KINETIC STUDY AND OPTIMIZATION OF EAF DUST ATMOSPHERIC LEACHING IN SULPHURIC ACID SOLUTION

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Abstract

This work deals with the possibility of hydrometallurgical treatment electric arc furnace (EAF) dust using dilute sulfuric acid solutions. The origin of the EAF dust sample was Železiarne Podbrezová a.s., Slovakia. Zinc content in the dust was 17.05 % and zinc was present both as zincite ZnO and zinc ferrite $ZnFe_2O_4$. The effect of temperature, acid concentration and leaching time on zinc, iron and calcium extraction into the solution was investigated in order to optimize leaching parameters. The leaching experiments were carried out in temperature range within 20 and 95°C in aqueous solutions of sulfuric acid with concentrations of 0.05, 0.1, 0.25, 0.5 and 1 M. The maximum zinc extraction of 95 % was achieved in 1 M H_2SO_4 at 80°C after 90 minutes of leaching, while the iron extraction under the same conditions was 66 %. The main objective of this study was to find out conditions at which the maximum amount of zinc passes into the solution while iron remains in the solid residue. Following conditions were specified as optimum: 0.1 M H_2SO_4, 60 °C. The zinc extraction under the given conditions was 65 %, while iron extraction was around 5 %.

Keywords: material recycling, hydrometallurgy, leaching kinetics, EAF dust, zinc

1. INTRODUCTION

Steelmaking industry is, as any other kind of industry, typical by production of significant amount of by-products – wastes, which are in many cases classified as hazardous waste. EAF dust is one of these industrial hazardous wastes, which is a material containing of iron oxides and oxides of heavy metals as Zn, Pb, Cd, Cr, etc., what means that EAF dust is classified as hazardous waste.

On the other hand, due to high content of iron (20 – 50 wt. %) and zinc (8 – 35 wt. %), this kind of waste can be considered as suitable secondary raw material for iron and/or zinc production. Zinc, in EAF dust, is mostly present as oxide ZnO and ferrite $ZnFe_2O_4$ while iron can be present as ferrite $ZnFe_2O_4$ and Fe_3O_4 and/or as an oxide Fe_2O_3. Calcium can be present in EAF dust mostly as an oxide CaO, hydroxide $Ca(OH)_2$ and a carbonate $CaCO_3$.

The main reason for recycling EAF dusts are:

- Zinc recovery – current zinc price is 2188 $/t,

- Obtaining Fe concentrate, which can be used as an input into blast furnaces or EAF, current price of iron ore is 139 $/t,

- Reducing the amount of hazardous waste or its transformation to non-hazardous waste.

The methods of processing EAF dust can be divided into pyrometallurgical, hydrometallurgical methods and their combination. The best known pyrometallurgical process for processing EAD dust is Waelz kiln process. Approximately, 80 % of EAF dust being produced, is processed by this process [1]. Except Walz kiln process, also other pyrometallurgical processes such as Primus, Fastmet, Radust, Tetronic, Dereco, Enviroplas, ISP, Contop and so on, were developed [2].

Hydrometallurgical processes for processing EAF dust were so far developed only in laboratory or in pilot plant scale. Hydrometallurgical processes developed in pilot plant scale include: Ezinex, Terra Gaia, Amax, UBC-Chapparal, Hatch, Cebedeau and Zincex process. The best known among these processes is Ezinex process, which is based on alkaline leaching [3].

Recently, mostly pyrometallurgical processes are used for recycling EAF dust. However, pyrometallurgical processes are economically competitive only if the annual amount of produced EAF dust reaches 100 000 tons, what is impossible to get in condition of Slovak Republic. In contrary to pyrometallurgical processes, hydrometallurgical processes are characterized by higher flexibility, lower energy consumption and possibility to get economical profit even if lower annual amount of EAF dust (10 000 tons) is being processed.

2. EXPERIMENTAL

2.1. Material and experiments

The sample of EAF dust was subjected to chemical analysis by AAS method with results given in Tab 1.

