



Comparative study of selective zinc leaching from EAFD using carboxylic agents

Estudio comparativo de la lixiviación selectiva de zinc a partir de EAFD utilizando agentes carboxílicos

J. Borda*, R. Torres

¹Universidad Pedagógica y Tecnológica de Colombia. Facultad de Ingeniería. Escuela de Metalurgia. Avenida central del norte Km 4, Edif. de Ingeniería 201, Tunja, Colombia.

Received: September 10, 2020; Accepted: October 27, 2020

Abstract

Recycling of industrial waste has become a process of highly positive impact on the environment, industry and human health. The management of the electric arc furnace dust (EAFD) is a necessary and interesting task due to the possible recovery of its elevated metallic content (Zn, Pb, Cu, etc.). This reduces the environmental pollution generated by the leachability of its heavy metals and produces new revenues for the steel industries. In this work, a hydrometallurgical route was studied to extract the zinc present in EAFD. The research carried out using two organic carboxylic anions: sodium citrate and oxalic acid at moderate concentrations (≤ 0.5 M). The effect of pH, molar concentration and stirring speed was analyzed. Under atmospheric pressure and room temperature, after 3 h of leaching, the results showed that both agents can leach zinc from waste, reaching metal extractions of approximately 50%. The more stable franklinite (ZnFe_2O_4) and hematite (Fe_2O_3) phases were not decomposed under these mild conditions. Citrate was especially promising due to its selectivity for zinc.

Keywords: EAFD, leaching, sodium-citrate, oxalic-acid, zinc.

Resumen

El reciclaje de residuos industriales se ha convertido en un proceso de impacto muy positivo en el medio ambiente, la industria y la salud humana. El manejo del polvo del horno de arco eléctrico (EAFD) es una tarea necesaria e interesante por la posibilidad de recuperar su elevado contenido metálico (Zn, Pb, Cu, etc.). Esto reduce la contaminación ambiental generada por la lixiviación de sus metales pesados y genera nuevos ingresos para las industrias del acero. En este trabajo se estudió una ruta hidrometalúrgica para extraer el zinc presente en EAFD. La investigación se llevó a cabo utilizando dos aniones carboxílicos orgánicos diferentes: citrato de sodio y ácido oxálico a concentraciones moderadas ($\leq 0,5$ M). Se analizó el efecto del pH, la concentración molar y la velocidad de agitación. Bajo presión y temperatura ambiente, luego de 3 h de lixiviación, los resultados mostraron que ambos agentes pueden lixiviar el zinc de los desechos, alcanzando extracciones de metales de aproximadamente el 50%. Las fases más estables de franklinita (ZnFe_2O_4) y hematita (Fe_2O_3) no lograron descomponerse en estas condiciones suaves. El citrato resultó especialmente prometedor debido a su lixiviación selectiva de zinc.

Palabras clave: EAFD, lixiviación, citrato de sodio, ácido oxálico, zinc.

1 Introduction

Zinc is a non-ferrous industrially important metal due to its role in the alloy production and galvanization processes. Because of its durability, it is widely used in the transportation, infrastructure, consumer goods and food production sectors (Asturiana de Zinc, 2017; Zhang *et al.*, 2014). Furthermore, its recycling capacity contributes to saving natural resources and

improving sustainability (Asturiana de Zinc, 2017). Previously, zinc production was limited to the extraction from its minerals through metallurgical processes, however, zinc has been identified as one of the elements whose supply may be potentially limited in nature (Al-harabsheh *et al.*, 2018a). For this reason, metal recovery from secondary resources and industrial waste is currently an interesting alternative (Zhu *et al.*, 2019).

*Corresponding author. E-mail: angela.johana.borda@uptc.edu.co

<https://doi.org/10.24275/rmiq/IA2022>

ISSN:1665-2738, issn-e: 2395-8472

Furthermore, it provides a solution to one of the major problems of the steel industry worldwide: the elimination and treatment of its waste produced as a result of the fusion and refining processes (Hagni *et al.*, 1991). For example, the electric arc furnace, generates exhaust gases that transport many fine particles which are retained in the filters of the gas purification system (Madias, 2009), known as Electric Arc Furnace dust (EAFD). Every year, the worldwide steel industry is estimated to produce over 4.6 million tons of EAFD (Hagni *et al.*, 1991). Due to its leachable metals, EAFD has been classified as a hazardous waste (Laforest and Duchesne, 2006). The steel industry generally does not treat this type of waste, opting to deposit it in storage facilities or landfills. This condition is not favorable from two points of view; firstly, it increases the environmental risk of the waste since it is in direct contact with soil, water, and wind, and secondly, it requires large area within the steelworks for its disposal. For those reasons, metals treatment and recycling EAFD could provide extensive added value in the steel industry. Hydro and pyrometallurgical techniques have been used for the recycling of EAFD, mainly for the extraction of zinc. Its use as a construction material or as a filler in acoustic and thermal insulators has also been studied (Al-harashsheh *et al.*, 2018). Pyrometallurgical processes have been the traditional recycling route: zinc and lead are volatilized and collected as oxides, while an iron-rich slag is obtained. For these processes, temperatures between 900 and 1000 °C are required (Gamboa, 2017) for the chemical reactions to occur. These routes require sizeable capital investments and energy consumption, in addition to the generation of a significant amount of toxic gases. Metals, such as copper and nickel cannot be recovered during these processes and remain in the slag (Buzin *et al.*, 2017).

