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Atmospheric leaching of EAF dust with diluted sulphuric acid

Tomas Havlik[a,*], Martina Turzakova[a], Srecko Stopic[b], Bernd Friedrich[b]

[a]*Department of Non-ferrous Metals and Waste Treatment, Faculty of Metallurgy, Technical University of Kosice, Letna 9, 04200 Kosice, Slovakia*
[b]*IME Process Metallurgy and Metal Recycling, RWTH, Intzestrasse 3,52056 Aachen, Germany*

Abstract

In this study the hydrometallurgical processing of EAF steelmaking dust (Paul Wurth S.A.) is investigated on a laboratory scale under normal temperature and pressure conditions. The behaviour of zinc and iron under the influence of sulphuric acid as the leaching agent is discussed. The dependency between the temperature and the liquid/solid ratio is investigated. The main aim is the transfer of zinc into the solution while iron ought to remain as a solid residue.

The hydrometallurgical recovery of zinc from EAF dust is feasible with a relatively high recovery yield, while iron mostly remains in the solid phase. Calcium, too, is transferred to the solution with a relatively high recovery yield. This results from the use of a low concentration of sulphuric acid. 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 an iron dissolution. However, the problem is that the chemical and mineralogical composition of each steelmaking dust is individual. Therefore, it is necessary to study the processing conditions for each one of them.
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1. Introduction

One of the most important issues with which steel producers are faced is the question of environmental protection. It refers e.g. to the necessity to utilise dusts resulting from the process of steel production from scrap in electric furnaces, containing mainly of Zn, Fe, Pb and a considerable amount of harmful elements, such as Cd, As, Cr and F. The composition of EAF dusts depends on the following aspects: on the scrap processed, on the type of steel to be produced, on operating conditions and on the degree recirculation of the dust to the process. The contents of the main elements in EAF dusts may vary between: 30% of Zn, 0.3–6% of Pb, 0.01–0.2% of Cd, 20–35% of Fe, 0.2–0.7% of Cr, 1–10% of Ca, etc. (Cruells et al., 1992).

The mineralogical analysis indicates the presence of iron in an oxide form, mostly as hematite Fe_2O_3, magnetite Fe_3O_4 and ferrite as franklinite $ZnFe_2O_4$. Zinc is present mostly in two basic compounds, namely as oxide ZnO and ferrite $ZnFe_2O_4$, and possibly as a complex ferrite, e.g. $(ZnMnFe)_2O_4$. The mineralogical form of the zinc presence seems to be the basic indicator for the effectiveness of the EAF dust treatment. ZnO in principle is an easily workable form for both the pyro- and the hydrometallurgical method, but the ferrite form is considerably complex and difficult.

Treatment technologies of zinc-bearing wastes represent various levels of development both of pyrometallurgical and hydrometallurgical processes. A brief overview of the methods, which have been used for the treatment of this material, was presented in our previous work (Havlik et al., 2004). These
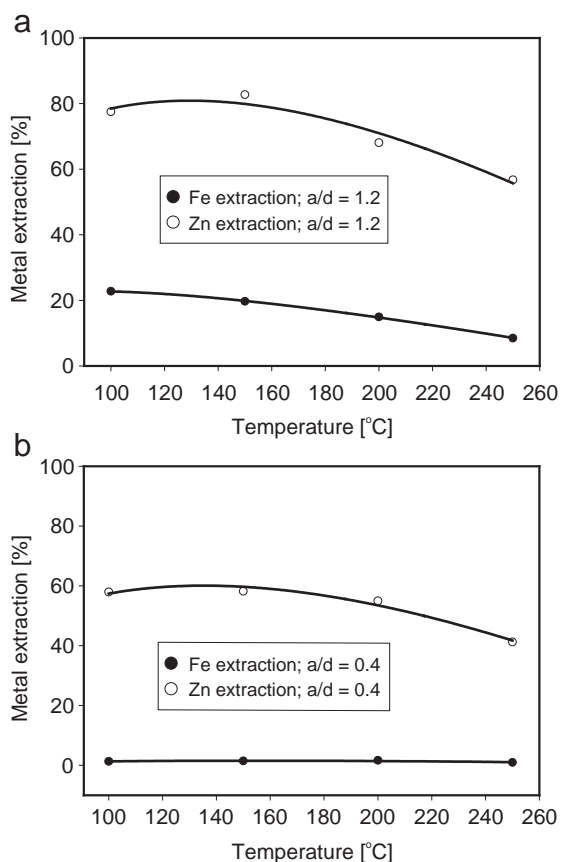
Table 1
Chemical analysis of EAF dust by Paul Wurth S.A.

Element	Fe	Zn	Pb	Si	Ca	Mn	Cu	Cr
[%]	27.8	20.9	2.7	2.1	4.3	3.2	0.36	0.77

Element	Ni	Ti	Cd	Sb	As	Cl$^-$	SO$_4^{2-}$	Loss of ignition
[%]	0.06	~0.04	0.027	0.069	<0.1	0.89	0	12.18

works were made by several investigators (Frenay et al., 1985, 1986; Jha and Duyvesteyn, 1985; Dreissinger et al., 1990; Barrett et al., 1992; McElroy and McClaren, 1994; McElroy and Murray, 1996; Lupi et al., 1996; Jandová et al., 2002), etc.

