Leaching of Slovak EAF steelmaking dust in sulfuric acid

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Abstract

The leaching characteristics of electric arc furnace steelmaking dust of Železiarne Podbrezová, a.s., Slovakia were investigated on a laboratory scale under normal temperature and pressure conditions in this study. The behavior of zinc and iron under the influence of sulphuric acid as the leaching agent is discussed. The dependence between temperature and acid concentration is investigated. It follows from results, that the hydrometallurgical recovery of zinc from electric arc furnace dust is feasible with relatively high recovery yield, while iron mostly remains in the solid phase. However, the problem is that the chemical and mineralogical composition of each steelmaking dust is individual and that is why it is necessary to set up the leaching conditions for each individual steelmaking dust.

Keywords: electric arc furnace steelmaking dust, zinc, iron, sulphuric acid, leaching, hydrometallurgy, industrial waste

1. Introduction

The accompaniment of the steel melting in the electric arc furnace is generation of relatively high amount of dust containing mostly iron oxides. Because of scrap melting, also significant amounts of volatile components are transferred into the dust such as oxides and complex oxides of mostly zinc, lead and cadmium. The dust composition is in very wide range: 2-35 % Zn, 30-45 % Fe, 0.5-2 % Pb, 0.1-03 % Cd, 1-7 % Ca, etc. It is impossible directly recycle such quality dust in the iron-making process. Moreover, the content of heavy metals classified this dust as hazardous waste.

There are existing several possibilities of EAF dust pre-treatment - pyrometallurgical, hydrometallurgical, and even combined one, but generally still doesn't exist effective and economic advantageous method for treatment of these wastes.

Hydrometallurgicaly can be EAF dust treated by several methods. By using of alkaline method the non-ferrous metals as zinc, lead and cadmium are transferred into solution while iron should remain in the solid phase. However, the disadvantage being relatively low efficiency and necessity to use of very concentrated solutions. Acid processes are more effectively, however the iron is more or less transferred into solution, too. It causes the problems with following solutions treatment.

The extraction of zinc significantly depends on its mineralogical form in the dust. Zinkite ZnO is easily and fast leachable compound. On other hand, ferrite form of zinc as franklinite $ZnFe_2O_4$ or complex franklinite $(Zn_x,Me_y)Fe_2O_4$ is rather refractory material.

The discussion on advantages and disadvantages of several hydrometallurgical methods of EAF dust treatment is given in [1-6]. The results of individual leaching experiments done on various EAF dusts (Paul Wurth- Luxembourg, Gerdau – Brazil) are described in [3-5]. The leaching of EAF dust of Železiarne Podbrezová, a.s., Slovakia, in laboratory scale under similar conditions is studied in this contribution.

2. Experimental part

From chemical analysis of studied EAF dust results the presence of main components as 32.09 % Fe, 18.96 % Zn, 2.05 % Pb, 3.42 % C, 3.42 % Ca. Total loss of ignition was 13.57 %. Mineralogical composition according to X-ray diffraction qualitative analysis shows presence of magnetite Fe_3O_4, franklinite $ZnFe_2O_4$ and zincite ZnO. Also silica SiO_2 and massicot PbO as minority phases were identified.

2.2 Experimental conditions and procedure

Leaching experiments were performed in the apparatus [4,5] whose project is shown in Fig. 1.

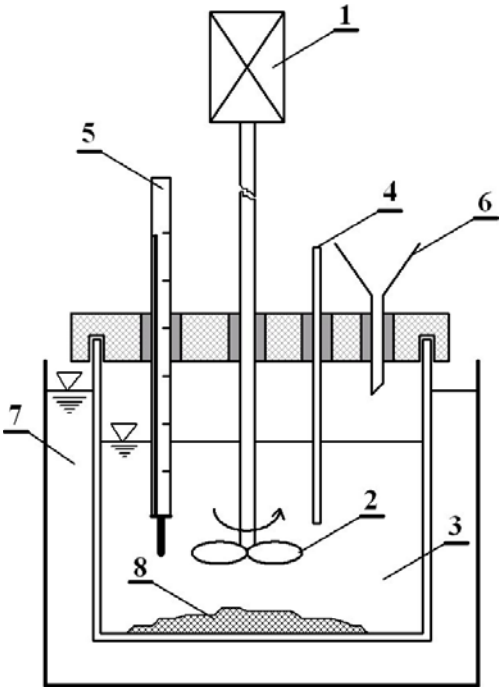


Fig. 1: Schematic view of the leaching apparatus
1 - stirrer engine; 2 - propeller; 3 - pulp; 4 - sampler; 5 - thermometer; 6 - feeder; 7 - water thermostat; 8 - EAF sample

