



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Halli, Petteri; Agarwal, Vivek; Partinen, Jere; Lundström, Mari

## Recovery of Pb and Zn from a citrate leach liquor of a roasted EAF dust using precipitation and solvent extraction

Published in: Separation and Purification Technology

DOI: 10.1016/j.seppur.2019.116264

Published: 01/04/2020

Document Version Publisher's PDF, also known as Version of record

Published under the following license: CC BY

Please cite the original version:

Halli, P., Agarwal, V., Partinen, J., & Lundström, M. (2020). Recovery of Pb and Zn from a citrate leach liquor of a roasted EAF dust using precipitation and solvent extraction. *Separation and Purification Technology*, 236, Article 116264. https://doi.org/10.1016/j.seppur.2019.116264

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.



Contents lists available at ScienceDirect

## Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

# Recovery of Pb and Zn from a citrate leach liquor of a roasted EAF dust using precipitation and solvent extraction



Separation Purificatio

#### Petteri Halli, Vivek Agarwal, Jere Partinen, Mari Lundström\*

Aalto University, School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, The Research Group of Hydrometallurgy and Corrosion, Otakaari 3 J, P.O. Box 12200, FI-00076 Aalto, Finland

ARTICLE INFO	A B S T R A C T				
<i>Keywords:</i> Circular economy Sustainability Zn recovery D2EHPA Cyanex 572	Electric arc furnace (EAF) dust is globally one of the biggest metal-containing waste fractions, with a compo- sition that challenges the recycling of dust back to the steel process due to the high Zn and Pb content, which also prevents it from being landfilled. The current study presents a process flowsheet with zinc and lead removal from EAF dust via citric acid leaching, lead removal by precipitation, and further solvent extraction (SX) of zinc for recovery. The process produces fractions that can be directly routed back to a steel plant (leach residue), a zinc electrowinning process (pregnant leach solution, PLS), and a lead smelter (lead sulfate, PbSO <sub>4</sub> precipitate). Moreover, zinc separation by solvent extraction from citric acid leach solution originating from EAF was per- formed successfully with minimal impurity content in the final electrolyte, using di(2-ethylhexyl)phosphoric acid (D2EHPA). The total lead removal from PLS was achieved with an addition of only 0.012 M sulfate ion (from sulfuric acid) at room temperature. The optimization of zinc separation via SX was performed at a tem- perature range of 25–55 °C varying the D2EHPA concentration (10–25 vol-%) with different O/A ratios. With an optimized EAF SX process ( $pH = 5$ , $t = 15$ min, $T = 25$ °C, $C_{D2EHPA} = 20$ vol-%, $O/A = 1:1$ ) and stripping process ( $t = 15$ min, $T = 25$ °C, $C_{H2SO4} = 1$ M, $O/A = 3:1$ ), the zinc content in the electrolyte could be enriched up to 50 g/L, and the amount of impurities in the solution decreased down to a level where they have no adverse effect on the zinc electrowinning process and final zinc recovery. Moreover, the iron-rich leach residue was also shown to be chemically suitable as a raw material for the EAF process. With the proposed roasting-leaching-pre- cipitation-SX-EW unit operation. FAF dust can be converted into three different secondary raw material streams.				

### suitable for integration into state-of-the-art processes.

#### 1. Introduction

The electric arc furnace (EAF) is predominantly used in steel production. When smelting scrap steel in an EAF, three output streams are produced: iron matte, slag, and dust. The global production of EAF dust in steel production is approximately 12 Mt/year [1,2] and therefore, recycling it could bring new secondary raw material streams into steel, zinc, and lead production. Landfilling such material should not be promoted due to the toxic and carcinogenic nature of the dust. In addition, both the EC (European Commission) and the EU (European Union) strongly regulate the amount of lead fed into EAF processes, as well as its content in the final product [3,4]. However, it was demonstrated earlier [5,6] that citric acid as a leaching medium can be used as a lixiviant to treat EAF dust. Furthermore, citric acid is known to favor zinc solubility over other heavy metals [7]. The earlier research [5,6] produced a fully recyclable iron residue, but also a Zn-rich PLS (pregnant leach solution), which requires further purification in order to produce secondary zinc and lead.

In primary production, zinc is recovered mainly via electrowinning (EW) [8–11], where the feed electrolyte originates from the purified leach solution of zinc-containing minerals [12–14]. The process is rather energy-intensive (3.0–3.3 kWh/kg) due to the high cell voltage [8,13,15,16] and requires a great deal of chemicals with high consumption rates  $(0.5–2.2 \text{ M H}_2\text{SO}_4 \text{ /kg})$  [12–14]. Moreover, the zinc EW process requires a rather high (50–70 g/L) zinc content in the electrolyte [11,17–20] when minimizing the content of impurities [21–24]. The impurities in Zn electrolyte are often categorized into groups 1–3: category 1 includes the worst impurities, i.e., Ge, Sb, Te, and Se; category 2 consists of worse impurities including As, Ni, Sn, Co, Ag, and Fe; and category 3 includes bad impurities, i.e., Ga, Bi, Cd, Hg, In, and Pb [25]. These impurities have an adverse effect on Zn EW, for example by increasing the energy consumption of the EW process by decreasing

\* Corresponding author.

E-mail address: mari.lundstrom@aalto.fi (M. Lundström).

https://doi.org/10.1016/j.seppur.2019.116264

Received 17 July 2019; Received in revised form 27 September 2019; Accepted 26 October 2019 Available online 04 November 2019 1383-5866/ © 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license

(http://creativecommons.org/licenses/BY/4.0/).

the hydrogen evolution overpotential or depositing on the cathode together with zinc, which reduces the purity of the final zinc cathode product. Therefore the zinc leach solution needs to be purified to a level where category 1 impurities are below 0.01 ppm and category 2 impurities below 1 ppm [25].

The purification of the leachate can be done via several different stages, e.g., cementation [26,27], precipitation [28-31], or solvent extraction (SX) [17,32-37]. The most commonly used SX reagents for Zn extraction are organophosphorus extractants, i.e., di(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethyl hexyl ester (PC88A) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cvanex 272) [34,38–40]. Of these extractants, D2EHPA has been used extensively to extract Zn along with other elements, e.g., Fe and V [41-43]. Most of the primary zinc processes such as the HydroZinc process of Teck Cominco, Canada [44,45], the ZINCEX process of Técnicas Reunidas, Spain [44], the Skorpion Zinc plant of Anglo American, Namibia [44,46] and MIM Holdings Ltd. (now Glencore) [45,47] use D2EHPA as an extractant for Zn recovery in the SX process. However, in primary Ni/Co processing (e.g., Murrin Murrin, Australia), Cyanex 272 was preferred over D2EHPA for Zn extraction to avoid the risks associated with cross-contamination [48]. Furthermore, D2EHPA is known to extract Zn at lower pH (< 2) values compared to Cyanex 272 under similar experimental conditions [49], and Zn can also be selectively stripped from D2EHPA in the presence of other impurities such as Fe at low acid concentration [45]. Cyanex 572, which is a novel commercial extractant and considered a mixture of phosphonic and phosphinic acids [50,51], has been mainly used in the separation and extraction of rare earth elements (REEs) until the time of writing [51-53]. However, recent studies have shown that Cyanex 572 has the potential to selectively extract Zn in the presence of other impurities (Mn, Fe) from municipal solid waste incineration (MSWI) fly ash [54,55]. Both the organic reagents (D2EHPA and Cyanex 572) used in present work are organophosphorus acidic extractants. Therefore, the possible extraction reaction of divalent metal ions could be cation exchange mechanism. From literature, the extraction mechanism of divalent metal ions (M<sup>2+</sup>) like Zn or Mn, using D2EHPA and Cyanex 572 can be represented using Equation (1), [54-56], where HR represents the organic extractant and MR<sub>2</sub> represents the metal-extractant complex:

