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Direct hydrometallurgical separation of Zn(II) from brine leaching solution of zinc filter cake by simple solvent extraction process

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Abstract: The zinc leaching filter cake residue as a secondary resource is used for hydrometallurgical lead production from brine (chloride) media. In this method, zinc accumulation caused decrease in the lead leaching efficiency in feed solution as well as a defective cycle flowsheet in production process. Therefore, an experiment was designed for the solvent extraction (SX) of zinc from brine solution after lead cementation stage. The results indicated that approximately 98% zinc with a little contamination of other metals was extracted under optimum conditions (193.5 g.dm^{-3} of D2EHPA in kerosene as diluent, pH=3.5, contact time=5 min, temperature=40±2 °C and aqueous: organic ratio (A:O)=1:1). Also, according to the differences of $\Delta pH_{0.5}$ and separation factor values among Zn and other ions, D2EHPA as an organophosphorous extractant has suitable capability for zinc selective extraction from brine solution. Moreover, H_2SO_4 solution which was used for stripping to transfer Zn^{2+} ions to zinc conventional production sulphate media achieved high efficiency of 99%. McCabe-Thiele diagram was simulated to counter-current extraction route. The results showed that two stages were needed for both extraction and stripping.

Keywords: Zn^{2+}, chloride leaching solution, sulphate filter cake, D2EHPA, SX

1. Introduction

Currently, zinc industrial residue is one of the most important secondary resources for Zn recovery and other valuable metals such as Cd, Ni, Co, etc. These residues are left from various stages of zinc hydrometallurgical production industry as well as flotation process and other related processing systems (Moradkhani et al., 2014). On the other hand, the presence of toxic elements that affects human health like Pb, Cd and Ag, and environmental legislations, restrict damping of such waste materials (Cole and Sole, 2003; Biswas et al., 2016; Balesini et al., 2013). Therefore, several works have been performed on utilization of zinc residues and wastes. Haghshenas et al. (2007) investigated the recovery of Zn, Mn and Co from hot filter cake by sulphate media leaching and determined optimal parameters for the process. Schlumberger et al. (2007) studied the Zn-SX from filter ash of thermal treatment waste and used bis (2, 4, 4-trimethylpentyl) phosphinic acid as extractant. Vahidi et al. (2009) reported solvent extraction of zinc from sulphate solution obtained from zinc industrial leach residue by D2EHPA and Tributyl Phosphate (TBP). In another study, Haghighi et al. (2015) investigated the separation and recovery of zinc from hot filter cakes that were obtained from cobalt neutralization stage in Zn hydrometallurgical production process. This filter cake was subjected to selective leaching by alkaline media and followed with electrowinning for zinc recovery. Ru et al. (2015) studied the leaching and recovery of Zn by membrane filter press from zinc calcine leaching residues. Separation/recovery of Zn^{2+} from chloride media is a conventional hydrometallurgical process, therefore a variety of researches have done on other industrial solutions such as fly ash, which was treated for zinc and copper separation by LIX860N and CYANEX923 from chloride leaching solution (Tang and Steenari, 2015). In other study, the 95% of Cu and 61% of Zn content in ash residue was separated using LIX860N and CYANEX572,

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respectively (Tang et al., 2018). SX of the different synthetic solutions with several extractants have been studied too. For example, Lin (1993) investigated the zinc extraction from chloride media by DBBP in Escaid 110. Pyridine carboxamides were used as extractants for zinc separation from zinc chloride solution and the type of complexes were suggested (Borowiak et al., 2010). Wieszczycka (2013) studied the effect of pyridyl ketoximes on zinc solvent extraction over Cu, Fe (II) and Fe (III). Azizitorghabeh et al. (2016) examined the zinc and iron separation by the mixture of D2EHPA and TBP. The best result obtained for $\Delta pH_{0.5}$ between zinc and iron was 2.5 and 80% of zinc extracted. Cheng et al. (2016) studied the effect of various synergistic systems on the sulphate and chloride solutions by oximes and organophosphorous extractants for Zn, Cu, Ni and Co extraction. Pyridine carboxamides and diketone are the other extractants that are used in three steps of SX process (extraction and scrubbing and stripping) for zinc separation (Stasiak, 2016). Jafari et al. (2018) studied Zn separation from Cd and Mn from chloride solution with D2EHPA, and reported the optimal parameters. Table 1 summarizes the reagents and extractants for zinc and manganese extraction (Biswas et al., 2016).

Table 1. Summary of Zn and Mn extractions using various organophosphorous extractants (Biswas et al., 2016)

Organic phase			Aqueous phase				Eq.	Exn.
Ext.	[Ext] ($g.dm^{-3}$)	Diluent	Anion	pH	[Mn^2] ($g.dm^{-3}$)	[Zn^{2+}] ($g.dm^{-3}$)	time (min)	(%)
D2EHPA	64.49	Kerosene	Cl^-	5.00	20.0	-	10	CE
	64.49	Kerosene	Cl^-	3.50	1.00	-	180	≈CE
	96.73	Kerosene	SO_4^{2-}	2.50	-	28.80	5	PE
	64.49	Benzene	SO_4^{2-}	4.50	0.20	-	10	≈CE
Na-D2EHPA	20.72	Kerosene	SO_4^{2-}	3.95	0.55	-	5	41
	20.72	Kerosene	SO_4^{2-}	3.95	-	0.65	5	97
Na-PC88A	19.76	Kerosene	SO_4^{2-}	4.20	0.55	-	5	4
	19.76	Kerosene	SO_4^{2-}	4.20	-	0.65	5	≈CE
Cyanex 272	14.52	Kerosene	$SO_4^{2-} - Ac^-$	6.00	1.00	-	10	≈CE
	29.04	Kerosene	SO_4^{2-}	5.00	-	1.00	5	98
	29.04	Xylene	SO_4^{2-}	4.00	-	0.07	15	≈CE
Na-Cyanex 272	18.81	Kerosene	SO_4^{2-}	5.95	0.55	-	15	51
	18.81	Kerosene	SO_4^{2-}	5.95	-	0.65	5	CE
Cyanex 302	516.08	-	Cl^-	0.75	70.20	-	-	8
	25.80	Kerosene	SO_4^{2-}	2.92	-	2.13	5	CE
Cyanex 301	1032.16	-	Cl^-	2.80	70.20	-	-	96
	25.80	Kerosene	SO_4^{2-}	0.00	-	2.00	5	CE

Note: % in 3rd column is in v/v, Ext.=extractant, Exn.=extraction, CE=complete extraction, PE=partial extraction, Eq.=equilibrium

In conventional zinc production process, after sulphuric acid leaching and neutralization stage, the solution is filtrated and leaching filter cake is removed (Moradkhani et al., 2013). Zinc leaching filter cake (ZLFC) is one of the important residues in zinc plants. In some zinc plants, ZLFC is stored in depot for lead recovery in future and considered as hazardous residue due to its harmful elements in content such as cadmium (Turan et al., 2004). For this reason, in the first step for lead recovery from ZLFC, chloride or brine leaching is suggested by some previous works. Ruşen et al. (2008) reported H_2SO_4 and NaCl leaching for Zn and Pb extraction from Çinkur leach residue sequentially. Also, some study use Taguchi's experiment method for parameter optimization in brine leaching of hydrometallurgical residue to maximize lead and zinc recovery (Guo et al., 2010; Behnajady et al., 2012). Wang et al. (2015) investigated acidic $CaCl_2$ aqueous solution leaching process as an alternative approach for brine leaching of zinc hydrometallurgical residue.

