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Leaching of Zinc and Iron from Blast Furnace Dust in Sulphuric Acid Solutions

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During the production of pig iron in a blast furnace a large quantity of dust is generated. The main compounds of dust are iron oxides with a share of heavy non-ferrous metal oxides, mainly zinc. This work focuses on the leaching of blast furnace (BF) dust under normal conditions of temperature and pressure in dilute sulphuric acid. Leaching experiments were carried out using a solution of 0.5 M, 1M and 2 M H_2SO_4 at the temperatures of 20, 50 and 80 °C. The main objective of this work was to leach the maximum amount of zinc into the solution with the minimum amount of iron passing into the solution. On the basis of the obtained results, it can be said that it is possible to effectively obtain zinc from BF dust by leaching, whilst iron remains in the solid residue, which can be recycled in the pig iron production process.

The issue of environmental protection is one of the major problems faced by iron and steel producers. In the material flow of the pig iron and steel production and processing a wide range of waste is produced, such as dust, sludge, wastewater containing heavy non-ferrous metals and so on. Yet, these wastes are not effectively processed. In consideration of increasing metal prices and environmental charges for landfilling, this task is getting more and more important.

The chemical analysis of BF dusts shows the presence of mainly iron. Other elements present in BF dust are usually Si, Mn, C and also heavy metals Zn, Pb, Cd, Ni, Cr, etc. The mineralogical analysis shows the presence of iron in oxidic form as hematite Fe_2O_3, magnetite Fe_3O_4 and ferite $ZnFe_2O_4$. Zinc is present mostly in the two compounds, as zinc oxide ZnO (zincite) and as ferite $ZnFe_2O_4$ (franklinite) or as complex franklinite, e.g. $(ZnMnFe)_2O_4$ [1, 2]. The mineralogical form of the presence of zinc is an essential indicator of efficient processing of wastes from iron and steel production. In principle, ZnO is an easily treatable form of zinc for both pyrometallurgical and hydrometallurgical methods, but ferrites are generally very resistant to treatment.

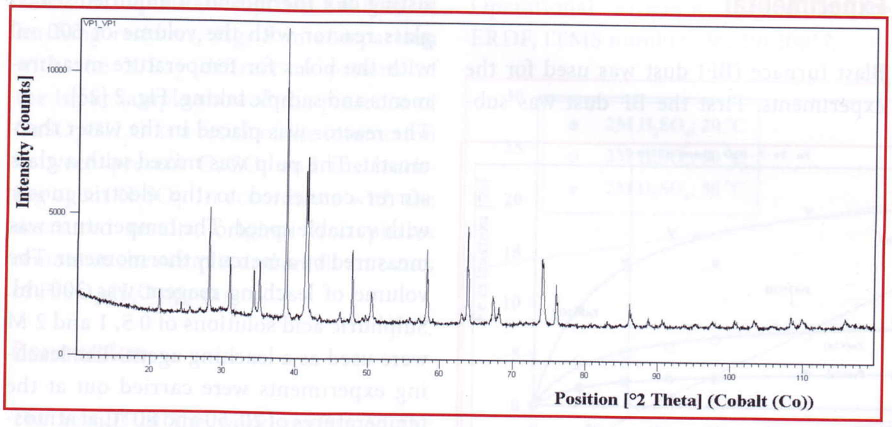

Fig. 1: XRD pattern of BF dust

Element	Fe	Si	Zn	Pb	Sb	Sn	Cu	Cr	LOI*
Content [%]	32.94	5.58	1.54	0.15	0.15	0.17	0.24	trace	20.24

Table 1: The chemical analysis of the most commonly occurring elements in the studied dust [%]

In order to solve the problem, several hydrometallurgical and pyrometallurgical methods and processes have been developed so far. The best known pyrometallurgical processes include: the Waelz process [3], the Rotary Hearth Furnace process [4], the Primus process [5] or plasma technology [6]. The main objective of pyrometallurgical processes is to obtain iron concentrate and/or pig iron, whilst zinc is obtained as ZnO clinker of poor commercial quality.

