THERMODYNAMIC ANALYSIS OF EAFD GENERATION AIMING AT THE RECYCLING: SYSTEM Fe-O-Zn[1]

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Abstract

The steel production in semi-integrated mills generates process residues, among which there is the electric arc furnace dust (EAFD). The EAFD contains the element zinc that bears economic interests capable to motivate its extraction. Based on a computational thermodynamics tool, theoretical considerations are made on iron and zinc compounds which can form during the production of steel in electric arc furnace, in particular the conditions for ZnO formation. In this work a study was made also of the compositions of the solid and liquid phases from the systems Fe-O and Fe-O-Zn. It follows that an increase in the zinc content in the EAF charge tends to increase the ZnO content of the EAFD which favors the use of hydrometallurgical processes for recovery of zinc from the EAFD.

Key words: EAFD; EAFD mineralogy; Computational thermodynamics.

ANÁLISE TERMODINÂMICA DA GERAÇÃO DO PAE OBJETIVANDO A RECICLAGEM: SISTEMA Fe-O-Zn

Resumo

A produção siderúrgica em usinas semi-integradas gera resíduos de processo, dentre os quais pó de aciaria elétrica (PAE). O PAE possui o elemento zinco que apresenta interesse econômico capaz de motivar a sua extração. Com base na ferramenta termodinâmica computacional são feitas considerações teóricas sobre os compostos de ferro e zinco que podem se formar durante a produção de aço na aciaria elétrica, especialmente as condições de formação da ZnO. Neste trabalho foram estudadas também as composições das diferentes fases sólidas e líquidas dos sistemas Fe-O e Fe-O-Zn. Conclui-se que um incremento do teor de zinco na carga do FEA tende a elevar o teor de ZnO no PAE o que favorece a utilização de processos hidrometalúrgicos de recuperação do zinco do PAE.

Palavras-chave: PAE; Mineralogia da PAE; Termodinâmica computacional.

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1 INTRODUCTION

1.1 EAFD and Its Recycling/ Processing

During the production of steel in semi-integrated plants, the generation of waste such as slag, mill scale and dust from electric arc furnace (EAFD) is unavoidable.

Some of these wastes show a higher metal content, *e.g.* mill scale and EAFD. The mill scale is generated mostly in casting and rolling operations and is primarily constituted of iron oxides (the combined amount of mill scale and EAFD generated can reach between 3 to 4 [wt.%] of the crude steel production). EAFD is constituted basically of oxides of iron; nevertheless, when galvanized scrap is used in electric steelmaking, the main constituents of EAFD are oxides of iron and zinc.

Waste generation during the operation of electric arc furnace (EAF) occurs by vaporization of ferrous and nonferrous metals and ejection and dragging of steel and slag particles.

Due to the raw materials, temperatures and pressures used, compounds like Zincite (ZnO) and Franklinite ($ZnFe_2O_4$) are generated; also Iron is present in EAFD, (apart from Franklinite), mostly as Magnetite;(1) yet several other elements are present. Accordingly, EAFD is considered a hazardous waste in most industrialized countries since it fails the toxicity test for lead, cadmium and chromium.(2)

The costs for disposal of these wastes are not negligible (specially when considering the transportation costs to the place of processing or final disposal).

Alternatives for disposal have been discussed in previous studies,(3,4) including the co-processing in the cement clinker production. The mill scale has good disposition in this co-processing, however, EAFD has encountered difficulties, due to its high chlorine content.

Along with the alternatives already studied, the reintroduction of these wastes in the electric steelmaking process as self-reducing briquettes consisting of iron oxides (mill scale and EAFD) agglomerated with a binder and reducing agents, like charcoal fines has been suggested.(3,5)

'Compound briquettes' (produced by a mixture of mill scale with EAFD) show better mechanical strength than those made with EAFD only. These briquettes were already tested and results from preliminary trials were encouraging.(3)

Nevertheless, in order to consider the use of briquettes as a feedstock of the EAF, they must present also the ability to 'autoreduce' their metal oxides within the dynamics of operation for this equipment. This is particularly true since, currently, with shorter tap-to-tap times and optimization of energy consumption, the EAF reaches up to be a challenge as a reactor for waste oxide recycling.