After brine leaching of ZLFC, in the second stage, aluminium powder was used for lead cementation process. Farahmand et al. (2009) reported optimum conditions for lead cementation obtained from brine leaching filtrate of lead-bearing zinc plant residue which resulted in lead sponge recovery of about 95%. In another study, optimal parameters for lead cementation with Al powder from zinc

hydrometallurgical residue brine leaching solution was investigated (Abdollahi et al., 2015). After leaching and cementation stages, lead sponge was separated and collected. Then, raffinate solution containing zinc, lead, cadmium, manganese, etc was repeatedly recycled to brine leaching and cementation steps. After three to four times of recycling, lead dissolution decreased and zinc as well as other impurities concentration increased.

Therefore, to avoid the environmental friendly issues and obligations by chloride solution, zinc separation stage has to be performed. Present research discusses the solvent extraction (SX) procedure for zinc selective separation and creates a closed cycle as an innovative method in process flowsheet.

For this purpose, di-2-ethyl hexyl phosphoric acid (D2EHPA) as an effective reagent for metals extraction from chloride media such as hydrochloric acid was selected for solvent extraction process and identifying optimal parameters (Jin et al., 2014).

2. Materials and methods

2.1. Feed solution preparation

A sample of typical sulphate leaching filter cake residue from conventional hydrometallurgical treatment of Angouran zinc concentrate (Zanjan Zinc Khalessazan Industries Co., Iran) was used for brine leaching and lead cementation stages (Table 2).

Table 2. Chemical analysis of major metal ions in* ZLFC (Dry basis)

Element	Zn	Pb	Fe	Cd	Mn	Ni	Co	Cu
Content (wt %)**	6.80	4.60	3.40	0.13	0.16	0.08	0.02	0.01

*:Note: other main ions in ZLFC are calcium, sodium, silicon and sulphate that don't have any role in process.

** : weight percentage

Brine leaching of ZLFC in the 300 $g.dm^{-3}$ of NaCl solution was performed at pH=3, T= 25 (°C), solid: liquid ratio (S:L)=1:4 and t=120 min. Brine leaching filtrate obtained from this stage was subjected to cementation for lead separation by using aluminium scrap pieces. After lead sponge collection, raffinate solution was recycled to brine leaching stage (Behnajady et al., 2012). After three times of brine leaching and lead cementation, final industrial feed solution was obtained for zinc solvent extraction (Table 3).

Table 3. Chemical analysis of ZLFC final feed solution for SX process (after three times of leaching and cementation)

Element	Zn	Pb	Fe	Cd	Mn	Ni	Co	Cu
Feed solution content ($mg.dm^{-3}$)	26884.0	55.3	2.8	742.3	327.2	21.2	29.5	1.1

2.2. Reagents

The D2EHPA reagent was diluted in kerosene (Tehran Oil Refinery Company, TORC) to give 96.7, 145.1, 193.5 and 241.8 ($g.dm^{-3}$) to determine optimum extractant concentration. Ammonia (255.5 $g.dm^{-3}$) and HCl (91.2 $g.dm^{-3}$) solutions (Merck Co.) were used for adjusting the pH of the solution during solvent extraction experiments.

2.3. Extraction procedure

Extraction percentage versus equilibrium pH was determined by single-stage batch experiments to reach the optimum pH and $\Delta pH_{0.5}$ values for Zn extraction from industrial feed solution. In a typical run, about 100-500 cm^3 of the leach solution and an equal volume of the organic phase (A:O=1:1) were mixed with a mechanical stirrer. Sampling was done after 10 min of adjusting the initial pH value of the solutions to the desired condition.

The effect of equilibrium pH, D2EHPA concentration, contact time, temperature and A:O ratio was carried out using a thermostatic water bath (Memmert Co.). pH was measured by a Metrohm pH meter. Metal ions contents of aqueous solutions were determined by atomic absorption spectroscopy (AAS) technique (Varian AA240) and their concentrations in the respective organic phases were calculated by mass balance. The distribution ratio (D) was calculated from the Eq. 1:

$$D = \frac{\bar{C}_M}{C_M} \quad (1)$$

where $\bar{C}_M$ and C_M are the concentration of M in organic and aqueous phases after solvent extraction, respectively. The separation factor of two different metal ions M_1 and M_2 (β_{M_1/M_2}) was determined from the Eq. 2:

$$\beta_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}} \quad (2)$$

2.4. Stripping procedure

The loaded organic solutions were accompanied with H_2SO_4 (196.2 g.dm^{-3}) solutions for 15 min at 25 °C, and metals ions were transferred from organic phase into the sulphate aqueous media. Also, the aqueous solution samples were analyzed with ASS method and stripping percentages were calculated.

3. Results and discussion

3.1. Effect of pH on extraction isotherm

Determining pH value of equilibrium is one of the important parameters in solvent extraction processes. So, experiments were carried out to optimize pH range for Zn^{2+} extraction from other metal ions in chloride solution that were obtained from brine leaching and cementation raffinate (Table 3) by D2EHPA extractant.

