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Pb-Zn recovery from a malic leach solution of a carbonate type ore flotation tailing by precipitation and solvent extraction

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ABSTRACT

The recovery of zinc and lead from a malic leach solution of a carbonate type ore flotation tailing by precipitation with sulfuric acid followed by solvent extraction using di(2-ethylhexyl)phosphoric acid (D2EHPA) as extractant was investigated. The separation of lead via precipitation was essentially complete from the malic acid leach solution by adding sulphuric acid to reach a pH of 0.25 at 25 °C. The precipitate product was identified by XRD as anglesite ($PbSO_4$). The pregnant leach solution after lead precipitation was then subjected to solvent extraction using D2EHPA. The optimum solvent extraction conditions were determined as 10% D2EHPA concentration, 25 °C temperature, 10 min contact time and phase ratio of unity. Under these conditions, 99.3% of zinc was extracted into the organic phase at a pH of 4.2 in a single contact alongside a substantial amount of Ca (76.6%), and minor amounts of Fe (19.2%) and Mg (18%). Complete stripping of zinc and calcium from the loaded organic solution along with 47.8% of Mg was achieved at a pH 0.5 under room temperature. No iron stripping was observed from the loaded organic. The zinc content in the loaded strip solution could be enriched and then sent to the electrowinning (EW) stage. It is noted that the calcium and magnesium impurities in the loaded strip solution had no adverse effect on the zinc EW process. Based on the experimental results, a flowsheet was proposed for the recovery of Pb and Zn from the malic acid leach solution. With the proposed precipitation and solvent extraction process, two different material streams are produced.

1. Introduction

The recycling of mine wastes and tailings to recover valuable metals has gained increasing interest over the years. One of the central subject in this area is the recovery of lead and zinc from flotation tailings [1]. This is because the utilization of lead and zinc flotation tailings to recover the two metals simultaneously reduces the existing toxic and hazardous mine wastes volume, particularly due to the presence of lead and arsenic, while produces values to meet Pb and Zn demands without further degrading the land. This is also driven by the fact that high-grade ores of Pb and Zn are continuously dwindling by the day [2].

Zn has a wide range of applications in the metallurgical, chemical and textile industries making it the fourth most used metal in the world after iron, aluminium and copper [3–5]. The demand for zinc is expected to continue to increase in the foreseeable future, but the future supply of Zn from natural resources is expected to decrease with time due to the depletion of reserves [6]. Therefore, attempts to recovery Zn from secondary resources have been studied extensively in recent years [7–8].

Hydrometallurgical methods appear to be more economical and environmentally-friendly than pyrometallurgical methods to recover Zn from secondary resources [9]. Leaching of the Zn-bearing materials can be done by using either inorganic or organic acids. Given the worldwide strive for greener technologies, there is increasing attention to the use of organic acids as lixiviant as they are biodegradable. Halli et al., 2017 reported that the performance of citric acid to dissolve Zn from an electric-arc furnace dust sample was comparable to those of sulphuric, nitric and hydrochloric acid [10]. They also tested other organic acids namely acetic, formic and oxalic acid but these acids performed much poorer than these three inorganic acids. Later, Kaya et al., 2020, who studied leaching of non-sulphide Pb-Zn flotation tailings in various inorganic and organic acids, showed that malic acid can yield about 90% Zn dissolution, which is close to Zn dissolution with citric acid [7].

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Depending on the impurities present, purification of a pregnant leach solution (PLS) is usually comprised of a precipitation and solvent extraction step. Pb is commonly present in a leach solution of Zn-bearing materials when sulphuric acid was not used as lixiviant. Halli et al., 2020 reported that Pb can be completely and selectively removed from a citric acid leach solution via precipitation by adding sulphuric acid at room temperature. Solvent extraction is then usually used to separate Zn from the other impurities [11]. The most common extractants that are used for this purpose are the organophosphorus extractants such as di(2-ethylhexyl)phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272). Among these extractants, D2EHPA is the most popular because it is the most cost-effective option among the three as evident by its use in most zinc refineries in the world [11–12]. The extraction mechanism and nature of the metal complexes formed using D2EHPA are dependent on the following factors: nature of the organic solvent, acidity of the aqueous phase concentration of the metal cations, and the type of the extracted cations [13].

There exist non-linear equilibria between ions found in the extract phase and the raffinate phase, as far as the chemistry of the extraction–stripping processes for metallic systems is concerned. Taking the case of zinc extraction with D2EHPA dissolved in an aliphatic diluent, the equilibrium can be represented by:

$$Zn^{2+}(aq) + 1.5(RH)_2(org) = ZnR.2RH(org) + 2H^{+}(aq) \quad \text{at the liquid} - \text{liquid interface} \tag{1}$$

$$2ZnR.2RH(org) = 2ZnR_2(org) + (RH)_2(org) \quad \text{in the extract phase} \tag{2}$$

where RH represents the extractant, the (aq) and (org) subscripts represent aqueous and organic constituents, respectively [14]. Eqs. (1) and (2) show that Zn extraction with D2EHPA entails heterogeneous and homogeneous complex reactions that occur in both liquids simultaneously, leading to two metal-complex species in the extract phase. At low loading levels of Zn in the extract phase, the heterogeneous reaction is higher. However, at intermediate and high loading levels, there is a co-existence between the complexes ZnR.2RH and ZnR_2, as indicated by the statistical analysis of Zn-D2EHPA equilibrium data by Mansur et al., 2002 [14].

