

Evaluation of Reduction of Electric Arc Furnace (EAF) Dust Using Volatile Matter of Non-Coking Coal

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Abstract

In this present research, the reduction of iron and zinc oxides of Electric Arc Furnace (EAF) dust using volatile matter of non-coking coal was investigated. Reduction was performed by two types of coals at three different heating rates in the temperature range of 25-950 °C. The weight percentages of volatile matters in types 1 and 2 of the coal were 37% and 24%, respectively. Factsage 6.1 software was used to determine thermodynamic feasibility of the reduction process. The chemical composition of the dust was determined by ICP method, before and after the reduction process. The results of thermodynamic simulations show that decreasing the heating rate of the coal from 18.4 to 13.5 °C /min leads to complete reduction of iron and zinc oxides in both types of coals. A higher amount of volatile matter in coal 1 has caused higher amounts of reduction degree. Experiments show that at high heating rates of the coal, only small fraction of iron and zinc oxides are reduced. At lower heating rates, reduction degree increases, and the results of experiments are closer to the those of thermodynamic simulations. The best results were obtained at a heating rate of 13.5 °C /min for coal 1. Under these conditions, reduction of iron and zinc oxides takes place by 75% and 89%, respectively. In addition, the weight percentage of iron in the dust has increased from 31% to 46% that provides the possibility of dust recharge into the furnace.

Keywords: Electric Arc Furnace Dust; Non-Coking Coal; Volatile Matter; Coal Heating Rate; Reduction.

1. Introduction

In recent decades, one of the growing problems due to the development of advanced technologies is the environmental problems of new processes and materials. Solving the problem is often uneconomical, therefore increases production costs, and ultimately

increases the price of the final product. One method to reduce the environmental hazards of toxic materials is to reuse them in production processes instead of releasing them into the environment ¹⁻².

Electric arc furnace dust (EAFD) is one of the by-products of the steel industry, which contains heavy metals as well as toxic and hazardous compounds ³. Therefore, the Environmental Protection Agency (EPA) classifies it as a hazardous waste ⁴⁻⁵. It is estimated that more than 12 million tons of EAFD will be produced annually in the world ⁶. The high cost of landfilling in accordance with environmental regulations, as well as the high levels of iron and zinc in the dust, have encouraged many steel industry researchers to EAFD recovery. Dust recovery mainly involves the reduction of iron and

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zinc oxides by a carbon reducing agent such as coal ⁴⁻⁵).

Coal, as a reducing agent, plays an important role in iron production processes in the world. Coking coal is used in blast furnaces and non-coking coal is used in coal-based iron production processes ⁷⁻⁸). The most important problem of coal is its environmental problems. These problems are caused by volatile matter of coal, which is a complex set of light and heavy hydrocarbon compounds, water, hydrogen, carbon dioxide, carbon monoxide, sulfur dioxide, and so on ⁹). These compounds are released during heating of coal from the ambient temperature to high temperatures (950 °C) and have a polluting role ⁹). Non-coking coals (containing 10-40% of volatiles) are considered as cheap coals. In most iron production methods, coal volatiles do not participate in the reduction process and are considered as non-useful and undesirable materials ¹⁰). Therefore, applying techniques that allow the use of non-coking coal as the main reductant decreases production costs as well as its environmental problems.

The aim of the work is to investigate the possibility of using volatile matter of coal as reducing agent for reduction of EAFD in non-isothermal conditions. Volatile matter was used for the reduction of iron and zinc oxide of the dust. Although limited researches have been done on the reduction of iron oxides by the coal volatiles, their use to reduce EAFD has never been reported ¹⁰). The main advantage of this idea is the production of iron and zinc from two very cheap materials. This reduces the cost of dust recovery and increases desirability of its recycling for manufacturers.

The use of non-coking coal not only reduces the cost of dust recovery, but also decreases the temperature of the recovery process. Industrial zinc recovery processes of dust are mainly performed in the temperature range of 1100-1300 °C, while in the proposed method, the reduction temperature is reduced to 950 °C. On the other hand, due to the non-consumption of fixed carbon of the coal, it is possible to reuse the remaining coal. Another important feature of this research is the performance of experiments in non-isothermal conditions with the help of natural materials. Non-isothermal experiments are closer to industrial processes and provide more useful information. The experiments were designed so that the heating rate and temperature of coal in the furnace were lower than the temperature and heating rate for dust. This causes the volatile materials, which are mainly released at temperatures below 700 °C, to react with the dust at higher temperatures, thus allowing separation of reduced zinc on the gas phase. The release of zinc in the gas phase allows it to be recovered with high purity. On the other hand, reduction of iron and zinc oxides of the dust compounds increases the weight percentage of iron in the remaining solid and make it possible to recycle solid residue to the furnace.

In this research, a new set-up was designed to investigate the effect of coal heating rate on reduction

degree of zinc and iron oxides. Two types of non-coking coal have been used to investigate the effect of the amount of volatile matter on the reduction efficiency of coal.

2. Materials and Methods

The EAF dust used in the experiments was collected from Esfarayen Steel Complex in Iran. Particle size distribution of the dust was determined by SHIMADZU-SALD-2101. The specific surface area (S_{BET}) of the dust particles was measured by nitrogen adsorption method. Inductively coupled plasma emission spectroscopy (ICP-ES-Spectro) was used to determine the chemical composition of the dust. The amount of chlorine was determined by gas chromatography. The X-ray pattern of the initial and final dust was also measured by XRD (Siemens D-500 – Cu ($K\alpha$)) in the range of 0-80 degrees.

Two types of non-coking coal with high volatiles were used as reducing agents. Approximate analysis of the coals was determined according to ASTM D 3172-07A method. The particle size of the coal powders was in the range of 180-300 microns. The gravimetric analysis was applied to measure weight loss of the coals as a function of temperature. Heating was done in an air atmosphere from ambient temperature to 950 °C with the rate of 21 °C/min.

Alumina powder was used as a separating layer between the dust and the coals. Alumina doesn't react with the coals and dust in the temperature range of heating process.