The operating conditions were as the following: concentration of D2EHPA= 193.5 g.dm^{-3}, A:O ratio=1:1, temperature= 40±2 °C and organic-aqueous contact time=5 min. It was observed that the pH value for 50% metals extraction ($pH_{0.5}$) for Zn was around 1.6, for Mn around 3.75 and for other metals was out of range (Fig.1). ($pH_{0.5}^{Mn}$-$pH_{0.5}^{Zn}$) shows the difference between 50% of overall extraction for each elements individually (zinc and manganese in this section) at a specific pH value. The 50% extraction point pH for Mn and Zn ($pH_{0.5}^{Mn}$-$pH_{0.5}^{Zn}$) reported to be 2.15 pH unit. Considering the metal ions concentrations, this $\Delta pH_{0.5}$ is excellent compared to Versatic 10 and Versatic 10+ LIX 63 (Cheng et al., 2016).On the other hand, Zn extraction yield increases from 16.1% to 99.1% by increasing equilibrium pH value from 1 to 6. The optimum equilibrium pH value for maximum zinc extraction percentage and minimum extraction of impurities are represented in Fig. 1. It is observed that at 3<pH<4, approximately 97 to 99% (equal to 26.6 g.dm^{-3}) Zn with a little contamination of other metals (Mn<190, Cd<150, Pb<15, Co<5 and the rest of metal ions<1 mg.dm^{-3}) can be extracted from feed solution. Therefore, according to Fig. 1, the optimum average pH value for zinc extraction is 3.5.

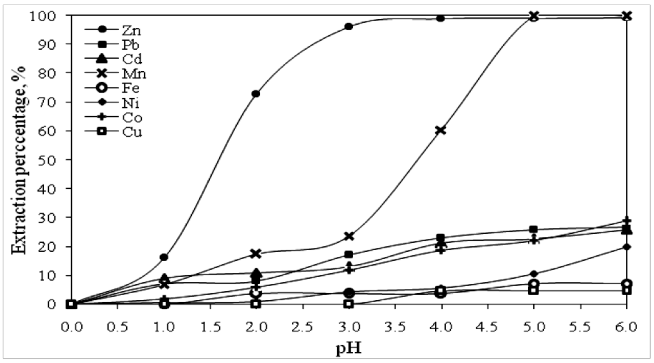

Fig. 1. Diagram of Extraction percentage of metal ions vs. pH from industrial chloride feed solution by D2EHPA=193.5 g.dm^{-3}, A:O=1:1, T=40±2 °C and contact time=5 min

3.2. Effect of extractant concentration on extraction isotherm

The effect of reagent concentration on zinc solvent extraction from industrial aqueous solution was studied using D2EHPA concentration varying from 96.7 to 241.8 (g.dm^{-3}) diluted in kerosene. Figure 2 shows that, Zn extraction percentage rises with increase in D2EHPA concentration. So, increasing D2EHPA concentration from 96.7 to 241.8 (g.dm^{-3}) caused $pH_{0.5}^{Zn}$ to decrease from 2 to 1.3 (Table 4).

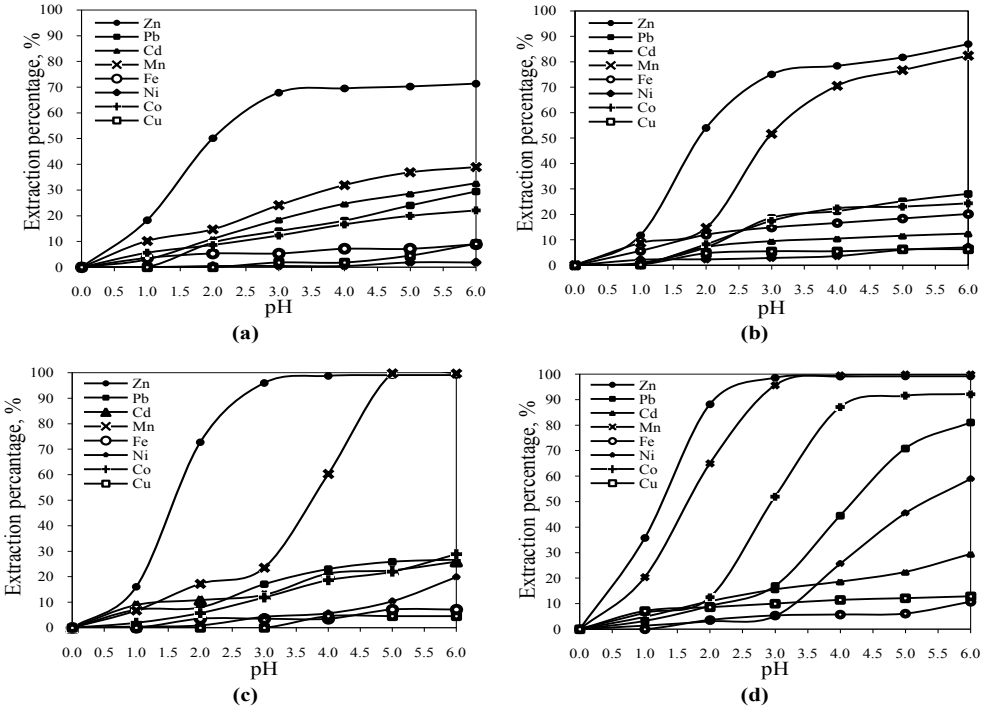

Fig. 2. D2EHPA concentration effect on zinc extraction from industrial chloride feed solution at T=40±2 °C, A:O=1:1 and contact time=5 min by D2EHPA concentration: (a) 96.7, (b) 145.1, (c) 193.5 and (d) 241.8 g.dm^{-3}

Table 4. Metals pH_{50} and ΔpH_{50} extraction values by different D2EHPA concentrations (96.7, 145.1, 193.5 and 241.8 g.dm^{-3} diluted in kerosene), T=40±2 °C, A:O=1:1 and contact time=5 min

D2EHPA (g.dm^{-3})	96.7	145.1	193.5	241.8	D2EHPA (g.dm^{-3})	96.7	145.1	193.5	241.8
$pH_{0.5}^{Zn}$	2.00	1.90	1.60	1.30	$\Delta pH_{0.5}^{(Mn-Zn)}$	-*	1.05	2.15	0.40
$pH_{0.5}^{Mn}$	>6.00	2.95	3.75	1.70	$\Delta pH_{0.5}^{(Pb-Zn)}$	-	-	-	2.90
$pH_{0.5}^{Pb}$	>6.00	>6.00	>6.00	4.20	$\Delta pH_{0.5}^{(Cd-Zn)}$	-	-	-	-
$pH_{0.5}^{Cd}$	>6.00	>6.00	>6.00	>6.00	$\Delta pH_{0.5}^{(Fe-Zn)}$	-	-	-	-
$pH_{0.5}^{Fe}$	>6.00	>6.00	>6.00	>6.00	$\Delta pH_{0.5}^{(Ni-Zn)}$	-	-	-	-
$pH_{0.5}^{Ni}$	>6.00	>6.00	>6.00	5.30	$\Delta pH_{0.5}^{(Co-Zn)}$	-	-	-	4.00
$pH_{0.5}^{Co}$	>6.00	>6.00	>6.00	2.95	$\Delta pH_{0.5}^{(Cu-Zn)}$	-	-	-	1.65
$pH_{0.5}^{Cu}$	>6.00	>6.00	>6.00	>6.00					

