



## Acidic leaching both of zinc and iron from basic oxygen furnace sludge

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### ABSTRACT

During the steel production in the basic oxygen furnace (BOF), approximately 7–15 kg of dust per tonne of produced steel is generated. This dust contains approximately 1.4–3.2% Zn and 54–70% Fe. Regarding the zinc content, the BOF dust is considered to be highly problematic, and therefore new technological processes for recycling dusts and sludge from metallurgical production are still searched for. In this study the hydrometallurgical processing of BOF sludge in the sulphuric acid solutions under atmospheric pressure and temperatures up to 100 °C is investigated on laboratory scale. The influence of sulphuric acid concentration, temperature, time and liquid to solid ratio (L:S) on the leaching process was studied. The main aim of this study was to determine optimal conditions when the maximum amount of zinc passes into the solution whilst iron remains in a solid residue.

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## 1. Introduction

The generation of steelmaking dusts is an integral part of melting in steelmaking plants. Steelmaking dusts are waste oxide materials, whose major components are iron oxides. These steelmaking dusts are obtained either in the form of dust, from dry dust separation, or in the form of sludge from wet dust separation. Due to the zinc content in the steelmaking dusts and sludge they cannot be recycled, hence they are deposited in landfills.

Large grain size scattering as well as varied chemical and mineralogical composition are typical features of steelmaking dusts. Table 1 shows the percentage of zinc and iron in BOF dust and sludge according to various authors.

Both BOF dust and sludge are categorized as hazardous wastes [14]. Several methods for the processing of steelmaking dusts have been already designed; however, there is still not enough information about how to process BOF dust. This is probably caused by relatively low content of zinc compared with electric arc furnace dust. The steelmaking dust can be processed by pyrometallurgical methods, hydrometallurgical methods or by combination of both [15]. Each of these methods has its advantages as well as disadvantages. The advantage of hydrometallurgical processes is their higher flexibility in plants. Hydrometallurgical processes are also more economical because of lower capital and operating costs. In

addition, hydrometallurgy offers the possibility of getting valuable metals from the dust or sludge. There are also environmental benefits in comparison with pyrometallurgy because of no problems associated with off-gases, dust nuisance and noise.

However, hydrometallurgy does not offer a solution to the steelmaking waste processing by only one versatile way. The leaching methods are individual and depend not only on the type of the processed waste but on the physical, physico-chemical, chemical and mineralogical properties as well. Research in the field of hydrometallurgical processing is becoming more and more intensive. It is mainly because of the need to process complex raw materials, environmental aspects and also due to the legislative pressure for environmental protection.

This work focuses on a study of the influence of the temperature and sulphuric acid concentration on zinc extraction into the solution as well as the determination of the optimal conditions under which the maximum amount of zinc passes into the solution and iron remains in solid residue. The aim is to design a recycling method for BOF sludge.

## 2. Experimental

### 2.1. Material

The sample of BOF sludge was dried and homogenized before the leaching experiments. The chemical analysis was performed by atomic absorption spectrometry (AAS). The chemical composition of dust from converter gas treatment is shown in Table 2.

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**Table 1**  
Zinc and iron contents in BOF dust and sludge according to various authors.

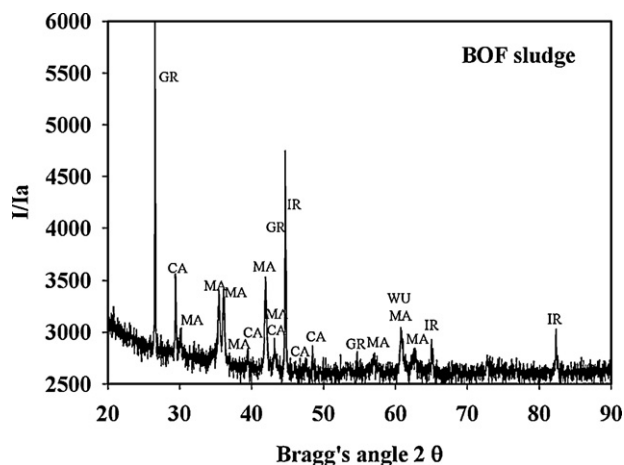
Zn (%)	0.5–3.5	0.1–1	0.01–0.9	1.4–3.2	0.05–4	0.02	1.20	0.200
Fe (%)	53–63	59–67	52–72	54–62	45–62	62.3	59.8	64.8
Ref.	[1]	[1]	[1]	[1]	[1]	[1]	[1]	[1]
Zn (%)	1–10	14.1	7.80	1.10	5.10	6.00	1.50	1.70
Fe (%)	55–65	57.1	57.9	64.8	57.1	55.7	56.7	55.4
Ref.	[2]	[3]	[3]	[4]	[4]	[4]	[4]	[5]
Zn (%)	0.6–5	2.86	0.480	0.9–2.5	1–2	0.208	1.40	7.55
Fe (%)	56–64	67.86	87.2	60–64	60.0	74.8	73.8	44.2
Ref.	[6]	[7]	[7]	[8]	[9]	[10]	[10]	[10]
Zn (%)	0.070	0.380	3.99	2.54				
Fe (%)	82.1	63.0	59.7	53.6				
Ref.	[11]	[11]	[12]	[13]				
<i>Average values</i>								
Zn amount (wt.%)		2.57						
Fe amount (wt.%)		61.4						

**Table 2**  
The chemical composition of dust from converter gas treatment.

Element	Amount [%]
Fe	47.7
Zn	2.74
Pb	0.180
Si	0.610
Sb	0.310
Sn	0.200
Cu	0.100
Cr	0.010
Ca	6.80
Mg	0.550
Mn	0.490
Ni	0.090
Co	0.020
LOI	12.5

LOI – lost of ignition.

