

METALLURGY
OF NONFERROUS METALS

Thermodynamic Analysis of Zinc Ferrite Decomposition in Electric Arc Furnace Dust by Lime

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Abstract—Scientific basis of pyrometallurgical processing technology of dusts of electric steelmaking containing zinc ferrites was investigated. The thermodynamic analysis of the decomposition of zinc ferrite with lime was carried out. The analysis of calculated data has shown that, in order to decompose more than 90% $ZnFe_2O_4$, it is necessary to add no less than 46% CaO for dust, while to decompose more than 95% $ZnFe_2O_4$, no less than 60% CaO is necessary. The results of the calculation were verified experimentally using a laboratory furnace. The experimental calcination of dust in air with the addition of lime in an amount of 60% of the dust weight at 1000°C with a holding time of 4 h confirmed that the decomposition of zinc ferrite with calcium oxide with the formation of zinc oxide and dicalcium ferrite occurs. In addition, sublimates were also formed in an amount of 50 kg per 1 t of dust containing 29% of lead and 15% of zinc. Dust calcination with lime can be applied to transform zinc from ferrite into a soluble oxide form. Intermediate products for the recovery of zinc and lead can be obtained by the calcination. After zinc leaching, it is possible to obtain an iron-containing product, which can be used in ferrous metallurgy. This approach has a series of process advantages compared with the well-known Waelz technology. In particular, calcination with lime requires lower temperature (1000°C) than the known technology (1250°C), it eliminates the second stage of the Waelz treatment necessary to purify zinc oxide fed for leaching from halides, considerably reduces coke consumption, and significantly simplifies gas cleaning from dust due to a decrease in the amount of sublimates by a factor of 6–8.

Keywords: zinc ferrite, calcium ferrite, calcium oxide, zinc oxide, thermodynamic analysis, Waelz process, EAF dust

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INTRODUCTION

Dust of electric arc furnaces (EAF) of steelmaking is waste of the IV hazard class. Their accumulation can lead to serious environmental damages. Among the variety [1–14] of technologies developed worldwide to process EAF dust, the Waelz process is the most efficient. According to certain evaluations, about 85% of the total quantity of EAF dust involved in recycling in world industrial practice is processed using the Waelz method. Processing EAF dust using the hydrometallurgical method is hampered; the main factor preventing its commercially profitable use is the high content of difficult-to-decompose zinc ferrite. Chlorine and fluorine, which are not removed during leaching, also create additional problems associated with the failure

of the cathode and anode, as well as zinc separation from the cathode during the further electrolytic recovery of zinc [15].

The decomposition of zinc ferrite in practice of the Waelz process is provided by carbothermal reduction at above 1250°C [16]. High-cost coke is applied in this case (up to 200 kg/t_{dust}). To decompose $ZnFe_2O_4$ in various materials, process flowsheets have also been developed with preliminary calcination at low temperatures in the presence of Na_2CO_3 [17], carbothermal reduction in a weakly reducing atmosphere [18], roasting with elemental sulfur [19], etc. The authors [20, 21], in order to reduce ferrite formation and decompose zinc and cadmium ferrites, proposed to use calcium oxide in roasting of zinc concentrates.

In this study, calcium oxide was tested as a component promoting the decomposition of zinc ferrite in the EAF dust during pyrometallurgical processing without using coke fines combined with the removal of chlorine and fluorine. The possibility of such metallurgical processing was verified by thermodynamic calculations and experiments using a laboratory furnace.

EXPERIMENTAL

Calculations of the necessary amount of lime to decompose ZnFe_2O_4 were carried out using the HSC Chemistry 5.11 software [22]. The equilibrium composition of components was determined using the minimization method of the Gibbs free energy for isobaric-isothermal conditions. Equilibrium states were calculated for $t = 1000^\circ\text{C}$ and total pressure $P = 1$ atm. The calculation was performed for 100 kg of the EAF dust. The gas phase with the composition 20% O_2 + 80% N_2 was specified. The experiment based on the results of calculations was performed using a laboratory furnace.

