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Abstract:

Dust from blast furnace (BF) and basic oxygen furnace (BOF) is recycled as iron source for sintering process. However, dust recycling rate is limited due to the zinc in dust. Thus, it is necessary to remove zinc from dust to improve the dust recycling rate. In this study, zinc-separating process of BF dust using hydrometallurgical system is proposed with an iron-recovery process. Laboratory-scale experiments using BF dust were conducted to investigate zinc and iron behavior. This process was composed of acid leaching, iron-recovery from leachate and zinc-recovery. With this process, 68 wt% of the zinc in dust was successfully separated and the sludge containing over 40 wt% of zinc was obtained. A long-term continuous test at Chiba Works was conducted to clarify long-term stability of this process. As a result, the average zinc removal rate was 66 wt% and the average zinc content in the zinc concentrated sludge was 41 wt%. This process can promote BF dust recycling.

1. Introduction

Since the total amount of blast furnace (BF) dust and basic oxygen furnace (BOF) dust generated in Japan is about 5.8 million t/y¹⁾, steel works have pro-

tilation and liquid permeation²⁾. Therefore, the recycling rate of BF and BOF dust is limited by the content of zinc. In order to further promote recycling of these types of dust, it is necessary to separate zinc from these dusts.

Practical zinc separation methods include dry and

hydrometallurgical (wet) processes. The main practical dry processes are the rotary kiln method³⁾, rotary hearth furnace (RHF) method⁴⁾ and shaft furnace method⁵⁾. The purposes of these methods are zinc separation and production of reduced iron. Because these methods are characterized by the volatilization and separation of zinc under a high temperature atmosphere over 1 000°C in order to achieve a high zinc removal rate, it can be said that they are large energy-consuming processes. Moreover, they also tend to require large proc

in the experiment. The dried dust was analyzed by ICP-AES.

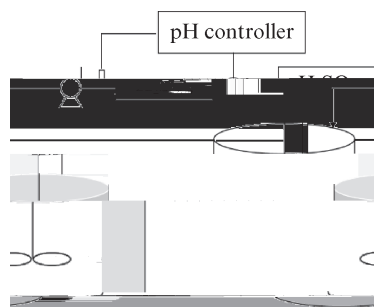
2.2 Zinc Leaching from BF Dust by Sulfuric Acid

In order to improve the recycling rate of BF dust, the treatment conditions under which iron leaching was suppressed and zinc could be leached and removed to a level that did not hinder recycling were investigated. The leaching test with sulfuric acid was performed with the apparatus shown in **Figure 1**. 50 g of the BF dust was suspended in 500 mL of distilled water (solid-liquid ratio = 1 : 10), and the suspension was stirred at 500 rpm at 25°C. Due to the increased content of leached iron at pH values below 2.0, this condition was excluded from the test. Since the concentration of zinc in the leachate became saturated in about 1 h, a treatment time of 1 h was used in all cases in the following study. After 1 h, the pH-controlled suspension was filtrated to separate the leachate and residue, and the zinc and iron in the leachate were analyzed by ICP-AES.

The ZnO, ZnS and ZnFe₂O₄ contained in the BF dust and the residue after leaching were determined according to Fujimoto's method⁸⁾ in order to investigate the effect of the zinc compound morphology on the zinc leaching rate.

2.3 Zinc Leaching from BF Dust by Sulfuric Acid

During the treatment described in the previous sec-



tion, not only zinc but also other metals such as iron were leached. When an alkaline reagent was added to this leachate, zinc and other metals were co-precipitated and the precipitate had a low content of zinc, which reduced the value of this precipitate as a zinc source. In order to increase the zinc content, purification of the leachate by precipitation and recovery of other metals such as iron from the sulfuric acid leachate, namely, zinc purification, was conducted by using the difference of the pH for hydroxide precipitation formation of each metal species. The process flow is shown in **Figure 2** (a). An oxidizing agent (hydrogen peroxide) and an aqueous sodium hydroxide solution were added to the sulfuric acid leachate, and iron was precipitated and separated as iron hydroxide.