$$M^{2+} + 2HR_{(org.)} \leftrightarrow MR_{2(org.)} + 2H^{+}$$
(1)

Globally, the main zinc-containing secondary raw materials are galvanized steel and scrap brass [57,58]. Zinc recycling is predominantly conducted by employing a Waelz kiln reactor [57,59] but other technologies have also been developed to treat such hazardous material, e.g., the rotary hearth furnace (RHF) or in-process separation (IPS) [60]. Another way to recycle zinc is the leaching of scrap galvanized steel in an alkaline medium followed by EW [58]. Furthermore, EAF dust is also a major source for secondary zinc [58] and, in terms of the circular economy, the usage of secondary raw materials is highly recommended. However, as stated above, after the citric acid leaching of EAF dust, a zinc-rich PLS is produced that still contains several impurities such as Fe, Pb, Na, Al, Ca, and Mn. Therefore, the PLS is not suitable for direct zinc EW without further purification and enrichment steps.

Consequently, the current study develops the EAF dust recycling process further. The work continues from the work of Halli et al. [5,6] and focuses on the development of Pb removal and Zn solvent extraction. In this work, D2EHPA and Cyanex 572 are compared in terms of recovering Zn from EAF dust citric acid PLS. Furthermore, the current study addresses the challenges related to solution purification and Zn enrichment for further recovery of zinc, thus completing the process flowsheet for the novel citric acid treatment of EAF.

Table 1Composition of the EAF dust citric acid PLS.

LOD = limit of detection

#### 2. Experimental procedure

#### 2.1. Materials

The roasted EAF dust employed in citric acid leaching was obtained from the Ovako Imatra Oy Ab steel plant in Finland. The details about the raw material and the pre-treatment (roasting), as well as citric acid leaching, were published in the previous work [5,6]. Table 1 presents the solution composition achieved after leaching of roasted EAF dust in 0.8 M citric acid [6], used as the raw material in the current study. As can be seen, the contents of Zn and Na are rather high in comparison with other elements present in the PLS. The Zn originated from the EAF dust and the Na from the roasting step. The iron content presented in Table 1 is the total iron content in the PLS whereas by redox potentiometric titration (with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) [61] it was confirmed that Fe(II) content was only ~14 mg/L. Moreover, halogen species (e.g. Cl<sup>-</sup>, F<sup>-</sup>, etc.) are known to occur at significant amounts in the EAF dust and other similar metallurgical residues as well [62-66]. Furthermore, only Cl<sup>-</sup> was found from the employed raw material, EAF dust in small quantities, ~1.5 wt-%. However, Cl<sup>-</sup> present in the EAF dust, and therefore ending up to the PLS, were not analyzed from the solution because thermodynamically it is likely that majority of it ends up into the gaseous phase during NaOH roasting due to high vapour pressure at low temperatures (< 300 °C) [63,67]. Additionally, no other halogens were detected from the roasted EAF dust [6].

Low odor kerosene (Sigma-Aldrich, USA), 97% D2EHPA (Sigma-Aldrich, USA) and Cyanex 572 (Solvay, the Netherlands) were used in solvent extraction (SX) experiments and 95% sulfuric acid (VWR Chemicals, Belgium) in stripping experiments. Sodium hydroxide powder, 99% NaOH (VWR Chemicals, Belgium) was used together with sulfuric acid for pH modification. All the employed chemicals were of technical grade and the stripping and pH modification solutions were made in Milli-Q (Merck Millipore, USA) deionized water.

#### 2.2. SX experiments

The experiments were carried out in a 100 mL separation funnel, with shaking at 250 revolutions per minute (RPM) using a KS 3000i control incubated shaker (IKA, Germany). In the optimized conditions, both SX and stripping were also performed in a 500 mL separation funnel in order to simulate upscaling. After finishing the experiment, the separation funnels were allowed to settle for 5 min to allow phase disengagement. The collected aqueous phases were analyzed by AAS or ICP-OES. The metal extractions were calculated using Eqs. (2) and (3) [68]:

Extraction (%) = 
$$\left(\frac{C_{MR_n} \cdot V_{org}}{C_{MR_n} \cdot V_{org} + C_M^{n+} \cdot V_{aq}}\right) \cdot 100$$
 (2)

Stripping (%) = 
$$\left(\frac{C_{M^{n+}} \cdot V_{aq}}{C_{MRT} \cdot V_{org}}\right) \cdot 100$$
 (3)

where  $C_{MR_n}$  and  $C_{M^{n+}}$  are the equilibrium concentrations of metal ions in organic and aqueous phases,  $C_{MR_T}$  is the total concentration of metal ions in the loaded organic phase before stripping, and  $V_{org}$  and  $V_{aq}$  are the volumes of organic and aqueous phases, respectively. The pH of the aqueous phase was adjusted by adding 18 M H<sub>2</sub>SO<sub>4</sub> or 20 M NaOH solution. An S210 SevenCompact<sup>TM</sup> pH meter (Mettler Toledo, USA) was employed when monitoring the pH. The distribution coefficient (D) and separation factor ( $\beta$ ) were calculated using Eqs. (4) and (5), respectively:

$$D = \frac{C_{MR_n}}{C_{M^{n+}}}$$
(4)

$$\beta_{\frac{M_2}{M_1}} = \frac{D_2}{D_1} \tag{5}$$

where  $D_1$  and  $D_2$  are the distribution coefficients of elements 1 and 2, respectively, in a specific solvent system. A McCabe-Thiele diagram of zinc extraction from citric acid solution using D2EHPA was plotted by varying the O/A (organic to aqueous) ratio from 1:5 to 5:1 at constant time (15 min), pH (5), and temperature (25 °C).

The effect of two different acidic organophosphorus extractants (Cyanex 572 and D2EHPA) on the extractions of Zn, Fe, and Mn from PLS was studied in a pH range of 2 to 6. Table 2 presents the investigated parameters in the SX and stripping experiments. In each experiment, only one parameter at a time was changed while keeping the others constant.

