CALCIUM BEHAVIOR IN EAF STEELMAKING DUST ACIDIC LEACHING

Tomas Havlik[1]*, Frantisek Kukurugya[1], Tomas Vindt[1], Andrea Miskufova[1]
[1] Technical University of Košice, Faculty of Metallurgy, Košice, Slovakia

*Corresponding author: e-mail: tomas.havlik@tuke.sk, Tel.: (+421) 055 / 6022428, Department of non-ferrous metals and waste treatment, Faculty of Metallurgy, Technical University of Košice, Letná 9, 042 00 Košice, Slovakia

Abstract
In this study the hydrometallurgical processing of EAF steelmaking dust (Ironworks Podbrezova) was investigated in laboratory scale. The behavior of calcium under the influence of sulphuric acid as the leaching agent is discussed. The main aim is the transfer of zinc into the solution while iron ought to remain as a solid residue. Calcium, too, is transferred to the solution, but due to its low solubility it is precipitated from solution into solid residue. Acid is continuously consumed, spending gradually calcium phase from EAF dust and also other zinc and iron containing phases. In such a way, it is possible to set up the conditions for the leaching of EAF dust, namely sufficient sulphuric acid concentration in order to achieve an optimum zinc yield to the solution without iron dissolution. However, the problem is that the calcium content of each steelmaking dust is individual. Therefore, it is necessary to study the processing conditions for each one of them.

Keywords: EAF steelmaking dust; Industrial waste; Zinc; Iron; Calcium; Sulphuric acid; Leaching; Hydrometallurgy

1   Introduction

During the production of steel from scrap in electric arc furnaces some amount of dust is recovered in gas cleaning units per tone of steel produced. The presence of leachable zinc, lead, cadmium, chromium, and other elements in the dust has in recent years caused the material to be widely regarded as a toxic waste which is unsuitable for disposal in landfill. From the same reason it is very complicated to use this waste as secondary raw material for iron or steel production. There is a very wide of presence of heavy metals in steel making dusts, for example 2 – 30 % Zn, 0.3 – 6% Pb, 0.01 – 0.2 % Cd, etc. Moreover, a big scale of minorities is present such as Al, As, Ba, Ca, Cl, Cr, Cu, Hg, K, Mg, Mn, Mo, Na, Ni, P, Se, Si, Ti, Zr [1].

Mineralogical analysis shows iron presence in oxide form, mostly as magnetite Fe_3O_4 and franklinite $ZnFe_2O_4$. Zinc is present mostly in two basic compounds, namely as oxide ZnO and ferrite $ZnFe_2O_4$, eventually complex ferrite, e.g. $(ZnMnFe)_2O_4$. The form of zinc presence seems to be the basic indicator for effective method of the EAF dust treatment. ZnO is in principle easy workable form for both of pyro and hydro method, but ferrite form is considerable refractory. Moreover, it is practically impossible prognosticate the form of zinc compound presence. The negotiability of chosen process is of course affected by amount of heavy metals present in the dust.

On other hand, EAF dusts contain also further elements, present in various forms. These also participate on the processes of EAF dust treatment, although the main aim is the valorization both of iron and zinc. Lead, manganese and calcium except of iron and zinc are present in interesting amounts. Heavy metals are present in the EAF dust due to their presence in the

melted scrap, the calcium is transferred into EAF dust from fluxes. Its amount is changed from case to case and varies within the range 0.4-14 %. The average amount is around 5 % [2].

It follows from published results, that calcium in EAF dust is present in various form as CaO [3], $Ca(OH)_2$ [3], $CaCO_3$ [1, 4], complex oxide [5] and other. The nature of calcium compound depends on history of origination and also on duration time of EAF dust existence and its positioning.

Calcium ferrites originate during melting of scrap at high temperatures by chemical reaction between scrap parts, fluxes and working atmosphere.