The elemental composition of the dust and clinker samples was investigated by atomic emission, atomic absorption, and X-ray fluorescent spectroscopy using Jobin-Yvon Ultima 2 (France), Therm Fisher Scientific iCE3500 (United States), and ARL QUANT'X (Switzerland) devices, respectively. The sulfur and carbon contents were determined using a Leco SC-400 device (United States). The phase composition of the samples was investigated using an ARL X'TRA diffractometer (Switzerland) with X-ray radiation CuK_α . Iron-containing phases were analyzed using Ms-1104Em Mössbauer spectrometer (Russia) in a constant acceleration mode with the Co-57 source in an Rh matrix.

RESULTS AND DISCUSSION

The elemental composition of the EAF dust is presented below, %:

Fe	19.57	C	1.68
Zn	21.46	Cl	2.41
Pb	1.59	Na	6.36
Ca	7.59	Al	0.61
Si	3.56	P	0.25
Mn	3.11	Cr	0.42
K	2.75	Cu	0.28
Mg	1.54	Ti	0.12
S	0.88		

X-ray phase analysis has shown that the dust contains fractions of franklinite (ZnFe_2O_4), zincite (ZnO), magnetite (Fe_3O_4), graphite (C), sodium chloride (NaCl), and potassium chloride (KCl). Spectral lines that we failed to reliably prescribe to the phases most likely correspond to parameters of compounds $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, Mn_2O_3 , and PbO.

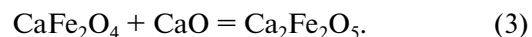
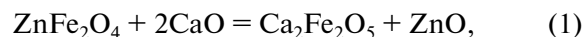
The analysis of iron phases of the dust by the Mössbauer spectroscopy indicates that 66% of iron atoms is present in ZnFe_2O_4 , while 34% is a part of Fe_3O_4 .

Based on the data of the chemical analysis, X-ray phase analysis with the Rietveld refinement, and an analysis of iron phases by the Mössbauer method, the composition of the EAF dust for further thermodynamic calculations was accepted as follows (components with a low content were not taken into account), %: 51.1 ZnFe_2O_4 , 30 ZnO , 2.9 Fe_3O_4 , 7.6 $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, 1.9 NaCl, 1.2 KCl, 2.5 C, 0.4 PbO, and 2.4 Mn_2O_3 .

Figure 1 shows the dependence of equilibrium amounts of compounds based on zinc, iron, and calcium in the dust on the weight of added CaO.

Thermodynamic calculations point out the transition possibility of zinc oxide into an independent phase. It is established by calculations that, in order to decompose 90% ZnFe_2O_4 , it is necessary to add no less than 46% CaO, while in order to decompose more than 95% ZnFe_2O_4 , no less than 60% CaO should be added.

The decomposition of zinc ferrite with calcium oxide occurs according to reactions



In addition, thermodynamic calculations have indicated the possibility of the almost total sublimation of chlorine and fluorine—mainly in the form of sodium, potassium, and zinc halogenides, as well as of lead in the form of chloride and oxide.

Figure 2 shows the influence of temperature on the change of Gibbs energy of reactions (1)–(3). It follows from these data that these reactions are thermodynamically possible. The formation reaction of dicalcium ferrite is most probable.

