CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 52 (2016) 143–151

Contents lists available at ScienceDirect

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

journal homepage: www.elsevier.com/locate/calphad

Invited article

Thermodynamic analysis of the carbothermic reduction of electric arc furnace dust in the presence of ferrosilicon

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ARTICLE INFO

Article history:
Received 1 September 2015
Received in revised form
29 November 2015
Accepted 29 November 2015
Available online 7 January 2016

Keywords:
Electric arc furnace dust
Ferrosilicon
Zinc recovery
Slag formation
Kinetic condition

ABSTRACT

Thermodynamic analysis of zinc recovery from electric arc furnace (EAF) dust by carbon in the presence of ferrosilicon was studied. A preheating process was performed to remove volatile compounds from dust to avoid impurities in the final zinc product. The main process includes reduction of zinc oxide and gasification and condensation of zinc vapor. Equilibrium condition was computed using FactSage program for the processes of reduction and gasification. The effect of ferrosilicon addition on the recovery of zinc was investigated for the temperature range of 950–1050 °C at the constant pressure of one atmosphere. It is shown that ferrosilicon provides a better kinetic condition for zinc recovery by facilitating slag formation. The preferred condition for formation of liquid slag was predicted based on thermodynamic calculations and verified by performing some experiments. The experimental results show that good agreement between calculations and experiments can be obtained with higher amounts of silicon contents and at higher temperatures where liquid slag is presented. A mixture of the dust with 10% C and 7% FeSi(75%) can be used to achieve over 97% zinc recovery.

1. Introduction

Electric arc furnace dust is classified as a hazardous material because of the presence of heavy metal constituents (i.e., leachable lead, cadmium and hexavalent chromium) [1–4]. More than 6 million tons of EAF dust is annually produced worldwide, which has to be treated to comply with the environmental regulations. One common choice of treating this toxic material is stabilization and landfilling. EAF dust contains significant amounts of zinc and iron. Since the use of galvanized steel continues to increase in the automotive industry, the amount of zinc in the dust will rise concurrently. There are many different processes to recover zinc from EAF dust [5–12].

Today, about 30% of the industrial zinc is produced by recovery from secondary zinc resources such as galvanized sheets and steelmaking dusts [13]. Zinc recovery from EAF dust is economically feasible when zinc concentration is more than 15% [14]. Pyro-metallurgical treatments are main industrial technologies for zinc recovery from EAF dust whereas 80% of recycled dust is treated by Waelz kiln process. In pyro-metallurgical methods EAF dust is reduced at a high temperature. Zinc can be recovered from the vapor and the iron can be recovered in the form of liquid metal.

Many researchers have studied different aspects of zinc recovery from EAF dust in pyrometallurgical processes. In most of these works carbonaceous materials are used as the reductant. Pickles [15] studied the reaction of EAF dust with solid iron powder in argon atmosphere and reported zinc recovery of 87% at 1050 °C. In another work [16] he considered the reaction of EAF dust with molten pig iron containing carbon and silicon. He showed that in this process, zinc can be completely reduced and recovered in the form of crude zinc oxide.

Silicon can be an alternative reducing agent for carbonaceous materials. Fig.1 shows changes in standard free energy of oxidation for silicon, zinc, iron, wustite and magnetite by considering the following reactions.

$$4Fe_3O_4(s)+O_2(g)=6Fe_2O_3(s) \quad (1)$$

$$6FeO(s)+O_2(g)=2Fe_3O_4(s) \quad (2)$$

$$2Fe(s)+O_2(g)=2FeO(s) \quad (3)$$

$$2Zn(s)+O_2(g)=2ZnO(s) \quad (4)$$

$$Si(s)+O_2(g)=SiO_2(s) \quad (5)$$

As it can be seen in Fig. 1, silica is more stable than zinc and iron oxides and therefore reduction of these oxides by silicon is

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http://dx.doi.org/10.1016/j.calphad.2015.11.003
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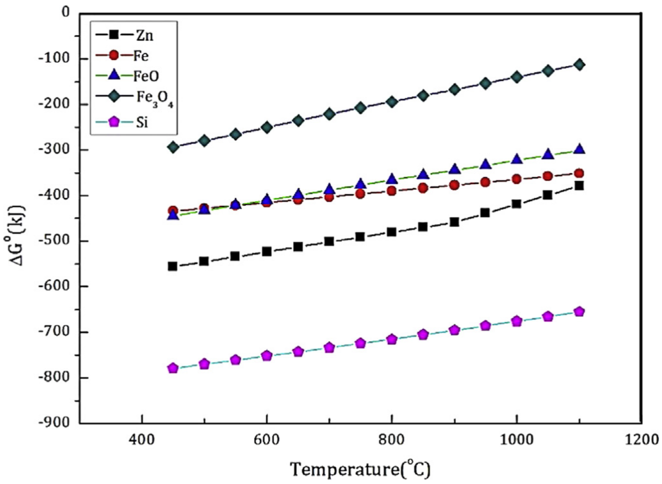

Fig. 1. Standard free energy changes of oxidation for Zn, Fe, FeO, Fe_3O_4 and Si according to reactions (1–5).