The mineralogical composition was determined by XRD phase analysis (Fig. 1). Dust from steelmaking furnaces is mainly generated at high temperatures, which gives rise to an assumption of generating more complex bonds between particular elements and possibly new synthetic compounds. In the sample the phases such as magnetite  $\text{Fe}_3\text{O}_4$ , wuestite  $\text{FeO}$ , calcite  $\text{CaCO}_3$ , graphite C, and metallic Fe are found with high probability. Phases such as maghemite  $\text{Fe}_2\text{O}_3$ , ferrite phases and  $\text{SiO}_2$  were found with less

**Fig. 1.** X-ray diffraction pattern of the input sample (MA – magnetite, CA – calcite, GR – graphite, IR – iron, WU – wuestite).

probability. Other phases, if they are present following the chemical composition, are in minor amounts and vanishing in the background of the XRD pattern.

In the sample of BOF sludge no phase containing zinc was identified. This can be caused by the following reasons:

- Small amounts of Zn in the sample, 0.1–3%. These amounts create a small amount of phases, and if zinc is distributed to various phases (zinkite, franklinite, and complex franklinite) their diffractions can vanish in the background of the XRD pattern.
- The diffraction measurement was carried out on Cu  $K\alpha$  radiation. In principle, this radiation is not very suitable for samples with high iron content, because fluorescent radiation is activated, which results in the increased background of the diffraction pattern, and therefore small diffraction peaks are vanishing in the background.
- It is assumed that a part of the sample, in regard to its origin, is not totally crystallized. Amorphous parts result in the increased background of the diffraction pattern. In addition, the carbon present causes similar effects.
- Another reason can be the fact that franklinite and magnetite are isostructural and the diffraction peaks appear approximately at the same diffraction angles.
- However, the most important fact seems to be the existence of isomorphous structures, which are created by ferrites very often. The analysis results also showed the presence of various ferrites and/or structurally very similar substances.

Fig. 2 shows the input sample of the BOF sludge from optical microscopy. It can be seen that the input sample, from a viewpoint of granularity, is a heterogeneous material, where bigger particles are densely coated by smaller particles.

The input sample of the sludge was further analyzed by the sedimentation analysis for particles distribution on the Scanning photo sedimentograph Fritsch Analysette 20. The sample of BOF sludge was dispersed by ultrasound for 2 min before analysis.

The outcomes of the analysis are displayed in Table 3, which shows the high proportion of the particles (below 36%) with granularity less than 10  $\mu\text{m}$ .

Distribution and cumulative curves of scatter for the BOF sludge sample are shown in Fig. 3. The distribution curve shows that the mostly represented fraction is fraction +14 to 22  $\mu\text{m}$ , however the fraction +1 to 2.5  $\mu\text{m}$  is not negligible, either. From the cumulative curve it results that 93% of sludge has its grain size below 30  $\mu\text{m}$ .

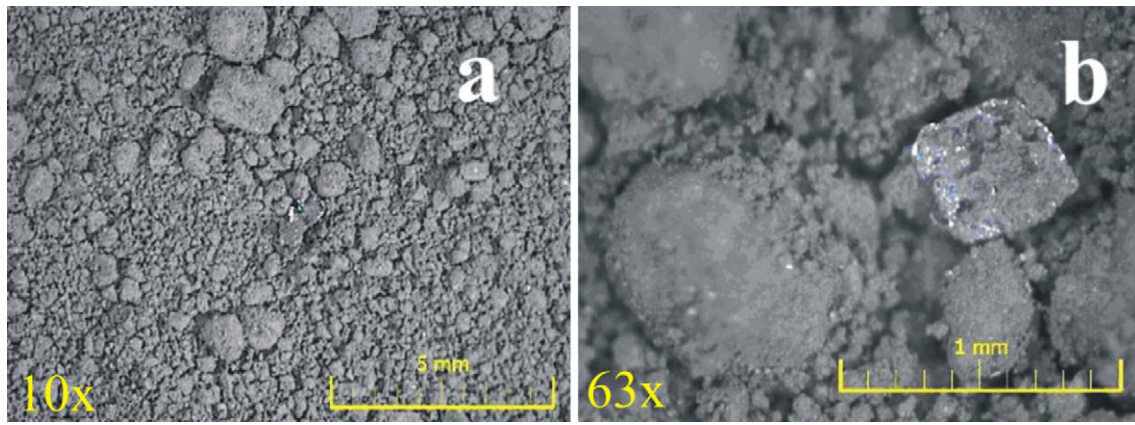


Fig. 2. View of the input sample from optical microscopy.

**Table 3**  
Granularity analysis of the BOF sludge input sample.

Particles size [ $\mu\text{m}$ ]	<0.7	<1	<2.5	<6	<10	<14	<22	<30	<43
Cumulative [%]	4	10	25	30	36	50	85	93	100
Distributive [%]	4	6	15	5	6	14	35	8	7
$Q_{(10)} = 36\%$	$Q_{(40)} = 99.5\%$			$Q_{(63)} = 100\%$					

## 2.2. Experimental set-up

The leaching experiments were carried out in the apparatus, which is shown in Fig. 4 [16].

A glass reactor of 800 ml, which was placed in a water thermostat, was used for the leaching. Leaching experiments were carried out with 400 ml solution of 0.1, 0.2, 0.4, 1.0 M  $\text{H}_2\text{SO}_4$  at the temperatures of 20, 40, 60 and 80 °C. In each of the experiments the revolutions of the glass stirrer equal to 300  $\text{min}^{-1}$  were used. The sample weights for the leaching experiments were 40 g, with L:S ratio equal to 10. The liquid samples for chemical analysis were taken at the fixed time intervals after 2, 15, 30, 45 and 60 min.