In study (Havlik et al., 2004), the hydrometallurgical pressure processing of EAF steelmaking dust, provided by Paul Wurth S.A., Luxembourg, was investigated on a laboratory scale in the temperature range of 100 to 250 °C. The behaviour of zinc, iron

Fig. 1. Metal extraction vs. leaching temperature dependence (Havlik et al., 2004). (a) a/d ratio=1.2; (b) a/d ratio=0.4 (a/d=grams of concentrated H_2SO_4 to grams of dust).
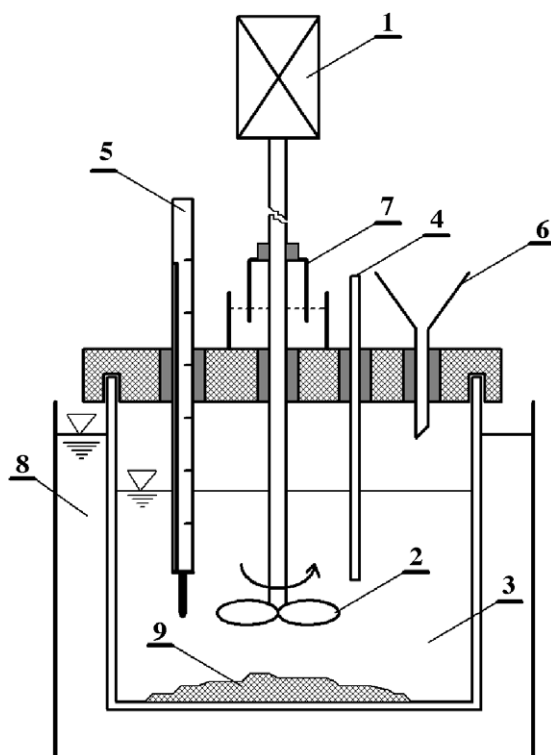

Fig. 2. Schematic view of the leaching apparatus. 1—Stirrer engine; 2—propeller; 3—pulp; 4—sampler; 5—thermometer; 6—feeder; 7—water seal; 8—water thermostat; 9—EAF sample.

and calcium under influence of sulphuric acid as the leaching agent was discussed.

According to the results obtained in this work, the high pressure hydrometallurgical recovery of zinc from EAF dust is feasible at a reasonable recovery yield, while iron mostly remains in the solid phase. The latter is due to the use of the low concentration of sulphuric acid of approximately 0.4 mol $H_2SO_4 \cdot dm^{-3}$. Three ratios of the free acid weight to solid, with the value of a/d (acid/dust) of 1.2, 0.6, and 0.4, were used. The maximal value of selectivity was obtained by the a/d ratio of 0.4. Higher temperatures and pressures moderately increase the zinc yield.

Fig. 1a to b show the results for the metal extraction depending on temperature/pressure and a/d ratios obtained in study (Havlik et al., 2004).

These results show promise. However, it is necessary to compare such results with those obtained

by the same hydrometallurgical route but under normal conditions concerning both temperature and pressure. This is the concept of the present study. The main factors investigated are the effects of temperature on the dissolution of Zn, Fe and Ca by use of sulphuric acid as the extractant at an atmospheric pressure of 0.1 MPa.