Hydrometallurgical processes for zinc recovery have been implemented using conventional inorganic acids and alternative solutions. The leaching processes have been successful at extreme conditions of pH, concentration, pressure and temperature. The authors have studied EAFD dissolutions with HNO₃, HCl and H₂SO₄ to obtain elevated zinc leaching rates); however, these methods present some disadvantages that are consistent with the work of other authors: 1) in addition to zinc extraction, the undesired metals (i.e., iron, copper, etc.) are also dissolve into the solution and 2) the acidic solution is corrosive to the metallurgical instruments, leading to a higher cost of recovery. The operation using HNO₃ is expensive,

non-ecological and generally unsafe (Al-harashsheh *et al.*, 2018a). With H₂SO₄, the dissolution of the metal is favored by increasing temperature: Extractions of 50%, 55% and slightly more than 60% of zinc were reached at temperatures between 20 and 80 °C (Havlik *et al.*, 2005; Oustadakis *et al.*, 2010], although with co-dissolution of large amounts of iron (approximately 45%). Studies carried out using some organic reagents (acetic and tartaric acid) (De La Torre *et al.*, 2013), also showed no selectivity, as the main drawback. Since EAFD originates from steel processes, the iron content in the EAFD is elevated. Its mass fraction is even higher in some iron ores that are currently depleted (Al-harashsheh *et al.*, 2018a).

Some routes of Pyro-hydrometallurgical operations to selectively extract zinc have been worked, by microwave treatment of EAFD mixed with tetrabromobisphenol A (TBBPA) and polyvinyl chloride (PVC) (Al-Harashsheh *et al.*, 2017; Al-Harashsheh *et al.*, 2014). The conditions microwave pyrolysis followed by water leaching were found to be not very efficient for recovery of Zn, using TBBPA-EAFD mixtures, due to the reduction of the metal into its metallic form by the carbonaceous materials left after TBBPA decomposition (Al-Harashsheh *et al.*, 2018b, 2018c; Al-Harashsheh *et al.*, 2017); on the other hand, the PVC-EAFD mixtures achieved 90% of Zn recovery but almost 30% for iron (Al-Harashsheh *et al.*, 2017); more works should be carried out to evaluate the possibility of hazardous emission (dioxins) by the pyrolysis of PVC (Al-Harashsheh *et al.*, 2014; Al-Harashsheh *et al.*, 2015).

A selective leach is necessary to avoid difficulties in the later stages of electrolytic recovery (Torres and Lapidus, 2017). Previous studies have shown that carboxylic agents, besides, to be efficient in the extraction of elements such as As, Pb, Mn, Zn, Cd, and Cr (García *et al.*, 2015), have the property of achieving an interesting selectivity in the dissolution of large amounts of metals such as zinc and only small amounts of iron, from industrial waste (Steer and Griffiths, 2013). For this reason, this research proposes a hydrometallurgical process to selectively extract zinc from the EAFD, under moderate conditions of concentration, pressure and temperature. To optimize the process, leaching was carried out using two different organic carboxylic anions to determine their efficacy: sodium citrate and oxalic acid. The use of these agents to recycle EAFD would enable a more ecofriendly process, since these leaching solutions can be reused in several leaching/ recovery cycles, without a considerable decline in their metal dissolution

capacity (Torres and Lapidus, 2017), producing an iron-rich residue for the reincorporation into the steel industry processes.

2 Materials and methods

2.1 Sample characterization

The EAFD employed in the present study was collected from off-gas cleaning system of an electric arc furnace that processes steel from scrap metal in Colombia. The granulometry of the waste was determined through wet sieving tests, using sieves of the ASTM-E-11 series. Table 1 reveals that the grain sizes (diameters) of the EAFD particles have a homogeneous trend. Therefore, for the investigation, EAFD sample was used as received from the steel plant. However, to avoid possible biases in the selection of the sample, the batch was mixed before each test.

The digestion was carried out by reacting 0.1 g of EAFD with 100 ml of aqua regia (HCl: HNO₃ 3: 1 v/v) at 80 °C. An analog magnetic stirrer (MR-3001 C / C HEIDOLPH®) was used; the stirring speed was fixed at 150 rpm. The samples were analyzed by emission spectroscopy: inductively coupled plasma (Agilent 4210 MP-AES), by using the patterns and conditions suggested by the manufacturer. Table 2 shows that the main metals of the EAFD are Zn and Fe, while Cu, Pb, K, Cr and Mn are found in lower proportions. Therefore, due to their low concentration in the EAFD, and their negligible dissolution in leaching (data not included), these elements will not be taken into account in the present study. Likewise, compounds such as silicates, (characteristic of electric arc furnace slag), which are not dissolved by the aqua regia, would hardly achieve it in less aggressive

solutions (such as the 2 carboxylic agents studied). The solid from the digestion showed a weight loss of approximately 75%.

The mineralogical phases present were determined by X-ray diffraction analysis (XRD) (Panalytical X'pert Pro), using Bragg-Brentane geometry with a cobalt tube. Being a steel waste, EAFD is expected to consist mainly of Fe and alloying elements contained in scrap. Due to the oxygen injection intensity and process temperature in different periods of melting, most of these elements should appear combined with oxygen (Buzin *et al.*, 2017). The ICDD® database (International Center for Diffraction Data) allowed contrasting the peaks shown in the diffractogram (Fig. 1). Effectively, the identified major phases were mixed oxides, corresponding to magnetite (Fe₃O₄), franklinite (ZnFe₂O₄) and less stable oxides such as the zincite (ZnO) and hematite (Fe₂O₃). Small peaks of other compounds were also found in the dust as PbO, Cu₂O and SiO₂. The X-ray diffraction pattern of this EAFD sample agrees with the findings of other authors (Hagni *et al.*, 1991; Buzin *et al.*, 2017).

