

New EAF Dust Treatment Process with the Aid of Strong Magnetic Field

Satoshi ITOH,¹⁾ Akira TSUBONE,²⁾ Kazuyo MATSUBAE-YOKOYAMA,³⁾ Kenichi NAKAJIMA⁴⁾ and Tetsuya NAGASAKA³⁾

1) Graduate School of Engineering, Tohoku University, Sendai 980-8579 Japan 2) Aichi Steel Corp., Tokai 476-8666 Japan.
3) Graduate School of Environmental Studies, Tohoku University, Sendai 980-8579 Japan. 4) National Institute of Environmental Studies, Tsukuba 305-8506 Japan.

(Received on May 29, 2008; accepted on July 14, 2008)

A new EAF dust treatment process named as “Lime Addition and Magnetic Separation Process (LAMS Process)” has been proposed to recover zinc oxide from the dust and to use solid residue as a flux for steel refining. The LAMS Process consists of the reaction of EAF dust with CaO followed by the adequate crushing and high gradient magnetic separation. The basic principle of this process has been established by revealing the phase equilibria in the CaO–Fe₂O₃–ZnO system where Ca₂Fe₂O₅ can be in equilibrium with pure ZnO rather than ZnFe₂O₄, which is the major component of EAF dust, at higher CaO region. The conversion of zinc ferrite in EAF dust to ZnO and Ca₂Fe₂O₅ has been experimentally demonstrated by heating the dust with double molar amount of CaO at 1 173 and 1 373 K. It has also been demonstrated that the formed ZnO and Ca₂Fe₂O₅ can be separated by the strong magnetic field. Therefore, it may be possible to recover ZnO from EAF dust without the carbothermic reduction like Waelz process.

KEY WORDS: EAF dust; electric arc furnace; recycling; magnetic separation; zinc ferrite.

1. Introduction

One of the main environmental concerns associated with the Electric Arc Furnace (EAF) steelmaking process is the generation of dusts together with CO₂ and dioxin emissions. EAF steelmaking process commonly generates approximately 15 kg of dusts (EAF dust) for 1 ton of steel production. The composition of EAF dust strongly depends on the operating conditions such as the characteristics of scrap charged in the furnace, operating period, specification of the steel produced and so on, while it is known that EAF dust generally consists of zinc, iron, lead, cadmium and halogens (chlorine and fluorine). Generally zinc content in the dust is around 20 mass%¹⁾ and it is sometimes higher than 30 mass% if the recycling of dust to EAF is promoted.

The authors²⁾ have pointed out in their analysis of substance flow of zinc through Japanese iron and steel industry that EAF dust generation and the amount of zinc accompanied with the dust in 2005 have been estimated as 0.433×10^6 ton and 0.865×10^5 ton-Zn, respectively. Among total zinc in EAF dust, 0.495×10^5 ton of zinc is estimated to be recovered as crude zinc oxide (ZnO) by the intermediate treatment processes. Crude ZnO is used as a zinc resource by the nonferrous industry such as Imperial Smelting Process (ISP).³⁾ The amount of the recovered zinc from EAF dust corresponds to about 12.8% of total domestic zinc production in 2005 (6.75×10^5 ton). Except for process scrap of zinc from the galvanization of steel and die-castings, EAF dust is essentially the one and only recycling path of zinc from the end-of-life products.

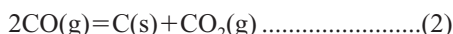
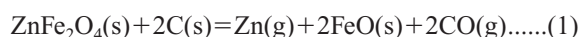
For the recycling or stabilization of steelmaking dusts, the intermediate treatment process acts an essential role to recover zinc and other heavy metals together with the removal of halogens from the dust. Due to the industrial importance, several techniques have been developed or proposed as the intermediate treatment process based on the hydro-metallurgical process,^{1,4–17)} carbothermic reduction,¹⁸⁾ iron-reduction distillation process of zinc oxide in the dust,^{19,20)} chlorination of heavy metals with PVC²¹⁾ and so on. In addition, fundamental studies on the characterization of the dust components,²²⁾ behavior of halogens during the carbothermic reduction,²³⁾ thermodynamic simulation on the selective carbothermic reduction of dust components,²⁴⁾ reutilization of the dust as a catalyst of waste water treatment,²⁵⁾ suppression of dust generation in EAF operation²⁶⁾ have also been reported. Among them, the principal commercial method is the Waelz process which is commonly employed worldwide. However, some problems are pointed out from environmental aspects.^{2,3,27)}

The objective of the present work is to establish the basic principle of the new EAF dust treatment process which enables to recover crude zinc oxide from the dust without carbothermic reduction.

