HYDROMETALLURGICAL PROCESSING OF BLAST FURNACE FLUE DUST CONTAINING ZINC

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Abstract

With every tonne of pig iron being produced, over 10 kg of flue dust is generated. Direct recycling of this material is unacceptable mainly due to its high zinc content. This waste often ends up on landfills, which is not ideal because of its heavy metal content and fine-grained character. There are several pyrometallurgical methods for recycling this type of material, but due to high energy consumption and low zinc content it's not ideal choice. On the other hand, hydrometallurgy is suitable for low zinc content with possibility of selective leaching. In this work, leaching of the dust with sulphuric acid was observed. Thermodynamic and kinetic aspects of zinc leaching were studied. Experiments were carried out under atmospheric pressure and effect of acid concentration and temperature was investigated. The goal was to set the conditions for maximum zinc leaching while minimum amount of iron is transferred into solution. Ideal conditions for selective leaching were achieved using 50 °C and 1 ÷ 0.5 M sulphuric acid solution. Higher temperature and concentration caused higher iron leaching ratio. With optimal conditions, iron recovery was in the range 5 ÷ 10 % while all of the zinc was leached out. Solid residue, obtained by this method is relatively zinc-free and can be reused in blast furnace (BF) process.

Keywords: Zinc, blast furnace flue dust, leaching, hydrometallurgy, material recycling

1. INTRODUCTION

Steel and iron production generates significant amounts of waste materials containing heavy non-ferrous metals. This waste is often deposited on landfills [1]. Flue dust from the BF contains iron, so it makes it valuable secondary material for re-use, but heavy metals must be removed [2].

This can be achieved by three ways: pyrometallurgical, hydrometallurgical and combined method. The best known pyrometallurgical full-plant and pilot plant processes include: the Waelz process, the Primus process, the Rotary Heart Furnace process, AUSMELT and RAPID, processes [3]. Hydrometallurgical processes are generally less sensitive to scatter of input composition. Also, there are advantages like lower energy consumption, no air pollution and possibility of small-scale processing. Hydrometallurgical leaching can be carried out by alkaline or acidic method. The main advantage of alkaline leaching is high selectivity of leached non-ferrous metals from iron, which remains in a solid phase. The disadvantages are relatively low efficiency and need for concentrated solutions. The acidic method brings a possibility to use less concentrated solution with higher effectively but lower selectivity. The best known hydrometallurgical processes, suitable for BF dust recycling are: Ezinex, Zincex Cardiff, Terra Gaia [3-5].

Most of these processes are optimized for relatively high concentration of zinc (over 10%). Leaching ability of zinc and overall kinetics of the hydrometallurgical treatment depends on the mineralogical form of the zinc. Several studies have shown that there are two possible phases containing zinc in dust - zincite (ZnO) and franklinite ($ZnFe_2O_4$) [6, 7]. Zincite is leachable in sulfuric acid under normal conditions; however franklinite is stable, refractory phase.

BF dust contains less zinc than dusts from secondary steel production, such as electric arc furnace (EAF) and basic oxygen furnace (BOF) dusts and slags. Behavior of EAF steelmaking dust has been studied [8, 9]. The main difference between EAF and BF flue dust is in the zinc quantity. The EAF dust contains 14 % to 21 % of zinc, while in BF flue dust the percentage of zinc content lies between 0.5 % and 5 % [10, 4].

As a suitable, relatively low cost and widely available leaching medium, appears sulphuric acid. Obtaining metals from sulfuric acid solution is relatively cheap and well-known process. Current effort should focus on the finding a process, in which heavy metals passes into solution and iron stays in the solid phase. This paper focuses to study of leaching relatively low zinc concentrated BF flue dust in the sulfuric acid solution.

2. EXPERIMENTAL

2.1. Material

Used BF flue dust was dried and crushed to fine particle size under 0.1 mm. Homogenous representative sample was obtained and characterized by atomic absorption spectroscopy (AAS). The results from chemical analysis were: 32.94 % Fe, 5.58 % Si, 1.54 % Zn, 0.24 % Cu and 0.15 % Pb (in wt.%). The loss of ignition was 20.24 %. The XRD qualitative phase analysis identified presence of hematite (Fe_2O_3), magnetite (Fe_3O_4), calcium carbonate ($CaCO_3$) and silicon dioxide (SiO_2). No zinc containing phase was identified. The reason could be relatively low content of zinc.

Leaching experiments were carried out in glass apparatus according to **Fig. 1**. Solid to liquid ratio (S:L) of 1:6 was used. Normal conditions of temperature and pressure were used, i.e. temperature range 20 to 80 °C and atmospheric pressure 0.1 MPa. Concentrations of sulfuric acid solution were 0.5, 1 and 2 M. Stirring was done by mechanical stirrer with constant speed 300 rpm.

