Article

Recovery of Zn and Fe from Steelmaking By-Products by Ar Plasma Smelting

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Abstract: Iron-containing by-products have high recycling value as an iron source due to the high content of Fe. However, some impurities in by-products limit their recycling. In particular, zinc in by-products are repeatedly vaporized and recrystallized inside a blast furnace, which deteriorates the operation. It is necessary to remove zinc from by-products by the zinc removal process such as RHF (rotary hearth furnace). However, due to the low removal ratio of zinc in RHF using coal as reducing agent, it is difficult to achieve carbon neutrality. This research investigated the removal of zinc and the recovery of zinc and iron from zinc-containing by-products by Ar plasma smelting. Two kinds of by-products used in this study contained 0.89 and 3.39 wt% of zinc oxide, respectively. One by-product (BP-A) resulted in a mixture of metallic iron and FeO remaining inside the crucible after Ar plasma smelting. The recovery ratio of iron in the product was evaluated as 94.2%, and the removal ratio of zinc was calculated to be 95.6%. The recovery ratio of zinc collected in the form of dust outside the crucible was calculated as 92.5%. The other by-product (BP-B), produced because of Ar plasma, was mostly FeO, and 82.6% of iron was recovered. In total, 96.4% of zinc from BP-B was removed, and 73.1% of zinc was recovered as dust. By the thermodynamic calculation in terms of FactSage 8.2, the temperature of the sample during plasma smelting was expected to be 2500 °C. The main gases generated during smelting were H₂, CO and CO₂ which were formed at the initial stage of the process.

Keywords: by-products; plasma smelting; zinc removal; zinc recovery; argon plasma

1. Introduction

Recycling by-products is of great importance as one of the recent issues in the steel industry [1]. Although some of the by-products have economical and environmental values as iron source, it is more or less difficult to directly use them in the sintering process and the blast furnace since most of them contain Zn [1,2]. In case such by-products are charged into the blast furnace, zinc is repeatedly vaporized and recrystallized on the refractory bricks, which gradually deteriorates the blast furnace operation [1–6]. Therefore, it is necessary to remove Zn from the by-products before recycling.

Zn can be recovered by two representative methods, hydrometallurgy and pyrometallurgy. Rodriguez et al. [4] investigated the leaching process of BOF (basic oxygen furnace) sludge where the highest leaching efficiency of zinc was evaluated to be 80% of BOF sludge for 3 h. A more common process to remove zinc from by-products is to employ RHF (rotary hearth furnace) in the steel industry [2,7–9]. In the RHF process, coal and its by-products are mixed in the form of pellets, and then heated. During the heating, the coal reduces the oxides of zinc and iron in the by-products to produce zinc oxide and DRI (direct reduced iron). However, it is difficult to achieve higher than a 90% zinc removal ratio, and the RHF process produces CO₂. Accordingly, it is necessary to alternatively develop a new process to achieve carbon neutrality.
The necessary conditions of the zinc removal process from by-products are high temperature and reducing atmosphere. Since the vaporization temperature of metallic zinc is about 900 °C, it is easy to separate zinc at high temperatures [2,3,9,10]. Therefore, thermal plasma might be used as one of the new technologies to remove zinc from by-products. Thermal plasma can reach a high temperature of over 3000 °C [11–15] and has a high reducing power because ejected gas is ionized [16–19].

Several studies [20–24] reported the recovery of valuable metals from by-products with plasma. Mohai et al. [20] reported the removal of zinc from the mixture of reagent-grade hematite, zinc oxide and some by-products. According to thermodynamic calculation, it is possible to remove zinc in gaseous form with plasma above 1000 °C. However, there are few reports on the recovery efficiency of zinc and iron from by-products, a change in the phase of produced zinc and iron and the formation of gas during the process. The current study investigated the removal and recovery of zinc from by-products employing the Ar plasma-smelting process. In addition, the recovery ratio of zinc and iron was evaluated by analyzing the chemical and phase compositions of recovered samples, and the gases that evolved during the process. This research might underline the new treatment technology that can achieve carbon neutrality while improving the removal of zinc in the steel industry.

