Liquidus Surface of Newly Defined "Ferrous Calcium Silicate Slag" and its Metallurgical Implications

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ABSTRACT

Ferrous calcium silicate (FCS) slag is defined as a new slag consisting of FeOx, CaO and SiO_2 with a nominal composition near the di-calcium silicate surface. This slag is expected to solve the drawbacks of the "fayalite" and ferrite slags. However, the detailed knowledge of the liquidus surface of this new slag is not available in literature. Based on the authors' first article on the liquidus surface of FeOx-SiO_2-CaO system containing Al_2O_3, MgO and Cu_2O, the available liquid region of FCS slag is confirmed under relevant oxygen potentials along with the effect of minor oxides, especially Al_2O_3. The liquidus temperature is lowered by dissolution of copper oxide, and thus, FCS slag seems to be useful especially in the converting and direct smelting of copper. The obtained knowledge of the liquidus surface accompanied by further proper extensions can also be useful for the understanding of various metallurgical processes.

INTRODUCTION

Ferrous calcium silicate (FCS) slag is defined by the authors(1) as a new slag consisting of FeOx, CaO and SiO_2 with a nominal composition near the di-calcium silicate surface. This slag is expected to be a third copper smelting slag after "fayalite" and calcium ferrite slags. The traditional slags have several well-known drawbacks. "Fayalite" slag has high viscosity, low removal ability of arsenic and is disturbed by the precipitation of solid magnetite, while ferrite slag has low silica solubility, low removal ability of lead and is very aggressive toward refractories. Ferrous calcium silicate slag not only may solve these difficulties but it also presents the additional advantage of low loss of oxidic copper by dissolution. The detailed knowledge of the liquidus surface of this new slag, however, is not available in literature. In fact, in a broader spectrum, despite the increasing interest in the copper continuous converting and direct smelting of copper concentrates, the detailed knowledge of the liquidus surface of FeOx-SiO_2-CaO slag containing several minor oxides under the relevant oxygen pressures has been missing in literature. In the author's first article (2), the liquidus surface of FeOx-SiO_2-CaO system is quantified for the first time at intermediate oxygen partial pressures along with the effect of minor oxides and oxygen potentials. In the present article, based on the first one, the available liquid regions of ferrous calcium silicate slag are confirmed under relevant oxygen potentials. This work (2,6-7) is a normal continuation of the previous work (3-5) in which the liquidus surface of FeO-Fe_2O_3-SiO_2-CaO slag containing Al_2O_3 and MgO was quantified at predominantly low oxygen potentials.

OVERVIEW OF METALLURGICAL SLAGS IN FeOx-SiO_2-CaO SYSTEM

Figure 1 shows the liquidus surface of four limiting ternaries of FeO-Fe_2O_3-SiO_2-CaO quaternary system compiled from the literature data (8-9). The compositions of various metallurgical slags are also illustrated. Figure (a) is well known as FeO-SiO_2-CaO system in coexistence with metallic iron and is very important in the reductive smelting and iron making. In the middle of this figure, at a smelting temperature of 1300°C, a wide homogeneous liquid region is observed starting from the fayalite phase (Fe_2SiO_4). On the olivine (fayalite) surface, liquidus temperature decreases by addition of CaO and reaches below 1100°C. In this area, the liquid, which consists mainly of FeOx and SiO_2, is the most common nonferrous slag usually known as "fayalite" slag.

Figure (b) shows Fe_2O_3-SiO_2-CaO system in air, where the liquidus surfaces of olivine and wustite are replaced by spinel (Fe_3O_4) and hematite (Fe_2O_3). Liquidus temperatures are generally higher than those of Figure (a) and the liquid region at 1300°C is limited to the middle part region of silicate melt and the upper-left region of calcium ferrite melt (CF). Looking through (a) and (b) from the top to the bottom, it can be seen that two low temperature valleys exist in the middle of the diagram. The right-side valley that includes fayalite slag is limited by the cliff of silica-saturation and the left-side valley that includes FCS slag is limited by the cliff of Ca_2SiO_4-saturation.

It should be noted that Figures (a) and (b) correspond respectively to extreme low and high oxygen potentials. Despite their importance in the copper smelting and iron ore sintering, no data on the liquidus surface at oxygen potentials of 10^{-9} to 10^{-5} atm are found in literature.

