Acid leaching of BOF (basic oxygen furnace) sludge

Z. Hoang-Trung, F. Kukurugya, Z. Takáčová, T. Havlík
Technical University of Kosice, Faculty of Metallurgy, Department of Non-ferrous Metals and Waste Treatment, Letna 9, 042 00 Kosice, Slovak Republic
O. Forsén
Aalto University School of Science and Technology, Department of Material Science and Engineering, PO BOX 6200, FI-02015, Espoo, Finland

ABSTRACT: During steel production in the basic oxygen furnace (BOF) approximately 7 to 15 kg of dust per ton of produced steel is generated. Coarse dust contains approximately 0.01 - 0.4 % Zn and 30 – 85 % Fe. Fine dust contains 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 dusts and sludge from metallurgical production are still searched for. Next reason for processing this kind of waste is to recover zinc that nowadays becomes scarce metal. 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 a 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.

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. In regard to form the steelmaking dusts are obtained in the form of dust from dry dust separation or in the form of sludge from wet dust separation.

Coarse dust is usually returned into the steelmaking process after pretreatment or it is recycled in the sintering plant.The fine dust contains a considerably higher content of zinc compared with the coarse dust. Due to the zinc content, dusts and sludge cannot be recycled, hence they are stored in landfills.

Large scatter of grain, chemical and mineralogical composition is a typical feature of steelmaking dust. Tab. 1 shows percentage composition of zinc and iron in BOF dust and sludge according to various authors.

Tab. 1: Zinc and iron contents in BOF dust and sludge according to various authors [1 - 13]

Zn (%)	1-10	14.10	7.8	1.10	5.10	6.00	1.50	1.7
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	0.48	0.5 - 3.5	0.1 - 1	0.01-0.9	1.4 - 3.2	0.05 - 4
Fe (%)	56 - 64	67.86	87.2	53 - 63	59 - 67	52 -72	54 - 62	45 - 62
Ref.	6	7	7	1	1	1	1	1
Zn (%)	0.02	1.2	0.2	0.9-2.5	1-2	0.208	1.396	7.55
Fe (%)	62.3	59.8	64.8	60 - 64	60	74.8	73.75	44.2
Ref.	1	1	1	8	9	10	10	10
Zn (%)	0.07	0.38	3.99	2.54				
Fe (%)	82.1	63	59.70	53.6				
Ref.	11	11	12	13				

Average value	
Zn Amount (wt %)	2.57
Fe Amount (wt. %)	61.41

Both BOF dust and sludge are categorized as hazardous waste [14]. Several methods for the processing of steelmaking dust have been already designed; however, there is still a lack of information on how to process the BOF dust. This is probably caused by a relatively low content of zinc compared with electric arc furnace dust, where steel scrap is melted. The steelmaking dust can be processed by the three main groups of methods: pyrometallurgy, hydrometallurgy or a combination of both methods [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.

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.

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 both coarse and fine dust from converter gas treatment is shown in Tab. 2.

Tab. 2: The chemical composition of coarse and fine dust from converter gas treatment

Parameter	Coarse dust [%]	Fine dust [%]
Total Fe	30 - 85	54 - 70
Metallic Fe	72	20
CaO	8 - 21	3 - 11
Zn	0.01 – 0.4	1.4 – 3.2
Pb	0.01 – 0.04	0.2 – 1.0
S	0.02 – 0.06	0.07 – 0.12
C	1.4	0.7

The mineralogical composition was determined by XRD phase analysis. In the sample the phases such as magnetite (Fe_3O_4), wustite (FeO), calcite ($CaCO_3$), graphite (C), and metallic Fe are found with high probability. Phases such as hematite (Fe_2O_3), ferritic phases and SiO_2 were found with less probability. Other phases, if they are present following the chemical composition, are in minor amounts and vanishing in the background of the XRD pattern.

Fig. 1 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.

