

Effect of Acid Treatment on the Recovery of Valuable Metals from Steel Plant Exhaust

Zeeshan A. Hameed¹, Junaid Saleem^{2,3,*}, Hira Lal², Ahsan Abdul Ghani² and Muhammad Shoaib²

¹Department of Quality Assurance, Peoples Steel Mills Ltd., Karachi, Pakistan

²Department of Chemical Engineering, University of Karachi, Karachi, Pakistan

³Department of Mechanical Engineering, DHA Suffa University, Karachi, Pakistan

Abstract: The response of different metals such as Zn, Fe, Pb, Cr and Mn during leaching of Electric Arc Furnace (EAF) dust in acid medium has been investigated. The major proportion of EAF dust constitutes of these metals and their recovery by means of a chemical process is not only economical but also imparts positive impact on the environment. The leaching of metals from dust is achieved using different concentration of sulphuric acid, and the dust samples have been characterized both before and after leaching. Based on the results, several recommendations have been suggested for the optimization of H₂SO₄ concentration, that lead to the maximum recovery of these metals. Under the optimized conditions, it has been determined that the satisfactory leaching yield of Zn (95%) can be obtained at a concentration of 1M.

Keywords: Electric arc furnace dust, Sulphuric acid, Leaching, Sustainable environment, Zn recovery.

1. INTRODUCTION

Steel manufacturing industry recycles around 30 million tons waste per year. These waste materials in powdered form, produced by two major routes: Basic Oxygen Furnace (BOF), uses primary sources such as iron oxide with addition of base chemical, and Electric Arc Furnace (EAF), which is used primarily to re-melt scrap steel for making special type of steel with the advantage of energy saving system [1]. In 2008, the BOF related to about 67.1% of steel making while EAF was 30.6% of the steel produced in same year [2]. Both technologies have certain environmental impacts, EAF technique is advantageous for economic reason [3].

Nowadays the production of steel through EAF is one of the fastest emerging sector of manufacturing industries all over the world, and accounts for a little over one third of total world output. During the steelmaking process, temperature of electric arc furnace (EAF) can reach up to 1600°C or more, and many components in the feed, including: lead, zinc, chromium, manganese, iron and cadmium are converted into the vapour phase [4], and release in large quantity as a critical hazardous waste (class I, code K061), according to the European Waste Catalogue and Hazardous Waste List. Inhalation of Cd and Pb fumes or particles may cause kidney damage and diminish intellectual capacity; nose bleeding has been observed among workers in industries that

produce compound of Pb and Cr [5], these heavy metals are released beyond the range of disposable landfills as per EPA, USA [6]. Due to depletion of high grade natural ores/concentrates and increasing metals prices, these types of industrial wastes are gaining significance for the maximum recovery of valuable metals [7, 8]. The world generation of EAF dust is estimated to be 5–7 million tons per year [9, 12]; steel production through EAF produces about 15-20kg per ton of steel which contain Zn, Pb and Cr(VI) together with Fe; whereas Zn, due to the relatively large amount present, is the most valuable component [10, 11]. Therefore, the maximum recovery of Zn from EAF dust is a feasible option due to its low production cost [12].

In this connection different methods are developed: mineral beneficiation (mechanical, physical and physiochemical) and extractive metallurgy (Pyrometallurgical and hydrometallurgical), to process these powders with the aim of leaching the valuable metals [13, 14]. Pyrometallurgical processes are classified taking into account the technology used, the main technologies including: plasma technology, converter technology, electric arc technology and Waelz kiln technology (the most common one) [15, 16]; which work in large-scale and therefore the dust must be assembled from various sources and conveyed to relatively large processing plant. These processes are operated at high temperature and only 70% of total zinc recovery can be obtained [17, 18]. Also product of pyrometallurgical process has high consumption of reducing agent, usually have low commercial value and represented by impure ZnO [19].