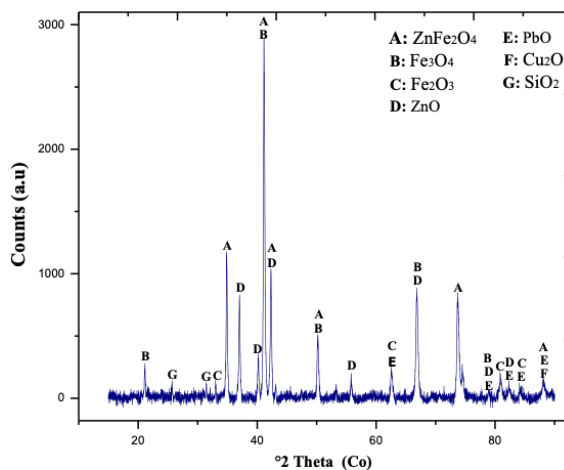


Fig. 1. Diffractogram of EAFD as received.

Table 1. Particle size distribution of EAFD.

Diameter opening, μm	+425	+250	+150	+106	+75	+63	-63	Total
% Retention	15.9	12.3	17.2	12.4	14.8	10.8	16.6	100

Table 2. Heavy metal content of EAFD.

Element	Fe	Zn	Pb	Cu	K	Cr	Mn
Content (%)	31.6	24.7	1.7	0.22	0.94	0.15	1.96

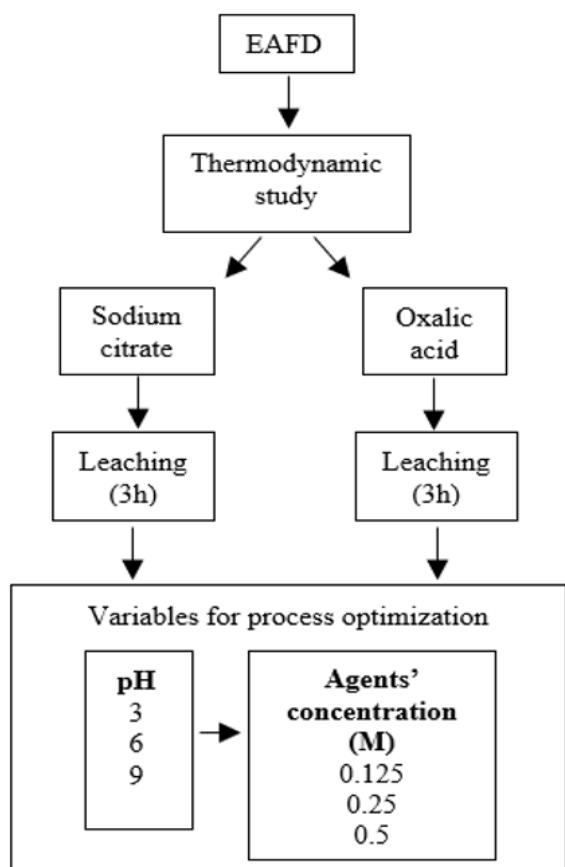


Fig. 2. Diagram of the experimental procedure.

2.2 Leaching experiments

Leaching solutions were prepared using deionized water and analytical grade reagents (J.T. Baker™); the concentrations were specific for each experiment. The pH was adjusted with a dilute solution of HNO_3 and NaHCO_3 .

The leaching experiments were carried out in a glass reactor with a solid: liquid ratio of 25 g per liter, at 17°C and ambient pressure (1.022 bar). Compact digital agitators (Model 50006-03, COLE-PARMER), with shovel-type propellers, were used. In preliminary studies, the leaching rate found to be independent of stirring speeds above 250 rpm. Samples of the leaching solution were taken each hour and their metal content was quantified by inductively coupled plasma atomic emission spectroscopy. All of the thermodynamic data of soluble species used in the document were obtained from the NIST database (NIST, 2004). The corresponding predominance diagrams were designed

using the MEDUSA® software (Making Equilibrium Diagrams Using Simple Algorithms) (Eriksson, 1979; Puigdomenech, 2004). The solution potential was monitored by using a saturated Ag / AgCl electrode (Oakton pH ORP 700 Benchtop Meter); all values were later adjusted to the standard hydrogen electrode (SHE). Some of the leaching parameters were varied to determine their effect on the efficiency of each agent in zinc leaching. The experimental methodology is described in Figure 2.

3 Results and discussion

3.1 Thermodynamic study

For the hydrometallurgical process, predominance diagrams are an important tool to determine conditions of potential and pH, that favor the chemical reaction between the carboxylic acids and metal ions contained in the EAFD.

Figure 3 shows the stability zones for the formation of soluble complexes. Since the experimentally measured potentials in both systems were 390-470 mV and 412-640 mV for sodium citrate and oxalic acid, respectively, the predominant iron species was Fe(III). Consequently, for both agents, the formation of soluble metal species with the two reagents is limited by pH and not by potential (Fig. 3) and the solution potential will not be discussed in this study. Both sodium citrate (hereinafter Cit) and oxalic acid (hereinafter Ox) dissolve zinc in a pH range between 1 and 10.7, and its maximum is limited by the stability line with the solid species ZnO (Fig 3a; 3c). This wide pH range for the formation of soluble species is due to the interaction between the strong bonds of the organic anions Cit and Ox and the Zn ions (Pinna *et al.*, 2019).

Thermodynamic analysis for iron shows that the only solid-state species (Fe_2O_3) occurs at a pH greater than 6.5 for both carboxylic agents (Fig. 3b-3d). Iron can dissolve at pH 3 and 6; however, only solid species are expected to form at higher pH values. In this manner, selective zinc leaching could be achieved in alkaline pH values, where Cit and Ox complexes show a wide range of pH stability. To establish the condition that dissolves the largest amount of zinc, 3 different pH values were tested. The experiments were carried out varying the pH in 3, 6 and 9.