The use of D2EHPA to extract Zn from inorganic leach solutions have been studied extensively by numerous investigators [15–26]. Most of these studies reported that more than 95% of Zn can be extracted with D2EHPA at pH between 1 and 3, a temperature between 25 and 40 °C and a contact time of less than 10 min. Sometimes tributyl phosphate (TBP) is added into the organic phase as a modifier to improve Zn extraction [16,19,27–28].

In contrast, little attention has been given to the solvent extraction of Zn from organic leach solutions using D2EHPA. Halli et al., 2020 reported the extractions of Zn, Fe and Mn from citric acid leach solutions with D2EHPA [11]. Unlike those from inorganic leach solutions, they reported that high Zn extractions can only be achieved at pHs higher than 4 with 5 being the optimum. These suggest that the extraction behaviours of metal ions in organic leach solutions may be different from those in inorganic solutions.

In this study, we focus on the purification of a PLS obtained from leaching of carbonate type Pb-Zn flotation tailing with malic acid. The leach conditions have been optimized in the work of Hussaini et al., 2021 [29]. They reported that at an optimum condition, 90% of Zn can be extracted from a carbonate type Pb-Zn flotation tailing with malic acid, which was very close to the 90.6% extraction that was achieved with citric acid at its optimum condition. The use of malic acid also showed a higher leaching selectivity against Fe compared to using citric acid. The objective of this present study was to investigate the recovery of Pb and Zn from the malic acid leach solution of a carbonate type ore flotation tailing via selective precipitation with sulfuric as precipitation agent and solvent extraction with D2EHPA as extractant.

Table 1
The chemical components of pregnant leach solution after malic acid leaching (pH: 2.20).

Elements	Zn	Pb	Fe	As	Ca	Mg
Concentration (mg/L)	5050	387	1200	470	570	228

2. Materials and method

2.1. Materials

The flotation tailing used for the leaching experiments were supplied by Orex Mining Co. plant in Kayseri, Turkey. The details about the flotation tailing and sulfuric, citric, oxalic, malic acids leaching, were published in the previous works [7,30]. Table 1 shows the concentration of the major elements in the pregnant leach used in the present study, which was obtained after leaching of the flotation tailing in a 1 mol/L technical grade malic acid (Detsan, Turkey) at 80 °C, a solid-to-liquid ratio of 1/10 for 60 min. Industrial grade di-(2-ethylhexyl) phosphoric acid (D2EHPA) and analytical grade Hexane (Sigma-Aldrich, USA) were used as the extractant and diluent, respectively, for the solvent extraction experiments. Analytical grade sulfuric acid (Merck, Belgium) and sodium hydroxide powder (Merck, Belgium) were used for pH adjustment. Deionized water was used for diluting the inorganic reagents when needed.

2.2. Method

Prior to the solvent extraction experiments, Pb precipitation tests were carried out using 5 mol/L sulfuric acid solutions at a mixing speed of 200 rpm as Pb was one of the main impurities in the PLS. The pH of the PLS was measured by a pH meter (Hach HQ40d) equipped with IntelliCAL PHC 28101 probe. The precipitation experiments were conducted at 25 °C. After the precipitation experiments, the solutions were measured and filtered with Whatman 1 filter paper and then analyzed by atomic absorption spectroscopy (AAS, PerkinElmer or ThermoScientific) at Nanotechnology Engineering Department of Abdullah Gul University (AGU), Mining Engineering Department of Eskisehir Osmangazi University to calculate precipitation percentages of Pb along with other metal ions. The mineralogical composition of the precipitates was identified using an X-ray diffraction (XRD) instrument (Bruker Discover) at AGU's Central Research Laboratory, which was calibrated with a silicon standard for alignment of the $2\theta = 5$–85° using radiation generated at 40 mA and 40 kV. Diffrac Suite EVA software equipped with the current ICDD PDF-2/Minerals database was used for the determination of mineral phases. The precipitation percentage of the metal ions as a function of pH was calculated based on the difference of the metal concentration in the solution before and after the precipitation experiment according to the following equation:

$$Precipitation(\%) = \frac{C_1 \times V_1 - C_2 \times V_2}{C_1 \times V_1} \times 100\% \tag{3}$$