2. Materials and Methods

2.1. Materials Preparation

The current study conducted plasma smelting experiments of by-products. Two zinc-containing by-products from the steelmaking process were used. Their chemical composition is shown in Table 1.

<table>
<thead>
<tr>
<th>By-Products</th>
<th>T.Fe</th>
<th>FeO</th>
<th>M.Fe</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP-A</td>
<td>73.70</td>
<td>25.90</td>
<td>45.50</td>
<td>11.54</td>
<td>9.11</td>
<td>1.69</td>
<td>0.50</td>
<td>0.89</td>
</tr>
<tr>
<td>BP-B</td>
<td>62.10</td>
<td>22.40</td>
<td>11.80</td>
<td>47.02</td>
<td>6.68</td>
<td>1.25</td>
<td>0.2</td>
<td>3.39</td>
</tr>
</tbody>
</table>

The first by-product (BP-A) has metallic Fe as the main phase and contains 0.89 wt% of zinc oxide. But the 2nd by-product (BP-B) has Fe₂O₃ as the main phase and contains 3.39 wt% of zinc oxide. The previous studies [1,2,4,6] have identified the phases of zinc existing in by-products to be zinc oxide (ZnO), zinc ferrite (ZnO·Fe₂O₃) and zinc silicate (2ZnO·SiO₂). BP-A and BP-B contained zinc in the form of zinc ferrite and zinc silicate, respectively, as shown in Figure 1.

![Figure 1. Phase composition of the two by-products identified by X-ray diffraction: (a) BP-A and (b) BP-B.](image-url)
2.2. Experimental Apparatus and Procedure

A laboratory-scale plasma reactor was employed for the Ar plasma smelting of by-products. Figure 2 shows the schematic diagram of the plasma reactor coupled with a gas analysis system.

Table 2. Chemical composition of Fe crucible (wt%).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe crucible</td>
<td>&lt;0.25</td>
<td>&lt;0.45</td>
<td>&lt;1.5</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

A tungsten tip was used as the cathode for the formation of plasma, and the Fe crucible and molten by-products were used as the anode. The experiments were completed when...
there was no change in gas composition through the QMS analysis. The samples obtained after the experiment were analyzed for the phase and composition of zinc and iron by X-ray diffraction (D8-Advance Davinci, Bruker, Billerica, MA, USA), ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy, SPECTRO (Kleve, Germany), ARCOS-III) and XRF (X-Ray Fluorescence) to evaluate the recovery ratio of zinc from by-products. The stable phases with changing temperature by thermodynamic calculations were estimated through Factsage in the current study. In the FactSage calculation, FactPS (pure substance database), FToxide (compounds and solutions) and gaseous ions (plasma) were used.

3. Results and Discussion

3.1. Removal and Recovery of Zn from By-Products

About half of BP-A is composed of metallic Fe along with some iron oxide. It contains 0.89 wt% of zinc oxide. After the Ar plasma-smelting process, iron oxide and metallic iron remained in the crucible, and some dust was generated around the reactor. After cooling, the iron oxide and metallic Fe in the crucible were separated and supplied for phase analysis by X-ray diffraction. Iron oxide was present on the top and surroundings of the metallic Fe, and the two parts were easily separated. Figure 3 identifies the phases of metallic iron, iron oxide and zinc-containing dust.

![Figure 3. Cont.](image-url)
Figure 3. Phase identification of three products: (a) Product 1, (b) Product 2 and (c) Dust 1.

Figure 3a shows the phase of metallic Fe obtained as residue after the Ar plasma smelting of the BP-A sample, which showed that the residue of BP-A was almost pure metallic Fe. Figure 3b showed that the oxide part was identified to be iron oxide after the BP-A argon smelting process where the main phase was wustite, and minor phases were $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ and metallic Fe. Table 3 shows the chemical composition of three products obtained from BP-A plasma smelting.