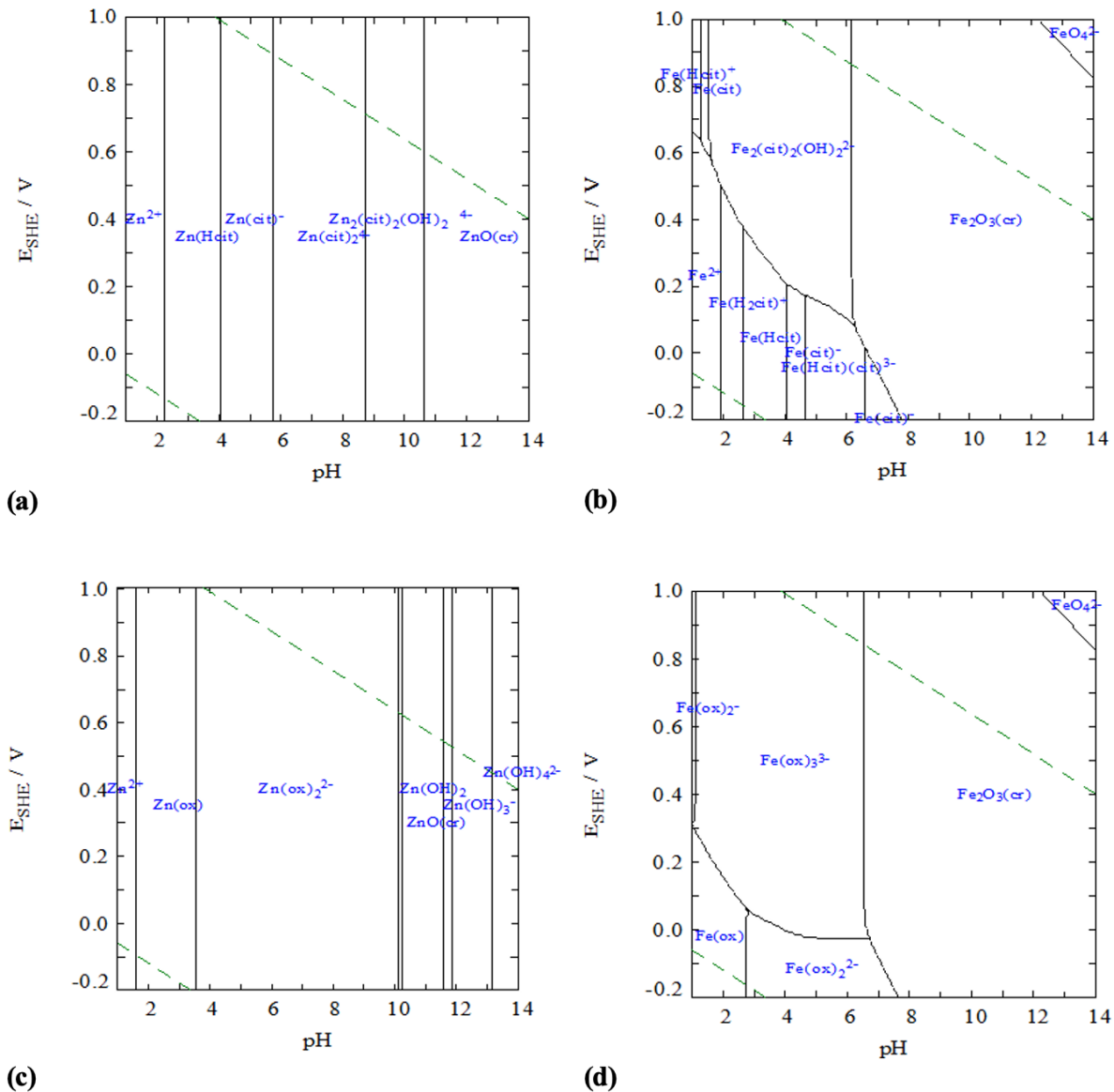


Fig. 3. Predominance diagrams for zinc and iron at 25°C, in the presence of Citrate (Cit) or Oxalate (Ox) ions. Conditions: 0.5 M Cit- or Ox-; 0.06 M Zn and 0.1 M Fe. Designed with MEDUSA ® software.

3.2 Effect of pH in citrate solutions

Leaching tests with citrate were favorable at pH 3 and 6, while under alkaline conditions, only 10% of the zinc dissolved (Fig. 4). The formation of complexes from the organic ligand Cit³⁻ and the divalent cation Zn²⁺, is dependent on pH; according to the energies of each reaction, the system evolution reaches the most stable energy state under acidic conditions

(Appendix A). The leaching process is selective since the dissolution of iron is almost negligible. This is due to the stability of its compounds (equations 4, and 5 from Appendix A) contained in the EAFD; as indicated in the X-ray diffraction study (Fig. 1), iron is mainly present in the form of fairly stable and poorly soluble spinels (Carriazo *et al.*, 2017; Chairaksa-Fujimoto *et al.*, 2016; Langová *et al.*, 2009), which do not dissolve in the solution.

