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Characteristic of zinc ferrite decomposition by calcium and magnesium oxides

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Abstract. Electric arc furnace (EAF) dust generated in steelmaking is a valuable waste material with high content of zinc, lead and iron. Recovery of zinc by current industrial hydrometallurgical methods at zinc plants is difficult due to the presence of zinc in the hardly soluble ferrite form and high contents of chlorine and fluorine that are harmful impurities for further electrolysis. To decompose zinc ferrite and remove halogens from EAF dust there is a promising approach that promote zinc ferrite decomposition to highly soluble zinc oxide and volatilization of halogens in one pyrometallurgical stage, where EAF dust are calcined with lime at 900-1100°C. This paper aims to investigate kinetics of the reaction between pure ZnFe_2O_4 and CaO to determine its controlling step and evaluate its characteristics. The reaction between pure ZnFe_2O_4 and MgO is also considered. The investigation of the EAF dust sample has confirmed that majority of zinc is in the form of hardly soluble ferrite. The results of experiments have shown that the reaction of zinc ferrite with calcium oxide at 900-1000°C is kinetic controlled, so temperature has a significant effect of on the reaction rate. The degree of conversion of the reaction between zinc ferrite and magnesium oxide is negligible, so the application of MgO during the EAF dust processing is inexpedient at the studied temperatures.

1. Introduction

Electric arc furnace (EAF) dust generated in steel industry is a valuable by-product with high content of zinc, lead and iron. The content of zinc and lead in EAF dust is in large excess over their content in the base metal ores. Currently, about 45% of EAF dust generated in the world is recycled [1], primarily in Western Europe and North America for nonferrous metals extraction.

The EAF dust processing in order to extract zinc by current industrial hydrometallurgical methods at zinc plants is difficult due to the presence of zinc in the hardly soluble ferrite form [2], as well as high content of chlorine and fluorine that creates additional hindrances in the further electrolysis of obtained zinc-containing solutions [3]. Therefore, to decompose zinc ferrite and remove halogens from EAF dust many plants apply the Waelz process [4], which is the pyrometallurgical processing of dust with carbonaceous reducing agent in rotary kiln at 1200-1300°C. During the Waelz process, zinc, lead, chlorine and fluorine volatilize from the charge to Waelz-fume. For the separation of lead and halogens from zinc some producers use additional calcination of obtained Waelz-fume in a rotary kiln [5] or salt-water leaching [6]. Currently, the Waelz process is the most popular method of EAF dust recycling. Today, about 85% of the processed dust are recycled in the Waelz kilns [7]. In the practice of Waelz process, processing of EAF dust consumes up to 350 kg/ton of expensive coke breeze [8]. Due to the high-energy costs of such processing and need of the subsequent calcination of Waelz-



fume, it is necessary to look for new effective methods of EAF dust recycling. Other methods with processing of wastes in rotary-hearth furnace [9, 10], shaft furnace [11], multiple-hearth furnace [12], induction furnace [13], flash smelter [14], as well as leaching methods [15-17] have limited application for EAF dust recycling [8]. Thus, it is preferable to develop new methods based on the processing of EAF dust in rotary kiln as are used in the Waelz process. Authors [18-20] proposed a method to transform zinc ferrite to highly soluble zinc oxide and to remove halogens from EAF dust in one processing stage, where the dust is calcined with lime at 900-1100°C.

In this paper, kinetics of the reaction between pure ZnFe_2O_4 and CaO were studied to reveal its controlling step and evaluate its characteristics. Moreover, the reaction between pure ZnFe_2O_4 and MgO was analyzed because magnesium oxide also promotes zinc ferrite decomposition [21, 22].

2. Materials and Methods

Elemental composition of EAF dust of Vyksa Steel Works (AO VMZ) was investigated by X-ray fluorescence spectrometer Axios Advanced (Netherlands). The carbon and sulfur contents were analyzed by LECO CS-400 (USA). Phase composition of the dust was studied by diffractometer DRON-4 (Russia) with X-rays of $\text{Cu-K}\alpha$. The distribution of iron phases was analyzed by Mössbauer spectrometer Ms-1104Em (Russia) in constant acceleration mode with the source of Co-57 in Rh matrix.