2. Basic Principle

The basic principle of the Waelz process is a carbothermic reduction of zinc-ferrite (ZnFe₂O₄) and zinc oxide (ZnO) which are main components of zinc in the dust. Zinc in the ZnFe₂O₄ and ZnO is reduced to metallic form in the

Waelz rotary kiln and the formed metallic zinc subsequently evaporates into the gas phase at high temperature around 1473 K (1200°C). Halogens or halides volatilize jointly with the zinc and it is another function of this process while it is not discussed in this paper. Through controlled admission of air at the kiln outlet end and the chemical equilibrium in Zn–C–O–H system at lower temperature, however, zinc vapor is oxidized again and zinc is finally recovered in the form of ZnO rather than metallic zinc. The basic reactions in the Waelz process are given by the following equations.



$$\begin{aligned} \Delta G_1^\circ &= 603\,178 - 943.185T - 6.715 \times 10^{-3} T^2 \\ &\quad - 50.21 \times 10^5 / T + 58.316T \ln T \quad \text{J/mol} \\ &\quad (1\,179 \text{ K} < T < 1\,650 \text{ K}) \dots\dots\dots(4)^{28)} \end{aligned}$$

$$\begin{aligned} \Delta H_1^\circ &= 603\,178 - 58.316T + 6.715 \times 10^{-3} T^2 \\ &\quad - 100.41 \times 10^5 / T \quad \text{J/mol} \\ &\quad (1\,179 \text{ K} < T < 1\,650 \text{ K}) \dots\dots\dots(5)^{28)} \end{aligned}$$

The enthalpy change of Eq. (1) at 1180 K (just above boiling point of zinc) is 535 kJ/mol, indicating that the reaction of Eq. (1) is large endothermic at high temperature due to mainly the decomposition of zinc ferrite and the vaporization of zinc. The collected crude ZnO is supplied to zinc refinery. That is, this process acts as a concentration method of ZnO from the dust in spite of large energy input for the reduction and volatilization of zinc. Another concern of this process is the solid residue. The solid residue of the Waelz process containing the most of iron in the dust (Waelz clinker) was used to be utilized by the cement industry. However, the cement industry can no longer accept the Waelz clinker due to some environmental regulations and the clinker is presently stocked, landfilled or returned to EAF company. Therefore, the Waelz process is not the best choice for dust treatment in the view point of effective usage of energy and recovery of metals such as zinc and iron.

In order to improve large carbon consumption in the Waelz process, the authors have proposed new process for dust treatment.^{2,29)} If the following reaction takes place, ZnFe₂O₄ in the dust can react with CaO to form ZnO and Ca₂Fe₂O₅.



$$\begin{aligned} \Delta G_6^\circ &= -32\,114 + 11.329T + 4.201 \times 10^{-3} T^2 \\ &\quad - 5.46 \times 10^5 / T - 3.373T \ln T \quad \text{J/mol} \dots\dots(7)^{28)} \end{aligned}$$

$$\begin{aligned} \Delta H_6^\circ &= -32\,114 + 3.373T - 4.201 \times 10^{-3} T^2 \\ &\quad - 10.91 \times 10^5 / T \quad \text{J/mol} \dots\dots\dots(8)^{28)} \end{aligned}$$

The values of free energy and enthalpy changes of this reaction are both negative at elevated temperature. For example, ΔH_6° at 1180 K is -34.9 kJ/mol. Exothermic nature of this reaction is a benefit of the new process. In addition, this reaction can basically proceed in air and it enables to form