2.3.1 Effect of pH

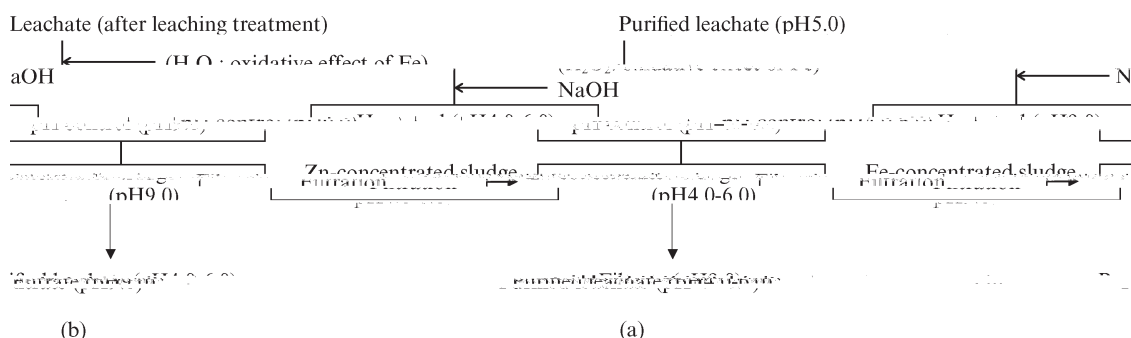
The element iron, which is the main object of precipitation and recovery in this process, is known to precipitate as a hydroxide under not only alkaline conditions but also weakly acidic conditions.

Therefore, the effect of pH on the precipitation behavior of iron was investigated. Using the experimental apparatus shown in Fig. 1, the leachate obtained by sulfuric acid leaching at pH 2.0, which showed the highest zinc leaching rate in the study in section 2. 2, was treated with an aqueous sodium hydroxide solution, and the pH was controlled to values from 4.0 to 6.0. The treatment temperature was 25°C, and the stirring intensity was 500 rpm. The treatment time was set to 1 h, as mentioned in the previous section.

2.3.2 Effect of hydrogen peroxide addition

Iron leached by sulfuric acid is known to exist in solution with the divalent cation⁹⁾, and as the iron hydroxide, Fe(OH)₃, in which iron is the trivalent cation, as a common compound form. Therefore, in order to efficiently precipitate and recover iron from the leachate, oxidation of Fe²⁺ to Fe³⁺ in the leachate was considered effective.

Hydrogen peroxide was added as an oxidizing agent



while controlling the pH of the leachate obtained by sulfuric acid treatment (Fig. 2 (a)). The pH was set to 5.0, which allowed more iron to be precipitated with

be pH 4.0 or 5.0. As for iron, the residual ratio tended to decrease with increasing pH, indicating that a high pH is necessary to precipitate iron. Therefore, pH 5.0 was found to be the most suitable pH for selective precipitation and recovery of iron while minimizing precipitation of zinc.

However, even at pH 5.0, 46 wt% of the iron remained in the leachate and could not be recovered, suggesting that further improvement of the efficiency of iron precipitation and recovery was necessary.

3.3.2 Effect of hydrogen peroxide addition

As described in the previous chapter, the iron in the leachate was predicted to be Fe^{2+} , and the iron in the iron hydroxide was predicted to be Fe^{3+} . Therefore, we attempted to improve the precipitation and recovery efficiency of iron by oxidizing the Fe^{2+} in the leachate by using a hydrogen peroxide solution as an oxidizing agent, and thereby precipitate the iron as Fe^{3+} .

At pH 5.0, which is suitable for selective iron precipitation, the residual rates of zinc and iron in the leachate when hydrogen peroxide was added were as shown in **Fig. 4**. When hydrogen peroxide was added, the residual iron ratio was 0, indicating that iron was completely precipitated and recovered.