At the melting temperature around 2100 °C the iron oxidation takes place according to [6]

$$4Fe + 3O_2 = 2Fe_2O_3 \qquad \Delta G^o_{2100} = -106.941 \text{ kJ/mol} \qquad (1)$$

The lime CaO is added into scrap melting as flux. Its reaction with s Fe_2O_3 takes place according to

$$CaO + Fe_2O_3 = CaFe_2O_4 \qquad \Delta G^o_{2100} = -106.291 \text{ kJ/mol} \qquad (2)$$

eventually

$$2CaO + Fe_2O_3 = 2CaO*Fe_2O_3 \qquad \Delta G^o_{2100} = -152.031 \text{ kJ/mol} \qquad (3)$$

Even additives would be present as $Ca(OH)_2$, or $CaCO_3$, at high melting temperatures in EAF higher than 2000 °C these are thermally dissociated originating CaO.

$$CaCO_3 = CaO + CO_{2(g)} \qquad \Delta G^o_{2100} = -140.803 \text{ kJ/mol} \qquad (4)$$
$$Ca(OH)_2 = CaO + H_2O_{(g)} \qquad \Delta G^o_{2100} = -116.943 \text{ kJ/mol} \qquad (5)$$

In the freshly collected EAF dust the calcium is present mostly as CaO, eventually as relatively stable ferrite. When this EAF dust is stored without restraint, the lime reacts with air atmosphere at ambient temperature according to

$$CaO + CO_{2(g)} = CaCO_3 \qquad \Delta G^o_{20} = -131.224 \text{ kJ/mol} \qquad (6)$$

or by particular reaction

$$CaO + H_2O_{(g)} = Ca(OH)_2 \qquad \Delta G^o_{20} = -67.078 \text{ kJ/mol} \qquad (7)$$

and originated hydroxide further reacts with CO_2 from air creating $CaCO_3$

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \quad \Delta G^o_{20} = -73.302 \text{ kJ/mol} \qquad (8)$$

In fact, this is the classic process of mortar hardening known from civil engineering. These reactions do not proceed immediately; the kinetics is relatively slow and depends on partial pressures of water steam and carbon dioxide in ambient atmosphere. It follows from above mentioned that the reactions proceed by different kinetics on the surface and different one inside of volume of stored dust.

The processes of acidic hydrometallurgical processing of EAF dust are rather frequently discussed in the literature. Hydrochloric acid [7, 8], nitric acid [9], ammonium chloride [10], acetic acid [11] are common used as lixviant in these processes, but mostly sulphuric acid is discussed as leaching agent for EAF dust leaching at the normal conditions both of temperature and pressure [12] or high temperature and pressure [13].

Main components of EAF dust react in sulphuric acid according to reactions:

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O \qquad \Delta G^o_{80} = -124.339 \text{ kJ/mol} \qquad (9)$$

$$ZnFe_2O_4 + 4H_2SO_4 = ZnSO_4 + Fe_2(SO_4)_3 + 4H_2O$$
$$\Delta G^o_{80} = -67.938 \text{ kJ/mol} \qquad (10)$$

$$ZnFe_2O_4 + H_2SO_4 + 2H_2O = ZnSO_4 + 2Fe(OH)_3$$
$$\Delta G^o_{80} = -45.996 \text{ kJ/mol} \qquad (11)$$

$$3ZnFe_2O_4 + 2H_2SO_4 = ZnO*2ZnSO_4 + 3Fe_2O_3 + 2H_2O$$
$$\Delta G^o_{80} = -52.729 \text{ kJ/mol} \qquad (12)$$

$$4Fe_3O_4 + 18H_2SO_4 + O_2 = 6Fe_2(SO_4)_3 + 18H_2O$$
$$\Delta G^o_{80} = -74.249 \text{ kJ/mol} \qquad (13)$$

$$CaO + H_2SO_4 = CaSO_4 + H_2O \qquad \Delta G^o_{80} = -268.025 \text{ kJ/mol} \qquad (14)$$

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2 \qquad \Delta G^o_{80} = -146.386 \text{ kJ/mol} \qquad (15)$$

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O \qquad \Delta G^o_{80} = -211.721 \text{ kJ/mol} \qquad (16)$$

From the thermodynamic point of view the most stable specie in the EAF leaching system in sulphuric acid at 80 ^{o}C, what is often used leaching temperature, is calcium sulphate. It follows from the comparison of values of standard Gibbs energy changes of individual components creation and it does not depend from which primary calcium compound the calcium sulphate originates. It means, that these calcium compounds, present in EAF dust, will react with sulphuric acid predominantly and hence they will the acid consume. This phenomenon is frequently used for the neutralization of waste acid solutions.