Cylindrical alumina crucibles with an inner diameter of 28 mm, a thickness of 2 mm and a height of 140 mm were used as reaction chamber. Fig. 1 shows the arrangement of materials in the crucibles. A layer of refractory blanket was wrapped around the bottom of the crucible to decrease heat transfer to the coal and thus reduce the coal heating rate. According to Fig. 1, by wrapping a refractory blanket in the lower part of the crucible, heat transfer in this area occurs at a lower speed, and therefore the coal temperature will reach the furnace temperature at longer time. Two thicknesses of 10 mm and 30 mm were selected for refractory blanket to create different coal heating rates. Steel wire was used to fasten the blanket around the crucible. Multilayer arrangement of materials was used to prepare the samples. First, a weighed amount of alumina powder was poured to a certain height on the crucible floor. This alumina was compressed to decrease heat transfer from the bottom of the crucible to the coal. The coal powder was then weighed and slowly poured onto the alumina layer. The secondary layer of alumina was slowly poured on the coal layer. EAF dust powder was the final layer that was weighed and poured on the alumina layer. The process of pouring the powders into the crucible was done in such a way that the created surfaces were completely smooth and horizontal. The weight ratio of the coal to the dust was considered 1:1. The amount of alumina was determined based on the predetermined thickness (approximately 20 mm).

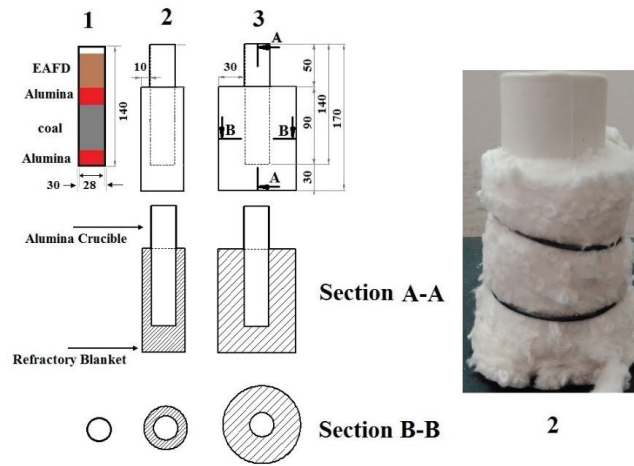


Fig. 1. Schematic representation of materials configuration in different samples.

After preparation and weighing, the samples were heated in an electric muffle furnace at 21 °C/min from ambient temperature to 950 °C. Fig. 2 shows a schematic of the heat treatment equipment. Argon was blown 15 minutes before heating and during heating into the furnace at a rate of 5 liters per minute to create a neutral atmosphere inside the furnace to prevent re-oxidation of the dust. Due to the heating, volatile matter of the coal is gradually removed and by passing through the dust layer, the iron and zinc oxides in the dust reduces. Other dust oxides such as calcium, aluminum and magnesium oxides are not reduced due to their high stability. To measure the heating rate of dust and coal layers, two k-type wire thermocouples were placed in the middle of each layer in the crucible. After reaching the coal temperature to the furnace temperature at 950 °C, the furnace was turned off and the sample was taken out. After cooling, each layer of the coal and the dust was carefully separated and weighed. Sampling was performed from solid residue of the dust to evaluate the amount of total iron, metallic iron and zinc. Metallic iron and total iron were measured by titration using 0.25 N

dichromate solution, and atomic absorption spectrometer was used to measure zinc.

As shown in Fig. 1, for each type of the coals, three samples were prepared and subjected to the reduction process. Comparison of the results of these three samples for each coal will show the effect of coal heating rate on the reduction capability of coal volatiles. Coal 1 is used in samples 1, 2 and 3 and coal 2 is used in samples 4, 5 and 6. Comparing the results of samples with different coal types determines the effect of coal composition on its reduction capability.

FactSage 6.1 software was used to study thermodynamic aspects of the reduction process. Thermodynamic studies make it possible to predict the maximum amount of reduction that can be performed during experiments. 'EQUILIB' package of the software receives composition and weight of initial materials as well as system temperature and pressure and determines the amount of each phase in the final equilibrium. The software calculations are based on minimizing the Gibbs free energy of the system at constant temperature and pressure.

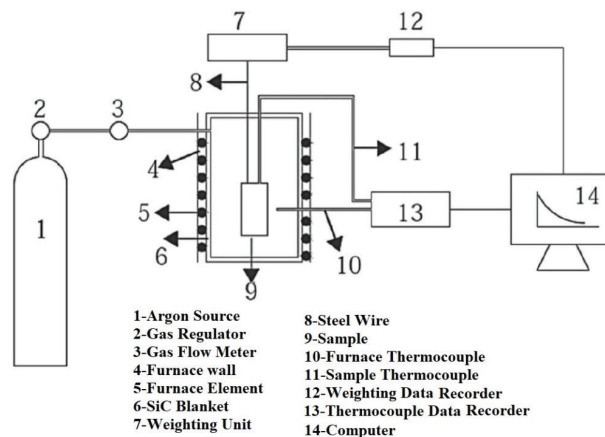


Fig. 2. Developed set up used in the reduction process.

In order to thermodynamically simulate the reduction process, 100 g of EAF dust with the composition mentioned in Table 1, was entered to ‘EQUILIB’. Considering the fact that the release of coal volatiles occurs at temperatures above 200 °C, the simulation was performed in the temperature range of 200-950°C in 16 steps (50 °C intervals). By knowing the coal temperature at any time, the weight loss of the coal can be measured from the TG diagram of the coal. This weight loss is entirely due to the release of volatiles from the coal. Therefore, it is possible to determine the weight of volatile matter released from the coals in each 50 °C intervals. The amount of carbon and hydrogen of the volatiles was then calculated and entered the software as reductants. It is assumed that all hydrogen and carbon of volatiles have reduction capability. It is also assumed that the percentage of carbon and hydrogen of the volatiles was constant over the entire computational temperature range. All calculations were performed at an atmospheric pressure assuming the gases were ideal. After determining the equilibrium state by the software, the weight percentage of each compound in solid and gas phases was obtained. The chemical composition of the residual dust at each temperature was considered as input data for the next temperature. In this way, the non-isothermal heating process of the samples in the furnace was simulated by isothermal processes in small temperature ranges (50 °C). The mentioned process was continued up to 950 °C and at each temperature, the

reduction degree of iron and zinc was calculated based on the following equations:

$$RD(Fe) = \left(1 - \frac{WO_r}{WO_i}\right) * 100 \quad \text{Eq. (1)}$$

$$RD(Zn) = \frac{WZn_g}{WZn_i} * 100 \quad \text{Eq. (2)}$$

Where WO_i and WO_r are the weight of oxygen in iron oxides before and after reduction at each temperature, respectively. WZn_g is the weight of zinc in the gas phase after reduction and WZn_i is the weight of zinc in the initial dust. The reduction degree of zinc is calculated based on the amount of zinc introduced into the gas phase. The part of reduced zinc which cannot enter the gas phase, cannot practically be recovered. Therefore, the degree of zinc reduction indicates the amount of zinc recovery in the gas phase.

