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EFFECT OF OXYGEN POTENTIAL AND FLUXING COMPONENTS ON PHASE RELATIONS DURING SINTERING OF IRON ORE

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Abstract

The optimal operation of the blast furnace depends considerably on the properties of the sinter fed into the furnace. As a result, the optimization of the sintering processes has a direct effect on the overall effectiveness of the iron making processes. In order to produce a good sinter special care needs to be taken in order to assure it has a good permeability and reducibility and it is able to retain these properties for a certain time. If the sinter starts to melt down early in the upper part of the blast furnace, where its solid state reduction is essential, permeability decreases, the gas channels get blocked, reductibility diminishes and serious problems may also follow. Among the factors that influences the above mentioned sinter properties are the oxygen potential and fluxing components. Nevertheless, their effect on the phase relations during sintering and sinter reduction conditions has not yet entirely clarified and confusion exists in literature. This quantification becomes even more important today where many new minor components such as Al_2O_3 and MgO enter the sinter through raw materials. This work quantifies the effect of oxygen potential and fluxing components such as alumina and magnesia on the liquidus and phase relations of the sinter primary melts in the iron rich portion of CaO-FeO-Fe_2O_3-SiO_2 system at sintering conditions. This is carried out by the means of new type of industrial diagrams in the form of Fe/CaO vs. SiO_2 that can directly help the optimization of the sintering processes.

Keywords: Sinter; Phase ralations; Melting; CaO; FeO; Fe_2O_3; SiO_2; Al_2O_3; MgO; Sintering process; Primary melts; Liquidus; Fe/CaO

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1. Introduction

The production of the homogeneous self-fluxing sinter is the first important step in the iron making process. The quality of the sinter considerably affects the important process parameters of the blast furnace such as its productivity and the product quality. A blast furnace operation without problems requires a sinter with good permeability and reductibility that is able to keep these properties for a certain period of time. If the sinter melts down precociously at an area where a solid state reduction is essential many problems may occur. The primary melt would block the porosity of the sinter as well as the gaps between its particles causing a low gas permeability and would decrease the effective surface area causing a low reductibility. Some of the factors that influence the quality of a sinter are the basic chemical composition, minor components, oxygen potential and other process conditions.

In the sintering process the CaO/SiO_2 ratio of the initial charge mixture of iron ore, flux and $CaCO_3$ is normally around 2. Following different solid state reactions in the charge, the mixture of free oxides (Fe_3O_4+CaO+SiO_2) is enriched with Al_2O_3 and MgO. At above 1150°C, two kinds of primary melts become possible. The first is calcium ferrite with a very high CaO/SiO_2 ratio and the second is a silicate melt with the CaO/SiO_2 ratio around unity.

It has been observed that the primary melts are enriched with Al_2O_3. Shigaki et al.[1], have experimentally found that along with the temperature increase the composition of silicate melt containing alumina shifts toward $CaSiO_3$. This is shown in Figure 1. However the effect of Al_2O_3 and MgO on the formation of the silicate melt and the shift of its composition are not yet clarified.

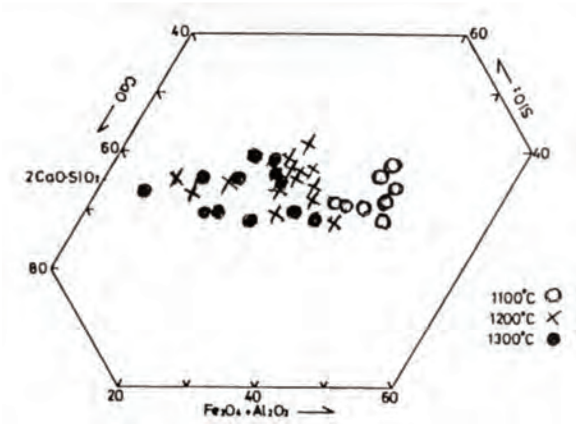

Figure 1 – Change of silicate melt composition during sintering according to [1]

The oxygen potential during sintering is widely scattered from 10^{-12} to10^{-4} atm as a result of various short time heterogeneous reactions. It depends on several factors such as the layer, temperature, coke size, its amount, etc. However the normal oxygen potential during sintering is considered to vary from 10^{-6} to 10^{-7} atm. It is also practically known that the silicate melt lies on the spinel saturation area. Despite these facts the phase relations and the behavior of spinel have not yet been clarified on these relevant oxygen potentials.