An increase of zinc concentration in EAFD can be expected in case of industrial feasibility for the introduction of briquettes composed of EAFD and scale in the electric arc furnace. This effect of increasing the percentage by weight of zinc in the furnace load is similar to the use of a greater amount of galvanized scrap.

The accumulation of zinc in EAF dust must be attributed to its low solubility in the molten steel and slag. Fundamentally, this is due to an increased vapor pressure of zinc in relation to iron, at the process temperatures.

The zinc vapor is loaded along with gases and particles forming compounds which comprise the EAFD.

With the possible use of the 'compounds briquettes', besides the possibility of recovering part of the iron oxides in the waste, which would be reduced to metallic iron and incorporated into the bath of molten steel, there would still be the generation of a EAFD with characteristics different from the dust collected presently.

Among them, an increasing in the concentration of zinc is clearly expected. The resulting EAFD, at some appropriate time to be defined in future, must be referred to an appropriate destination or, alternatively, to undergo a process of treatment and recovery of metals contained therein.

In general, and especially in industrialized countries, the EAFD treatments commonly used aim mainly at the recovery of zinc.

1.2 Motivation

Several authors(2,6-8) agree to point out that, in hydrometallurgical processes to recover zinc from EAFD, both in alkaline and acid media, the more reactive forms, such as ZnO do not cause obstacles for their dissolution. On the other hand, Franklinite, which proves to be a very stable compound, requires more energetic treatment.

This is the case of technological routes using hydrochloric and sulfuric acids, which lead to a greater iron dissolution – a clear drawback for these processes. In any event, zinc remaining in the residue is always associated with the compound Franklinite.

Xia and Pickles(2) in their study of the recovery of zinc from EAFD in basic medium, consider that the processes that employ hybrid pyrometallurgical treatments for *primary decomposition of Franklinite*, followed by hydrometallurgical steps for the recovery of nonferrous metals, may be more advantageous than treatments that do not consider this step.

Takano et al.(9) report that in the case of low amounts of zinc present in the flue dust, there is a need for its recirculation or recycling in the electric arc furnace before application of technologies for the recovery of zinc. Thus the zinc content of the residue is increased, which makes the recovery process for the metal more competitive.

Due to these reasons, aim of this study is to perform a theoretical analysis of the formation of compounds containing iron, oxygen and zinc found in EAFD. Special emphasis is given to the conditions of formation of ZnO, compound which can promote the hydrometallurgical routes for the recovery of zinc from EAFD.

Last but not least, the work is focused especially on the question: what are the phases formed when the conditions of pressure and temperature are known? This question, of course, will have a response influenced by the system composition – ultimately, by the EAF load. However, to maintain the problem in a simple level, only the systems Fe-O and the Fe-O-Zn were considered.

2 METHODOLOGY

The thermodynamic equilibrium state for every system under study in the present work was determined by using the *Equilib* module of the *FactSage* software (version 6.2) – software is described elsewhere by Bale et al.(10)

The following databases were employed:

- FSstel - FactSage steel intermetallic compounds and alloy solutions [2009];
- FToxid - FACT oxide compounds and solutions [2009];
- FACT53 - FactSage compound database [2009].

For the sake of simplicity, most of the analysis was conducted at the O_2 partial pressure of 0.21 [atm].

3 THEORETICAL CONSIDERATIONS ON EAFD GENESIS

The three most abundant elements on EAFD are: Fe, Zn and oxygen. A thermodynamic analysis, considering only these three elements, will be conducted later. A preliminary analysis of the EAFD genesis considering only the system Fe-O will be made first, in order to serve as background for the ternary system analysis.

3.1 System Fe-O

Considering the temperature range between 800°C and 1,700ºC and O_2 pressures ranging from 1 to 1×10^{-10} [atm], there are several phases in the Fe-O system which may be found in the state of thermodynamic equilibrium – some are solids, other are in the liquid state (Figure 1).