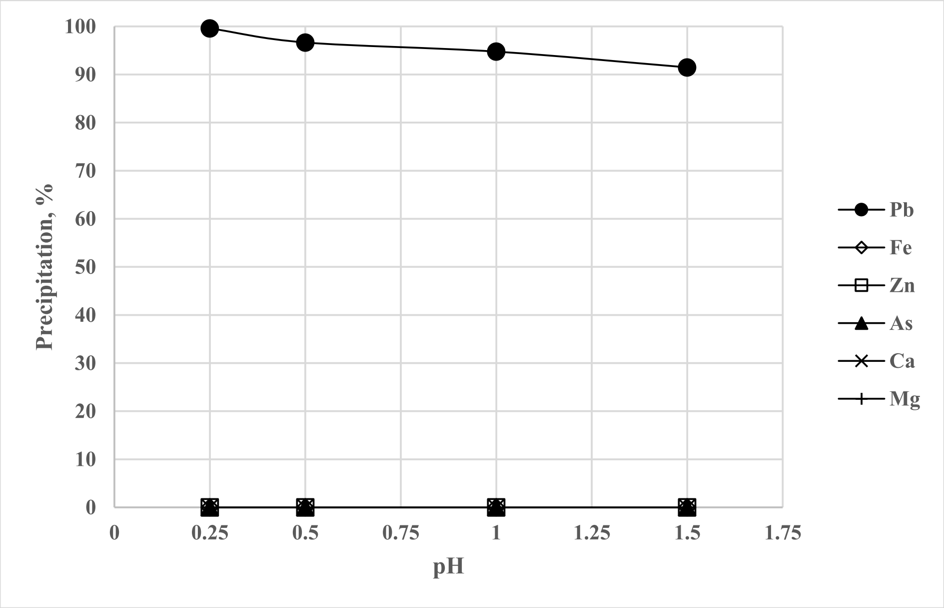

Fig. 1. Precipitation of metal ions using 5 M H_2SO_4 as a function of pH from the malic leach solution (Conditions: T: 25 °C, t:30 min.).

where C_1 is the initial metal concentration in the PLS (mg/L), C_2 the final metal concentration in the PLS (mg/L), V_1 the initial volume of the PLS (L) and V_2 the final volume of the PLS (L).

The solvent extraction experiments were carried out in a 150-mL glass reactor at a stirring speed of 400 rpm using a METOPS mechanical stirrer equipped with a three-blade stainless-steel impeller (35-mm diameter). A heating mantle (METOPS) was used for temperature control. The aqueous solution was contacted with an equal volume of the organic solution (A/O = 25 mL/25 mL), unless otherwise stated. The aqueous solution pH was controlled by small additions of NaOH (5 mol/L). After finishing the SX experiment, the mixture was allowed to stand for 10 min and then transferred into a separation funnel. The aqueous and organic phases were separated by Whatman 1PS phase separation filter paper to prevent any phase entrainment. The collected aqueous phase was analysed by inductively coupled plasma mass spectrometry (ICP-MS) at ALS Minerals in Izmir, Turkey. The concentration of metal ions in the organic phase was calculated by mass balance. The extraction percentage (E) of metal ions was calculated according to the following equation:

$$E = \frac{[M]_{org}}{[M]_{aq}} \times 100 \tag{4}$$

where [M]org and [M]aq demonstrate the concentration of metal ions in the organic and aqueous phase (mg L^{-1}), respectively.

The distribution coefficient (D) was calculated using the following equations:

$$D = \frac{C_{org}}{C_{aq}} \tag{5}$$

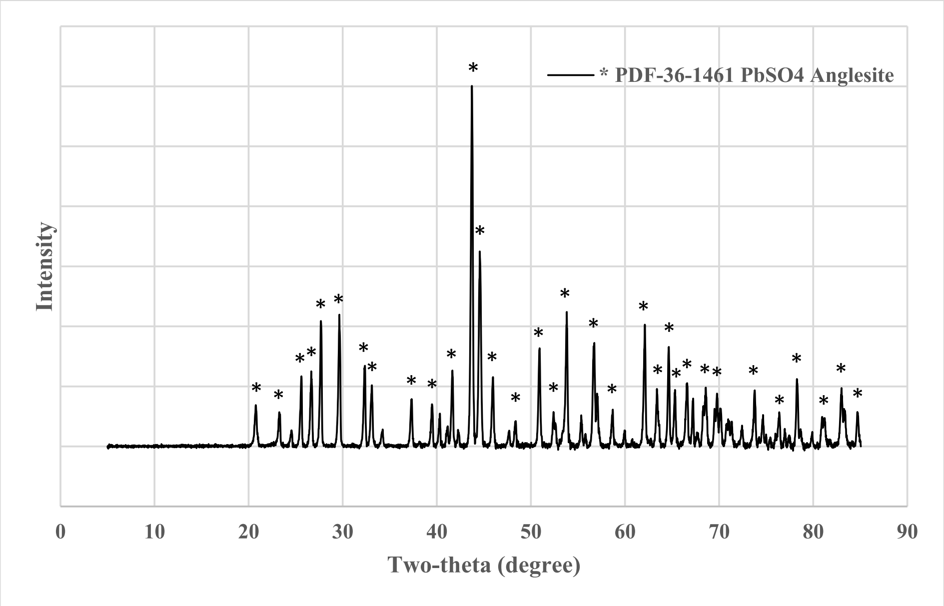

Fig. 2. XRD pattern of the precipitate at pH 0.25.

Table 2

The chemical component of pregnant leach solution after precipitation stage (pH: 0.25).

Elements	Zn	Fe	As	Ca	Mg
Concentration (mg/L)	5020	1095	441	512	212

where Corg and Caq are the equilibrium concentrations of metal ions in organic and aqueous phases, respectively. The separation factor (β) was calculated as:

$$\beta_{M2/M1} = \frac{D_2}{D_1} \tag{6}$$

where D1 and D2 are the distribution coefficients of elements 1 and 2, respectively, in a specific solvent system.

The McCabe-Thiele diagrams of Zn extraction from the malic acid solution using D2EHPA and Zn stripping from the loaded organic solution were constructed by changing the aqueous to organic ratio while keeping the other operating parameters constant.

3. Results and discussion

3.1. Separation of lead from zinc via selective precipitation

Fig. 1 shows the precipitation of metal ions as a function of pH. The addition of sulfuric acid resulted in the precipitation of Pb, while the other metal ions were completely stable in the aqueous phase. The highest Pb precipitation within the tested experimental range, which was 99.6%, was achieved at pH 0.25. This pH was then determined to be optimal.