3. Results and Discussion

3.1. Materials Characterization

Table 1 shows the chemical composition of the initial dust. As can be seen, zinc forms about 20 weight percent of the dust. According to the literature, zinc recovery from EAF dust is economically viable when zinc forms more than 15% by weight of the dust¹¹). Also, more than 30 weight percent of the dust is iron. As shown in the X-ray diffraction pattern of the initial dust in Fig. 3, iron is mainly in the form of hematite and magnetite.

Table 1. Elemental and mineralogical composition of the initial EAF dust.

Chemical composition of the EAF dust determined by ICP method												
Element	Fe	Zn	Cl	Mg	Ca	Na	K	Pb	Al	Cr	Si	O
Weight Percent	31.2	19.8	7.1	5.1	4.5	3	2.8	1	0.52	0.35	0.23	Balanced
Chemical composition of the EAF dust used in calculations in FactSage software												
Species	Fe ₂ O ₃	ZnO	MgO	NaCl	CaO	KCl	PbO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂		
Weight Percent	44.6	24.7	8.5	7.6	6.3	5.3	1.1	0.9	0.5	0.5		

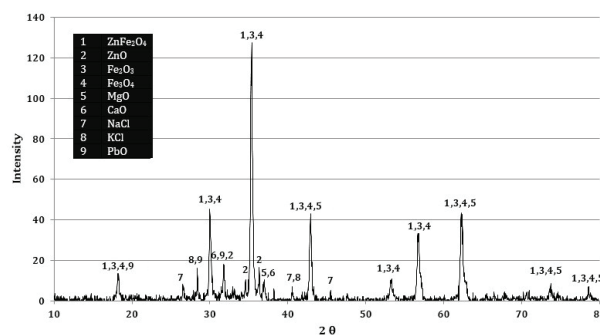


Fig. 3. XRD graph of the initial EAF dust.

Part of iron and zinc form a stable compound called zinc ferrite ($ZnO \cdot Fe_2O_3$), which does not decompose or dissolve easily. Determination of the amount of divalent and trivalent iron oxides occurs through the dissolution of the dust in strong acids. These acids are not able to completely dissolve zinc ferrite, and therefore part of the zinc and iron remain insoluble in the acids. Therefore, it is practically impossible to measure the exact weight percentage of zinc ferrite, hematite and magnetite in the dust. Comparing the results of the chemical analysis in different ways shows that the main part of iron is crystallized in the form of hematite.

In thermodynamic calculations, it is necessary to determine the initial composition of the dust as a mineral. It is assumed that in the dust, iron exists only in the form of Fe_2O_3 and zinc exists only in the form of ZnO . The mineral form of the other elements is based on what is seen in XRD pattern of the dust. Table 1 reports mineral composition of the initial dust used in thermodynamic calculations in FactSage software.

Particle size distribution of the initial dust is reported in Fig. 4. Type of particle size distribution is binormal which indicates there are two groups of particles with different dimensions in the dust. High temperature

of the dust particles when leaving the furnace causes partial surface melting and limited physical bonding at the interface of some particles, resulting in large agglomerate particles. This type of distribution has also been reported by other researchers¹²⁻¹³. The obtained peaks are related to particle diameter of 0.2 and 5 microns, respectively and the average particle size is 1.8 microns. Also, 98% of the particles are smaller than 20 microns. The specific surface area was measured for EAF dust being $0.7 \text{ m}^2/\text{g}$. The reported dimensions indicate that the dust is micronized. Because the reduction reactions are heterogeneous, reducing the particle size increases the external surface area of the particles where the reactions take place. This in turn leads to an increase in the kinetics of the reduction processes.

Chemical composition of the used coals is reported in Table 2. Volatile matter of coals 1 and 2 is 37.4% and 24.1%, respectively. The difference between fixed carbon and total carbon determines the amount of carbon in volatile matter. According to the results, 68% of the volatiles of coal 1 is carbon and 11% is hydrogen. The weight percentages of carbon and hydrogen in volatiles of coal 2 are 62% and 18%, respectively.

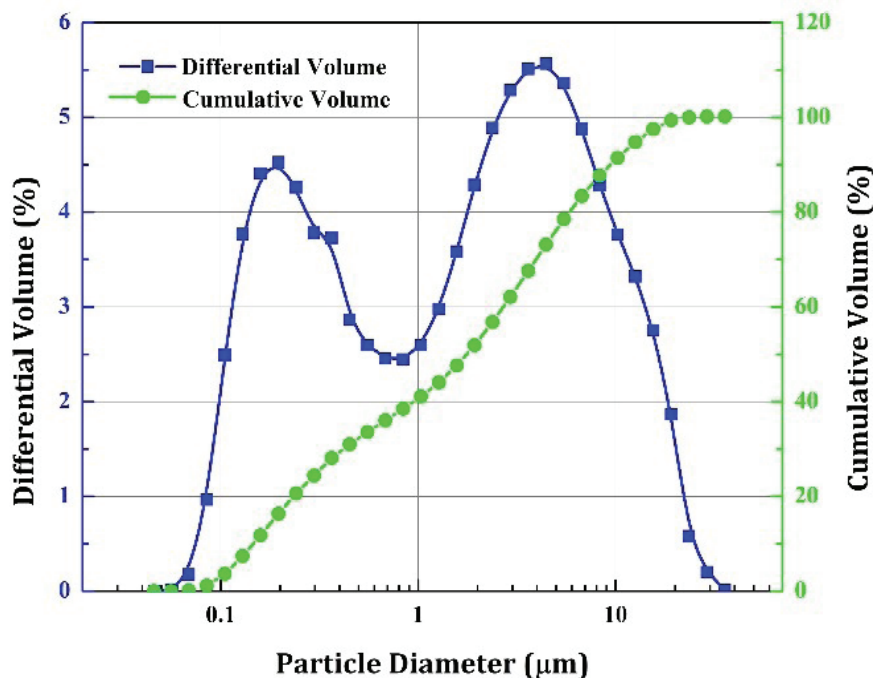


Fig. 4. Particle size distribution of the initial EAF dust.