#### 2.3. Pb removal

As lead was the main impurity of the EAF citric acid PLS (the highest content, ~1 g/L, in the PLS and harms zinc EW [24]), its removal was performed by sulfate precipitation [31] from the PLS (Table 3). The pH of the PLS was slowly adjusted at room temperature by droplets of 18 M  $H_2SO_4$  with a target pH of 0 under mixing of 200 rpm. The solution samples were taken at intervals of 0.5 pH after 10 min stabilization. According to the solution analysis, a pH value of 2 was confirmed to be the optimal pH in terms of minimizing chemical consumption while maximizing lead removal.

#### 2.4. Analysis

AAS (Atomic Absorption Spectroscopy, Thermo Scientific iCE 3000, USA) for Zn, Pb, Mn, and Fe and ICP-OES (inductively coupled plasma – optical emission spectroscopy, Perkin Elmer Optima 7100 DV, USA) for other elements were employed to determine the solution compositions. The dried residues were analyzed using XRD (X-Ray Diffraction, X'Pert PRO Powder, the Netherlands).

#### Table 2

Experimental	parameters	and	their	respective	levels

#### Table 3

Quantitative Rietveld refinement of the XRD histogram of the precipitate formed at pH 2.



**Fig. 1.** Sulfate ion consumption when modifying the pH of EAF dust citric acid PLS and the content of metals in the solution as a function of pH at room temperature.

#### 3. Results & discussion

#### 3.1. Lead removal

Fig. 1 presents the sulfate ion consumption and Pb and Mn precipitation as a function of pH. The sulfate ion consumption (by sulfuric acid addition) needed to achieve full Pb removal was 0.012 M (pH = 2). Simultaneously 30% of Mn was removed. With further sulfate addition, Mn precipitation was supported, with the addition of 0.09 M providing over 60% of Mn precipitation (pH = 0). The sulfate precipitation was carried out with sulfuric acid since, at the same time, the Na content in the solution was also decreased prior to Zn EW. Moreover, the Na content in the precipitate was rather high (Table 3, 52 wt-% Na vs. 42.8 wt-% Pb) compared to Pb. However, the solution samples were not analyzed for Na because it causes no major challenges in Zn EW [25].

Quantitative Rietveld analysis [69,70] suggested that the precipitated lead that was formed had a composition of  $PbSO_4$ , see Eq. (6). However, Mn precipitate could not be detected by XRD due to the relatively small amount (~0.1 wt-%, calculated based on the Mn solution analysis before and after the precipitation) compared to the other precipitates. The suggested precipitate route is presented in Eq. (7).

$$Pb^{2+}(aq) + H_2SO_4(aq) = PbSO_4(s) + 2H^+(aq)$$
 (6)

Solvent extraction							Stripping				
Experimental parameters	Levels						Experimental parameters	Levels			
Contact time (min)	1	2	5	10	15*	30	H <sub>2</sub> SO <sub>4</sub> (M)	0.005	0.1	1*	2
pH Temperature (°C)	1 25*	2 35	3 45	4 55	5* -	6	O/A ratio	1:1*	2:1	3:1	4:1
D2EHPA% (vol-%) O/A ratio	15 1:5	20* 1:2	25 1:1*	30 2:1	- 5:1	- -					

\* Value that was kept constant while other parameters were studied.



Fig. 2. Effect of two extractants (A) D2EHPA and (B) Cyanex 572 on the extraction of Zn, Fe, and Mn as a function of pH ([Extractant] = 20%, T = 25 °C, O/A = 1:1,  $t = 15 \, {\rm min}$ ).

$$Mn^{2+}(aq) + H_2SO_4(aq) = MnSO_4(s) + 2H^+(aq)$$
(7)

The lead sulfate precipitate formed can be transferred to secondary lead production where smelting of PbSO<sub>4</sub> into lead bullion takes place [71]. According to stoichiometry, to achieve 100% Pb and 30% Mn removal at pH 2, the amount of sulfate ions required is only  $\sim$ 0.007 M. Therefore, with the optimized parameters for Pb and Mn removal (Fig. 1), approximately 0.012 M of excess sulfuric ions was needed to fully remove all the Pb and 30% of the Mn from the PLS. This is around 1.8 times the stoichiometry, which can be explained by the precipitation of Na as Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Table 3.

#### 3.2. Effect of pH and extractant type

The purified PLS was subjected to a study of Zn separation. The main goal in solvent extraction was to achieve higher separation between zinc and dissolved iron. After lead removal, the composition of the Pb-free PLS was as presented in Table 1, excluding all lead and ~20% of Mn (~500 vs. ~400 mg/L), therefore, the remaining impurities in the PLS were Fe and Mn at significant concentrations. Fig. 2 shows that extractions of Zn and Mn using D2EHPA (Fig. 2A) and Cyanex 572 (Fig. 2B) are favored with increasing pH as predicted by Eq. (1) by cation exchange mechanism. Similar behaviors of Zn and Mn extraction with acidic extractants are also reported in the literature [32,34-37,44-47]. In contrast, Fe extraction was decreased significantly when pH was increased from 1 to 6 using D2EHPA and Cyanex 572. The possible reason for this behavior could be the complex formation of Fe with citrate ions. In literature, stability constant for Fecitrate complex is reported in the range of 11–15 [72,73] while similar values for Zn and Mn complexes are reported in the range of 4.2-4.9 and 3.5-4.2 [72,74], respectively. Speciation diagrams of Fe-citrate species in aqueous solution demonstrate that Fe could form very stable neutral [73] or anionic [75] complexes in the pH range of 1–6 and free iron species does not predominate at higher pH levels (> 1.5) [75]. This indicates that the formation of stable iron-citrate complexes could be preferentially rejected by the acidic extractants and therefore, the extraction of iron was decreased with increasing pH, Fig. 2. Furthermore, it was predicted in an investigation [76] that the addition of citrate ions in solution favors the formation of free species of zinc  $(Zn^{2+})$ , suggesting that extraction of Zn ions will increase at elevated pH levels via cation exchange mechanism (Eq. (1)).

The separation factors of zinc concerning Fe and Mn were calculated and compared between D2EHPA and Cyanex 572 in the pH range of 3-6, see Table 4. It was observed that, in general, D2EHPA was found to provide higher separation of zinc from iron compared to Cyanex 572. Separation of Zn from Mn was higher by D2EHPA at low pH (3), while

Table 4
Separation factors of Zn with respect to Fe and Mn using D2EHPA and Cyanex
572 in citric acid solutions

pH	D2EHPA		Cyanex 572		
	$\beta_{Zn/Fe}$	$\beta_{Zn/Mn}$	$\beta_{Zn/Fe}$	$\beta_{Zn/Mn}$	
3	2	39	3	19	
4	43	39	6	38	
5	63	23	9	20	
6	2629	14	14	50	

increasing the pH up to 5 resulted in similar separation efficiency for both extractants. At pH 6, Cyanex 572 was able to separate Zn from Mn more effectively, although not from Fe. Therefore, D2EHPA was selected as the SX extractant and pH 5 defined as the pH for Zn extraction.