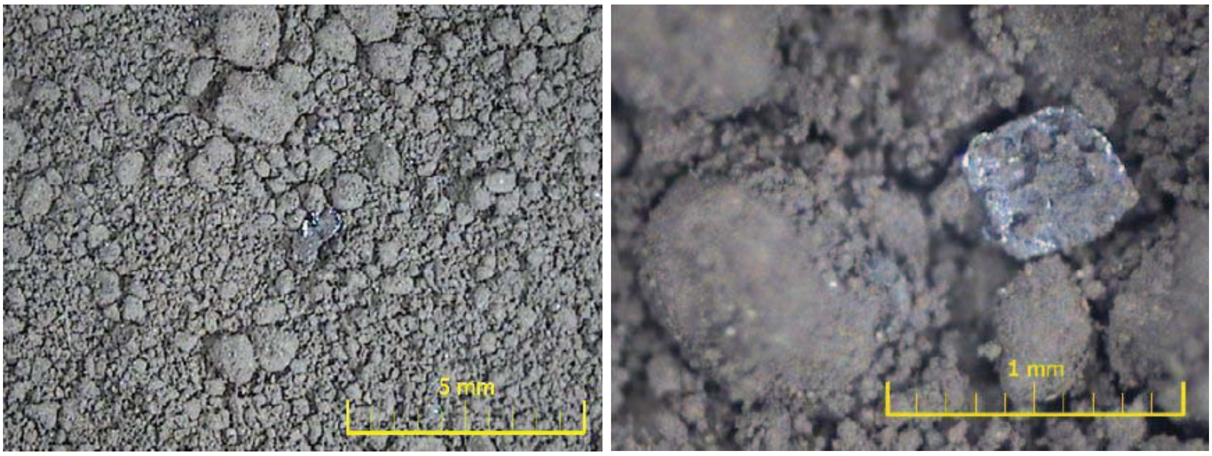


Fig.1: View of the input sample from optical microscopy

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 minutes before analysis.
Distribution and cumulative curves of scatter for BOF sludge sample are shown in Fig.2. The distribution curve shows that the mostly represented fraction is fraction +14 –22 µm, however the fraction +1 –2.5 µm is not negligible, either. From the cumulative passing curve it results that 93 % of sludge has its grain size below 30 µm.

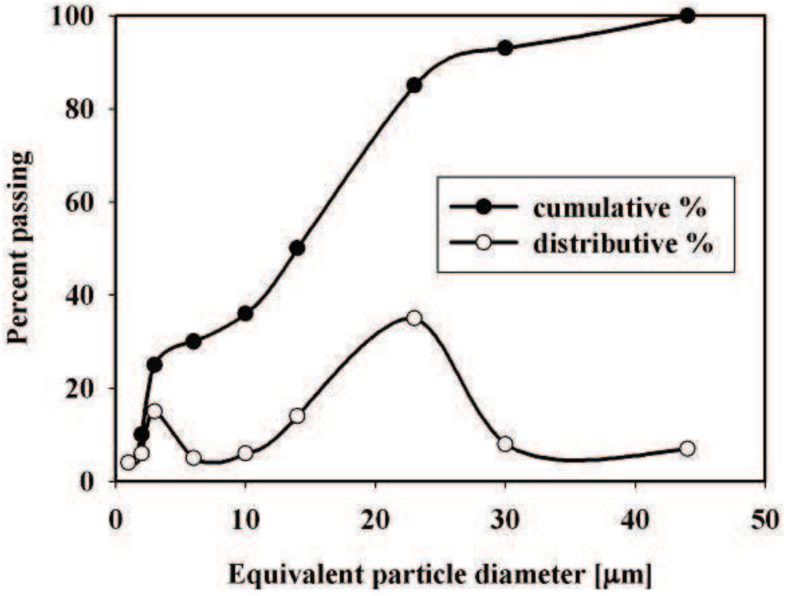


Fig.2: Curve of scatter for BOF sludge

2.2. *Experimental set-up*

The leaching experiments were carried out in the apparatus, which is shown in Fig. 3 [16]. A glass reactor of 800 ml, which was placed in a water thermostat, was used for the leaching. It allowed keeping the desired temperature of the leaching automatically. Leaching experiments were carried out with 400 ml solution of 0.1, 0.2, 0.4, 1 M H_2SO_4 at the temperatures of 20, 40, 60 and 80 °C. In each of experiments the revolutions of the glass stirrer equal to 300 min-1 were used. The sample weights for the leaching experiments were 40g, with liquid to solid ratio equal to 10. The liquid samples for chemical analysis were taken at the fixed time intervals after 2, 15, 30, 45 and 60 minutes. 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.