Table 2. Chemical composition of the coals used in the experiments.

Constituents	Total Carbon	Fixed Carbon	Volatile matter	Ash	Sulfur	Moisture
Coal 1 (wt%)	73.1	49.1	37.4	13	1.8	0.5
Coal 2 (wt%)	78.4	66.3	24.1	4.8	0.7	4.9

Weight loss of the coals as a function of temperature is shown in Fig. 5. This diagram can be classified into 4 separate areas based on the rate of volatile emission. The slope of the graph in the first region is low and about 3% weight loss of the coals has occurred in this region. The length of the first zone is shorter for coal 1 and continues up to a temperature of 400 °C. The length of this zone for coal 2 continues up to 470 °C. The highest rate of volatile emission for both coals occurs in zone 2. The weight loss in this area for coals 1 and 2 is 17% and 7%, respectively. For both coal types, this region continues up to 530 °C.

As the temperature of the coals increases, the emission velocity of the volatiles decreases. Zone 3 occurs for both coals in the temperature range of 530 to 680 °C. In this region, weight loss of the coals 1 and 2 are 9% and 8%, respectively. As the temperature rises above 680 °C, the remaining volatiles leave the coal at a slower rate. Zone 4 is in the temperature range of 680 to 950 °C. The emission rate of volatiles in this area is almost equal to zone 1. For both types of the coals, about 6% weight loss occurs in this area. Due to the high temperature of the coals in zones 3 and 4, the released

hydrocarbons are broken down into lighter ones and the dark color of the released gas gradually becomes transparent. According to Fig. 5, the amount of volatiles released from coal 1 is 35% by weight, which is 2% less than the amount reported in Table 2. It should be noted that the amount of volatiles is not recognized as an intrinsic property of the coal and changes under the influence of various factors such as heating rate, final temperature, pressure, particle size and type of coal¹⁴⁻¹⁵.

3.2. Reduction

3.2.1. Effect of Coal Heating Rate

The average heating rate of furnace, dust and coal in different samples is reported in Table 3. Temperature vs time curves, which are recorded with the help of suspended thermocouples in dust and coal, is shown in Fig. 6. Since the heating of all samples was done in a furnace with similar thermal program, the heating rate of the furnace was the same for all samples. This rate was 21 °C /min. In addition, dust heating rate was measured 18.4 °C /min for all samples.

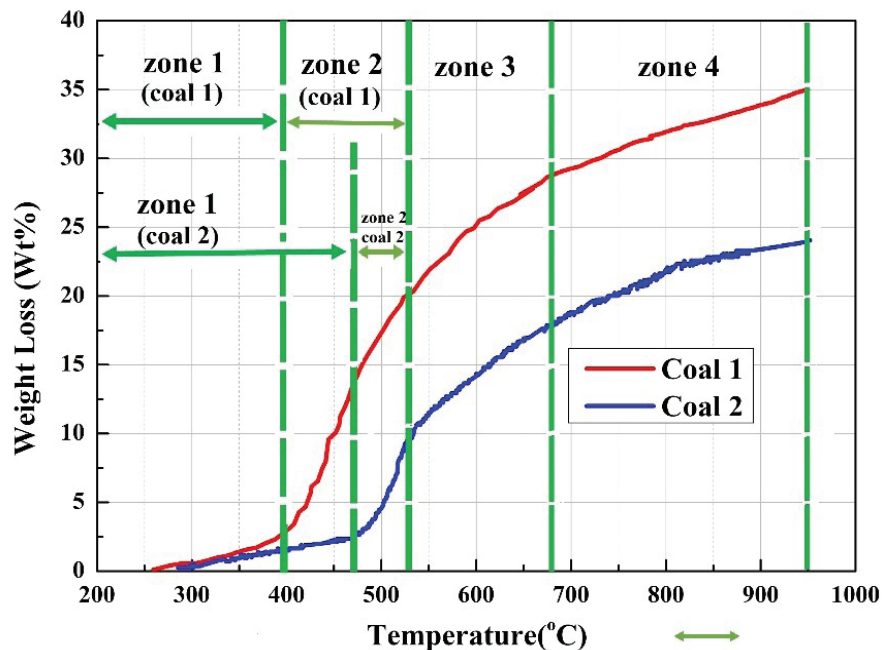


Fig. 5. Weight loss of the coals as a function of temperature.

Table 3. Heating rate of furnace, dust and coal in different samples.

Sample number	Blanket Thickness (mm)	Coal Type	Heat Rate (°C/min)		
			Furnace	Dust	Coal
1	0	1	21	18.4	18.4
2	10	1	21	18.4	16.3
3	30	1	21	18.4	13.5
4	0	2	21	18.4	18.4
5	10	2	21	18.4	16.3
6	30	2	21	18.4	13.5