Table 1 Chemical composition of the sample (AAS)

Metal	Zn	Fe	Ca	Pb	Cd	Mn	Cr	LOI
Content [wt.%]	17.05	27.23	4.42	1.28	0.09	1.03	0.81	7.08

Two main granular fractions are present in the sample, namely fine fraction (-22 +2 µm), which represents 37 % and coarse fraction (-47 +28 µm), which represents 35 % of all particles in the sample and 90 % of particles have size below 50 µm.

The XRD phase analysis proved the presence of zinc in the form of zincite – ZnO and in ferritic form as franklinite $ZnFe_2O_4$. Iron is present in the sample in ferritic form as franklinite and magnetite – Fe_3O_4. Calcium was present as oxide – CaO. Also the presence of SiO_2 was confirmed by the phase analysis.

The leaching experiments were performed in a glass reactor. Sulfuric acid solutions within the concentration range of 0.05 - 1 $M.l^{-1}$ were used as a leaching reagent. Kinetics measurements were carried out within the temperature range 20 - 95 °C. The chemical analysis, carried out in order to determine zinc, iron and calcium content, was made by means of the AAS method. The effect of temperature and sulfuric acid concentration on the extraction of zinc, iron and calcium into the solution was observed in this work.

3. RESULTS AND DISCUSSION

3.1. The behavior of zinc

Fig. 1 shows the kinetics dependencies of the zinc extraction at different sulfuric acid concentration (0.05 to 1M) and temperatures 20 to 95 °C.
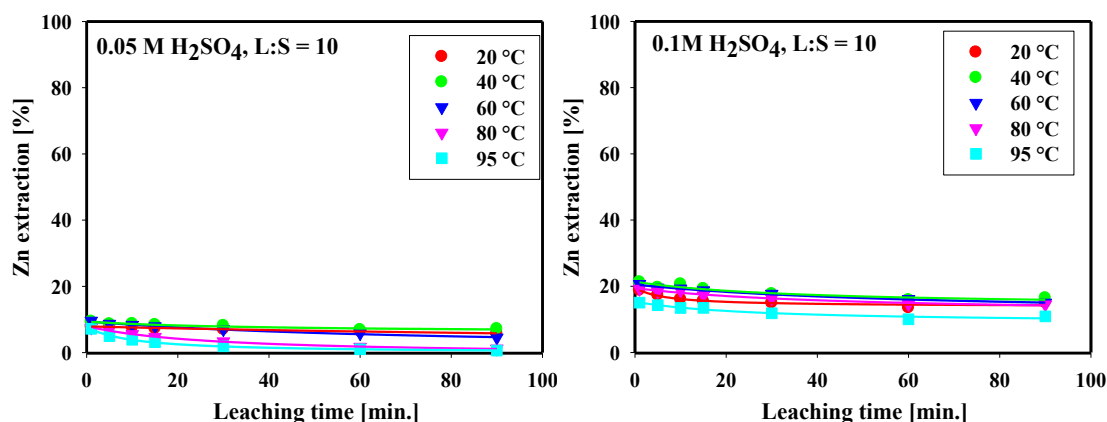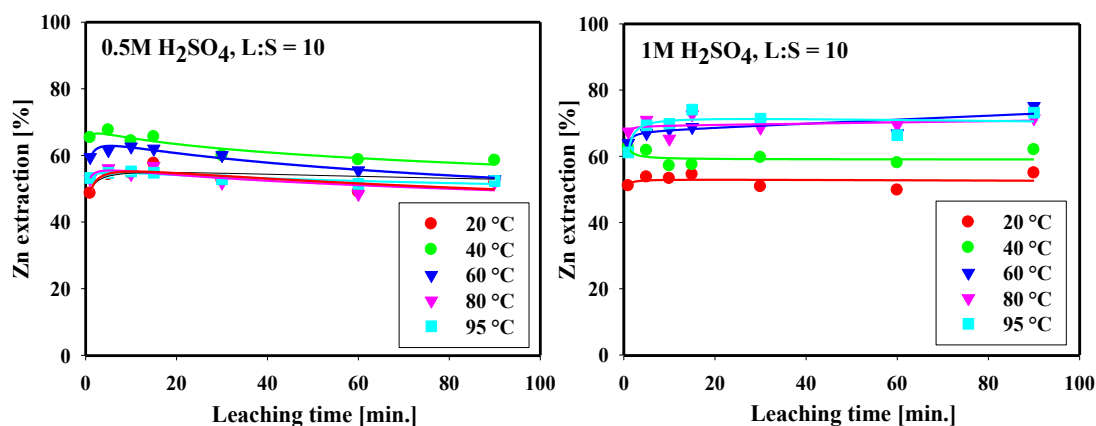
Fig. 1 Kinetics dependencies of the zinc extraction on the temperature at acid concentrations 0.05 to 1M H_2SO_4

