Zinc Separation Process for Blast Furnace Dust Using Hydrometallurgical System

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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/y[1)], steel works have promoted recycling of these types of dust by charging the recovered dust into blast furnaces and basic oxygen furnaces as iron sources. However, BF and BOF dust contain not only iron and carbon but also zinc and other elements which negatively affect the iron-making process. In particular, zinc is evaporated and deposited on the blast furnace wall, causing deterioration of ventilation and liquid permeation[2)]. 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 method[3)], rotary hearth furnace (RHF) method[4)] and shaft furnace method[5)]. 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 processing facilities and have a high construction cost. While the dry processes are suitable for large-scale treatment, application to small plants is not economically feasible, as these plants do not enjoy economies of scale.

On the other hand, the hydrometallurgical zinc separation process has not been applied practically in Japan. Very few reports have examined acid leaching of zinc in BF dust[6, 7)], and because expensive organic acids (dicarboxylic acid and carboxylic acid) were used, practical application was rather difficult, as the organic acids were more expensive than inorganic acids such as sulfuric acid and hydrochloric acid.

In order to improve the recycling rate of BF dust, the conditions for leaching and separation of zinc with sulfuric acid in the wet process and a technology for high purity recovery of the leached zinc were investigated, and a new zinc separation process using a hydrometallurgical system was proposed, as introduced in this study.

2. Experimental

2.1 Materials

In this study, BF dust in slurry form was collected at East Japan Works (Chiba District) of JFE Steel Corporation. This slurry was dried at 105°C for 12 h and used

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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 $ZnFe_2O_4$ contained in the BF dust and the residue after leaching were determined according to Fujimoto's method[8] 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 section, 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.

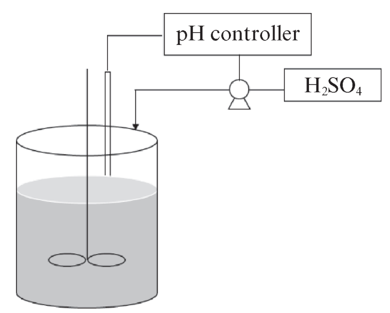

Fig. 1 Experimental apparatus for leaching treatment using sulfuric acid

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 cation[9], 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 Fe^{2+} to Fe^{3+} in the leachate was considered effective.

Hydrogen peroxide was added as an oxidizing agent

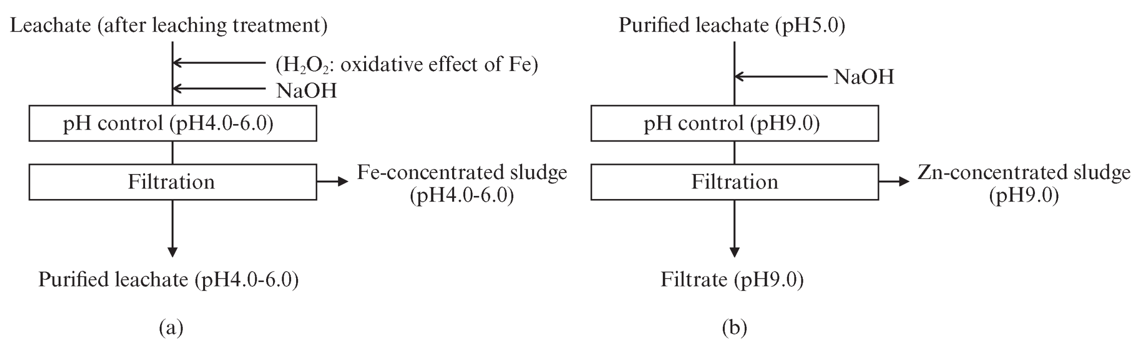

Fig. 2 Simplified process flowsheet. (a) Fe-recovery process, (b) Zn-recovery process

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 almost no zinc precipitation. One equivalent of hydrogen peroxide was added to the iron in the leachate determined by ICP-AES.

In both experiments, the treated solution was filtrated through a filter paper with a pore size of 1 μm, and the concentrations of the zinc and iron in the filtrate and residue were analyzed by ICP-AES.

