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Theme: Eletric Steelworks

EAFD GENERATION – TERMODINAMIC ANALISYS OF Fe-Zn-O-Cl-H-C SYSTEM*

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Abstract

The steel production in mini mills generates several process residues, among them there is the electric arc furnace dust (EAFD). This residue has as main elements Fe, O, and Zn, being classified as hazardous by the presence of Pb and Cd. Thermodynamic studies related to the formation of mineral species containing Fe, O and Zn elements were carried on due to the influence of these compounds in hydrometallurgical EAFD recycling processes. In recent years, a rise in the chlorine content of this residue was observed, mainly motivated by the increased use of scrap with polymeric impurities containing this element. In this work, based on computational thermodynamics tool FactSage, a general overview of gaseous and minerals species (found in EAFD) formed by Fe, Zn, O, Cl, H and C is shown – representing the organic origin of chlorine. For this study, the PVC polymer was used as the chlorine carrier substance which contaminates the EAF load.

Keywords: EAFD; Fe-Zn-O-Cl-H-C system; Computational thermodynamics.

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1 INTRODUCTION

1.1 Chlorine in EAFD

The technology used in steelmaking by most semi-integrated plants or *mini-mills* is the electric steel melting shop, which employs as scrap melting equipment the electric arc furnace, EAF, and as refining equipment the ladle furnace, LF. With the melting of the load, electric arc furnace dust, EAFD, generation occurs at a ratio ranging between 1 and 2 wt.% of the steel plant production. This waste comes from vaporization of ferrous and non-ferrous metals, ejection of particles from the metal bath, dragging of slag and other charge materials, etc. According to Guézennec *et al.* [1], the main dust forming mechanisms are: volatilization (27 wt.% of the EAFD) and bursting of carbon monoxide (CO) bubbles (60 wt.% of the EAFD); the direct fly-off of solid particles takes place, but is limited – provided that sufficient operating caution is taken. This residue, in the form of fine particles, is adduced from the oven together with gases from the melting and refining of the load, and intake air for post-combustion and cooling stage.

The EAFD composition depends on scrap and other process input materials. Formation mechanisms and the specific parameters of each plant interfere with the formation of different mineral species. Thus, EAFD is the end result of a series of phenomena that have occurred since their initial birth in the oven (type and amount of scrap, added materials, etc.), to the successive physical-chemical equilibria by which matter passes during its trajectory from the oven to the dust control system. In general, the major mineral species found in the EAFD are solid oxides of iron and zinc: zincite (ZnO) and franklinite ($ZnFe_2O_4$), iron found in EAFD, in addition to franklinite, is contained primarily in magnetite (Fe_3O_4) [2]. Other elements may also be present in varying concentrations in the EAFD.

In recent years an increase in chlorine content, motivated by the increased use of scrap containing this element as impurity, has been observed. Often chlorine becomes the most abundant element in EAFD after iron, zinc and oxygen. Average contents of about 5% by weight of chlorine in the dust have been reported [3]. Because of this, depending on the concentration, chlorine can interfere with formation of mineral species of iron and zinc, and in the reuse and treatment of EAFD, both pyrometallurgical as hydrometallurgical [4].

1.2 Chlorine Path in Electric Steelworks

The source of chlorine element in the EAFD may be located in materials of organic nature, such as polymers, paints, oils, waste rubber, etc., as well as in the inorganic materials (mineral species) accompanying the scrap; it is likely that contribution of organic matter is much greater than that of inorganic.

During the loading step of the EAF, through large buckets (baskets) carried by bridge crane, it is common to observe the formation of flames and fumes when the scrap load reaches the furnace. These emissions result from the pyrolysis of organic compounds adhered to scrap when it undergoes an abrupt warming in contact with the walls and the heated material present inside the EAF. The compounds formed by pyrolysis, in sequence, combust with the surrounding air forming gases, however, a possible formation of particulate matter can not be rule out during the operation.