The chemical analysis, carried out in order to determine Zn and Fe content, was made by means of AAS variant Spectrometer AA 20+. In each sample the pH value was measured. All results were recalculated due to the change of the pulp volume caused by sampling and evaporation.

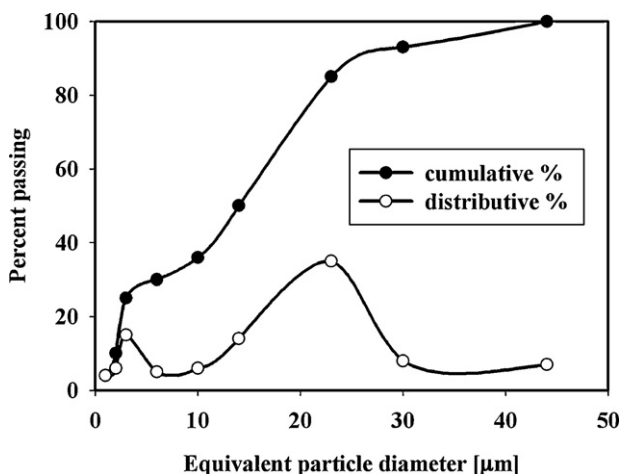


Fig. 3. Curve of scatter for the BOF sludge.

## 3. Results and discussion

During the BOF sludge leaching by sulphuric acid, the following chemical reactions are assumed:

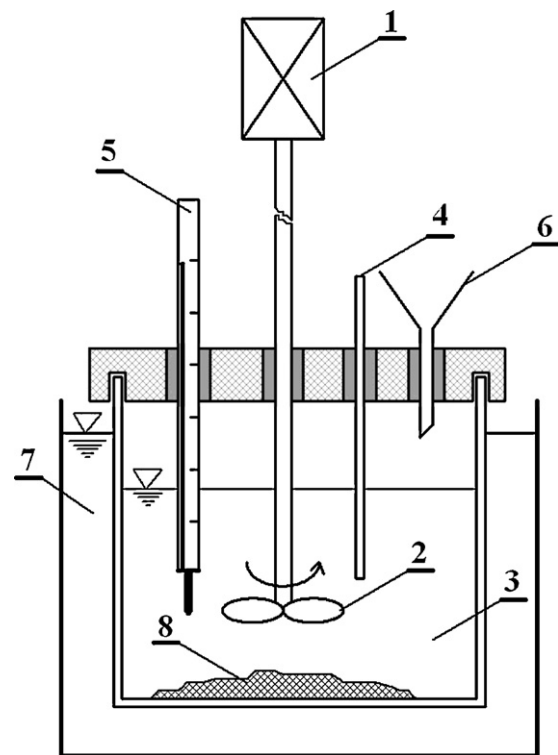
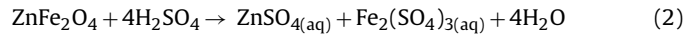
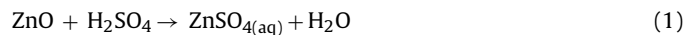


Fig. 4. Schematic view of the leaching apparatus [16]. 1 – mechanical stirrer; 2 – propeller; 3 – pulp; 4 – sampler; 5 – thermometer; 6 – feeder; 7 – water thermostat; 8 – BOF sample.

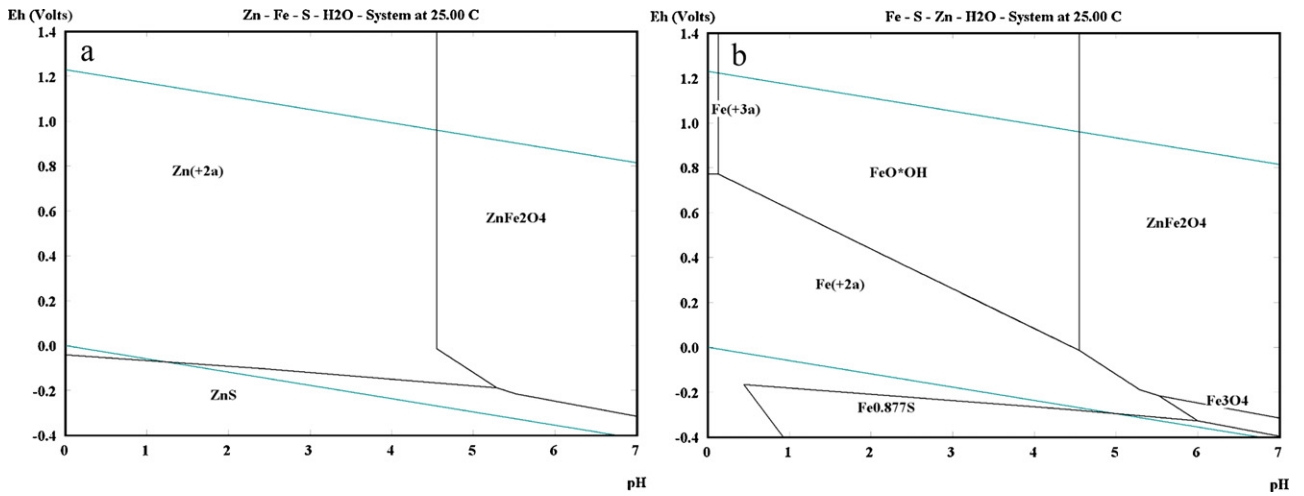


Fig. 5. E–pH diagrams of the Zn–S–H<sub>2</sub>O and Fe–S–H<sub>2</sub>O systems at 25 °C [17].

