

Available online at www.sciencedirect.com



Separation Purification Technology

Separation and Purification Technology 53 (2007) 89-96

www.elsevier.com/locate/seppur

# Recovery of zinc sulphate from industrial effluents by liquid–liquid extraction using D2EHPA (di-2-ethylhexyl phosphoric acid)

Daniel Dayrell Pereira<sup>a,1</sup>, Sônia Denise Ferreira Rocha<sup>b</sup>, Marcelo Borges Mansur<sup>b,\*</sup>

<sup>a</sup> Votorantim Metais, Zinco, Unidade Três Marias, Rodovia BH-Brasília BR 040, Km 284, 39205-000 Três Marias, MG, Brazil

<sup>b</sup> Departamento de Engenharia Química, Universidade Federal de Minas Gerais, Rua Espírito Santo, 35, 6° Andar, 30160-030 Belo Horizonte, MG, Brazil

Received 18 May 2006; received in revised form 19 June 2006; accepted 20 June 2006

#### Abstract

The liquid–liquid extraction of zinc using D2EHPA as extractant has been investigated in this paper in order to recover zinc sulphate from an industrial effluent produced by Votorantim Co. (Brazil) which contains several metallic species such as cadmium, cobalt, iron, lead, calcium, magnesium, manganese and nickel. The study was carried out in two main steps: (1) extraction and stripping laboratory scale tests in order to assess adequate operational conditions for the favourable recovery of zinc from the effluent and (2) continuous pilot scale tests using a mixer-settler battery aiming to reproduce the bench results. In the laboratory scale experiments, operating variables such as the pH of the aqueous effluent (0.5–5.0), concentration of D2EHPA (5–50%,w/w) and aqueous/organic volumetric phase ratio (1/5–5/1) were investigated for the zinc extraction process; for the zinc stripping process, the organic/aqueous volumetric phase ratio (1/1–10/1) was studied by contacting a metal loaded organic phase with an industrial acid solution produced by the company in the electrolysis of zinc. The continuous mixer-settler tests have shown that zinc can be selectively and quantitatively removed from the effluent (around 98%) using 3 extraction stages (pH 2.5, [D2EHPA]=20% (w/w) and A/O = 1), and other 3 stripping stages (O/A = 4). A final solution containing 125.7 g/L of zinc was obtained that could be sent directly to electrowinning. © 2006 Elsevier B.V. All rights reserved.

Keywords: Liquid-liquid extraction; Zinc; D2EHPA; Mixer-settler; Effluent treatment

# 1. Introduction

Liquid–liquid extraction is an important separation process with several applications in industries such as petrochemical, pharmaceutical and hydrometallurgical ones. On the regard of hydrometallurgical applications in commercial scale, it is commonly used for concentrating metals like zinc or copper for electrowinning [1–3], and also for separating complex metallic systems such as nickel/cobalt [4–6], uranium [7], mercury [8], rare earths [9,10] and many other metal ions. In the recent years, increasing attention has been given to the use of liquid–liquid extraction as an alternative method for the removal of metallic species from aqueous liquors or effluents that result from industrial activities.

The separation of solute(s) by liquid–liquid extraction may occur by solubility difference or by interfacial chemical reaction

as is the case of metal extraction processes where an extractant is dissolved into the solvent phase to react selectively with the metal(s) of interest. The chemistry of extraction-stripping processes for metallic systems frequently involves non-linear equilibria between the species present in the raffinate and extract phases. For example, in the case of zinc extraction with D2EHPA (di-2-ethylhexyl phosphoric acid) as extractant dissolved in aliphatic diluents, the equilibrium is given by the following scheme reactions [11]:

$$Zn^{2+}_{(aq)} + 1.5 (RH)_{2(org)} \hookrightarrow ZnR_2RH_{(org)} + 2H^+_{(aq)}$$
  
at the liquid-liquid interface (1)

$$2 ZnR_2RH_{(org)} \hookrightarrow 2 ZnR_{2(org)} + (RH)_{2(org)}$$
  
in the extract phase (2)

where RH represents the extractant species D2EHPA that acts like a liquid cationic ion exchanger, and subscripts (aq) and (org) refer to aqueous and organic species, respectively. According to the reaction scheme shown by Eqs. (1) and (2), zinc extraction involves heterogeneous and homogeneous complex

<sup>\*</sup> Corresponding author. Tel.: +55 31 3238 1778; fax: +55 31 3238 1789. *E-mail addresses:* danieldayrell@vmetais.com.br (D.D. Pereira), mansur@deq.ufmg.br (M.B. Mansur).