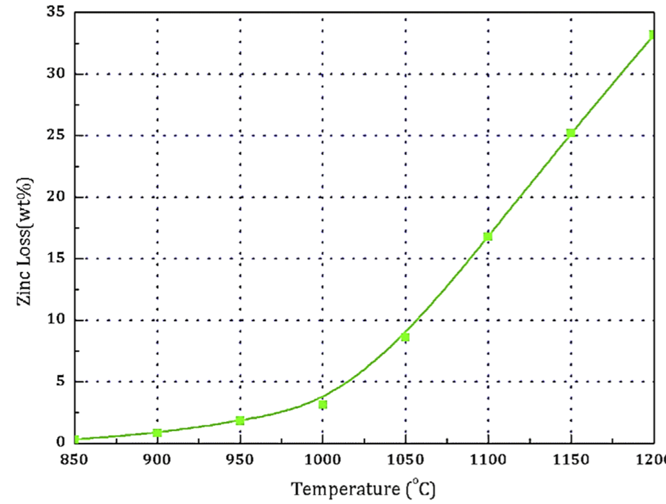

Fig. 2. Calculated zinc loss during the pretreatment of EAF dust.

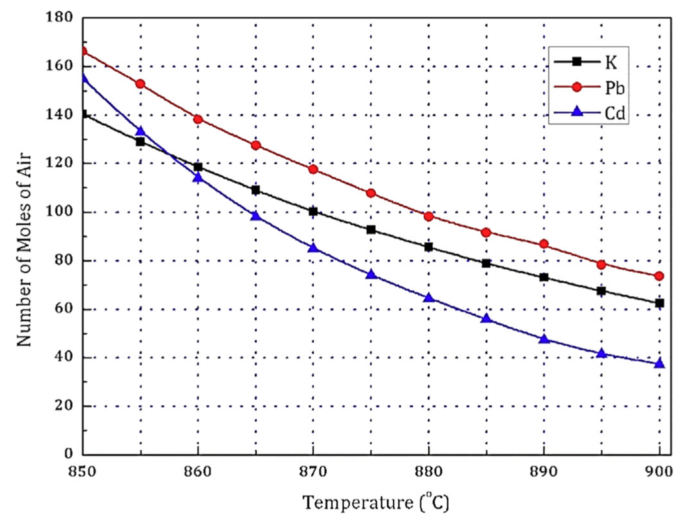

Fig. 3. Calculated amounts of air needed for 95% removal degree of volatile species during the pretreatment.

thermodynamically possible. Using silicon for reduction of EAF dust increases silica content of the residue and forms low melting temperature slag. This could enhance the rate of reactions by increasing the mass and heat transfer in the condense phases. Due to the higher cost of silicon use of a mixture of silicon and carbon are proposed as the reducing agent for the zinc recovery from EAF dust. The aim of the present research is to investigate the thermodynamic conditions for reduction of EAF dust by a mixture of carbon and ferrosilicon. Alkali halides and lead oxide are usually problematic in the recovery of zinc from EAF dust, especially in the zinc metal recovery processes. Therefore, according to the literature [17,18] a preheating step for removing the more volatile species from EAF dust at a lower temperature was suggested. In this pretreatment, volatile impurities such as PbO, NaCl, KCl and CdO are removed from EAF dust.

2. Thermodynamic calculations and experiments

2.1. Calculations

FactSage 6.1 program was used to study the equilibrium conditions of the reactions involved in the heat treatment process. EQUILIB (a module of FactSage) [19] utilizes the chemical composition of reactants in the form of compounds or elements as the input and determines the combination of the most stable products at any desired temperature and pressure. Calculations are based on minimization of Gibbs free energy of the system at isothermal and isobaric conditions.

For the pretreatment, heating of 100 g dust in the presence of different amounts of air as a carrier gas was studied. Then, computations of thermodynamic equilibrium of the pretreated dust (solid residue remaining from the pretreatment) with different amounts of carbon and ferrosilicon at different temperatures were performed. The amounts of carbon and ferrosilicon were increased from 1 to 20 g by a step size of 1 g. Temperature was increased from 850 °C to 900 °C in steps of 5 °C for pretreatment and from 950 °C to 1050 °C in steps of 10 °C for the reduction. Input data was introduced to EQUILIB program in the form of elemental composition. The chemical compositions of the real EAF dust samples before and after pretreatment were used.

2.2. Experiments

EAF dust was obtained from an alloy steelmaking company in Iran. Graphite powder was provided by Sinopharm Chemical Reagent Co. Ltd. and ferrosilicon powder containing 75% silicon and 25% iron from Iran Ferrosilice Co. was used. Chemical composition of the EAF dust and the residues of the pretreatment were analyzed by an inductively coupled plasma-mass spectrometer (ICP-MS, Spectro MS). The carbon content of the dust was determined by a Leco CS 244 analyzer.

For the pretreatment process, 100 g EAF dust was heated in an alumina boat (200 mm in length, 100 mm in width and 30 mm in height) by an electric furnace at 875 °C for 4 h and cooled inside

Table 1
Chemical composition of the EAF dust.

Element	Fe	Zn	Ca	Pb	Na	Mg	Al	Cd	Cr	K	Si	C	Cl
wt%	30.0	19.02	4.5	0.99	3.38	4.99	0.53	0.04	0.34	0.16	0.16	2.1	6.45