Dezincing Behavior from Iron and Steelmaking Dusts by Microwave Heating

Koki NISHIOKA, Takayuki MAEDA and Masakata SHIMIZU

Graduate Faculty of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581 Japan

Recycling of valuable metals such as Zn, Pb is a key issue for environmental protection and efficient utilizations of valuable metals. In order to recover Zn and Pb from iron and steelmaking dusts, the recovery process of these dusts by microwave heating was investigated.

Zn and Pb were almost 100% recovered from these dusts by microwave heating. In the first stage of this process, reduction of Fe₂O₃ proceeded prior to that of ZnO. In the second stage, when the temperature of the sample was above 900°C, ZnO was reduced and Zn was vaporized.

KEY WORDS: recovery of zinc; iron and steelmaking dusts; microwave heating.

1. Introduction

Recycling of valuable materials such as Zn, Pb is a key issue for environmental protection and efficient utilizations of valuable metals for decades. Iron and steelmaking dusts usually contain Zn, Pb and other valuable products, however the dusts are valuable second resource, about 30% of the dusts are wasted.

The dusts are recycled in sinter plants as raw materials, but reusable amount of the dusts is limited due to residual Zn in the dusts. Previously, rotary kiln and rotary hearth were used to recover Zn and Pb from the dusts. These processes have some problems, such as energy efficiency, generation of huge amount of CO₂ and high temperature exhaust gas.

In order to recover Zn and Pb from iron and steelmaking dusts without these problems, a new treatment process of the dusts is proposed in this study. Advantages of the process are; (1) small amount of waste gas due to burner-less process, (2) no drying process required for raw materials, (3) the facilities smaller than the current ones.

Microwave heating has the following potential; (1) rapid and selective heating of materials, (2) reactions can be catalyzed because the heating occurs on a molecular or atomic level, (3) the gas volume is reduced and the atmosphere can be controlled, (4) the materials is heated internally; and (5) the temperature of the refractory can be minimized. Microwave is able to heat various kinds of oxides and carbon contained in iron and steelmaking dusts selectively. For the reasons mentioned above, in this process, microwave heating was applied for the recovery of Zn and Pb.

Therefore, in this paper, availability of microwave heating on the recovery process of Zn and Pb from various dusts was investigated.

2. Experiments

2.1 Recovery of Zn and Pb from Blast Furnace Wet Dust (BFWD) and other dusts

20g of the Blast Furnace Wet Dust sample (BFWD), which is shown in Table 1, was prepared for the experiment.

Fe₂O₃, Fe₃O₄ and carbon existed in BFWD sample were identified by X-ray diffraction analysis. The BFWD contains enough amount of carbon for the reduction of Fe₂O₃, ZnO and PbO in the dust. On the contrary, BOFWD, BOFDD and EAFD contain inadequate amount of carbon for the reduction of Fe₂O₃, ZnO and PbO. For the reduction of these oxides in these dusts, enough amount of carbon should be added. The BFWD, BOFWD, BOFDD and EAFD shown in Table 1 contain 1.7-36.7%mass% of FeO, 1.7-36.7%mass% of C, 3.4%mass% of Zn, 0.23-3.4%mass% of Pb. Therefore, considering their chemical compositions, synthetic dusts were prepared by blending the proper amounts of reagent grade of Fe₂O₃, C, ZnO and PbO. Chemical compositions of the samples are shown in Table 2. 20g of the samples (Sample A – D) were used for the experiments.

Table 1. Chemical composition of iron and steelmaking dust (mass%)

<table>
<thead>
<tr>
<th></th>
<th>T-Fe</th>
<th>FeO</th>
<th>C</th>
<th>Zn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFWD</td>
<td>32.43</td>
<td>64</td>
<td>36.74</td>
<td>1.47</td>
<td>0.23</td>
</tr>
<tr>
<td>BOFWD</td>
<td>68.3</td>
<td>64.2</td>
<td>-</td>
<td>0.54</td>
<td>-</td>
</tr>
<tr>
<td>BOFDD</td>
<td>66.0</td>
<td>5.6</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>EAFD</td>
<td>30.2</td>
<td>2.8</td>
<td>1.7</td>
<td>19.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of synthesis dusts (mass%)

<table>
<thead>
<tr>
<th></th>
<th>Fe₂O₃</th>
<th>C</th>
<th>ZnO</th>
<th>PbO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>48.7</td>
<td>48.7</td>
<td>2.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Sample B</td>
<td>46.5</td>
<td>46.5</td>
<td>5.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Sample C</td>
<td>43.5</td>
<td>43.5</td>
<td>10.9</td>
<td>2.1</td>
</tr>
<tr>
<td>Sample D</td>
<td>38.5</td>
<td>38.5</td>
<td>19.2</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Figure 1 shows schematic diagrams of microwave heating apparatus. Experiments were conducted with a
Sharp, Model 4000, industrial microwave oven. The power output is variable from 0 to 1 kW at 2.45 GHz.

The samples were placed in an alumina crucible, which was covered with fine ceramic fiber to prevent heat loss to the surroundings, and located in a chamber. The alumina crucible was placed in a Pyrex glass chamber with inlet and outlet ports. A Chromel-Alumel thermocouple was inserted through the wall of the applicator of the microwave oven for monitoring the sample temperature. The chamber was placed on the center of the microwave oven, and the thermocouple was inserted into the center of the sample.

The argon gas was introduced at a flow rate of 8.33 × 10^6 m³/s to the chamber as a carrier gas. The sample was irradiated with 1 kW of microwave for 1800 seconds. Concentrations of CO and CO₂ of exhaust gas were measured continuously by an infrared analyzer. Concentrations of Zn and Pb of the sample at various appropriate reaction time were quantified by Inductively Coupled Plasma (ICP) analysis.