*Address correspondence to this author at the Department of Mechanical Engineering, DHA Suffa University, Karachi, Pakistan; Tel: 00922135244854; Fax: 00922135244855; E-mail: Junaidupm@gmail.com

These challenges were fulfilled by variety of hydrometallurgical processes which require low thermal energy such as atmospheric acid leaching [20], microwave caustic leaching [22], high pressure acid leaching [21], two-stage acid leaching [18] and the reactions with different acids [20, 23–26] or with concentrated alkaline solution have been studied [10, 18, 24, 26, 27]. The hybridization of pyrometallurgical or hydrometallurgical routes were also applied for the recovery of zinc from EAF dust [12]. Hydrometallurgy is an interesting way to recover zinc from EAF dusts as it consumes less energy [16, 23], and no problems associated with off-gases and dust nuisance [28]. The treating of EAF dust, directly in the primary hydrometallurgical zinc production has the advantages of sophisticated control, lower capital and operating costs compared with pyrometallurgical ones, and production of valuable metal of high commercial grade [29].

For the maximum recovery of zinc, an acid leaching step is required in which sulphuric or hydrochloric acid liquors can be used. Sulphuric acid leaching is considered more suitable in comparison with hydrochloric acid because of the absence of chloride ion, furthermore zinc recovery of around 75 – 90 wt% has also been achieved using sulphuric acid [23].

In Pakistan several types of zinc-containing waste material are available; these include: electric arc furnace flue dust, zinc scrap and spent dry cell batteries out of which major proportion of zinc found in EAF dust in different forms. The contents of Zn, Fe and Pb in EAF dust according to global perspective state that the highest percentage of zinc is available in Pakistani EAF flue dust [30–35], which is due to the fact that the scrap used in steelmaking is of old automobile galvanized steel Hence to meet economic benefit and stringent environmental rules, it is practical to recover zinc from flue dust.

2. EXPERIMENTAL SECTION

2.1. Characterization Techniques

Chemical composition of the dust sample was determined by wet chemical method (WCM). Trace elements were analyzed as pressed pellet through Axios^{max}, WD-XRF spectrometer of 3KW X-ray tube. The pressed pellets were prepared at 6:1 (sample: binder) with the help of Omnia standard application of PANalytical origin. Mineralogical structures of dried leaching residue and original samples were analyzed by X-ray diffraction spectrometer with CuK α radiation was used. The patterns were recorded over the range

10-90 degree 2 theta and counting time of 3 seconds per step.

2.2. Materials and Experimental Procedure

EAF flue dust used in this study having particle size (D_{50}) from 0.84-2.15 μm , was not exposed to any metallurgical pre-treatment; it is evident that smaller the particle size, faster is the dissolution rate. All experiments were performed at atmospheric pressure, elevated temperature and chemicals used were of analytical grade. These operational conditions were chosen in order to know the extent of leaching reaction; although leaching start at earlier stages that could not explain the complete residual analysis of leachates and leftover product. It is possible that working at higher temperature improve process and this has been investigated in this study.

The studies were carried out for selective leaching of zinc (and other heavy metals) out of EAF flue dust, and metals composition in residue left after completion of leaching (2 h). The main factors investigated in this work are the effect of different acid concentrations on fixed liquid-to-solid ratio (50 ml/gm), time (2 h) and agitation speed (300 rpm), on recovery of Zn, Fe, Pb, Mn and Cr. The quantitative analysis of residual solid was accomplished and the effect of residual metals composition was analyzed after completion of leaching.

2.2.1. Leaching Stage

EAF flue dust was provided by Peoples Steel Mills Ltd., Pakistan. EAF dust is firstly leached with distilled water to remove traces of soluble chlorides which could cause damage to electrode and complexities in reaction during electrowinning [36, 37].