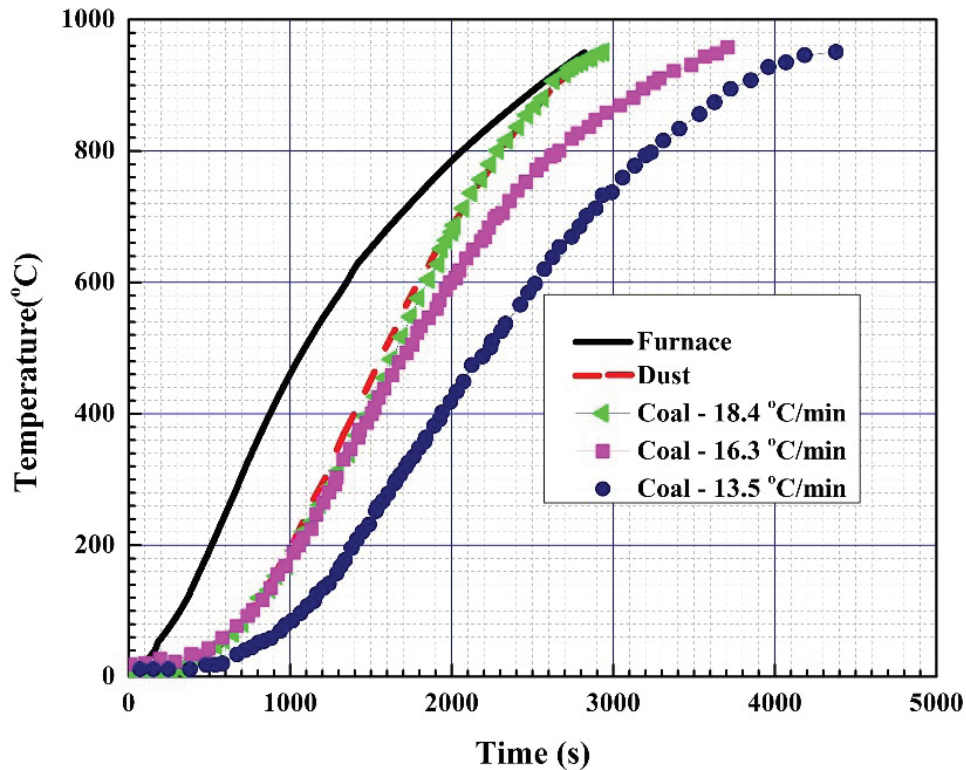
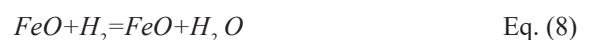
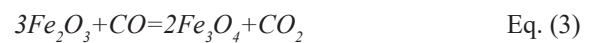


Fig. 6. Temperature vs. time curves for furnace, dust and coal in different samples.

Results indicate that the heating rate of the coal decreases by increasing the thickness of the refractory blanket wrapped around the lower region of the crucibles. The heating rate of coal in samples 3 and 6, which have the highest thickness of the refractory blanket, is the lowest and equal to 13.5 °C /min. In these samples, the dust was heated by an average of 5 °C /min more than the coal. For example, after 40 minutes, a temperature difference of 200 °C is obtained between the dust and the coal. According to Table 3, the heating rate recorded for samples 2 and 5 was equal to 16.3 °C /min and for samples 1 and 4 was equal to 18.4 °C /min.

Fig. 7 shows the weight changes of iron and zinc oxides as a function of temperature in samples 1-3 in which coal 1 was reduction agent. The degree of the reduction of iron and zinc is also plotted in this figure. Data were completely derived from thermodynamic calculations performed by FactSage software. Fig. 7 (a) is related to sample 1, which had the highest heating rate of the coal among all samples. As the reduction process begins, the weight of hematite is decreased, and the weight of magnetite is increased. These weight changes occurred based on Equations (3) and (4). The reduction reaction of hematite to magnetite has less Gibbs free energy compared to the reduction reactions of hematite to wustite and hematite to pure iron. Therefore, all hematite must first be reduced to magnetite to continue the process of reducing iron oxides. As heating continues, magnetite reduces to wustite and pure iron,

simultaneously. The reduction of the magnetite to pure iron at temperatures below 520 °C has less Gibbs free energy than the reduction of the magnetite to wustite (Equations (5) and (6)). Therefore, some portion of the magnetite is first reduced to pure iron (about 3 grams). Therefore, most of the magnetite is converted to wustite by reduction at higher temperatures. This sequence in the reduction of iron oxides has reported by other researchers¹⁶⁻¹⁷. The magnetite reduction is completed by reaching temperature to 600 °C where the amount of wustite reaches its maximum value. With a further increase in the temperature, the reduction of wustite to pure iron proceeds according to Equations (7) and (8) and is completed at 800 °C. At this temperature, all portion of the iron of the dust is in the form of metallic iron. Therefore, the degree of iron reduction reaches 100%.



Since the reduction of iron oxides has continued during the dust heating process, the degree of iron reduction has increased during heating. As more volatiles are removed from the coal at higher temperatures, more CO and H₂ are available for reduction reactions. Moreover, reduction reactions are mainly endothermic and therefore progress more at higher temperatures.

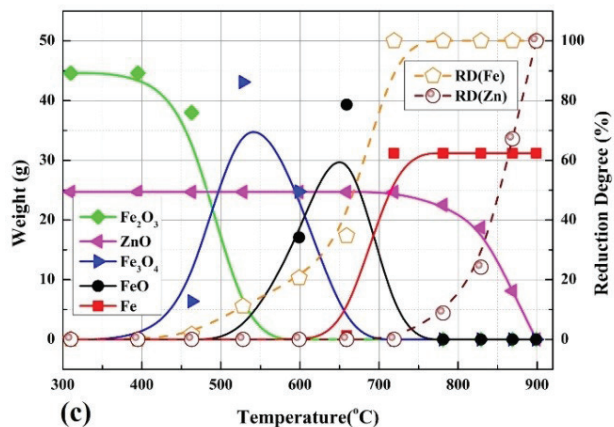
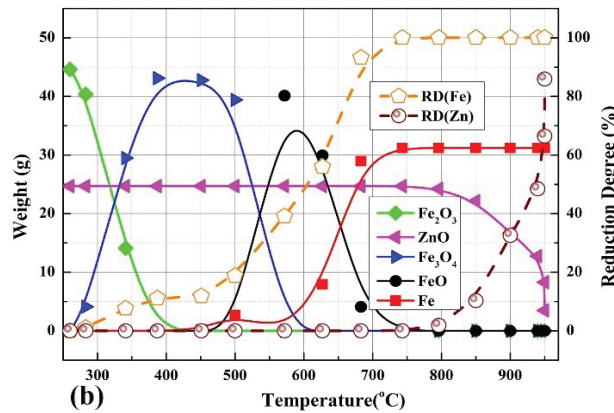
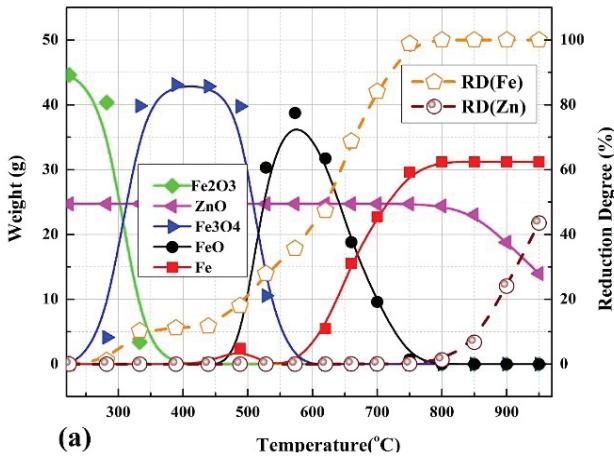


Fig. 7. Weight changes and the reduction degree of iron and zinc oxides in a) sample 1, b) sample 2 and c) sample 3.