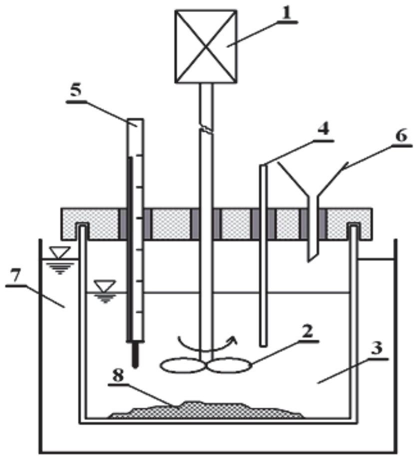

Fig. 1 Leaching apparatus [11]

The samples for the chemical analysis were taken in intervals: 15, 30, 45, 60, 90 and 120 minutes. The samples were then filtered from potential solid non-dissolved dust and analyzed by AAS. The effect of temperature and sulfuric acid concentration on the extraction of zinc and iron into the solution was observed.

2.2. Results

Leaching reactions of possible phases containing zinc are represented by reactions (1) - (3).

$$ZnO_{(s)} + H_2SO_{4\,(aq)} = ZnSO_{4\,(aq)} + H_2O_{(l)} \tag{1}$$

$$ZnFe_2O_{4(s)} + 4\ H_2SO_{4\,(aq)} = ZnSO_{4\,(aq)} + Fe_2(SO_4)_{3\,(aq)} + 4\ H_2O_{(l)} \tag{2}$$

$$ZnFe_2O_{4(s)} + H_2SO_{4\,(aq)} = ZnSO_{4\,(aq)} + Fe_2O_3 + H_2O_{(l)} \tag{3}$$

Reaction (2) is thermodynamically more preferable than reaction (3). All of the standard Gibbs energy changes of the reactions have increasing character with temperature, as shown on **Fig. 2**. It follows from that the higher temperatures doesn't have positive impact on leaching zinc from dust.

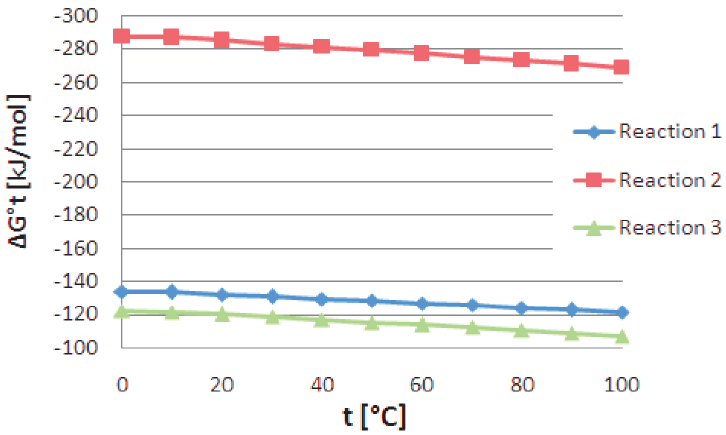

Fig. 2 Standard Gibbs energy as a function of temperature

On the other hand, kinetic experiments showed that with increasing temperature total zinc yield increases, as shown on **Fig. 3 a**. It is also visible, that with temperature of 80°C, the 100 % of Zn was extracted into solution within first 15 minutes of leaching. Increasing sulfuric acid to concentration over 1 M has weak effect on zinc leaching (as shown on **Fig. 3b**).

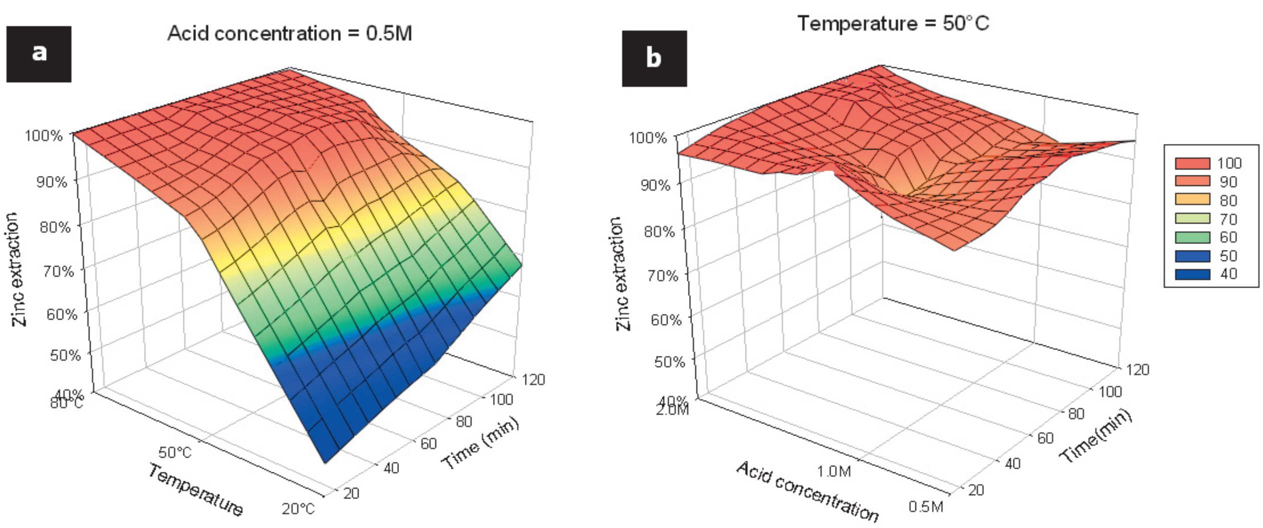

Fig. 3 Kinetic plots of zinc yielded from temperature (**a**) and acid concentration (**b**)

Fig. 4 a shows ideal conditions for leaching of zinc in 15th minute. It is clear, that reasonable amounts of zinc are leached with all used acid concentration and temperatures above 50 °C. **Fig. 4 b** shows iron yield status in 15th minute of experiment at varying conditions. Higher acid concentration and temperatures tends to increase iron leaching, which is undesired.

