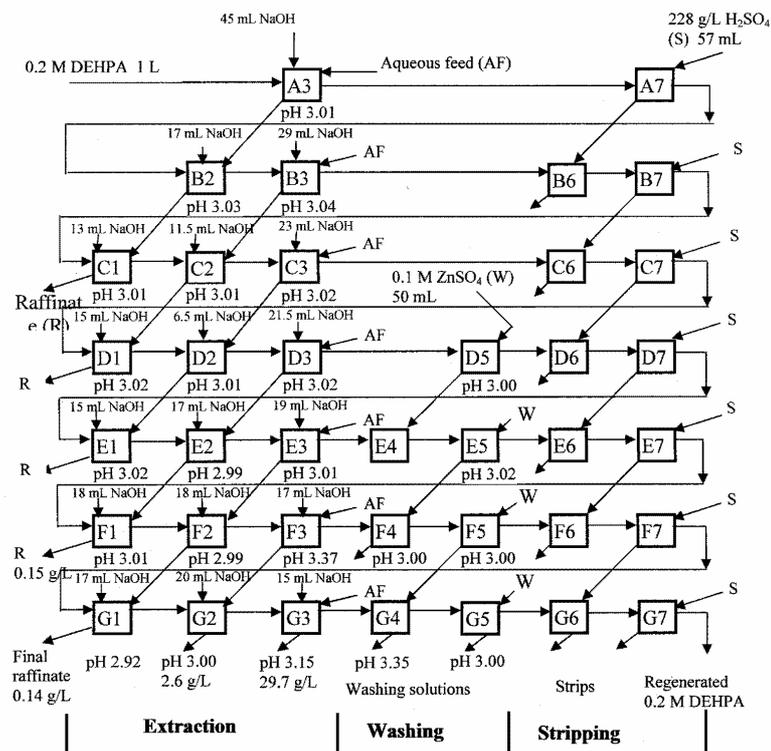


Fig. 2. Simulation of counter-current extraction-stripping process. 0.2 M DEHPA as extractant (117.5 mL of the aqueous feed (AF) used for extraction in each cycle A3-G3, 57 mL of 2.3 M sulphuric acid (S) used for stripping in each cycle A7-G7, different volumes of 5 M NaOH (N) used for pH adjustment in each extraction, 50 mL of 0.1 ZNSO<sub>4</sub> (W) used for washing in each cycle D5-G5)

The extraction-stripping process (2-2-2 and 3-2-2 for CYANEX 272 and DEHPA, where the subsequent digits denote the numbers of stages in extraction, washing and stripping, respectively) were simulated by contacting phases for 10 minutes in beakers (up to 2 L volume) and separating the phases in separatory funnels at a room temperature. pH was adjusted with 2.5 or 5 M NaOH to 3.5 and 4.0 in the first and second extraction stages with CYANEX 272, and to pH 3 in each extraction step with DEHPA. The same volume of 2.3 M (228.3 g/L) sulphuric acid was used for stripping in each stage (48 and 57 mL from CYANEX 272 and DEHPA, respectively). 0.1 M  $\text{ZnSO}_4$  was used for washing. Actual equilibrium pH values in each extraction stage are given in Figs. 1 and 2.

The simulation was carried out in the manner presented in Figs. 1 and 2. Seven extraction cycles (A-G) were carried out. The raffinate obtained in the first cycle (A2) was used as an aqueous feed in the second stage (B1) of extraction of cycle B, in which the regenerated organic phase (after stripping in A6) was used. Next the organic phase was contacted with the fresh feed solution in B2. In the same second cycle B, both the aqueous phase from the first cycle (A6→B5) and fresh sulphuric acid (in B6) were used for stripping. Washing was started from the fourth cycle (D) and was carried out in two stages in each subsequent cycle.

Atomic absorption spectroscopy was used to determine the contents of the components in the aqueous phases.

## RESULTS AND DISCUSSION

Initial experiments showed that equilibria of extraction stripping were obtained in 5 minutes of phase contact. The phases separated completely both in extraction and stripping.

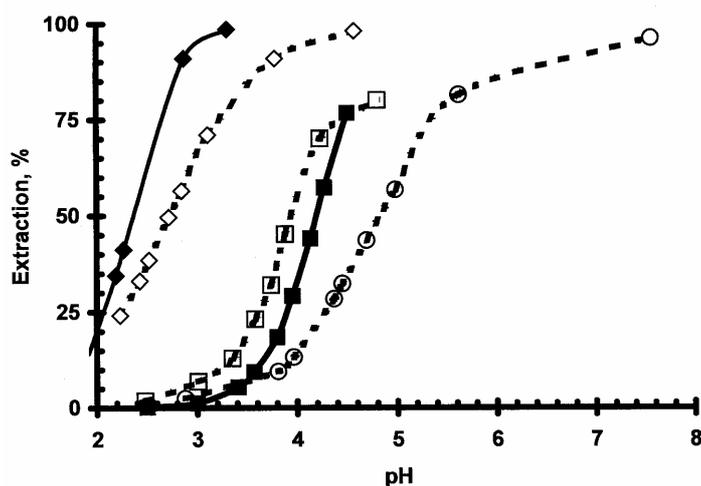


Fig. 3. Effect of pH on extraction of selected metal cations with 0.2 M CYANEX 272