* pH_{50} of metals with trace concentration is out of range, so there is no data subtraction

It can be seen that at pH lower than 4, Mn with over 50% yield was extracted from 145.1 (g.dm^{-3}) D2EHPA; while $pH_{0.5}^{Mn}$ in 193.5 (g.dm^{-3}) is equal to 3.75. Also, the extraction percentage of other metals in 145.1 and 193.5 (g.dm^{-3}) D2EHPA is less than 50%. Table 4 shows that in 241.8 (g.dm^{-3}) D2EHPA, extraction rate of other metals such as Co, Pb and Fe increased to 50%, so this concentration of extractant for optimal extraction of zinc is unacceptable. According to extraction percentages, $pH_{0.5}$ values and the contamination of the loaded organic phase with impurities, the optimum concentration for D2EHPA is 193.5 (g.dm^{-3}). On other hand, $\Delta pH_{0.5}^{Mn-Zn} (= pH_{0.5}^{Mn} - pH_{0.5}^{Zn})$ in 145.1 and 193.5 (g.dm^{-3}) M D2EHPA is equal to 1.05 and 2.15 pH unit, respectively. It was observed that at 3<pH<3.5, the extraction yield of zinc can reach 98% in aqueous solution with little contamination of the other metals by using 193.5 (g.dm^{-3}) D2EHPA. From data in Table 5, it can be calculated that the best separation factor between Zn^{2+} and Mn^{2+} ($\beta_{Zn/Mn}=D_{Zn}/D_{Mn}$) is equal to 51.6 when D2EHPA 193.5 (g.dm^{-3}) is used.

The complexation of zinc by organophosphorous acids extractants can be described as (Cole and Sole, 2003):

$$Zn_{(aq)}^{2+} + mHA_{(org)} \leftrightarrow ZnA_2.(m\text{-}2)HA_{(org)} + 2H_{(aq)}^{+} \quad (4)$$

Table 5. Metals separation factor values by different D2EHPA concentrations (96.7, 145.1, 193.5 and 241.8 g.dm^{-3} diluted in kerosene) from feed solution at T=40±2 °C, A:O=1:1, pH=3.5 and contact time=5 min

D2EHPA Concentration (g.dm^{-3})	96.7	145.1	193.5	241.8
$\beta_{(Zn/Pb)}$	11.7	13.2	148.8	182.3
$\beta_{(Zn/Cd)}$	8.0	29.6	180.8	393.6
$\beta_{(Zn/Mn)}$	5.6	2.1	51.6	2.0
$\beta_{(Zn/Fe)}$	32.9	17.6	1006.3	1379.6
$\beta_{(Zn/Ni)}$	462.3	97.5	715.2	447.7
$\beta_{(Zn/Co)}$	12.9	13.2	207.1	35.4
$\beta_{(Zn/Cu)}$	118.3	56.1	1602.6	673.7

where HA represents the D2EHPA reagent. In Eq. 4, m signifies the stoichiometry of HA in the reaction. The equilibrium constant ($K_{ext.}$) of the zinc extraction reaction is shown in Eq. 5:

$$K_{ext.} = \frac{[ZnA_2.(m-2)HA]_{(org)}.[H^+]^2_{(aq)}}{[Zn^{2+}]_{(aq)}.[HA]^m_{(org)}} \tag{5}$$

$$\log\left[\frac{[ZnA_2.(m-2)HA]_{(org)}}{[Zn^{2+}]_{(aq)}}\right] = \log K_{ext.} + m\log[HA] + 2pH \tag{6}$$

The distribution coefficient of Zn^{2+} (D_{Zn}) is calculated from the following equation:

$$D_{Zn} = \frac{[ZnA_2.(m-2)HA]_{(org)}}{[Zn^{2+}]_{(aq)}} \tag{7}$$

As a result:

$$\log[D_{Zn}] = \log K_{ext.} + m\log[HA] + 2pH \tag{8}$$

According to Eq. (8), the slope of the plot of $\log D_{Zn}$ vs. log[HA]=log[D2EHPA] (Fig. 3) would give the number of molecules of D2EHPA engaged in the reaction (Eq. 4),that is m=2.

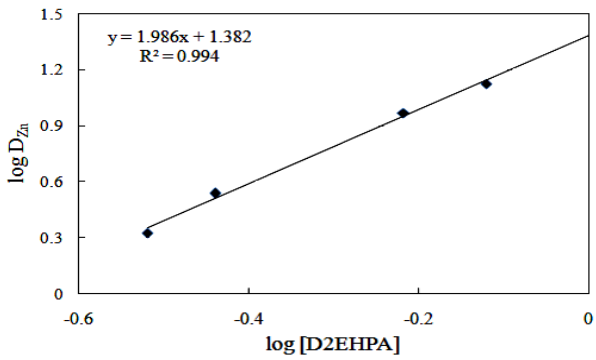

Fig. 3. D2EHPA concentration effect on the distribution coefficient of Zn^{2+} from industrial chloride feed solution at T=40±2 °C, pH=3.5, A:O=1:1 and contact time=5 min (based on chemical analysis in Table 3)

3.3. Effect of contact time on extraction isotherm

Figure 4 shows the evaluation of zinc extraction percentage vs. organic-aqueous phases contact at different time intervals. It was observed that the kinetics of zinc extraction is quick and more than 90% of Zn is extracted by organic phase within the first 0.5 min. After 2 min, the zinc extraction yield increases to 98% and stays constant up to 10 min. Also, it was observed that prolong organic-aqueous contact time had no adverse effect on extraction percentage. Further experiments were also subjected to 5 min for contact time of solutions, which confirms the results of previous work (Jafari et al. 2018).