<sup>&</sup>lt;sup>1</sup> Tel.: +55 38 3754 9143, fax: +55 38 3754 1397.

<sup>1383-5866/\$ –</sup> see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.seppur.2006.06.013

reactions that occur simultaneously in both liquids resulting in two metal-complex species in the extract phase. The heterogeneous reaction predominates at low loading levels of zinc in the extract while both complexes ZnR<sub>2</sub>RH and ZnR<sub>2</sub> co-exist at intermediate and high loading conditions as verified on statistical analysis of zinc-D2EHPA equilibrium data [11]. While the heterogeneous reaction is frequently accepted by several researchers [12-15], the homogeneous one as shown in Eq. (2) still requires further investigation. Recently, the zinc-complex species  $(ZnR_2)_2$  has been proposed instead of  $ZnR_2$  as shown in Eq. (2) based on the experimental evidence that the viscosity of the extract phase increases significantly (as much as 20 times) with the increase of the loading level of zinc (and cobalt) in diluents such as dodecane and benzene (aggregation theory) [16]. However, apart from the molecular structure of zinc-complexes with D2EHPA at high loading conditions, it seems that both models may describe equilibrium data well for engineering calculations as verified on the modelling of a pilot-scale packed column used to extract zinc with D2EHPA [17]. It is important to comment that the zinc-D2EHPA system has been recently adopted by the European Federation of Chemical Engineering as a test system for validating equipment design procedures when both mass transfer and chemical reaction rates have to be taken into account [18]. In addition, this reactive system is also used in industrial scale for recovering zinc as verified, for example, at the Anglo America's Skorpion Zinc refinery located in southern Namibia [5]. In an electrolytic zinc refinery process, the zinc sulphate solution is subjected to a series of purification steps to remove unwanted species such as iron, calcium, lead, manganese, magnesium, copper, etc. Some metals are rejected from the stream through the conventional zinc dust cementation process. Depending on the efficiency of the purification process, some streams containing predominantly zinc and several other metals in relatively low concentrations are produced. Such streams could be treated by liquid-liquid extraction process using D2EHPA as extractant in order to recover their zinc content instead of being considered as industrial effluents. Therefore, the zinc-D2EHPA system is relevant both from the academic and the commercial point of view.

Liquid–liquid extraction can be accomplished either in differential contactors or in staged extractors [19,20]. In the case of hydrometallurgical applications, staged mixer-settlers batteries are commonly used to separate and/or concentrate metal solutions. One mixer-settler unit consists of a mixing compartment where liquids are brought into contact by intense stirring, followed by a settling compartment where liquids are separated according to their density difference. Mixer-settlers are characterised by high capacity (flow rate higher than  $250 \text{ m}^3/\text{h}$ ), flexibility (any number of stages can be used and controlled individually) and they can handle high viscous solutions with density difference higher than  $0.10 \text{ g/cm}^3$  [21].

In this context, the main operating variables for the extraction of zinc sulphate by liquid–liquid extraction using D2EHPA as extractant has been investigated in this paper aiming to recover sulphate of zinc from an industrial effluent containing several other metals. The study has been carried out in two main steps: (1) laboratory or bench scale tests in order to assess adequate conditions for the favourable recovery of zinc from the effluent and (2) continuous pilot scale tests using a mixer-settler battery aiming to reproduce the bench scale results.

# 2. Experimental

## 2.1. Industrial effluent used in this study

The industrial effluent used in this study consisted of sulphuric acid liquor produced by the Votorantim Metais Co. (Zinco-Unidade Três Marias, located in the state of Minas Gerais, Brazil). The Votorantim group (www.votorantimmetais.com.br) is the fifth largest producer of zinc in the world, with total capacity of 400 thousand tons of zinc per year (Zinc SHG type with 99.995% purity). The effluent was collected directly from the stream pipe that feeds the effluent treatment sector of the company which is ISO 14001 certified. In order to obtain a representative solution, the effluent was periodically collected in samples of 1 L each during several weeks and stored in a tank of 400 L. After sedimentation of suspension matter for several days, the clean solution was transferred to another 400 L tank. A sample of this liquid hereafter named effluent was withdrawn for metal concentration analysis by atomic absorption (Perkin-Elmer, model AAnalyst 100). Its chemical composition is shown in Table 1 which also shows the concentration limits for several species for adequate disposal of industrial effluents into river waters, as determined by the environmental legislation of Minas Gerais state, in Brazil [22].