The reduction of zinc oxide by volatile matter of the coal is performed based on equations (9) and (10). Gibbs free energy of these reactions in the same ratio of CO / CO₂ or H₂ / H₂O is more than that of the reduction reactions of iron oxides. Therefore, from a thermodynamic point of view, the reduction of zinc oxide occurs after the reduction of iron oxides. Due to the high vapor pressure of zinc, at temperatures above 800 °C, recovery of zinc in the gas phase begins. Zinc is produced based on reactions (9) and (10) and evaporated and enters the gas phase at higher temperatures. The higher the temperature, the higher the vapor pressure of the zinc and the higher the amount of zinc entering the gas phase. The normal boiling point of zinc is 907 °C. At temperatures above 907 °C, all portion of the reduced zinc enters the vapor phase.



As can be seen in Fig. 7 (a), despite complete reduction of iron oxides, the reduction of zinc oxide at the end of the heating operation is only 44%. Thermodynamic simulations indicate that the amount of volatile matter of coal 1 is sufficient to complete reduction of the zinc oxide in the dust. However, since the main part of the coal volatiles releases at temperatures below 800 °C, they cannot be able to recover zinc in the gas phase.

Fig. 7 (b) and 7 (c) show the weight loss curves of the oxides and the degree of reduction for iron and zinc in samples 2 and 3, respectively. Based on these figures, as the coal heating rate decreases, the reduction degree of zinc oxide increases. The reduction degree of zinc oxide was increased from 44% in sample 1 to 86% in sample 2 and 100% in sample 3. The weight change curves for iron oxides have also shifted to higher temperatures. Both of these events are due to the greater temperature difference that occurs in these samples between the dust and the coal. During heat treatment of samples, at a certain temperature of the coal, the dust in sample 1 was at a lower temperature than that in samples 2 and 3. For example, in sample 1, when the coal was at 500 °C, the dust experienced a temperature of 528 °C. However, in sample 2, when the coal was at 500 °C, the dust temperature reached 572 °C, and in sample 3, the dust experienced a temperature of 783 °C. Table 4 reports the corresponding dust temperatures in different samples in terms of coal temperature. The higher temperature of the dust in sample 3 causes the reduction reactions to occur at higher temperatures and therefore more degree of iron and zinc reduction will be achieved. The reduction of zinc oxide at higher temperatures causes the

production of gaseous zinc and increases zinc reduction degree.

Table 4. Corresponding temperature of the dust and the coal in different samples.

Coal Temperature (°C)	Corresponding Temperature of the Dust (°C)		
	Samples 1 and 4	Samples 2 and 5	Samples 3 and 6
200	224	229	395
250	282	283	463
300	333	341	528
350	389	387	599
400	439	451	659
450	488	500	719
500	528	572	781
550	573	627	829
600	620	683	869
650	660	743	899
700	700	796	950
750	750	850	950
800	800	900	950
850	850	940	950
900	900	950	950
950	950	950	950

3.2.2. Effect of Coal Type

According to Table 3, coal 2 is used in samples 4-6 as a reduction agent. This coal has less volatiles than coal 1. Heat treatment was performed on samples 4-6, similar to samples 1-3. The heating rate of the furnace, dust and coal for these samples was obtained like that reported in Fig. 6 for samples 1-3. Therefore, in the thermodynamic simulation, the corresponding coal and dust temperatures were considered similar to those reported in Table 4. The results obtained from the thermodynamic calculations of FactSage are reported in Fig. 8.

Fig. 8 (a) shows the weight changes of iron and zinc oxides for sample 4. In this sample, the reduction of iron oxides has been completed and all portion of hematite has been converted to metallic iron. In this sample, reducing the amount of coal volatiles decreased reduction of zinc oxide compared to sample 1. The highest degree of zinc reduction in sample 4 reached 32%, which is 12% less than the value obtained for sample 1.

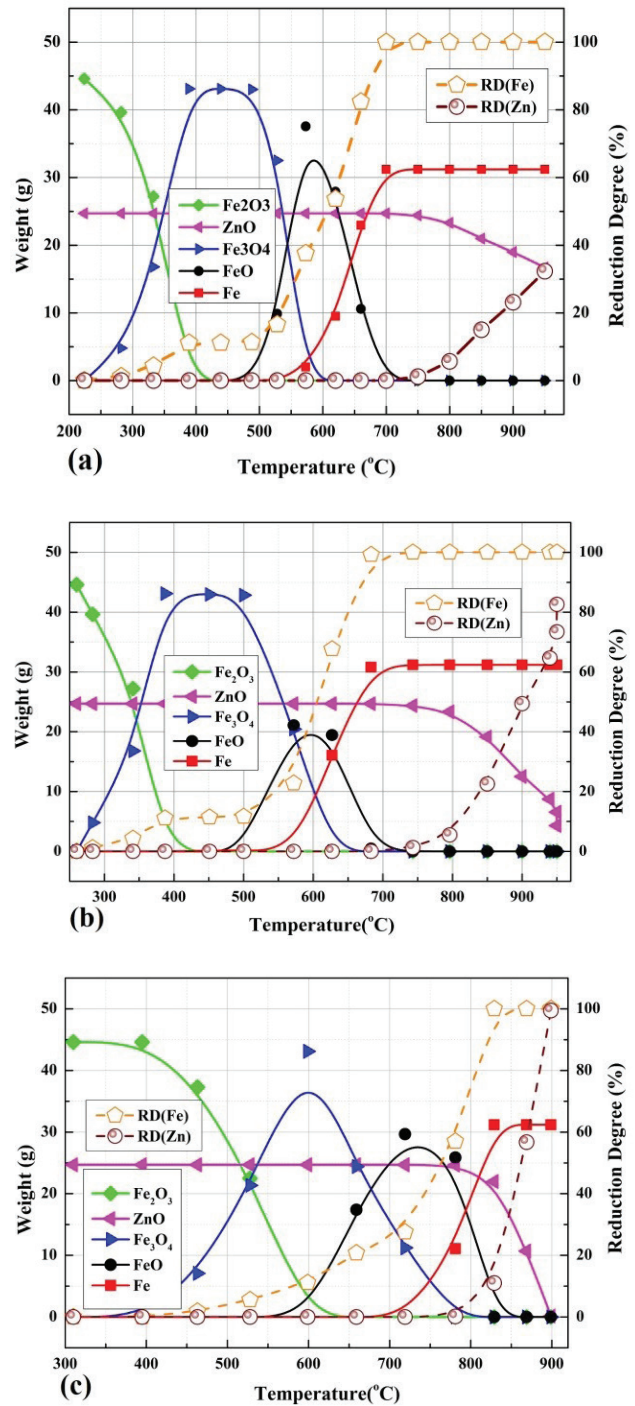


Fig. 8. Weight changes and the reduction degree of iron and zinc oxides in a) sample 4, b) sample 5 and c) sample 6.