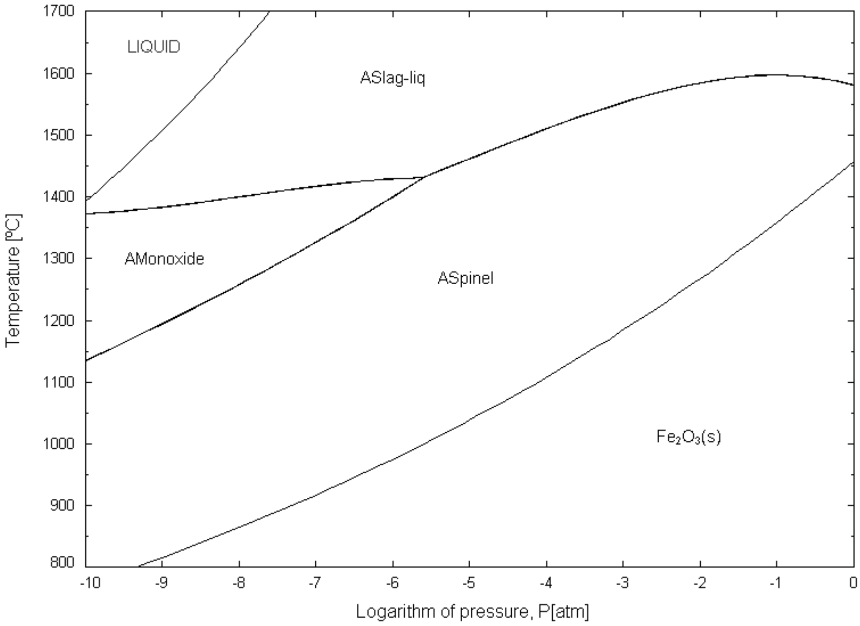

Figure 1. Fe-O phase diagram (temperature *versus* logarithm of pressure, pressure in atmospheres); denoted phases: LIQUID = solution of liquid iron with oxygen; ASlag-liq = liquid 'FeO' oxide; AMonoxide = FeO (wustite) solid solution; ASpinel = $FeO \cdot Fe_2O_3$ or magnetite (Fe_3O_4)

The Fe-O phase diagram depicted in Figure 1 is of the type which shows the stable phases (at a given temperature) as a function of oxygen chemical potential – though only the oxygen *pressure* is denoted. It is interesting to note, for binary systems of this type, no multiphase field exists.

It is apparent from this figure that the phase hematite (Fe_2O_3) is stable in a range of low temperatures combined with high oxygen partial pressures. If the partial pressure of this gas is reduced locally inside the EAF by injection of a reducing agent, or if the temperature is raised, there is a strong tendency to form the spinel phase (Fe_3O_4). Together, hematite and spinel cover up a wide range of temperatures and pressures and this can be the reason why they are so ubiquitous in EAFD.

For a combination of very low oxygen pressures with medium temperatures, FeO (wustite) solid solution will come to existence.

For higher temperatures – apart from the very low oxygen pressure corner –, all phases will be transformed into the liquid oxide phase. Particles of this phase in the EAFD would be recognized by the spherical form they should exhibit after solidification.

Given that all these phases are reported in the EAFD, it is undoubtedly clear that a wide range of oxygen potentials and temperatures do exist inside the electric arc furnace, or ducts by which the EAFD crosses in its way to the baghouse.

3.2 System Fe-Zn-O

In order to better study the Fe-Zn-O system, a slightly different approach was chosen. First, an oxygen partial pressure was fixed, which had the value of 0.21 [atm]. Only then the system composition was varied, with the zinc mass fraction being increased up to the value of 0.5.

For the above conditions, the stable phases in the system at the thermodynamic equilibrium state for the temperature range between 1,300°C and 1,600°C can be observed in Figure 2.