Figure 2 illustrates the calculated equilibrium oxygen and sulfur pressures during oxidative copper smelting. It can be seen that in the matte smelting and blister making converting, oxygen pressures at 1300°C can be respectively approximated as 10^{-8} and 10^{-6} atm. It should be kept in mind, however, that the oxygen potentials of the slag might drop below 10^{-9} atm during matte smelting at the solidification temperature or in the reductive slag-cleaning furnace.

Figures (c) and (d) show the available data in the FeO-Fe_2O_3-SiO_2 system(8-9) without CaO and FeO-Fe_2O_3-CaO system(10-11) without SiO_2, covering a wide range of oxygen potentials. Figure (c) is well known as the basis of the so-called "fayalite" slag. The oxygen potentials on the liquidus surface are also shown. It should be noticed that the liquidus surface changes from fayalite (olivine) to magnetite (spinel) at oxygen potentials above 10^{-9}-10^{-10} atm. Figure (d) was constructed by the authors as the basis of the calcium ferrite slag. Part of this figure at 1300°C is compared with "fayalite" slag in Figure 3 along with the oxygen potentials at this temperature. Taking into account the fact that at 1300°C the oxygen partial pressure in the blister making process is about 10^{-6} atm, the availability of ferrite slag in continuous converting is well recognized. However, both Figures (c) and (d) are also extreme cases, and the liquidus surface of FeO-Fe_2O_3-SiO_2-CaO system at various intermediate oxygen pressures has never been studied before. The quantification of this surface was carried out by the present authors in the first article(2) along with the effect of oxygen potential and minor oxides.

EFFECT OF OXYGEN POTENTIAL ON THE LIQUIDUS SURFACE OF FERROUS CALCIUM SILICATE SLAGS

Based on the authors' previous quantitative model predictions(2), the effect of oxygen potential on the liquid regions of $FeOx$-SiO_2-CaO system is summarized here in relation to the copper smelting. The results are shown in Figures 4 to 6. Figure 4 describes the homogeneous liquid regions of the slag at 1300°C and PO_2 of 10^{-5}, 10^{-8} and around 10^{-11} atm (co-existence with iron). It can be seen that the liquid region at $PO_2=10^{-8}$ atm, which corresponds to the oxidative matte smelting, is sufficiently wide compared to that at iron saturation, which corresponds to the reductive smelting. But, as it is also shown in Figure 5, this region gets narrower at 10^{-5} or 10^{-6} atm, which means that the selection of slag composition is easy during matte smelting, but not as easy in the copper making process.

Figure 5 shows the effect of temperature on the homogeneous liquid region at $PO_2=10^{-6}$atm. It suggests that, during the converting process, a small decrease in temperature causes the precipitation of solid magnetite (spinel). Both Figures 4 and 5 show that the liquidus regions are limited by almost four primary crystals, SiO_2, spinel (Fe_3O_4), Ca_2SiO_4 and wollastonite ($CaSiO_3$). In general, as can be seen from the figures, the liquidus region decreases with the decrease of temperature and the increase of oxygen potential. It decreases drastically on the spinel surface even for slight decreases in temperature or slight increases in the oxygen potential. This is the reason of the so-called "magnetite problem" in the "fayalite" slag. An increase on the oxygen potential, however, increases slightly the liquid region near the Ca_2SiO_4 saturation surface, which corresponds to the area of FCS slag.

Figure 6 is another recompiled figure of previous work(2). It demonstrates the effects of temperature, oxygen pressure and CaO content of the slag at a constant Fe/SiO_2 ratio, which is an well-accustomed parameter for practical engineers. The low CaO region at $Fe/SiO_2=1.1$

corresponds to the conventional "fayalite" slag, while the high CaO region at Fe/SiO_2=2.3 corresponds to FCS slag. In order to help the description of the liquidus temperature of FCS slag, these constant ratios are shown in Figure 5 with dotted straight lines. It is interesting to note that CaO additions decrease the melting temperature on the olivine surface in the iron-saturated reductive smelting, but increases it on the spinel surface at above PO_2 of 10^{-8} atm, due to the disappearance of olivine. However, in the region of high CaO content and high Fe/SiO_2 ratios such as 2.3, which correspond to the region of FCS slag, the liquidus temperature decreases at high oxygen potentials along with an increase of CaO content.

As described above, fayalite (olivine) surface disappears at oxygen potential above 10^{-9}atm. Nevertheless the iron silicate slag of composition near Fe_2SiO_4 has always been called "fayalite" slag regardless of the exposed oxygen potential. Because this name has been repeatedly used to "imagine" the approximate composition of the slag or to distinguish it from other slags, (exp. ferrite slags), it will continue to be used in this paper only in parenthesis in order to expose its irrelevant meaning at intermediate oxygen potentials.