Zinc can be removed hydrometallurgically using alkaline [7 – 9] or acid methods [10 – 16]. In addition to conventional sulphate and chloride leaching agents, also intensification methods such as using pressure [17, 18] or microwave leaching [19 – 22] are examined. The problem in removing zinc is the form in which it occurs. Zinc is usually present in the form of franklinite, which is highly resistant to leaching. Alkaline methods seem to be very effective, as heavy metals Zn, Pb, Cd etc. are leached out in alkaline agents, whilst iron is inert to the alkaline leaching. However, these methods require highly concentrated leaching solutions regardless of the fact that the leaching of zinc present in the form of franklinite is very difficult, and it is often necessary to include also an intermediate step of thermal processing. Acid leaching does not require as concentrated solutions as in the case of alkaline leaching, but part of iron also passes into the solution during acid leaching. Even in this case, franklinite is relatively resistant to processing, and therefore the benefits of acid leaching are determined in addition to operational costs also by a medium used in the leaching process, e.g.: relatively cheap acetic acid, cheap and available sulphuric acid, or more aggressive chlorine environment.

Obtaining metals from sulphuric acid solution is a relatively cheap and simple process. The remaining solid product can be either landfilled as non-hazardous waste or recycled in the iron or steel production process. The effort should focus on finding a process, in which heavy metals would pass into the solution by a cheap way, and iron would remain in the solid residue. After removing these metals from the leaching solution the solution can be recycled in the leaching step. This is the main objective of the work.

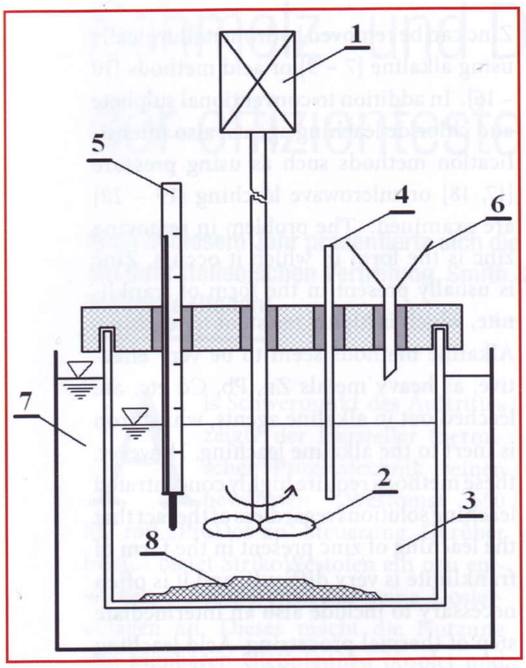

Fig. 2: The scheme of the leaching apparatus in the system solid – liquid phase

Experimental

Blast furnace (BF) dust was used for the experiments. First the BF dust was subjected to mechanical treatment, drying, crushing and screening on screens with grain size of 100 μm in order to obtain a fine fraction suitable for the hydrometallurgical processing. The chemical composition of treated dust is shown in Tab. 1.