2.4 Recovery of Zinc by Alkali Precipitation Method

The zinc in the purified leachate obtained as described in the previous section was recovered as a solid by a conventional alkaline precipitation method. The process flow is shown in Fig. 2 (b). An aqueous sodium hydroxide solution was added to the purified leachate, and the pH was controlled to 9.0 using the apparatus shown in Fig. 1. As in the previous section, the treatment temperature was 25˚C, the agitation intensity was 500 rpm and the treatment time was 1 h. After the treatment, the treated solution was filtrated through a filter paper with a pore size of 1 μm, and the concentrations of the zinc and iron in the filtrate and residue were analyzed by ICP-AES.

3. Results

3.1 Characteristic Analysis of Tested BF Dust

The results of a component analysis of the BF dust are shown in **Table 1**. The BF dust used in this study contained 1.04 wt% of zinc and 35.7 wt% of iron.

3.2 Results and Discussion

The effect of pH on the percentage of metal leached by sulfuric acid leaching is shown in **Figure 3**. The percentage of metal leached was calculated by the following Eq. (1).

$$y = \frac{x_{sol}}{x_{\text{int}}} \times 100 \quad \cdots\cdots (1)$$

x_{int}: metal in BF dust before acid leaching (g)
x_{sol}: metal in leachate after acid leaching (g)
y: percentage of metal leached (wt%)

The amount of leached zinc increased as the pH decreased. At pH 2.0, 68 wt% of the zinc was leached, whereas only 6.4 wt% of iron was leached, indicating that zinc can be selectively leached from BF dust without leaching large amounts of iron or other elements.

The ratios of the zinc compounds in the dust were compared before and after sulfuric acid treatment

Table 1 Chemical composition of BF dust used

	Chemical composition (wt%)	
	Zn	Fe
BF dust	1.04	35.7

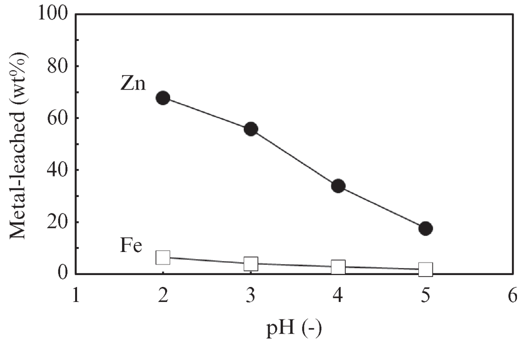

Fig. 3 Effect of pH on percentage of leached metal in sulfuric acid leaching treatment

Table 2 Quantitative analysis of Zn-compounds in BF dust before and after leaching treatment

	Zn compounds (wt%)		
	ZnO	ZnS	$ZnFe_2O_4$
BF dust (before treatment)	67	33	0.3
Residue at leaching treatment	6.6	31	0.3
	ZnO	ZnS	$ZnFe_2O_4$
Leaching rate	90	6.1	0

(leaching treatment at pH 2.0), as shown in **Table 2**. The ratios of the zinc compounds before sulfuric acid treatment were 67 wt% for ZnO and 33 wt% for ZnS, together with a very small amount (0.3 wt%) of $ZnFe_2O4$. The contents of ZnS and $ZnFe_2O_4$ in the dust were hardly changed by sulfuric acid treatment, proving that only ZnO was leached. The leaching rates of ZnO, ZnS and $ZnFe_2O_4$ were 90, 6.1 and 0 wt%, respectively.

3.3 Purification of Sulfuric Acid Leachate (Recovery of Iron)

3.3.1 Effect of pH

The effect of pH on the percentage of metal remaining in the leachate after the purification process is shown in **Figure 4**. In the leachate purification process, it is necessary to selectively precipitate and recover iron without precipitating zinc as much as possible. When the hydrogen peroxide solution was not added, almost 100% of the zinc remained in the leachate and did not precipitate under the conditions of pH 4.0 and 5.0, while at pH 6.0, part of zinc precipitated and the residual zinc ratio decreased to 83 wt%. Therefore, the conditions for avoiding zinc precipitation were found to