Consequently, although, the quality of the self-fluxing sinter depends simultaneously on the process conditions, chemical composition, minor components etc. the fluxing effects during sintering and sinter reduction have not yet been clarified. The effect of oxygen potential in the process has not normally been taken into account although it has a major influence on the phase relations. The presence of minor components in the iron ore feed, such as Al_2O_3 and MgO complicate things even more since they effect the phase relations and the conditions of the formation of the primary melts.

In previous work [2-21] the phase relations of several slag systems have been quantified along with the effect of some minor constituents.

The purpose of this work is to quantify the fluxing effect of oxygen potential and sinter major and minor components in the iron-rich corner of the basic $CaO\text{-}FeO\text{-}Fe_2O_3\text{-}SiO_2$ system at sintering conditions based on a new original physical model recently developed by FLOGEN® Technologies Inc.[22] for non-equilibrium conditions that incorporates in itself equilibrium conditions as a particular case. Some practical industrial diagrams that can directly help the optimization of the sintering processes are constructed in the form of Fe/CaO vs. SiO_2. This is convenient in some industrial conditions that work in this area and helps resolve the above mentioned problems that are frequently encountered in ferrous metallurgy.

2. Effect of Oxygen Potential

Figure 2 describes the liquidus surface of the iron-rich corner of $CaO\text{-}FeO\text{-}Fe_2O_3\text{-}SiO_2$ system. The superimposed curves at constant CaO/SiO_2 ratios are also shown since ferrous metallurgists sometimes use these ratios in the industrial practice. From this figure it can be seen that at a constant CaO/SiO_2 ratio and constant oxygen potential an increase of iron and a decrease of the lime content increases the liquidus temperature in the magnetite (spinel) saturation area and decreases it in the Ca_2SiO_4 and $Ca_2Fe_2O_5$ areas. In is shown in the diagram that the minimum liquidus temperatures are in the region where magnetite and Ca_2SiO_4 or $Ca_2Fe_2O_5$ reach each other.

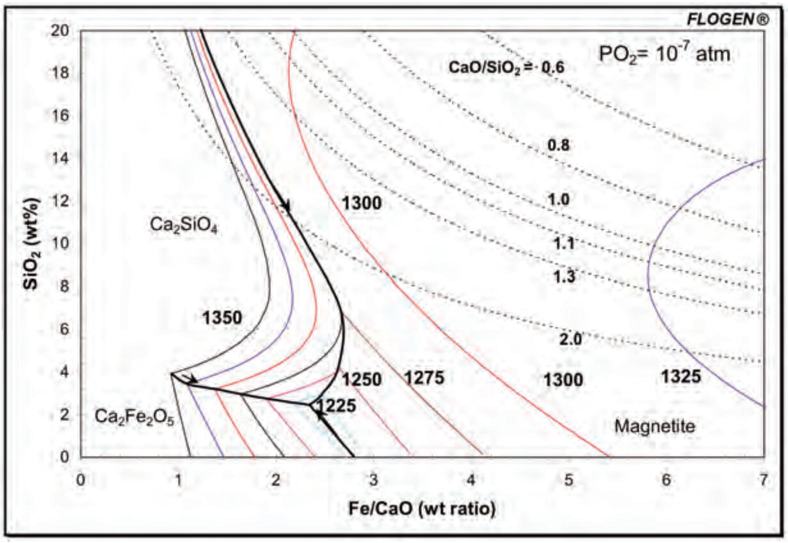

Figure 2 - Liquidus Surface of iron-rich corner of $CaO\text{-}FeO\text{-}Fe_2O_3\text{-}SiO_2$ System at PO_2 of 10^{-7} atm, along with the Curves of Constant CaO/SiO_2 Ratios

Figure 3 shows the iron-rich corner of $CaO-FeO-Fe_2O_3-SiO_2$ Slag at 1300°C, at 2 oxygen potentials along with the curves of constant CaO/SiO_2 ratios. It can be seen that at constant CaO/SiO_2 ratios a decrease of oxygen potential increases the liquid regions and the risk of primary melt formations.

3. Effect of Al_2O_3

Figure 4 gives the liquidus surface of the iron-rich corner of $CaO-FeO-Fe_2O_3-SiO_2-Al_2O_3$ system at PO_2 of 10^{-6} atm and 3% Al_2O_3 along with the curves at constant CaO/SiO_2 ratios.