Leaching experiments of EAF flue dust were performed in the semi-batch reactor, 500 ml capacity, made out of glass, provided with opening at top in which the axis of propeller type mechanical stirrer, for adjustable revolutions was placed. Stirring speed was kept at 300 rpm, since the leaching yield of zinc increased for increasing rpm (100; 200; 300) and remains almost constant when rpm exceeded by 300. Opening for sampling liquid specimen, alcoholic thermometer and powdered sampling were fitted at top of reactor and baffle fitted along the wall to break the vortex formed; this improves the mixing and enhance reaction rate. The reactor was made isothermal to conduct leaching at desired temperature using water bath controlled by a thermostat. To study kinetics, leaching experiments were performed with solution of

400 ml of different acid concentrations 0.1, 0.5, 1 and 1.5 M H₂SO₄ concentration. The sample weight was taken as 8 g, measured on analytical weight balance. A solution with acid-to-EAF dust ratio (ml/g) of 50 was used since high ratio will increase the recovery of metals present in the dust. The residual solid was analyzed for temperatures 90°C, under normal atmospheric pressure.

Eight grams of EAF dust sample containing 3.268 g of zinc were leached for total reacting of this zinc amount, 3.88 mL of concentrated H₂SO₄ are theoretically necessary. Volume needed at different concentration is given in Table 1.

Table 1: Amount of Sulphuric Acid Required at Different Concentration

H ₂ SO ₄ concentration (M)	H ₂ SO ₄ amount (ml)
0.1	2.76
0.5	13.77
1.0	27.55
1.5	41.6

2.2.2. Filtration Stage

The filtration step, made after each stage, took place in Whatman quantitative ash-free filter paper, Grade 50. Each filter paper weighed before filtration. Samples after filtration are collected into the vial bottles revealing clear solutions. The solution was colorless, weakly yellow or light green depending on leaching conditions and proportion of valuable component transferred into the solution.

2.2.3. Elemental Analysis Equipment

Residue left after leaching was weighed, then dried in an oven at around 120°C to remove all the moisture present. The residue was then analyzed using XRF for chemical analysis, these solid samples must be broken down in aqua regia-HF solution. All the samples were diluted in order to be in the calibration range. Trace elements in residue were analyzed as pressed pellet through Axios^{max}, WD-XRF spectrometer of 3KW X-ray tube. No other components in the rest of the solution were traced.

3. RESULTS AND DISCUSSION

3.1. Characterization of Samples

Chemical composition of dust samples is provided in Table 2, which shows that it is rich in valuable metals

including 41.446% Zn, 15.471% Fe and 2.03% Pb. In addition K and Ca are also present and can be easily leached out by ion exchange technique [28]. Chemical composition of EAF flue dust depends on types of steel, quality of scraps being processed, operating conditions, recycling of dust and efficiency of de-dusting plant to capture the dust and molten metal to slag thermodynamic reactions.

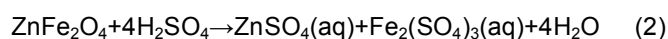
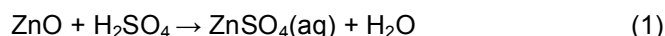
Table 2: Chemical Composition of EAFD by Wet Chemical & XRF Spectrometer

Substance	Composition (%)
Mg	0.694
Cu	0.226
Zn	41.446
Fe	15.471
Mn	0.905
K	1.019
Ca	0.914
Pb	2.031
Cr	0.260

The X-ray diffraction pattern of the indigenous EAF dust sample is shown in Figure 1. In the original sample major peaks of zincite (ZnO), franklinite (ZnFe₂O₄) and magnetite (Fe₃O₄) were identified in which ZnO has four distinct peaks with 2θ angle of 31.77°, 34.42°, 36.24° and 47.57° were observed. Other phases were also identified with insufficient amounts ashematite (Fe₂O₃) and wustite (FeO). At 0.1 M H₂SO₄ concentration, peak size of franklinite and magnetite was increased, this is due to the fact that ZnFe₂O₄ is slightly soluble in dilute solution of sulphuric acid however, at high concentration (1 M), reduction in peak is responsible for the reaction of same phase in sulphuric acid solution. Increase in concentration has completely suppressed the peak of franklinite and magnetite. It is also observed from XRD results that for all concentrations of H₂SO₄, the peak of zincite completely suppressed. From XRD results, it is also deduced that at higher concentrations of H₂SO₄, Zn has highest selectivity in comparison to other metals.