**Table 3. Chemical composition of three products obtained from BP-A.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw Material (90 g)</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>11.54</td>
</tr>
<tr>
<td>FeO</td>
<td>25.90</td>
</tr>
<tr>
<td>M.Fe</td>
<td>45.50</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.89</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.69</td>
</tr>
<tr>
<td>CaO</td>
<td>9.11</td>
</tr>
</tbody>
</table>

In the plasma-smelting process using 100 vol% of Ar, $\text{Fe}_2\text{O}_3$ was dissociated to FeO. Previous studies [25,26] also explained the reduction of $\text{Fe}_2\text{O}_3$ to $\text{Fe}_3\text{O}_4$ in an Ar plasma condition. This was explained by reduction at high temperatures and low oxygen partial pressures. As shown in Figure 4, the FactSage calculation predicts the change in phase of $\text{Fe}_2\text{O}_3$ in an inert atmosphere with increasing temperature from room temperature to 4000 °C.

The results show that $\text{Fe}_2\text{O}_3$ could be dissociated to $\text{Fe}_3\text{O}_4$ above 1500 °C, and then reduced to FeO above 2400 °C in an inert atmosphere. As mentioned in previous studies, the temperature of the plasma is higher than 4000 °C, so the temperature of the molten sample is expected to be higher than 2000 °C. Therefore, after the plasma-smelting process, $\text{Fe}_2\text{O}_3$ in BP-A was reduced to FeO, and remained on the metallic Fe. The dust formed inside the chamber was mostly composed of zinc oxide and wustite. After zinc oxide was decomposed at a high temperature, zinc was vaporized, and then recrystallized and reoxidized inside the reactor at relatively lower temperatures. The argon plasma-smelting process of BP-B also showed similar results where iron oxide remained in the crucible after the smelting process, causing two type of dusts to form inside the reactor. As shown in Figure 5, the phases of Product 3 remaining in the crucible were identified to be reduced
iron oxide (FeO and Fe) while Dust 2 and Dust 3 consisted of ZnO and iron oxide (FeO) with metallic Fe by X-ray diffraction.

![Graph](image)

**Figure 4.** Change in phase of 1 mol hematite in an inert atmosphere with increasing temperature.

In the case of BP-B, two kinds of dusts were obtained after the reaction: Dust 2 and Dust 3. Dust 2, which was a more yellow color, was easily removed from the wall of the reactor, while Dust 3, which was a more gray color, was strongly attached to the reactor. As shown in Figure 5b,c, identifying the phases by X-ray diffraction, Dust 2 was mostly composed of ZnO whereas Dust 3 was primarily comprised of iron oxide with a small amount of ZnO. Product 3 remained in the crucible after smelting and mostly consisted of wustite (FeO) along with a small amount of Fe. Unlike BP-A, about half of BP-B is composed of Fe₂O₃. However, the reduction of iron oxide to FeO was very similar. Table 4 shows the chemical composition of three products obtained from BP-B plasma smelting.
Figure 5. Cont.
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Table 4. Chemical composition of three products obtained from BP-B.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw Material (90 g)</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>47.02</td>
</tr>
<tr>
<td>FeO</td>
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<td>M.Fe</td>
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<tr>
<td>ZnO</td>
<td>3.39</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.25</td>
</tr>
<tr>
<td>CaO</td>
<td>6.68</td>
</tr>
</tbody>
</table>

As shown in Figure 4, FeO is the most stable phase of iron oxide above 2500 °C in an inert atmosphere according to FactSage calculation, and the experimental results are similar.