Experiments for the investigation of the reactions between pure zinc ferrite and calcium oxide were carried out on the laboratory muffle furnace. Reagent grade CaO and MgO were preliminarily calcined at 900°C for 2 hours to remove the hydration moisture. Pure zinc ferrite was obtained by the following method. Reagent grade Fe_2O_3 and ZnO were mixed in a 1:1.1 ratio (with a 10% molar excess of zinc oxide) in the V-shell blender. The briquettes obtained from mixtures were calcined in the muffle furnace at 1000°C for 6 hours. The obtained sample was milled and washed in aqueous solution of $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ to wash the remaining ZnO [23], then dried at 1000°C for 2 hours. All the initial components for the experiments were preliminarily tested by the X-ray phase analysis.

Experiments were carried out as follows. The briquetted mixtures of the $\text{ZnFe}_2\text{O}_4\text{--CaO}$ and $\text{ZnFe}_2\text{O}_4\text{--MgO}$ systems were placed to the preheated muffle furnace at 900°C or 1000°C in molar ratio 1:1.5, 1:3, 1:4.5 or 1:9. Every 1-15 minutes one sample was taken out from the furnace. Leaching of zinc in the soluble oxide form from the calcined samples was carried out by aqueous solution of $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ (22 g of NH_4Cl in a mixture of 80 ml of NH_4OH with density of 0.9 g/cm³ and 120 ml of water) according to the method [24]. The obtained zinc-containing solution was analyzed by the ICP AES method using Perkin Elmer Optima 3300RL (USA) device.

The controlling step of the reaction between ZnFe_2O_4 and CaO was evaluated using the corrected time method by comparison of experimental data with kinetic models based on the Yander (1), the contracting sphere (2), and Erofeev-Avrami (3) equations [25]:

$$[1 - (1 - \alpha)^{\frac{1}{3}}]^2 = K_Y \cdot \tau \quad (1)$$

$$[1 - (1 - \alpha)^{\frac{1}{3}}] = \frac{K_{\text{chem}}}{r_B} \cdot \tau \quad (2)$$

$$[-\ln(1 - \alpha)]^{1/n} = K_{\text{AE}} \cdot \tau \quad (3)$$

In the equations α is the conversion degree, τ is time, K_Y , K_{chem} , K_{AE} are the corresponding constants, r_B is the initial radius of the particle and n is the coefficient that considers shape and type of nucleuses (point nucleuses were taken in account, for which $n = 1$).

3. Results and Discussion

The chemical composition of the EAF dust sample was obtained as follows: 14.6% Zn; 25.4% Fe; 1.38% Pb; 0.62% Al; 1.85% Si; 11.9% Ca; 2.06% Mg; 1.61% Na; 1.7% K; 2% Mn; 0.31% Cr; 0.2% Cu; 3.69% Cl; 0.45% F; 1.63% C; 0.66% S; 0.11% P. Figure 1 shows XRD pattern of the sample.

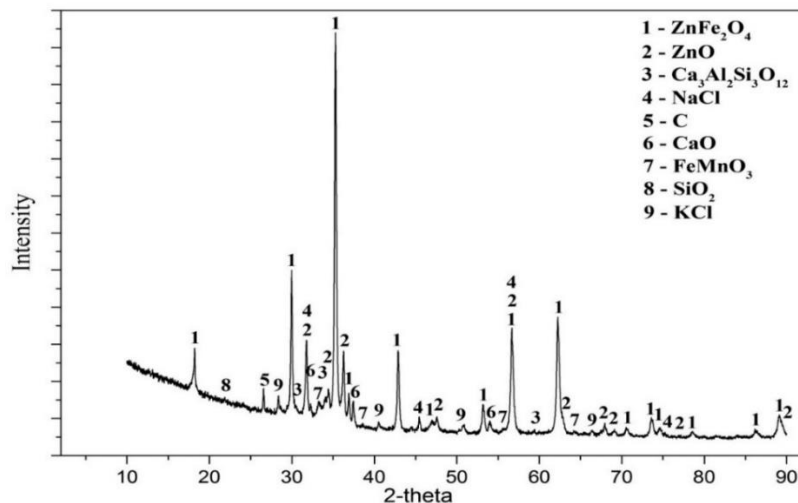


Figure 1. XRD pattern of the EAF dust sample.

