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A STUDY ON THE RECOVERY OF ZINC AND PIG IRON FROM BYPRODUCTS AFTER STEELMAKING DUST TREATMENT

In this study, a research was conducted to recover metallic zinc and pig iron and to improve the purity and the recovery rate through a reduction process for zinc and iron in the byproducts that are generated after steelmaking dust treatment. As the result of the calcination, it was confirmed that Cl (6.06%) and K (3.37%) decreased to Cl (2.75%) and K (0.22%), respectively. For the zinc powder that was recovered with reaction temperature of 1100°C, reaction time of 4 hours, and argon gas of 1L/min as the optimal conditions. The measurement for the purity of zinc was 99.8% and the recovery rate was 92.14%. The melt reduction for recovering pig iron from the residue was reacted under reaction temperature of 1600°C, flux composition ($CaO:SiO_2$) of 1:1, and reducing agent infusion ratio (residue: C) of 14:1, and the pig iron was measured to have a purity of 87.7% and a recovery rate of 91.81%.

Keywords: Steelmaking dust; Reduction; Recovery; Zinc; Pig Iron

1. Introduction

About 10 ~ 20 kg of dust is generated per ton of steel produced during the electric arc furnace steelmaking process [1]. Since the annual electric arc furnace crude steel production of Korea is about 20 million tons based on 2020, the amount of dust generated is estimated to be about 300,000 tons or more. Among them, the zinc content is about 25%, and about 100,000 tons of zinc is generated annually in the form of dust. This is called steelmaking dust, and steelmaking dust contains heavy metals like zinc, iron, lead, manganese, copper, cadmium, and anions like chlorine and fluorine. Zinc oxide is obtained from such dust by distilling zinc in a gaseous phase using a Rotary Reduction Kiln (Waelz kiln). This is called crude zinc oxide [2].

During the process of producing crude zinc oxide from steelmaking dust, zinc is volatilized and recovered from the filter, and residue remains inside the kiln. It contains the flux components that were added to prevent ring formation, zinc iron that have not volatilized yet, solid iron, etc. and they are recovered in clinker form. The process byproducts that are generated at this time are treated as waste without a separate treatment process and are used for landfill or as material for construction, cement material mixture, road pavement, etc. [3-7].

The process byproducts generated after the steelmaking dust treatment contain about 5 ~ 9wt.% of Zn and about 50 ~ 60wt.% of Fe, and they are mostly used for landfill due to lack of treatment technology and social interest. In addition to the landfill treatment cost, problems like surrounding soil contamination and water contamination due to landfills emerge and since they contain large amounts of iron and zinc, large amounts of economic losses occur because they are simply being buried without extracting valuable metals. Therefore, it is necessary to develop technology to recycle waste that are just being used for landfills.

In this study, research was conducted to selectively recover and produce zinc and iron from the byproducts that are generated after the steelmaking dust treatment. To do this, zinc was recovered first, and an experiment was carried out in accordance with conditions with the reaction temperature, the reducing agent, and the flux infusion amount to improve the purity and recovery rate of the pig iron

2. Experimental

The specimens used in this study were generated after the process of producing crude zinc oxide from steelmaking dust as the raw material. To analyze the phase and composition of

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the raw materials, analysis was performed by X-ray Diffraction (XRD) and X-ray Fluorescence (XRF), and the results are shown in Fig. 1(a). As the result of XRD analysis, it was found that Fe oxide and Fe-base mixed oxides were present in DRI (direct reduction iron), and as the result of XRF analysis, it was confirmed that the content of each element was 54.7% of Fe and 9.75% of Zn shown in TABLE 1.