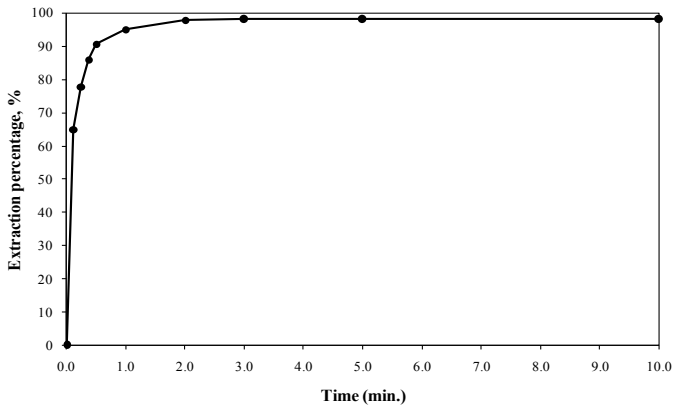

Fig. 4. Contact time effect on zinc solvent extraction from industrial chloride feed solution by D2EHPA=193.5 g.dm^{-3}, A:O=1:1, T=40±2 °C and pH=3.5 (based on chemical analysis in Table 3)

3.4. Effect of temperature on extraction isotherm

The impact of temperature on zinc solvent extraction was carried out using 193.5 (g.dm^{-3}) D2EHPA in A:O phase ratio=1, pH range from 1-6 and contact time= 5 min at temperatures 20, 30, 40 and 50±2 °C. Figure 5-(a) shows that zinc extraction percentage at 20±2 °C and 3<pH<3.5 is less than 90. Also, it was observed that $\Delta pH_{0.5}^{(Mn\text{-}Zn)}$ is 1.3 and 2.15 at 30 and 40±2 °C respectively (Fig. 5-(b and c)). Additionally, extraction of other metal ions at 50±2 °C is not only increased, but also $\Delta pH_{0.5}^{(Mn-Zn)}$ becomes almost equal to one pH unit (Fig. 5-(d)).

Moreover, $\beta_{(Zn/Mn)}$ at selected temperatures was calculated (Table 6). Finally, according to these data, optimal temperature value for other experiments was chosen 40±2 °C. $\beta_{(Zn/Mn)}$ increases from 20 °C up to 40 °C and then decreases at 50 °C.

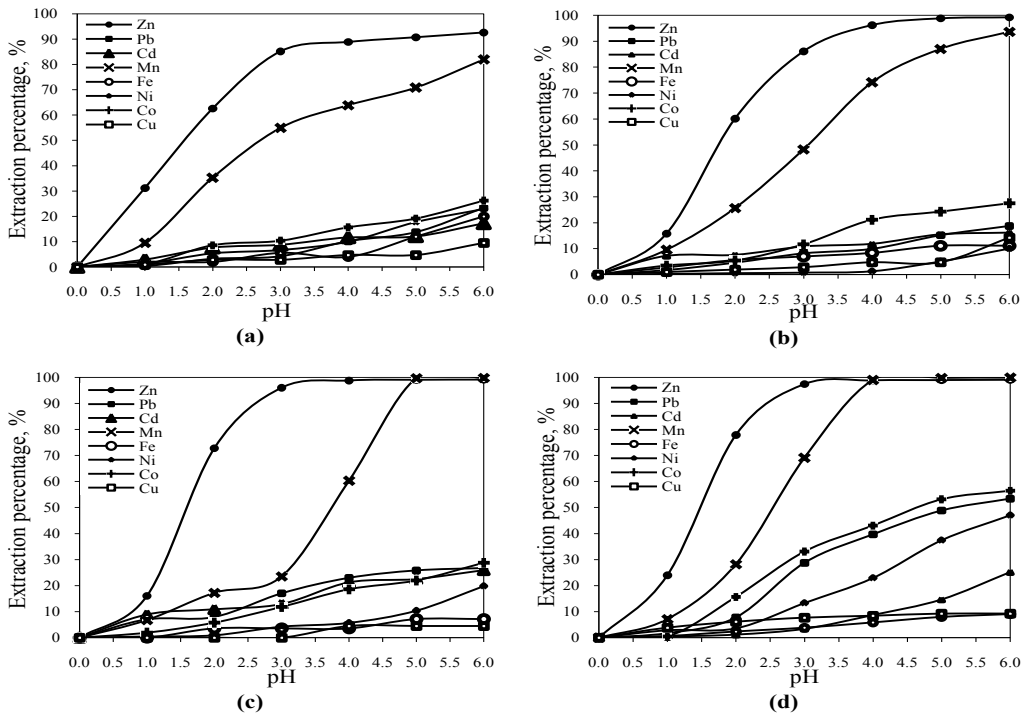

Fig. 5. Temperature effect on zinc SX from feed solution by D2EHPA=193.5 g.dm^{-3}, A:O=1:1, pH=3.5 and contact time=5 min at: (a) 20, (b) 30, (c) 40 and (d) 50±2 °C

Table 6. Metals separation factor ($\beta_{Zn/Metal}$) values at various temperatures (20, 30, 40 and 50±2 °C), D2EHPA=193.5 g.dm^{-3}, A:O=1:1, pH=3.5 and contact time=5 min

Temperature (°C)	20	30	40	50
$\beta_{(Zn/Pb)}$	86.7	104.4	148.8	100.1
$\beta_{(Zn/Cd)}$	59.1	80.9	180.8	807.3
$\beta_{(Zn/Mn)}$	4.6	6.5	51.6	9.9
$\beta_{(Zn/Fe)}$	133.2	125.0	1006.3	1017.1
$\beta_{(Zn/Ni)}$	73.7	1023.2	715.2	236.4
$\beta_{(Zn/Co)}$	45.0	52.6	207.1	84.9
$\beta_{(Zn/Cu)}$	169.5	261.0	1602.6	593.6

Moreover, Van't Hoff equation can be used for calculating the value of enthalpy change in zinc extraction (Mellah and Benachour, 2007):

$$\frac{\Delta \log D_{Zn}}{\Delta(1/T)} = -\frac{\Delta H}{2.303R} \tag{9}$$

Log D_{Zn} vs. 1/T is plotted (Fig. 7). It can be observed that the distribution coefficient values rise by incresce in temperature. According to the Eq. 9 and Fig. 6, zinc extraction enthalpy can be calculated by the slope of the liner relation. Consequently, ΔH= +6.07 kJ.mol^{-1} is determined, which clearly indicates that the Eq. 4 is an endothermic reaction and elevation of temperature improves the zinc extraction from aqueous solution by using D2EHPA.

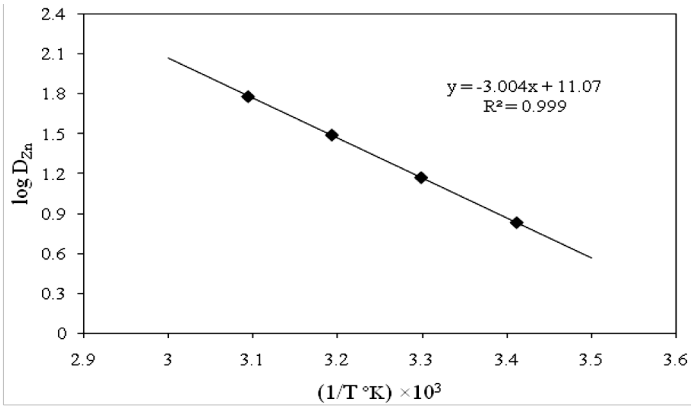

Fig. 6. Temperature effect on the distribution coefficient of Zn^{2+} from industrial chloride feed solution by D2EHPA

3.5. Extraction distribution isotherm and McCabe-Thiele Diagram

Aqueous to organic phase ratio (A:O) is one of the important parameters in solvent extraction processes. So, some experiments have been performed at 7 levels of A:O ratio: 10:1, 5:1, 2:1, 1:1, 1:2, 1:5 and 1:10.