Although the phase and amount of Zn present in the two by-products were different, the zinc was experimentally removed in the form of dust with Ar plasma smelting in both samples. In the case of BP-A, the phase of zinc was identified to be zinc ferrite (ZnO·Fe₂O₃) by XRD analysis. As shown in Figure 6, the most stable phase of Zn is expected to be zinc ferrite with an increasing temperature of up to 1500 °C by the FactSage calculation.
At 1500 °C, zinc ferrite decomposes into zinc oxide and magnetite, which releases oxygen. Subsequently, zinc oxide converts to zinc vapor and oxygen gas while magnetite is decomposed to wustite and oxygen gas. Therefore, when the estimated temperature of the sample reaches 2500 °C during smelting, zinc ferrite is expected to decompose into zinc vapor, oxygen and wustite according to thermodynamic calculation, and a similar result was obtained in the Ar plasma-smelting experiment using BP-A sample. In BP-B, zinc silicate was the main phase of zinc.

The phase transformation of zinc silicate is expected with increasing temperature in an inert atmosphere as shown in Figure 7. At 2000 °C, zinc silicate decomposes to zinc vapor, oxygen and SiO₂. This is a similar result to the thermodynamic calculation of zinc ferrite, and it is expected that zinc oxide decomposes to zinc vapor and oxygen at 2000 °C, although it might even combine with some oxides. Based on these results, in case the smelting temperature of by-products is higher than 2000 °C, it is possible to remove zinc through vaporization and to recover Fe in the form of FeO.
3.2. Recovery Evaluation of Zn and Fe from By-Products

The current study aims to achieve the optimal condition for increasing the recovery ratio of Zn and Fe from by-products. The recovery ratio of Zn can be evaluated in the form of ZnO because both the phase of zinc in the by-products and dust is ZnO. However, regardless of the oxidation degree of iron, the recovery of Fe was evaluated in the form of Fe since total Fe is the important factor as an iron source as shown in Equations (1) and (2). As previously mentioned, BP-A resulted in metallic iron (Product 1), iron oxide (Product 2) and zinc-containing dust (Dust 1) by Ar plasma smelting. In the case of BP-B, iron oxide (Product 3) and two kinds of dusts containing Zn (Dust 2 and Dust 3) were obtained. In this study, iron was recovered in the form of residue inside the crucible, and zinc was recovered in the form of zinc-containing dust on the reactor:

\[
R_{\text{ZnO}}(\%) = \frac{\text{Total amount of ZnO in dust on reactor (g)}}{\text{Total amount of ZnO in by-products (g)}} \times 100
\]  

\[
R_{\text{Fe}}(\%) = \frac{\text{Total amount of Fe in residue on crucible (g)}}{\text{Total amount of Fe in by-products (g)}} \times 100
\]

The initial amount of iron and zinc oxide in 90 g of the BP-A sample used in the experiment is 66.33 g and 0.80 g, respectively, based on the chemical composition shown in Table 1. As mentioned before, Product 1 and Product 2 were obtained inside the crucible by Ar plasma smelting of BP-A. Product 1 and Product 2 were obtained at 33.81 g and 40.05 g after the experiment, respectively. The amount of Fe and ZnO in two residues was calculated by the weight of each residue and the mass percent of the total Fe and ZnO analyzed with titration and ICP-OES and XRF analysis, respectively. For the quantitative...
analysis of ZnO, Fe, CaO and SiO$_2$, XRF and ICP-OES analysis were performed. In addition, Dust 1 amounted to 2.07 g, and the dust contained 0.95 g of iron and 0.74 g of zinc oxide, respectively. From the BP-A, most of the zinc oxide was reduced and removed by vapor during Ar plasma smelting, and most of the zinc oxide was recovered as dust. Table 5 shows the recovery ratios of zinc oxide and iron from BP-A with Ar plasma smelting.

Table 5. Recovery ratio of zinc oxide and iron from BP-A.