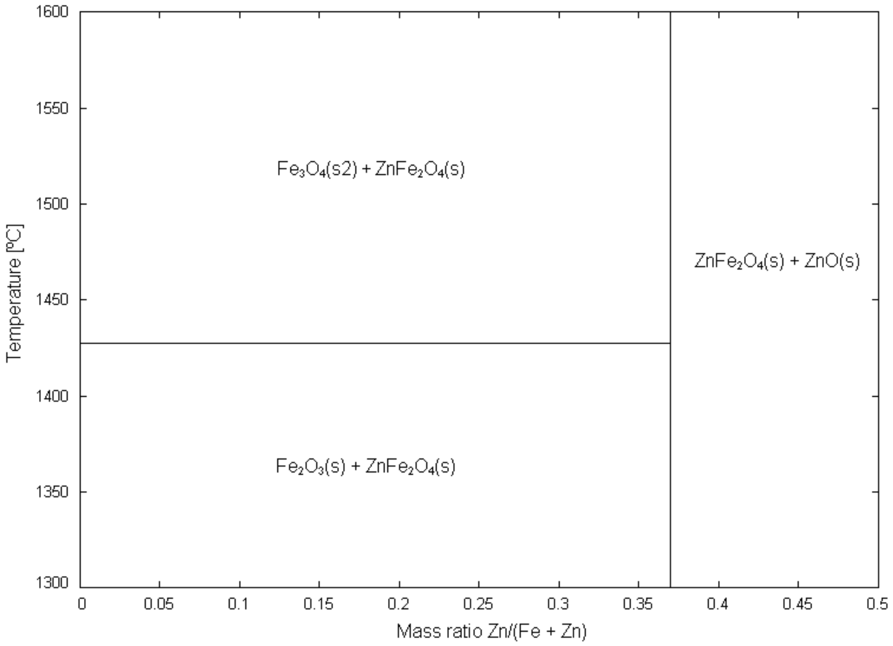

Figure 2. Fe-Zn-O phase diagram at system pO_2 = 0.21 [atm].

This figure can be seen as being a cross-sectional diagram at pO_2 = 0.21 [atm] in Figure 1.

With reference to that diagram, it becomes evident that the hematite/ magnetite transition temperature (Figure 2, *horizontal* line) is not fixed, being dependent on the oxygen partial pressure of the system – decreasing for a declining pO_2 pressure.

As only stoichiometric compounds were used to represent all the phases of the Fe-Zn-O system, the diagram is only schematic. Thus, the biphasic field displaying the mixture of magnetite (Fe_3O_4) and franklinite ($ZnFe_2O_4$) is in fact a monophasic field containing the single *solid solution* phase spinel, while the mixture between the phases franklinite and hematite, is, on the contrary, a *real* one.

This is an interesting fact because it shows a potential for ‘concentrating’ the Zn metal in the spinel phase if the EAFD is born in a temperature which is lower than the transition temperature.

That is, for a fixed mass fraction of Zn/ (Zn + Fe) between 0 and ~0.35, under a system temperature *lower* than the spinel-hematite transition temperature, metal Zn takes part solely of the spinel phase; conversely, iron bounded to the hematite phase is free from Zn (to be precise, the thermodynamic description of phase hematite, Me_2O_3, named 'FToxid-CORU' in FACT oxide database (FToxid), portrays a solid solution between several oxides other than zinc oxide).

When, instead of the stoichiometric compounds, *solid solution* phases are used to describe the thermodynamics of the Fe-O-Zn system, the phase boundaries changes drastically.

For instances, for a system temperature below the transition one, the biphasic hematite-spinel field is, in some way, drastically reduced (Figure 3).

Though, the effect just described, which is, the concentration of metal Zn in the spinel phase, is albeit clearly visible: for any composition from 0 to ~0.15 mass fraction Zn, Zn content in spinel phase is constant, *ca.* 10 wt.% Zn (Figure 4).

Above ~0.15 till around 0.35 mass fraction Zn, spinel is the sole phase present in the equilibrium state of the system. Within this range, zinc concentration grows steadily from 10% up to ~26 wt.% Zn.

Higher concentration of Zn can be found naturally in phase ZnO; nevertheless it occurs only above ~0.35 mass fraction Zn.

As seen before, for system temperatures higher than that of transition, the hematite field disappears (Figure 5), and spinel (now the only stable phase for Zn mass fraction up to *ca.* 0.35) will be slowly loading Zn, once an increasing fraction of this metal is taking part in the system (Figure 6).

As can be seen, the content of Zn in ZnO at 1,550ºC is somewhat lower than that of ZnO at 1,300ºC, but the relative amount of this phase at T above the transition temperature is higher.