EFFECT OF MINOR OXIDES ON THE LIQUIDUS SURFACE OF FERROUS CALCIUM SILICATE SLAGS

The liquidus surface at some intermediate conditions within the limiting diagrams of Figures (a) and (b) and (c) and (d) in Figure 1 are now clarified including the region of FCS slag. In practice, however, the existence of minor oxides affects considerably the slag liquidus temperature. The effect of Al_2O_3, MgO and Cu_2O on the liquidus surface of FeO-Fe_2O_3-SiO_2-CaO-Al_2O_3-MgO system at intermediate oxygen potentials was quantified previously by the present authors(2,6) through a new type of phase diagrams derived from a thermodynamic model. This work follows the previous one in which the effect of minor oxides was quantified at some predominantly low oxygen potentials (3-5). Figure 7 is a recompiled figure from previous work (2), which shows the effect of Al_2O_3 on the liquidus temperature of $FeOx$-SiO_2-CaO-Al_2O_3 system at $PO_2=10^{-8}$ atm and constant Fe/SiO_2 ratios of 1.1 and 2.3. In the low CaO region corresponding to "fayalite" slag, the liquidus temperature on the spinel surface increases respectively by 6-8 and 3-4 degrees per positive % increment of Al_2O_3 or CaO. At high CaO region, however, nearby Ca_2SiO_4 saturation, the effect of Al_2O_3 is not significant, and the difference of liquidus temperature between Fe/SiO_2=1.1 and 2.3 is not considerable. The effect of Al_2O_3 on similar "fayalite" slag of Fe/SiO_2=1.1 but in coexistence with metallic iron is also shown in the bottom part of the figure with dotted lines. Because of the reducing conditions, the liquidus temperature decreases on the olivine surface by addition of Al_2O_3.

The above-mentioned effect of Al_2O_3 on the liquidus region at $PO_2=10^{-8}$ atm and 1300°C is also illustrated on the triangle composition diagram in Figure 8. The general trends of the effect of Al_2O_3 are similar to those reported by Shigaki et al.(12), Yang et al. (13) and Tsukihashi(14), that is the liquidus region shifts to upper-left part by addition of Al_2O_3. These trends are important to be taken into consideration regarding the formation and reduction of the iron ore sinters(6).

Figure 9 shows the effect of Cu_2O on the liquidus temperature at Fe/SiO_2=1.1 and 2.3 in the similar way as Figures 6 and 7 but at PO_2 of 10^{-6} atm. Since Cu_2O is easily reduced into metal at lower oxygen potentials, the liquidus temperatures at the maximum dissolution of Cu_2O at this oxygen pressure are illustrated with the bottom lines labeled Cu-saturation. As shown in the figure, 1%Cu_2O decreases the liquidus temperature by around 3 degrees at low CaO "fayalite" slag and around 5 degrees at high-CaO, FCS slag. It has been repeatedly pointed out in the past that, at higher oxygen potentials, iron silicate slag is disturbed by the separation of solid magnetite unlike ferrite slag where this risk does not exists. However, the risk of magnetite (spinel) precipitation is considerably decreased when silicate slag dissolves fluxing oxides such as Cu_2O. Inversely, this risk increases when the slag contains refractory oxides such as MgO, which increase the liquidus temperature.

THE AVAILABILITY OF FERROUS CALCIUM SILICATE SLAG IN CONTINUOUS CONVERTING

Ferrous calcium silicate slag is defined as a new slag of composition near the di-calcium silicate surface in the ternary FeOx-SiO_2-CaO diagram. This slag has never been used for matte smelting because of high dissolution of sulfidic copper. However, when copper in the slag is only in the oxidic form, as in the converting process, this slag presents a minimum loss of copper by dissolution. This slag also has high removal ability of As and Sb, comparable to that of the ferrite slag, but it offers a better removal ability of Pb than that of ferrite slag. The viscosity of this slag will be somewhat lower than that of "fayalite" slag, but not as low as ferrite slag, which tends to attack refractories because of its fluidity.