Published works focused on material recycling of EAF dust by acid leaching are in principle narrowed by double direction. In one direction there is used relatively aggressive leaching agent, for example hydrochloric acid and hence almost all EAF components goes into solution from which they are gradually extracted for example by solvent extraction. Another works are focused on selective extraction of chosen component into solution, mostly zinc, whereas iron stays in solid residue and after treatment is recycled into iron and steel production. The last one is interesting from economical point of view, but on other hand, setting of necessary equilibrium in solution is very sensitive task.

It follows from thermodynamic study by using of E_h – pH diagrams of Zn-Fe-S-H_2O system, Fig. 1, that at the normal conditions zinc in soluble form creates wide stability area within the pH region from 0 to 4.5. This tendency is observed with increasing temperature, whereby the

equilibrium boundary between soluble Zn^{2+} ion and insoluble $ZnFe_2O_4$ is shifted toward to lower value pH = 3.4.
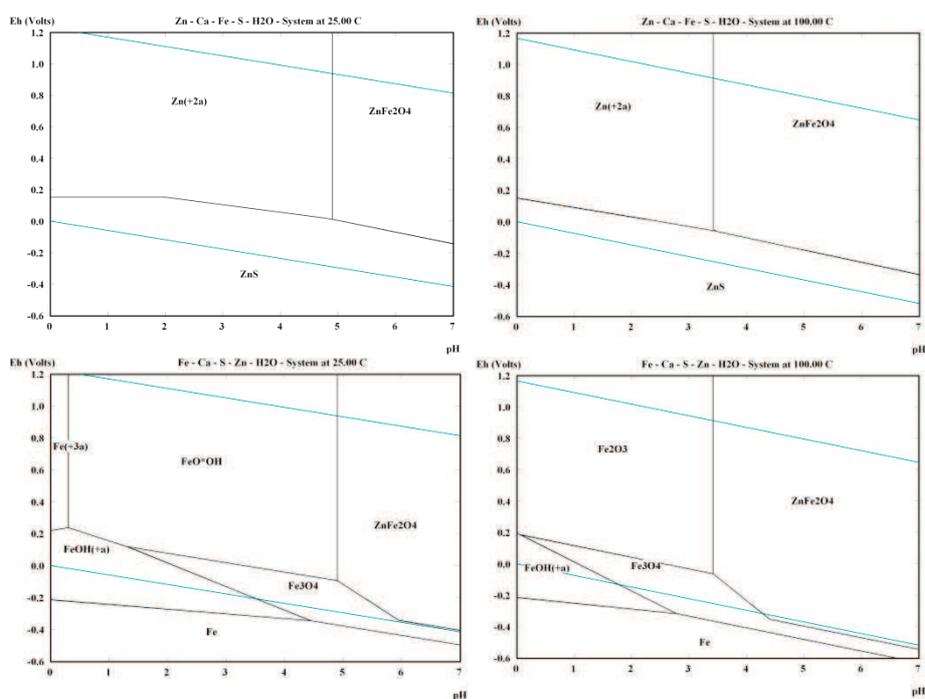
Fig. 1 Eh-pH diagrams of Zn-Fe-S-H_2O system at temperatures 20 and 100 ^{o}C

However, in acidic area soluble iron ions form narrow stability area only and by increasing pH value over pH = 0.5 iron precipitates as oxide or hydroxide.