ZnO without carbothermic reduction of the dust, so that the dust may be treated at elevated temperature in air. The reaction products, ZnO and Ca₂Fe₂O₅, may be separated with an adequate technique such as magnetic separation. Another great benefit of this process is that steel industry can use Ca₂Fe₂O₅ as a dephosphorization agent or raw material for sintering plant. Ye and Burstrom^{10,11)} have also proposed the elimination of zinc ferrite, which is hard to be leached, by the reaction with CaO for the pretreatment of EAF dust followed by the leaching process named as EZINEX. They experimentally confirmed the conversion of ZnFe₂O₄ to free ZnO and Ca₂Fe₂O₅ at 1373 K. Their basic concept is based on the phase diagram of CaO–Fe₂O₃–ZnO system estimated by FactSageTM5.2. On the other hand, it is hard to precisely predict phase equilibria of unknown system without experimental information. If ternary intermediate compound, which is unloaded in the data base of FactSage, exists in ZnO–ZnFe₂O₄–Ca₂Fe₂O₅ sub-system, the above-mentioned principle is no longer expected. Actually the authors have found unknown ternary compound in CaO–Fe₂O₃–ZnO system as it will be mentioned in the later section.

The present work aims to establish the basic principle of the carbon free dust treatment process. Phase diagram of CaO–Fe₂O₃–ZnO system at around 1273 K and the chemical/physical properties of the reaction products for the following separation process have been experimentally revealed.

3. Experimental

3.1. Measurement of the Phase Equilibrium

The specimen for the phase equilibrium measurement was prepared as follows: reagent grade CaCO₃, Fe₂O₃ and ZnO were well mixed at the aimed compositions and then pressed into the 10 mm diameter 1.5 g tablet under the pressure of about 400 MPa. This tablet was put in a platinum crucible and heated with the SiC resistance furnace in air for a desired holding time at temperature of 1173 or 1373 K. After the attainment of the equilibrium, the specimen was quenched. For the perfect establishment of the equilibrium, the specimen was held for 5 d at the experimental temperature. The phase equilibria were determined by the phase identification using X-ray diffraction technique (XRD: Rigaku Corp. RINT2200) together with the microscopic observation.

3.2. Magnetic Separation

The magnetic properties of ZnFe₂O₄ and Ca₂Fe₂O₅ were measured in the present work as part of a quantitative investigation of the possibility of magnetic separation of ZnO and Ca₂Fe₂O₅. The preliminary synthesized ZnFe₂O₄ and Ca₂Fe₂O₅ were supplied for the magnetization curve measurement with a vibrating sample magnetometer (VSM: Rigaku Corp. BHV-55). ZnFe₂O₄ and Ca₂Fe₂O₅ were prepared by mixing ZnO and Fe₂O₃ with 1 : 1 and CaCO₃ and Fe₂O₃ with 2 : 1 in molar ratio (total 15 g in both cases) and heating in platinum crucible for 60 h at 1373 K and then for 3 d at 1173 K. The formation of each compound phase was confirmed by XRD.

In order to verify whether the individual recovery of ZnO and Ca₂Fe₂O₅ from the treated dust is actually feasible, we

carried out a magnetic separation experiment using a strong magnetic-field generator of the superconducting bulk-magnet type. The detailed procedure of the magnetic separation has been described elsewhere.^{30,31)} The maximum magnetic field strength on the surface of the bulk magnet was 5 T, and the magnetic field gradient near the surface of magnet was measured with a Gauss-meter as approximately 1.1 T/cm.

The vertical pyrex (inner diameter was about 30 mm) tubing was set at the center of the magnet. The inside of the tubing was filled with the distilled water and the bottom end was closed at this moment. 16 pieces of stainless steel mesh filter (grid distance was less than 0.6 mm) were horizontally placed at the center in the tubing. Approximately 1 g of the mixture of ZnO and $\text{Ca}_2\text{Fe}_2\text{O}_5$ (average particle size was about 150 μm) was dispersed in 0.25 L of distilled water. Then this mixture was charged into the pyrex tubing from the upper end and at the same time bottom end was opened to flow the water. After all of the water was exhausted from the tubing, inside was washed with 0.5 L of distilled water. The unmagnetized substance exhausted from the bottom of the tubing and the magnetized substance trapped on the filter were collected and chemically analyzed by ICP-AES (Shimazu Corp., ICPS-8100).