3.4 Recovery of Zinc by Alkali Precipitation Method

Zinc was recovered from the leachate obtained in the previous section by the alkaline precipitation method.

iron and 42.6 wt% of zinc.

5. Long-Term Continuous Test

Based on the results in the previous sections, a continuous test apparatus (treatment capacity: 5 L/h) for treating BF dust was manufactured and a long-term continuous test was carried out at East Japan Works (Chiba District) of JFE Steel Corporation. The process flow of the test is shown in **Figure 7**.

Tank 1 is the leaching process using sulfuric acid. The slurry was controlled to pH 2 in a 25 wt% sulfuric acid aqueous solution.

Tank 2 (tank volume: 5 L) is the recovery process of iron in the leachate. Here, the slurry was controlled to pH 5 by a 10 wt% calcium hydroxide slurry, and the oxidation-reduction potential of the slurry was simultaneously controlled to over 0.55 V by 35 wt% hydrogen peroxide. Next, solid/liquid separation of the slurry was carried out by a solid/liquid separator (PC separator type A, manufactured by AION Co., Ltd.). The residue after solid-liquid separation (Zn-reduced dust) was dried in a thermostatic dryer at 105°C for 24 h and then subjected to analysis. The filtrate was fed to Tank 3 at 5 L/h by a roller pump.

Tank 3 (tank volume: 5 L) is the zinc recovery process. The filtrate was controlled to pH 9 by a 30 wt% aqueous sodium hydroxide solution. Solid/liquid separation was carried out by gravitational settling in a solid/liquid separation tank (tank volume: 20 L), and

was not stable, and only 54 wt% of the iron could be precipitated and recovered. In contrast, in the system containing hydrogen peroxide, the oxidation-reduction potential of the solution could be raised to the potential in the region where iron precipitates as a hydroxide, resulting in complete precipitation and recovery of iron at pH 5.0.

4.3 Recovery of Zinc by Alkali Precipitation Method

According to Fig. 6, both zinc and iron precipitate as hydroxides in the pH 9.0 region. Therefore, when the alkaline precipitation method was applied directly to the acid leachate, the residual iron in the leachate was precipitated as iron hydroxide. As a result, zinc hydroxide was diluted by iron hydroxide, and the zinc content in the precipitate (Zn-concentrated sludge) remained at 8.1 wt%.

Introduction of the leachate purification step, in which iron is precipitated and recovered before zinc recovery by the alkaline precipitation method, made it possible to recover iron before zinc recovery and obtain a Zn-concentrated sludge containing only 0.03 wt% of

Zn_{in} : Zn content in BF dust before treatment (wt%)

Zn_{out} : Zn content in Zn-reduced dust (wt%)

z : Zn removal rate (wt%)

5.1 Results of Long-Term Continuous Experiment

Figure 8 shows the results of a long-term continuous test. The Zn content in the Zn-reduced dust obtained after the treatment decreased to less than 1 wt%.

Based on Eq. (2), the average zinc removal rate in the long-term continuous test was about 66 wt%, which was almost equivalent to the zinc leaching rate obtained in section 3.2. The average zinc content and iron content in the Zn-concentrated sludge were 41.0 wt% and 0.03 wt%, respectively, and this Zn-concentrated sludge was equivalent to the sludge obtained in Section 3.4.

These results suggest that stable removal of zinc in BF dust can be achieved by a process consisting of (1) leaching with sulfuric acid, (2) recovery of the iron in the leachate and (3) recovery of zinc, as shown in Fig. 7.

6. Conclusion

A zinc separation process for blast furnace (BF) dust was investigated experimentally, and the following findings were obtained.

(1) Leaching of zinc in dust by using sulfuric acid

The influence of pH on the leaching of zinc and iron in sulfuric acid treatment was investigated by using BF dust generated by an actual steel works. As a result, 68 wt% of the zinc in the BF dust was leached and separated from iron under the condition of pH 2.0. The leaching rate of iron was limited to 6.4 wt%, and zinc could be leached preferentially under more moderate treatment conditions than in previous studies.

(2)