Extraction data of zinc in both aqueous and organic phases affected by the phase ratio (A:O) are summarized in Table 7. According to the experimental results, zinc extraction percentage was more than 95% for A:O=1:1, 1:2, 1:5 and 1:10, while it was reduced to 9.2% for the ratio of 10:1. At the same time, the distribution coefficient of zinc (D_{Zn}) in A:O=1:1 and 1:2 was more than 20. Also, it was observed that separation factors for other metal ions over zinc in feed solution at A:O=1:1 were more than other ratios (Table 7). Therefore, this ratio was chosen as the optimum to provide high zinc extraction yield and low contamination from other metals.

Figure 7 shows McCabe-Thiele distribution isotherm for zinc extraction from feed solution in different phase ratios by using data in Table 7. It was observed that when operating line is set up on A:O=1.3:1, zinc continuous extraction can be suggested at two stages. It can also be deduced from Fig. 7 that in this ratio, the actual loading capacity of organic phase for Zn^{2+} ions may be regarded to be slightly over 23 (g.dm^{-3}) under the experimental conditions employed in the present study.

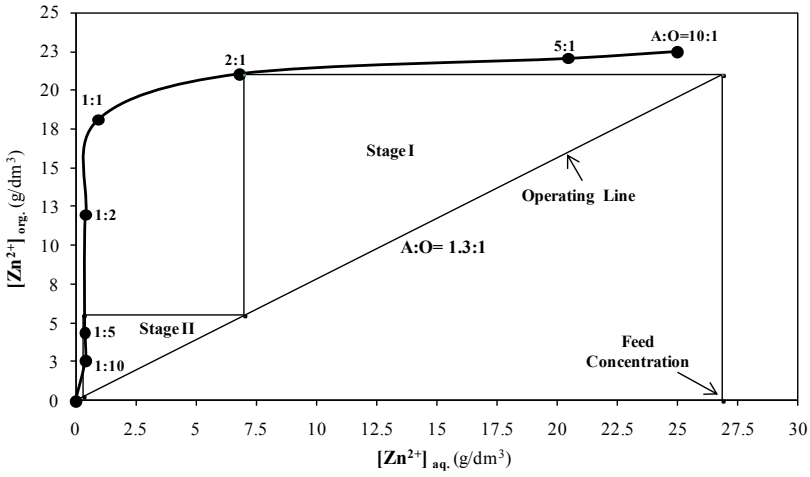

Fig. 7. McCabe-Thiele distribution isotherm for zinc from industrial chloride feed solution by D2EHPA

Table 7. Variation of extraction percentage and distribution ratio of Zn with phase ratio for industrial chloride feed solution and separation factors by D2EHPA=193.5 g.dm^{-3}, T=40±2 °C, pH=3.5 and contact time=5 min

A:O ratio	Concentration (g.dm^{-3})		Distribution Coefficient (D_M)	Extraction Percentage (%)	Separation Factor (β)						
	Aqueous	Organic			Zn/Pb	Zn/Cd	Zn/Mn	Zn/Fe	Zn/Ni	Zn/Co	Zn/Cu
1:10	0.4	2.6	6.8	98.6	72.7	465.7	0.2	103.3	27.0	17.3	39.6
1:5	0.4	4.4	11.9	98.7	145.4	767.6	0.2	93.3	31.8	17.4	38.3
1:2	0.4	12.0	29.8	98.5	420.0	2642.2	0.5	175.4	183.9	33.8	48.9
1:1	0.9	18.1	20.1	96.7	665.0	4389.2	15.5	275.6	1169.2	99.8	62.6
2:1	6.8	21.0	3.1	75.4	60.0	223.4	13.0	46.1	199.7	99.8	41.5
5:1	20.5	22.1	1.1	25.6	29.1	78.1	14.4	11.2	70.8	62.6	17.7
10:1	25.0	22.5	0.9	9.2	31.6	71.0	14.5	13.8	70.4	62.2	17.5

3.6. Stripping of loaded organic phase

In conventional zinc hydrometallurgical industry, one of the aims in this research is transporting of zinc metal ions from loaded organic phase to sulphate aqueous media for processing. Therefore, according to the optimum extraction conditions, the loaded D2EHPA solution (Table 8) was subjected to stripping experiments employing a sulphuric acid (196.2 g.dm^{-3}) solution.

Table 8. Chemical analysis of metal ions in loaded organic phase

Element	Zn	Pb	Fe	Cd	Mn	Ni	Co	Cu
Content (mg.dm^{-3})	26448.5	11.1	0.1	126.9	133.9	1.1	4.5	0.1

The extent of Zn stripping percentage vs. equilibrium pH value at 25 and 40±2 °C is presented in Fig. 8. It can be observed that the stripping efficiency increases with decreasing in equilibrium pH value. When the pH value is lowered from 2 to 0.5, stripping yield increased from 0.5% to 75% and 12% to 98% at 25 and 40±2 °C, respectively. Therefore, 0<pH<1 range (average pH ≈ 0.5) and T=40±2 °C are desirable conditions for zinc stripping.

Also, to determine the number of stages required for stripping, the loaded D2EHPA was conducted with sulphuric acid solution at various A:O ratios (1:10, 1:5, 1:2, 1:1, 2:1, 5:1 and 10:1) while the total volume of phases was constant. Distribution isotherm of Zn stripping and McCabe-Thiele diagram is plotted (Fig. 9). It is shown that two continuous stages are required for zinc stripping from loaded organic phase with 99% efficiency employing A:O ratio equal to 2.5:1.