Based on above mentioned it is existing the idea of EAF dust processing by leaching in weak sulphuric acid solution where the individual EAF dust components will be leached out and at the same time the acid will be consumed. Such way the pH value will increase. After achieving pH values over ~ 1 will iron precipitated back from the solution as oxide while zinc stays in the solution. After phase separation the solution will be individually treated in order to zinc recovery and solid residue is going to be recycled into iron and steel production [12, 13].

2   Experimental

The EAF sample supplied by Ironworks Podbrezova, Slovakia was used for the experiments of leaching in order to transfer zinc into solution, while iron should stay in solid residue. The chemical analysis of used material is shown in Tab. 1.

Tab. 1 Chemical composition of the EAF dust sample from Ironworks Podbrezova

Element	Zn	Fe	Ni	Cr	Mn	Pb	Cd	Ca	LOI
Amount [%]	17.05	27.23	0	0.81	1.03	1.28	0.09	4.42	7.08

In order to identify the mineralogical composition, the EAF dust sample was subjected to X-ray (XRD) qualitative diffraction analysis on an X-ray diffractometer PANalytical X'Pert PRO MRD using CoKα radiation. EAF dust contains following phases $ZnFe_2O_4$, ZnO, Fe_2O_3, $CaCO_3$, C as results from phase diffraction analysis.

This sample was subjected to leaching experiments in sulphuric acid. Eight different concentrations were used for this purpose, namely 0, 0.05, 0.1, 0.25, 0.5, 0.75, 1 and 2 M H_2SO_4. Leaching temperature was 60 °C, solid to liquid ratio S:L = 20, leaching time was 30 minutes. Liquid sample were taken in 3, 5, 10, 15, and 30 minute of leaching for analysis of Zn, Fe and Ca by AAS ethod. pH was measured continuously during each experiment.

A typical leaching experiment shows, that zinc, iron and calcium as well are leached out from EAF dust into solution very fast, in minutes, while temperature influences metal extraction not significantly [12, 13].
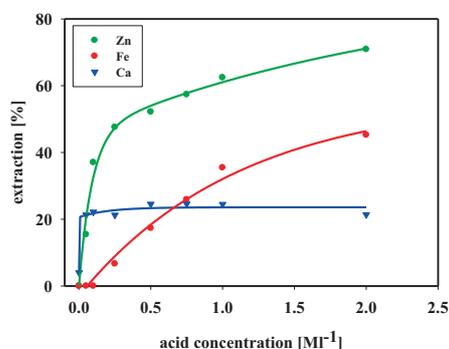
Fig. 2 Acid concentration influence on metal extraction

In contrary, the solution acidity influences the process significantly, Fig. 2. However, zinc, iron and calcium behavior is different. Zinc extraction is governed by monotonous leaching curve, the iron is not leached at low acid concentration and calcium is leached out on certain level, around 22 % in this case, and the process stop. The pH value change during leaching, Fig. 3, reveals that acid consumption continues during whole process and it is not accompany by jump change as should follow from the comparison Figs 2 and 3.
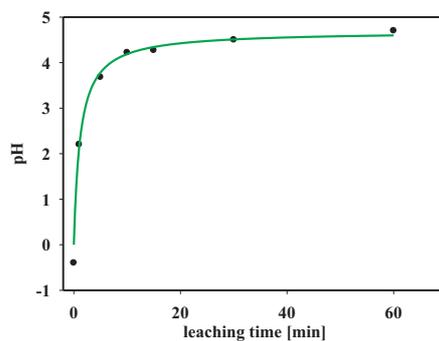
Fig. 3 pH change vs leaching time dependence

The temperature does not influence the metals extraction into solution significantly. However, the metals extraction, mostly calcium, is influenced by pulp concentration change, Fig. 4. The change liquid to solid ratio (L:S) causes leaching of calcium in short time on maximum level at given conditions. Then amount of dissolved calcium in the solution is stabilized or even slightly diminished.
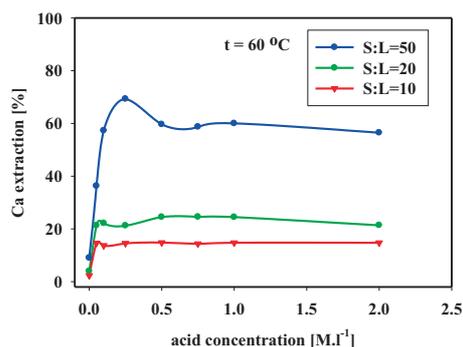
Fig. 4 Calcium extraction depending on L:S ratio