<table>
<thead>
<tr>
<th></th>
<th>Zinc Oxide (g)</th>
<th>Iron (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before experiment</td>
<td>0.80</td>
<td>66.33</td>
</tr>
<tr>
<td>After experiment</td>
<td>0.74</td>
<td>62.47</td>
</tr>
<tr>
<td>Recovery ratio (%)</td>
<td>92.50</td>
<td>94.18</td>
</tr>
</tbody>
</table>

From BP-A used in the experiment, iron was recovered as residues in the crucible after the experiment, and about 94% was recovered. In the case of zinc oxide, the recovery ratio was 93 wt% of the dust found inside the reactor. And the removal ratio of zinc oxide from BP-A through plasma smelting is 96%. The removal ratio of zinc from by-products was calculated by comparing the initial amount of zinc (0.8 g) and that in residue is (0.035 g).

In the case of BP-B, Product 3, Dust 2 and Dust 3 were obtained after the smelting experiment. In total, 46.19 g of iron was recovered in the form of FeO and metallic Fe, and the recovery ratio of iron was evaluated to be 82.6% with respect to the initial amount (55.89 g) of iron in BP-B. The amount of Product 3 was 60.17 g and the content of zinc oxide in iron oxide was 0.182 wt%. The total amount of zinc oxide in Product 3 was evaluated to be 0.11 g. Through this calculation, the removal ratio of zinc from BP-B was evaluated to be 96%. For the evaluating recovery ratio of zinc oxide from BP-B, the content of zinc oxide in Dust 2 and Dust 3 was analyzed, respectively. A total of 2.07 and 0.16 g of zinc oxide was contained in Dust 2 and Dust 3, respectively. In 90 g of BP-B used, 2.23 g of zinc oxide was recovered as dust with respect to 3.05 g of initial zinc oxide, and the recovery ratio of zinc oxide was calculated to be 73%. Table 6 shows the recovery ratio of zinc and iron from BP-B.

Table 6. Recovery ratio of zinc oxide and iron obtained from plasma smelting of BP-B.

<table>
<thead>
<tr>
<th></th>
<th>Zinc Oxide (g)</th>
<th>Iron (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before experiment</td>
<td>3.05</td>
<td>55.89</td>
</tr>
<tr>
<td>After experiment</td>
<td>2.23</td>
<td>46.19</td>
</tr>
<tr>
<td>Recovery ratio (%)</td>
<td>73.11</td>
<td>82.64</td>
</tr>
</tbody>
</table>

Iron from by-products was obtained in the form of FeO regardless of the type of by-products. In this study, the smelting experiments were conducted in an inert atmosphere. The reduction of Fe$_2$O$_3$, Fe$_3$O$_4$ and ZnO in two by-products proceeded because of the low partial pressure of oxygen. Figure 8 shows the oxygen content in the output gas during smelting experiments.
Figure 8. Oxygen content in output gas during smelting experiments.

In both cases, the maximum content of oxygen gas was 0.1 vol% and the average oxygen content was 0.05 vol%. Since the experiments were conducted at atmospheric pressure, the volume percent of oxygen means the partial pressure of oxygen. Depending on the partial pressure of oxygen, the stable phase of iron oxide would be changed, and Figure 9 shows the change in the stable phase of iron with a different level of oxygen partial pressure and temperature.

Figure 9. Phase of iron oxide with changing partial pressure of oxygen and temperature.
Based on the FactSage calculation, the most stable phase of iron oxide is liquid FeO at 0.05–0.1 partial pressure of oxygen at experimental condition. For the further reduction of FeO to metallic Fe, it is necessary to form a reducing atmosphere by adding hydrogen gas as reducing agent or maintaining a lower oxygen partial pressure. Contrary to thermodynamic calculation results of iron oxide, the reduction of zinc oxide proceeded at a relatively higher oxygen partial pressure. Figure 10 shows the change in the zinc oxide phase with changing oxygen partial pressure and temperature. Based on the FactSage calculation, zinc oxide would easily be reduced to gaseous zinc than that of hematite to wustite. This indicates that it is not necessary to add hydrogen to induce a stronger reducing atmosphere for the removal of zinc oxide from iron-containing by-products.