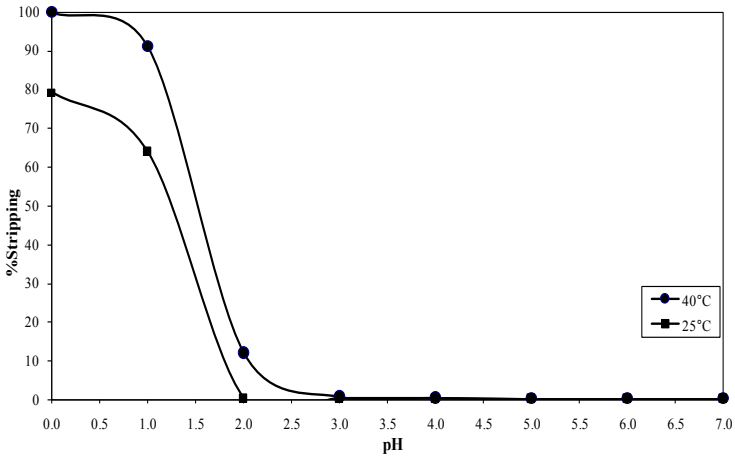

Fig. 8. Zinc stripping percentage vs. pH from loaded D2EHPA at T=25 and 40±2 °C (based on chemical analysis in Table 8)

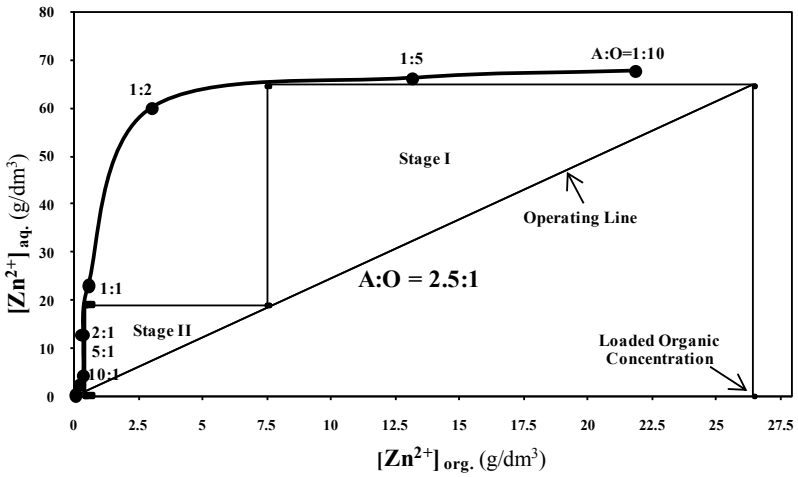

Fig. 9. McCabe-Thiele distribution isotherm for zinc stripping from loaded D2EHPA at T=40±2 °C and pH≈0.5

4. Conclusions

On the basis of obtained results, a closed-cycle flowsheet in lead process by D2EHPA diluted in kerosene was suggested for zinc extraction (Fig. 10). The effect of some parameters such as pH, extractant concentration, contact time, temperature and phases ratio was studied in zinc extraction and stripping steps. The summary of the conclusions is as follows:

(1) Under optimum conditions, $pH_{0.5}^{Zn}$=1.6, $pH_{0.5}^{Mn}$=3.75 and for other metals $pH_{0.5}$ are out of experiments range due to trace concentration ($pH_{0.5}$ >6). Also, $\Delta pH_{0.5}^{(Mn-Zn)}$=2.15.

(2) About 98% of zinc together with a little contamination of other metal ions was extracted in a two counter-current route stages validating the prediction of McCabe-Thiele plot.

(3) Zinc extraction enthalpy change (ΔH) equal +6.07 kJ.mol^{-1} was obtained.

(4) For transferring of Zn^{2+} to hydrometallurgical zinc production process, loaded organic phase was stripped by using H_2SO_4 solution to form zinc sulphate phase. Therefore, almost 99% Zn (II) at T=40±2 °C and average pH ≈ 0.5 can be stripped in a two-stage counter-current process at the A:O ratio of 2.5:1.

(5) Zinc was successfully separated from the raffinate of lead brine solution with solvent extraction.

Consequently, the results suggest a hydrometallurgical approach for ZLFC residue management, zinc selective extraction as a by-product and completion of the lead brine production treatment.

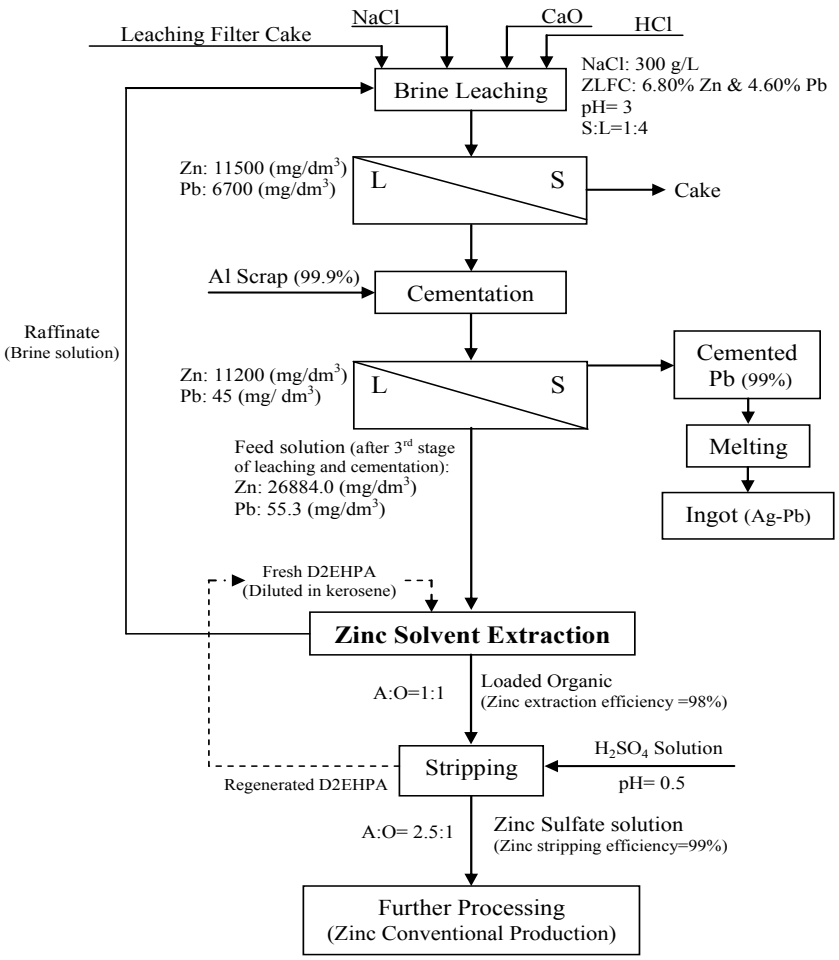

Fig. 10. Flowsheet of the proposed process for zinc and lead co-extraction from ZLFC

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References

ABDOLLAHI P., YOOZBASHIZADEH H., MORADKHANI D., BEHNIAN D., 2015. *A study on cementation process of lead from brine leaching solution by aluminum powder*, Open Access Library J. 2, 1-6.