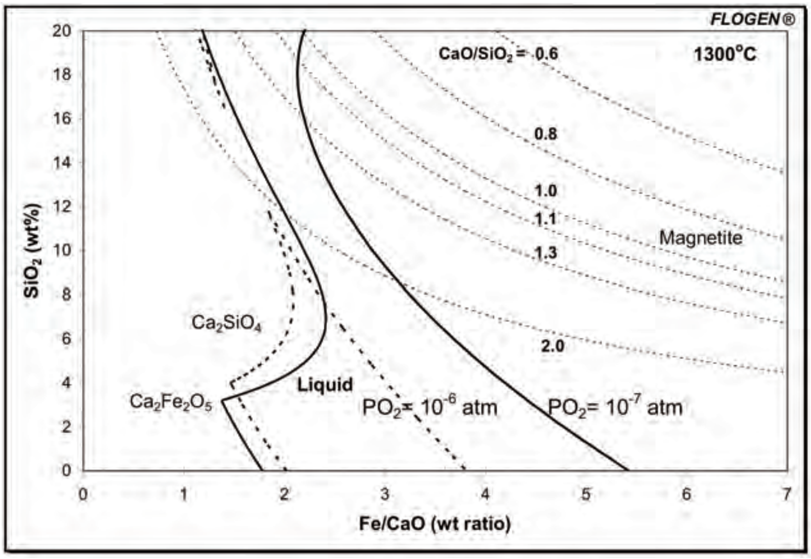

Figure 3 - Liquid regions of $CaO-FeO-Fe_2O_3-SiO_2$ Slag at 1300°C and various PO_2 along with the Curves of Constant CaO/SiO_2 Ratios

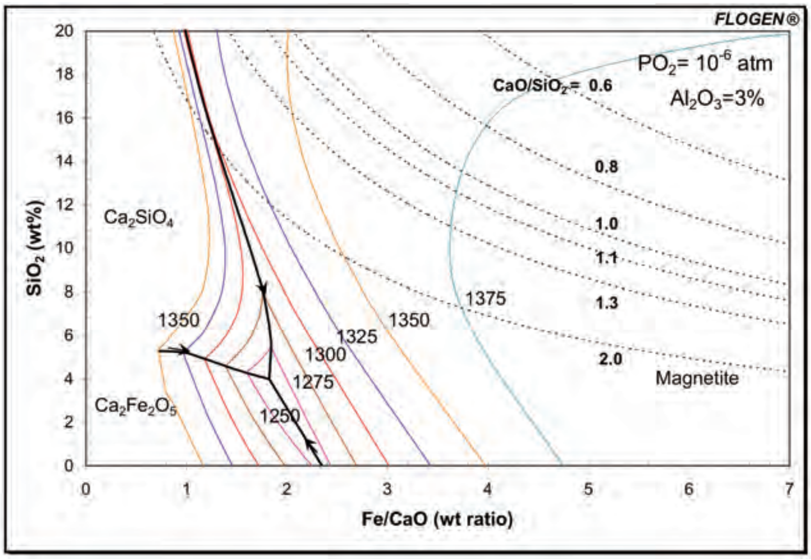

Figure 4 – Liquidus surface of iron-rich corner of $CaO-FeO-Fe_2O_3-SiO_2-Al_2O_3$ System at PO_2 of 10^{-6} atm and 3% Al_2O_3 along with the Curves of Constant CaO/SiO_2 Ratios

Figure 5 shows the liquid regions of iron-rich corner of the CaO-FeO-Fe_2O_3-SiO_2-Al_2O_3 slag at 1350°C, PO_2 of 10^{-6} atm at 0 and 3% Al_2O_3. It can be seen that at constant CaO/SiO_2 ratio an increase of alumina content decreases the liquid region of the slag in the magnetite saturation area and increases it in the Ca_2SiO_4 or $Ca_2Fe_2O_5$ area.