The weight changes of iron and zinc oxides as well as the degree of reduction for sample 5 are shown in Fig. 8 (b). General trend of the curves is similar to sample 4. The degree of zinc reduction has significantly increased from 32% to 83%. Also, the height of the wustite curve is significantly reduced. The maximum amount of wustite in sample 4 reaches 38 grams during heat treatment,

while for sample 5, this amount is 21 grams. It seems that the maximum amount of wustite (equal to 41 grams) occurs in the temperature range of 625-572 °C which is not visible in the figure. Because the thermodynamic simulations were performed in temperature ranges of 50 °C, the exact temperature at which the maximum value of the wustite occurred was not observable. Results also indicate that, during the magnetite reduction process, no pure iron was produced in samples 4 and 5. This means that production of metallic iron starts after the complete reduction of magnetite to wustite.

According to Fig. 8 (c), the weight curves of iron oxides shift to higher temperatures for sample 6. In sample 4, the magnetite was completely reduced below 600 °C. However, the reduction of magnetite for samples 5 and 6 were completed at 650 and 800 °C, respectively. Similar trends are observed for the weight curves of hematite, wustite and metallic iron. As mentioned earlier, moving the curves to the right is due to the fact that in samples with lower coal heating rate, the gases emitted from the coal, met the dust at higher temperatures. Therefore, the reactions are transferred to higher temperatures. A significant proportion of the volatile matter of the coal in samples 3 and 6 met the dust at temperatures above 800 °C. High vapor pressure of zinc at this temperature causes a large part of the produced zinc to enter the vapor phase and increase the zinc reduction degree (according to Equation (2)). Complete recovery of zinc in the gas phase happened for samples 3 and 6, which had the lowest heating rates.

3.3. Verification of Thermodynamic Simulations

In order to verify the accuracy of the results of thermodynamic simulations, the chemical composition of the residual dust in different samples at the end of heating has been analyzed. Chemical analysis shows that in all samples the iron in the residual dust is in the form of metallic iron and FeO. This means that the reduction of hematite to magnetite and magnetite to wustite is completely done. Reduction degree of iron and zinc for each sample is determined based on Equations (1) and (2). Fig. 9 shows reduction degree of iron and the percentage of iron in the residual dust. Thermodynamic calculations show that a 100% reduction degree for iron is obtained in all samples. However, according to the experiments (Fig. 9), 75% of reduction has occurred in the best conditions (in sample 3). The results of the experiments also indicate that iron reduction degree in sample 1, in which the heating rate of coal and dust was approximately equal, is 47%. Furthermore, the ratio of metallic iron to total iron in sample 1 was measured 6.8%. Similar results have been reported by Hemmati et al.¹⁰. They investigated the effect of volatile matter of non-coking coal on the reduction of Fe₂O₃. They reported a reduction degree of 45% and a ratio of metallic iron to total iron of 6.5%. The type and size of the used coal and the heating rate of the furnace were the same in both studies, while the weight ratio of coal to hematite in their study was 3:4.

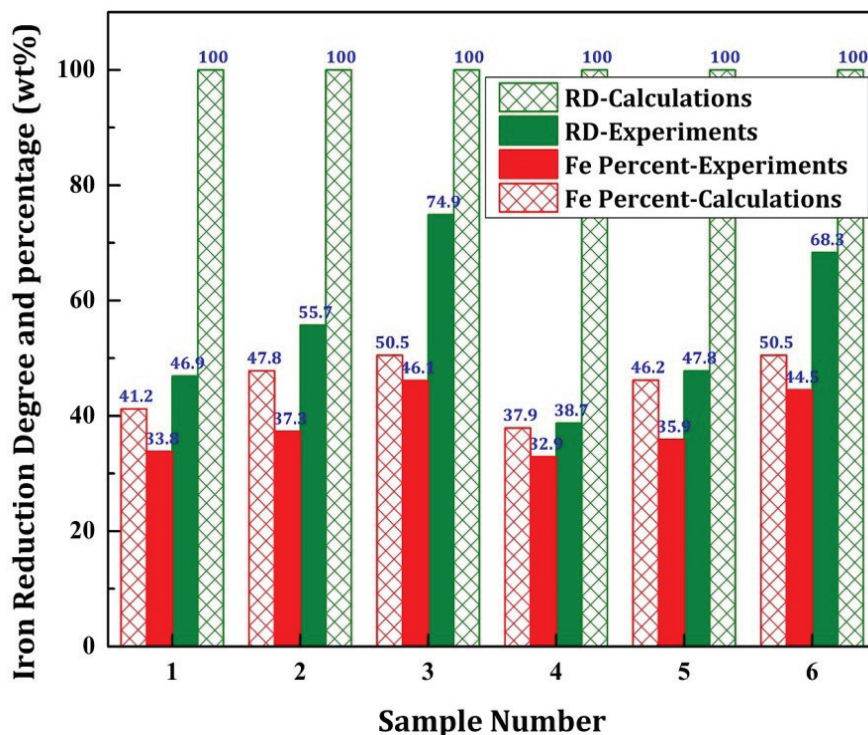


Fig. 9. Comparison of the results of the experiments and thermodynamic simulations for iron.