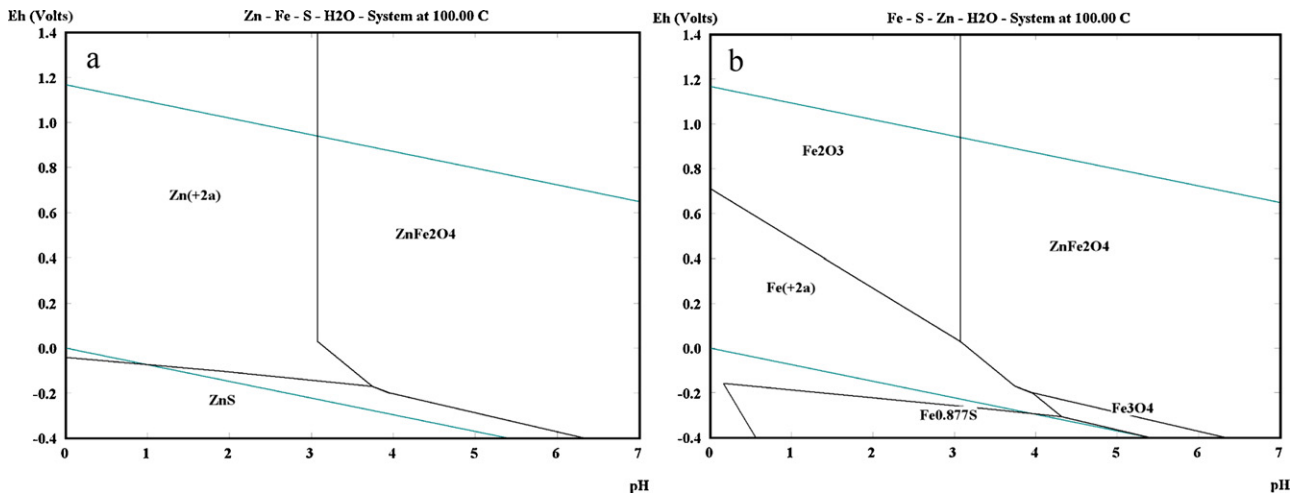


Fig. 6. E–pH diagrams of the Zn–S–H<sub>2</sub>O and Fe–S–H<sub>2</sub>O systems at 100 °C [17].

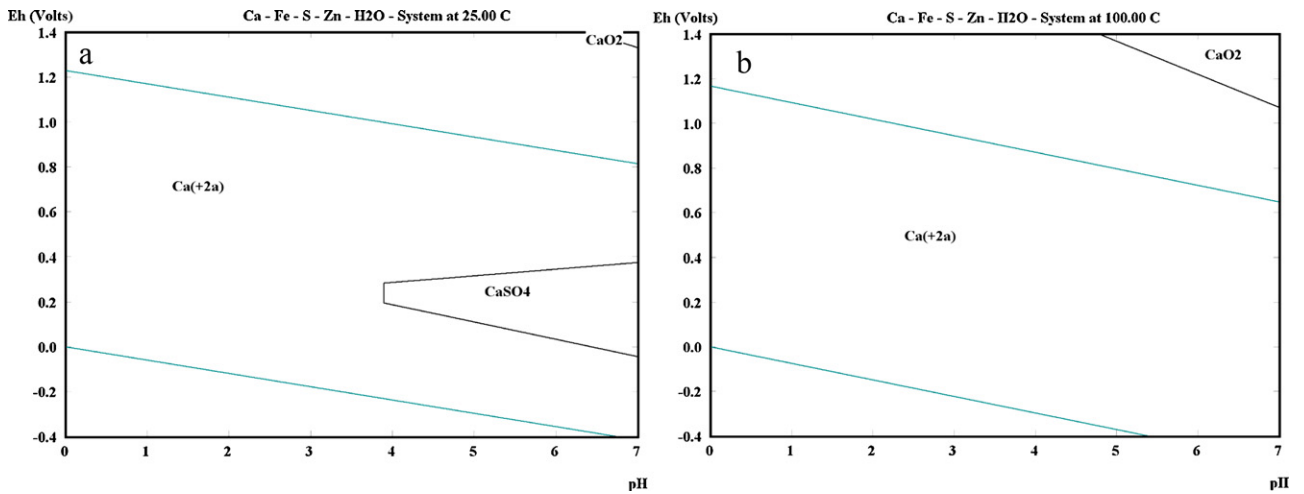


Fig. 7. E–pH diagrams of the Ca–Fe–S–Zn–H<sub>2</sub>O system at 25 and 100 °C [17].