This gas stream is collected by the hood and routed to the dedusting system, which mixes it with the general gas flow from the operation of the exhaust system. At the

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end of this step, the solid particles are retained in filter bags, and come to constitute a part of EAFD.

The melting of the load starts after the closing of the dome roof of the EAF and the introduction of graphite electrodes. At this stage the formation of the EAFD itself begins, since the reached temperatures are increasing and the zinc is volatilizing in the scrap. During this step the pyrolysis of the remaining organic compounds also occurs; consequently the conditions for the occurrence of the reactions between iron, oxygen and other existing elements in the load are being established.

Thus, both during loading and during melting of the charge, the pyrolysis of organic compounds containing chlorine leads to simpler gas compounds, especially hydrochloric acid [5]. However, due to the high reactivity of this chemical element, during its passage through the stages of the process he must engage in various chemical reactions with the transmutation of the chemical species containing it, because of the different conditions to which it is subject. And in the end, it may interfere even with the formation of zinc and iron oxides found in EAFD.

Consequently, the species containing chlorine (and its concentration), both in gaseous emissions, as well as in the dust collected in the dust collection system will be established mainly as a function of (i) the other chemical species present in the scrap and (ii) the prevailing physico-chemical conditions in the production of steel in electric steelmaking process.

Studies aiming to analyze the various nearby conditions and the mineral species (and thermodynamic phases) constituents of EAFD that are established from the three main elements of the dust, namely: iron, zinc and oxygen, were made in some previous works [6,7]. In this work, a new thermodynamic approach is taken, considering besides, the presence of the elements chlorine, hydrogen and carbon originating from the pyrolysis and combustion of organic matter.

One should distinguish this work from others [8,9], which aim to study the possibility of recovering metals from PAE using chlorine and are included chemically in the processes of chloridizing roasting.

The objective of this work is therefore to study the role and influence of chlorine, hydrogen and carbon (Fe-Zn-O-Cl-H-C system) in forming gas and mineral species present in EAFD.

2 METHODOLOGY

2.1 Software and Databases

The thermodynamic equilibrium states for every system under study in the present work were determined using the *Equilib* module of *FactSage* software (version 6.4) – software is described elsewhere by Bale *et al.* [10].

The following databases were employed:

- FSstel - FactSage steel intermetallic compounds and alloy solutions;
- FToxid - FACT oxide compounds and solutions database;
- FactPS - FactSage compound database.

2.2 Simulation Conditions

In the study of dust from electric arc furnaces with the presence of the element chlorine (plus H and C) by means of thermodynamics was considered a hypothetical

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composition for EAFD, as indicated in Table 1, which is based on characterization data exposed in the literature.

Table 1. EAFD hypothetical composition

Element	Fe	Zn	O	Cl	Other
Wt.%	44	11	21	5	19

The amount of chlorine effectively used was obtained by trial and error, adding the input amount of material and, next, controlling the outcome of the final composition of EAFD (it is noteworthy that the amount of chlorine is something bigger than that refered in EAFD, because the chlorine is carried out with the gaseous emissions).

Chlorine was added in the system followed by the carbon and the hydrogen, reflecting its probable organic origin. The ratio of C, H and Cl in the compound Polyvinyl chloride (C_2H_3Cl), PVC, was chosen, so that three moles of hydrogen and two moles of carbon are introduced into the system each time a mole of chlorine is added.

Reflecting what succeeds in post-combustion system, (excess) air was added to the system until the nitrogen content of the gas stream composition had a partial pressure close to that of air (~78 vol.%).

It was considered that the air had a relative humidity value of 60%, at 25ºC of temperature, reflecting a common value, found in many places in the world.

The weight fraction of Fe with respect to iron and zinc in the system (Fe/(Fe + Zn)) was selected and maintained in 80%, *i.e.*, according to previous publications, it means that the dust would be mineralogically a mixture of minerals franklinite and hematite.