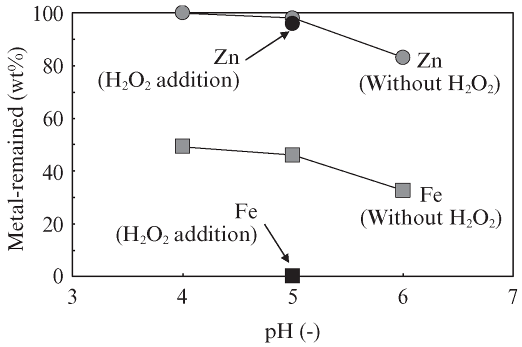

Fig. 4 Effect of pH on percentage of Zn and Fe-remained in leachate

Table 3 Chemical composition of Zn-concentrated sludge and BF dust

	Chemical composition (wt%)	
	Zn	Fe
Zn-concentrated sludge	42.6	0.03
BF dust (before treatment)	1.04	35.7

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. **Table 3** shows the comparison of the zinc and iron concentrations of the Zn-concentrated sludge and the initial BF dust. The concentrations of zinc and iron

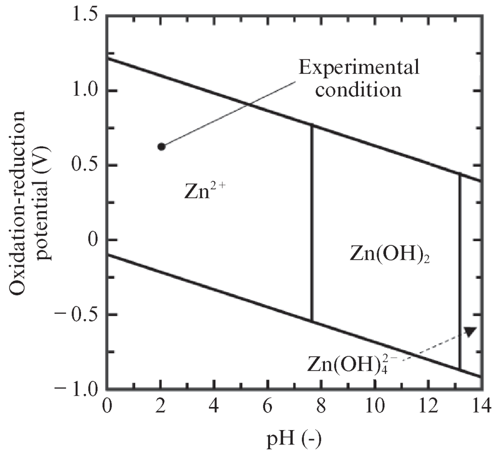

Fig. 5 Potential-pH diagram of Zn-water system[10)]

in the sludge were 42.6 wt% and 0.03 wt%, respectively. Thus, it was found that the 1.04 wt% of zinc contained in the BF dust could be concentrated to 42.6 wt% in the sludge.

4. Discussion

4.1 Behavior of Zinc in Sulfuric Acid Leaching Treatment

Figure 5 shows the potential-pH diagram of zinc[10)]. Zinc is mainly leached as Zn^{2+}. However, the leaching rate of zinc at pH 2.0 was only 68 wt%, which is not complete leaching. As a result of an investigation of the leaching behavior of zinc depending on the forms of the zinc compounds in the BF dust, 90 wt% leaching was achieved with ZnO, while leaching of ZnS and $ZnFe_2O_4$ was slight. This fact suggests that ZnS and $ZnFe_2O_4$ are less likely than ZnO to leach into sulfuric acid. At pH 2.0, the ZnO in the dust was leached selectively, which means the zinc leaching rate in this study was determined by the content of ZnO in the dust.

4.2 Behavior of Iron in Sulfuric Acid Leachate Purification Process

Figure 6 shows the potential-pH diagram of the Zn-Fe-O-H system[10)]. At pH 5.0, Zn^{2+} is the dominant form of zinc in a solution, while the dominant form of iron depends on the oxidation-reduction potential of the solution. The oxidation-reduction potential at pH 5.0 was measured with an ORP meter, and was 0.39 V without addition of hydrogen peroxide and 0.60 V with addition of hydrogen peroxide. As shown in **Fig. 6**, the oxidation-reduction potential of the system without addition of hydrogen peroxide is near the boundary between the region where iron dissolves as Fe^{2+} and the region where iron precipitates as iron hydroxide. As a result, the form of iron in the solution

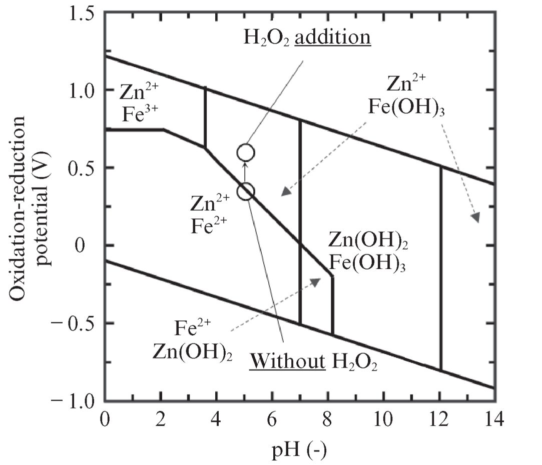

Fig. 6 Potential-pH diagram of Zn-Fe-O-H system[10)]

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 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 the residue was subjected to analysis after drying at 105°C for 24 h in a thermostatic dryer.