![Figure 10. Phases of zinc with changing oxygen partial pressure and temperature.](image)

### 3.3. Evolution of Gases during Ar Plasma Smelting

In the present study, the gases generated during the smelting of by-products were analyzed through the QMS in situ gas analyzer. This is because the composition of the flue gas during the process is one of the important factors for the utilization and treatment of the flue gas. The analyzed gases included O₂, H₂, CO and CO₂ along with Ar as the main gas. Figure 11a,b show the formation of gases during the smelting of BP-A and BP-B, respectively.
Figure 11. Formation of gases during Ar plasma smelting of: (a) BP-A and (b) BP-B.

In both cases, a negligible amount of oxygen gas was formed, and \( \text{H}_2 \), CO and \( \text{CO}_2 \) were the main gases formed during smelting. Because carbon sources such as coal and coke were not added, it is necessary to find the source of carbon that formed CO and \( \text{CO}_2 \). Accordingly, the carbon content of two by-products was analyzed to be 0.53 and 0.52 wt% of carbon for BP-A and BP-B, respectively. In addition, it is believed that the oxygen forming \( \text{CO} \) and \( \text{CO}_2 \) originated from the reduction of \( \text{Fe}_2\text{O}_3 \) in the by-products to wustite. With reference to the 0.47 g of carbon contained in the 90 g of two by-products...
used in each experiment, about 0.79 g of carbon was calculated from 0.88 L of CO and 0.61 L of CO$_2$ formed during the experiment of BP-A. The slight difference might be within the uncertainty of gas analysis employing QMS since N$_2$ and CO have a similar amu (atomic mass unit) in the gas analyzer. However, in the case of BP-B, most of the carbon in the by-products was evolved in the form of CO and CO$_2$ where 0.54 L of CO and 0.81 L of CO$_2$ were formed during Ar plasma smelting. That is, more CO$_2$ was formed than CO in BP-B, which might have resulted from the difference in their composition. As mentioned before, BP-B contains a high amount of Fe$_2$O$_3$ which releases more oxygen by the reduction during smelting.

Hydrogen was commonly formed in both by-products as the main gas during the smelting process. This might have originated from the moisture contained in the by-products which decomposed at the high-temperature Ar plasma. Figure 12 shows the stable phases of water with increasing temperature which was estimated by FactSage.

![Equilibrium diagram of 1 mole H$_2$O at high temperatures.](image)

Figure 12. Equilibrium diagram of 1 mole H$_2$O at high temperatures.

At temperatures above 2000 °C, H$_2$O was decomposed to H$_2$, OH and O$_2$ based on this thermodynamic calculation. BP-A and BP-B contain 0.82 and 5.91 wt% of moisture, respectively. However, the amount of hydrogen formed during the smelting process was higher for BP-A of 0.87 L than BP-B of 0.64 L. BP-B is mostly composed of Fe$_2$O$_3$, which during smelting produced more oxygen reacting with more hydrogen. The gases generated during the smelting process can result from the interaction of iron oxide, carbon and moisture in by-products. The phase equilibrium of Fe$_2$O$_3$, carbon and H$_2$O at high temperatures can be estimated by FactSage as shown in Figure 13.
Figure 13. Equilibrium diagram of mixture of 2 mole of Fe$_2$O$_3$, 1 mole of H$_2$O and 1 mole of carbon from room temperature to 4000 °C.

With 2500 °C as the sample temperature, CO can be detected with minor gases of CO$_2$ and H$_2$ in case the mixture consists of 2 mole of Fe$_2$O$_3$, 1 mole of H$_2$O and 1 mole of carbon. The relative ratio of the three gases obtained by thermodynamic calculation might be different from the experimental results. Since the gases were evolved at the initial stage of the entire experimental time, the part of the sample reaching 2500 °C might be fairly localized. Figure 13 shows that more CO$_2$ is formed than CO at temperatures below 1000 °C. As the gases are formed in the beginning of the experiment, the sample temperature for forming gases is expected to widely vary from 100 to 2500 °C.