2. Experimental

2.1. Material

The materials used in these experiments are the same as in study (Havlik et al., 2004), i.e. EAF dust given by Paul Wurth S.A., Luxembourg. Its chemical analysis, given in Table 1, was determined by the ICP method.
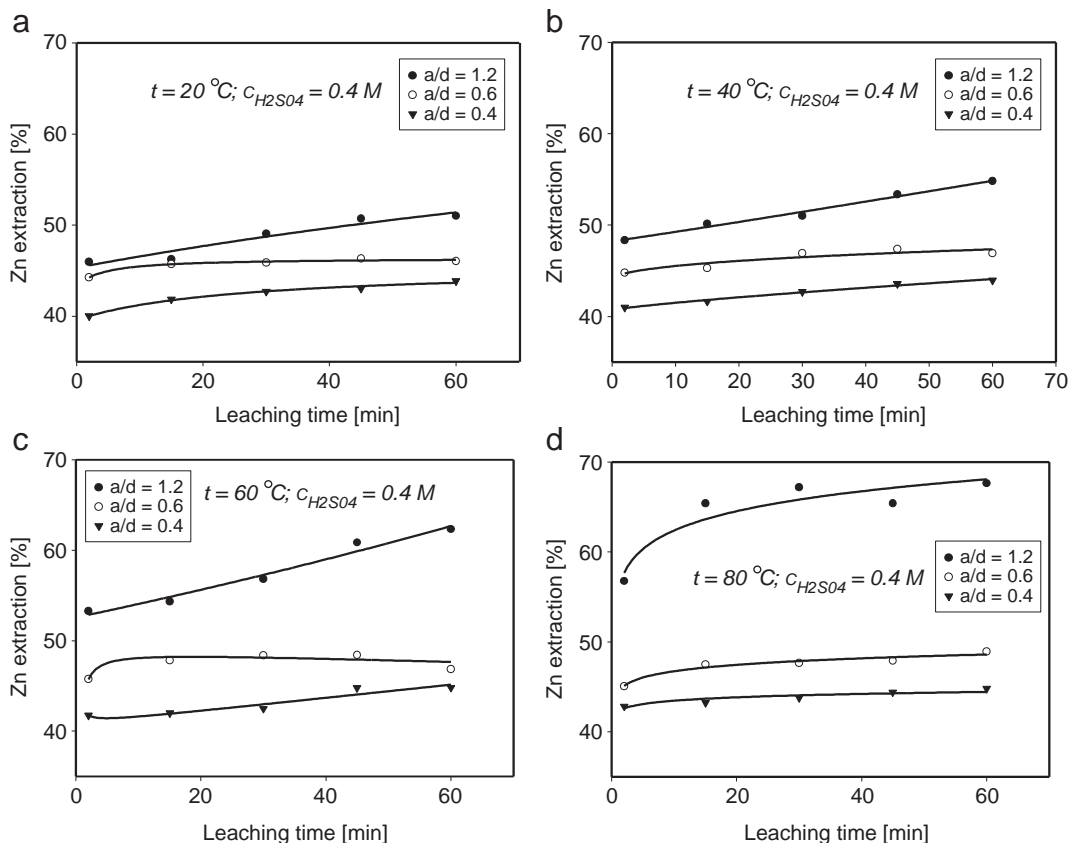

Fig. 3. (a) Extraction of Zn by sulphuric acid at a temperature of 20 °C. (b) Extraction of Zn by sulphuric acid at a temperature of 40 °C. (c) Extraction of Zn by sulphuric acid at a temperature of 60 °C. (d) Extraction of Zn by sulphuric acid at a temperature of 80 °C.

The results of the X-ray diffraction qualitative analysis show the presence of compounds such as franklinite Zn_2FeO_4, zincite ZnO, magnetite Fe_3O_4, cristobalite SiO_2. Other phases, which, on the basis of the chemical analysis, could be present, are probably below the detection limit.

2.2. Experimental set-up and procedure

Leaching tests are performed in the apparatus, of which a scheme is given in Fig. 2.

The leaching experiments are performed in a glass reactor of 600 mL provided with a Teflon cap in the central hole in which the axis of a glass stirrer for adjustable revolutions is placed. Openings for a mercury thermometer, a sampling liquid specimen, and an input of the powdered sample are situated in the perimeter of the cap. The reactor is placed in a water bath controlled by a thermostat. This allows to conduct the leaching at the desired temperature.

Leaching tests are performed with a solution of 300 mL of 0.4 M H_2SO_4. The sample weight is in the range of 10 to 30 g. A solution with an acid-to-EAF dust ratio a/d of between 0.4 and 1.2 is used. The temperatures being used are 20, 40, 60, and 80 °C, under normal atmospheric pressure.