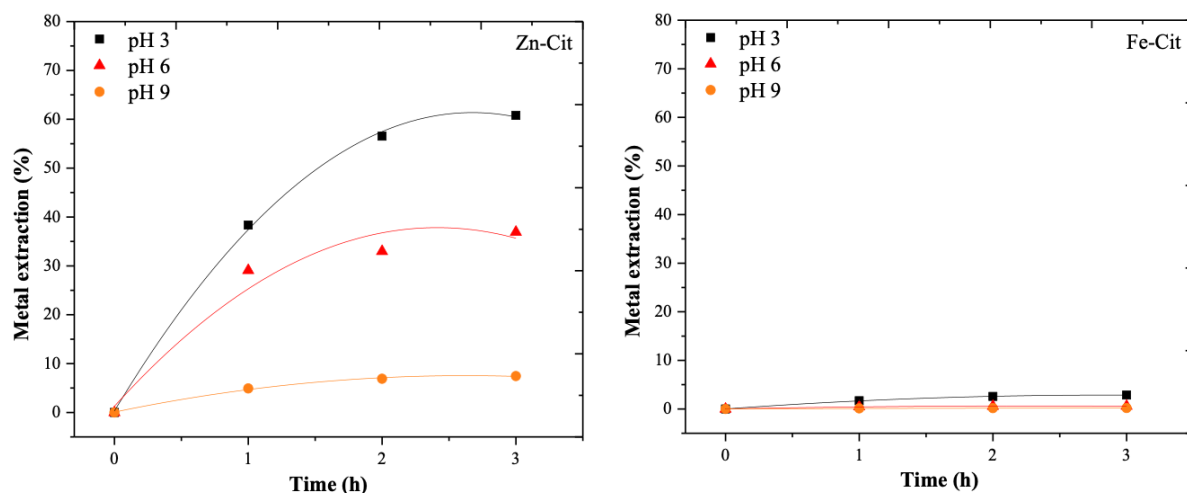


Fig. 4. Effect of pH (3,6,9) on the extraction zinc and iron from EAFD in citrate solutions. Conditions: Cit 0.5 M; 500 rpm; 25 g EAFD /1 L.

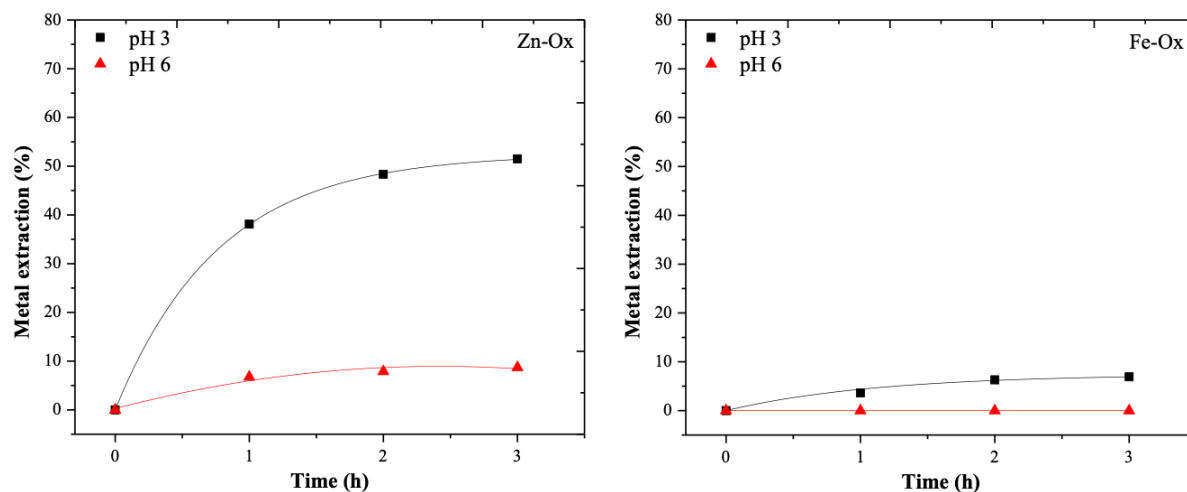
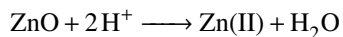


Fig. 5. Effect of pH (3,6) on the extraction zinc and iron from EAFD in oxalate solutions. Conditions: Ox 0.5 M; 500 rpm; 25 g EAFD /1 L.

The kinetics of zinc leaching at pH 3 is dictated by the solid species and the leaching solution. There are two main zinc phases in this residue, ZnO and ZnFe₂O₄; the latter phase is quite refractory, as may be observed in (Appendix A). The high initial extraction slope in the first hour is highly dependent on the acid concentration and is probably due to the dissolution of ZnO:



When the curve takes on an asymptotic behavior, it is probably indicating that the leachable specie ZnO is running out and only spinel phase remains, evidenced by the negligible amount of iron leached. The specific criteria of process kinetics are beyond the scope of this study and are in the process of publication by the authors.

3.3 Effect of pH in Ox solutions

The effect of pH on zinc and iron extractions in oxalate solutions was determined by applying the

same method as for citrate. However, the experiment at pH 9 was not possible due to the low solubility of the oxalate ion: 3.7 g /100 mL. In Ox solutions, metals dissolution even more dependent on pH (Fig.5), achieving very little extraction at pH 6.

The main driving force for leaching metal cations with Ox comes from the action of the H^+ ions present in the medium (Wu *et al.*, 2018; Mazurek, 2013). However, the increased iron extraction at pH 3 could be due to its elevated stability of iron oxalate complexes, as shown in Appendix A.

3.4 Use of Cit Vs Ox in zinc leaching

According to the results described above, the zinc dissolution in the oxidized state is favored in acidic media; therefore, pH 3 was the chosen condition for the continuation of this study. The two carboxylic agents, as n-dentate ligands, form soluble zinc chelates (Fig. 6). The solubility of Zinc is due to its affinity with organic ligands that form complexes and make dissolution possible (García *et al.*, 2015). After 3 hours of leaching zinc extraction was favored with both agents, although Cit achieved better results over Ox.