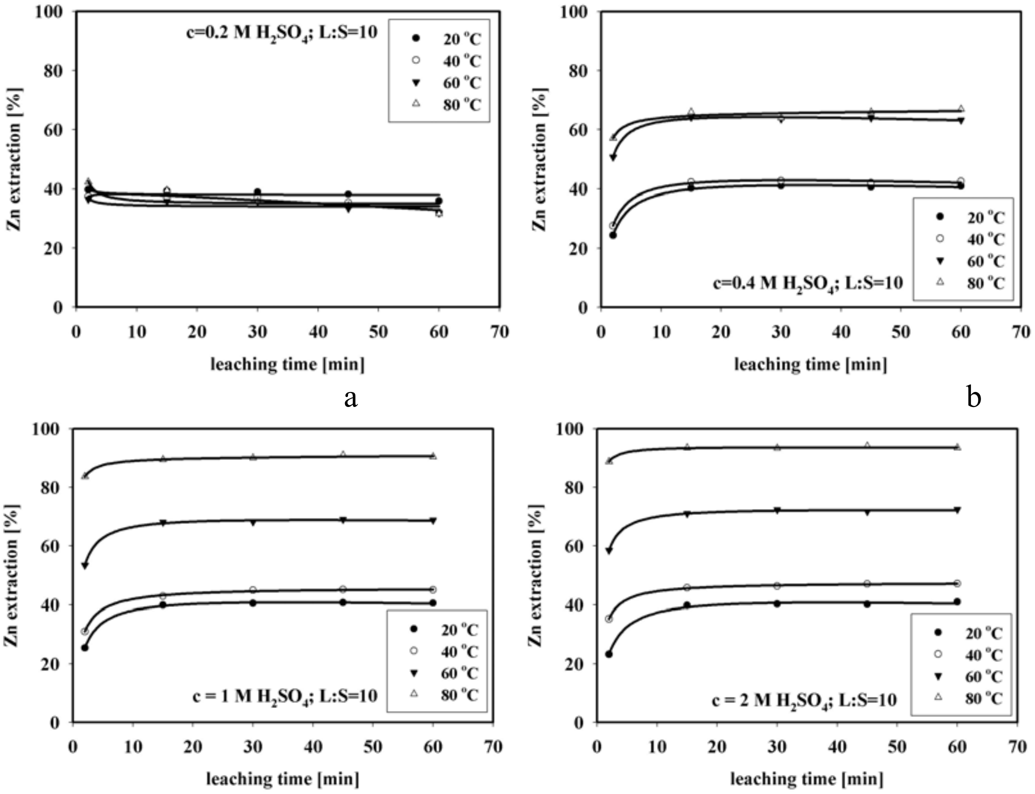
The leaching experiments were performed in a glass reactor of 800 ml provided with a cap in the central hole in which the axis of a glass stirrer for adjustable revolutions is placed (300 rev/min in each experiment). Openings for a mercury thermometer, a sampling liquid specimen, and an input of the powdered sample were situated in cap. The reactor was placed in a water bath controlled by a thermostat. This allowed the conducting of the leaching at the desired temperature. Leaching tests were performed with a solution of 400 ml of 0.2, 0.4, 1.0 and 2.0 M H_2SO_4. The sample weight was 40, 26.7 and 13.5 g with a liquid to solid ration L: S equal to 10, 15 and 30.

A solution with an acid-to-EAF dust ratio of 12.5 and 25 was used. The temperatures being used were 20, 40, 60, and 80 ^{o}C, under normal atmospheric pressure. The samples for the chemical analysis were taken according to a fixed-schedule after 2, 10, 15, 30, 45 and 60 minutes. The samples were then filtered and inserted into test tubes. A clear solution was obtained. The chemical analysis, carried out in order to determine Zn and Fe**,** was made by means of AAS method. All results were recalculated because of the change of the pulp volume due to the sampling and evaporation.