The samples for the chemical analysis are taken according to a fixed-schedule after 2, 15, 30, 45 and 60 min. Then the samples are filtered into test tubes and, thus, a clear solution is obtained. Like during the pressure leaching described in work (Havlik et al., 2004), the solution is colourless, weakly yellow or weakly emerald depending on the leaching conditions. In some samples, again the
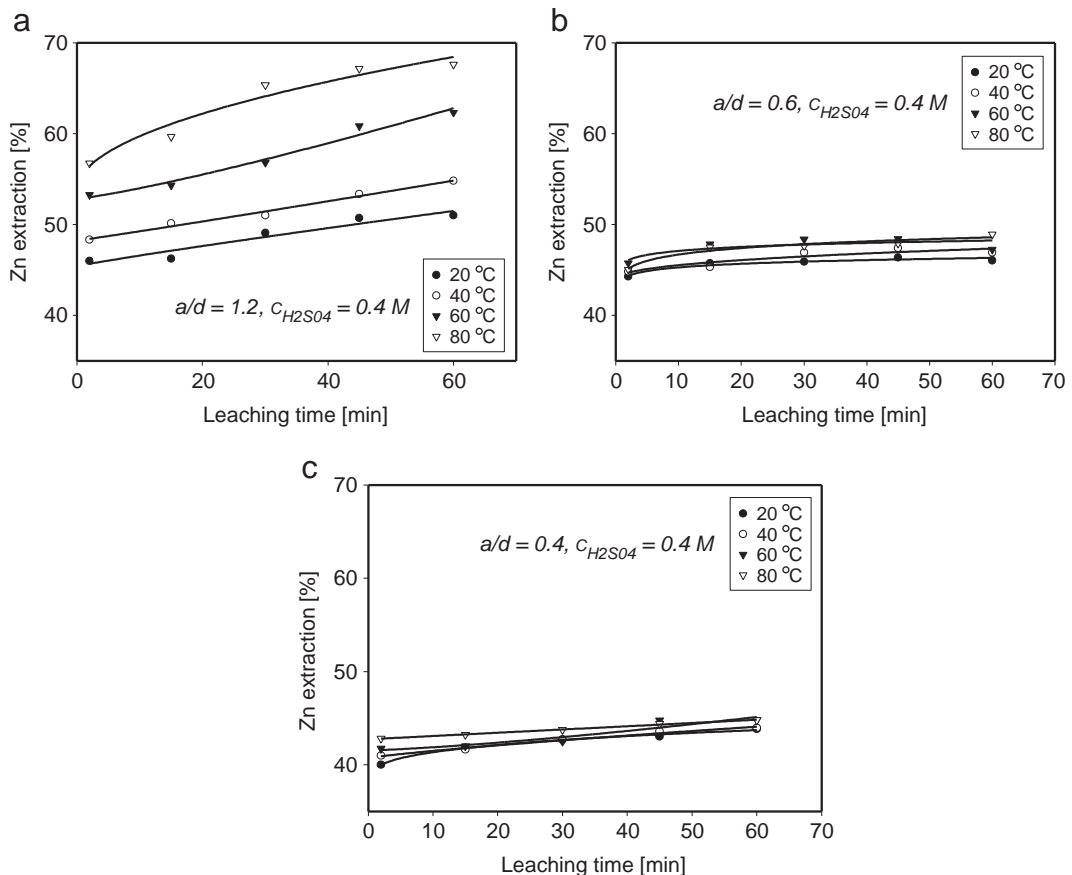

Fig. 4. (a) Extraction of Zn by sulphuric acid for a 10 g charge under various temperatures. (b) Extraction of Zn by sulphuric acid for a 20 g charge under various temperatures. (c) Extraction of Zn by sulphuric acid for a 30 g charge under various temperatures.

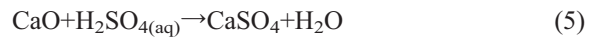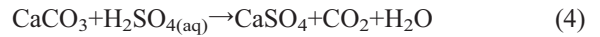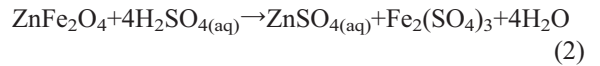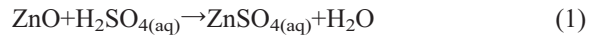white precipitate of calcium sulphate appears after 1 or 2 days.

The chemical analysis, carried out in order to determine Zn, Fe, and Ca, was made by means of an AAS Varian Spectrometer AA 20+. Moreover, the amount of free acid as well as the pH is measured. All results are recalculated because of the change of the pulp volume due to the sampling and evaporation.

3. Results and discussion

3.1. Leaching reactions

As already described in Havlik et al. (2004), the reactions of the main species occurring in the

sample and their stoichiometry can be stated as follows:

$$ZnO+H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)}+H_2O \qquad (1)$$

$$ZnFe_2O_4+4H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)}+Fe_2(SO_4)_3+4H_2O \qquad (2)$$

$$ZnFe_2O_4+H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)}+Fe_2O_3+H_2O \qquad (3)$$