The other elements in the system have been considered inert, not interfering in chemical reactions with the six main elements.

The simulation results were followed over a decreasing temperature, simulating a cooling process.

3 RESULTS AND DISCUSSION

The present thermodynamic analysis was made considering only six elements on EAFD – namely: Fe, O, Zn, Cl, H and C. Any analysis considering few elements, *i.e.* taking into consideration a system that is far more simpler than a real one – like the intricate situation existing inside an EAF –, is subject to error. Yet, simplicity is frequently essential for clarity and understanding of complex problems. Moreover, knowledge of the phase relations in lower order (binary and ternary) systems is crucial for a better understanding of higher order (quaternary, quinary etc.) systems.

3.1 Analysis of the Gas Phase

The concentration of the gas phase constituents at equilibrium were determined and their minor components are presented as a function of temperature in Figure 1.

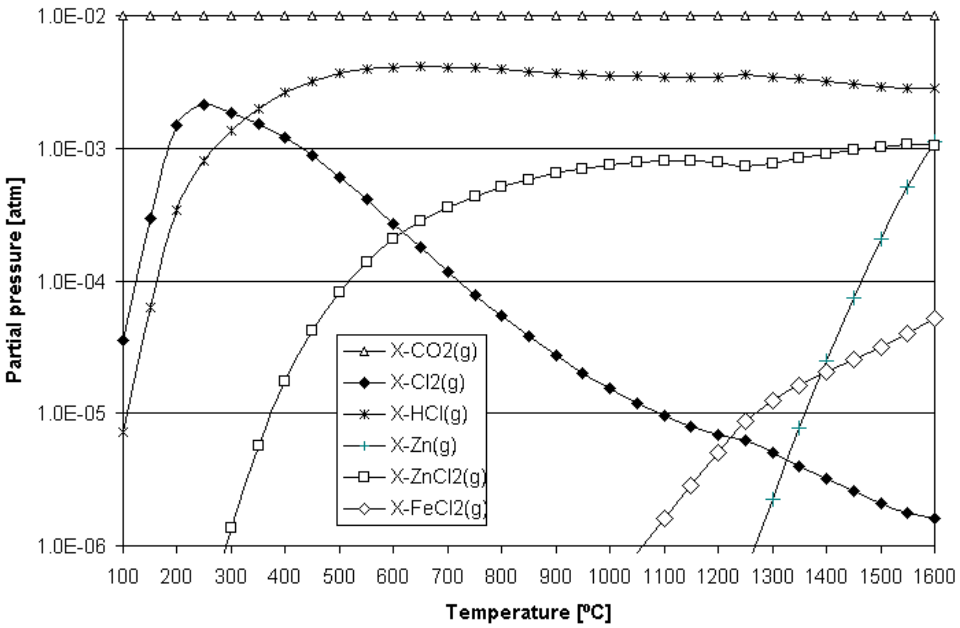

Figure 1. Concentration of the minor constituents of the gas phase as a function of the temperature.

Analysis of the minor constituents of the gaseous phase show that, at high temperatures, the chlorides of zinc, iron chloride and gaseous Zn coexist. Along with them, with the highest molar fraction is HCl. With the cooling of the gas phase, the chlorides disappear, but not HCl, which only shows the same trend of decline when the temperature is reduced to below 300-400ºC. Opposed to this trend, chlorine gas, gradually increases its share, to the extent that the temperature decreases. But this trend is reversed (suddenly) at ~250ºC. To find a reasonable explanation for this phenomenon, one must analyze the condensed phases.

3.2 Analysis of the Condensed Phases

Initially, in order to provide a reference, the phases (and the proportions between them) will be presented in the system at equilibrium, without the presence of elements Cl, H and C, as a function of temperature, Figure 2.