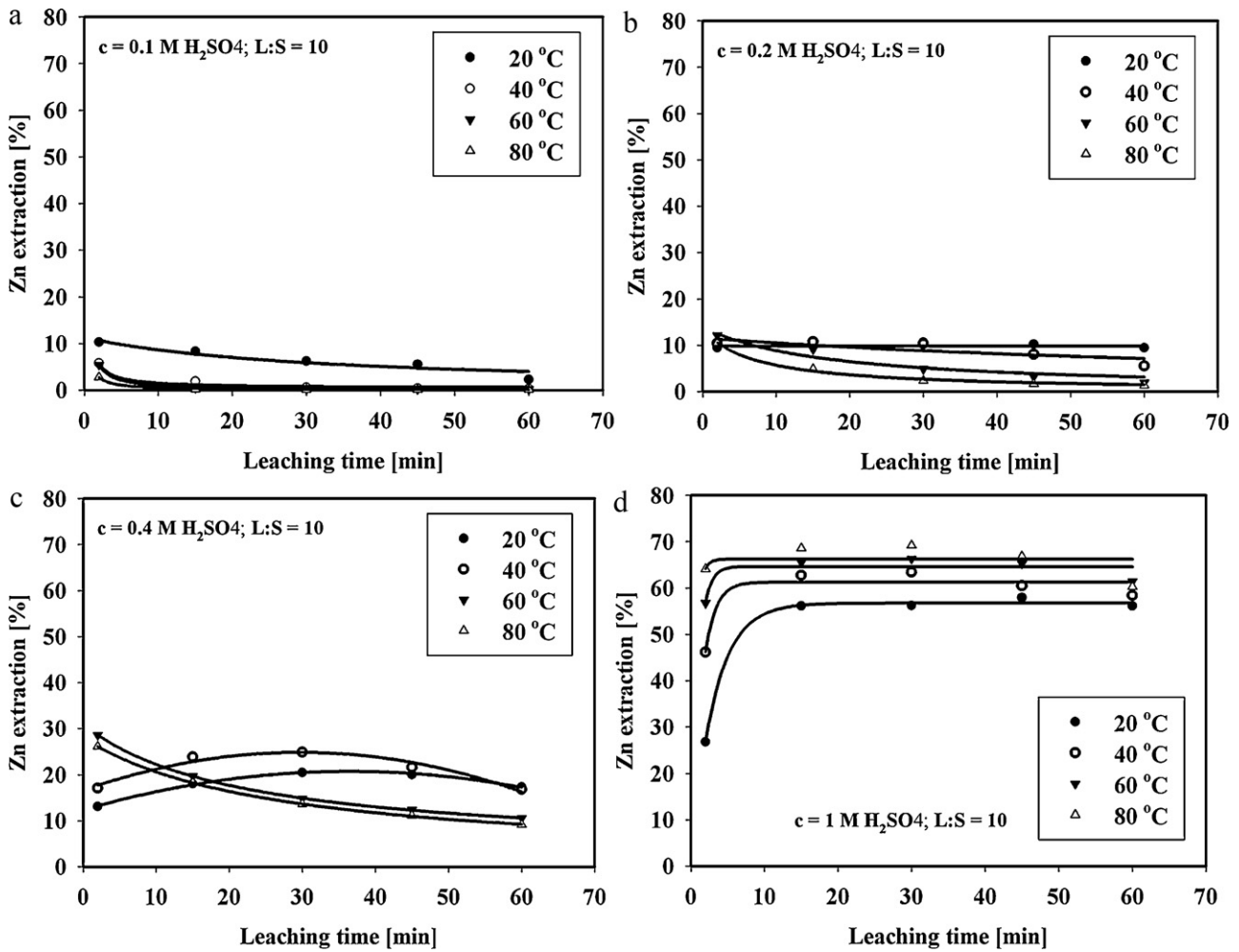
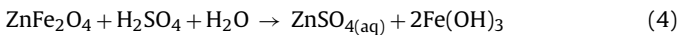
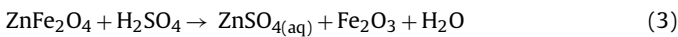
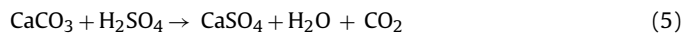


Fig. 8. Kinetics dependencies of leached zinc on temperature at different acid concentration and liquid to solid ratio L:S=10.



Reaction (2) is thermodynamically preferable to Eqs. (3) and (4) within the whole temperature range used in the experiments.

Calcium present in the input sample of the BOF sludge was identified as calcite CaCO<sub>3</sub>. This will react in the system as follows:



Several facts result from the thermodynamic study [17,18] by means of E–pH diagrams (Figs. 5 and 6). The E–pH diagrams of the Zn–S–H<sub>2</sub>O and Fe–S–H<sub>2</sub>O systems show the stability areas of Zn<sup>2+</sup>

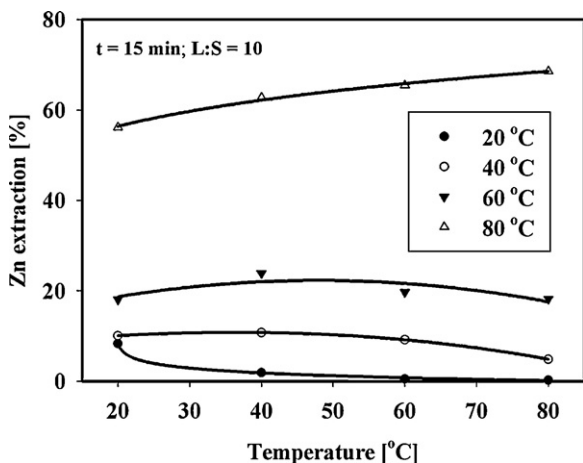


Fig. 9. Dependence of leached zinc on sulphuric acid concentration at 20–80 °C and liquid to solid ratio L:S=10 after 15 min of leaching.

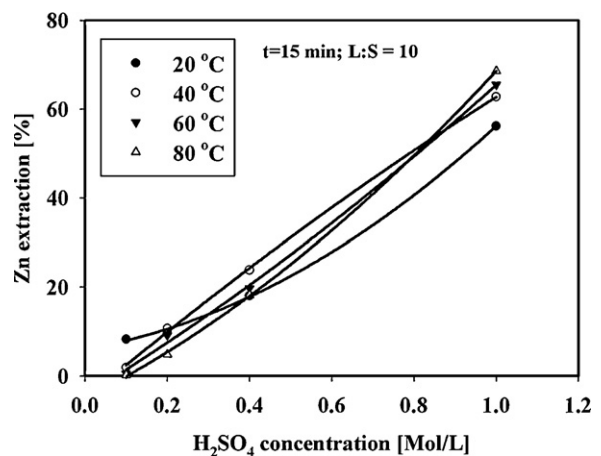


Fig. 10. Dependence of leached zinc on sulphuric acid concentration at 20–80 °C and liquid to solid ratio L:S=10 after 15 min of leaching.