#### 3.3. Effect of solvent extraction parameters

Fig. 3A shows that extraction of both zinc and manganese was fast (approx. 1 min) and approximately the same regardless of the SX time employed; however, the extraction of iron slowly increased with increased SX time (up to 15 min). Similar behavior for iron extraction has also been reported earlier [41]. However, an SX duration of 15 min was selected for the optimal conditions even though iron extraction increased when increasing the time.

The effect of D2EHPA concentration, see Fig. 3B, was studied in the range of 10 to 25 vol-%. The extraction of Zn, but also impurities (Fe and Mn), rose with increasing extractant concentration. With the lowest 10 vol-% D2EHPA concentration, the extractions of Fe and Mn were marginal but also only 50% of Zn could be extracted. A D2EHPA concentration of 20 vol-% was selected as the optimal concentration (Zn 90%, Fe 18%, Mn 38%) since the separation between Zn and Fe was the highest. Comparable extraction behavior regarding Fe and Zn in a different base medium has also been reported by other authors [35,42,43].

As can be seen in Fig. 4, the temperature did not have a significant effect on Zn extraction, and that of manganese also stayed approximately at the same level. While iron extraction decreased when raising the temperature. Although, increasing temperature favors the separation between Zn and Fe, however, 25 °C was chosen as an optimum temperature to keep the cost of the process low and to improve safety in operations. Furthermore, Mn extraction was slightly favored by increasing the temperature, suggesting the extraction reaction of Mn with D2EHPA in citric acid media is endothermically driven. In contrast, there was a slight decrease in Zn extraction and a significant decrease in iron extraction observed, suggesting that the extraction reactions of Fe



Fig. 3. Effect of (A) time and (B) D2EHPA concentration on extraction of Zn, Fe, and Mn (T = 25 °C, O/A = 1:1, pH = 5).



**Fig. 4.** Effect of temperature on extraction of Zn, Fe, and Mn from citric acid solution ([D2EHPA] = 20%, pH = 5, O/A = 1:1, t = 15 min).

and Zn with D2EHPA in citric acid media are exothermically driven.

#### 3.4. McCabe-Thiele analysis

McCabe-Thiele analysis, see Fig. 5, shows that almost all the zinc could be loaded into the organic phase using two theoretical countercurrent stages at an operating line (O/A ratio) of 1:1. An organic phase loaded with  $\sim$ 20 g/L of zinc could be obtained from a feed solution containing  $\sim$ 20 g/L of Zn, with a zinc recovery of over 99%.

For stripping studies, the organic phase was loaded with  $\sim 18.5$  g/L of zinc,  $\sim 100 \text{ mg/L}$  of iron, and  $\sim 180 \text{ mg/L}$  of manganese by a single stage extraction at pH 5, room temperature, and unit phase ratio. First, the stripping of zinc into sulfuric acid was carried out in a concentration range of 0.005 to 2 M at room temperature and a stripping time of 15 min. Fig. 6 presents the results obtained after stripping Zn from the loaded organic solution. As can be seen, the lowest H<sub>2</sub>SO<sub>4</sub> concentration (0.005 M) resulted in very poor stripping efficiency compared to higher acid concentrations where ~93% of zinc was successfully stripped in a 1 M H<sub>2</sub>SO<sub>4</sub> solution. Therefore, 1 M acid concentration was chosen for further study. It is noteworthy that such a short stripping time (15 min) did not provide any iron to the aqueous phase; all of the iron (~100 mg/L) remained in the loaded organic phase. A similar slow iron stripping rate has also been observed by other authors [43]. However, as the total iron content in D2EHPA is very low, the organic solution can be recycled several times before the cumulative content of



**Fig. 5.** McCabe-Thiele diagram for extraction of Zn using D2EHPA in citric acid media ([D2EHPA] = 20%, T = 25 °C, t = 15 min, pH = 5).



**Fig. 6.** Effect of  $H_2SO_4$  concentration on stripping efficiency of Zn, Fe and Mn (T = 25 °C, t = 15 min, O/A = 1:1).

iron in D2EHPA increases to such a level that it requires purification. Furthermore, iron stripping from D2EHPA is known to require a rather strong acid concentration [77–79], but one experimental run conducted



Fig. 7. McCabe-Thiele diagram for stripping of Zn using  $H_2SO_4$  solution (T = 25 °C, t = 15 min,  $[H_2SO_4] = 1$  M).

with 0.8 M citric acid at pH 5 with an O/A ratio of 1/1 at room temperature for 60 min resulted in 30% Fe stripping efficiency.

Similarly to Fig. 5 for Zn extraction, a McCabe-Thiele diagram for zinc stripping was also plotted by varying the phase ratio (O/A) from 1:1 to 6:1, as shown in Fig. 7. It was determined that at an operating line of 3:1 (O/A ratio), three theoretical countercurrent stages were required to completely strip Zn from organic solution to  $1 \text{ M H}_2\text{SO}_4$  solution, giving rise to ~55 g/L Zn solution. This kind of solution could be effectively processed by electrowinning for Zn recovery.

To simulate the predicted results at optimized conditions, a single stage SX experiment (pH = 5, t = 15 min, T = 25 °C,  $C_{D2EHPA} = 20$  vol-%, and O/A = 1:1) was performed followed by a single stage stripping experiment (t = 15 min, T = 25 °C,  $C_{H_2SO_4} = 1$  M, and O/A = 3:1) to produce a zinc-rich solution (Table 5), applicable for state-of-the-art zinc electrowinning. As can be seen, the zinc enrichment ratio is over 2.5 (20000 mg/L vs. 51990 mg/L) and the content of all the other elements has decreased. Moreover, the content of Mn has stayed at approximately the same level (504 mg/L vs. 585 mg/L), although manganese is known not to cause problems during Zn EW [11,17,20,24,25,15,18,19,80]. Therefore, the composition presented in Table 5 can be utilized in a state-of-the-art Zn EW process [18,19].

#### 3.5. Process flowsheet

Fig. 8 outlines a multistage recycling process for iron, lead, and zinc from EAF dust including roasting, leaching, precipitation, and solvent extraction followed by electrowinning. EAF dust is firstly roasted with caustic soda (at a ratio of 2:1) and then leached in 0.8 M citric acid

#### Table 5

Composition of zinc electrolyte after optimized solvent extraction and stripping circuits.