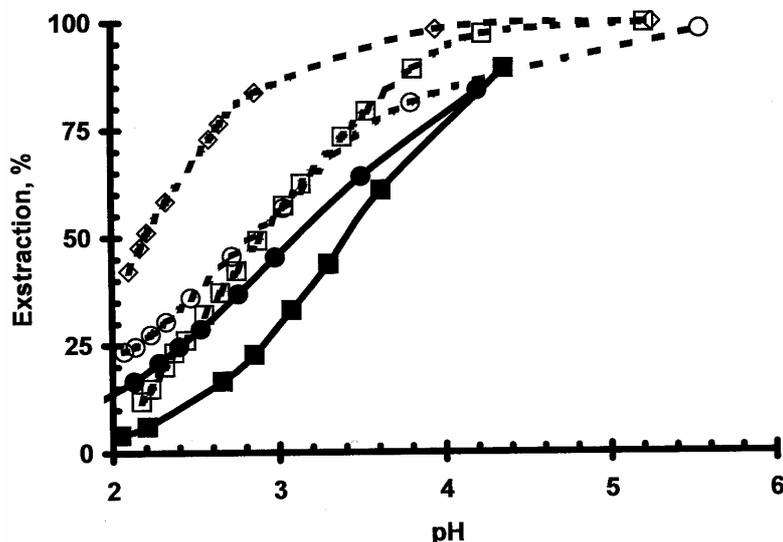


Fig. 4. Effect of pH on extraction of selected metal cations with 0.2 DEHPA

Figures 3 and 4 show the effect of equilibrium pH on the extraction of selected metal cations with 0.2 M solutions of CYANEX 272 and DEHPA. Such relationships are usually given in reagent catalogues. However, the position of the curves of % extraction vs. pH depends on the extraction conditions, i.e., concentrations of reagents in both phases and the diluent. The isotherms given in Figs. 3 and 4 correspond to the experimental conditions used in this work. In the both considered systems, zinc(II) was better extracted than other cations. DEHPA extracted zinc(II) at lower pH than did CYANEX 272.  $pH_{0.5}$  values determined for metal sulphate concentration equal to 0.5 M amounted as follows: 0.2 DEHPA – Zn 2.21, Cd 2.83, Cu 2.90 and 0.2 M CYANEX 272 – Zn 2.72, Cd 4.82, Cu 3.93. Bigger gaps between the curves of % extraction vs. pH were observed for CYANEX 272.

Extraction isotherms of zinc concentration in the organic phase versus zinc concentration in the aqueous phase (Fig. 5) indicated that the loading capacities of the organic phases (0.2 M) were in the range 6-8 g/L for the considered equilibrium pH. Such low capacities indicated that i) the organic phase could easily be totally loaded with zinc(II) and, due to the crowd-out effect, the selectivity of zinc extraction could be improved, and ii) a significant volume excess of the organic phase would be needed to efficiently recover zinc(II) from concentrated aqueous feeds (68.6 g/L Zn(II)). The extraction should then be carried out in 2-3 counter-current stages.

The compositions of the selected aqueous phases and recoveries of contaminated components are given in Tables 1 and 2. A higher recovery of zinc(II) (99.997%) was obtained using DEHPA. However, the final aqueous phase contained significant amounts of metal contaminants. About 50% Cu(II), 30% Cd(II), 20% K(I) and 3.5%

Mg(II) present in the aqueous feed was transferred to the final strip. The content of sodium increased drastically from 4.4 g/L up to 7.6 g/L. That high concentration of sodium could result from the great difference in the volumes of phases in the stripping (1 L of organic phase and 57 mL of strip phase). The organic phase was not totally loaded with zinc(II) and accumulated sodium. Additional washing with a diluted acid should be necessary to remove sodium. However, some amounts of zinc(II) would be also washed out as a result.

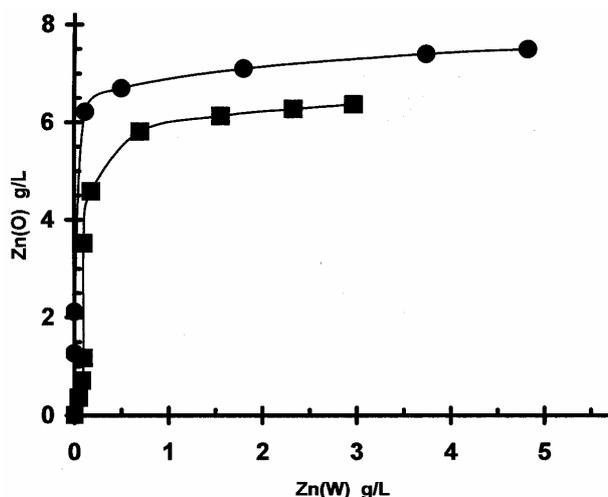


Fig. 5. Extraction isotherms for zinc(II) extraction with 0.2 DEHPA (pH 3.0) and 0.2 M CYANEX 272 (pH 4)