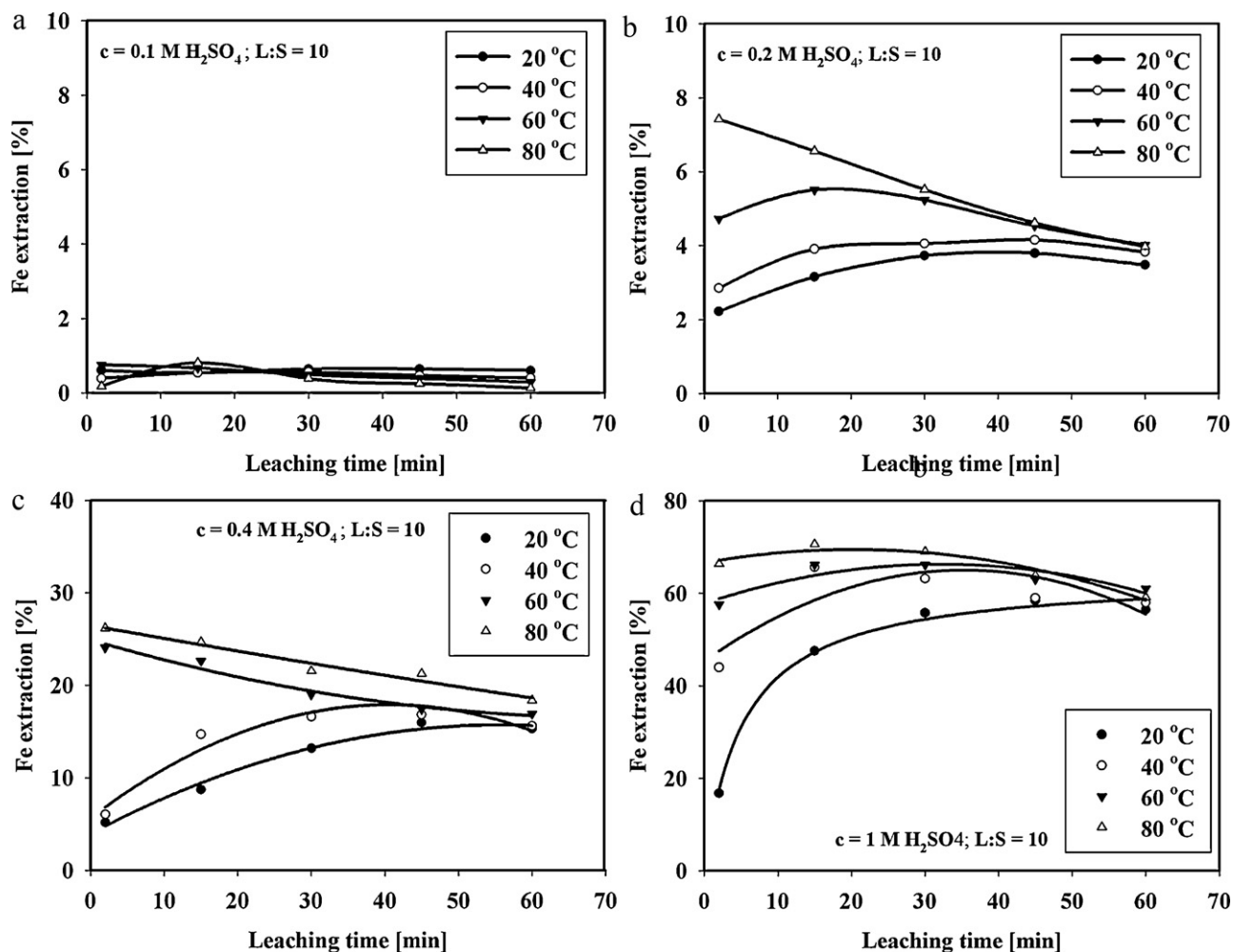


Fig. 11. Kinetics dependencies of leached iron on temperature at different acid concentrations and liquid to solid ratio L:S=10.

ions and the limited stability area of  $\text{Fe}^{2+}$  ions or  $\text{Fe}^{3+}$  in the solution. This fact offers a good opportunity for separating zinc from iron directly in the solution by selecting proper pH. Practically, the entire amount of sulphuric acid should be used during the leaching, and this amount can be calculated from molar Zn to Fe ratio present in the sample.

Fig. 5 shows the  $E$ -pH diagrams of the Zn-S- $\text{H}_2\text{O}$  and Fe-S- $\text{H}_2\text{O}$  systems at the temperature of 25 °C. The system allocates the stability area of  $\text{Zn}^{2+}$  ion in a wide range of pH values from 0 to 6.5 at the ambient temperature. Similarly, iron allocates the stability area of soluble  $\text{Fe}^{2+}$  ions practically in the same range of pH values. Increasing the redox potential value causes narrowing of the stability area of  $\text{Fe}^{2+}$  ions with pH whilst iron creates the stability area of insoluble hydroxyl ions. Neither sulphuric acid nor its aqueous solution is an oxidizing acid, and therefore it is not possible to expect strong oxidizing conditions in the system.

From the thermodynamic point of view increasing the temperature in the leaching system does not change the situation significantly, Fig. 6. The stability area of soluble iron ions is moderately narrowed into pH values  $\sim 4$ , however the same occurs with the stability area of soluble  $\text{Zn}^{2+}$  ions.