3.2. Leaching Reactions

The reactions of the main species occurring in the sample and their stoichiometry are as follows:



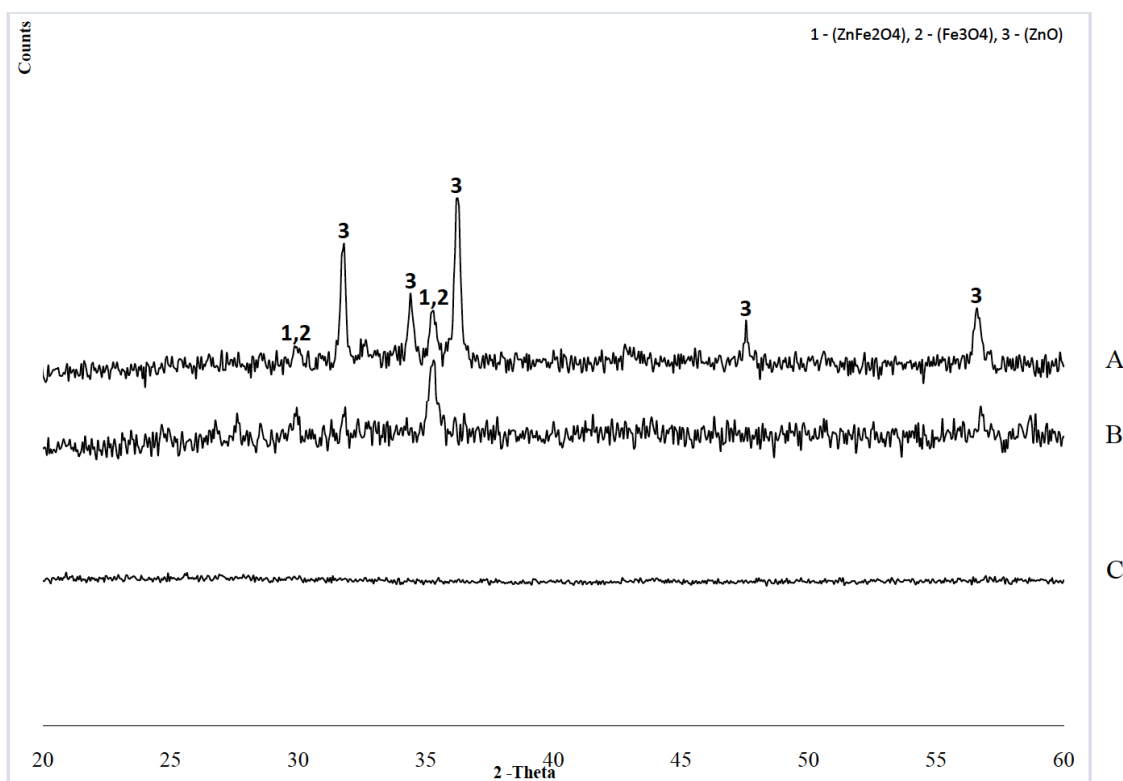
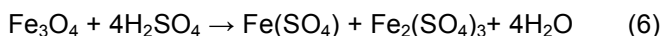
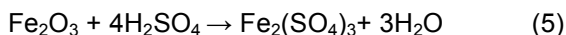
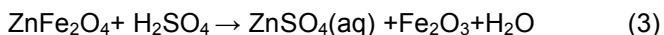


Figure 1: X-ray diffraction results of EAF dust samples (A) Untreated dust, (B) Leaching residue at 0.1 M H₂SO₄, (C) Leaching residue at 1M H₂SO₄.