$$CaCO_3+H_2SO_{4(aq)} \rightarrow CaSO_4+CO_2+H_2O \qquad (4)$$

$$CaO+H_2SO_{4(aq)} \rightarrow CaSO_4+H_2O \qquad (5)$$

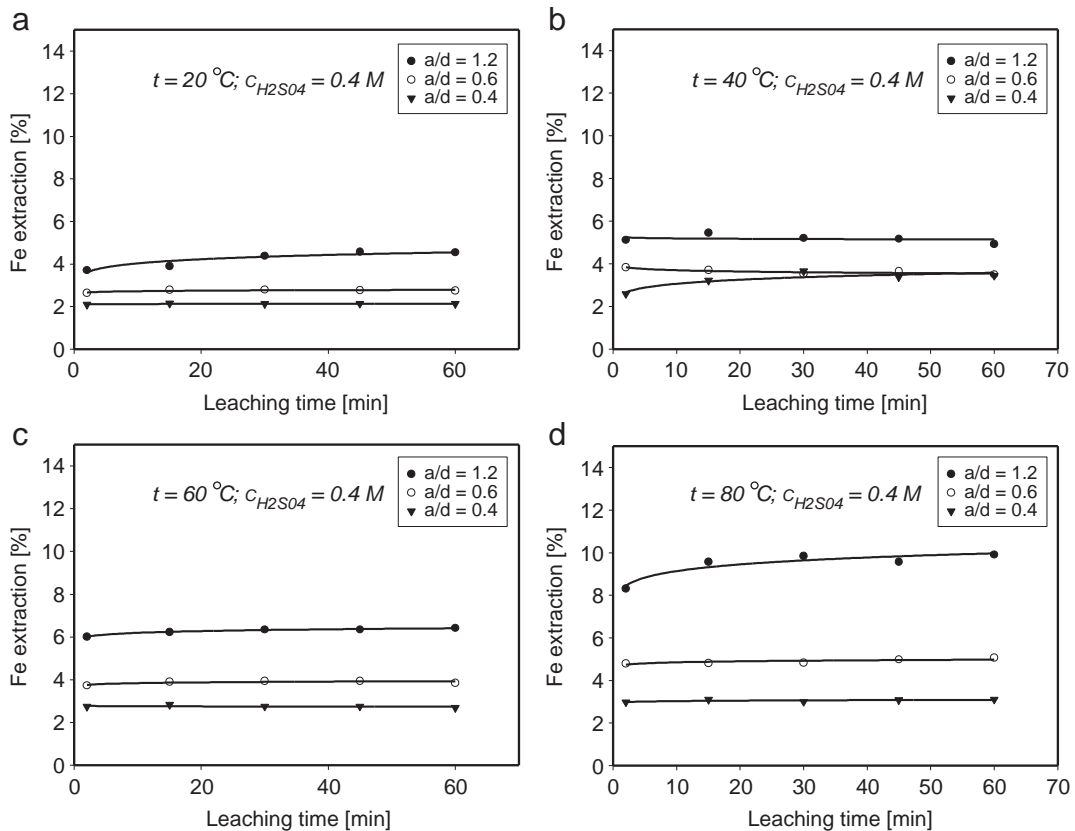Reaction (2) occurs slowly at room temperature, but runs at a high rate at elevated temperatures.

Fig. 5. (a) Extraction of Fe by sulphuric acid at a temperature of 20 °C. (b) Extraction of Fe by sulphuric acid at a temperature of 40 °C. (c) Extraction of Fe by sulphuric acid at a temperature of 60 °C. (d) Extraction of Fe by sulphuric acid at a temperature of 80 °C.

3.2. Leaching studies with sulphuric acid

In Fig. 3a to d the extraction curves at 0.4 M H_2SO_4 and various acid/dust (a/d) ratios for Zn at different temperatures are presented.

The temperature has a considerable effect on the yield of the zinc extraction. This is valid for each solid/liquid ratio being studied, as demonstrated in Fig. 4a to c. Since an increase of the quantity of the charge causes the reduction of the zinc yield, the concentration of sulphuric acid (or the a/d ratio) seems to be the second important factor for the zinc extraction. The maximum value for the zinc extraction of 67% is obtained at a temperature of 80 °C, in a time of 60 min and with a concentration of sulphuric acid of 0.4 mol·dm^{-3} (Fig. 3d). However, the curves in general show a progressive run. This means that the prolongation of the

leaching time should result in an increase of zinc extraction.

Fig. 5a to d illustrate the extraction curves for iron under the same conditions. In these cases, the increase of temperature causes the increase of the iron yield, although the total amount of iron in the solution does not exceed 10%.

The temperature effect on iron extraction is shown in Fig. 6a to c at various a/d ratio. It was observed in the high temperature/pressure leaching of EAF dust (Havlik et al., 2004) that calcium sulphate was precipitated from the same solution after the leaching and cooling of the leaching solution. In the present experiments, under normal conditions concerning both temperature and pressure the white precipitate of calcium sulphate rarely occurs. Fig. 7a to d demonstrate the extraction of the calcium during the leaching under various conditions.
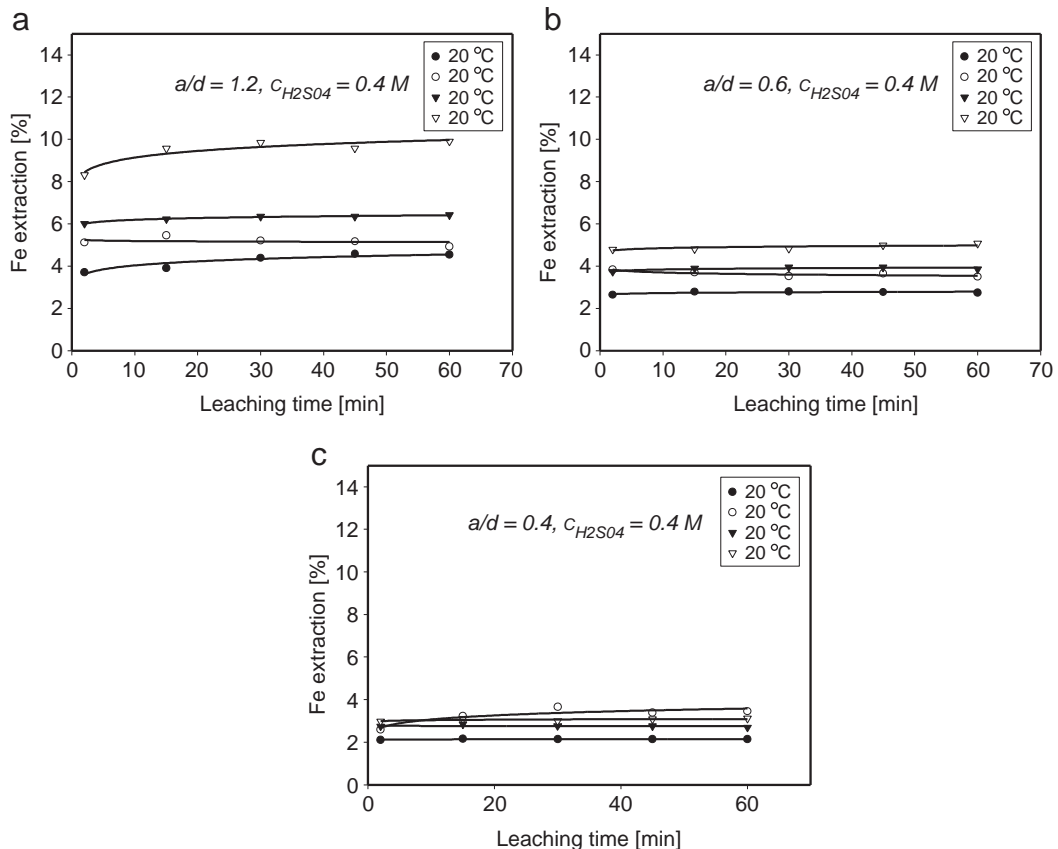