As for iron, Ox is a good reducing and complexing agent for many Fe^{3+} containing metal oxides (spinel in which much of the iron is found Fig. 1) (Avery, 1974; Wentworth and Ladner, 1975). The extraction achieved by Ox was twice that of Cit. This result does not favor the process since greater iron dissolution into the solution creates problems in subsequent electrical recovery processes. This highlights the efficiency of sodium Cit, by allowing more selective zinc leaching.

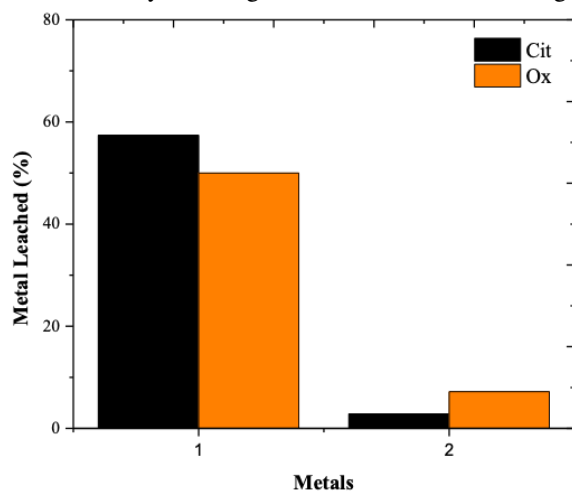


Fig. 6. Cit vs Ox in the final extraction of Zn (1) and Fe (2). Conditions: Cit and Ox 0.5 M, pH 3; 500 rpm; 25g EAFD / 1 L.

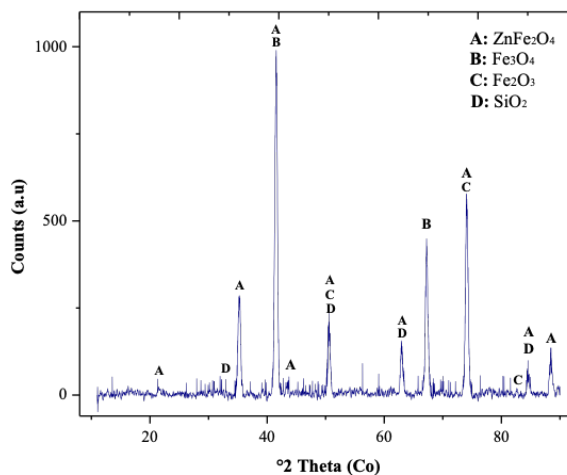


Fig. 7. Diffractogram of EAFD after leaching with Cit pH 3.

Both systems exhibit progressive recovery and rapid kinetics of ZnO, allowing good extractions to be achieved in a short time. The presence of franklinite did not allow total zinc extraction from the EAFD; this is corroborated with the figure 7. The diffraction pattern shows that the major difference between the leached and non-leached EAFD is the disappearance of zincite, cuprite and litharge.

Franklinite peaks remain after leaching, indicating that the percentage of recovered zinc corresponds completely to the zincite dissolution. However, it is difficult for franklinite to provide a conclusion about its exact presence in EAFD before and after leaching, because its XRD pattern is similar to that of magnetite. After leaching, the main EAFD phases are magnetite and / or franklinite and SiO_2 ; the carboxylic anion cannot dissolve them. The franklinite stability requires reducing conditions for its decomposition (Zhang *et al.*, 2011), although this would probably also lead to more iron dissolution.

3.5 Effects of carboxylic agents' concentration

The effect of the Ox and Cit concentrations on the zinc and iron extractions was examined using three different values: 0.125 M, 0.25 M and 0.5. In general, and as expected, metal extraction increased with increasing agents' concentration (Fig. 8). Although Cit achieved the best extractions at all concentrations tested, the increase in extraction was most noticeable with Ox.

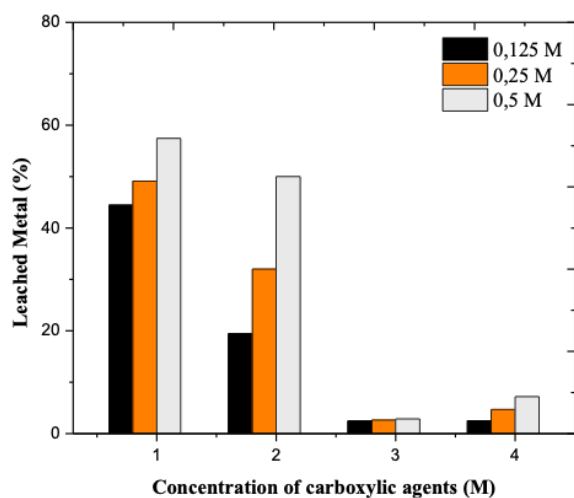


Fig. 8. Effect of concentration of citrate (1=Zn, 3=Fe) and oxalate (2=Zn, 4=Fe). Conditions: Cit and Ox at pH 3; 500 rpm; 25 g EAFD/1 L.

It should be noted that oxalate has the disadvantage of its limited solubility in aqueous media. At higher concentrations, saturation of the solution occurs, which reduces its efficiency.

Conclusions

The extraction of zinc from EAFD was investigated using two different organic carboxylic anions, to achieve a selective leaching (high levels of zinc and low levels of iron). Under ambient conditions and moderate concentrations, a selective leaching route using carboxylic agents, is possible. Reaction kinetics were strongly dependent upon the solution pH, achieving the best zinc extractions under acidic conditions. Metallic extraction increases with increasing molar concentration of the complexing agent. Under the same operating conditions, citrate achieves 10% more zinc extraction and 5% less iron than Ox. The low aqueous solubility of the zinc ferrite in the residue did not allow further zinc extraction under the study conditions. Citrate is suggested as an adequate leaching agent for EAFD, to achieve selective extractions under ambient operating conditions: pH 3, 0.5 M, 25 g EAFD per liter.