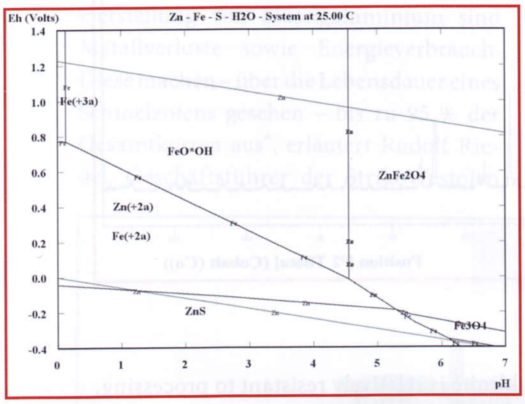

Fig. 3: E-pH diagram of the system Zn-Fe-S-H_2O at 25 °C

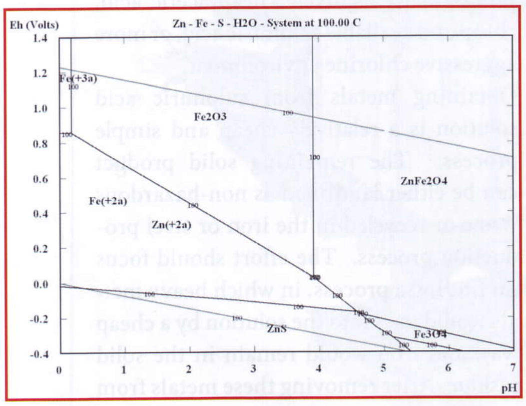

Fig. 4: E-pH diagram of the system Zn-Fe-S-H_2O at 100 °C

The X – Ray diffraction qualitative phase analysis shows the mineralogical composition of BF dust, Fig. 1, from which it follows that hematite Fe_2O_3, silicon oxide SiO_2, magnetite Fe_3O_4 and calcium carbonate $CaCO_3$ are present with a relatively high probability.

No zinc containing phase was confirmed. The reason is a relatively low zinc content, 1.54 %, which causes that potential zinc containing phases are suppressed into the background of the XRD pattern. Another reason is that zinc may be present in the form of franklinite, $ZnFe_2O_4$, which has almost the same diffraction pattern as magnetite, which was identified in the initial sample.

The leaching experiments of treated BF dust were carried out in the apparatus consisting of a thermostat, a modified sealed glass reactor with the volume of 600 ml with the holes for temperature measurements and sample taking, Fig. 2 [23].

The reactor was placed in the water thermostat. The pulp was mixed with a glass stirrer connected to the electric motor with variable speed. The temperature was measured by a mercury thermometer. The volume of leaching reagent was 300 ml. Sulphuric acid solutions of 0.5, 1 and 2 M were used as a leaching agent. The leaching experiments were carried out at the temperatures of 20, 50 and 80 °C at atmospheric pressure. The sample weight for the leaching experiments was 50 g. After heating up the leaching solution, the sample of BF dust was put into the reactor and the time measurement began. The liquid samples with the volume of 5 ml were taken at the fixed time intervals after 15, 30, 45, 60, 90 and 120 minutes. The samples were filtrated and analyzed for zinc and iron content by atomic absorption spectrometry (Varian Spectrometer AA 20+). After leaching, the remaining solution was subjected to filtration. The final volume was measured for the purpose of correction values in zinc and iron as a result of sampling and evaporation. The pH value was measured using a digital pH meter OP-110. In each experiment, the pulp was stirred at a constant speed of 300 rpm. After having been flushed with water and dried, the leaching residues were subjected to XRD qualitative phase analysis.

Results and discussion

The leaching reactions of the selected compounds in the system are governed by the following equations:

$$ZnO + H_2SO_4 \rightarrow ZnSO_{4(aq)} + H_2O \tag{1}$$

$$ZnFe_2O_4 + 4\,H_2SO_4 \rightarrow ZnSO_{4(aq)} + Fe_2(SO_4)_{3(aq)} + 4\,H_2O \tag{2}$$

$$ZnFe_2O_4 + H_2SO_4 \rightarrow ZnSO_{4(aq)} + Fe_2O_3 + H_2O \tag{3}$$

$$ZnFe_2O_4 + H_2SO_4 + H_2O \rightarrow ZnSO_{4(aq)} + Fe(OH)_3 \tag{4}$$

while reaction (2) is thermodynamically more favorable than equations (3) and (4) in the whole range of considered temperatures.

The following facts result from the thermodynamical study [24] of E – pH diagrams, Fig. 3 and 4.

In acidic area, there is a stability area of soluble ions $Zn^{2+}_{(aq)}$ and $Fe^{2+}_{(aq)}$. The increase of pH and the decrease of potential cause that soluble ferrous ions start to precipitate from the solution in the form of FeOOH precipitate, whilst zinc remains in the solution in the soluble form. In a very acidic area at pH~0, there is a stability area of ferrous ions. Those ions participate in leaching as a strong oxidant, while they reduce themselves; and as sulphuric acid is consumed by the leaching reactions, they precipitate from the solution as FeOOH. With the increase of the temperature, the stability area of $Fe^{3+}_{(aq)}$ ions widens and a potential border $Fe^{2+}_{(aq)}$/ $Fe^{3+}_{(aq)}$ moves towards higher values of redox potential. The thermodynamic study shows the possibility of ensuring the transfer of zinc into the solution, while iron remains in the solid residue by pH control.