Zn [mg/L] 51,990 Pb [mg/L] < LOD Ba [mg/L] < LOD	Fe [mg/L] < LOD Sn [mg/L] < LOD Ni [mg/L] < LOD Sb [mg/L] 20	Ca [mg/L] 580 Ga [mg/L] < LOD Sn [mg/L] < LOD Ag [mg/L] < LOD	Mg [mg/L] 36 Ge [mg/L] < LOD Co [mg/L] < LOD Cd [mg/L] < LOD	Al [mg/L] < LOD In [mg/L] < LOD Se [mg/L] < LOD K [mg/L] 460	Cr [mg/L] < LOD As [mg/L] < LOD Si [mg/L] < LOD Na [mg/L] 66	Mn [mg/L] 585 S [mg/L] 30,700 Bi [mg/L] < LOD
--	---	--	---	---	---	---

LOD = limit of detection

media at 40 °C with constant oxygen feed and agitation for 120 min [6]. After leaching, the solution is filtered and the residue is transferred to a pelletizing plant with suitable binder materials, e.g., bentonite [81], to produce a suitable iron feed for an EAF process [6]. After filtration, the remaining solution is transferred to a lead precipitation unit process followed by a secondary filtration unit. The zinc-rich filtrate is further routed to solvent extraction and stripping units and finally, state-of-theart zinc electrowinning can be performed for the purified solution with 52 g/L of Zn and  $\sim 100 \text{ g/L}$  of H<sub>2</sub>SO<sub>4</sub> in the solution, suitable for Zn EW process [11 16,19,20,22,23]. In the main process flow, three different excess streams are produced, i.e., zinc-free aqueous solution after solvent extraction, zinc depleted organic solution after stripping process. and spent zinc electrolyte. The zinc-free aqueous solution can be transferred back to the citric acid leaching unit and mixed with fresh 0.8 M citric acid solution and the spent Zn electrolyte can be transferred to the stripping stage mixed with fresh 1 M H<sub>2</sub>SO<sub>4</sub>. Zn depleted organic solution or regenerated D2EHPA solution could be recycled back to solvent extraction stage.

#### 4. Conclusions

A novel hydrometallurgical process flowsheet for Zn, Pb recovery by precipitation and solvent extraction from citric acid leach solution of EAF dust was suggested. The proposed flowsheet allows EAF dust to be suitable raw material not only for secondary steel production but also for secondary lead and zinc production. The conclusions of this study from the different stages are the following:

- (1) From EAF dust citric acid PLS, lead was removed as lead sulfate (PbSO<sub>4</sub>) by sulfate precipitation with the addition of sulphuric acid at pH 2. The sulfate precipitation was found to be very efficient for Pb and somewhat selective for Mn too, with relatively low acid consumption,  $0.0012 \text{ M} [\text{SO}_4^-]$ . Moreover, Zn losses were minimal in the process.
- (2) Further purification of lead-free leach solution was performed by solvent extraction where D2EHPA was found to surpass Cyanex 572 when comparing the selectivity of Zn over Fe at pH 2.
- (3) McCabe-Thiele results indicated that at optimized solvent extraction conditions (pH = 5, t = 15 min, T = 25 °C,  $C_{D2EHPA} = 20$  vol%), Zn (~20 g/L) could be loaded completely in organic solution in two counter-current stages at an operating line (O/A) of 1:1.
- (4) The Zn loaded D2EHPA solution was further treated with sulfuric acid and at optimized stripping conditions ( $[H_2SO_4] = 1 \text{ M}$ , t = 15 min,  $T = 25 \degree \text{C}$ , O/A = 3:1), Zn rich solution (~55 g/L) could be produced in three counter-current stages at an operating line (O/A) of 3:1.
- (5) The purified Zn solution is suitable for direct integration in Zn electrowinning process. Therefore, EAF dust what is considered waste, can be transferred into three different streams (Zn, Fe, and Pb) of secondary metal production.

#### **Declaration of Competing Interest**

The authors declared that there is no conflict of interest.

#### Acknowledgements

This work has been financed and supported by the Association of Finnish Steel and Metal Producers (METSEK project) together with the "NoWASTE" project, ML, (Grant 297962) and the "GoldTail" project, PH, (Grant 319691) funded by the Academy of Finland. The research also made use of the Academy of Finland funded "RawMatTERS Finland Infrastructure" (RAMI), based at Aalto University. Ovako Imatra Oy Ab, is gratefully acknowledged by the authors.



**Fig. 8.** Schematic of the proposed route for Fe, Pb, and Zn recovery from EAF dust. The blue box refers to previous findings [6] and green is the focus of this study. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

#### References

- L.E.K. Holappa, Energy efficiency and sustainability in steel production, Applications of Process Engineering Principles in Materials Processing, Energy and Environmental Technologies, Springer International Publishing, 2017, pp. 401–410.
- [2] A.J.B. Dutra, P.R.P. Paiva, L.M. Tavares, Alkaline leaching of zinc from electric arc furnace steel dust, Miner. Eng. 19 (5) (2006) 478–845, https://doi.org/10.1016/j. mineng.2005.08.013.
- [3] E.U. Council, Council Decision 2003/33/EC of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC, 2003, Off. J. Eur. Commun. 16 (2003) L11.
- [4] European Commission DG ENV.E3, Heavy metals in waste, final report, project ENV.E3/ETU/2000/0058.COWI A/S, 2002, Denmark.
- [5] P. Halli, J. Hamuyuni, H. Revitzer, M. Lundström, Selection of leaching media for metal dissolution from electric arc furnace dust, J. Cleaner Prod. 164 (2017) 265–276, https://doi.org/10.1016/j.jclepro.2017.06.212.
- [6] P. Halli, J. Hamuyuni, M. Leikola, M. Lundström, Developing a sustainable solution for recycling electric arc furnace dust via organic acid leaching, Miner. Eng. 124 (2018) 1–9, https://doi.org/10.1016/j.mineng.2018.05.011.

- [7] S.R. Burckharda, A.P. Schwabb, M.K. Banks, The effects of organic acids on the leaching of heavy metals from mine tailings, J. Hazard. Mater. 41 (2–3) (1995) 135–145, https://doi.org/10.1016/0304-3894(94)00104-0.
- [8] A.P. Brown, J.H. Meisenhelder, N.P. Yao, The alkaline electrolytic process for zinc production: a critical evaluation, Ind. Eng. Chem. Prod. Res. Dev. 22 (2) (1983) 263–272, https://doi.org/10.1021/i300010a020.
- [9] B.C. Tripathy, S.C. Das, G.T. Hefter, P. Singh, Zinc electrowinning from acidic sulfate solutions: Part I: Effects of sodium lauryl sulfate, J. Appl. Electrochem. 27 (6) (1997) 673–678, https://doi.org/10.1023/A:1018431619595.
- [10] S.t. Rashkov, T.s. Bobrev, Z. Noncheva, Y. Stefanov, B. Rashkova, M. Petrova, Lead-cobalt anodes for electrowinning of zinc from sulphate electrolytes, Hydrometallurgy 52 (3) (1999) 223–230, https://doi.org/10.1016/S0304-386X (99)00005-5.
- [11] P. Guillaume, N. Leclerc, C. Boulanger, J.M. Lecuire, F. Lapicque, Investigation of optimal conditions for zinc electrowinning from aqueous sulfuric acid electrolytes, J. Appl. Electrochem. 37 (11) (2007) 1237–1243, https://doi.org/10.1007/s10800-007-9377-2.
- [12] T. Pecina, T. Franco, P. Castillo, E. Orrantia, Leaching of a zinc concentrate in H<sub>2</sub>SO<sub>4</sub> solutions containing H<sub>2</sub>O<sub>2</sub> and complexing agents, Miner. Eng. 21 (1) (2008) 23–30, https://doi.org/10.1016/j.mineng.2007.07.006.
- [13] Z. Chenglong, Z. Youcai, G. Guixiang, H. Xi, L. Hongjiang, Leaching of zinc sulfide in alkaline solution via chemical conversion with lead carbonate, Hydrometallurgy

90 (1) (2008) 19-25, https://doi.org/10.1016/j.hydromet.2007.09.007.