The raw material contains impurity (Cl and K) components, which cause detrimental effect for the purity of the zinc and they must be reduced in prevision step. Therefore, to remove the impurities that are the low melting point materials in the raw material, a calcination was carried out at a temperature of 900°C, which is lower than the boiling point of zinc (907°C), for a reaction time of 1 ~ 3 hrs. Subsequently, to increase the purity and recovery rate of zinc, the experiment was conducted by varying each condition with the reaction temperature, the reaction time, and the argon gas injection amount. After calcination, 100 g of the reducing agent was mixed with 3 kg of the specimen and charged into a crucible. Then, they were reacted using a distillation furnace of electric furnace type under the following conditions: reaction temperature of 900~1100°C, reaction time of 2~5 hrs, and argon gas injection amount of 1~4 l/min. The zinc powder was collected at room temperature after reaction was done, and the recovered powder was subjected to analyze phase and chemical component using XRD and XRF shown in Fig. 1. The thermodynamic reaction of the zinc oxide with reducing agent is shown below. The values of Gibbs free energy are calculated by HSC Chemistry software.

$$ZnO_{(s)} + C_{(s)} \rightarrow Zn_{(s)} + CO_{(g)} \; \Delta G_{1000\sim1200°C} = = -1.424 \sim -10.656 \text{ kcal/mol} \quad (1)$$

$$2ZnO_{(s)} + C_{(s)} \rightarrow 2Zn_{(s)} + CO_{2(g)} \; \Delta G_{1200°C} = = -0.599 \text{ kcal/mol} \quad (2)$$

After the zinc recovery experiment, a melting reduction experiment was conducted to recover the pig iron from the residue, and slag composition was controlled by infusing flux to control the impurities in the residue. A 100 g of the residue was reacted with reducing agent using an induction furnace under the following conditions: reaction temperature of 1600°C, reaction time of 5 ~ 25 mins, reducing agent infusion ratio (residue: C) of 14:1, 7:1, 4:1, and flux composition (CaO:SiO_2) of 0.5:1, 1:1, 2:1. For the chemical composition of the recovered pig iron, analysis was implemented with XRF, and ICP analysis was carried out for the slag. The thermodynamic reduction reaction of the iron oxide in the residue is shown below. The values of Gibbs free energy are calculated by HSC Chemistry software.

$$Fe_2O_{3(s)} + 1.5C_{(s)} \rightarrow 2Fe_{(s)} + 1.5CO_{2(g)} \; \Delta G_{800\text{-}1600°C} = = -12.607 \sim -60.165 \text{ kcal/mol} \quad (3)$$

$$Fe_3O_{4(s)} + 4C_{(s)} \rightarrow 3Fe_{(s)} + 4CO_{(g)} \; \Delta G_{700°C\text{-}1600} = = -6.646 \sim -115.558 \text{ kcal/mol} \quad (4)$$

3. Results and discussion

TABLE 1 shows the results of an experiment in which impurities were removed and measured over time at 900°C. As a result of the experiment, it can be confirmed that Cl (6.06%) and K (3.37%) contained in the raw material decreased to Cl (2.75%) and K (0.22%), respectively. As a result of an XRF analysis on the specimen after the calcination experiment. Almost no change was shown in the component content of Cl and K over time.

Fig. 2 shows the results of the experiment for zinc recovery under the following conditions: reaction temperature, reaction time, and argon gas injection amount. The starting material of this experiment is used after calcination conducted at 900°C. The re-

TABLE 1

XRF component analysis results

	Fe	Zn	Cl	K	Na	Mg	Al	Si	P	S	Ca	Cr	Mn	Ni
DRI	54.7	9.75	**6.06**	**3.37**	2.02	1.58	1.44	3.56	0.204	2.25	6.29	0.876	5.74	0.09
Roasting	58.4	9.86	**2.75**	**0.22**	2.31	1.75	1.47	5.44	0.204	2.25	6.29	0.87	5.76	0.094
Zn powder		99.8				0.0856	0.033	0.032		0.009				
Residue	67.2	0.14		0.1	1.87	2.57	4.3	6.86	0.24	0.75	8.12	1.03	6.52	
Pig iron	87.7		0.087			0.219	0.174	11.3	0.03	0.074	0.13	0.064	0.059	0.077