As shown in Table 1, the concentration of various metals encountered in the effluent has surpassed the superior limit determined by legislation, so it must be adequately treated. The concentration of zinc and sulphate ions in the effluent is relatively high. In addition, the concentration of cadmium, iron, lead, calcium and magnesium are also high while nickel, cobalt and cupper are quite low. It has been observed that the pH of effluent is favourable for zinc extraction with D2EHPA [23].

## 2.2. Equilibrium laboratory scale investigation

Equilibrium bench scale experiments were carried out at  $28 \pm 1$  °C in order to assess favourable operating conditions for

Table 1	
Chemical composition of the industrial effluent used in the study	

Species	Concentration in the effluent (mg/L)	Superior limit by legislation (mg/L) [22]
Zn	13462.6	5.0
Cd	22.7	0.1
Со	0.66	_
Cu	4.6	0.5
Total Fe	240.6	10.0
Pb	5.38	0.1
Ca	564.2	_
Mg	2375.2	_
Mn	745.3	1.0
Ni	0.84	1.0
$SO_4^{2-}$	39460	_
pН	3.1	6.5-8.5 (±0.5)

the extraction and stripping of zinc sulphate using D2EHPA as extractant. The solvent phase consisted of commercial di-2-ethyhexyl phosphoric acid (D2EHPA, 97% purity, Rhodia) dissolved in commercial kerosene Exxsol D-80 (Exxon Mobil, mostly aliphatic, aromatic max. of 0.5 wt%). Tests were carried out by contacting specific volumes of aqueous and organic solutions in a beaker for 10 min (as determined in preliminary tests). In the extraction tests, 100 mL of the aqueous phase (effluent) was kept constant at changing volumes of the organic phase while 50 mL of the stripping acid solution was used at changing volumes of the loaded organic phase (extract) in the stripping tests. Both phases were brought together by mechanical stirring using a glass impeller marinetype. The pH of the aqueous phase was monitored using a pH-meter (model D-20 Micronal) attached to a temperature electrode for pH control. In the extraction tests, the pH was kept constant by adding NaOH or H<sub>2</sub>SO<sub>4</sub> solutions (analytical grade reagents). The equilibrium concentration of metals Zn, Cd, Co, Ni, Fe, Mg, Mn, Ca and Pb in the aqueous phase (rafinate) was determined by atomic absorption spectrophotometry while that in the organic phase (extract) was calculated by mass balance difference. The concentration of ions  $SO_4^{2-}$  was determined by atomic emission spectrophotometry (ICP plasma Spectro, model Spectroflame). No third phase formation was observed for the experimental conditions studied.

The following variables were investigated in the extraction tests: pH of the aqueous phase (0.5–5.0), concentration of extractant (5–50%, w/w) and aqueous/organic volumetric phase ratio (1/5–5/1). In the stripping tests, the organic/aqueous volumetric phase ratio (1/1–10/1) was investigated by contacting a loaded organic phase (extract) with a typical industrial acid solution produced in the zinc electrolysis step by Votorantim Co. (Brazil). The loaded organic phase was obtained by contacting an organic solution containing 20% (w/w) D2EHPA with the effluent at A/O ratio equal to 1.0 at constant pH 2.5 and room temperature (28 ± 1 °C). The chemical composition of the loaded organic phase and the industrial acidic solution used as stripping liquor are shown in Table 2.