Based on calculations, we performed an experiment using a laboratory furnace. The EAF dust was mixed with powderlike lime in an amount of 60% of the dust weight and the CaO content in lime was 79%. The granulated and slightly dried mixture was preliminarily calcined in a laboratory rotary furnace in air at $t = 1000^\circ\text{C}$ for 4 h. The elemental composition of the formed clinker is presented below, %:

Fe	12.61	C	0.15
Zn	14.93	Cl	0.02
Ca	30.37	Pb	0.14
Si	4.37	Al	0.53
Mn	1.77	P	0.13
K	0.50	Cr	0.23
Mg	0.71	Cu	0.19
S	1.97		

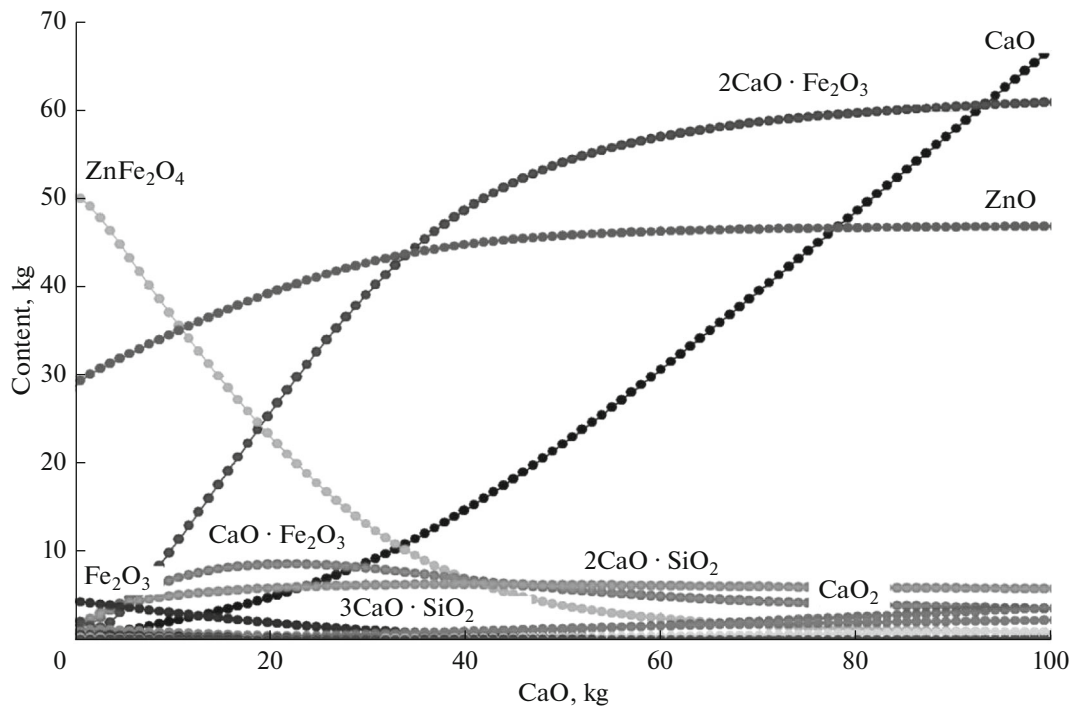


Fig. 1. Dependence of equilibrium contents of compounds based on Zn, Ca, and Fe in the EAF dust on the amount of CaO added under oxidizing conditions at $t = 1000^{\circ}\text{C}$.