The separation of Pb from Zn via selective precipitation by adding sulphuric acid was possible due to the very low solubility of $PbSO_4$ in aqueous solutions. The XRD analysis of the precipitate shown in Fig. 2 confirmed that $PbSO_4$ (anglesite) was the reaction product. The overall precipitation reaction can, therefore, be written as:

$$Pb^{2+}(aq) + H_2SO_4(aq) = PbSO_4(s) + 2H^+(aq) \tag{7}$$

3.2. Separation of zinc from impurities by solvent extraction

The PLS was subjected to an SX process after the lead precipitation process to separate Zn from the major impurities, namely Fe, As, Ca and Mg. The extractant D2EHPA was investigated for this purpose. The chemical composition of the PLS after precipitation was relatively changed except for Pb, which was almost completely removed from the solution (Table 2).

Fig. 3 shows that the extraction of the metal ions with D2EHPA as a function of pH at different extractant concentrations ranging from 5% to 15%. The ranges of the tested pH are different in the three graphs as extractions at the higher pH than those required to achieve an essentially quantitative Zn extraction were not pursued. The extraction of Zn generally increases with pH using the three extractant concentrations. This is a common characteristic of D2EHPA as an acidic extractant, which have been shown by previous investigators who also used D2EHPA to extract Zn from various acidic aqueous solutions [1,12,20,31–32]. Zn is extracted in preference to the other impurities in all the tested pH ranges. The extraction of Ca followed a similar trend to that of Zn. Fe, on the other hand, showed a different trend. The extraction of Fe initially increased when the pH was increased from 0.3 to 1.3 at a D2EHPA concentrations of 5%, but then decreased when the pH increased further up to 5.4. The extractions of Mg and As were relatively low in all the tested ranges.

The observed behaviour of Fe was probably due to its interaction with the malate ions, which competed with the reaction between Fe and

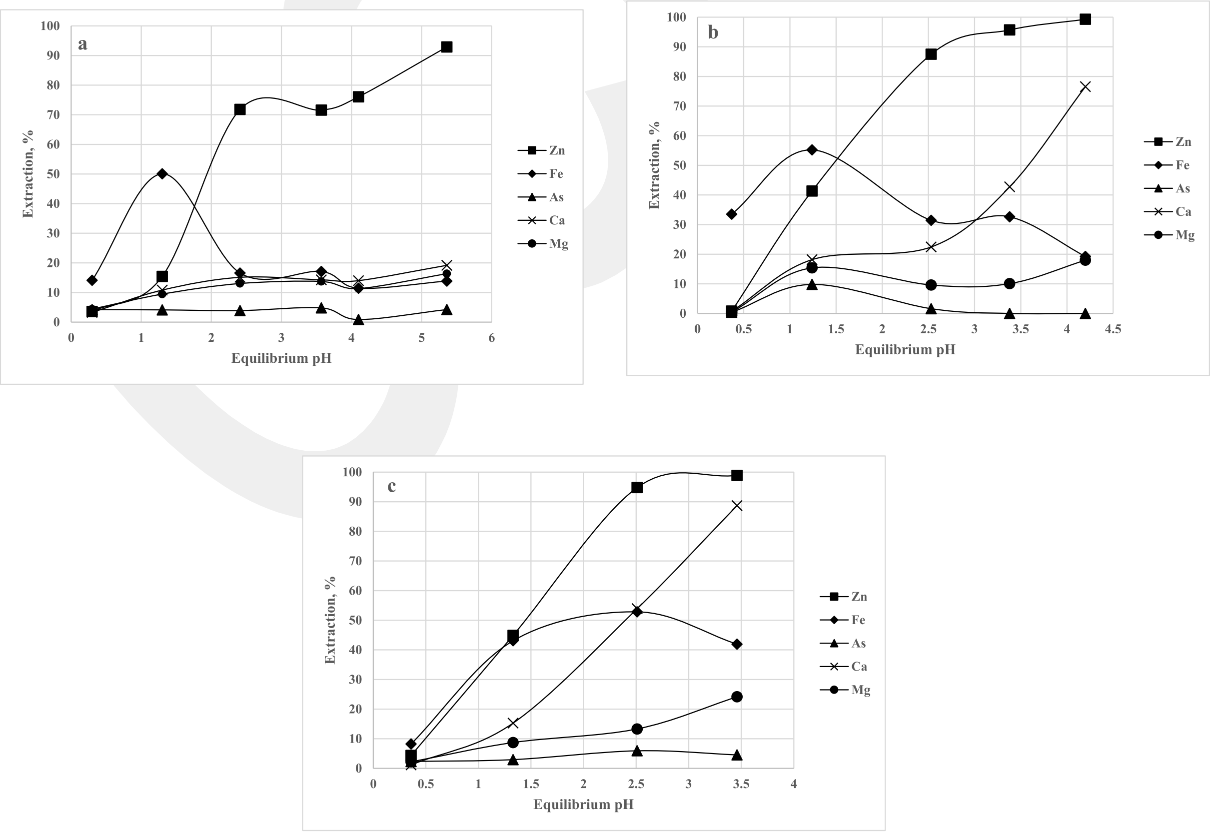

Fig. 3. Extraction of metal ions as a function of pH (a-5% D2EHPA, b-10% D2EHPA, c-15% D2EHPA, Conditions: T: 25 °C, t:10 min.).

Table 3

Separation factors of Zn with respect to Fe using D2EHPA in malic acid solution.