The result of these determinations shows that for the composition chosen for the system, at a temperature of 1600ºC, among the various condensed phases that could participate in the equilibrium state, there is in fact only spinel. This phase increases its mass slightly but, in the temperature range between 1250 and 700ºC, there is a steep decrease. At 1250ºC, hematite phase also appears in the system. The hematite, on the contrary, makes the opposite direction, increasing its mass in the same direction of the decreasing temperature. The masses of the two phases finally stabilize and the ratio between them is fixed at a constant value between 700 and 100ºC.

Therefore, at the end of the cooling stage there is no other phase in the system behind the gas phase, hematite and spinel.

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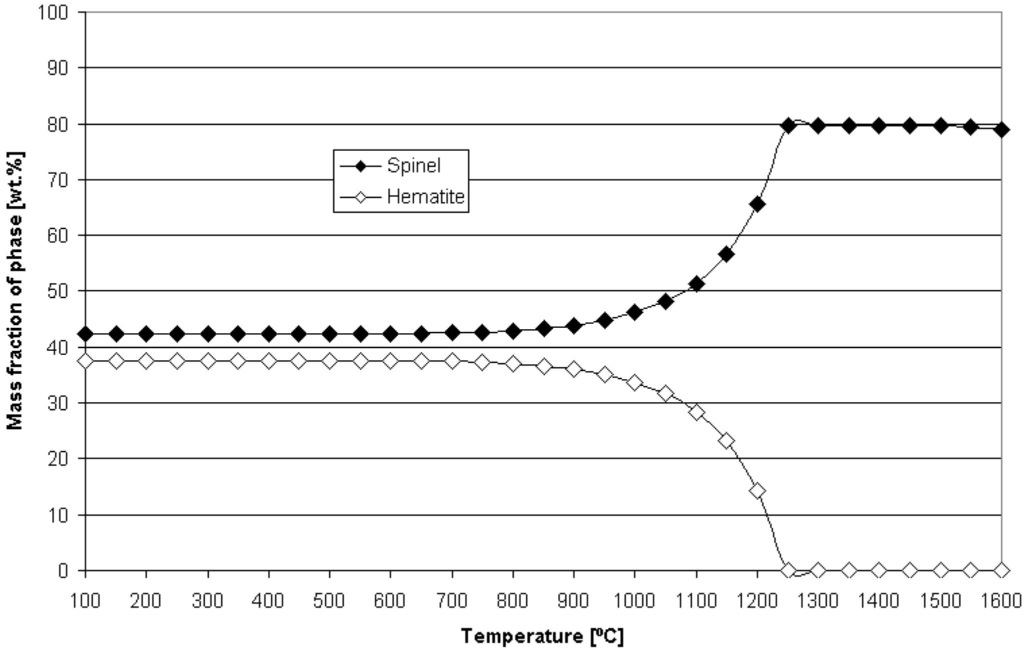

Figure 2. Schematic representation showing the condensed phase amount as a function of the temperature; Fe-Zn-O reference system.