Analysis of the results

The objective of the experimental part was both to prove leachability of BF dust in sulphuric acid, and to achieve the highest extraction of zinc into the solution. Fig. 5 shows kinetics curves of zinc extraction and Fig. 6 shows kinetics curves of iron extraction depending on the sulphuric acid concentration and temperature.

The extraction of zinc in the solution increases with leaching time at each temperature and also a positive influence of acid concentration is evident. Practi-

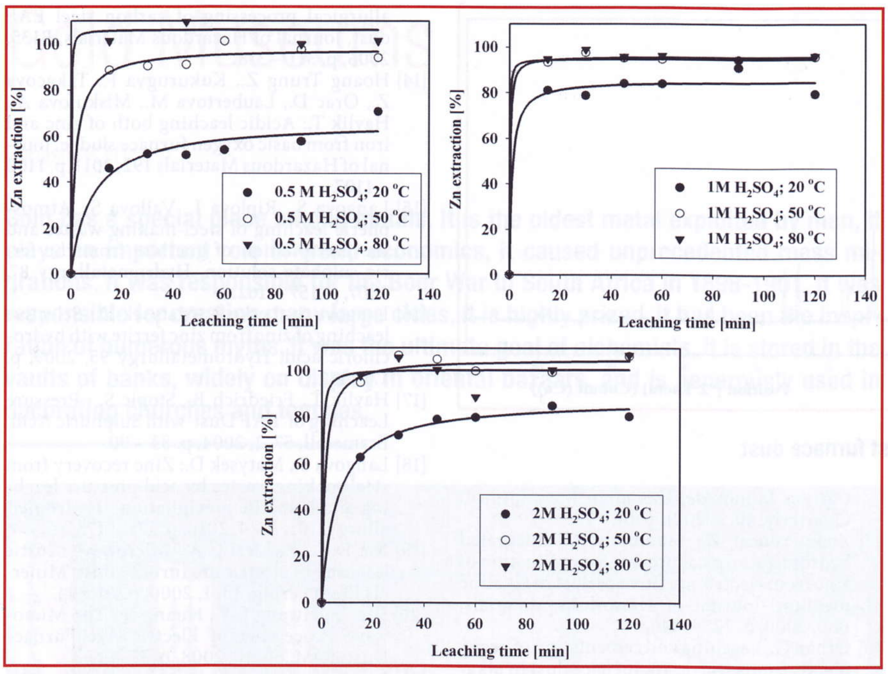

Fig. 5: Kinetics curves of zinc extraction at temperatures 20, 50 and 80 °C with sulphuric acid concentrations 0.5, 1, 2 M and L:S ratio = 6

cally, zinc is completely leached out in short time periods, in a few minutes, at acid concentrations of 1 M and higher, as shown in Fig. 7.

By increasing the acid concentration, the amount of leached iron increases as well, while this amount depends on the temperature. The amount of leached iron at 20 °C is relatively low at each used acid concentration, but this amount increases with increasing temperature. The use of concentrated acid (2 M) at high temperature (80 °C) results in a significant part of iron passing into the solution.

It can be seen from the kinetics curves that the amount of leached metal in different sulphuric acid concentrations depends on both temperature and leaching time. Iron passes into the solution in smaller amounts and little by little, while zinc almost immediately.

Fig. 7 shows the dependence of zinc and iron extractions on the acid concentration in the 30th minute of the leaching for the used temperatures. It follows that at elevated temperatures, the high zinc extraction in the solution is achieved in short time period also at low acid concentration, while iron is leached only slightly. It provides a good basis for the direct separation of zinc and iron directly in the solution during the leaching process, and the subsequent use of products for recycling in blast furnace or zinc recovery from the solution after the refining process.

The XRD qualitative phase analysis of leaching residues, Fig. 8 in comparison with the X-Ray diffraction pattern of the input sample showed the presence of $CaSO_4 \cdot 5H_2O$ as a result of the interaction between present $CaCO_3$ and the leaching agent H_2SO_4. In accordance with the measured results, original iron phases remain in the sample, and small amounts of $FeSO_4 \cdot H_2O$ appear.