It results from Fig. 1 that leaching zinc into the solution is a very fast process. Maximum amount of zinc which is able to pass into the solution will do that in first minutes of the leaching. The maximum zinc extraction ~75 % was achieved in 1M H_2SO_4 at temperatures over 60 °C. In case of zinc leaching the influence of temperature is very low. Moderate influence of temperature on zinc extraction can be visible only in case of 1M H_2SO_4. Fig. 2 shows the dependence of leached zinc on sulfuric acid concentration after 60 minutes of leaching. Curves in Fig. 2 indicate that maximum zinc extraction was achieved in 1M H_2SO_4 at all studied temperature. Moreover, it can be seen that further increasing sulfuric acid concentration would lead to further gentle increasing in zinc extraction.
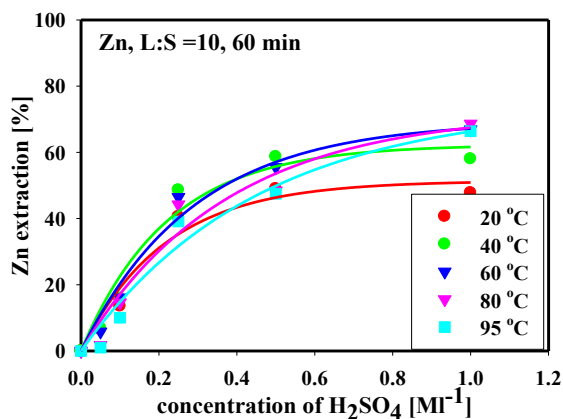

Fig. 2 Dependence of leached zinc on sulfuric acid concentration at given temperatures after 60 minutes of leaching

3.2. The behavior of iron

Fig. 3 shows the kinetics dependencies of the iron extraction at sulfuric acid concentration 0.5 and 1M and temperatures 20 to 95 °C. As the iron extraction in case of sulfuric acid concentrations 0.05, 0.1 and 0.25M was under 0.1 %, kinetics curves for these concentrations are not presented in this work.
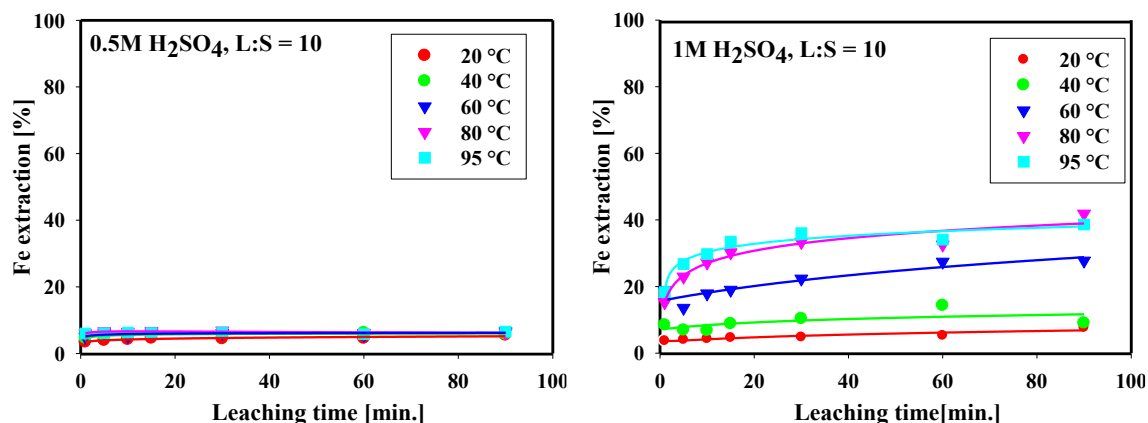
Fig. 3 Kinetics dependencies of the iron extraction on the temperature at acid concentrations 0.5 and 1M H_2SO_4