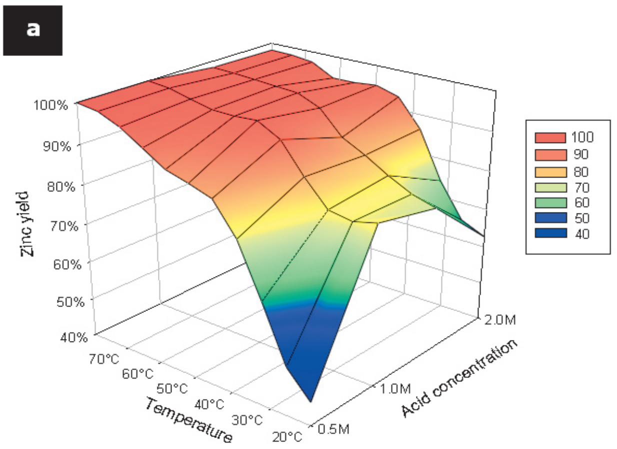

Fig. 4 Zinc (**a**) and iron (**b**) leached illustrated as a function of temperature and acid concentration in 15th minute of experiment

Iron behavior with time is illustrated with kinetic plots on **Fig. 5**. From the plots is clear, that iron yield is increasing with time and acid concentration. Maximum of iron leached was achieved with 2 M sulfuric acid and 80 °C in 120th minute of leaching. The maximum iron yield was 19.72 %.

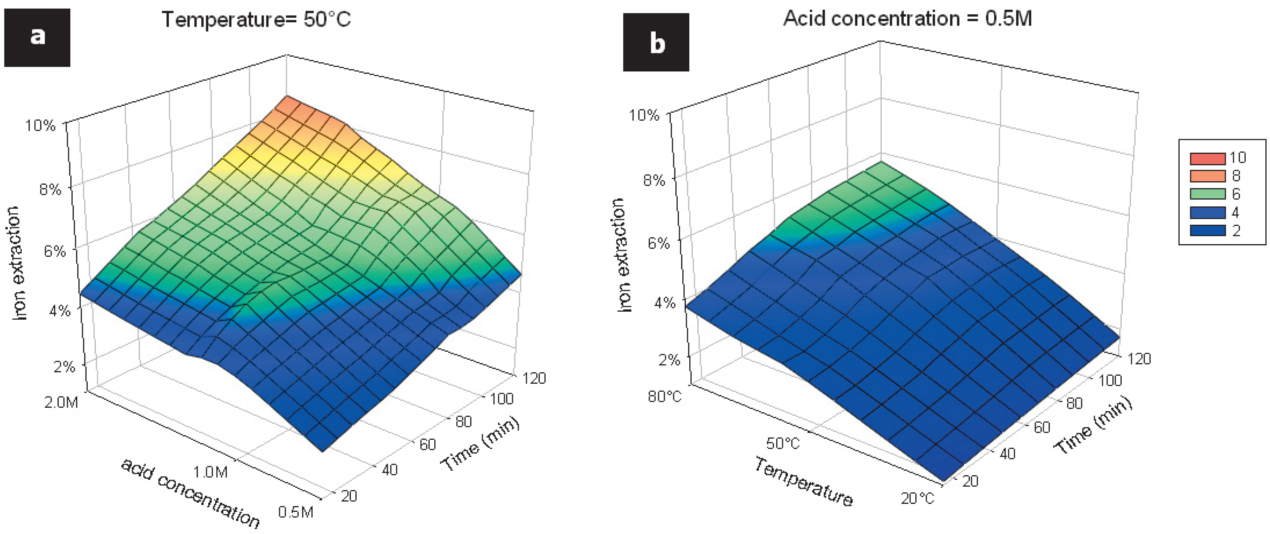

Fig. 5 Kinetic plots of iron yielded from temperature (**a**) and acid concentration (**b**)

3. CONCLUSION

The objective of the experiments was to show the possibility to leach BF flue dust in sulfuric acid with the highest possible extraction into solution. The results confirmed the possibility of hydrometallurgical processing BF dust. Process of zinc leaching is very rapid and with almost all temperatures and concentrations the metal yield reached maximum within first 15 minutes.

It is impossible to achieve selective leaching zinc from iron with this configuration and used material, however form kinetic aspects is clear that iron leaching is not as rapid as zinc. The 100 % of zinc was extracted within first 15 minutes of leaching with these conditions: 0.5M acid and 80°C. S:L ratio was 1:6 and experiments was carried out under atmospheric pressure. Maximum iron yield was 4.4 % at these conditions.

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