Table 2

Chemical composition of the extract and the industrial acidic solutions used in the stripping experiments

Species	Concentration of the extract (mg/L)	Concentration of the stripping solution (mg/L)		
Zn	11900	73600		
Cd	0.12	0.10		
Co	0.46	0.39		
Fe	2.70	1.03		
Pb	0.76	0.87		
$H_2SO_4$	_	181300		
Mn	6.82	3200		
Ca	2.38	344		
Mg	3.25	18400		
Ni	0.77	0.54		
Cu	0.03	0.09		
$SO_4$	-	358.80		

#### 2.3. Continuous mixer-settler pilot scale tests

The mixer-settler cascade used in this work was composed of box-type mixer-settlers made of Teflon with similar internal arrangement and dimension (width = 260 mm, depth = 60 mmand height = 240 mm including the motor head). The active volume of one mixer-settler or stage was 600 mL while the ratio of the mixer and settler volumes was 1:4 (120 and 480 mL, respectively). The stirring speed used was 1800 rpm. The horizontal area of each settler was 603 cm<sup>2</sup>. The connection between mixer and settler units was made by means of a central hole; a vertical wall containing seven small vertical slots was placed 10 mm apart from the mixer in order to diminish any turbulence in the settler. Each mixer unit was provided with a pump-mixer impeller also made of Teflon, which ensured the flow of both phases between the stages. The mixer-settlers were tightly connected into 2 sections of 3 stages each, one for extraction and other for stripping of zinc. The operating conditions were chosen such that the residence time of each phase in the mixer was 5 min, so the flow rate for the feed and solvent streams was 12 mL/min in the extraction section, and 3 mL/min for the stripping solution stream in the stripping section. The equipment was used for the extraction of zinc sulphate from the effluent using a solution containing 20% (w/w) D2EHPA dissolved in Exception Exception D-80(A/O = 1) followed by the zinc stripping from the extract using  $1.85 \text{ mol/L H}_2\text{SO}_4$  industrial solution (O/A = 4). In the extraction section, the pH of the aqueous phase in the mixers was kept constant at pH 2.5 by the continuous addition of a solution NaOH 50% (w/w). All runs were carried out at  $28 \pm 1 \,^{\circ}\text{C}.$ 

# 3. Results and discussion

## 3.1. Equilibrium laboratory scale investigation

The extraction-stripping process of zinc sulphate with D2EHPA was studied at laboratory scale according to the following operating variables ( $T = 28 \degree$ C): pH of the aqueous phase, concentration of D2EHPA and A/O volumetric ratio. The results are discussed as follows. Preliminary experiments have shown that zinc is rapidly and quantitatively extracted from the effluent. Equilibrium was reached within 5 min for the range of operating conditions investigated, so all laboratory scale tests were carried out within 10 min in order to ensure the liquid–liquid equilibrium was reached. Fast kinetics for the zinc-D2EHPA system has been also found elsewhere [11–13,24].

Fig. 1 shows the effect of the equilibrium pH of the aqueous phase on the extraction of various metals from the effluent. As expected, the increase on pH (lower proton concentration) results in higher metal extraction. Such behaviour is typical for the extraction of metal cations by cationic extractants as is the case of D2EHPA as shown by the following reaction:

$$M^{m+}_{(aq)} + n (RH)_{2(org)} \leftrightarrows MR_2(RH)_{2n-2(org)} + m H^+_{(aq)}$$
 (3)

where M represents metals Zn, Cd, Co, Fe, Pb, Ca and Mg, RH is the molecule of D2EHPA, m metal valence, n the stoichio-

metric coefficient and subscripts (aq) and (org) refer to aqueous and organic species, respectively. The distribution of the metal ions between the organic and the aqueous phases depends on a number of variables such as solution composition, equilibrium pH, type of diluent, etc. According to Eq. (3), the increase in the concentration of protons favours the stripping reaction.

The following metal extraction sequence with D2EHPA was obtained as shown in Fig. 1:  $Zn \gg Fe \sim Pb > Cd \sim Ca > Mg \sim Co$ . Based on the experimental  $pH_{1/2}$  values, four separating metal groups can be distinguished, e.g., Zn ( $pH_{1/2} \sim 0.9$ ), Fe and Pb ( $pH_{1/2} \sim 2.0-2.2$ ), Cd and Ca ( $pH_{1/2} \sim 2.9-3.2$ ) and Mg and Co ( $pH_{1/2} \sim 4.3-4.8$ ). Therefore, zinc can be selectively separated from the effluent ahead all other metals analysed at low pH values.