3.3. Reaction of EAF Dust with CaO

The reaction efficiency of actual EAF dust with CaO was also tested in the kinetic view point. **Table 1** shows the zinc, iron and Ca contents in the dust supplied from EAF company. The composition listed here was determined by ICP-AES with the alkaline fusion technique using $\text{K}_2\text{S}_2\text{O}_7$. The ratio of ZnO and ZnFe_2O_4 was determined by each relative peak intensity of XRD pattern.³²⁾ Two kinds of heating method were tested for the reaction of dust with CaO. One

Table 1. Composition of EAF dust supplied from EAF company.

mass%Zn	mass%Fe	mass%Ca
14.8	21.3	1.5

Table 2. Experimental compositions for the measurement of CaO– Fe_2O_3 –ZnO system and observed equilibrium phases at 1 173 and 1 373 K. ZF, CF, C_2F and θ denote ZnFe_2O_4 , CaF_2O_4 , $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{ZnCa}_2\text{Fe}_{14}\text{O}_{24}$, respectively.

Sample No.	X_{ZnO}	$X_{\text{Fe}_2\text{O}_3}$	X_{CaO}	identified phases	experimental temperature
1	0.15	0.65	0.20	ZF+CF+ θ	1173K
2	0.14	0.66	0.20	ZF+CF+ θ	1373K
3	0.00	0.85	0.15	CF+ Fe_2O_3	1373K
4	0.50	0.35	0.15	ZnO+ZF+ C_2F	1173K, 1373K
5	0.25	0.50	0.25	ZF+CF	1373K
6	0.20	0.15	0.65	ZnO+ C_2F +CaO	1173K, 1373K
7	0.20	0.60	0.20	ZF+CF+ θ	1173K, 1373K
8	0.15	0.45	0.40	ZF+ C_2F +CF	1173K, 1373K
9	0.10	0.60	0.30	ZF+CF+ θ	1173K, 1373K
10	0.20	0.75	0.05	ZF+ θ + Fe_2O_3	1373K
11	0.13	0.64	0.23	ZF+CF+ θ	1373K
12	0.10	0.70	0.20	θ	1373K
13	0.20	0.70	0.10	ZF+ θ + Fe_2O_3	1173K, 1373K
14	0.33	0.67	0.00	ZF+ Fe_2O_3	1173K
15	0.00	0.60	0.40	CF+ Fe_2O_3	1373K
16	0.05	0.55	0.40	ZF+CF+ θ	1373K
17	0.20	0.55	0.25	ZF+CF+ θ	1373K
18	0.05	0.70	0.25	CF+ θ + Fe_2O_3	1173K, 1373K

is the static heating and another is the dynamic heating with the kiln type reactor shown in **Fig. 1**. In the static method, the dust or synthesized ZnFe_2O_4 was mixed with CaCO_3 and 1.5 g of this mixture was pressed into the tablet of 10 mm diameter under the pressure of about 400 MPa. This tablet was put in a platinum crucible and heated with the SiC resistance furnace in air for a desired reaction time. In the latter case, the mixed powder sample of ZnFe_2O_4 with CaCO_3 was charged at the center of the stainless steel pipe of kiln type reactor, where four small impellers were equipped at the inner wall, and heated in air with the rotation of the pipe at 1 rpm for the continuous convection. The experimental temperature was at 1 173 or 1 373 K and the molar ratio of ZnFe_2O_4 and CaCO_3 in the sample mixture was adjusted at 1 : 2. After the desired period from 3 to 6 h, the sample was discharged from each reactor and supplied for XRD analysis after cooling. The reaction degree per unit operation time was determined from the ratio of relative intensities of XRD peaks of ZnO and ZnFe_2O_4 .³²⁾

4. Results and Discussion

4.1. Phase Equilibria in the CaO– Fe_2O_3 –ZnO System

The experimental compositions and identified equilibrium phases at each composition are listed in **Table 2**. It was found that CaO– Fe_2O_3 –ZnO system exhibits completely the same phase equilibria at 1 173 and 1 373 K. **Fig.**

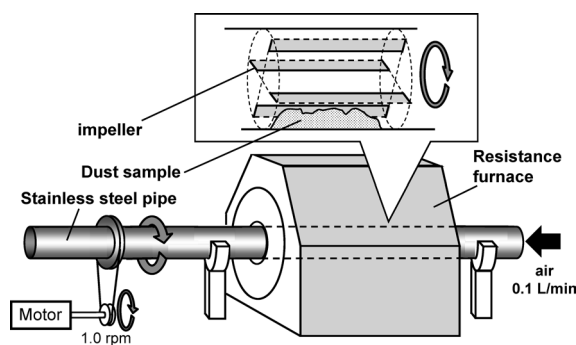


Fig. 1. Schematic diagram of the kiln type furnace used in the dynamic heating method.