3.3. Effect of Different Sulphuric Acid Concentrations

The effect of sulphuric acid concentrations was investigated by keeping other conditions constant as liquid-to-solid ratio of 50 ml/g and temperature 90°C in the concentration range of 0.1-1.5 M. The results obtained are shown in Figures 2 and 3.

The effect of H₂SO₄ concentration on Zn, Fe, Pb, Mn and Cr in residue has been determined using XRF technique. Figure 2 shows that increasing concentration sharply decreases the Zn, Fe and Mn percentages in the residue; this indicates Zn preferentially recovered more than Fe and Mn, therefore, leaching of Zn Fe and Mn are strongly dependent on H₂SO₄ concentration. In case of Pb and Cr, increasing acid concentration increases the Pb and Cr in the residue, hence Pb and Cr recovery is poor at the end of the leaching reaction.

Figure 3 shows that recovery of heavy metals increase with increasing acid concentration and follow different pattern for each metal. Leaching yield of Zn increases with the increasing H₂SO₄ concentration up to 1M, however it remains nearly constant after increasing concentration at this point. The effect of leaching time on the dissolution of Zn is evident that at the end of leaching reaction, the zinc recovery at 1 M acid concentration increased up to 95%. Leaching yield of Mn and Cr also increase up to 92 wt% and 88 wt% at high acid concentration i.e. 1.5 M. Recovery rate of Cr is more sluggish initially, and varies linearly at higher concentration of H₂SO₄ while the recovery of Mn increases rapidly at low acid concentration and then the response becomes slow at higher concentration. From recovery trend it is obvious that, due to increasing recovery of Mn and Cr with acid concentration, the cost also increases for separation of pure zinc. XRD patterns of leaching residue indicates that peak of ZnO has suppressed as concentration of acid was raised to 1 M which confirms the shift of Zn from ZnO to ZnSO₄ as the concentration is increased.

4. CONCLUSIONS

In the present study, residual analysis of heavy metals in electric arc furnace flue dust at different sulphuric acid concentration was investigated.

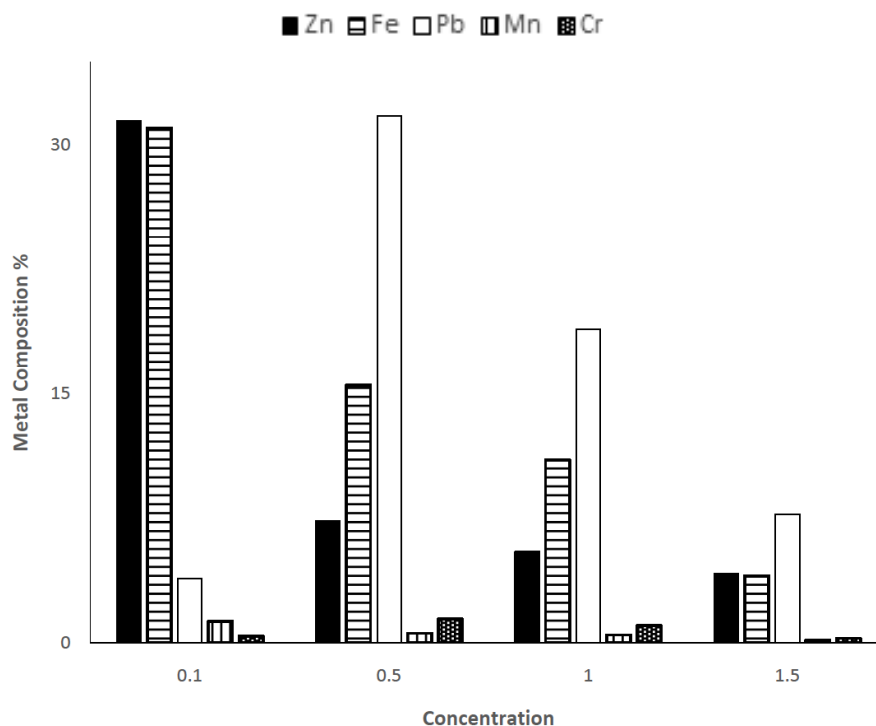


Figure 2: Metal composition (%) in residue at 0.1 M, 0.5 M, 1.0 M and 1.5 M H_2SO_4 after completing of leaching (t: 2 h, N: 300 rpm, T: 90 °C).