3. Achieved results and discussion

It follows from theoretical study by E-pH diagrams [5] that at certain pH of solution zinc could be transferred into solution while iron stays in the solid residue. The increasing of the pH values and the decreasing of the redox potential of solution cause that the soluble Fe^{2+} ions are precipitated from the solution while zinc stay in the solution in the soluble form. The stability area of the Fe^{3+} ions also exists in the very acid area at pH~0. They participate on the leaching as considerably strong oxidant and precipitate as FeOOH while sulphuric acid is spent and pH increases. The increasing of temperature cause that the stability area of the Fe^{3+} ions is extended and the potential line between Fe^{2+} and Fe^{3+} ions is moved to the higher values of the redox potential. The line precipitation of the Zn^{2+} ions from the solution is moved to the lower pH values, from $pH_{25} = 4.55$ to $pH_{100} = 3.91$. This value is still enough high in compare with line precipitation of iron ions from the solution. At the same time the reactions of the other presented elements from EAF dust also will take place. Therefore, it is necessary to find the optimum acid concentrations so that the free acid content will be spent and pH solution increases to the desired values in which iron precipitates from the solution.

Figure 2 shows the kinetic curves of zinc leaching from EAF dust depending on temperature and sulphuric acid concentration.



a b

c d

Fig. 2a-d Kinetic curves of zinc extraction from EAF dust at various acid concentrations

As follows from results given above, process is very fast and immediately after the beginning of the leaching, the maximum amount of the zinc from EAF dust is dissolved. Both of acid concentration and temperature affected the amount of zinc extracted.

Fig. 3 shows the dependence of zinc extraction on acid concentration and temperature suggesting that at the individual temperature the amount of zinc extraction with increasing of acid concentration changes only a little. The exception makes only using low acid concentration in this case 0.2 M H_2SO_4.

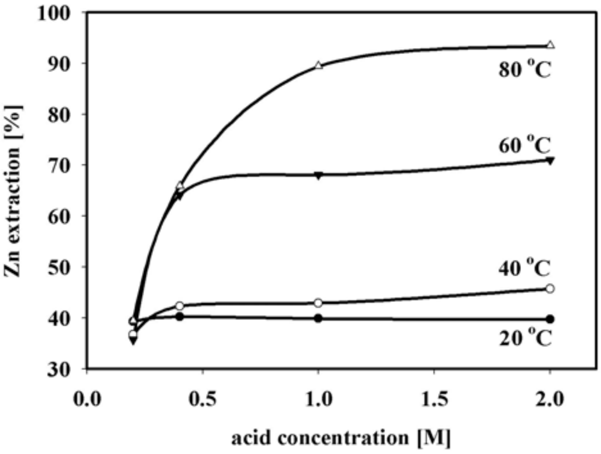


Fig. 3 Extraction of zinc on acid concentration and temperature after 15 minutes of leaching

Figure 4 shows the kinetic curves of iron extraction from EAF dust depending on both of temperature and sulphuric acid concentration. No iron extraction is occurred in whole temperature range when low acid concentration 0.2 mol.dm^{-3} H_2SO_4 is used for leaching. However, the increasing of acid concentration results in the iron dissolving and this amount considerably depends on the temperature. At lower temperature the amount of the iron dissolved is low, but increasing of temperature causes the increasing of iron dissolving. Initially, at the low acid concentration, amount of iron in the solution is higher but latter it decreases. Iron precipitates from the solution forasmuch as the free acid content is spent by reaction with zinc and other elements. As result of it, pH value of solution increases out of range of the stability area of the dissolved iron ions in accordance with E-pH diagrams of the system Fe-S-H_2O [5].

Necessary amount of acid for this EAF dust follows from the Fig. 5, in which the dependence of pH on temperature is shown. The pH values of 0.2 mol.dm^{-3} H_2SO_4 are during leaching increased up to pH = 5 while the pH values of the more concentrated solution increased only to pH = 1.5. The pH = 2 of the initial leaching solution didn't increase therefore it's obvious that there is sufficient amount of free acid for reaction with heavy metals and also with iron. It results in high iron content in the solution, especially at the high temperatures, when process kinetics gains important.