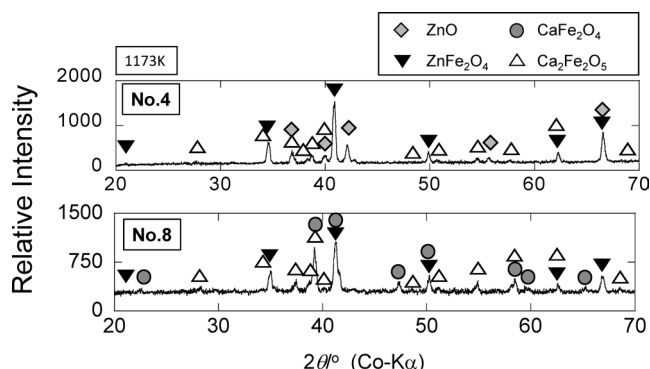


Fig. 2. XRD patterns of the samples No. 4 and No. 8 at 1173 K.

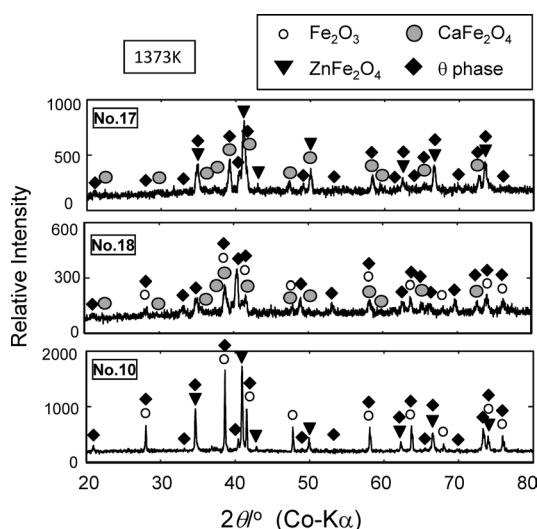


Fig. 3. XRD patterns of the samples No. 10, No. 17 and No. 18 at 1373 K.

Figure 2 shows the XRD pattern of No. 4 and No. 8 after the establishment of the equilibrium. These specimens consist of respectively ZnO–Ca₂Fe₂O₅–ZnFe₂O₄ (No. 4) and Ca₂Fe₂O₅–CaFe₂O₄–ZnFe₂O₄ (No. 8) three phases, indicating that ZnO can be in equilibrium with Ca₂Fe₂O₅ rather than CaFe₂O₄ and the Alkemade line should be joined between Ca₂Fe₂O₅ and ZnFe₂O₄. As shown in Fig. 3, unknown phase was observed near Fe₂O₃ corner. This phase was deduced as ternary intermediate compound. From the results of EPMA analysis, its stoichiometric formula has been specified as ZnCa₂Fe₁₄O₂₄. This ternary compound phase is named as θ phase in this paper. Figure 4 represents XRD pattern of sample No. 12 whose composition was adjusted to that of θ phase. This sample basically consisted of single phase and its diffraction pattern show reasonable agreement with that of unknown phase observed in other samples.

The phase diagram of the CaO–Fe₂O₃–ZnO system established in the present work is illustrated in Fig. 5. This diagram is identical at both temperature of 1173 and 1373 K. The phase diagram of this ternary system is more complex than that estimated by Ye and Burstrom,^{10,11)} and it consists of 6 sub-ternary systems. The most important fact is that ZnO can be in equilibrium with Ca₂Fe₂O₅, suggesting that ZnFe₂O₄ can be transformed into ZnO and Ca₂Fe₂O₅, as it was expected, at the equilibrium state if CaO is added to ZnFe₂O₄ with the enough amount beyond the Alkemade

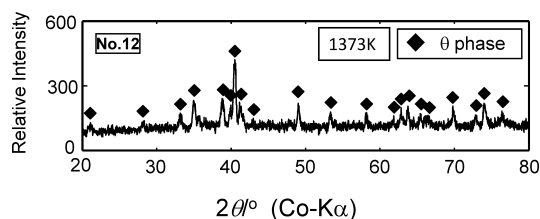


Fig. 4. XRD patterns of the samples No. 12 which essentially consists of single phase of θ at 1373 K.