- [14] H. Xu, C. Wei, C. Li, G. Fan, Z. Deng, M. Li, X. Li, Sulfuric acid leaching of zinc silicate ore under pressure, Hydrometallurgy 105 (1–2) (2010) 186–190, https:// doi.org/10.1016/j.hydromet.2010.07.014.
- [15] S. Gürmen, M. Emre, A laboratory-scale investigation of alkaline zinc electrowinning, Miner. Eng. 16 (6) (2003) 559–562, https://doi.org/10.1016/S0892-6875(03)00081-5.
- [16] G.W. Barton, A.C. Scott, A validated mathematical model for a zinc electrowinning cell, J. Appl. Electrochem. 22 (2) (1992) 104–115, https://doi.org/10.1007/ BF01023811.
- [17] M.K. Jha, V. Kumar, R.J. Singh, Review of hydrometallurgical recovery of zinc from industrial wastes, Resources Conserv. Recycl. 33 (1) (2001) 1–22, https://doi.org/ 10.1016/S0921-3449(00)00095-1.
- [18] B.C. Tripathy, S.C. Das, V.N. Misra, Effect of antimony(III) on the electrocrystallisation of zinc from sulphate solutions containing SLS, Hydrometallurgy 69 (1–3) (2003) 81–88, https://doi.org/10.1016/S0304-386X(02)00204-9.
- [19] J.T. Hinatsu, V.D. Tran, F.R. Foulkes, Electrical conductivities of aqueous ZnSO<sub>4</sub> – H<sub>2</sub>SO<sub>4</sub> solutions, J. Appl. Electrochem. 22 (3) (1992) 215–223, https://doi. org/10.1007/BF01030180.
- [20] A.C. Scott, R.M. Pitblado, G.W. Barton, A.R. Ault, Experimental determination of the factors affecting zinc electrowinning efficiency, J. Appl. Electrochem. 18 (1) (1988) 120–127, https://doi.org/10.1007/BF01016215.
- [21] L. Mureşan, G. Maurin, L. Oniciu, D. Gaga, Influence of metallic impurities on zinc electrowinning from sulphate electrolyte, Hydrometallurgy 43 (1–3) (1996) 345–354, https://doi.org/10.1016/0304-386X(96)00012-6.
- [22] E.J. Frazer, T. Lwin, Identification of optimum conditions for zinc electrowinning in high-purity synthetic electrolytes, J. Appl. Electrochem. 17 (3) (1987) 453–462, https://doi.org/10.1007/BF01084118.
- [23] A.M. Alfantazi, D.B. Dreisinger, The role of zinc and sulfuric acid concentrations on zinc electrowinning from industrial sulfate based electrolyte, J. Appl. Electrochem. 31 (6) (2001) 641–646, https://doi.org/10.1023/A:1017569400346.
- [24] A.R. Ault, E.J. Frazer, Effects of certain impurities on zinc electrowinning in highpurity synthetic solutions, J. Appl. Electrochem. 18 (4) (1988) 583–589, https:// doi.org/10.1007/BF01022254.
- [25] K. Tozawa, T. Nishimura, M. Akahori, M.A. Malaga, Comparison between purification processes for zinc leach solutions with arsenic and antimony trioxides, Hydrometallurgy 30 (1–3) (1992) 445–461, https://doi.org/10.1016/0304-386X (92)90099-L.
- [26] T.M. Dreher, A. Nelson, G. Demopoulos, D. Filippou, The kinetics of cobalt removal by cementation from an industrial zinc electrolyte in the presence of Cu, Cd, Pb, Sb and Sn additives, Hydrometallurgy 60 (2) (2001) 105–116, https://doi.org/10. 1016/S0304-386X(00)00152-3.
- [27] B.S. Boyanov, V.V. Konareva, N.K. Kolev, Purification of zinc sulfate solutions from cobalt and nickel through activated cementation, Hydrometallurgy 73 (1–2) (2004) 163–168, https://doi.org/10.1016/j.hydromet.2003.09.002.
- [28] Y. Zhao, R. Stanforth, Production of Zn powder by alkaline treatment of smithsonite Zn-Pb ores, Hydrometallurgy 56 (2) (2000) 237–249, https://doi.org/10.1016/ S0304-386X(00)00079-7.
- [29] E. Kim, L. Horckmans, J. Spooren, K.C. Vrancken, M. Quaghebeur, K. Broos, Selective leaching of Pb, Cu, Ni and Zn from secondary lead smelting residues, Hydrometallurgy 169 (2017) 372–381, https://doi.org/10.1016/j.hydromet.2017. 02.027.
- [30] R. Zárate-Gutiérrez, G.T. Lapidus, R.D. Morales, Aqueous oxidation of galena and pyrite with nitric acid at moderate temperatures, Hydrometallurgy 115–116 (2012) 57–63, https://doi.org/10.1016/j.hydromet.2011.12.010.
- [31] A.E. Lewis, Review of metal sulphide precipitation, Hydrometallurgy 104 (2) (2010) 222–234, https://doi.org/10.1016/j.hydromet.2010.06.010.
- [32] S. Amer, J.M. Figueiredo, A. Luis, The recovery of zinc from the leach liquors of the CENIM-LNETI process by solvent extraction with di(-2-ethylhexyl)phosphoric acid, Hydrometallurgy 37 (3) (1995) 323–337, https://doi.org/10.1016/0304-386X(94) 00040-A.
- [33] A.L. Salgado, A.M. Veloso, D.D. Pereira, G.S. Gontijo, A. Salum, M.B. Mansur, Recovery of zinc and manganese from spent alkaline batteries by liquid–liquid extraction with Cyanex 272, J. Power Sources 115 (2) (2003) 367–373, https://doi. org/10.1016/S0378-7753(03)00025-9.
- [34] E. Vahidi, F. Rashchi, D. Moradkhani, Recovery of zinc from an industrial zinc leach residue by solvent extraction using D2EHPA, Miner. Eng. 22 (2) (2009) 204–206, https://doi.org/10.1016/j.mineng.2008.05.002.
- [35] N.B. Devi, K.C. Nathsarma, V. Chakravortty, Separation of divalent manganese and cobalt ions from sulphate solutions using sodium salts of D2EHPA, PC 88A and Cyanex 272, Hydrometallurgy 54 (2–3) (2000) 117–131, https://doi.org/10.1016/ S0304-386X(99)00054-7.
- [36] D.D. Pereira, S.D.F. Rocha, M.B. Mansur, Recovery of zinc sulphate from industrial effluents by liquid–liquid extraction using D2EHPA (di-2-ethylhexyl phosphoric acid), Sep. Purif. Technol. 53 (1) (2007) 89–96, https://doi.org/10.1016/j.seppur. 2006.06.013.
- [37] T. Hosseini, F. Rashchi, E. Vahidi, N. Mostoufi, Investigating the synergistic effect of D2EHPA and Cyanex 302 on zinc and manganese separation, Sep. Sci. Technol. 45 (8) (2010) 1158–1164, https://doi.org/10.1080/01496391003727908.
- [38] L.R. Gouvea, C.A. Morais, Development of a process for the separation of zinc and copper from sulfuric liquor obtained from the leaching of an industrial residue by solvent extraction, Miner. Eng. 23 (6) (2010) 492–497, https://doi.org/10.1016/j. mineng.2010.01.001.
- [39] P.E. Tsakiridis, P. Oustadakis, A. Katsiapi, S. Agatzini-Leonardou, Hydrometallurgical process for zinc recovery from electric arc furnace dust (EAFD). Part II: Downstream processing and zinc recovery by electrowinning, J. Hazardous