The main phases of the dust are franklinite ZnFe_2O_4 , zincite ZnO , sylvite KCl , halite NaCl . Zinc is in both ferrite and oxide forms. The presence of a few amount of graphite is probably due to the carry-over of carbonaceous materials in the steelmaking process that used for foaming of slag.

Mössbauer analysis indicates that more than 55% of iron is in ferritic form, about 40% is in the form of magnetite, the rest is part of other compounds.

Figure 2 (a, b) shows XRD patterns of the calcined samples of $\text{ZnFe}_2\text{O}_4\text{--CaO}$ and $\text{ZnFe}_2\text{O}_4\text{--MgO}$ systems at 1000°C during 4 hours with 1:3 and 1:5 molar ratios respectively. The molar ratios are due to thermodynamic probability of at least 95% zinc ferrite decomposition in accordance with the thermodynamic calculation in [26].

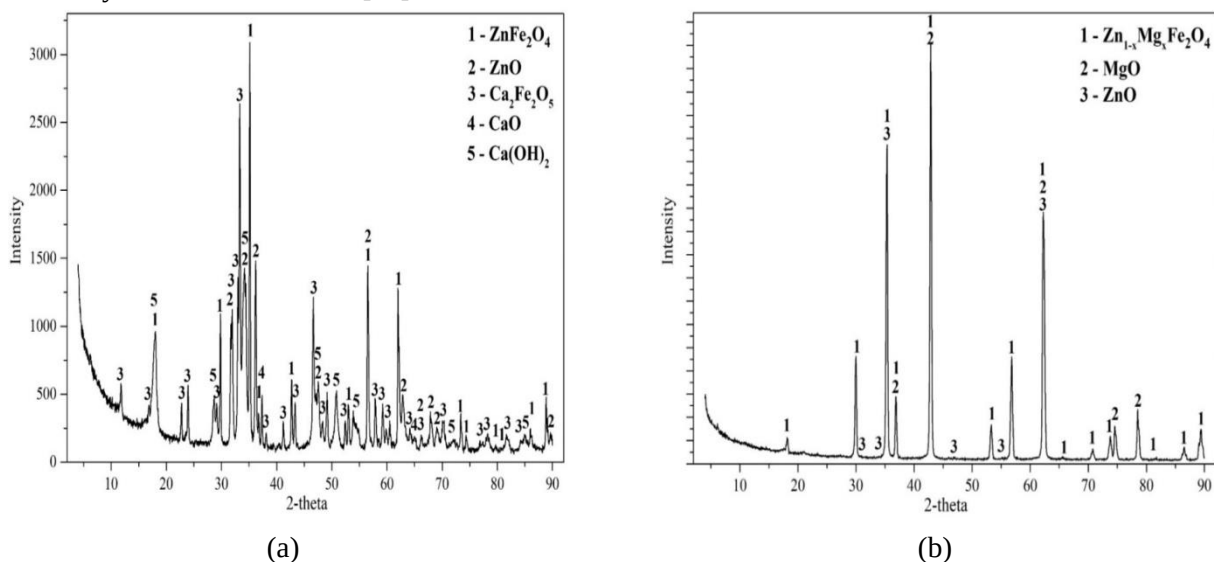
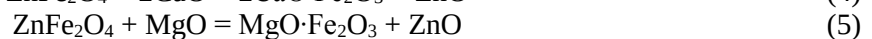
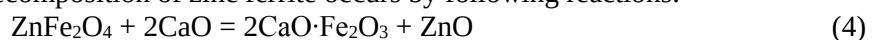


Figure 2. XRD pattern of the calcined sample $\text{ZnFe}_2\text{O}_4\text{--CaO}$ (a) and $\text{ZnFe}_2\text{O}_4\text{--MgO}$ (b) systems at 1000°C during 4 hours with 1:3 and 1:5 molar ratios respectively.