Table 1. Composition of selected aqueous phases and recoveries from the feed. 0.2 M CYANEX 272 as extractant

Solution		Concentrations, g/L							
		Cu	Cd	K	Na	Mg	As	Fe	Zn
Aqueous feed		3.4	0.38	9.4	4.4	3.05	0.053		68.6
F5	Strip	0.026	0.0034	0.14	0.94	0.036	0.013	0.006	110
G5	Strip	0.011	0.0021	0.10	1.01	0.018	0.010	0.004	140
F1	Raffinate	1.99	0.22	5.49	27.4	1.78	0.027	-	2.00
G1	Raffinate	1.98	0.22	5.50	26.2	1.79	0.028	-	4.25
G2	Raffinate	-	-	-	-	-	-	-	54.0
		Recovery, %							
F5	Strip	0.37	0.43	0.72	-	0.57	11.8	-	94.8
G5	Strip	0.16	0.27	0.51	-	0.28	8.9	-	89.4

CYANEX 272 extracted less zinc(II) (near 90%) but transferred significantly less metal contaminants. Thus, the use of CYANEX 272 was preferred because the reagent coextracted 150-300 times less copper(II), 70-100 times less cadmium(II), 35-45 times less potassium, 9-12 times less magnesium(II) and 6-8 times less sodium than DEHPA. Only the level of arsenic(V) was 1.3 times higher when CYANEX 272 was used.

Table 2. Composition of selected aqueous phases and recoveries from the feed. DEHPA as extractant.

Solution		Concentration, g/L						
		Cu	Cd	K	Na	Mg	As	Zn
Aqueous feed		3.4	0.38	9.4	4.4	3.05	0.053	68.6
F6	Strip	3.95	0.25	4.75	7.63	0.33	<0.007	150
G6	Strip	3.63	0.22	4.50	5.75	0.22	<0.007	150
F1	Raffinate	1.00	0.175	4.79	19.1	1.95	0.033	0.14
G1	Raffinate	1.12	0.187	4.94	19.2	2.02	0.034	0.15
G2	Raffinate	-	-	-	-	-	-	2.6
G3	Raffinate	-	-	-	-	-	-	29.7
		Recovery, %						
F5	Strip	56.4	31.9	24.5	-	5.25	<6.5	99.997
G5	Strip	51.8	28.1	23.2	-	3.50	<6.5	99.997

A higher selectivity of zinc(II) extraction with CYANEX 272 was obtained, although the equilibrium pH of the aqueous phases in the extraction (3.1-4, mainly near 4) was near 1 unit higher in comparison with the process in which DEHPA was used (near 3). At the same pH the advantage of using CYANEX 272 would be significantly higher. However, the strip solution needed further purification before electrowinning to reduce the content of Cu(II) and Cd(II) down to the level of 0.0001-0.0005 g/L. Such purification could be accomplished by cementation with zinc.

The use of Cyanex 272 was also more convenient because the formation of cruds was not observed. Contrary, the cruds were formed after a few cycles of extraction and stripping when DEHPA was used. The DEHPA organic phase became more viscous than the phase containing CYANEX 272.

## CONCLUSIONS

The simulation of the counter-current extraction-stripping process enabled CYANEX 272 to be selected for the recovery of zinc(II) from acidic sulphate solutions. A higher selectivity of zinc(II) extraction was the main benefit of using CYANEX 272. Technologically significant conclusions could be arrived at only when process solutions with metal contaminants were used for the studies and several extraction-washing-stripping cycles were carried out. The studies of individual extraction and/or stripping using model solutions could only be considered as an initial step and were of a limited technological value.

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**Gotfryd L., Szymanowski J.**, *Odzysk cynku(II) z kwaśnych roztworów siarczanowych. Symulacja przeciwprądowego procesu ekstrakcyjno-reekstrakcyjnego*, Physicochemical Problems of Mineral Processing, 38, (2004) 113-120 (w jęz. ang.).

Cyanex 272 oraz kwas di(2-etyloheksylo)fosforowy (DEHPA) zastosowano do ekstrakcji cynku(II) z procesowych roztworów siarczanowych zawierających dodatkowo Cu(II), Cd(II), Na(I), K(I), Mg(II), Ca(II) i As(V). Symulowano przeciwprądowy proces ekstrakcyjno-reekstrakcyjny. Symulacja pozwoliła wytypować Cyanex 272 jako odpowiedni ekstrahent do selektywnej ekstrakcji cynku(II) wobec występujących zanieczyszczeń. Tylko zastosowanie prawdziwych roztworów technologicznych i prowadzenie pełnego cyklu ekstrakcji – przemywania i reekstrakcji umożliwia wyprowadzenie technologicznie rozsądnych wniosków. Badanie indywidualnego etapu ekstrakcji lub reekstrakcji posiada ograniczone technologiczne znaczenie.