Mater. 179 (1-3) (2010) 8-14, https://doi.org/10.1016/j.jhazmat.2010.04.004.

- [40] K.C. Nathsarma, N. Devi, Separation of Zn (II) and Mn (II) from sulphate solutions using sodium salts of D2EHPA, PC88A and Cyanex 272, Hydrometallurgy 84 (3-4) (2006) 149–154, https://doi.org/10.1016/j.hydromet.2006.05.004.
- [41] F. Principe, G.P. Demopoulos, Comparative study of iron(III) separation from zinc sulphate-sulphuric acid solutions using the organophosphorus extractants, OPAP and D2EHPA: Part I: Extraction, Hydrometallurgy 74 (1-2) (2004) 93–102, https:// doi.org/10.1016/j.hydromet.2004.01.004.
- [42] X. Li, C. Wei, Z. Deng, M. Li, C. Li, G. Fan, Selective solvent extraction of vanadium over iron from a stone coal/black shale acid leach solution by D2EHPA/TBP, Hydrometallurgy 105 (3–4) (2011) 359–363, https://doi.org/10.1016/j.hydromet. 2010.10.006.
- [43] G. Hu, D. Chen, L. Wang, J.-C. Liu, H. Zhao, Y. Liu, T. Qi, C. Zhang, P. Yu, Extraction of vanadium from chloride solution with high concentration of iron by solvent extraction using D2EHPA, Sep. Purif. Technol. 125 (2014) 59–65, https://doi.org/ 10.1016/j.seppur.2014.01.031.
- [44] W. Zhang, C.Y. Cheng, Manganese metallurgy review. Part III: Manganese control in zinc and copper electrolytes, Hydrometallurgy 89 (3–4) (2007) 178–188, https:// doi.org/10.1016/j.hydromet.2007.08.011.
- [45] A. Deep, J.M.R. de Carvalho, Review on the recent developments in the solvent extraction of zinc, Solvent Extr. Ion Exch. 26 (4) (2008) 375–404, https://doi.org/ 10.1080/07366290802179267.
- [46] P.M. Cole, K.C. Sole, Solvent extraction in the primary and secondary processing of zinc, J. South Afr. Inst. Min. Metall. 102 (8) (2002) 451–456.
- [47] P.M. Cole, K.C. Sole, Zinc solvent extraction in the process industries, Miner. Process. Extr. Metall. Rev. 24 (2) (2003) 91–137, https://doi.org/10.1080/ 08827500306897.
- [48] D.S. Flett, Solvent extraction in hydrometallurgy: the role of organophosphorus extractants, J. Organomet. Chem. 690 (10) (2005) 2426–2438, https://doi.org/10. 1016/j.jorganchem.2004.11.037.
- [49] M. Gharabaghi, M. Irannajad, A.R. Azadmehr, Separation of nickel and zinc ions in a synthetic acidic solution by solvent extraction using D2EHPA and Cyanex 272, Physicochem. Probl. Miner. Process. 49 (1) (2013) 233–242, https://doi.org/10. 5277/ppmp130121.
- [50] C. Tunsu, J.B. Lapp, C. Ekberg, T. Retegan, Selective separation of yttrium and europium using Cyanex 572 for applications in fluorescent lamp waste processing, Hydrometallurgy 166 (2016) 98–106, https://doi.org/10.1016/j.hydromet.2016. 10.012.
- [51] V. Agarwal, M.S. Safarzadeh, J.T. Bendler, Solvent extraction of Eu (III) from hydrochloric acid solutions using PC88A and Cyanex 572 in kerosene, Hydrometallurgy 177 (2018) 152–160, https://doi.org/10.1016/j.hydromet.2018. 03.011.
- [52] J.E. Quinn, K.H. Soldenhoff, G.W. Stevens, N.A. Lengkeek, Solvent extraction of rare earth elements using phosphonic/phosphinic acid mixtures, Hydrometallurgy 157 (2015) 298–305, https://doi.org/10.1016/j.hydromet.2015.09.005.
- [53] E. Kolar, R.P.R. Catthoor, F.H. Kriel, R. Sedev, S. Middlemas, E. Klier, G. Hatch, C. Priest, Microfluidic solvent extraction of rare earth elements from a mixed oxide concentrate leach solution using Cyanex<sup>®</sup> 572, Chem. Eng. Sci. 148 (2016) 212–218, https://doi.org/10.1016/j.ces.2016.04.009.
  [54] J. Tang, M. Su, H. Zhang, T. Xiao, Y. Liu, Y. Liu, L. Wei, C. Ekberg, B.-M. Steenari,
- [54] J. Tang, M. Su, H. Zhang, T. Xiao, Y. Liu, Y. Liu, L. Wei, C. Ekberg, B.-M. Steenari, Assessment of copper and zinc recovery from MSWI fly ash in Guangzhou based on a hydrometallurgical process, Waste Manage. 76 (2018) 225–233, https://doi.org/ 10.1016/j.wasman.2018.02.040.
- [55] J. Tang, R. Ylmén, M. Petranikova, C. Ekberg, B.-M. Steenari, Comparative study of the application of traditional and novel extractants for the separation of metals from MSWI fly ash leachates, J. Cleaner Prod. 172 (2018) 143–154, https://doi.org/10. 1016/j.jclepro.2017.10.152.
- [56] H. Jafari, H. Abdollahi, M. Gharabaghi, A.A. Balesini, Solvent extraction of zinc from synthetic Zn-Cd-Mn chloride solution using D2EHPA: Optimization and thermodynamic studies, Sep. Purif. Technol. 197 (2018) 210–219, https://doi.org/10. 1016/j.seppur.2018.01.020.
- [57] OECD, Recycling of copper, lead and zinc bearing wastes, OCDE/GD(95)78, Environment monographs N° 109, Paris 1995, 29 pages, Internet: http://www.oecd. org/environment/publicationsdocuments/reports/73/ [Accessed 17.6.2019].
- [58] R.B. Gordon, T.E. Graedal, M. Bertram, K. Fuse, R. Lifset, H. Rechberger, S. Spatari, The characterization of technological zinc cycles, Resour. Conserv. Recycl. 39 (2) (2003) 107–135, https://doi.org/10.1016/S0921-3449(02)00166-0.
- [59] Z. Doug, What to do with your EAF dust, Steel Times Int. 20 (3) (1996) 46–50 ISSN 01437798.
- [60] T. Suetens, B. Klaasen, K. Van Acker, B. Blanpain, Comparison of electric arc furnace dust treatment technologies using exergy efficiency, J. Cleaner Prod. 65 (2014) 152–167, https://doi.org/10.1016/j.jclepro.2013.09.053.
- [61] J. Knop, Diphenylamine as indicator in the titration of iron with dichromate solution, J. Am. Chem. Soc. 46 (2) (1924) 263–269, https://doi.org/10.1021/ ja01667a001.
- [62] N. Menad, J.N. Ayala, F. Garcia-Carcedo, E. Ruiz-Ayúcar, A. Hernández, Study of the presence of fluorine in the recycled fractions during carbothermal treatment of EAF dust, Waste Manage. 23 (6) (2003) 483–491, https://doi.org/10.1016/S0956-0533(02)00151-4.
- [63] G.-S. Lee, Y.J. Song, Recycling EAF dust by heat treatment with PVC, Miner. Eng. 20 (8) (2007) 739–746, https://doi.org/10.1016/j.mineng.2007.03.001.
- [64] Y. Kashiwaya, A. Tsubone, K. Ishii, H. Sasamoto, Thermodynamic analysis on the dust generation from EAF for the recycling of dust, Iron Steel Inst. Jpn. Int. 44 (10) (2004) 1774–1779, https://doi.org/10.2355/isijinternational.44.1774.
- [65] P.J.W. Keglevich de Buzin, N.C. Heck, A.C.F. Vilela, EAF dust: An overview on the influences of physical, chemical and mineral features in its recycling and waste