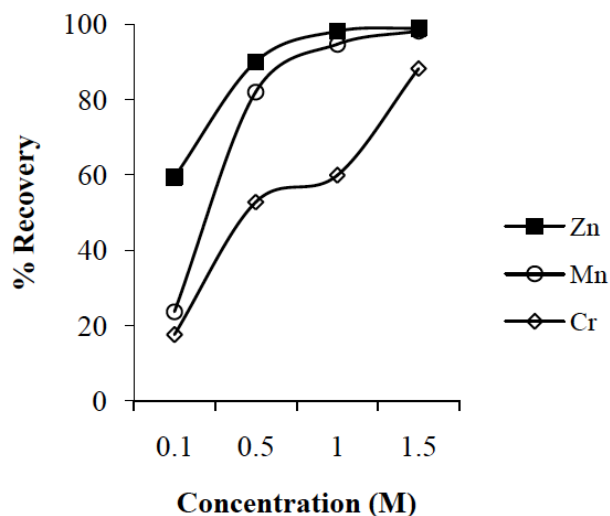


Figure 3: (%) Recovery of different metals vs. acid concentrations (t: 2 h, N: 300 rpm, T: 90°C).

It was found that leaching yield of Zn, Fe and Pb were strongly dependent on sulphuric acid concentration. Zn recovery is preferentially higher than other heavy metals. The optimum leaching conditions were found to be H_2SO_4 concentration: 1M, T: 90 °C, t: 2 h, L/S: 50 ml/gm, N: 300 RPM. Under the optimized conditions, it has been determined that the satisfactory leaching yield of Zn (95%) can be obtained. The leaching recoveries of Mn and Cr were also seeming to be increasing with acid concentration. The leaching

reaction was not isothermal and desired temperature maintained through heating mantle.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of Higher Education Commission Pakistan with grant number 21-470. Authors are also grateful to University of Karachi, Peoples Steel Mills and University of Peshawar for their support in characterizations and lab facilities.

REFERENCES

- [1] Boyanov BS, Baev TB. Utilization of zinc in powders from electric arc furnaces in steel production. *J Min Metall Sect B Metall* 2009; 45(1): 15-22. <http://dx.doi.org/10.2298/JMMB0901015B>
- [2] Grillo FF, Coleti JL, Espinosa DCR, Oliveira JR, Tenório JAS. Zn and Fe Recovery from Electric Arc Furnace Dusts. *Mater Trans* 2014; 55(2): 351-356.
- [3] Montenegro V, Oustadakis P, Tsakiridis P. Hydrometallurgical Treatment of EAF Dust by Direct Sulphuric Acid Leaching at Atmospheric Pressure. *Waste and Biomass Valorization* 2016: 1-18.
- [4] Youcai Z, Stanforth R. Integrated hydrometallurgical process for production of zinc from electric arc furnace dust in alkaline medium. *J Hazard Mater* 2000 223-240. [http://dx.doi.org/10.1016/S0304-3894\(00\)00305-8](http://dx.doi.org/10.1016/S0304-3894(00)00305-8)
- [5] Järup L. Hazards of heavy metal contamination. *Br Med Bull* 2003; 68: 167-82. <http://dx.doi.org/10.1093/bmb/ldg032>
- [6] Environmental Protection Agency, "Land disposal Restrictions for Electric Arc Furnace Dust,," 1991; 56(160): 41164.