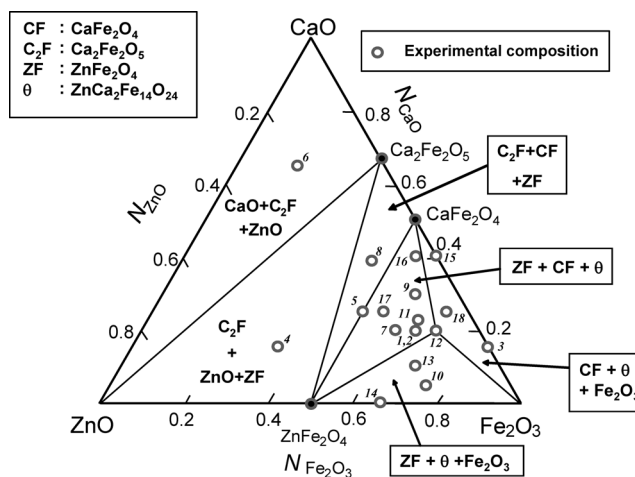


Fig. 5. Phase diagram of CaO–Fe₂O₃–ZnO system at 1173 and 1373 K.

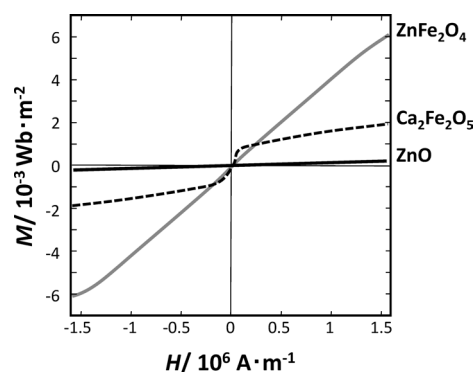


Fig. 6. Magnetization curve of ZnFe₂O₄, Ca₂Fe₂O₅ and ZnO.

line between ZnO and Ca₂Fe₂O₅ (CaO:ZnFe₂O₄>2:1 in mol). Ye and Burstrom have utilized such phase equilibrium to eliminate ZnFe₂O₄ which is basically insoluble in the leaching process while the present authors have aimed to obtain ZnO from ZnFe₂O₄ without carbothermic reduction.

4.2. Magnetic Separation

Figure 6 shows the magnetization curves of ZnO, ZnFe₂O₄ and Ca₂Fe₂O₅. It is found that ZnO, Ca₂Fe₂O₅ and ZnFe₂O₄ are non-magnetic, paramagnetic and ferromagnetic materials, respectively, and the difference between the magnetic susceptibility of ZnO and that of Ca₂Fe₂O₅ is remarkable. This indicates that ZnO can be separated magnetically from Ca₂Fe₂O₅ under a high gradient magnetic field.

The experimental result of magnetic separation using the simulated dust of ZnO+Ca₂Fe₂O₅ powder mixture is represented in Fig. 7. In the Waelz process, the purity of the crude ZnO is generally 75–80% and this crude ZnO is

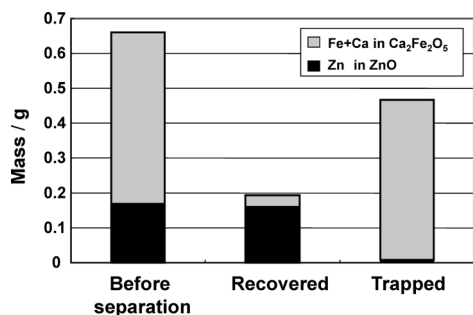


Fig. 7. Experimental results of magnetic separation for ZnO+Ca₂Fe₂O₅ mixture at 5 T.

heated again in another kiln at 1473 K for up-grading if necessary. On the other hand, ZnO and Ca₂Fe₂O₅ were well separated by the magnetic separation process and 95% of ZnO in the initial simulated dust was recovered. Although about 6% of Ca₂Fe₂O₅ was contaminated into the recovered ZnO and 5% of ZnO was lost into the trapped Ca₂Fe₂O₅, purity of the recovered ZnO was higher than 90%. According to these results, it is concluded that the basic principle of this new process is confirmed. The detail investigation on the optimum conditions for magnetic separation will be presented in our next paper. The key technology may be the design of the reactor for the reaction of Eq. (6) and the crushing of the treated dust. The authors have named this new process as Lime Addition and Magnetic Separation process (LAMS process).