5% D2EHPA		10% D2EHPA		15% D2EHPA	
pH	βZn/Fe	pH	βZn/Fe	pH	βZn/Fe
2.41	12.8	2.53	15.3	1.33	1.1
3.57	12.2	3.38	46	2.51	16.3
4.1	24.5	4.2	597	3.46	124
5.36	81				

the extractant. Hamada et al., 2005 reported that in the presence of malic acid, Fe did not precipitate at pHs ranging from 2.5 to 11.5 [33]. They proposed that the malate ions acted as chelating ligands to keep both the divalent and trivalent ions of Fe in the solution. The chelate effect forces the hydroxyl group to participate in the metal chelation, forming the stable fused five and six-membered chelating rings. Their finding is supported by the experimental results of Vukosav et al., 2010 that the soluble species of Fe in malic acid are stable in the aqueous phase for at least a year at a pH range of 1.5 to 11.5 [34].

Increases in the extractant concentration increased the extraction of Ca and Fe into the aqueous phase along with Zn at the same pH. This suggests that the crowding effect may also be responsible for the decreases in Fe extraction at pH higher than 2.5 as Ca and Mg were increasingly more preferred to be extracted. While the extraction of Ca became substantial at the higher extractant concentrations, increases in Fe extraction were relatively low compared to those of Zn leading to higher separation factor (β) between Zn and Fe (Table 3). The highest separation factor ($\beta_{Zn/Fe} = 597$) was obtained at pH 4.2 using D2EHPA concentration of 10%. Notably, Ca has no deleterious effect on zinc electrowinning at low concentrations [35] and As was not extracted at

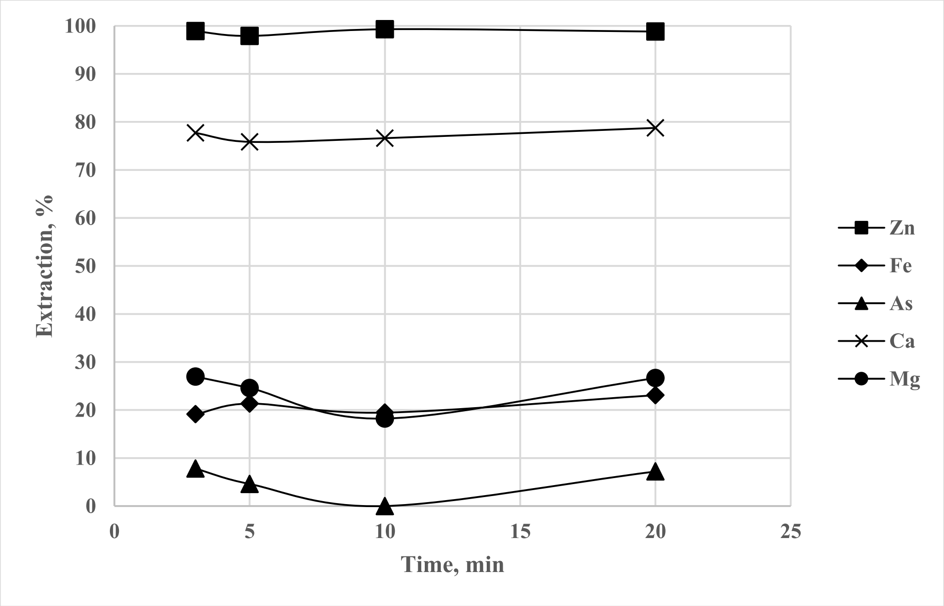

Fig. 4. Extraction of metal ions as a function of time (Conditions: 10% D2EHPA, pH: 4.2, T: 25 °C).

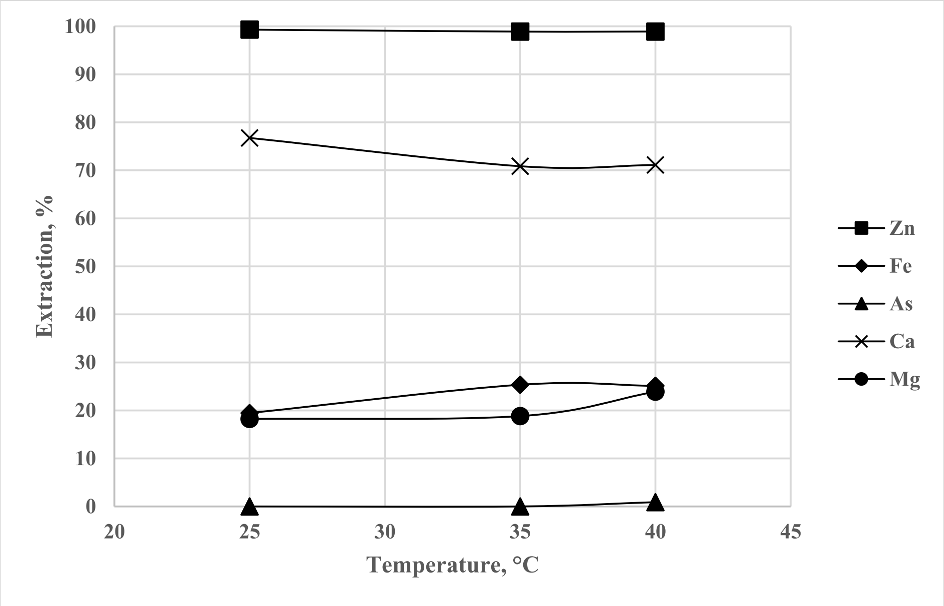

Fig. 5. Extraction of metal ions as a function of temperature (Conditions: 10% D2EHPA, pH: 4.2, t:10 min.).