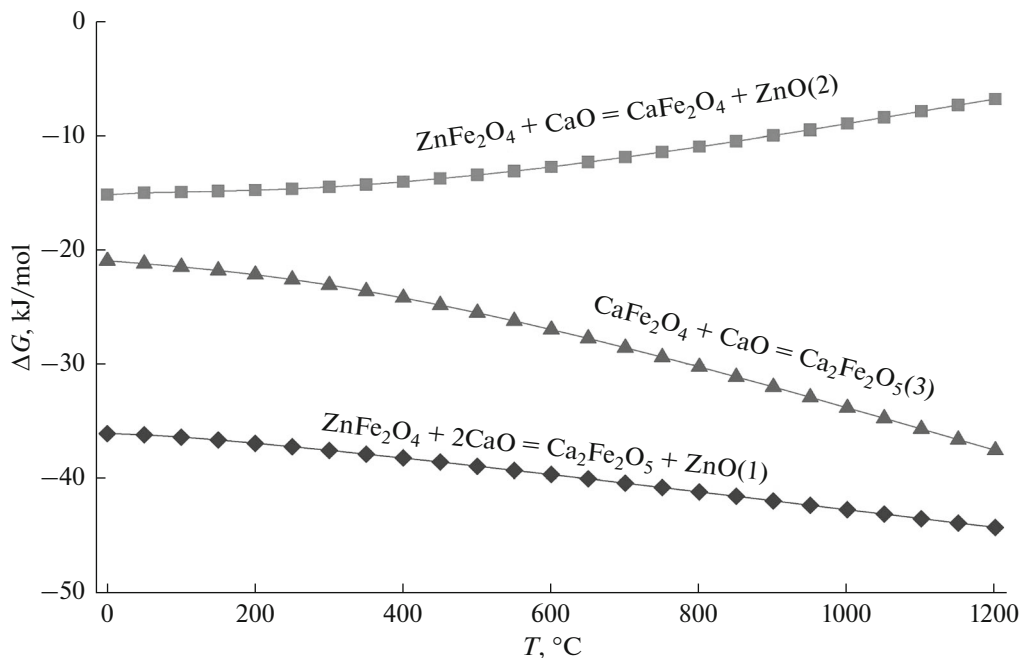


Fig. 2. Influence of temperature on change of Gibbs energy of reactions (1)–(3).

According to the X-ray phase analysis data, the clinker contains phases of dicalcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$), franklinite (ZnFe_2O_4), zincite (ZnO),

dicalcium silicate (Ca_2SiO_4), and calcium sulfate (CaSO_4). The calculation of the Mössbauer spectrum of the clinker shows the following distribution of iron

atoms: 19% is present in $ZnFe_2O_4$ and 81% is a part of $Ca_2Fe_2O_5$. The results have indicated on the decomposition of zinc ferrite according to the most thermodynamically probable reaction (1). The yield of sublimates was 50 kg per 1 t of the EAF dust, and sublimates contained, %: 29 Pb, 15 Zn, 17 Cl, 0.2 F, 0.5 Fe, 3CaO, and 5 (K + Na).

Thus, investigations of the elemental and phase compositions of the samples have shown that an increase in the amount of zinc in a soluble form and sublimation of halogenides, mainly of lead and alkali metals, were observed during the 4-h calcination of the EAF dust with 60% lime at $t = 1000^\circ\text{C}$. However, no complete transition of zinc into a soluble form has occurred, as it was predicted based on the results of calculations graphically shown in Fig. 1. In order to transform zinc ferrite into a soluble oxide form, the lime consumption should be increased.

CONCLUSIONS

Our investigations have shown that the calcination of electric arc furnace dust in the presence of lime can apply to transform zinc from ferrite into a soluble oxide form. Intermediate products for the recovery of zinc (clinker) and lead (sublimates) can be obtained from the calcination. After zinc leaching, an iron-containing product applicable in ferrous metallurgy can be prepared.

The proposed process has the following advantages when compared with the well-known Waelz technology, where coke is used as a reducing agent, while zinc also transfers into sublimates in addition to halides and lead:

(i) the amount of zinc remains almost invariable during the entire process (zinc remains in clinker);

(ii) the process occurs in a furnace, where zinc oxide in a ferrite structure is separated as ZnO by the reaction with CaO to form stable $Ca_2Fe_2O_5$;

(iii) coke is not almost consumed as a reducing agent;

(iv) the second Waelz stage necessary to purify zinc oxide fed for leaching from halides is excluded;

(v) the leaching residue is $Ca_2Fe_2O_5$, which is an efficient slag component for steel production;

(vi) the process occurs at a lower temperature (1000°C) when compared with the well-known technology (1250°C);

(vii) the system of gas cleaning from dust is simplified (the yield of sublimates reduces by a factor of 6–8);

(viii) the formed sublimates have a high lead content and can be used in lead production.

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