The apparent reduction rate constants of each sample were calculated from the slope of the fractional reduction curves where the fractional reduction was 0.5.

Table 3. Chemical composition of samples (mass%)

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>C</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>50</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>Sample 2</td>
<td>-</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

3. Results and Discussions

3.1 Recovery of Zn and Pb from BFWD

Figure 3 shows the temperature and concentration-time curves of Zn and Pb in a BFWD sample obtained by microwave heating at a power of 1 kW. In the first stage of the reaction, the temperature of the sample raised rapidly, after that, kept rising gradually, reached over 1300°C in 20 minutes. During the first stage of heating, up to 5 minutes, there was no change in the concentrations of Zn and Pb. Almost 100% of Zn and Pb were recovered by 20 minutes of microwave heating.

In iron and steelmaking dusts, zinc exists as zinc oxide. As can be seen from Figs. 3 and 4, at temperature above...
1000°C, in CO-CO₂ atmosphere, zinc oxide is reduced by carbon mono oxide and zinc vaporizes. Carbon mono oxide is regenerated by the reaction with solid carbon, as follows.

\[
\begin{align*}
\text{ZnO(s)} + \text{CO(g)} &\rightarrow \text{CO₂(g)} + \text{Zn(g)} \quad (1) \\
\text{C(s)} + \text{CO₂(g)} &\rightarrow 2\text{CO(g)} \quad (2)
\end{align*}
\]

In Fig. 4, CO-CO₂ compositions of exhaust gas of BFWD sample were plotted on the equilibrium diagram of Fe-C-O system. In this process, reduction of Fe₂O₃ and ZnO proceeded along with the equilibrium of Boudouard reaction Eq.(2). Therefore, it is supposed that the reduction of Fe₂O₃ or that of ZnO is rate-controlling stage.

The phases in the sample irradiated for 0, 5, 10 minutes were determined by X-ray diffraction analysis. The raw sample contained Fe₃O₄ and FeO₄. The sample irradiated for 5 minutes contained Fe₂O₃, Fe₃O₄, and Fe. Only Fe was detected from the sample irradiated for 10 minutes. Therefore, at first, reduction of Fe₂O₃ occurred, and then, atomic vaporization by reduction of ZnO occurred when the temperature of the sample reached enough temperature for the reduction of ZnO.

3.3 Apparent Reduction Rate

Fractional reduction curve of Sample 1 (mixture of ZnO and graphite) and Sample 2 (mixture of Fe₂O₃ and graphite) are shown in Figs. 6 and 7, respectively. The reduction of Sample 1 strongly depended on the temperature of the sample. On the contrary, the reduction of Sample 2 was relatively fast, and showed weak dependency on the reaction temperature.

3.2 Recovery of Zn from Synthetic Dusts

Figure 5 shows concentration change of Zn in the synthetic dusts listed in Table 2. The concentrations of Zn of the samples began to decrease in 5 minutes as well as the BFWD. Almost 100% of Zn was recovered by 20 minutes heating of microwave. Additionally, almost 100% of Pb was also recovered by 20 minutes heating of microwave. Therefore, it is supposed that steelmaking dust, which contain huge amount of Zn and Pb, can be reduced by microwave heating by adding enough amount of graphite, which works as reductant and heat generating source.

Fig. 6. Fractional reduction-time curves of sample 1.

Fig. 7. Fractional reduction-time curves of sample 2.
Reduction rate constants of each sample were calculated from the slope of the fractional reduction curves where the fractional reduction was 0.5. The reaction rate constants are shown in Table 4, and the Arrhenius plots of the rate constants are shown in Fig. 8. As can be seen from Table 4 and Fig. 8, rate constants of Fe₂O₃ were larger than that of ZnO. Therefore, the rate-controlling stage of this process was reduction of ZnO.

At 1000°C, the rate constant of Fe₂O₃ is about 8 times larger than that of ZnO. On the other hand, the rate constant of Fe₂O₃ at 1200°C is only about 3 times larger than that of ZnO at the same temperature. In this manner, as increasing the temperature, difference of the rate constants between Fe₂O₃ and ZnO becomes small.

In the first stage of this process, reduction of Fe₂O₃ proceeded prior to that of ZnO, because ZnO was stable below 900°C. When the temperature of the sample becomes above 900°C, reduction of ZnO and vaporization of Zn start. In the second stage of the process, when the temperature becomes more than 1200°C, the reduction rate of ZnO becomes large, and then almost 100% of Zn is recovered.

Table 4. Reaction rate constants and activation energies.

<table>
<thead>
<tr>
<th></th>
<th>1000°C</th>
<th>1100°C</th>
<th>1200°C</th>
<th>E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO-C</td>
<td>0.449</td>
<td>2.01</td>
<td>4.64</td>
<td>182.9</td>
</tr>
<tr>
<td>Fe₂O₃-C</td>
<td>3.53</td>
<td>10.32</td>
<td>14.17</td>
<td>109.4</td>
</tr>
</tbody>
</table>

Fig. 8. Arrhenius plots of rate constants of Fe₂O₃ and ZnO.

4. Conclusion

1) Almost 100% of Zn and Pb were recovered from BFWD and other synthetic dusts by microwave heating. It is considered that both metallic Zn and Pb can be recovered from steel making dusts by adding graphite as a reductant and a heating resource.

2) In the first stage of this process, reduction of Fe₂O₃ proceeded prior to that of ZnO. In the second stage, when the temperature of the sample was above 900°C, ZnO was reduced and Zn was vaporized.

REFERENCES


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