Leaching of basic oxygen furnace sludge with sulphuric acid

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In this study the hydrometallurgical processing of BOF sludge in the sulphuric acid solutions under atmospheric pressure and temperatures up to 100 $^{\circ}$ 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.

Key words: basic oxygen furnace dust and sludge, hydrometallurgy, leaching, zinc, sulphuric acid

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.

This dust is usually returned into the steelmaking process after pretreatment or it is recycled in the sintering plant. In the European Union only small amount of dust is stored in landfills. The dust contains a considerably high content of zinc. 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. Both BOF dust and sludge are categorized as hazardous waste [1]. 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 [2]. Each of these methods has its advantages as well as disadvantages. The advantage of hydrometallurgical processes is their higher flexibility in plants. 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 offgases, 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.

Experimental

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 mineralogical composition was determined by XRD phase analysis. 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 (Fe₃O₄), wustite (FeO), calcite (CaCO₃), graphite (C), and metallic Fe are found with high probability. Phases such as hematite (Fe₂O₃), ferritic phases and SiO₂ 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.

In the sample of BOF sludge no phase containing zinc was identified. This can be caused by small amounts of Zn in the sample. The small amount of zinc in the sample, 0.1 - 3 %, causes that diffraction of zinc phases can vanish in the background of the XRD pattern.

Experimental set - up

The leaching experiments were carried out in the apparatus, which is shown in Fig. 1 [3].¹

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 $0.1, 0.2, 0.4, 1.0M H_2SO_4$ at the temperatures of 20, 40, 60 and 80 °C. In each of experiments

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the revolutions of the glass stirrer equal to 300 rpm 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 content, was made by means of AAS Varian 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. 1. Schematic view of the leaching apparatus [4], 1 – mechanical stirrer; 2 – propeller; 3 – pulp; 4 – sampler; 5 – thermometer; 6 – feeder; 7 – water thermostat; 8 – BOF sample.

Results and discussion

Fig. 2 shows the kinetic dependences of the zinc leaching from BOF sludge in dependence on the leaching time at different concentration of sulphuric acid, liquid to solid ratio L:S = 10 and temperature 20 - 80 °C. 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 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 1 M 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. 2. Kinetics dependencies of leached zinc on the leaching time at different acid concentrations, liquid to solid ratio L:S = 10 and temperature 20 - 80 °C.

Fig. 3 shows kinetics dependencies of leached zinc on temperature at different sulphuric acid concentration 0.1 - 1 M 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

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decrease of leached zinc. However, by increasing the sulphuric acid concentration over $0.4 \text{ M H}_2\text{SO}_4$ 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. 3. 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.

Fig. 4 shows the kinetics dependencies of leached zinc on sulphuric acid concentration at 20 - 80 °C and liquid to solid ratio L:S = 10 after 15 minutes of leaching. From the kinetics curves it results that with the increase of sulphuric acid concentration the zinc extraction raises rapidly, while the influence of the temperature is minimal.



Fig. 4. Kinetics dependencies of leached zinc on sulphuric acid concentration at 20 - 80 °C and liquid to solid ratio L:S = 10 after 15 minutes of leaching.

Conclusion

The aim of the experimental work was to verify the zinc leachability from 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 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 in big amount. 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 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.

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