Conclusion

The results of the work confirmed the possibility of processing BF dust using simple hydrometallurgical processes. It was experimentally confirmed that the zinc leaching process is very fast and takes only a few minutes. The amount of leached zinc is affected by the sulphuric acid concentration and temperature. The 100 % zinc extraction was achieved using sulphuric acid solutions. On this basis, it can be assumed that zinc in the BF dust sample was present as easily leachable zinc oxide, although it has not been identified by the XRD diffraction phase analysis due to its low representation.

The amount of leached iron at different acid concentrations depends on the temperature used during the leaching. With increasing the acid concentration, the amount of leached zinc increases as well. The optimal conditions for passing zinc into the solution, with respect to the iron extraction, are achieved using 0.5 – 1 M sulphuric acid as a leaching agent at the temperature of 50 – 80 °C. However, these conditions are valid only for specific BF dust, as each BF dust has its own chemical and mineralogical composition. For leaching optimization of each BF dust it is recommended to examine the processing conditions for each material separately. On the other hand, it can be assumed that in the standard blast furnace process the leaching conditions will not vary widely.

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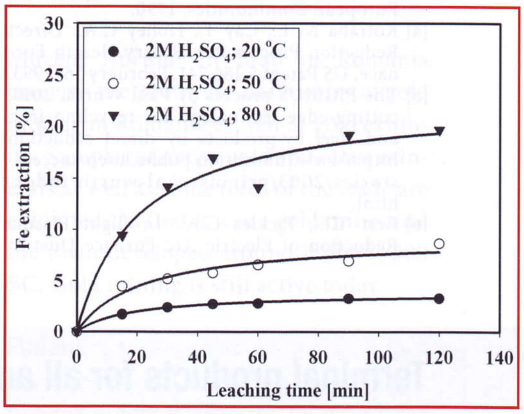

Fig. 6: Kinetics curves of iron extraction at temperatures 20, 50 and 80 °C with sulphuric acid concentration 2 M and L:S ratio = 6

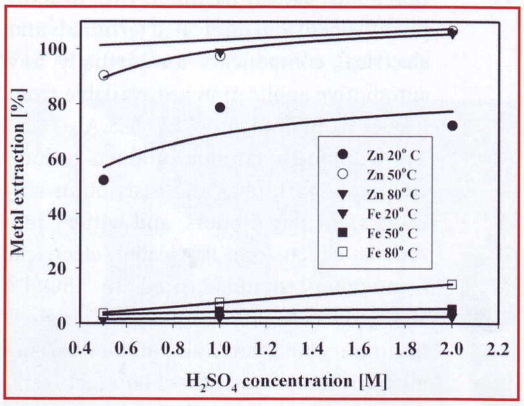

Fig. 7: The dependence of zinc and iron extraction on H_2SO_4 concentration in 30. minutes at different temperatures

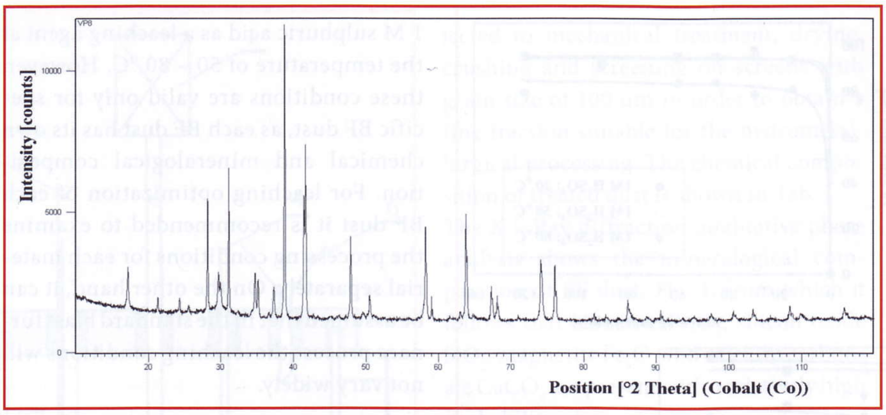

Fig. 8: XRD pattern of leaching residues of blast furnace dust

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