The explanation is in $CaSO_4$ solubility [15]. The solubility of calcium sulphate dihydrate is 0.26 g.l^{-1}, the solubility of calcium sulphate hemihydrate is 0.164 g.l^{-1} at 60 ^{o}C.

The keynote of EAF dust leaching in sulphuric acid is in this case as follows: Remove zinc into solution whereas iron stays in solid insoluble residue. This will be attached so, that pH of solution will be kept in the range ~1 < pH < ~4. Original pH value of solution is determined by input acid concentration, but this one will be spent in leaching process for $ZnSO_4$, $Fe_2(SO_4)_3$ and $CaSO_4$ creation according to equations (9),(10),(15), eventually (14) and (16). According to measured extraction values of zinc, iron and calcium, Fig. 5, the EAF dust leaching mechanism was often interpreted so, that the acid is spent and leaching of components stopped.
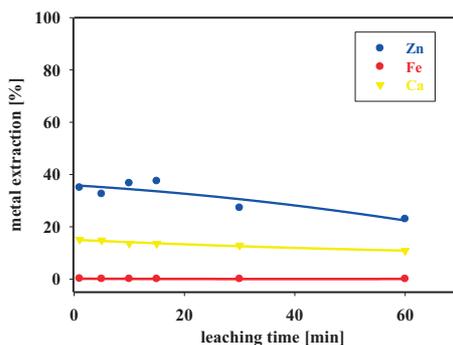
Fig. 5 Kinetic curves of zinc, iron and calcium leaching from EAF dust

On other hand, the pH dependence on concentration and L:S ratio on acid concentration as well reveals different mechanism. Because of low solubility of calcium sulphate in water

solution, during EAF dust leaching this sulphate precipitated from solution into solid and that is why next portion of EAF dust component containing calcium is leached out. Because these reactions are thermodynamically most favorable, the acid is consumed predominantly, what is crucial moment in leaching of EAF dust.

Fig. 6 shows precipitated white precipitate in leaching solution from EAF dust leaching

Fig. 6 White precipitate after leaching EAF dust

X-Ray diffraction qualitative phase analysis, Fig. 7, proved, that it is calcium sulphate containing water $CaSO_4*4H_2O$.
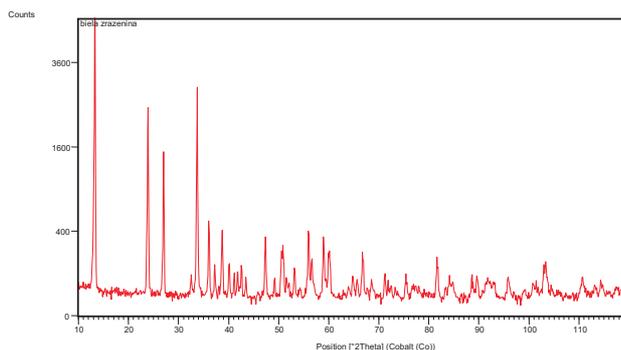
Fig. 7 X-Ray diffraction pattern of white precipitate

The morphological analysis and chemical microanalysis of particles as well (57 % Ca, 37.2 % S) on the Fig. 8 confirms XRD phase analysis.
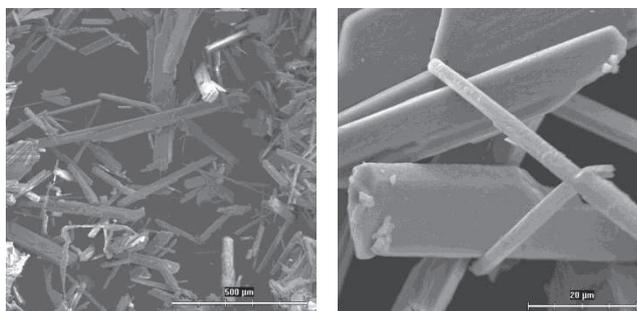
Fig. 8 Morphological observation on white precipitate