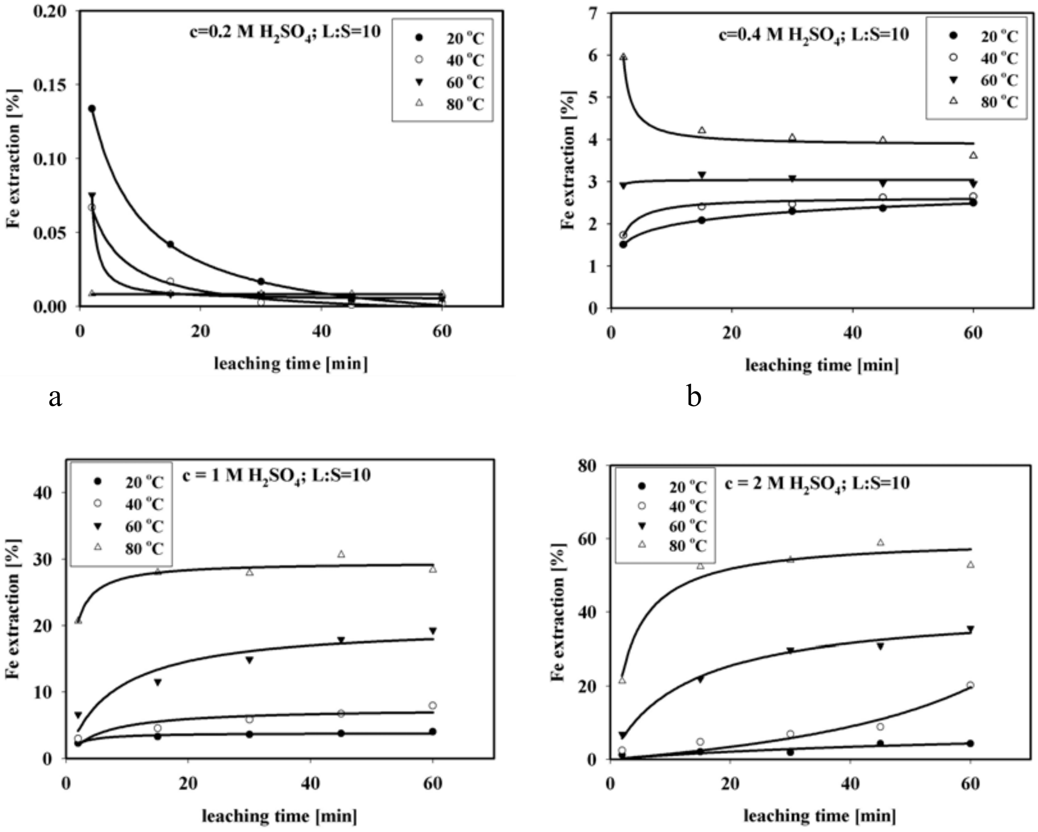


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Fig. 4a-d Kinetic curves of iron extraction from EAF dust at various acid concentrations

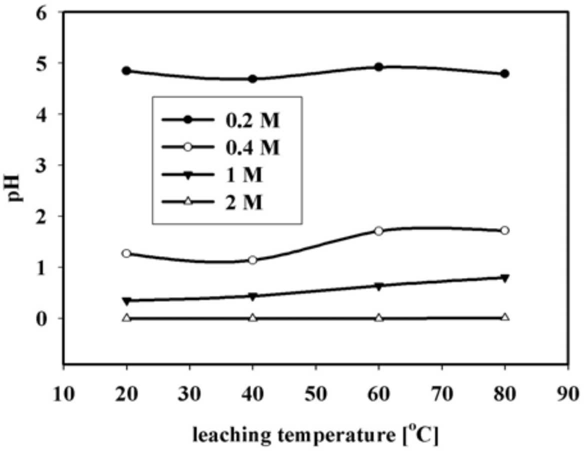

Fig. 5 Temperature dependence on the pH change of leaching solutions

Leaching of EAF dust depending on the change of a liquid:solid ratio showed only small changes in the results. The quantity of the dissolved zinc and iron always depends on the amount of free acid in the leaching solution. Hence, relative amount of the dissolved metals rises with increasing of liquid:solid ratio.

Conclusion

From the experimental study of Slovak EAF dust leaching can be deduced the following conclusions:

1. Zinc leaching from EAF dust is very fast running within minutes.
2. Zinc leaching depends on sulphuric acid concentration. The maximum zinc extraction of 95 % is achieved when acid concentration is higher than 1 mol.dm^{-3}.
3. The temperature has a considerable effect on the yield of the zinc extraction.
4. The iron isn't extracted at the low concentration of the used acids.
5. The increasing of acid concentration result in increasing amount of the iron extraction.
6. The amount of iron extraction for given concentrations depends on used of the leaching temperature.
7. The optimum conditions for removing zinc from EAF dust with a minimum iron extraction are obtained at the temperatures from 60 to 80 °C and concentration of sulphuric acid of 0.4 mol.dm^{-3} as well.

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