XRD patterns indicate that decomposition of zinc ferrite occurs by following reactions:



There was a partial decomposition of zinc ferrite by reaction (4) and insignificant by reaction (5). The presence of Ca(OH)_2 in one sample is due to the hygroscopicity of unreacted calcium oxide. Leaching of zinc and subsequent chemical analysis has shown that 43% of zinc transforms into the

oxide from the calcium-containing sample, and only 1.7% is converted to ZnO from the magnesium-containing sample.

Figure 3 (a, b) shows kinetic curves for the calcium-containing system.

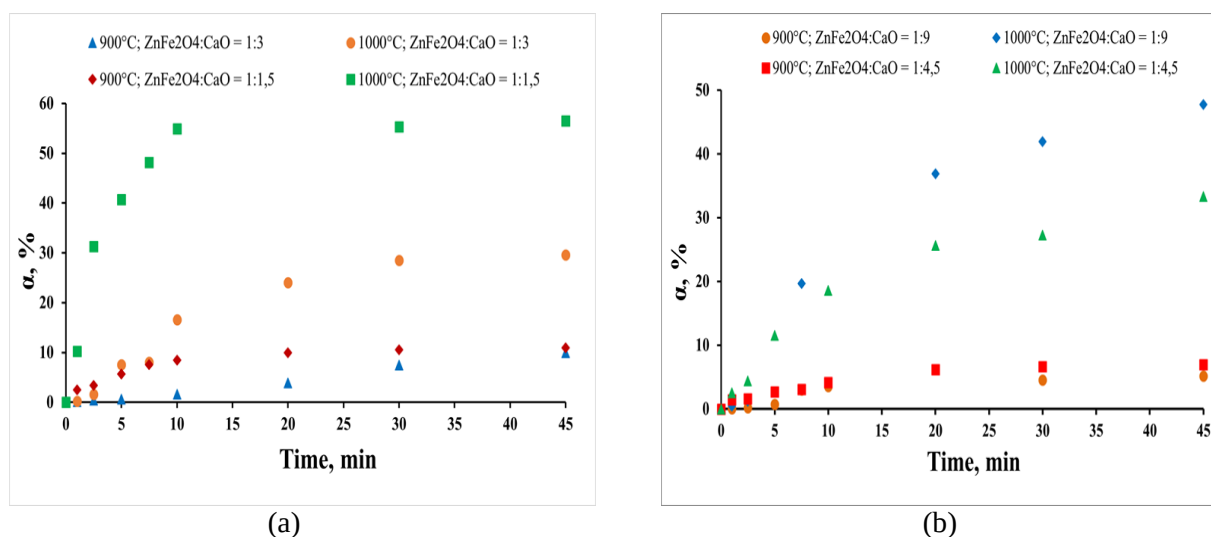


Figure 3. The kinetic curves for 1:1.5 and 1:3 (a), 1:4.5 and 1:9 (b) molar ratios of ZnFe₂O₄-CaO system at 900°C and 1000°C

The obtained data indicates that the reactions of the initial components at all studied ratios and temperatures have a similar development trend corresponding to a typical solid-phase reaction. It is possible to distinguish a stage of growing rate associated with the formation of the reaction products and increasing their amount, as well as a stage of reducing rate during which a continuous layer of reaction products is formed and contact of reactants is broken. The kinetic curves point out that increasing of temperature speeds up the reaction by several times.

Figure 4 (a, b) shows experimental and calculated effect of the corrected time on the degree of conversion for a 1:3 ratio at 900°C and 1000°C respectively. There is clear evidence shown in figures 4 (a, b) that the Yander and the Erofeev-Avrami equations corresponding to the diffusion and formation of nucleuses controlling steps respectively are mismatched with the experimental dependences. In the case of using other values of the coefficient n the Erofeev-Avrami equation is even more at variance with the experimental curves. The best match of calculated and experimental data is observed while using the contracting sphere equation. It should be mentioned that similar trends were obtained for all experimental ratios. The calculated values of the activation energy for all selected ratios are in the range of 175-210 kJ/mol.