The BF dust before treatment and the Zn-reduced dust were periodically sampled, and the Zn removal rate was calculated based on Eq. (2).

$$z = \left(1 - \frac{Zn_{out}}{Zn_{in}}\right) \times 100 \quad \cdots\cdots (2)$$

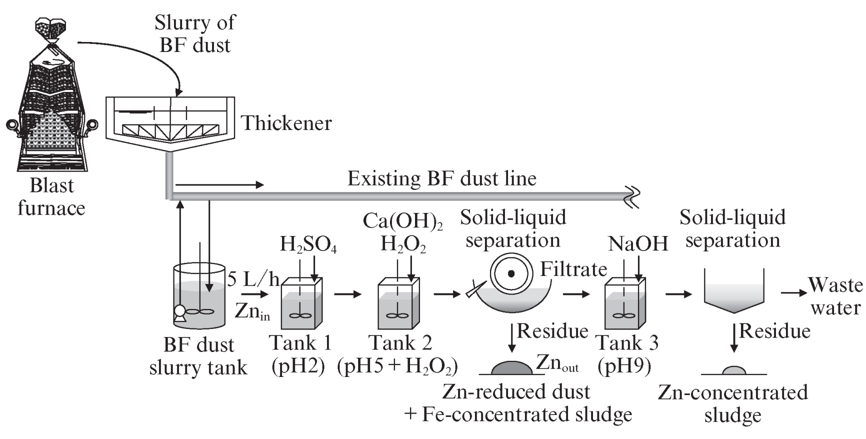

Fig. 7 Experimental apparatus for the long-term continuous test

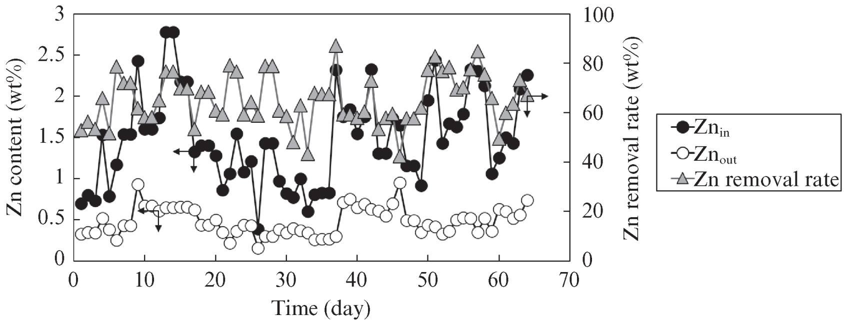

Fig. 8 Results of the long-term continuous test at Chiba Works

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) Purification of sulfuric acid leachate (recovery of iron)

A new leachate purification step was introduced to selectively precipitate the iron in the leachate. At pH 5.0, substantially 100% of the iron could be precipitated and recovered, while 96 wt% of the zinc remained dissolved in the leachate when the oxidation-reduction potential of the solution was set to a high potential by adding hydrogen peroxide.

(3) Recovery of zinc by alkaline precipitation

The zinc in the leachate was recovered as a hydroxide precipitate at pH 9.0. As a result, a Zn- concentrated sludge which contained almost no iron and 42.6 wt% zinc was obtained.

(4) Long-term continuous test

A continuous test was carried out at East Japan Works (Chiba District) of JFE Steel Corporation, using a process consisting of (1) leaching with sulfuric acid, (2) recovery of iron in the leachate, and (3) recovery of zinc. The results of this test demonstrated that zinc in BF dust can be stably removed by the proposed process.

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