Based on the previous results, the effect of the concentration of D2EHPA on the extraction of metals present in the effluent was evaluated at distinct pH levels (1.5 and 2.5), as respectively shown in Fig. 2(a) and (b). As expected, the increase in the concentration of D2EHPA resulted in higher metal extractions, independently of the pH level investigated. It occurs due to the higher amount of free D2EHPA for reaction as evidenced by Eq. (3). According to Fig. 2, the following metal extraction sequences were obtained depending on the pH level of the aqueous phase:

- for pH 1.5:  $Zn \gg Ca > Fe \sim Mg \sim Ni \sim Pb > Cd \sim Co \sim Mn$ 

- for pH 2.5: 
$$Zn \gg Fe > Pb \sim Ca \sim Mn \sim Cd > Mg \sim Co \sim Ni$$

In both cases, zinc was preferentially extracted but distinct zinc extraction levels were obtained. For pH 1.5, the extraction of zinc increased from 35 to 80% when the concentration of D2EHPA was raised from 10 to 30% (w/w). For pH 2.5, practically 100% of zinc was extracted at D2EHPA concentration levels higher than 25% (w/w). In addition, a relatively less contaminated extract was obtained at pH 1.5, so it seems more advantageous to treat the effluent at the lower pH level. However, the shift in the metal extraction sequence (mainly calcium, magnesium and iron) verified at distinct levels of the equilibrium pH and concentration of D2EHPA seems interesting from the operational point of view in the company because signifi-



Fig. 1. Effect of pH on the extraction of metals ([D2EHPA] = 30% (w/w) and A/O = 1).



Fig. 2. Effect of the concentration of D2EHPA on the extraction of metals at distinct pH levels (A/O = 1): (a) pH 1.5 and (b) pH 2.5.

cantly less calcium and magnesium were extracted at pH 2.5. At 20% (w/w) of D2EHPA, for instance, the extraction of calcium drops from 30 to 14% while the extraction of magnesium drops from around 20% to null, respectively. On the other hand, iron extraction increases from 18 to 60% while zinc goes from 65 to 95%. This result points out that zinc and iron are preferably extracted by D2EHPA than calcium and magnesium at higher pH values. In this context, the considerable reduction on the magnesium extraction at the expense of the increase of iron extraction seems more convenient because (1) the concentration of magnesium in the feed is comparatively higher so 60% of iron extracted at pH 2.5 corresponds to 156.4 mg/L Fe in the extract while 21% of magnesium extracted at pH 1.5 corresponds to 520 mg/L Mg in this phase (the same can be drawn for calcium as well), (2) for Votorantim Co., zinc and magnesium must be preferentially separated in this step in order to reduce the amount of magnesium in the industrial circuit and (3) around 98% of zinc is extracted at pH 2.5 so a lesser number of mixer-settlers will be required. Therefore, the following operating variables were defined in order to treat the effluent under investigation: pH 2.5 and [D2EHPA] = 20% (w/w).

Fig. 3 shows the experimental isotherm of zinc with D2EHPA. It has been obtained by contacting the effluent at pH 2.5 and the solvent containing 20% (w/w) of D2EHPA at changing A/O volumetric ratios. The total zinc concentration in the extract phase was predicted well by the model of Mansur et al. [11] (10.0% deviation). As shown in Fig. 4, the concentra-



Fig. 3. Isotherm of zinc (pH 2.5, [D2EHPA] = 20% (w/w), T = 28 °C).

tion of zinc and the total concentration of the remaining metals (Cd, Cu, Co, Ni, Pb, Fe, Mn, Ca and Mg) in the aqueous phase decreases as the A/O volumetric ratio reduce because a relatively smaller quantity of D2EHPA is contacted with a relatively larger volume of effluent. It is interesting to notice that the zinc concentration decreases monotonically with A/O ratio for the whole range investigated, reaching a very low concentration (high zinc extraction level) when A/O ratio  $\geq 1/2$ . On the other hand, the curve of total concentration which is similar to those of feed (low extraction level of remaining metals) at A/O ratios  $\geq 1$ , having a significant drop at A/O ratios < 1 thus indicating that the remaining metals have quantitatively reacted with D2EHPA. Therefore, it seems more economical to extract zinc from the studied effluent at A/O ratio of unity.

The graphical method of McCabe-Thiele was used to calculate the number of theoretical equilibrium stages for the extraction of zinc with D2EHPA from the industrial effluent. As shown in Fig. 5, all zinc was practically extracted from the effluent in two stages operated at pH 2.5, [D2EHPA] = 20% (w/w) and A/O = 1.