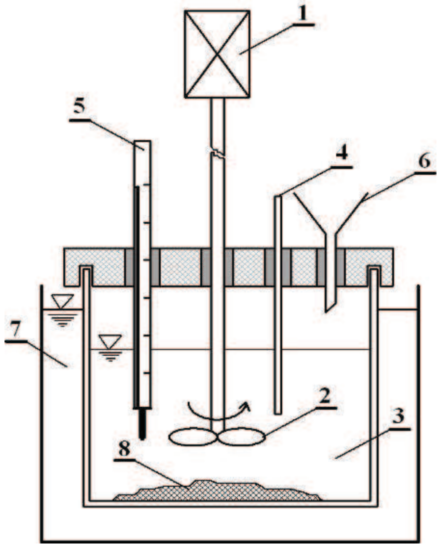
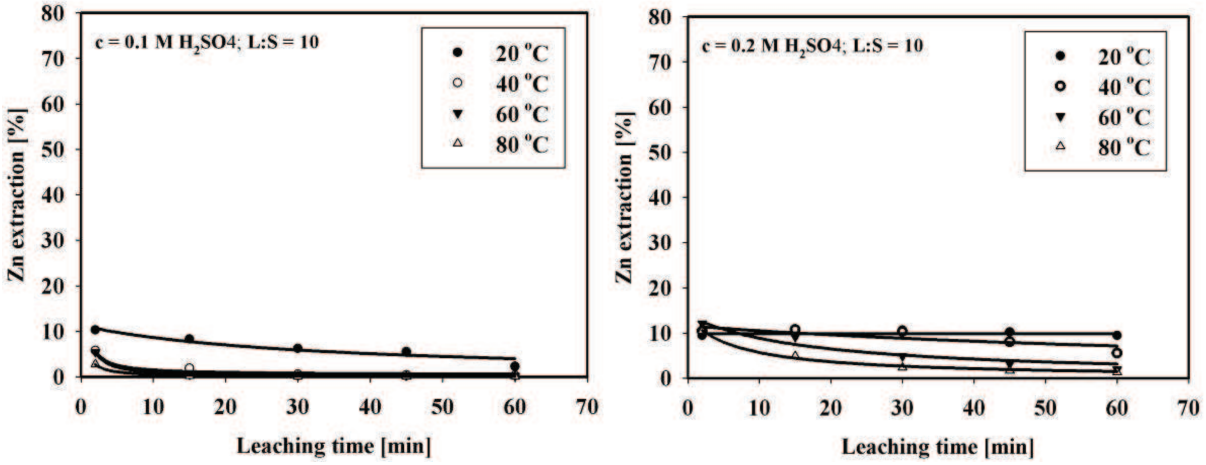


Fig. 3: Schematic view of the leaching apparatus
(1 – mechanical stirrer; 2 – propeller; 3 – pulp; 4 – sampler;
5 – thermometer; 6 – feeder; 7 – water thermostat; 8 – BOF sample)

3. RESULTS AND DISCUSSION

Fig. 4 shows the kinetic dependences of the zinc leaching from BOF sludge in dependence on the leaching time at different concentrations of sulphuric acid, liquid to solid ratio L:S = 10 and temperature 20 – 80 °C. The leaching results showed that when using 0.1M 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 minutes. The amount of leached zinc decreases with the leaching time. A visible change from the viewpoint of the temperature impact on the zinc extraction occurs when using 1M sulphuric acid. The amount of leached zinc increases with increasing the temperature, while the highest extraction was reached within the first 15 minutes of taking the sample.