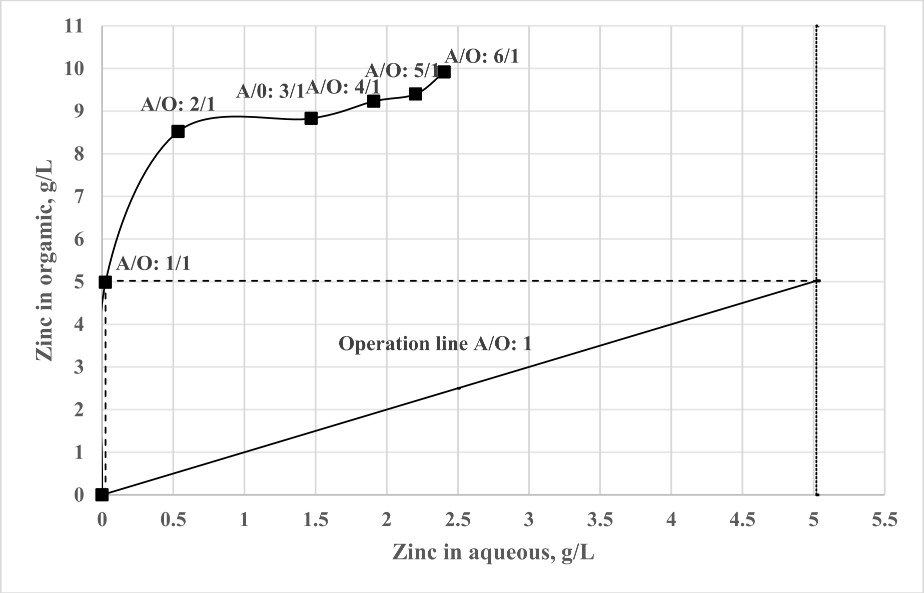

Fig. 6. McCabe-Thiele diagram for extraction of Zn using D2EHPA in malic acid solution (Conditions: 10% D2EHPA, T: 25 °C, t: 10 min., pH: 4.2).

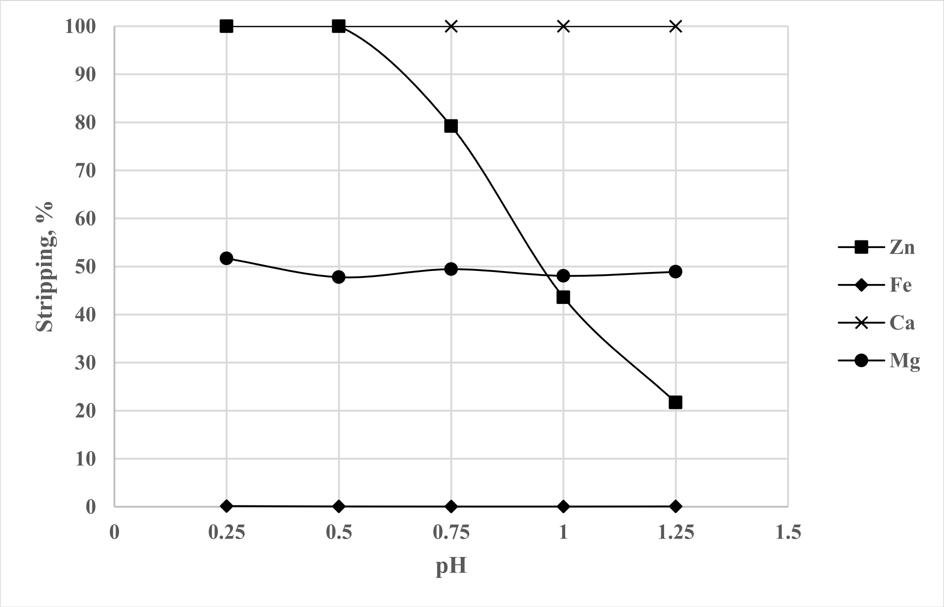

Fig. 7. Stripping of the loaded organic solution at different pHs using H_2SO_4(Conditions: T: 25 °C, t: 10 min, pH: 0.5).

this extraction condition. Therefore, the use of an extractant concentration of 10% and a pH of 4.2, wherein 99.3% of Zn was extracted along with 76.6% of Ca, 19.2% of Fe and 18% of Mg in a single contact, was determined to be optimum for separating Zn from the impurities.

3.3. *Effect of contact time and temperature on the solvent extraction process*

Fig. 4 shows the extraction of metal ions as a function of time at a pH of 4.2 and a temperature of 25 °C using 10% D2EHPA. The extractions of the metals ions after the first 3 min and 20 min of contact time were essentially the same showing that the bulk of the extraction reactions occurred quickly in less than 3 min. The staggered extraction percentages of the metal ions, particularly those of As and Mg, however, suggest that equilibrium has still not been reached within 20 min of contact time. The unsteady extractions of As and Mg appeared to be beneficial as fewer impurities were loaded into the organic phase along with Zn.