Through gas analysis, it is measured that the gas formed during the process of plasma smelting contains H$_2$ and CO, and it is expected that the value of recycling off-gas is high because it has high reducing potential. In this study, recovery of Zn and Fe, phases of products and gas composition of off-gas was analyzed, and Table 7 shows the summary of this research results.

Table 7. Summary of removal ratio of zinc, recovery ratios of zinc and iron and main phases of residues.

<table>
<thead>
<tr>
<th>Results</th>
<th>BP-A</th>
<th>BP-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal ratio of zinc (%)</td>
<td>95.63</td>
<td>96.41</td>
</tr>
<tr>
<td>Recovery ratio of zinc (%)</td>
<td>92.50</td>
<td>73.11</td>
</tr>
<tr>
<td>Recovery ratio of iron (%)</td>
<td>94.18</td>
<td>82.64</td>
</tr>
<tr>
<td>Phase of recovered zinc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase of residues</td>
<td>Metallic Fe and FeO</td>
<td>ZnO</td>
</tr>
<tr>
<td>Formation of gases</td>
<td>H$_2$, CO$_2$ and CO</td>
<td>FeO</td>
</tr>
</tbody>
</table>
4. Conclusions

The current study investigated the removal of zinc and the recovery of zinc and iron from by-products employing Ar plasma smelting. Since Ar plasma smelting does not use a carbon source such as coke and coal, there is the possibility of using this process as a by-product treatment process to achieve carbon neutrality. The gases generated during experiments were analyzed in terms of in situ monitoring of their change in composition. While zinc was formed as dust in the reactor, iron was recovered as residues in the crucible.

1. The first by-product, BP-A, contains metallic iron as the main phase along with 0.89 wt% of zinc oxide in the form of zinc ferrite (ZnO·Fe₂O₃). After Ar plasma smelting, the product obtained inside the crucible was identified to be metallic iron and FeO, where the removal ratio of zinc was evaluated to be 96% and recovery of iron was calculated to be 94%. The dust formed outside the crucible mainly consisted of zinc oxide and iron oxide where the recovery ratio of zinc was calculated to be 93%.

2. The second by-product, BP-B contains Fe₂O₃ as the main phase along with 3.39 wt% of zinc oxide in the form of zinc silicate (2ZnO·SiO₂). After the smelting process, the product obtained inside the crucible was mostly composed of FeO along with 0.18 wt% of zinc oxide where the removal ratio of zinc was evaluated to be 96%, and the recovery ratio of iron was calculated to be 83%. The dust formed outside the crucible was identified to contain 70 wt% of zinc oxide where the recovery ratio of zinc oxide was estimated to be 73%.

3. Ar plasma smelting successfully removed zinc oxide whose phase in two kinds of by-products are different. In the thermodynamic calculation by FactSage, it was expected that zinc oxide would be reduced to zinc vapor at temperatures above 2000 °C and that Fe₂O₃ be reduced to FeO from 2500 °C. In actual experiments employing Ar plasma, zinc oxide was removed from by-products in terms of reduction and vaporization. One product consisting of metallic iron and FeO was obtained inside the crucible. The reduction of ZnO and Fe₂O₃ proceeded with Ar plasma smelting around 2500 °C.

4. The main gases formed during Ar plasma smelting were H₂, CO and CO₂. Moisture and carbon in the by-products interactively reacted to produce H₂, CO and CO₂ by a high temperature of the plasma. The oxygen was originated from the reduction of Fe₂O₃ to FeO. Most of the gases were formed at the initial stage of experiments. Therefore, since the temperature of the sample did not reach equilibrium, the experimental results were different from those expected at a specific temperature by thermodynamic calculation.

Author Contributions: Writing—original draft, S.C.; writing—review & editing, L.T.D.R.; supervision, S.-M.J.; project administration, S.-W.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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