incorporation routes, J. Mater. Res. Technol. 6 (2) (2017) 194-202, https://doi. org/10.1016/j.jmrt.2016.10.002.

- [66] M.C. Mantovani, C. Takano, P.M. Büchler, EAF and secondary dust characterisation, Iron Steelmak. Process. Prod. Appl. 31 (4) (2004) 325–332, https://doi.org/10. 1179/030192304225018163.
- [67] W.-S. Chen, Y.-H. Shen, M.-S. Tsai, F.-C. Chang, Removal of chloride from electric arc furnace dust, J. Hazardous Mater. 190 (1–3) (2011) 639–644, https://doi.org/ 10.1016/j.jhazmat.2011.03.096.
- [68] M.L. Free, Hydrometallurgy: Fundamentals and Applications, John Wiley & Sons., The Minerals, Metals & Materials Society, 2003, 432 p, ISBN: 9781118732465.
  [69] R.A. Young, The Rietveld Method, International Union of Crystallography, 1993,
- [09] I.A. Toung, the reference method, international official of crystallography, 1995, vol. 5, 308p, ISBN: 9780198559122.
   [70] D.I. Bick, S.A. Hourger, Ourprinting phase analysis using the Pietrald method. J.
- [70] D.L. Bish, S.A. Howard, Quantitative phase analysis using the Rietveld method, J. Appl. Crystallogr. 21 (2) (1988) 86–91, https://doi.org/10.1107/ S0021889887009415.
- [71] A.M. Abdel-Rehim, Thermal and XRD analysis of Egyptian galena, J. Therm. Anal. Calorim. 86 (2) (2006) 393–401, https://doi.org/10.1007/s10973-005-6785-6.
- [72] V. Nischwitz, B. Michalke, Electrospray ionisation with selected reaction monitoring for the determination of Mn-citrate, Fe-citrate, Cu-citrate and Zn-citrate, Rapid Commun. Mass Spectrometry 23 (15) (2009) 2338–2346, https://doi.org/10. 1002/rcm.4156.
- [73] T.B. Field, J.L. McCourt, W.A.E. McBryde, Composition and stability of iron and copper citrate complexes in aqueous solution, Can. J. Chem. 52 (17) (1974) 3119–3124, https://doi.org/10.1139/v74-458.
- [74] D. Wyrzykowski, L. Chmurzyński, Thermodynamics of citrate complexation with Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> ions, J. Therm. Anal. Calorim. 102 (1) (2010) 61–64,

https://doi.org/10.1007/s10973-009-0523-4.

- [75] M. Pazos, S. Gouveia, M.A. Sanromán, C. Cameselle, Electromigration of Mn, Fe, Cu and Zn with citric acid in contaminated clay, J. Environ. Sci. Health Part A, Toxic/ Hazardous Substances Environ. Eng. 43 (8) (2008) 823–831, https://doi.org/10. 1080/10934520801974004.
- [76] K. Kabra, R. Chaudhary, R.L. Sawhney, Solar photocatalytic removal of Cu(II), Ni (II), Zn(II) and Pb(II): speciation modeling of metal–citric acid complexes, J. Hazard. Mater. 155 (3) (2008) 424–432, https://doi.org/10.1016/j.jhazmat.2007. 11.083.
- [77] M.R.C. Ismael, J.M.R. Carvalho, Iron recovery from sulphate leach liquors in zinc hydrometallurgy, Miner. Eng. 16 (1) (2003) 31–39, https://doi.org/10.1016/ S0892-6875(02)00310-2.
- [78] M. Bartkowska, M. Regel-Rosocka, J. Szymanowski, Extraction of zinc(II), iron(III) and iron(II) with binary mixtures containing tributyl phosphate and di(2-ethylhexyl)phosphoric acid or cyanex 302, Physicochem. Probl. Miner. Process. 36 (1) (2002) 217–224.
- [79] J. Sun, T.J. O'Keefe, An evaluation of steel scrap as a reducing agent in the galvanic stripping of iron from D2EHPA, Miner. Eng. 15 (3) (2002) 177–185, https://doi. org/10.1016/S0892-6875(02)00004-3.
- [80] Z. Youcai, R. Stanforth, Integrated hydrometallurgical process for production of zinc from electric arc furnace dust in alkaline medium, J. Hazard. Mater. 80 (1–3) (2000) 223–240, https://doi.org/10.1016/S0304-3894(00)00305-8.
- [81] T.C. Eisele, S.K. Kawatra, A review of binders in iron ore pelletization, Miner. Process. Extr. Metall. Rev. 24 (1) (2003) 1–90, https://doi.org/10.1080/ 08827500306896.