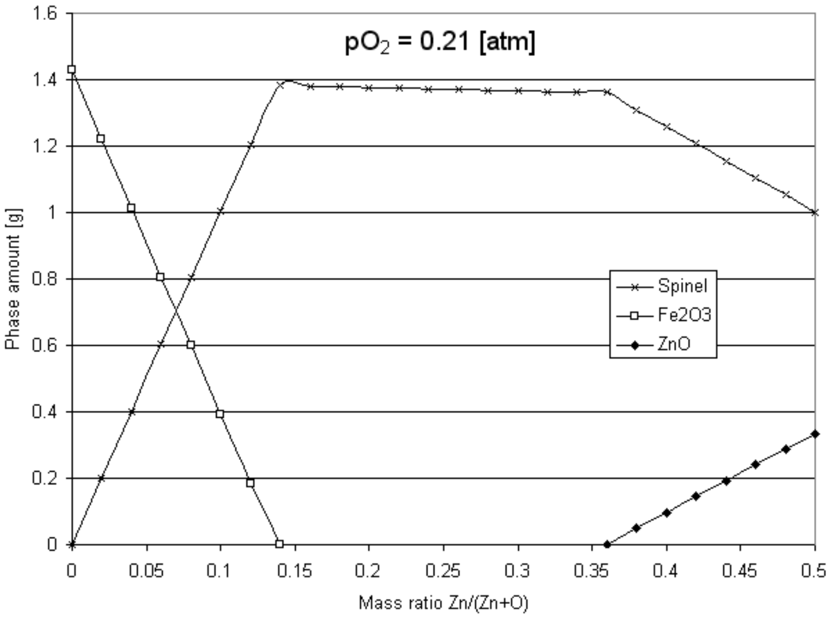

Figure 3. Phase amount (Fe_2O_3, spinel and ZnO) as a function of composition; temperature1,300ºC (below transition temperature); pO_2 = 0.21 [atm]

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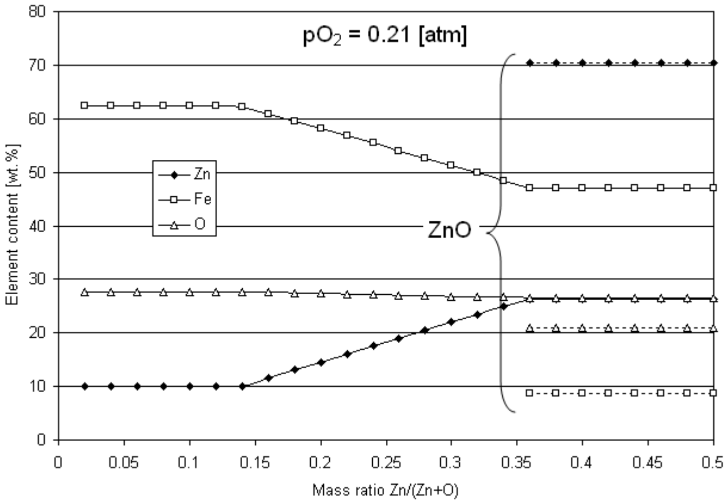

Figure 4. Element content (Zn, O and Fe) in spinel and ZnO solid solution phases as a function of composition; temperature1,300ºC (below transition temperature); pO_2 = 0.21 [atm].