4. Effect of MgO

Figure 6 describes the liquidus surface of the iron-rich corner of CaO-FeO-Fe_2O_3-SiO_2-MgO System at PO_2 of 10^{-8} atm and

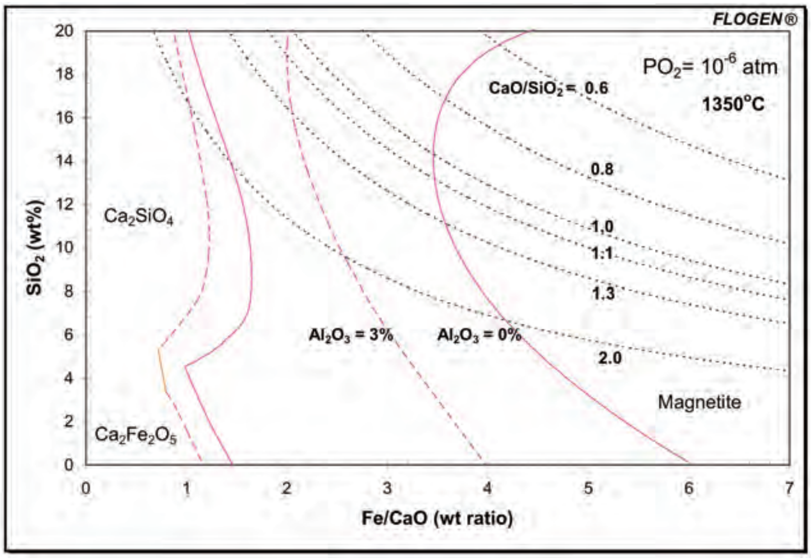

Figure 5 – Liquid regions of CaO-FeO-Fe_2O_3-SiO_2-Al_2O_3 Slag at 1350°C, PO_2 of 10^{-6} atm at 0 and 3% Al_2O_3 along with the Curves of Constant CaO/SiO_2 Ratios

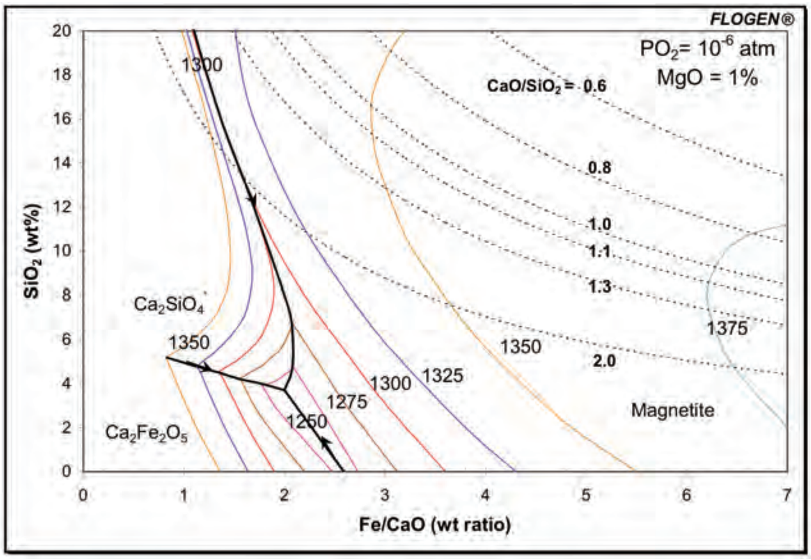

Figure 6 - Liquidus surface of iron-rich corner of CaO-FeO-Fe_2O_3-SiO_2-MgO Slag at PO_2 of 10^{-6} atm and 1% MgO along with the Curves of Constant CaO/SiO_2 Ratios

1% MgO.

Figure 7 shows the liquid regions of iron rich corner of the CaO-FeO-Fe_2O_3-SiO_2-MgO system at 1250°C, PO_2 of 10^{-6} atm at 0 and 1% MgO. It can be seen that at constant CaO/SiO_2 ratio an increase of MgO content decreases the liquid region of the slag in the magnetite saturation area and slightly increases it in the Ca_2SiO_4 and $Ca_2Fe_2O_5$ areas.