It can be clearly seen from Fig. 3, that kinetics of iron passing into the solution differs from kinetics of zinc. In case of iron, it is not as fast process as it was in case of zinc. Temperature has significant influence on iron extraction. Maximal iron extraction ~ 40 % was achieved in 1M H_2SO_4 at the temperature 80 °C. As the maximum iron extraction was achieved after 90 minutes, there is an assumption that extension of leaching time would led to higher iron extraction. As can be seen from Fig 4 also sulfuric acid concentration has significant influence on iron extraction.
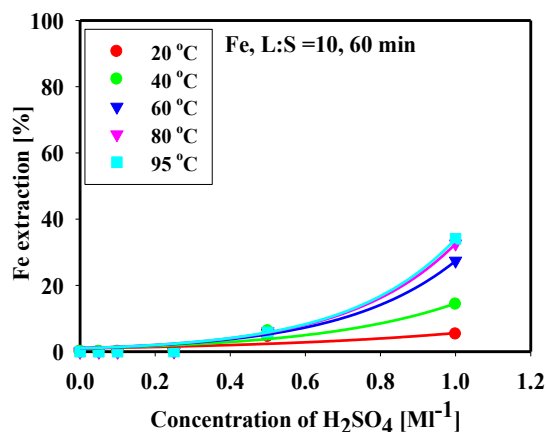

Fig. 4 Dependence of leached iron on sulfuric acid concentration at given temperatures after 60 minutes of leaching

Fig. 5 shows the kinetics dependencies of the calcium extraction at different sulfuric acid concentration (0.05 to 1M) and temperatures 20 to 95 °C.
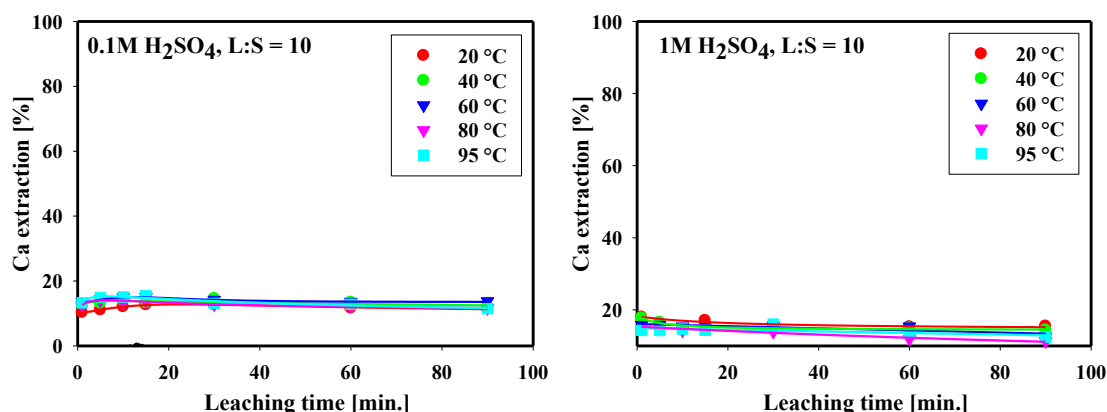
Fig. 5 Kinetics dependencies of the calcium extraction on the temperature at acid concentrations 0.05 to 1M H_2SO_4

It results from Fig. 5, that calcium extraction is not significantly affected by experimental conditions (temperature, acid concentration). Maximal concentration was around 20 % and was not depending on neither temperature nor acid concentration.