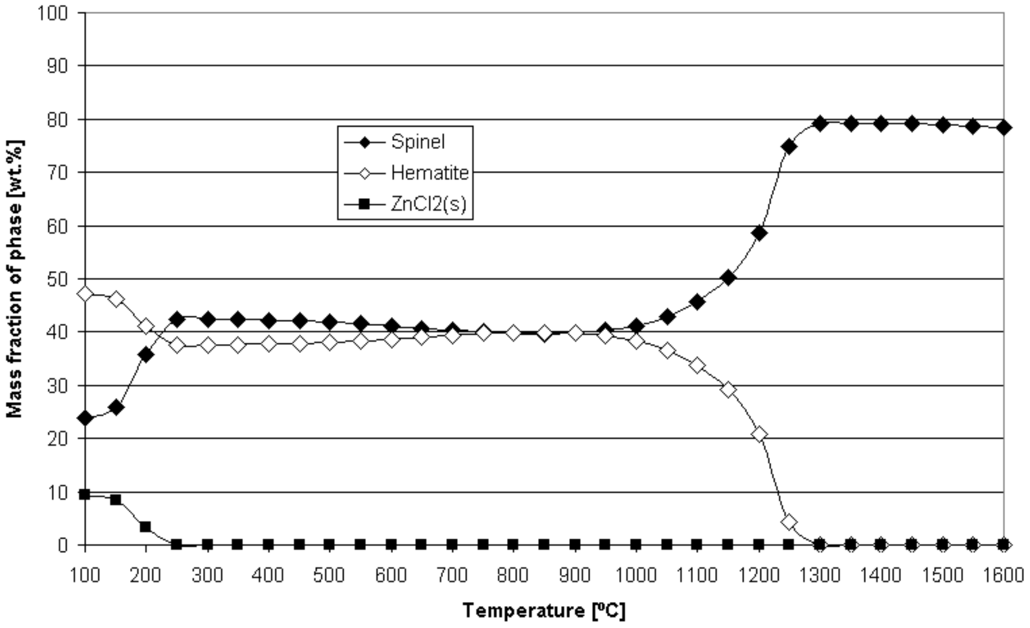

Figure 3. Schematic representation showing the condensed phase amount as a function of the temperature; Fe-Zn-O-Cl-H-C system.

Having the presence of Cl, H, and C in the system, the content of the spinel phase present at equilibrium is already somewhat lower compared to the system without those elements, at a temperature of 1600ºC. Between 1250 and 700ºC, in comparison with the reference system, the amount of spinel is smaller (at most equal to) the corresponding value of the reference system, while the opposite happens with the hematite phase.

In a few words, this means that chlorine in the gas phase 'extracts' zinc from franklinita (spinel) transforming it into hematite. This trend reaches its peak at 1000ºC. For lower temperatures the trend reverses slowly and finally, around 250ºC,

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the masses of spinel and hematite result to be exactly those existing in the system without chlorine, hydrogen and carbon.

From then on the two systems move away again, with a sudden lowering of the mass of the spinel phase, accompanied by the rapid growth of hematite. The condensed phase $ZnCl_2$ appears concomitantly; this fact may explain, ultimately, the decrease in the levels of chlorine gas and HCl previously observed in the analysis of gas phase.

There would be enough energy in the system to overcome the activation energy barrier that would trigger these transformations? The answer to this question is difficult to be given only by thermodynamics. One can, however, speculate that if this does not occur, then the level of gaseous species containing chlorine probably will not change, and the relatively high concentrations found in average temperatures will be maintained.

In any case, by the data from chemical analysis, it is known that there are chlorine-containing phases in EAFD.

3.3 Other (Numerical) Results

Some determinations were made on the atmosphere for Fe-Zn-O-CH-Cl system. They refer to the temperature of 105°C. The results can be seen in Table 2.

Table 2. Concentration of selected chemical species in gas hase

Chemical species	Unit	Value
$HCl_{(g)}$	mg/Nm^3	15.01
Cl as Cl_2	mg/Nm^3	142.7
Air humidity	%.Vv.	2.68
CO_2	%.Vv.	1.02
O_2	%.Vv.	17.3
N_2	%.Vv.	79.0

4 CONCLUSIONS

The thermodynamic simulation on EAFD genesis within the Fe-O-Zn-Cl-H-C system, considering the limited temperature range and the fixed composition of the mass input, showed that primarily iron oxides – mostly hematite and spinel (of iron and zinc – are generated), according to the proportion of components Fe and Zn in the charge.

The lone condensed phase containing chlorine appears at the end of the cooling process, below 250ºC, and is $ZnCl_2$.

Chlorine, in the intermediate zone of temperatures, concentrates in the gas phase with the chemical gaseous species HCl, Cl_2, $ZnCl_2$.

It should be noted that the speciation of chlorine compounds presented here refers only to the Fe-Zn-O-CH-Cl system. The presence of other elements in the system can change the formation of the species described here.

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