Figure 8 shows the effect of Al_2O_3 and MgO on the liquidus temperature of the same system for various CaO/SiO_2 ratios. As it can be seen while both MgO and Al_2O_3 increase

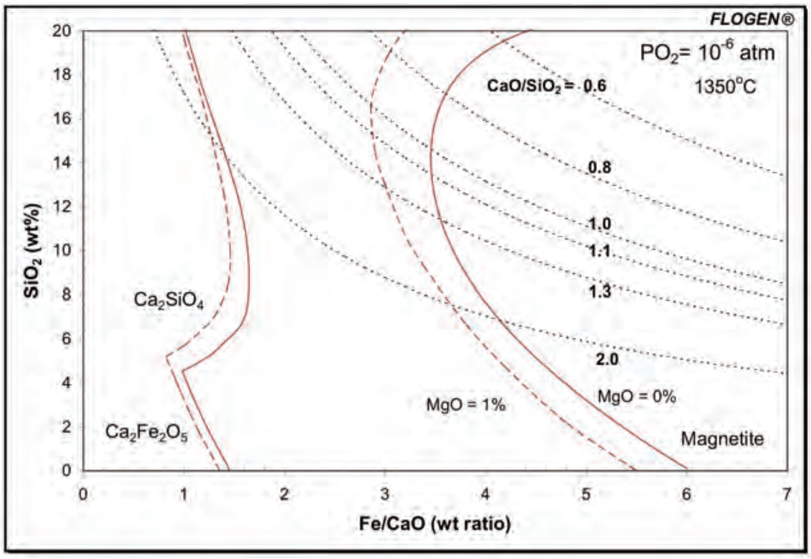

Figure 7 - Liquid regions of iron-rich corner of CaO-FeO-Fe_2O_3-SiO_2-MgO Slag at 1350°C, PO_2 of 10^{-6} atm and 0 and 1% MgO along with the Curves of Constant CaO/SiO_2 Ratios

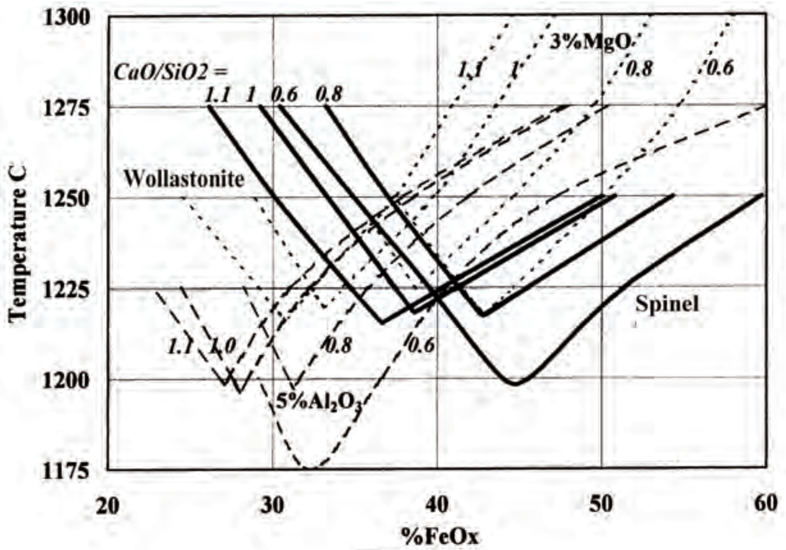

Figure 8 - Liquidus Surface of CaO-FeO-Fe_2O_3-SiO_2 Slag at PO_2 of 10^{-8} atm, for Various CaO/SiO_2 Ratios and MgO and Al_2O_3 Contents

liquidus temperature in the spinel saturation area, they also shift the eutectic line toward low FeOx side and low temperatures which makes the acidic mixture containing Al_2O_3 very fusible. For this reason optimum amounts of MgO and Al_2O_3 are needed in order to increase the liquidus temperature of the sinter so as to prevent its early melt down in the blast furnace and to avoid an acidic sinter of high SiO_2 and Al_2O_3 which have low eutectic temperatures.

5. Conclusions

The phase relations and the liquidus surface of the sinter primary melts in the iron-rich corner of CaO-FeO-Fe_2O_3-SiO_2 system at sintering conditions have been quantified through a new original, recently developed, physical model and a new type of industrial diagrams in the form of Fe/CaO vs. SiO_2.

The fluxing effects of the oxygen potential, Al_2O_3 and MgO have been quantified. It was found that the effect of oxygen potential, Al_2O_3 and MgO at constant CaO/SiO_2 ratios are not uniform and are closely related to the primary precipitate phases.

The presented diagrams can directly help to resolve the problems of permeability and reductibility that are frequently encountered in ferrous metallurgy and the optimization of the entire sintering processes.

The quantification of the effects of Al_2O_3 and MgO on the primary melts of other regions as well as the quantification of sinter softening behavior are authors' ongoing research.

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