Fig. 4. Concentration of zinc and total concentration of the remaining metals in the aqueous phase at changing A/O ratios (pH 2.5 and [D2EHPA] = 20%,w/w).



Fig. 5. Calculation of the number of theoretical stages of extraction by the method of McCabe-Thiele (pH 2.5, [D2EHPA] = 20% (w/w) A/O = 1).

The stripping results at changing O/A volumetric ratios are shown in Table 3. In these tests, the initial zinc concentration in the extract is quite similar to that predicted by the McCabe-Thiele method. According to Table 3, the concentration of zinc in the aqueous phase has increased considerably when higher O/A ratios were contacted. The percentage of zinc extracted with O/A ratio is shown in Fig. 6. In addition, the concentration of all remaining metals in the stripping solution did not change significantly, so a highly concentrated zinc solution can be obtained and submitted directly to eletrowinning. Ali et al. [25] have found that stripping percent of zinc from a loaded organic phase using bis(2,4,4-trimethylpentyl) phosphinic acid (trade name of Cyanex 272) as extractant takes the order  $HNO_3 > HCl > H_2SO_4$ but sulphuric acid was chosen for their further studies due to the ease of electrowinning of zinc from non-oxidising acids.

The number of theoretical stages of zinc stripping was calculated using the McCabe-Thiele method as shown in Fig. 7. The analysis has been done at O/A = 4 based on the percentage of zinc stripping (around 42% in one single stage). According to theoretical calculations, the concentration of zinc in the extract could be reduced from 11.9 g/L to around 2.0 g/L while



Fig. 6. Percentage of zinc stripping at changing O/A volumetric ratios.

Table 3			
Stripping results	at changing	O/A	ratios

Test	Zn (g/L)	Cd (mg/L)	Co (mg/L)	Ni (mg/L)	Ca (mg/L)	Mg (mg/L)	Mn (mg/L)	Fe (mg/L)	SO <sub>4</sub> (mg/L)	Pb (mg/L)	Cu (mg/L)
Initial extract	11.9	0.12	0.46	0.77	2.380	3.25	6.82	2.70	_	0.76	0.03
Initial stripping solution	73.6	0.10	0.39	0.54	0.344	18.4	3.20	1.03	358.8	0.87	0.09
O/A = 1	83.9	0.11	0.39	0.53	0.346	17.4	3.08	1.03	297.0	0.87	0.08
O/A = 2	94.5	0.10	0.38	0.54	0.338	17.4	3.08	1.03	313.2	0.87	0.08
O/A = 4	104.6	0.12	0.36	0.50	0.330	17.6	3.10	1.03	304.8	0.87	0.08
O/A = 6	109.5	0.12	0.36	0.50	0.340	17.2	3.02	1.04	321.0	0.87	0.08
O/A = 8	129.6	0.13	0.36	0.52	0.335	17.4	3.08	1.05	306.0	0.87	0.09
O/A = 10	126.5	0.10	0.34	0.48	0.320	15.8	2.82	1.03	279.6	0.84	0.08



Fig. 7. Calculation of the number of theoretical stages of stripping by the method of McCabe-Thiele (O/A = 4).

the zinc concentration in the aqueous phase could be increased from 74 g/L to almost 120 g/L in two counter-current stages.

## 3.2. Continuous mixer-settler pilot scale tests

Based on the bench scale equilibrium results, a continuous counter-current extraction pilot scale plant using a cascade of

six mixer-settlers containing 3 extraction stages and 3 stripping stages was designed for the recovery of zinc from the industrial effluent depicted in Section 2.1. The operating flow rates were determined such as the residence time of each phase in the mixer (volume of mixer = 120 mL) was 5 min in order to reach equilibrium as previously verified experimentally. So, in the extraction section, both streams were fed to the unit at 12 mL/min (A/O = 1) and, in the stripping section, the stream of industrial sulphuric acid solution was fed to the unit at 3 mL/min (O/A = 4). A scheme of the mixer-settler cascade used in this study is shown in Fig. 8.