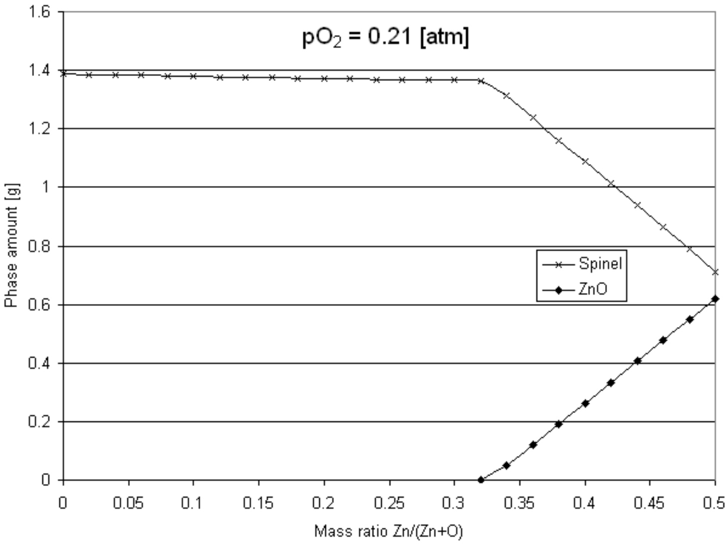

Figure 5. Phase amount (spinel and ZnO) as a function of composition; temperature1,550ºC (above transition temperature); pO_2 = 0.21 [atm].

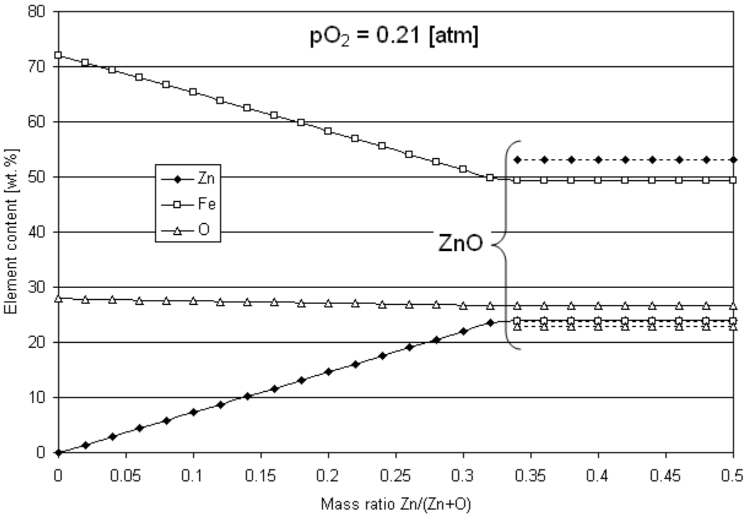

Figure 6. Element content (Zn, O and Fe) in spinel and ZnO solid solution phases as a function of composition; temperature1,550ºC (above transition temperature); pO_2 = 0.21 [atm].

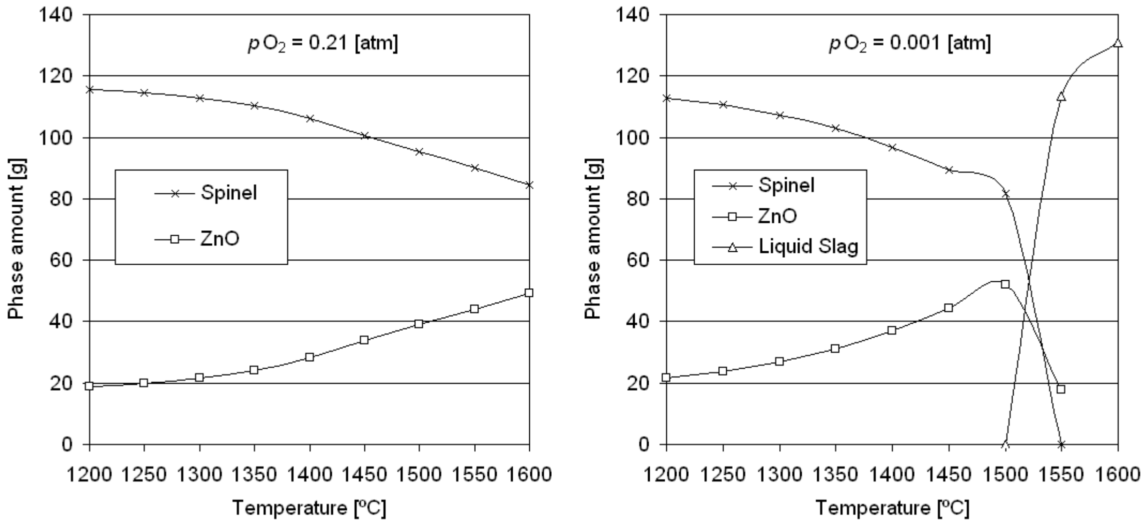

Figure 7. Phase amount (spinel, ZnO and liquid slag) as a function of temperature; Zn mass ratio = 0.45; pO_2 = 0.21 (left) and 0.001 [atm] (right).