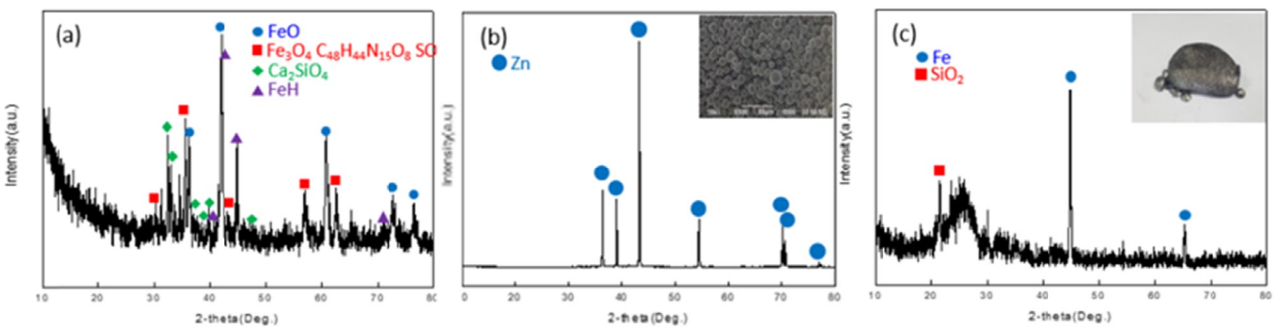

Fig. 1. 1 XRD Patterns of each specimen ((a)Steelmaking dust treated DRI raw material (b) Recovered zinc dust (c) Produced pig iron)

covery rate of zinc was calculated by considering the total amount of output by weight as a percentage of the amount by weight of input. At 900°C, the recovery rate of zinc was 56.21%, confirming that a significant amount of unreacted zinc oxide remained in the raw material. At 1000°C and 1100°C, the recovery rate of zinc was reached to 92.14% and 91.9%, respectively, showing almost no change in the recovery rate. Fig. 2(b) shows the results of the zinc recovery rate for each reaction time. At reaction time for 2 hrs and 3 hrs, the recovery rate of zinc was 51.0% and 68.0%, respectively. It is confirming that a significant amount of zinc oxide remained in the raw material. At 4 hrs and 5hrs, the recovery rate of zinc was 91.2% and 91.5%, respectively. It is showing no change in the recovery rate after 4 hrs. A Fig. 2(c) is the result of the zinc reduction distillation according to the argon gas infusion amount. At the condition of 1 l/min, 2 l/min, 3 l/min, and 4 l/min, the recovery rate was 90.9%, 89.9%, 91.1%, and 88.5%, respectively, showing almost no change in the recovery rate according to the gas infusion amount.

Fig. 3 shows the results of the melting reduction experiment under the following conditions: reaction time, flux composition, and reducing agent infusion amount. A Fig. 3(a) is a graph showing the change in the content of iron in the slag according to the reaction time. It was confirmed that the iron content in the slag decreased as the reaction time increased. The minimum holding time was set to 30 mins since almost no Fe in the slag was detected 30 mins after the melting reduction. Fig. 3(b) is graph showing the residual amount of Fe in the slag according to change in the ratio between the residue and the flux composition (CaO: SiO_2 = 0.5:1, 1:1, 2:1). When CaO: SiO_2 was 1:1, the content of iron was detected to be the highest at 69.5% and it was confirmed that the residual rate was the lowest at the iron content of 0.15% in the slag. Fig. 3 (c) is a graph showing the results of the smelting reduction experiment according to the reduction agent infusion ratio (residue: C = 1 4:1, 7:1, 4:1). At the ration of 14:1, the highest detection was confirmed with the iron content of 87.7% and the recovery rate of 91.81%.

4. Conclusions

In this study, distillation-reduction processes were conducted to selectively recover zinc and iron from the steelmaking dust treated DRI. After the calcination experiment, optimal conditions were derived for each reaction temperature, reaction time, and argon gas injection amount to recover zinc. Furthermore, optimal conditions were found for each reaction time, flux composition, and the reducing agent infusion amount to recover iron. After the experiment, the purity and recovery rate of zinc and iron were examined by XRD and XRF analysis. As the result of the experiment, the optimal process conditions to selectively recover zinc and iron were derived to be 1100°C, 4 hrs, and 1 l/min for zinc, and reaction temperature of 1600°C, flux composition (CaO:SiO_2) of 1:1 and reducing agent infusion ratio (residue:C) of 14:1 for iron. For zinc and iron, it was confirmed that the purity was found to be 99.8%, 87.7%, and the recovery rate was found to be 92.14%, 91.81%, respectively.