Fig. 5 shows that the extractions of As were consistently below 1% even at different operating temperatures ranging from 25 to 40 °C when the contact time was set to 10 min. This confirms the beneficial effect of the use of 10 min contact time to minimize impurities extraction. Mg and Fe extractions increased when the temperature increased to 40 °C. Differently, the extraction of Ca decreased with increasing temperature indicating that the extraction of Ca with D2EHPA from the malic acid solution was exothermically driven. The extraction of Zn, however, remained relatively constant throughout the tested ranges. Since there was no apparent benefit from increasing the temperature, operating at 25 °C using 10 min of contact time was determined to be optimum.

3.4. *McCabe-Thiele diagrams*

The McCabe-Thiele analysis, shown in Fig. 6, suggests that Zn was

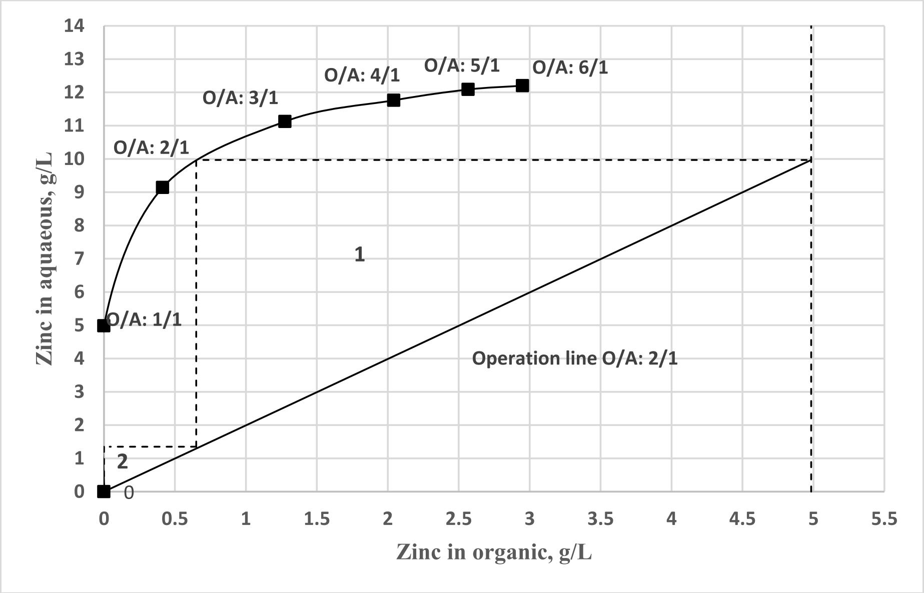

Fig. 8. McCabe-Thiele diagram for stripping of Zn (Conditions: T: 25 °C, t: 10 min, pH: 0.5).

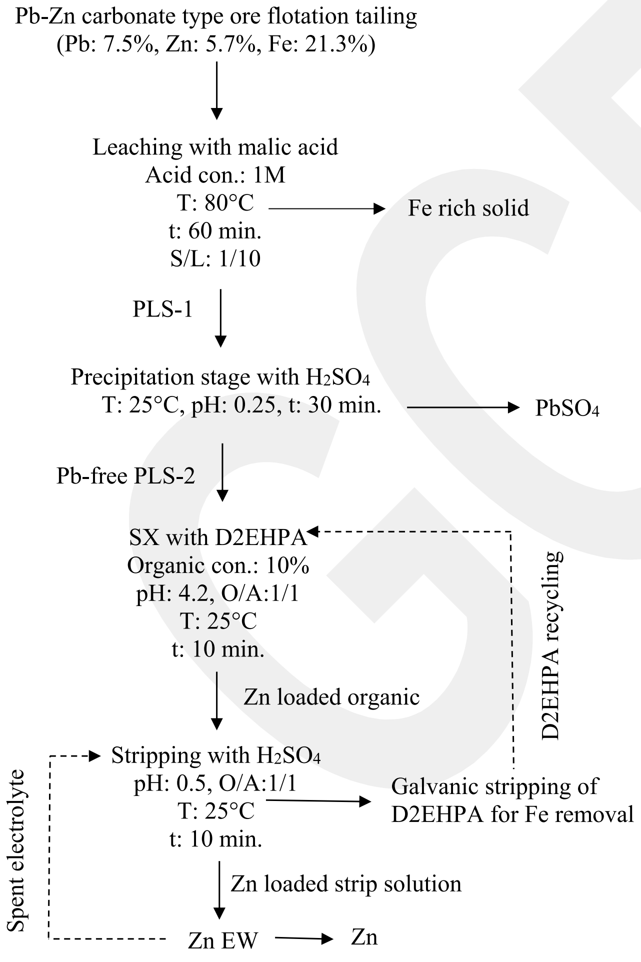

Fig. 9. Proposed flowsheet for the Pb-Zn recovery from a malic leach solution.

almost completely loaded into the organic phase using one theoretical counter-current stage at an operating line unity. An organic phase loaded with 4984 mg/L of Zn was obtained from a feed solution consisting of 5020 mg/L of Zn. The organic phase loaded with 4984 mg/L of Zn, 392 mg/L of Ca, 210 mg/L of Fe and 38 mg/L of Mg by a single-stage extraction at pH 4.2, 25 °C, and O/A ratio of unity was then subjected to stripping tests. The stripping of Zn from the loaded organic was carried out in a pH range of 0.25 to 1.25 using sulfuric acid solutions at room temperature and a stripping time of 10 min.