When the heating rate of the coals decreases, the experimental results become closer to the simulation results. For example, in the experiments, reduction degree of iron increased from 47% for sample 1 to 56% and 75% for samples 2 and 3, respectively. Also, in samples 4-6, the degree of iron reduction has increased from 39% for sample 4 to 48% and 68% for samples 5 and 6, respectively. Based on thermodynamic calculations in all these samples, an iron reduction degree of 100% is obtained. The percentage of metallic iron has followed a similar trend. By reducing the heating rate of coal, not only has the percentage of metallic iron in the final dust increased but also the experimental results have become closer to those of computer simulations.

The degree of the reduction of iron and the percentage of metallic iron in the experiments for samples containing coal 2 was less than the samples containing coal 1. The percentage of metallic iron in the final dust for sample 3 was 46.4% while for sample 6, it was 44.5%. Since the amount of volatiles in coal 2 was less than in coal 1 (Table 2), the reducing capacity of volatiles in coal 1 was higher.

The degree of zinc reduction for 6 samples is plotted in Fig. 10. In sample 1, only about 5% of zinc was reduced and entered the vapor phase, while 43% zinc can be recovered based on thermodynamic simulations. In sample 4, which had similar heating rate and different coal type, no recovery of zinc was observed. According to experiments, as the coal heating rate decreases, zinc recovery increases. In samples 3 and 6, which had the lowest heating rate, zinc recoveries were 68% and 89%, respectively.

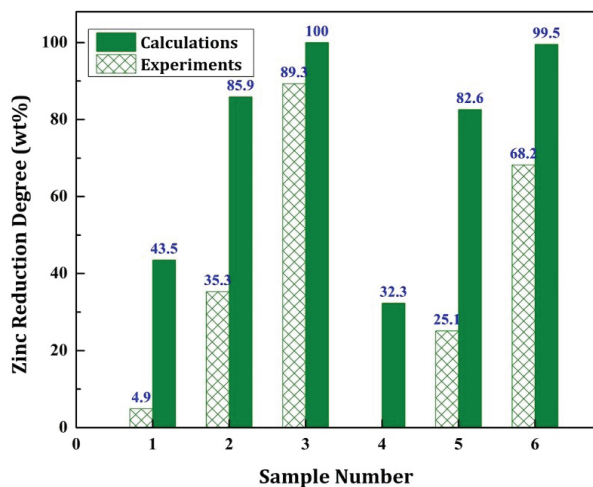


Fig. 10. Comparison of the results of the experiments and thermodynamic simulations for zinc.

According to stoichiometric calculations, volatiles of both types of coals can easily reduce all iron and zinc oxides in the dust. Low efficiency of reducing gases in the experiments relates to their high rate of volatilization.

In other words, volatile matter of the coals are in contact with the dust for a short time and therefore there is not enough time to perform reduction reactions. Therefore, to reduce coal consumption and increase reduction efficiency, we must reduce the heating rate of coal (to less than 13.5 °C/min).

Other factors, such as particle size of the coal and heating rate of the furnace affect reduction degree of the EAF dust. With increasing particle size of the dust, gasification rate of the coal volatiles is decreased. Therefore, increasing particle size of the dust will be similar to reducing the heating speed of the coal. Also, reducing the heating rate of the furnace can reduce the heating speed of the dust and the coal, simultaneously. Investigating the effect of these two parameters can be the subject of another research in this field.

Therefore the effect of reducing the heating speed of the coal. Also, reducing the heating speed of the furnace can reduce the heating speed of dust and coal, which requires more accurate laboratory studies.

Weight loss of the dust, due to the reduction process, has an important role in increasing the percentage of metallic iron in the final dust. Maximum weight loss of 30% was obtained for the dust in sample 3. The removal of oxygen from iron and zinc oxides by reduction reactions (Equations (3)-(9)) and the release of gaseous zinc at high temperatures are the main reasons for this weight loss. Fig. 11 shows the X-ray diffraction patterns for the residual dusts in samples 1 and 3. The comparison of these graphs with the XRD graph for the initial dust, demonstrates that due to dust reduction, the amount of metallic iron has increased and the amounts of iron and zinc oxides have decreased. As shown in Fig. 9 and 10, in samples where complete reduction of iron and zinc oxides occurs, iron concentration in the residual dust increases to 46 wt%. Increasing iron concentration in the residual dust allows it to be recharged to the furnace.

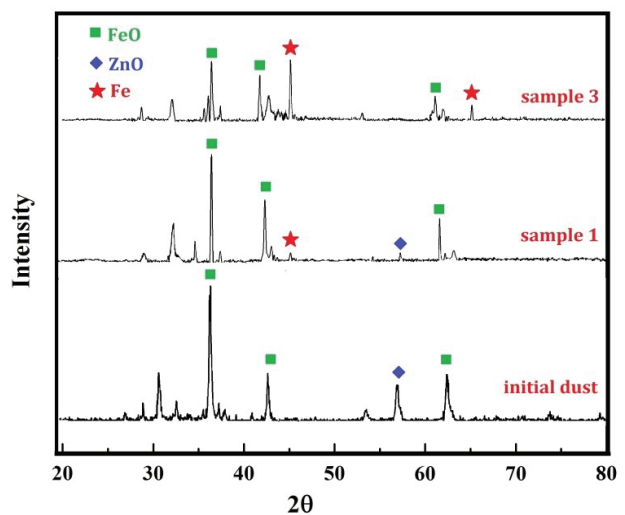


Fig. 11. XRD graphs of the residual dust in samples 1 and 3.

4. Conclusion

In this research, a simple method to recovery of zinc from EAF dust using a cheap reductant is suggested. EAF Dust reduction was performed by volatile matter of non-coking coal in the temperature range of 25-950 °C. The effect of coal heating rate and coal type on the reduction of iron and zinc oxides was investigated. Thermodynamic simulations indicate that decreasing the heating rate of coal 1 from 18.4 to 13.5 °C/min increases zinc recovery from 43% to 100%. A similar trend was observed in experiments. The change in the type of coal, accompanied by a decrease in coal volatiles, has reduced the rate of recovery. Experiments show that reducing the heating rate of coal facilitates the reduction of iron and zinc oxides in the dust. Furthermore, by decreasing coal heating rate, the reduction values in the experiments are closer to the values obtained in thermodynamic simulations. The best results were obtained in sample 3, in which the reduction degrees for iron and zinc were 75% and 89%, respectively. It can be predicted that by further decreasing the heating rate of coal, the rate of the reduction of zinc and iron can be increased to higher values.

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