Taking into account these properties, ferrous calcium silicate slag was newly proposed last year(1) in order to relieve the drawbacks of the conventional "fayalite" and ferrite slags. At that time the detailed data on liquidus temperature were not available. As shown in the above newly compiled figures, the homogeneous liquid region of FCS slag is not so wide as in "fayalite" slag, but it still might be available below 1300°C especially when copper oxide is dissolved. Figure 10 shows the variation of the liquid region for several Cu_2O contents of the slag at 1275°C and $PO_2=10^{-6}$ atm. Under these conditions, the liquid region of FeOx-SiO_2-CaO slag without Cu_2O is very narrow, but when the slag is in coexistence with liquid copper, the liquid region is broaden considerably by the help of the dissolution of several up to 10% Cu_2O. In this figure, FCS denotes the region of liquid ferrous calcium silicate slag, and N or O the "fayalite" type continuous converting slag used by Noranda and Olympic Dam.

Figure 11 also demonstrates the effect of Cu_2O on the slag liquidus temperature at $PO_2=10^{-6}$ atm corresponding to the oxygen potential at continuous converting. In this figure, the liquidus temperatures of FeOx-SiO_2-CaO-Cu_2O slag co-existing with liquid Cu are given at Fe/SiO_2 ratios of 1.1 and 2.3. The estimated liquidus temperatures of ferrite slag at $PO_2=10^{-6}$ atm are also illustrated. The labels F, CF and FCS denote the regions of "fayalite" slag, calcium ferrite slag and ferrous calcium silicate slag. Since the dissolution of other minor