Fig. 6. (a) Extraction of Fe by sulphuric acid for 10 g charge under various temperatures. (b) Extraction of Fe by sulphuric acid for 20 g charge under various temperatures. (c) Extraction of Fe by sulphuric acid for a 30 g charge under various temperatures.
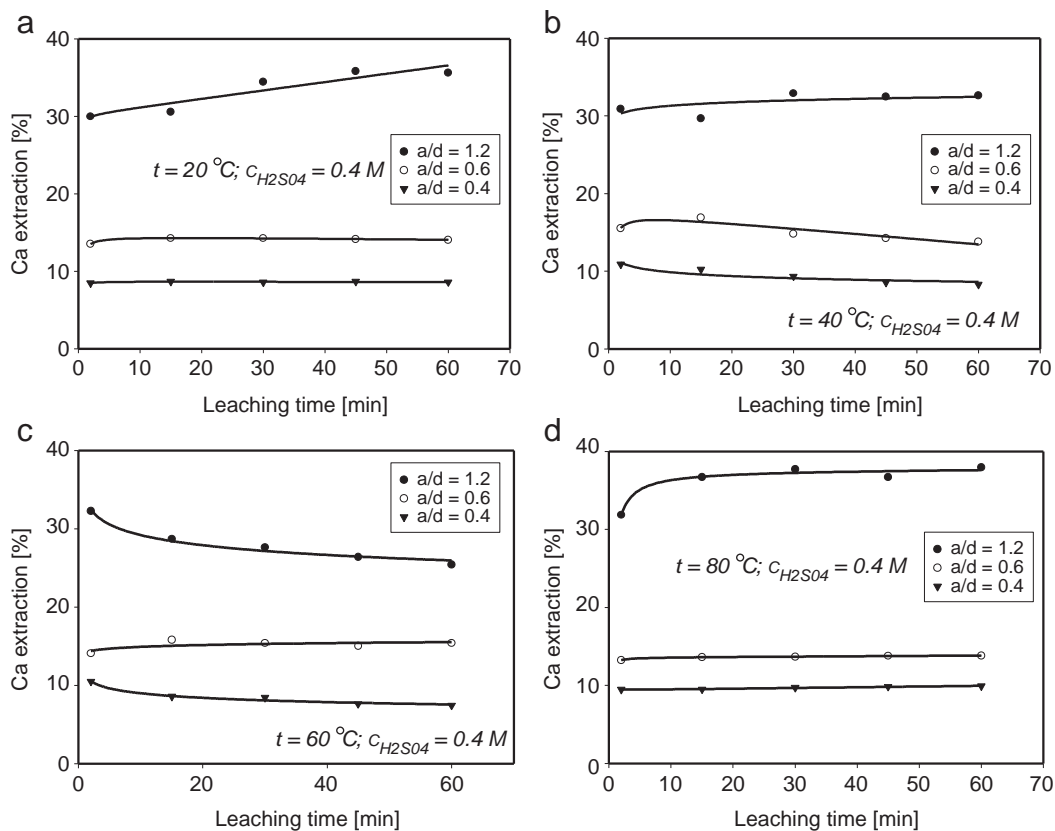
Fig. 7. (a) Extraction of Ca by sulphuric acid at a temperature of 20 °C. (b) Extraction of Ca by sulphuric acid at a temperature of 40 °C. (c) Extraction of Ca by sulphuric acid at a temperature of 60 °C. (d) Extraction of Ca by sulphuric acid at a temperature of 80 °C.

Although the amount of dissolved calcium is rather high, it is considerably decreased by the increase of the charge, as it is demonstrated in Fig. 8a to c.