- [7] Erdem M, Yurten M. Kinetics of Pb and Zn leaching from zinc plant residue by sodium hydroxide. *J Min Metall Sect B Metall* 2015; 51(1): 89-95.
<http://dx.doi.org/10.2298/JMMB140503012E>
- [8] Yan H, Chai LY, Peng B, Li M.. A novel method to recover zinc and iron from zinc leaching residue. *Min Engg* 2014; 103-110.
- [9] Kekki A, Aromaa J, Forsen O. Leaching characteristics of eaf and aod stainless steel production dusts. *Physicochem Prob of Min Processing* 2012; 48(2): 599-606.
- [10] Dutra AJB, Paiva PRP, Tavares LM. Alkaline leaching of zinc from electric arc furnace steel dust. *Miner Eng* 2006; 19(5): 478-85.
<http://dx.doi.org/10.1016/j.mineng.2005.08.013>
- [11] Jezierski J, Janerka K. Selected aspects of metallurgical and foundry furnace dust utilization. *PL. J Envir. Stud* 2011; 20(1): 101-105.
- [12] Kul M, Oskay KO, Şimur M, Subutay H, Kirgezen H. Optimization of selective leaching of Zn from electric arc furnace steelmaking dust using response surface methodology. *Trans Nonferrous Met Soc China* 2015; 25(8): 2753-62.
[http://dx.doi.org/10.1016/S1003-6326\(15\)63900-0](http://dx.doi.org/10.1016/S1003-6326(15)63900-0)
- [13] Dodson JR, Hunt AJ, Parker HL, Yang Y, Clark JH. Elemental sustainability: Towards the total recovery of scarce metals. *Chem Eng Process Process Intensif. Elsevier B.V.*; 2012; 51: 69-78.
- [14] Habashi F. Recent trends in extractive metallurgy. *J Min Metall Sect B Metall* 2009; 45(1): 1-13.
<http://dx.doi.org/10.2298/JMMB0901001H>
- [15] Nyirenda RL. The processing of steelmaking flue-dust: A review. *Miner Eng* 1991; 4(7-11): 1003-25.
[http://dx.doi.org/10.1016/0892-6875\(91\)90080-F](http://dx.doi.org/10.1016/0892-6875(91)90080-F)
- [16] Havlik T, Souza B, Bernardes A, Schneider I, Miskufova A. Hydrometallurgical processing of carbon steel EAF dust. *J Hazard Mater* 2006; 135(1-3): 311-8.
<http://dx.doi.org/10.1016/j.jhazmat.2005.11.067>
- [17] Cui J, Zhang L. Metallurgical recovery of metals from electronic waste: A review. *J Hazard Mater* 2008; 158(2-3): 228-56.
<http://dx.doi.org/10.1016/j.jhazmat.2008.02.001>
- [18] Zhang Y, Yu X, Li X. Zinc recovery from franklinite by sulphation roasting. *Hydrometallurgy. Elsevier B.V.*; 2011; 109(3-4): 211-4.
<http://dx.doi.org/10.1016/j.hydromet.2011.07.002>
- [19] Kukurugya F, Vindt T, Havlik T. Behavior of zinc, iron and calcium from electric arc furnace (EAF) dust in hydrometallurgical processing in sulfuric acid solutions: Thermodynamic and kinetic aspects. *Hydrometallurgy* 2015; 154: 20-32.
- [20] Havlik T, Turzakova M, Stopic S, Friedrich B. Atmospheric leaching of EAF dust with diluted sulphuric acid. In: *Hydrometallurgy* 2005.
<http://dx.doi.org/10.1016/j.hydromet.2015.03.008>
- [21] Havlik T, Friedrich B, Stopic S. Pressure leaching of EAF dust with sulphuric acid. *Erzmetall* 2004; 113-20.
- [22] D.K. Xiaş CAP. Microwave caustic leaching of electric arc furnace dust. *Miner Eng* 2000; 13(1): 79-94.
[http://dx.doi.org/10.1016/S0892-6875\(99\)00151-X](http://dx.doi.org/10.1016/S0892-6875(99)00151-X)