oxides such as Na_2O would further decrease the liquidus temperatures, these slags can be available in continuous converting below 1300°C. As described above, Al_2O_3 increases the melting temperature of the so-called "fayalite" slag, but not the one of the FCS slag. Undoubtedly, ferrite slag is the best from the standpoint of slag temperature, but FCS slag would be an interesting alternative to solve the inherent drawbacks of existing slags.

CONCLUSIONS

Using the results of the thermodynamic model predictions of the liquidus surface of FeOx-SiO_2-CaO-Al_2O_3-MgO system(2), the liquidus surface of the newly proposed ferrous calcium silicate slag has been clarified. It was found that this slag, which has the possibility to relieve the drawbacks of the "fayalite" and ferrite slag, might be available below 1300°C especially in the continuous converting. The present results of the liquidus surface accompanied by further proper extensions can also be useful for the understanding of other processes such as iron ore sintering and sinter reduction in the blast furnace (6). Furthermore, the composition of the ferrous calcium silicate slag is not considerably different from those of zinc and lead smelting slags and a proper extension of the present results may also be useful for the reductive smelting slags of various nonferrous metals. These subjects as well as the quantification of the effects of other minor oxides are ongoing research (7) and may be published in the future.

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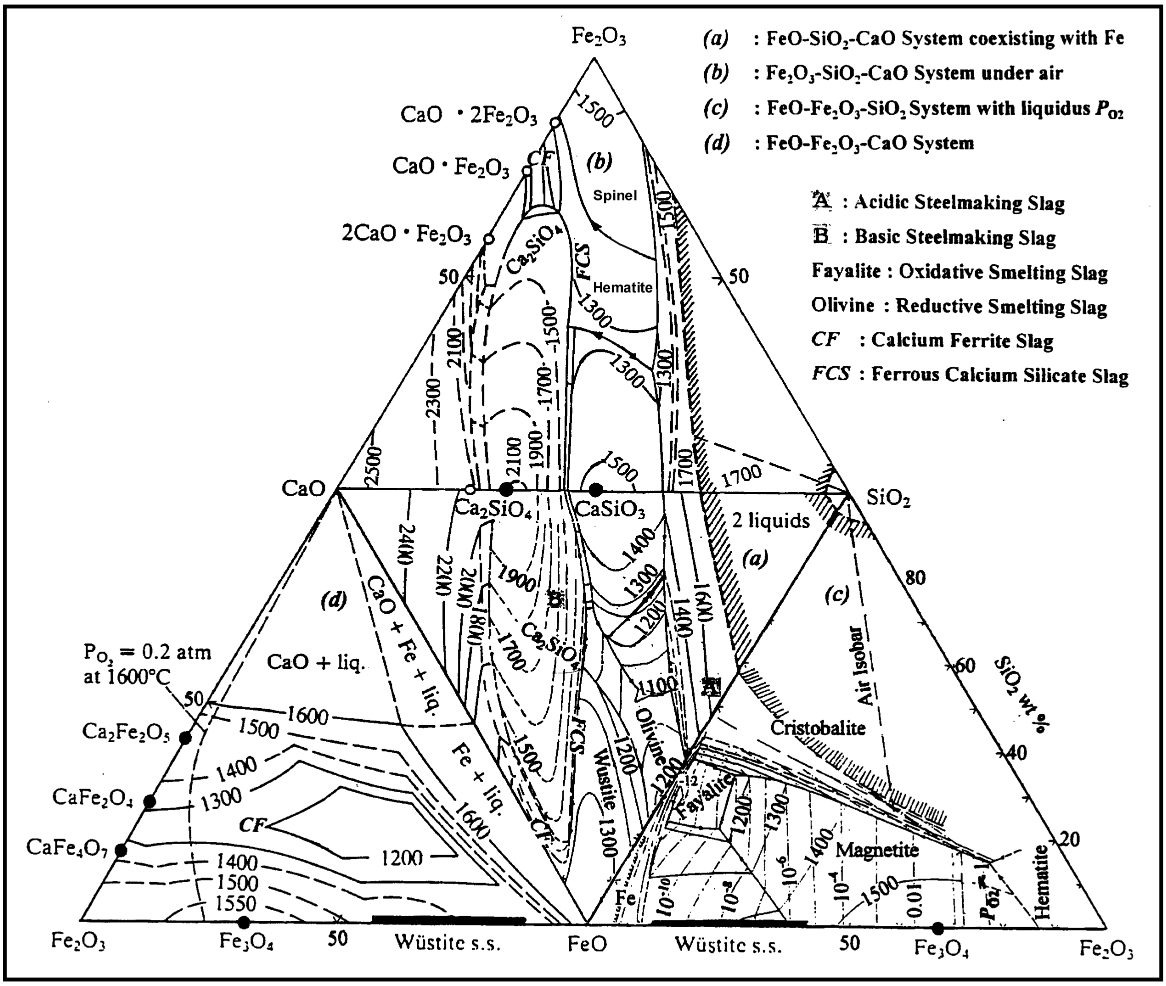