Table 4 shows the concentration of all metals analysed in the aqueous streams. Almost 99% of zinc was extracted from the effluent using three extraction stages. In the raffinate, the concentration of zinc is still higher than those allowed by environmental legislation, so it could be treated by precipitation in order to remove all remaining metals and allow the safe disposition of the liquid stream as treated effluent. In addition, the extraction of iron and magnesium was low, around 38.5 and 6.0%, respectively. In the stripping unit, around 98% of zinc was recovered from the extract phase thus resulting in a zinc concentrated solution containing 125.7 g/L that can be sent directly to electrowinning. In addition, the concentration of the remaining metals in the acid solution was quite unchanged, so it could be reused in the process.



Fig. 8. Scheme of the mixer-settler cascade for the recovery of zinc sulphate (continuous lines = aqueous streams, dashed lines = organic streams).

 Table 4

 Concentration of metals in the aqueous phases in the mixer-settler battery

	Extraction sect	ion			Stripping section				
	Feed (mg/L)	Stage 1 (mg/L)	Stage 2 (mg/L)	Stage 3 (mg/L)	Feed (mg/L)	Stage 1 (mg/L)	Stage 2 (mg/L)	Stage 3 (mg/L)	
Zn	13462.6	12080	8690	152	73600	75400	91200	125700	
Cd	22.70	22.35	22.39	22.01	0.10	0.11	0.12	0.11	
Co	0.66	0.63	0.60	0.61	0.39	0.36	0.36	0.35	
Ni	0.84	0.82	0.83	0.81	0.54	0.53	0.53	0.50	
Ca	564.2	546.2	524.7	440.1	0.34	0.32	0.33	0.29	
Mg	2375.2	2242.2	2113.9	2107.2	18400	17400	17200	16800	
Mn	745.3	730.4	718.5	683.4	3.200	3220	3100	2950	
Fe	240.6	187.6	173.2	115.5	1.03	1.01	1.15	1.22	
Pb	5.38	5.27	5.30	5.02	0.87	0.88	0.86	0.89	

## 4. Conclusions

The recovery of zinc from an industrial sulphate effluent has been investigated by liquid–liquid extraction using D2EHPA as extractant. The main conclusions are summarised as follows:

- D2EHPA extracts zinc very rapidly. Equilibrium was reached within 5 min.
- Zinc was preferentially extracted with D2EHPA at low pH levels (below 2.5). The following metal extraction sequence was obtained at pH 2.5: Zn ≫ Fe ~ Pb > Cd ~ Ca > Mg ~ Co.
- Practically all zinc was extracted from the effluent ahead of magnesium at pH 2.5 and [D2EHPA] = 20% (w/w). At this operational condition, zinc could be quantitatively and selectively extracted by two theoretical stages at A/O ratio = 1, as calculated by the McCabe-Thiele method.
- According to the method of McCabe-Thiele, the concentration of zinc in the extract could be reduced from 11.9 g/L to around 2.0 g/L while the zinc concentration in the aqueous phase could be increased from 74 g/L to almost 120 g/L in two counter-current stages operated at O/A ratio = 4.
- The continuous operation of a mixer-settler cascade containing 3 extraction stages and 3 stripping stages operated in counter-current manner have demonstrated that zinc can be removed quantitatively and selectively from the effluent (overall efficiency higher than 98%).

Finally, the present approach demonstrates the treatment of generated effluents and the recovery of zinc of high purity and value.

## Acknowledgement

Sincere thanks to Votorantim Metals Co. (Brazil) for technical and analytical support.

# References

- C. Forrest, M.A. Hughes, The separation of Zn from Cu by D2EHPA—an equilibrium study, Hydrometallurgy 3 (1978) 327–342.
- [2] G. Owusu, Selective extractions of Zn and Cd from Zn-Cd-Co-Ni sulphate solution using di-2-ethylhexyl phosphoric acid extractant, Hydrometallurgy 47 (1998) 205–215.