4.3. Reaction of Dust with CaO

It is needless to say that a faster reaction rate and a lower operating temperature are desirable in the practical view point. Static and dynamic heating methods for the reaction of EAF dust with CaO were tested in the present work while the detailed kinetic study will be made in the future work. Since the basic components in Eq. (6), ZnFe₂O₄, ZnO, Ca₂Fe₂O₅ and CaO, have no mutual solubility as shown in Fig. 5 and free energy change of Eq. (6) exhibits relatively large negative value of approximately -42 kJ/mol at 1173 to 1373 K, it is expected that Eq. (6) can spontaneously proceed toward right hand side.

The experimental results of two heating methods are demonstrated in Fig. 8. Normalized reaction degree obtained after 3 h operation at 1173 and 1373 K is presented with comparing two heating methods. The reaction rates by the static heating were insufficient even at 1373 K. They were 7 and 27% at 1173 and 1373 K at 3 h, respectively. However, the reaction rate was drastically improved by using the kiln type reactor shown in Fig. 1. Approximately 77% of ZnFe₂O₄ was able to be converted to ZnO and Ca₂Fe₂O₅ at 1373 K. The general operating condition of the Waelz process is 6 to 8 h treatment at around 1500 K.³³⁾ Therefore, it may be possible to complete the reaction of Eq. (6) at lower temperature and somewhat shorter operating time than those of the Waelz process. Ye and Burstrom^{10,11)} have also demonstrated that the most of ZnFe₂O₄ in the dust can be eliminated with the reaction of CaO while the reaction method and the holding time are unknown.

As it has been indicated by the authors,²⁾ life cycle energy consumption and CO₂ emission for the dust treatment

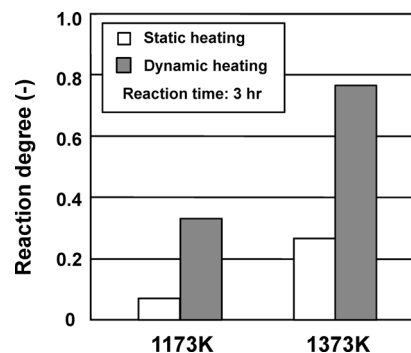


Fig. 8. The reaction efficiency of the dust with CaO by two kinds of heating methods at 1173 and 1373 K.

may be much improved by the LAMS process since this process is basically carbon reduction free process.

5. Conclusions

A new EAF dust treatment process to recover zinc oxide from the dust is proposed by the authors. It consists of the reaction of dust with CaO followed by the adequate crushing and high gradient magnetic separation. For the establishment of basic principle of this process, phase equilibria in the CaO-Fe₂O₃-ZnO system and magnetic properties of ZnO, ZnFe₂O₄ and Ca₂Fe₂O₅ have been investigated. Zinc ferrite in the EAF dust can be converted to ZnO and Ca₂Fe₂O₅ by the reaction with double molar amount of CaO at around 1273 K based on the phase equilibria revealed in the present work. The formed ZnO and Ca₂Fe₂O₅ can be separated by the strong magnetic field. It may be possible to convert zinc ferrite to ZnO and Ca₂Fe₂O₅ by this new process named as the Lime Addition and Magnetic Separation Process (LAMS Process) with much better efficiency than the conventional process.

Acknowledgements

The authors wish to thank K. Ono, N. Umeda and Y. Inoue, Graduate School of Environmental Studies, Tohoku University, for their experimental assistance. Special thanks is due to Dr. N. Hirota and Dr. H. Okada, Tsukuba Magnet Laboratory, National Institute for Materials Science, for their great help of magnetic separation experiment. Financial supports from a Research for Promoting Technological Seeds, the Japan Science and Technology Agency (JST) in 2007 and 2008, ISIJ Innovative Program for Advanced Technology, The Iron and Steel Institute of Japan, in 2008 and Advanced Research and Education Center for Steel (ARECS) of Tohoku University are also gratefully acknowledged.

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