Figure 1 – Phase diagrams of (a) FeO-SiO$_2$-CaO system in contact with metallic iron, (b) Fe$_2$O$_3$-SiO$_2$-CaO in air, (c) FeO-Fe$_2$O$_3$-SiO$_2$ and (d) FeO-Fe$_2$O$_3$-CaO

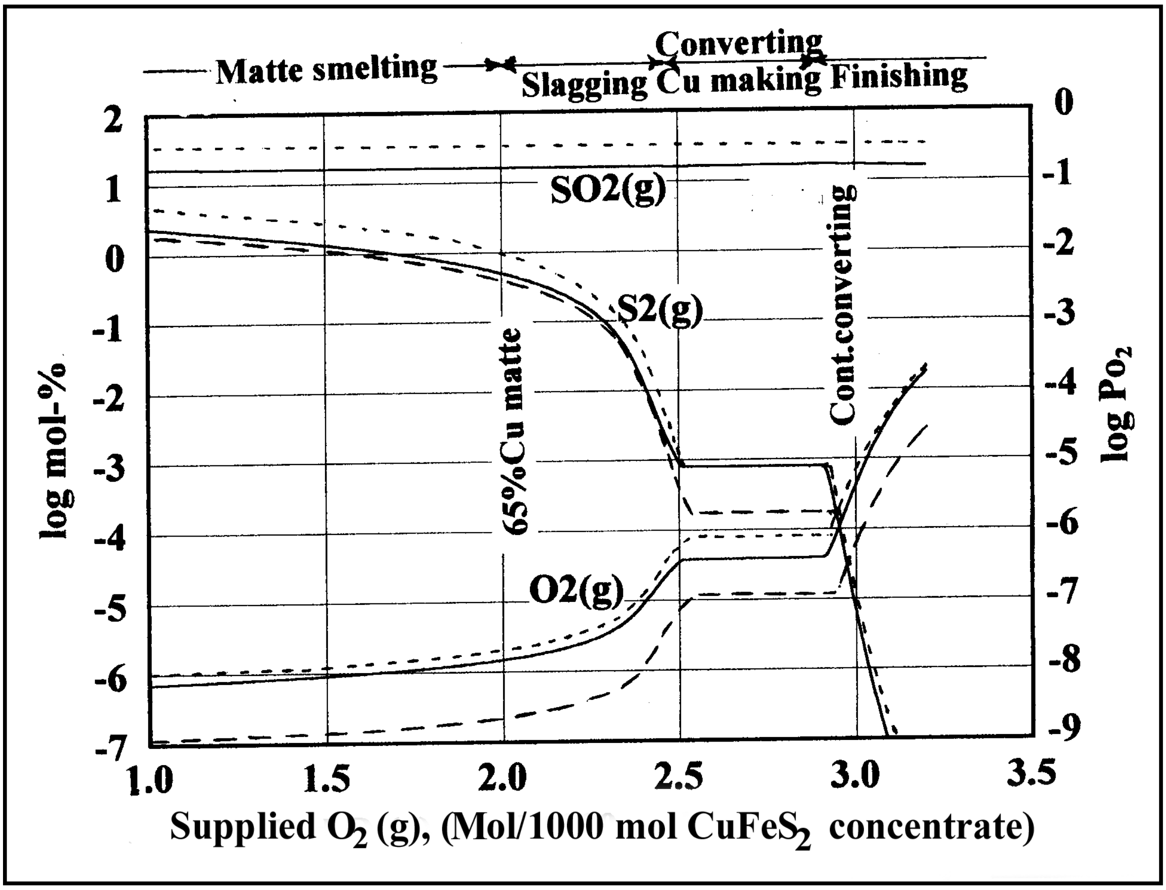

Figure 2 – Variations of equilibrium oxygen and sulfur pressures during oxidative matte smelting and converting. 1000 moles $CuFeS_2$ concentrate is assumed to be oxidized with air or oxygen enriched air at 1200 and 1300°C. (____: 1300°C Air blow; ------ 1300°C, 40%O_2 blow; - - - - - 1200°C, Air blow)

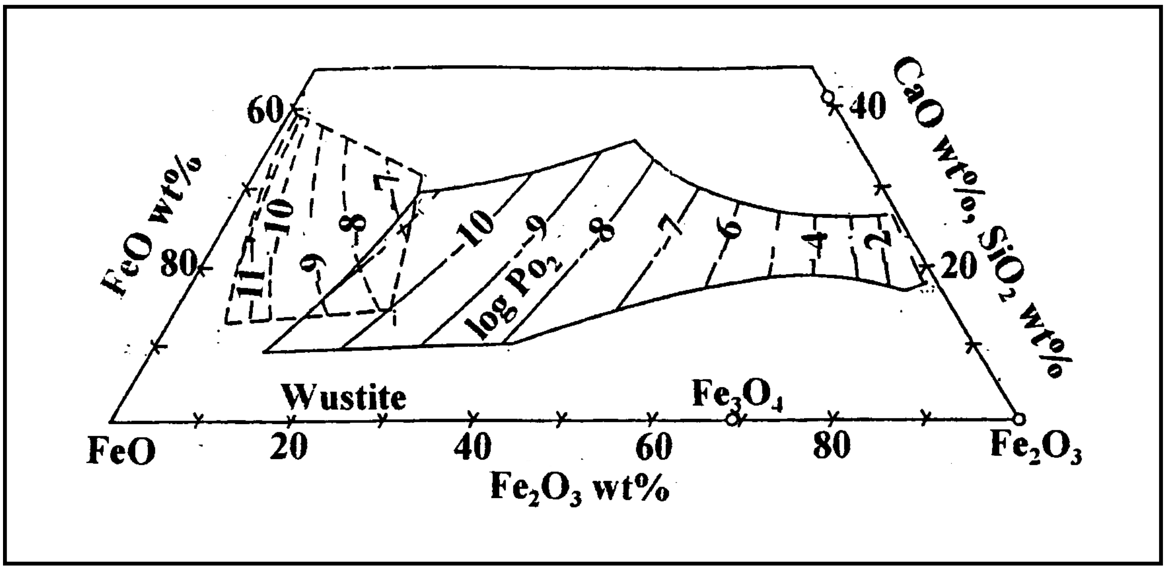

Figure 3 – Liquidus isotherms and oxygen isobars at 1300°C for FeO-Fe_2O_3-CaO (solid lines) and FeO-Fe_2O_3-SiO_2 (dashed lines) systems