Acknowledgements

The authors are grateful for the support received from the VIE - SGI project to carry out this research, as well

as the Grupo Metalurgia No Ferrosa of the Universidad Pedagógica y Tecnológica de Colombia UPTC.

References

- Al-harahsheh M, Al-Nu'airat J, Al-Otoom A, Al-hammouri I, Al-jabali H, Al-zoubi M, Al'asal SA. (2018a). Treatments of electric arc furnace dust and halogenated plastic wastes: A review. *Journal of Environmental Chemical Engineering*. <https://doi.org/10.1016/j.jece.2018.102856>
- Al-Harahsheh, M., Aljarrah, M., Al-Otoom, A., Altarawneh, M., & Kingman, S. (2018b). Pyrolysis kinetics of tetrabromobisphenol a (TBBPA) and electric arc furnace dust mixtures. *Thermochimica Acta* 660, 61-69. <https://doi.org/10.1016/j.tca.2017.12.022>
- Al-Harahsheh, M., Aljarrah, M., Rummanah, F., Abdel-Latif, K., & Kingman, S. (2017). Leaching of valuable metals from electric arc furnace dust–Tetrabromobisphenol A pyrolysis residues. *Journal of Analytical and Applied Pyrolysis* 125, 50-60. <https://doi.org/10.1016/j.jaap.2017.04.019>
- Al-Harahsheh, M., Al-Otoom, A., Al-Jarrah, M., Altarawneh, M., & Kingman, S. (2018c). Thermal analysis on the pyrolysis of tetrabromobisphenol a and electric arc furnace dust mixtures. *Metallurgical and Materials Transactions B* 49, 45-60. <https://doi.org/10.1007/s11663-017-1121-7>
- Al-Harahsheh, M., Al-Otoom, A., Al-Makhadmah, L., Hamilton, I. E., Kingman, S., Al-Asheh, S., & Hararah, M. (2015). Pyrolysis of poly(vinyl chloride) and–Electric arc furnacedust mixtures. *Journal of Hazardous Materials* 299, 425-436. <https://doi.org/10.1016/j.jhazmat.2015.06.041>
- Al-harahsheh, M., Kingman, S., Al-Makhadmah, L., & Hamilton, I. E. (2014). Microwave treatment of electric arc furnace dust with PVC: Dielectric characterization and pyrolysis-leaching. *Journal of Hazardous Materials* 274, 87-97. <https://doi.org/10.1016/j.jhazmat.2014.03.019>

- Asturiana de Zinc (2017). *Principales aplicaciones del zinc*. Disponible en: <https://www.azsa.es/es/CalidadProductos/todo-sobre-el-zinc/Paginas/Principales-Aplicaciones-del-Zinc.aspx>. Consultado: 14 de agosto de 2020
- Avery, H.E. (1974). *Basic Reaction Kinetics and Mechanisms*, London, England: Macmillan Publishers Ltd.
- Buzin, P. J. W. K. de, Heck, N. C., & Vilela, A. C. F. (2017). EAF dust: An overview on the influences of physical, chemical and mineral features in its recycling and waste incorporation routes. *Journal of Materials Research and Technology* 6, pp. 194-202. <https://doi.org/10.1016/j.jmrt.2016.10.002>
- Carriazo, J. G., Noval, V. E., and Ochoa, C. (2017). Magnetita (Fe₃O₄): Una estructura inorgánica con múltiples aplicaciones en catálisis heterogénea. *Revista Colombiana de Química* 46, pp. 42. <https://doi.org/10.15446/rev.colomb.quim.v46n1.62831>
- Chairaksa-Fujimoto, R., Maruyama, K., Miki, T., and Nagasaka, T. (2016). The selective alkaline leaching of zinc oxide from Electric Arc Furnace dust pre-treated with calcium oxide. *Hydrometallurgy* 159, pp. 120-125. <https://doi.org/10.1016/j.hydromet.2015.11.009>
- De La Torre, E., Guevara, A. and Espinoza, C. (2013). Valorización de polvos de acería, mediante recuperación de zinc por lixiviación y electrólisis. *Revista Politécnica* 32, pp. 51-56.
- Eriksson, G. (1979). An algorithm for the computation of aqueous multicomponent, multiphase equilibria. *Anal. Chim. Acta* 112, pp. 375-383.
- Gamboa, O. (2017). *Optimización de los Parámetros de Operación del Proceso de Reciclado de Zinc*. Tesis de maestría en Ciencias de Ingeniería Metalúrgica. Instituto Politécnico Nacional, Ciudad de México, México.
- García-Arreola, M.E; Soriano-Pérez, S.H; Flores-Vélez, L.M; Cano-Rodríguez, I; Alonso-Dávila, P.A. (2015). Comparación de ensayos de lixiviación estáticos de elementos tóxicos en residuos mineros. *Revista Mexicana de Ingeniería Química* 14, 109-117.
- Hagni, A.M., Hagni, R.D. and Demars, C. (1991). Mineralogical characteristics of electric arc furnace dusts. *JOM* 43, pp. 28-30. <https://doi.org/10.1007/bf03220543>
- Havlik, T., Turzakova, M., Stopic, S., and Friedrich, B. (2005). Atmospheric leaching of EAF dust with diluted sulphuric acid. *Hydrometallurgy* 77, pp. 41-5. <https://doi.org/10.1016/j.hydromet.2004.10.008>
- Laforest, G., and Duchesne, J., (2006). Stabilization of electric arc furnace dust by the use of cementitious materials: Ionic competition and long-term leachability. *Cement and Concrete Research* 36, pp. 1628-1634. <https://doi.org/10.1016/j.cemconres.2006.05.012>
- Langová, S., Leško, J., and Matýsek, D. (2009). Selective leaching of zinc from zinc ferrite with hydrochloric acid. *Hydrometallurgy* 95, pp. 179-182. <https://doi.org/10.1016/j.hydromet.2008.05.040>
- Madias, J. (2009). Reciclado de polvos de horno eléctrico. *Acero Latinoamericano* 23, 38.
- Mazurek, K. (2013). Recovery of vanadium, potassium and iron from a spent vanadium catalyst by oxalic acid solution leaching, precipitation and ion exchange processes. *Hydrometallurgy* 134, pp. 26-31. <https://doi.org/10.1016/j.hydromet.2013.01.011>
- NIST, (2004). *Critically Selected Stability Constants of Metal Compls*. NIST Standard Reference Database 46, Version 8.0.
- Oustadakis, P., Tsakiridis, P. E., Katsiapi, A., and Agatzini-Leonardou, S. (2010). Hydrometallurgical process for zinc recovery from electric arc furnace dust (EAFD). *Journal of Hazardous Materials* 179, pp. 1-7. <https://doi.org/10.1016/j.jhazmat.2010.01.059>
- Pinna, E.G.; Martinez, A.A; Tunez, F.M; Drajlín, D.S; Rodríguez, M.H. (2019). Acid leaching of LiCoO₂ from LiBs: Thermodynamic study and reducing agent effect. *Revista Mexicana de Ingeniería Química* 18, 441-450. <https://doi.org/10.24275/uam/izt/dcbi/revmexingquim/2019v18n2/Pinna>