Fig. 7 shows the stripping percentages of the metal ions from the loaded organic solution as a function of pH. As can be seen, Zn was completely stripped from the loaded organic solution at pHs ranging from 0.25 to 0.5. The stripping percentages of the other metal ions were relatively constant at tested pH ranges with Ca at 100%, Fe at 0% and Mg at about 50%. Fe is known to form a strong complex with D2EHPA that is difficult to be stripped with an inorganic acid. Yu and Chen, 1989 proposed that this is because Fe forms octahedral complexes with D2EHPA and the hydrophobic end of the complex will be directed toward the organic phase, whereas the hydrogen ions and the acid anions of inorganic acid are highly hydrated [36]. This results in only low concentrations of the extracted complexes and the inorganic acids exist at the interface to allow stripping of Fe from the organic phase. Hu et al., 2014 reported that the stripping of Fe was very slow and even with 4.0 mol/L of sulphuric acid only less than 40% of Fe was stripped from Fe-loaded D2EHPA solution [37]. They, however, showed that complete stripping of Fe from the organic phase to recycling the D2EHPA solution can be achieved via reductive stripping using 7% oxalic acid solution. Similarly, other methods involving reduction of Fe from its trivalent to divalent states have been shown to able to completely strip Fe from loaded D2EHPA solution such as the so-called galvanic stripping by, for example, adding Zn metal as reductant when contacting the loaded organic solution with mild sulphuric acid solution [38,39]. This aspect was outside the scope of this study.

A McCabe-Thiele diagram for Zn stripping was constructed by varying the phase ratio between the organic and aqueous phase (O/A) from 1:1 to 6:1 (Fig. 8). The diagram suggests that at an operating line of 2:1 (O/A ratio), two counter-current contacting stages were needed to completely strip Zn from organic solution at a pH of 0.5, which increased the Zn concentration up to 9968 mg/L in the loaded strip solution.

3.5. *Process development*

Fig. 9 presents a proposed process to recover lead and zinc from a malic leach solution of a non-sulphide flotation tailing by precipitation and solvent extraction. The flotation tailing was firstly leached in 1 M malic acid at 80 °C, solid to liquid ratio of 1/10 for 60 min. After leaching, the slurry was filtered and the filtered pregnant leach solution was sent to a precipitation step by adding sulphuric acid to obtain a Pb-free solution. In the present study, 99.6% of Pb precipitation was achieved at a pH of 0.25. The Pb-free aqueous solution was subjected to a solvent extraction and stripping process. Zn extraction of as high as 99.3% along with 76.6% of Ca, 19.2% of Fe and 18% of Mg was achieved in a single contact using 10% D2EHPA at a pH of 4.2, a temperature of 25% and an O/A of 1/1. The loaded organic was sent to the stripping stage and 100% of Zn was stripped out of the organic phase with a mild sulphuric acid solution at a pH of 0.5 along with 100% of Ca and 47.8% of Mg. It is reported that calcium has no deleterious effect on zinc electrowinning at low concentration [35] while magnesium presents no cathode problems, but $MgSO_4$ can adversely affect filtering, settling and electrolyte conductivity [40]. Fe remained in the loaded organic phase and its stripping require a reductive condition. For example, the galvanic stripping technique can be used to regenerate and recycle D2EHPA back to the solvent extraction circuit.

4. Conclusions

The recovery of Pb and Zn from a malic leach solution of a non-sulphide flotation tailing by precipitation and solvent extraction was conceived and experimentally explored. The Pb precipitation was achieved at pH 0.25 from the malic acid leach solution. The precipitate was determined to be $PbSO_4$ (anglesite). The sulfate precipitation was determined to be an efficient way for Pb removal with relatively minimal Zn losses. The filtrate was then subjected to solvent extraction stage using D2EHPA. 99.3% Zn was taken into the organic phase at pH 4.2 along with a substantial amount of Ca (76.6%) and a minor amount of Fe (19.2%), Mg (18%) using 10% D2EHPA, A/O ratio of unity at 25 °C for 10 min. The highest separation factor (β) between Zn and Fe was found to be 597. McCabe-Thiele results revealed that at optimized solvent extraction conditions, 4984 mg/L of Zn was loaded in organic solution in one counter-current stage at an operating line (O/A) of 1:1. 100% of Zn and Ca was stripped out from the loaded organic phase along with 47.8% of Mg at pH 0.5, O/A ratio of 1:1 for 10 min. Zn-rich solution (9968 mg/L) was produced in two counter-current stages at an operating line (O/A) of 2:1. The iron stripping has not been observed from the loaded organic, which is overcome by galvanic stripping. The calcium and magnesium-containing loaded strip solution had no reverse effect on the zinc EW process. Based on the experimental results obtained from the bench-scale study, a new hydrometallurgical process flowsheet for the recovery of Pb and Zn from malic acid leach solution was proposed. The flowsheet shows that separate product streams of Pb and Zn could be produced after malic acid leaching from Pb-Zn containing tailings and possibly from Pb-Zn ores.

CRediT authorship contribution statement

Shokrullah Hussaini: Investigation, Writing - original draft, Visualization, Data curation. **Angela Manka Tita:** Investigation, Writing - original draft, Visualization, Data curation. **Sait Kursunoglu:** Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing, Visualization, Supervision. **Soner Top:** Investigation, Writing - review & editing, Visualization. **Zela Tanlega Ichlas:** Investigation, Writing - original draft, Writing - review & editing, Visualization. **Umut Kar:** Investigation, Visualization. **Muammer Kaya:** Conceptualization, Methodology, Investigation, Writing - review & editing, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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