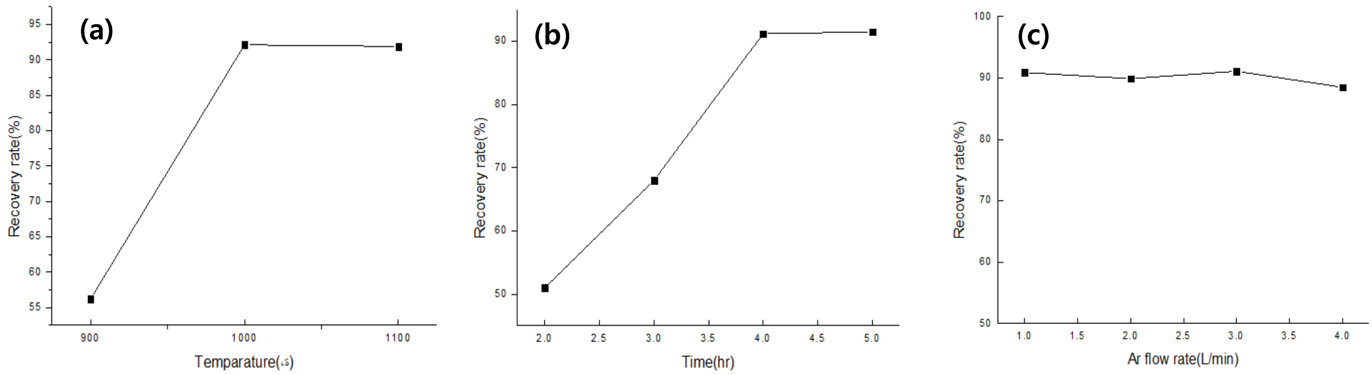

Fig. 2. Zinc recovery rate for each condition ((a) Recovery rate according to the temperature (b) Recovery rate according to the holding time (c) Recovery rate according to the Ar gas flow)

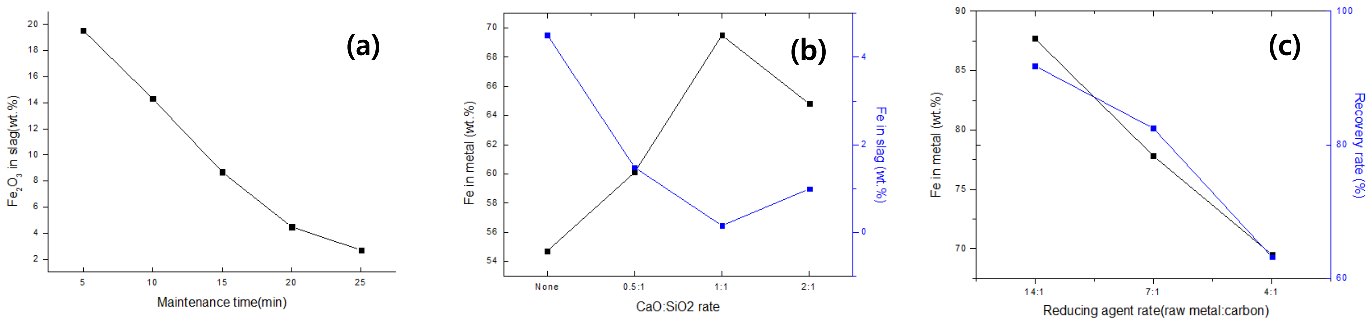

Fig. 3. Pig iron recovery process ((a) Iron oxide content in the slag according to the holding time (b) Fe content in the metal and the Fe content in the slag according to the additive ratio (c) Fe content in the metal and the Fe recovery rate according to the reducing agent addition rate

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