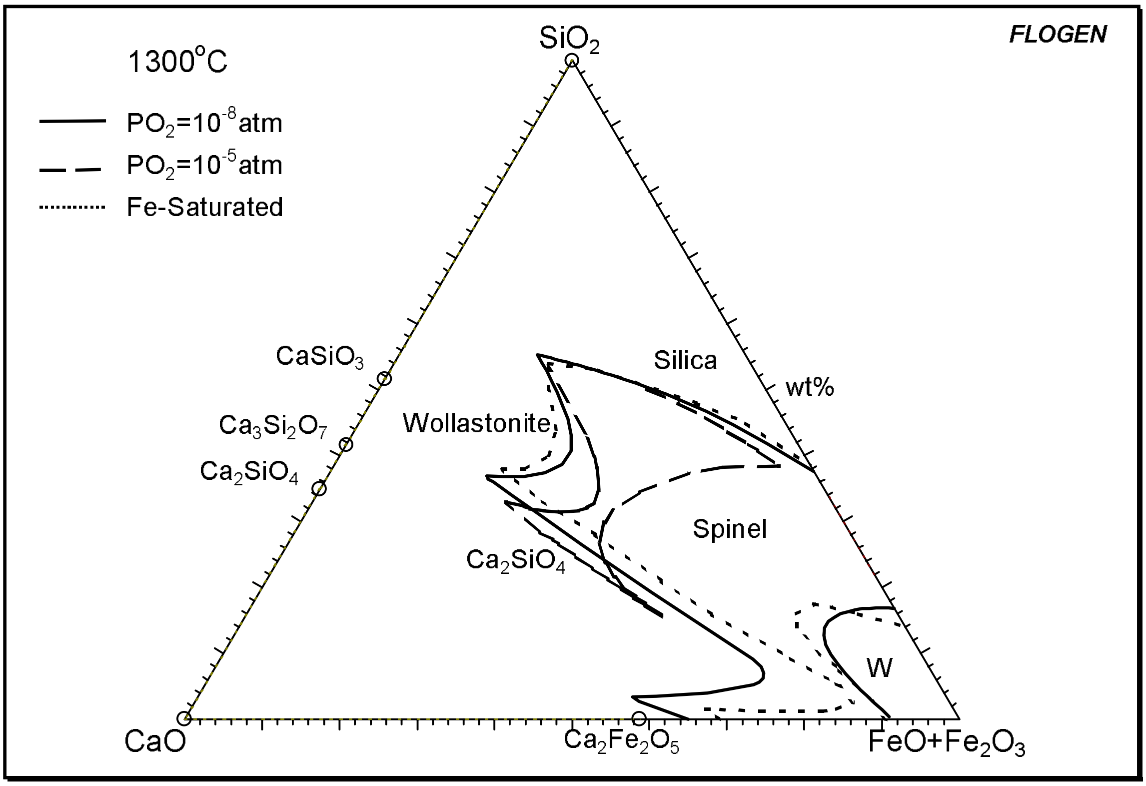

Figure 4 – Effect of oxygen potential on the homogenous liquid region of FeOx-SiO_2-CaO system at 1300°C