AZIZITORGHABEH A., RASHCHI F., BABAKHANI A., 2016. *Stoichiometry and structural studies of Fe (III) and Zn(II) solvent extraction using D2EHPA/TBP*, Sep. Pur. Tech. 171, 197-205.

BALESINI A.A., ZAKERI A., RAZAVIZADEH H., KHANI A., 2013. *Nickel solvent extraction from cold purification filter cakes of Angouran mine concentrate using LIX984N,* Int. J. Min. Metal. Mat. 20(11), 1-6.

BEHNAJADY B., MOGHADDAM J., BEHNAJADY M.A., RASHCHI F., 2012. *Determination of optimum conditions for the leaching of lead from zinc plant residues in NaCl-H_2SO_4-$Ca(OH)_2$ media by the Taguchi's method,* Ind. Eng. Chem. Res. 51, 3887-3894.

BISWAS R.K., HABIB M.A., KUMAR A.K., TANZIN S., 2016. *Recovery of manganese and zinc from waste Zn-C cell powder: mutual separation of Mn (II) and Zn (II) from leach liquor by SX technique*, Wast. Man. 51, 149-156.

BOROWIAK R.A., CHLEBOWSKA H., GIEZEK M., 2010. *Zinc extraction from chloride solutions with N-alkyl-and N, N -dialkylpyridinecarboxamides*, Hydrometallurgy 103(1-4), 158-166.

CHENG C.Y., BARNARD K.R., ZHANG W., ZHU Z., PRANOLO Y., 2016. *Recovery of nickel, cobalt, copper and zinc in sulphate and chloride solutions using synergistic solvent extraction*, Chinese J. Chemical Eng. 24(2), 237-248.

COLE P., SOLE K., 2003, *Zinc solvent extraction in the process industries*, Min. Process. Ext. Metal. Rev. 24 (2), 91-137.

FARAHMAND F., MORADKHANI D., SAFARZADEH M.S., RASHCHI F., 2009. *Optimization and kinetics of the cementation of lead with aluminum powder,* Hydrometallurgy 98, 81-85.

GUO Z., PAN F., XIAO X., ZHANG L., JIANG K., 2010. *Optimization of brine leaching of metals from hydrometallurgical residue*, Trans. Nonfer. Metal Soc. China 20, 2000-2005.

HAGHIGHI H.K., MORADKHANI D., SARDARI M.H., SEDAGHAT B., 2015. *Production of zinc powder from Co-Zn plant residue using selective alkaline leaching following by electrowinning*, Phys. Prob. Min. Proc. 51(2), 411-425.

HAGHSHENAS D.F., DARVISHI D., SHABESTARI Z.M., ALAMDARI E.K., SADRNEZHAAD S.K., 2007. *Leaching recovery of zinc, cobalt and manganese from zinc purification residue,* IJE Transactions B 20(2), 133-140.

JAFARI H., ABDOLLAHI H., GARABAGHI M., BALESINI A.A., 2018. *Solvent extraction of zinc from synthetic Zn-Cd-Mn chloride solution: optimization and thermodynamic studies*, Sep. Pur. Tech. 197, 210-219.

JIN Y., MA Y., WENG Y., JIA X., LI J., 2014, *Solvent extraction of Fe^{3+} from the hydrochloric acid route phosphoric acid by D2EHPA in kerosene*, J. Industrial Eng. Chem. 20(5), 3446-3452.

LIN H.K., 1993. *Extraction of zinc chloride with dibutyl butylphosphonate*, Metal. Mate. Trans. B 24(1), No. 1, 11-15.

MELLAH A., BENACHOUR D., 2007. *the solvent extraction of zinc, cadmium and chromium from phosphoric acid solutions by tri-n butyl phosphate in kerosene diluent*, Sep. Pur. Tech. 56(2), 220-224.

MORADKHANI D., ESKANDARI S, SEDAGHAT B., RAJAIE., 2013. *A study on heavy metals mobility from zinc plant residues in Iran*, Phys. Prob. Min. Proc. 49(2), 567- 574.

MORADKHANI D., SEDAGHAT B., KHODAKARAMI M., ATAEI I., 2014. *Recovery of valuable metals from zinc plant residue through separation between manganese and cobalt with N- N- reagent*, Phys. Prob. Min. Proc. 50(2), 735- 746.

RU Z.G., PAN C.X., LIU G.H., WANG X.T., DOU G.Y., ZHU K.S., 2015. *Leaching and recovery of zinc from leaching residue of zinc calcine based on membrane filter press,* Trans. Nonfer. Metal Soc. China 25(2), 622-627.

RUŞEN A., SUNKAR A.S., TOPKAYA Y.A., 2008. *Zinc and lead extraction from Ćinkur leach residues by using hydrometallurgical method*, Hydrometallurgy 93, 40-45.

SCHLUMBERGER S, SCHUSTER M, RINGMANN S, KORALEWSKA R., 2007. *Recovery of high purity zinc from filter ash produced during the thermal treatment of waste and inerting of residual materials*, Wast. Manage. Res. 25, 547-555.

STASIAK M., REGEL R.M., BOROWIAK R.A., 2016. *Zinc extraction from chloride solutions with mixtures of solvating and chelating reagents*, Hydrometallurgy 162, 57-62.

TANG J., STEENARI B.M., 2015. *Solvent extraction separation of copper and zinc from MSWI fly ash leachates*, Wast. Manag. 44(1), 147-154.

TANG J., SU M., ZHANG H., XIAO T., LIU Y., LIU Y., WEI L., EKBERG C., STEENARI B., 2018. *Assessment of copper and zinc recovery from MSWI fly ash in Guangzhou based on a hydrometallurgical process*, Wast. Manage. 76(1), 225-230.

TURAN M.D., ALTUNDOĞAN H.S., TŰMEN F., 2004. *Recovery of zinc and lead from zinc plant residue*, Hydrometallurgy 75, 169-176.

VAHIDI E., RASHCHI F., MORADKHANI D., 2009. *Recovery of zinc from industrial zinc leach residue by solvent extraction using D2EHPA*, Mineral. Eng. 22(2), 204-206.

WANG L., MU W., SHEN H., LIU S., ZHAI Y., 2015. *Leaching of lead from zinc leach residue in acidic calcium chloride aqueous solution*, Int. J. Min. Metal. Mat. 22, 460-466.

WIESZCZYCKA K., 2013. *Recovery of Zn (II) from multielemental acidic chloride solution with hydrophobic 3-pyridineketoxime*, Sep. Pur. Tech. 114, 17-23.