The concentration of H_2SO_4 used for these experiments, i.e. 0.4 mol·dm^{-3}, results from previous experiments described in study (Havlik et al., 2004). The thermodynamic considerations and calculations reveal that this concentration should mostly be spent for the dissolution of zinc, but less for iron and calcium. Fig. 9 shows the acid consumption during leaching, determined as the dependence of the pH-value on the charge amount at various temperatures.

The results reveal that the a/d ratio, i.e. the charge amount, plays an important role in the metal extraction. pH values were increased according to the increase of the a/d ratio due to a higher consumption of sulphuric acid during leaching. Since small charges are used, the zinc extraction is consid-

erably high. The maximum value for zinc extraction α=67% is obtained at a temperature of 80 °C, in a time of 60 min and at a used concentration of sulphuric acid of 0.4 mol·dm^{-3}, Figs. 3d and 4a. A further increase of the leaching time would probably result in same zinc extraction increasing as follows from Figs. 3d and 4a.

The increase of the charge amount results in the decreasing of the zinc extraction. In these cases, however, temperature plays a less important role. This probably means that the sulphuric acid concentration is a limiting factor for the dissolution of zinc.

This applies to iron and calcium, too. The maximum of iron dissolved is less than 10%, (Figs. 5d and 6a), but in case of calcium it is up to 40% (Figs. 7d and 8a).

Comparing of the results obtained in this work with those obtained in the study of high temperature/
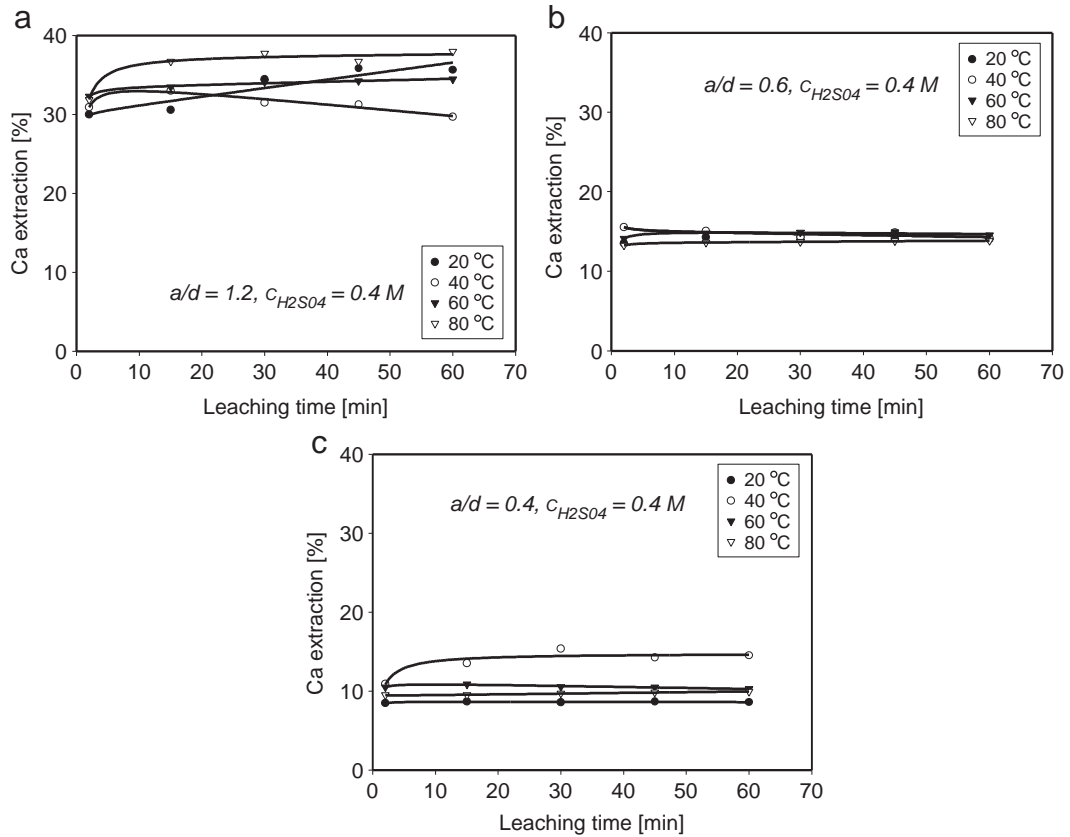
Fig. 8. (a) Extraction of Ca by sulphuric acid for a 10 g charge under various temperatures. (b) Extraction of Ca by sulphuric acid for a 20 g charge under various temperatures. (c) Extraction of Ca by sulphuric acid for a 30 g charge under various temperatures.

pressure leaching (Havlik et al., 2004) under similar conditions shows that the leaching under normal conditions results in the lower extraction of zinc, even

Fig. 9. pH vs. charge amount dependence for various temperatures.

though there is the tendency for the further dissolution of zinc. In high temperature/pressure leaching the leaching ceases after a short time at a fixed value. The maximum value is, at best, at $\alpha = 84\%$.