- [23] Herrero D, Arias PL, Güemez B, Barrio VL, Cambra JF, Requies J. Hydrometallurgical process development for the production of a zinc sulphate liquor suitable for electrowinning. *Miner Eng. Elsevier Ltd*; 2010; 23(6): 511-7.
- [24] Ruiz O, Clemente C AM. Recycling of an electric arc furnace flue dust to obtain high grade ZnO. *J Hazard Mater* 2006; 141(1): 33-6.
<http://dx.doi.org/10.1016/j.jhazmat.2006.06.079>
- [25] Shawabkeh RA. Hydrometallurgical extraction of zinc from Jordanian electric arc furnace dust. *Hydrometallurgy* 2010; 104: 61-65.
<http://dx.doi.org/10.1016/j.hydromet.2010.04.014>
- [26] Asadi Zeydabadi B, Mowla D, Shariat MH, Fathi Kalajahi J. Zinc recovery from blast furnace flue dust. *Hydrometallurgy* 1997; 47(1): 113-25.
[http://dx.doi.org/10.1016/S0304-386X\(97\)00039-X](http://dx.doi.org/10.1016/S0304-386X(97)00039-X)
- [27] D K X, Pickles C a. Microwave caustic leaching of electric arc furnace dust. *Miner Eng* 2000; 13(1): 79-94.
[http://dx.doi.org/10.1016/S0892-6875\(99\)00151-X](http://dx.doi.org/10.1016/S0892-6875(99)00151-X)
- [28] Trung ZH, Kukurugya F, Takacova Z, Orac D, Laubertova M, Miskufova A, *et al.* Acidic leaching both of zinc and iron from basic oxygen furnace sludge. *J Hazard Mater. Elsevier B.V.*; 2011; 192(3): 1100-7.
- [29] Tomas H. "The possibility of treatment of the EAF dusts and sludges. Present Futur Metall Mater Sci Refract Proc 50th Anniv Metall Fac Tech Univ Kosice, 2002; 93.
- [30] Langová Š, Leško J, Matýsek D. Selective leaching of zinc from zinc ferrite with hydrochloric acid. *Hydrometallurgy* 2009; 95(3-4): 179-82.
<http://dx.doi.org/10.1016/j.hydromet.2008.05.040>
- [31] Mordoğan H, Çiçek T, Işık a. Caustic soda leach of electric arc furnace dust. *Turkish J Eng Environ Sci* 1999; 23(3): 199-207.
- [32] Jezierski J, Janerka K. Selected aspects of metallurgical and foundry furnace dust utilization. *Polish J Environ Stud* 2011; 20(1): 101-5.
- [33] Lenz DMM, Martins F. B. Lead and zinc selective precipitation from leach electric arc furnace dust solutions. *Rev Matéria* 2007; 12(3): 503-9.
<http://dx.doi.org/10.1590/s1517-70762007000300011>
- [34] Wang JC, Hepworth MT, Reid KJ. Recovering Zn, Pb, Cd and Fe from electric furnace dust. *JOM.* 42(4): 42-5.
<http://dx.doi.org/10.1007/BF03220923>
- [35] Hong-xu L, Yang W, Da-qiang C. Zinc leaching from electric arc furnace dust in alkaline medium. *J Cent South Univ Technol (Engl Ed)* 2010; 17(6): 967-71.
- [36] Yu B-S, Wang Y-R, Chang T-C. Hydrothermal treatment of electric arc furnace dust. *J Hazard Mater. Elsevier B.V.*; 2011; 190(1-3): 397-402.
- [37] Gargul K, Boryczko B. Removal of zinc from dusts and sludges from basic oxygen furnaces in the process of ammoniacal leaching. *Arch of Civil and Mech Eng* 2015; 15: 179-187.

Received on 15-06-2016

Accepted on 27-06-2016

Published on 29-07-2016

<http://dx.doi.org/10.6000/1927-5129.2016.12.50>© 2016 Hameed *et al.*; Licensee Lifescience Global.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.