From the thermodynamic study it results that zinc creates soluble sulphates in the wide range of pH values in the acid area at normal temperatures, and the stability area of this ion widens with decreasing temperature. Iron also creates a wide stability area in the acid area in the range of pH values similar to the stability area of soluble zinc ions. From the viewpoint of the redox potential val-

ues zinc creates a stability area of  $\text{Zn}^{2+}$  ions within the whole range of a stability area of water, but this is not valid for  $\text{Fe}^{2+}$  ions. They are oxidized to  $\text{Fe}^{3+}$  ions with increasing the potential value in a very acid area at pH values  $\sim 0.5$ . However, by increasing the pH values it precipitates from the solution in the form of insoluble salts. This offers us a great opportunity to separate zinc and iron directly in the solution by suitable process control.

As it was found during the test experiments, under certain conditions a white coagulation is precipitated from the solution. Following the chemical analysis and calculation it was specified, that the white coagulation is calcium sulphate. The  $E$ -pH diagram, Fig. 7, shows the stability areas in the Ca-Fe-Zn-S- $\text{H}_2\text{O}$  system within the temperature range under consideration.

Fig. 8 shows the kinetic dependences of the zinc leaching from BOF sludge in dependence on the temperature at different concentrations of sulphuric acid and liquid to solid ratio L:S=10. The leaching results showed that when using 0.1 M sulphuric acid the temperature does not have a large impact on the zinc extraction, on the contrary zinc passes into the solution with the same efficiency already after 2 min. The amount of leached zinc decreases with the leaching time, what could be caused by increasing pH value in the solution. A visible change from the viewpoint of the temperature impact on the zinc extraction occurs when using 1 M sulphuric acid. The amount of leached zinc increases with increasing the temperature, whilst the highest extraction was reached within the first 15 min of taking the sample. The low zinc extraction at room temperature and low acid concentration (0.1 and 0.2 M) may be

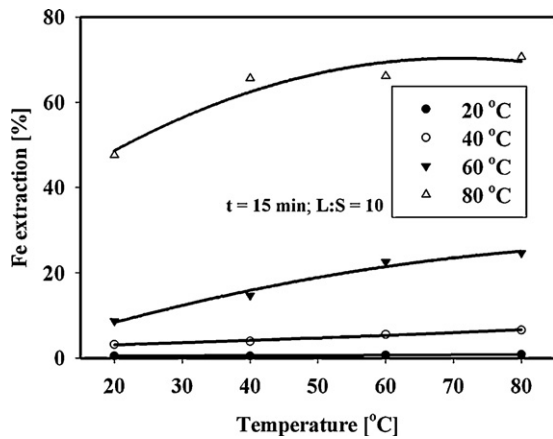


Fig. 12. Dependence of leached iron on sulphuric acid concentration at 20–80 °C and liquid to solid ratio L:S = 10 after 15 min of leaching.

explained by leaching zinc in the form of oxide whilst at higher temperatures and higher concentrations (0.4 and 1 M) also zinc from zinc ferrite was leached out. The explanation is also confirmed by iron extraction, Fig. 11.

Fig. 9 shows dependence of leached zinc on sulphuric acid concentration at 20–80 °C and liquid to solid ratio L:S = 10 after 15 min of leaching. In the area of low concentrations approaching zero the leaching runs only in small scale, and with the increase of the temperature there is a small decrease of leached zinc. However, by increasing the sulphuric acid concentration over 0.4 M  $H_2SO_4$  the process is rapidly accelerated. The highest zinc extraction of 70% was achieved at the temperature of 80 °C after 15 min of leaching.

Fig. 10 shows the dependence of leached zinc on sulphuric acid concentration at 20–80 °C and liquid to solid ratio L:S = 10 after 15 min of leaching. The figure illustrates the dependence of leached zinc on change of acid concentration more clearly. From the kinetics curves it results that with the increase of sulphuric acid concentration the zinc extraction raises rapidly, whilst the influence of the temperature is minimal.

In Fig. 11 the kinetics dependencies of leached iron on the temperature at different acid concentrations and liquid to solid ratio L:S = 10 are displayed. During the leaching in 0.1 M  $H_2SO_4$  practically no iron passes into the solution within the entire temperature range. By increasing the acid concentration the iron begins to pass into the solution, too; and this amount significantly depends on the temperature. At each acid concentration the relative amount of leached iron is low at lower temperatures but when the temperature increases this amount increases as well. The significant change can be observed when using 1 M  $H_2SO_4$ , when the iron extraction about 70% at 80 °C was achieved analogously to the zinc extraction.

From Fig. 11 results that in some cases the iron content in solution decreases with leaching time what can be caused by increasing pH value as acid is consumed. In that case iron can be precipitated as goethite as it follows from E–pH diagram, Fig. 5.

Fig. 12 shows the dependence of leached iron on sulphuric acid concentration at 20–80 °C and liquid to solid ratio L:S = 10 after 15 min of leaching. At low  $H_2SO_4$  concentrations the iron is leached into the solution with low efficiency. The iron extraction rises with increasing acid concentration and temperature.

Fig. 13 shows the dependence of leached iron on sulphuric acid concentration at 20–80 °C and liquid to solid ratio L:S = 10 after 15 min of leaching. The figure illustrates the dependence of leached iron on change of acid concentration more clearly. It results from this dependency that at given temperatures the amount of iron leached into the solution rapidly rises with the increase of the acid concentration as well as in the zinc leaching process.