Furthermore, in regard to iron, the study shows that the maximum value of iron dissolved under normal leaching conditions is about 10%, in contrast to high temperature/pressure leaching in which, at the worst, more than 20% is achieved. In high temperature/pressure leaching at best around 1% of dissolved iron is achieved. Under normal leaching conditions, regarding both temperature and pressure, the minimum value for the iron dissolution is about 2%.

The quantity of dissolved calcium is rather high. With a sulphuric acid concentration of 0.4 mol·dm^{-3}, only in one case the white precipitate of calcium sulphate is formed. However, this only applies for temperatures of 100 and 150 °C (concerning high
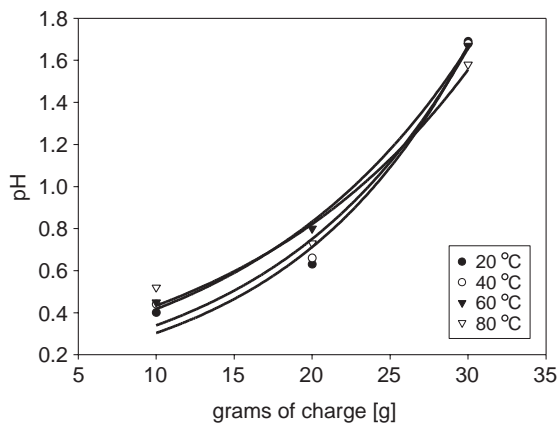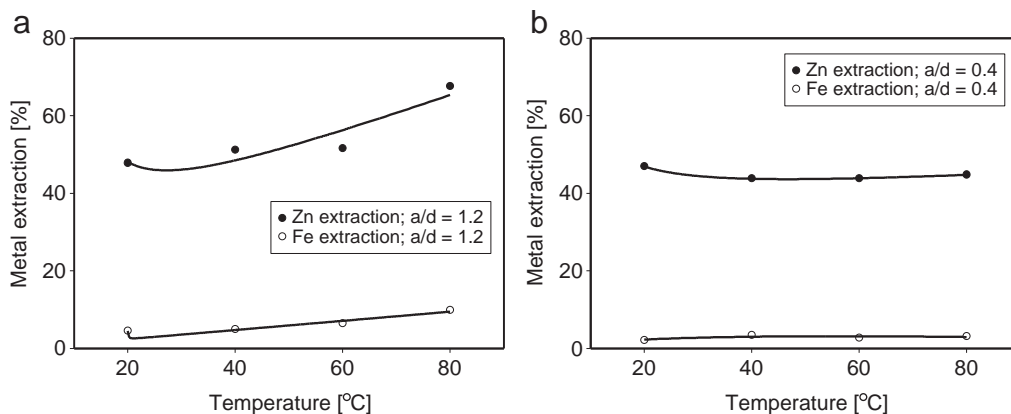
Fig. 10. (a) Dependency of metal extraction vs. leaching temperature at a/d=1.2. (b) Dependency of metal extraction vs. leaching temperature at a/d=0.4.

temperature/pressure leaching). This is the reason that only a small amount of calcium remains in the solution.

Fig. 10a to b show the dependencies of metal extraction on the leaching temperature for the highest and lowest dust charge, each in relation to the amount of acid available for the leaching. For the lowest charge amount of a/d=1.2, the zinc extraction is higher having the tendency to increase at a higher temperature. Yet, when using the lowest charge amount, also the quantity of the dissolved iron is higher compared to a/d=0.4. The comparison with the experiment at 100 °C, presented in work (Havlik et al., 2004), reveals that this, under normal temperature/pressure conditions, is the optimum temperature for the maximal zinc extraction. However, the amount of extracted iron is several times higher at 100 °C than at 80 °C. It seems that higher values of selectivity are obtained by lower temperature and, perhaps, a/d ratios.

4. Conclusion

According to the results obtained in this work, the hydrometallurgical recovery of zinc from EAF dust is feasible with a relatively high recovery yield, while iron mostly stays in solid phase. A similar conclusion can be drawn in the case of high temperature/pressure leaching under equivalent experimental conditions. Comparing the results of this work with those obtained by high temperature/pressure leaching man-

ifest that, concerning the zinc extraction, the last is more effective. Yet, this does not relate to iron. Additionally, calcium permanently remains in the solution. Although in high temperature/pressure leaching calcium is dissolved first, it later precipitates as calcium sulphate. This does only relate to temperatures up to 150 °C and pressures up to 4.1 bar. Even in higher temperatures/pressures leaching calcium permanently remains in the solution. This behaviour results from using a low concentration of sulphuric acid. This also causes in fact a decrease in the zinc yield, yet the amount of dissolved iron is low. In such a way, it can be possible to set up the conditions for an optimum zinc yield into the solution with a minimised iron dissolution. However, the problem persists that the chemical and mineralogical composition of each steelmaking dust is individual and that for each one the conditions of processing have to be studied.

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