- Puigdomenech, I. (2004). *Make Equilibrium Diagrams Using Sophisticated Algorithms (MEDUSA)*. Inorganic Chemistry, Royal Institute of technology. <https://sites.google.com/site/chemdiagr/>
- Steer, J. M., and Griffiths, A. J. (2013). Investigation of carboxylic acids and non-aqueous solvents for the selective leaching of zinc from blast furnace dust slurry. *Hydrometallurgy* 140, pp. 34-41. <https://doi.org/10.1016/j.hydromet.2013.08.011>
- Torres, R., and Lapidus, G. T. (2017). Closed circuit recovery of copper, lead and iron from electronic waste with citrate solutions. *Waste Management* 60, pp. 561-568. <https://doi.org/10.1016/j.wasman.2016.12.001>
- Wentworth, WE. & Ladner, SJ. (1975). *Fundamentos de Química Física*. Barcelona, España: Reverté.
- Wu, W., Wang, C., Bao, W., and Li, H. (2018). Selective reduction leaching of vanadium and iron by oxalic acid from spent V₂O₅-WO₃/TiO₂ catalyst, *Hydrometallurgy* 179, pp. 52-5. <https://doi.org/10.1016/j.hydromet.2018.05.021>
- Zhang, Y., Deng, J., Chen, J., Yu, R., and Xing, X. (2014). The electrowinning of zinc from sodium hydroxide solutions. *Hydrometallurgy* 146, 59-63, <https://doi.org/10.1016/j.hydromet.2014.03.006>
- Zhang, Y., Yu, X., and Li, X. (2011). Zinc recovery from franklinite by sulphation roasting. *Hydrometallurgy* 109, pp. 211-214. <https://doi.org/10.1016/j.hydromet.2011.07.002>
- Zhu, X., Xu, C., Tang, J., Hua, Y., Zhang, Q., Liu, H., Wang, X., and HUANG, M. (2019). Selective recovery of zinc from zinc oxide dust using choline chloride based deep eutectic solvents. *Transactions of Nonferrous Metals Society of China* 29, pp. 2222-2228. [https://doi.org/10.1016/s1003-6326\(19\)65128-9](https://doi.org/10.1016/s1003-6326(19)65128-9)

Appendix

Thermochemical data for the reaction product of Zn and Fe leaching (NIST, 2004).

Equation	ΔG , J/mol
$Zn^{2+} + H^+ + Cit^{3-} = Zn(HCit)$	-58,544 (1)
$Zn^{2+} + 2 Cit^{3-} = Zn(Cit)_2^{4-}$	-42,624 (2)
$2 Zn^{2+} + 2 Cit^{3-} + 2 OH^- = Zn_2(Cit)_2(OH)_2^{4-}$	-148,299 (3)
$Fe^{3+} + Cit^{3-} = Fe(Cit)$	-75,407 (4)
$2 Fe^{3+} + 2 Cit^{3-} + 2 OH^- = Fe_2(Cit)_2(OH)_2^{2-}$	-299,280 (5)
$2 Fe^{3+} + 6 OH^- = Fe_2O_{3(s)} + 3 H_2O$	-476,965 (6)
$Zn^{2+} + 2 OH^- = ZnO_{(s)}$	-95,861 (7)
$Zn^{2+} + 2 Fe_3^+ + 8 OH^- = ZnFe_2O_{4(s)} + 4 H_2O$	-581,882 (8)
$Zn^{2+} + Ox^{2-} = Zn(Ox)$	-27,788 (9)
$Zn^{2+} + 2 Ox^{2-} = Zn(Ox)_2^{2-}$	-43,879 (10)
$Fe^{3+} + 2 Ox^{2-} = Fe(Ox)_2^-$	-92,723 (11)
$Fe^{3+} + 3 Ox^{2-} = Fe(Ox)_3^{3-}$	-116,859 (12)