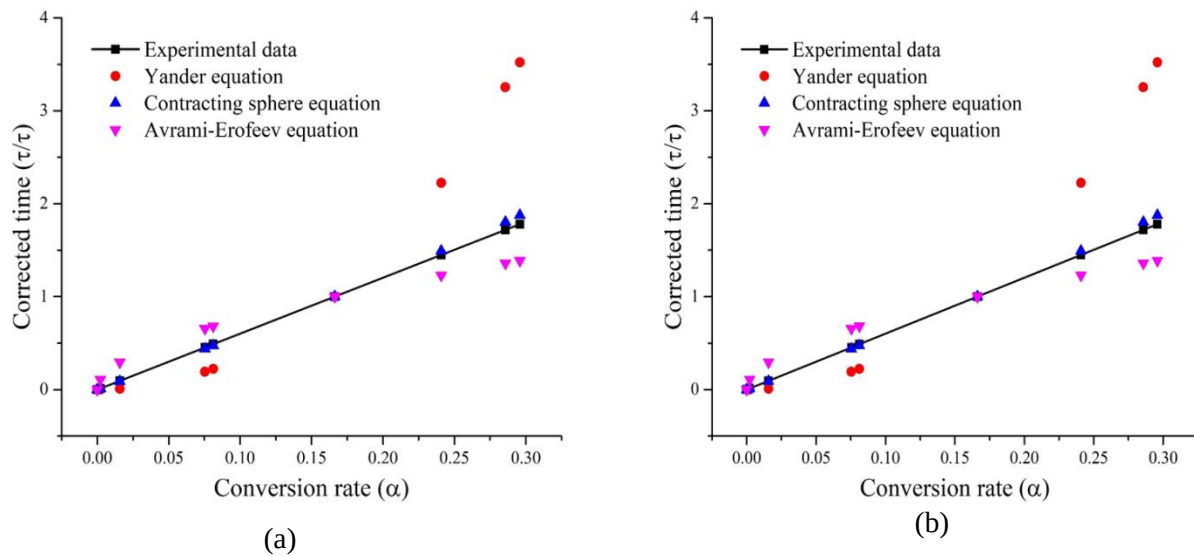


Figure 4. Experimental and calculated effect of the corrected time on the degree of conversion for a 1:3 ratio at 900°C (a) and 1000°C (b).

Table 1 shows the kinetic data for the magnesium-containing system.

Table 1. Experimental data for 1:5 molar ratio of ZnFe_2O_4 – MgO system at 900°C and 1000°C.

900°C		1000°C	
Time, min	Conversion degree, %	Time, min	Conversion degree, %
10	3.53	10	2.03
20	2.68	20	2.52
30	3.15	30	2.29
45	1.68	45	2.26
60	2.31	60	2.27
75	1.95	75	2.36

The obtained data points out that kinetic dependences for the ZnFe_2O_4 – MgO system are unreliable. The degree of conversion values are insignificant, which indicates the inefficient application of magnesium oxide during the processing of EAF dust containing zinc ferrite at 900–1000°C. The results obtained in [22] that have shown a quite high efficiency of magnesium oxide are probably due to the method of leaching experiments. For the selective dissolution of zinc oxide from calcined samples the authors have applied 7% sulfuric acid that promotes partial passing into the solution of zinc ferrite [27].

4. Conclusion

Thus, the analysis of the EAF dust sample has confirmed that a considerable part of zinc is in the form of hardly soluble ferrite. The experiments with pure components have shown that the reaction of zinc ferrite with calcium oxide at 900–1000°C is kinetic controlled, which indicates a significant effect of temperature on the reaction rate and an ability to control the process through its adjustment.

In practice, decreasing of the process rate due to the formation of a continuous layer of reaction products can be avoided by continuous mixing of the charge. The mixing process facilitates the continuous renewal of the contact surface of the reacting particles and therefore increase the

conversion degree. Such conditions can be achieved, for example, during the calcination in a rotary kiln. It is necessary to verify the obtained data by experiments using waste material (EAF dust).

The degree of conversion of the reaction between zinc ferrite and magnesium oxide is insignificant that makes the application of MgO at 900-1000°C for the calcination of EAF dust inexpedient.

Acknowledgments

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