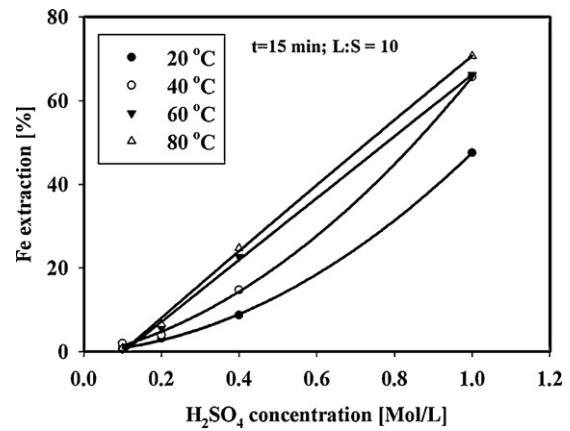


Fig. 13. Dependence of leached iron on sulphuric acid concentration at 20–80 °C and liquid to solid ratio L:S = 10 after 15 min of leaching.

#### 4. Conclusion

The aim of the experimental work was to verify the zinc leachability from fine-grain BOF sludge in acid medium. The BOF sludge is a very heterogeneous material, and therefore it is difficult to choose suitable concentration of the leaching medium. The sulphuric acid solution in the concentration range up to 1 M was selected as the leaching medium for the BOF sludge. The experimental results prove that the amount of leached zinc was the highest (70%) when using 1 M concentration of sulphuric acid with the leaching time up to 15 min and at temperature of 80 °C. The biggest contribution of this work is the fact that by choosing the right leaching conditions it is possible to leach zinc into the solution, however the disadvantage that iron passes into the solution as well still remains. On the other hand, by suitable adjusting of pH value it is possible to remove iron from the solution. The optimal conditions for simple zinc recovery from BOF sludge under given conditions are created when using 1 M sulphuric acid for leaching at 80 °C and a minimum of 15 min leaching time. Naturally, these conditions are valid only for the particular BOF sludge because the chemical and mineralogical composition of each steelmaking dust is individual, and therefore it is necessary to carry out leaching control tests. The next step for leaching liquor treatment should be purification of solution with the aim of iron removal. There are several processes for iron precipitation such as: hematite process, jarosite process and goethite process. These processes will be studied next.

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#### References

- [1] J. Legemza, Theoretical, Technological and Ecological Aspects Utilization of Steelmaking Dust, PhD thesis, TU Kosice, 1998.
- [2] U. Meurer, U. Buntbach, Recycling processes for residues of the steel industry – treatment of stainless steel production residues and alloy recycling, in: Copper and Nickel, Zinc and Lead, Environment, Proceedings of European Metallurgical Conference EMC, vol. 1, 2001, pp. 239–258.
- [3] P. Dvorak, J. Jandova, Recycling of blast furnace and basic oxygen furnace dust, Waste Forum 6 (2002) 22–24.

- [4] S.M. Hay, W.J. Rankin, M. Waladan, Recovery of iron and zinc from blast furnace and basic oxygen furnace dust: a laboratory investigation, in: *Extraction and Processing for the Treatment and Minimization of Waster*, The Minerals, Metals and Materials Society, 1993.
- [5] S.M. Hay, W.J. Rankin, Recovery of iron and zinc from blast furnace and basic oxygen furnace dust: a thermodynamic evaluation, *Minerals Engineering* 7 (1994) 985–1001.
- [6] P. Cengel, M. Pivovarci, Some information about pollution of steelmaking dust by zinc, *Metallurgical Journal* 9 (2000) 3–4.
- [7] D. Kristofova, V. Cablik, P. Fecko, Biological–chemical leaching of converter sludge, *Acta Metallurgica Slovaca* 8 (2002) 391–395.
- [8] V. Romenetes, V. Valavin, Y. Pokhvisnev, S. Vandariiev, V. Zaytsev, Processing industrial wastes with the liquid-phase reduction Romelt process, *JOM* (1999) 33–37.
- [9] J. Curilla, I. Jelc, New information and processes for evaluate some steelmaking dust, in: *Proceedings 30 years of Steel Production in Basic Oxygen Furnace in VSZ II, Kosice*, 1996, pp. 141–146.
- [10] I. Imris, L. Komorova, Zinc and lead removal from steelmaking dust, *Metallurgical Journal* 2 (1978) 93–99.
- [11] M. Kursá, D. Kristofova, T. Karník, J. Kret, J. Lesko, J. Botula, Heavy metals in fine-grain metallurgical wastes and recovery possibilities, *Acta Metallurgica Slovaca* 4 (1998) 131–136 (Special Issue 3).
- [12] Z. Ruzickova, J. Srb, New possibilities utilization of steelmaking dust, *Metallurgical Journal* 9 (1976) 626–631.
- [13] J.M. McClelland, G.E. Metius, Recycling ferrous and nonferrous waste streams with FASTMET JOM (2003) 30–34.
- [14] Regulation of Ministry of Environment of the Slovak Republic No. 284/2001, Website, 2010. <http://www.censo.sk/zakonyavhylasky/v284.2001%20Katalog%20odpadov.pdf>.
- [15] A.D. Zunkel, Recovering Zinc and Lead From Electric Arc Furnace Dust: A Technology Status Report, Website, 2006. <http://hometown.aol.com/dzunkel/myhomepage/index.html>.
- [16] T. Havlik, B. Vidor, E. Souza, A.M. Bernardes, I.A.H. Schneider, A. Miskufova, Hydrometallurgical processing of carbon steel electric arc furnace dust, *Acta Metallurgica Slovaca* 12 (2006) 42–53.
- [17] A. Roine, HSC Chemistry<sup>®</sup>, ver. 6.0, Software Outotec Research Oy.
- [18] T. Havlik, B. Friedrich, S. Stopic, Pressure leaching of EAF dust with sulphuric acid, *Erzmetall* 57 (2004) 83–90.