The two-phase field ZnO-Spinel was also an object of analysis.

For a fixed mass fraction amount of Zn / (Zn + Fe) = 0.45, mass of the phases and the content of the elements Zn, O, and Fe in all condensed phases were determined. Here again the O_2 pressure of air (pO_2 = 0.21 [atm]) was employed; in addition to this, another pressure ($1x10^{-3}$ [atm]) was also used.

The results show that for lower temperatures, the phases are relatively the same for both situations; however, for higher temperatures and reduced pressures, the liquid slag phase begins to participate in the equilibrium state (Figure 7).

In terms of concentration, a very similar Zn content in spinel phase, for the two pressures tested can observed, with Zn content falling in a slightly greater extent in the system with a lower pressure (Figure 8).

In the phase ZnO, the amount of Zn falls rapidly, from 73 [wt.%] to some value in the vicinity of 50 [wt.%], as the temperature rises (Figure 9).

Liquid slag phase has a concentration of Zn intermediate between that of the spinel phase and ZnO phase, closer to the spinel phase.

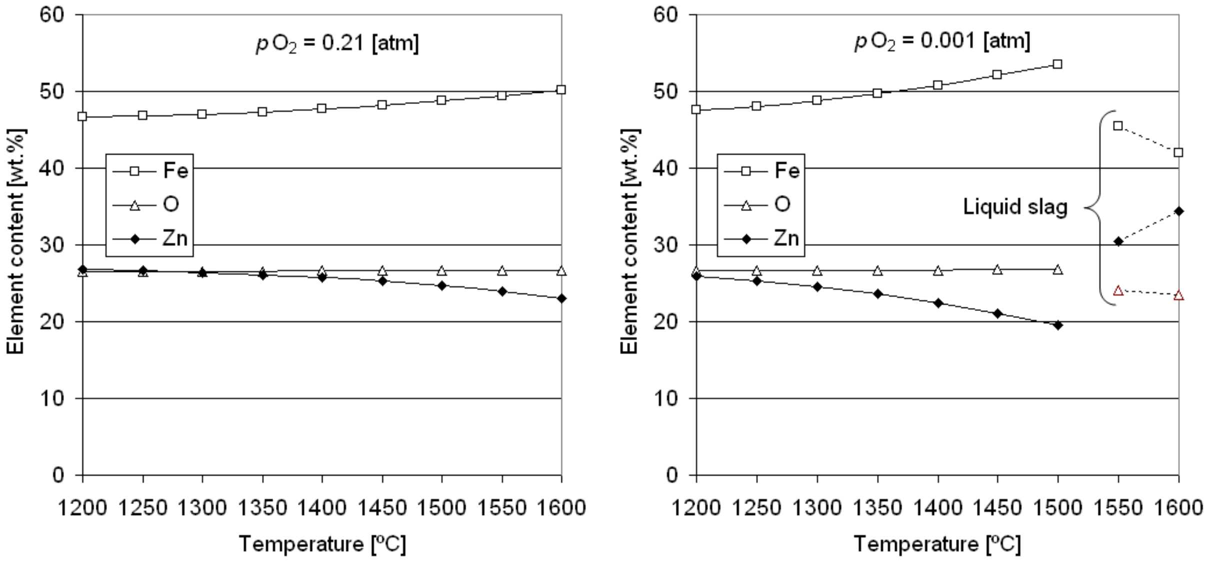

Figure 8. Element content (Zn, O and Fe) in spinel solid solution phase (and liquid slag) as a function of temperature; Zn mass ratio = 0.45; pO_2 = 0.21 (left) and 0.001 [atm] (right).