- [3] K. Kongolo, M.D. Mwema, A.N. Banza, E. Gock, Cobalt and zinc recovery from copper sulphate solution by solvent extraction, Miner. Eng. 16 (2003) 1371–1374.
- [4] C.Y. Cheng, Purification of synthetic laterite leach solution by solvent extraction using D2EHPA, Hydrometallurgy 56 (2000) 369– 386.
- [5] K.C. Sole, A.M. Feather, P.M. Cole, Solvent extraction in southern Africa: an update of some recent hydrometallurgical developments, Hydrometallurgy 78 (2005) 52–78.
- [6] D. Darvishi, D.F. Haghshenas, E. Keshavarz Alamdari, S.K. Sadrnezhaad, M. Halali, Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA, Hydrometallurgy 77 (2005) 227–238.
- [7] H. Singh, S.L. Mishra, R. Vijayalakshmi, Uranium recovery from phosphoric acid by solvent extraction using a synergistic mixture of di-nonyl phenyl phosphoric acid and tri-*n*-butyl phosphate, Hydrometallurgy 73 (2004) 63–70.
- [8] T. Francis, T.P. Rao, M.L.P. Reddy, Cyanex 471X as extractant for the recovery of Hg(II) from industrial wastes, Hydrometallurgy 57 (2000) 263–268.
- [9] J.S. Preston, A.C. du Preez, P.M. Cole, M.H. Fox, The recovery of rare earth oxides from a phosphoric acid by-product. Part 3. The separation of the middle and light rare earth fractions and the preparation of pure europium oxide, Hydrometallurgy 42 (1996) 131– 149.
- [10] C.A. Morais, V.S.T. Ciminelli, Process development for the recovery of high-grade lanthanum by solvent extraction, Hydrometallurgy 73 (2004) 237–244.
- [11] M.B. Mansur, M.J. Slater, E.C. Biscaia Jr., Equilibrium analysis of the reactive liquid–liquid test system ZnSO<sub>4</sub>/D2EHPA/*n*-heptane, Hydrometallurgy 63 (2002) 117–126.
- [12] L.A. Ajawin, E.S. Pérez de Ortiz, H. Sawistowski, Extraction of zinc by di(2-ethylhexyl) phosphoric acid, Chem. Eng. Res. Des. 61 (1983) 62–66.
- [13] T.-C. Huang, R.-S. Juang, Kinetics and mechanism of zinc extraction from sulfate medium with di(2-ethylhexyl) phosphoric acid, J. Chem. Eng. Jpn. 19 (1986) 379–386.
- [14] C.I. Sainz-Diaz, H. Klocker, R. Marr, H.-J. Bart, New approach in the modelling of the extraction equilibrium of zinc with bis-(2-ethylhexyl) phosphoric acid, Hydrometallurgy 42 (1996) 1–11.
- [15] M. Mörters, H.-J. Bart, Extraction equilibria of zinc with bis(2ethylhexyl) phosphoric acid, J. Chem. Eng. Data 45 (2000) 82– 85.
- [16] S. Kumar, G.L. Tulasi, Aggregation vs. breakup of the organic phase complex, Hydrometallurgy 78 (2005) 79–91.
- [17] J. Ji, K.H. Mensforth, J.M. Perera, G.W. Stevens, The role of kinetics in the extraction of zinc with D2EHPA in a packed column, Hydrometallurgy, in press.
- [18] B.S. Morais, M.B. Mansur, Characterisation of the reactive test system ZnSO<sub>4</sub>/D2EHPA in *n*-heptane, Hydrometallurgy 74 (2004) 11–18.
- [19] G.M. Ritcey, Development of industrial solvent extraction processes, in: J. Rydberg, C. Musikas, G.R. Choppin (Eds.), Principles and Practices of Solvent Extraction, Marcel Dekker, USA, 1992, pp. 449–510.

- [20] J.C. Godfrey, M.J. Slater (Eds.), Liquid–Liquid Extraction Equipment, John Wiley & Sons, 1994.
- [21] T.C. Lo, M.H.I. Baird, C. Hanson (Eds.), Handbook of Solvent Extraction, John Wiley & Sons, 1983.
- [22] COPAM, no. 10, Minas Gerais state normative legislation by 16/12/1986, Brazil.
- [23] G.M. Ritcey, A.W. Ashbrook, Solvent extraction: principles and applications to process metallurgy, in: Process Metallurgy, Part 1, Elsevier, 1984.
- [24] J. Aparicio, M. Muhammed, Extraction kinetics of zinc from aqueous perchlorate solution by D2EHPA dissolved in Isopar-H, Hydrometallurgy 21 (1989) 385–399.
- [25] A.M.I. Ali, I.M. Ahmad, J.A. Daoud, CYANEX 272 for the extraction and recovery of zinc from aqueous waste solution using a mixer-settler unit, Sep. Purif. Technol. 47 (2006) 135–140.