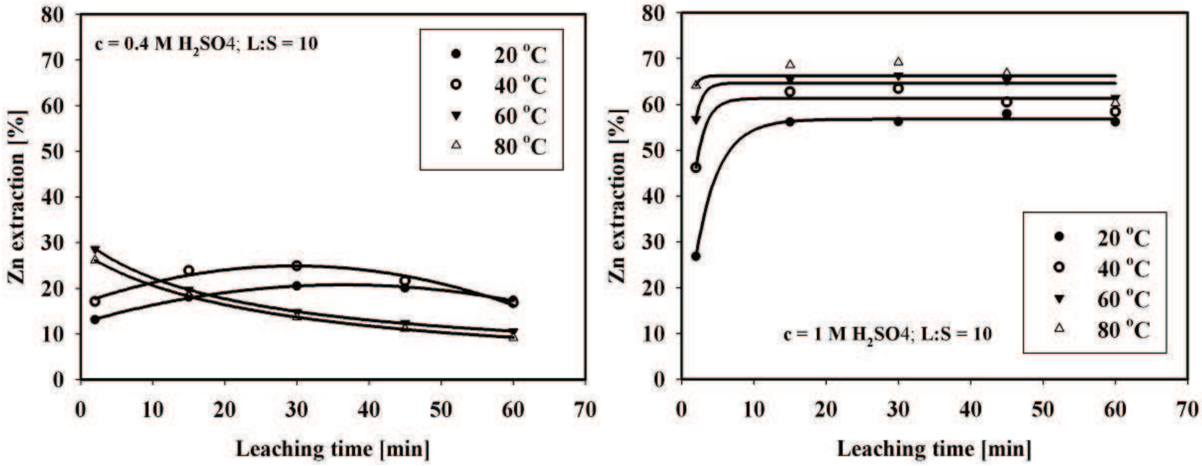


Fig. 4: Kinetics dependencies of leached zinc on leaching time at different acid concentration, liquid to solid ratio L:S = 10 and temperature 20 – 80 °C

Fig.4 shows that shape of the kinetics curve at 1M H_2SO_4 is different from shape of kinetics curves at lower concentration of H_2SO_4 (0.1, 0.2 and 0.4) in first 10 minutes. This difference can be caused by the fact that at lower concentrations entire acid was consumed immediately at the beginning of the experiment what caused that the Zn extraction did not change significantly with time. In case of 1M H_2SO_4 there was enough amount of sulphuric acid for increasing the Zn extraction in first 10 minutes.

Fig. 5 shows kinetics dependencies of leached zinc on temperature at sulphuric acid concentration 0.1 – 1M and liquid to solid ratio L:S = 10 after 15 minutes 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 0.4M H_2SO_4 the process is rapidly accelerated. The highest zinc extraction of 70 % was achieved at the temperature of 80 °C after 15 minutes of leaching.

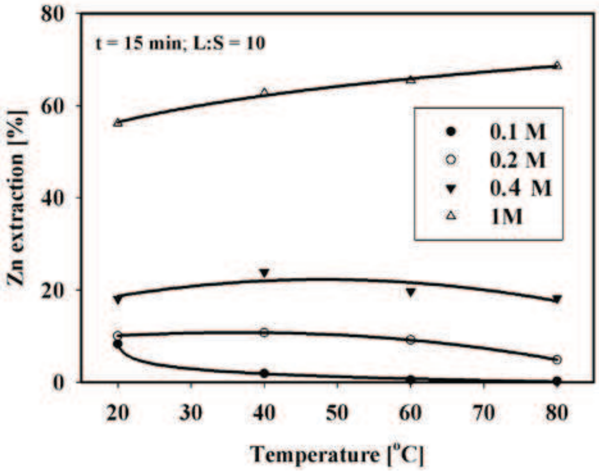


Fig. 5: Kinetics dependencies of leached zinc on temperature at sulphuric acid concentration 0.1 – 1M and liquid to solid ratio L:S = 10 after 15 minutes of leaching

In Fig. 6 the kinetics dependencies of leached iron on leaching time at different acid concentrations, liquid to solid ratio L:S = 10 and temperature 20 – 80 °C are displayed. During the leaching in 0.1M 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 1M H_2SO_4, when the iron extraction about 70 % at 80 °C was achieved analogously to the zinc extraction.