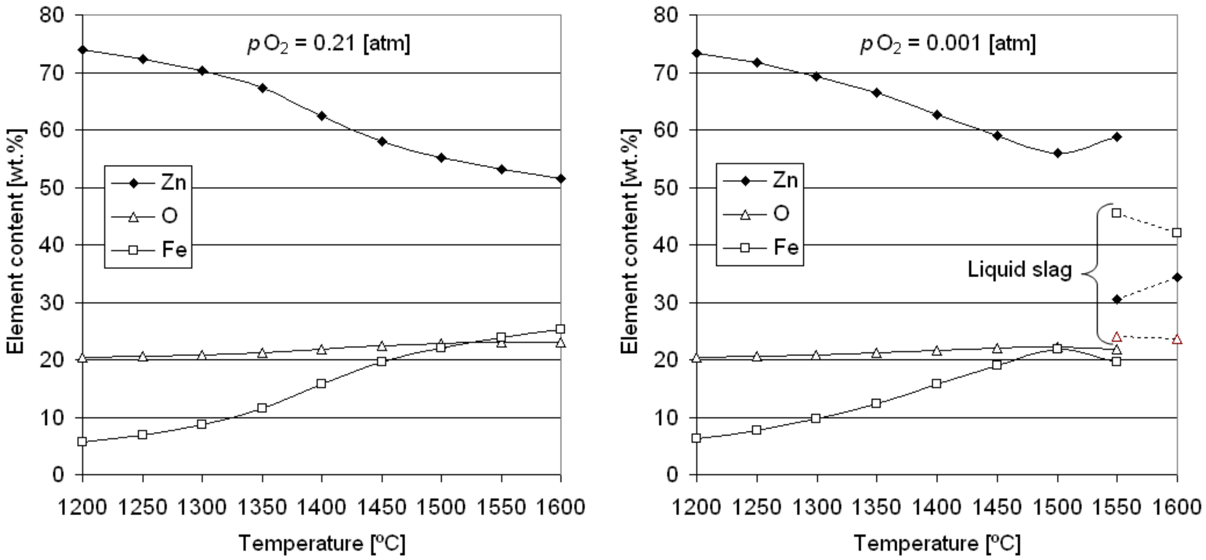

Figure 9. Element content (Zn, O and Fe) in ZnO solid solution phase (and liquid slag) as a function of temperature; Zn mass ratio = 0.45; pO_2 = 0.21 (left) and 0.001 [atm] (right).

4 CONCLUSIONS

The thermodynamic simulations on EAFD genesis – considering the limited temperature, pressure and composition ranges of the simulation – showed that primarily iron oxides (mostly magnetite) and spinels of iron and zinc are generated, according to the proportion of components Fe and Zn in the charge, depending on the different equilibria that can establish in the system Fe-O-Zn.

The generated EAFD can present several phases of oxidized Fe, depending on the conditions prevailing inside the furnace. Once the conditions inside the furnace are not uniform, one must expect in the EAFD a mixture of several of these phases. Even the possibility of phase change – even partially – can not be excluded, with the conversion of an iron oxide initially formed in other, if the temperature is sufficiently high as to guarantee the supply of energy required to overcome the energy barriers presented by the activation energy of reactions or transformations.

If feasible, the introduction of selfreducing briquettes composed of EAFD and scales in the production of steel by EAF, advantages such as reducing the amount of waste generated and an increase of zinc content in EAFD may be obtained. These effects translate into lower costs of disposal or recycling of these wastes.

Given this situation, an additional hydrometallurgical process for the recovery of zinc and other metals from flue dust, may be performed close to the place of steel manufacture, with lower use of capital and operating costs. This can be a decisive factor for the economic viability of any procedure, coupled with the fact that residues of the hydrometallurgical process may return to the EAF again for a new recovery stage.

In any event, reducing the amount of flue dust generated and the increase of zinc are advantageous even for the transport of smaller amounts of residue to the local of processing. A higher zinc content in the EAFD can also help to reduce costs for processing or even to reach a level where economic value can be assigned to this residue.

An adverse factor which comes about with the reintroduction of EAFD into the EAF must be taken into consideration, which is the concentration of undesirable impurities like chlorides, and other metals such as cadmium and lead. This tendency, however,

can be controlled by monitoring and, if appropriate, by applying a pre-treatment on the EAFD generated before recovery of the zinc itself can take place.
More studies should be made to explore these possibilities.

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