Absolute calcium concentration in the solution after leaching was in range 400 – 700 µg/ml. This is evidence of the fact, that calcium concentration in the solution is primarily given by its limited solubility of $CaSO_4.2H_2O$ and secondly by experimental conditions.

Solubility of $CaSO_4.2H_2O$, according to literature sources [4,5] is 2.6 g/l (at the temperature 25°C in diluted sulfuric acid solution), what represents concentration of Ca^{2+} in saturated sulfate solution around 600 µg/ml.

Fig. 6 confirms the fact that by increasing acid concentration and/or temperature will not lead to higher calcium concentration in the solution.
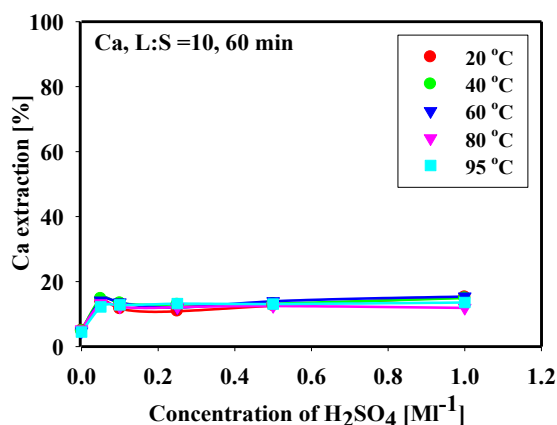

Fig. 6 Dependence of leached calcium on sulfuric acid concentration at given temperatures after 60 minutes of leaching

4.   CONCLUSION

The main aim of this paper was kinetics study of leaching zinc, iron and calcium from EAF dust in sulfuric acid solution at L:S ratio equal to 10. Before leaching experiments, also characterization of the EAF dust sample was carried out. The sample contains 17.05 % Zn, 27.23 % Fe and 4.42 % Ca. By XRD phase analysis phases ZnO, $ZnFe_2O_4$, Fe_3O_4, SiO_2 and CaO were identified.

Results of experimental study showed, that passing of zinc into the solution is a very fast process and maximum zinc extraction, at given conditions, can be reached already in first 15 minutes of leaching. Maximal zinc extraction was around 75 % and it was achieved in 1M H_2SO_4 at temperature over 60 °C.

From kinetics curves of iron can be clearly seen, that passing iron into the solution is not as fast as it was in case of zinc. Iron was passing into the solution gradually where influence of temperature was more significant than in case of zinc. Highest iron extraction, 40%, was reached in 1M H_2SO_4 at 80 °C after 90 minutes of leaching.

Maximum calcium extraction was 20 % and was not affected by experimental conditions. Absolute calcium concentration in the solution was ~ 600 µg/ml and it was given by limited solubility of $CaSO_4.2H_2O$.

Fig. 7 shows dependence of zinc, iron and calcium extraction on sulfuric acid concentration at 60 °C after 60 minutes of leaching.
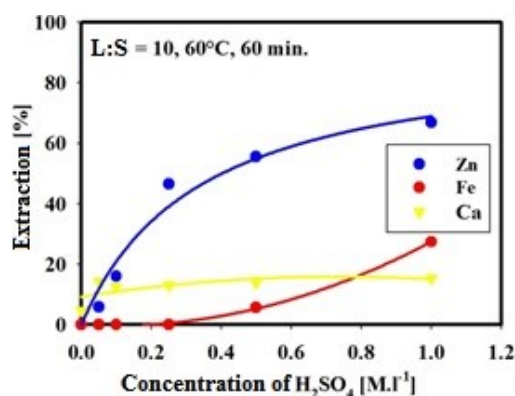

Fig. 7 Dependence of leached zinc, iron a calcium on sulfuric acid concentration at given temperatures after 60 minutes of leaching

From Fig. 7 can be seen that, when selective extraction of zinc is needed, maximum 0.25M H_2SO_4 can be used. At these concentration 50 % of zinc can be leached out into the solution without iron passing into the solution

ACKNOWLEDGEMENTS

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