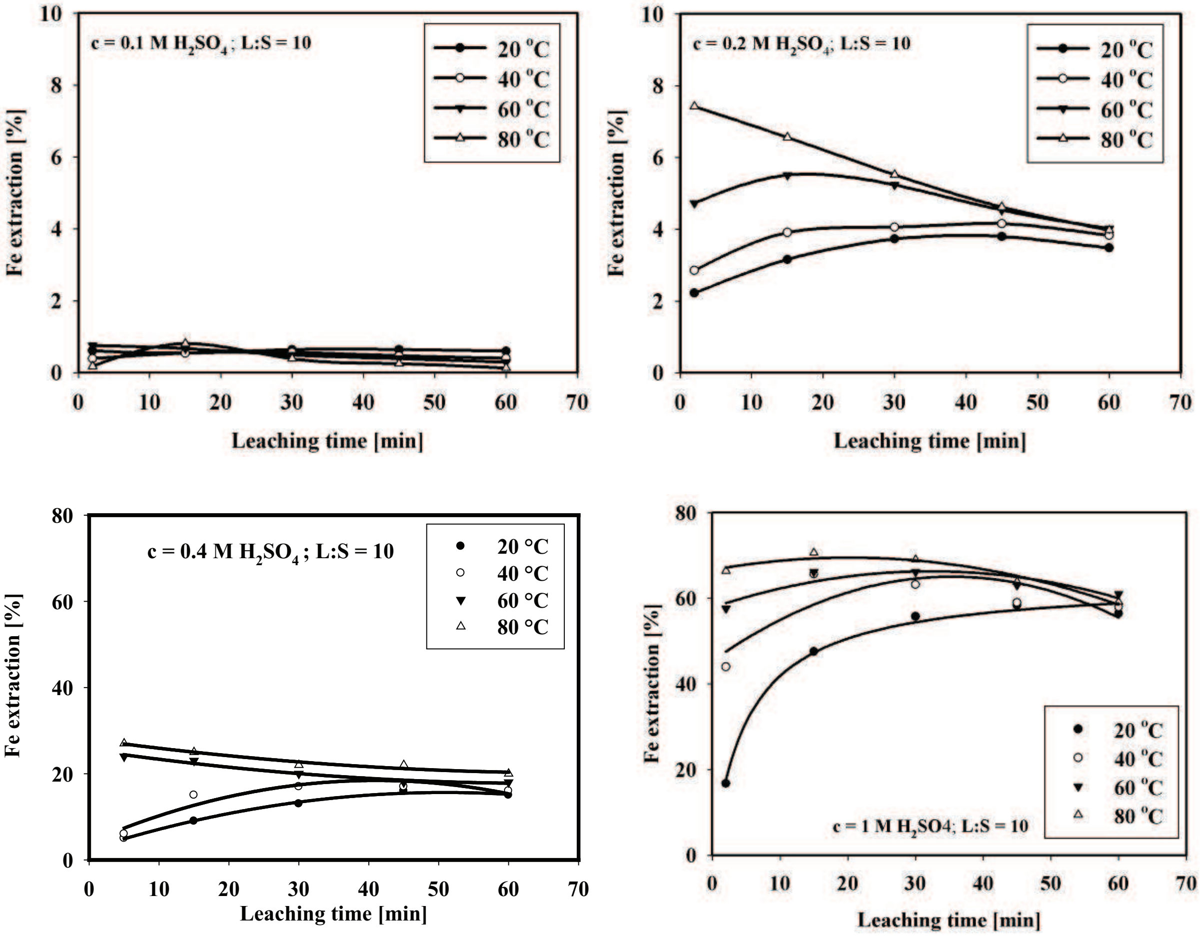


Fig. 6: Kinetics dependencies of leached iron on leaching time at different acid concentrations, liquid to solid ratio L:S = 10 and temperature 20 – 80 °C

Fig.7 shows kinetics dependencies of leached iron on temperature at sulphuric acid concentration 0.1 – 1M and liquid to solid ratio L:S = 10 after 15 minutes of leaching. At low H2SO4 concentrations the iron is leached into the solution with low efficiency. The iron extraction rises with increasing acid concentration and temperature.

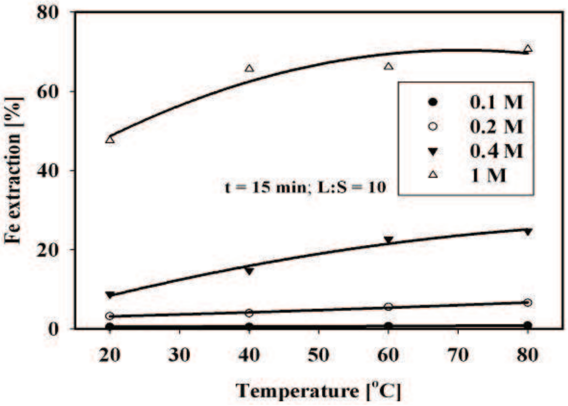


Fig. 7: Kinetics dependencies of leached iron on temperature at sulphuric acid concentration 0.1 – 1M and liquid to solid ratio L:S = 10 after 15 minutes of leaching

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 1M. 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 1M concentration of sulphuric acid with the leaching time up to 15 minutes 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 1M sulphuric acid for leaching at 80 °C and a minimum of 15 minutes 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.

5. ACKNOWLEDGEMENTS

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