3   Conclusion

The mechanism of EAF dust leaching is controlled predominantly by leaching of phases containing calcium followed by calcium sulphate precipitation. Precipitation process proceeds not immediately, it depends on temperature and time as well. The duration of precipitation vary within the range of some hours and some days.

It follows from described that process of selective zinc recovery (and other present non-ferrous metals) from the solution, as iron stays in solid residue, is significantly complicated by calcium content in EAF dust. The calcium compounds control leaching solution acidity during leaching. Tab. 2 shows chemical composition of three EAF dust samples, obtained in various time and space. The calcium content difference is significant.

Tab. 2 Chemical composition of three different EAF dust sample

element	Fe	Zn	Ca	Pb	Mn	Sb	Sn	Al	Cu	Cr	Ni	Co	Cd	LOI
dust I	29.66	18.96	4.1	1.94	1.35	0.17	0.16	0.37	0.3	0.12	0.07	0.02	0.05	7.08
dust II	29.71	10.47	9.84	1.19	2.14	0.05	trace	trace	0.179	0.31	0	0	0	7.24
dust III	28.8	14.85	10.3	1.95	2.4	0.06	trace	0.02	0.179	0.18	0.03	0.02	0	10.22

4   References

[1]   M. Cruells et al, Electric arc furnace flue dusts, characterization and leaching with sulphuric acid, Hydrometallurgy, 1992, 213-231

[2]   T. Havlik et al., Acidic Leaching of EAF Steelmaking Dust, Erzmetall, 65, 1, 2012, 48-56

[3]   F. Kukurugya et al,, Chemical and Structural Characterization of Steelmaking Dust from Stainless Steel Production, Proc. EMC 2011, vol. 4, Dusseldorf , 1171-1183, 2011

[4]   F.A. Lopez, et al, Electric Arc Furnace Flue Dust, Characterization and Toxicity with Photobacterium Phosphoreum, Int. J. of Environment and Pollution, 3 (4) 1993, 269-283

[5]   T. Sofilic et al, Characterization of steel mill electric-arc furnace dust, Journal of Hazardous Materials B109, 2004, 59–70

[6]   A. Roine, HSC chemistry®, ver. 6.1 – software Outotec Research Oy

[7]   Š. Langová et al, Selective leaching of zinc ferrite with hydrochloric acid, Hydrometallurgy 95, 2009, 179 – 182

[8]   D.S. Baik, D.J. Fray, Recovery of zinc from electric-arc furnace dust by leaching with aqueous hydrochloric acid, plating of zinc and regeneration of electrolyte, Trans. Instn Min. Metall., 109, C121-C128, 2000

[9]   R. A. Shawabkeh, Hydrometallurgical extraction of zinc from Jordanian electric arc furnace dust, Hydrometallurgy, 104, 2010, 61 – 65

[10]   M. C. Mantovani et al, EAF dust, Characterization and leaching with sulphuric acid and ammonium chloride, Dept. of Chemical Engineering, Brazil, 1 – 32

[11]   S. Nagib, K. Inoue, Recovery of lead and zinc from fly ash generated from municipal incineration plants by means of acid and/or alkaline leaching, Hydrom., 56, 2000, 269–292

[12]   T. Havlik et al, Atmospheric leaching of EAF dust with diluted sulphuric acid, Hydrometallurgy, 77, 2005, 41-51

[13]   T. Havlik et al, Pressure Leaching of EAF Dust with Sulphuric Acid, Erzmetall 57, 2, 2004, 113-120

[14]   M. Broul, J. Nývlt, O. Sohnel, Tabulky rozpustnosti anorganických látek ve vode, Academia, Praha, 1979