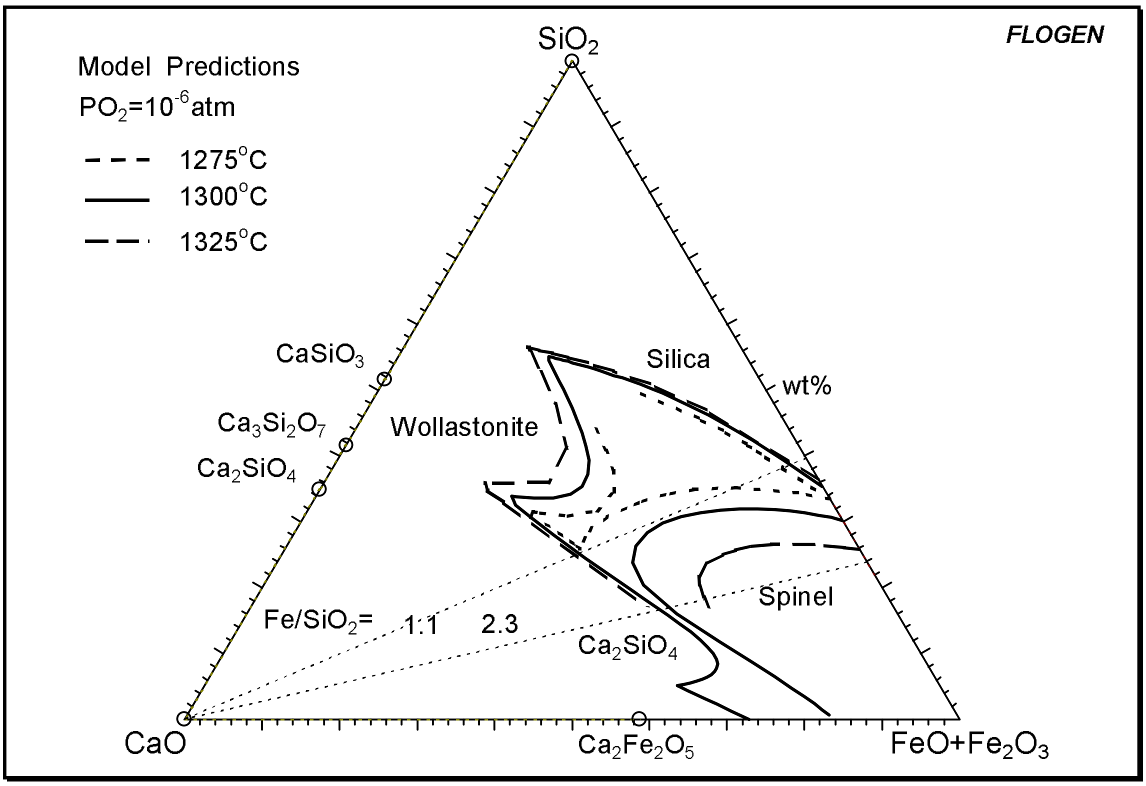

Figure 5 - Effect of temperature on the homogenous liquid region of FeOx-SiO_2-CaO system at $PO_2=10^{-6}$ atm

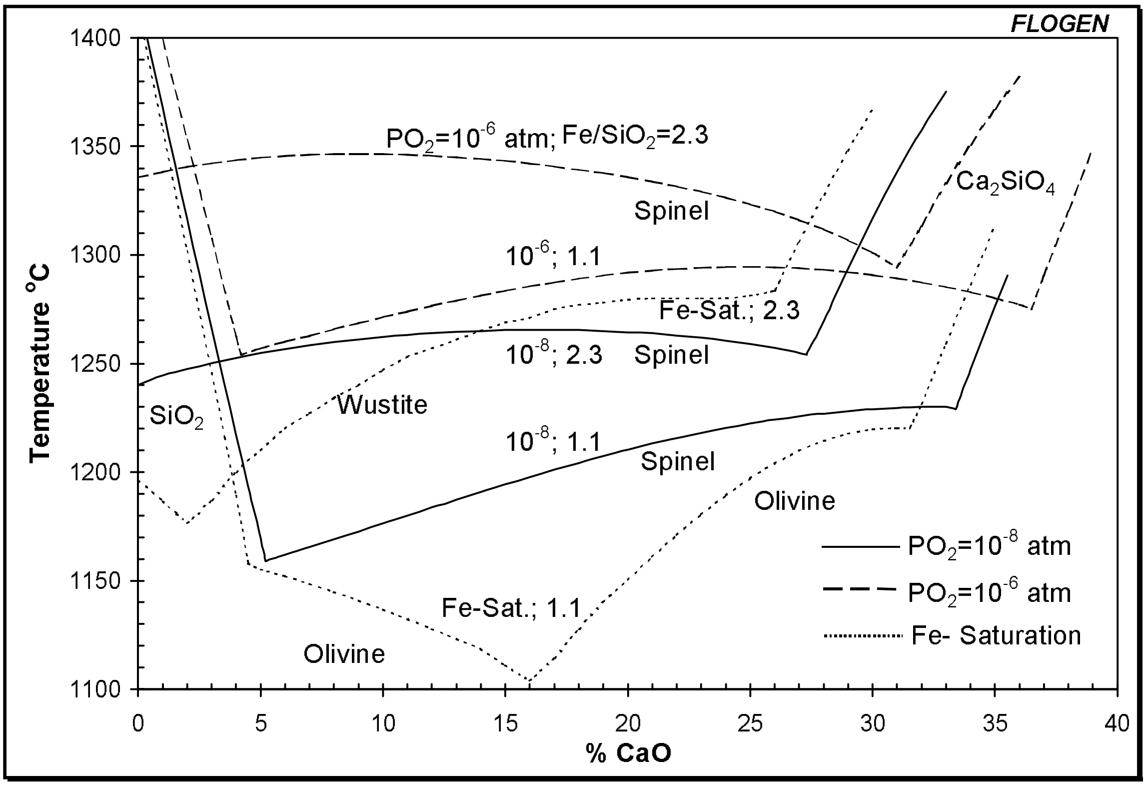

Figure 6 - Effect of CaO and oxygen potential on the liquidus temperature of FeOx-SiO_2-CaO system at several constant Fe/SiO_2 ratios.

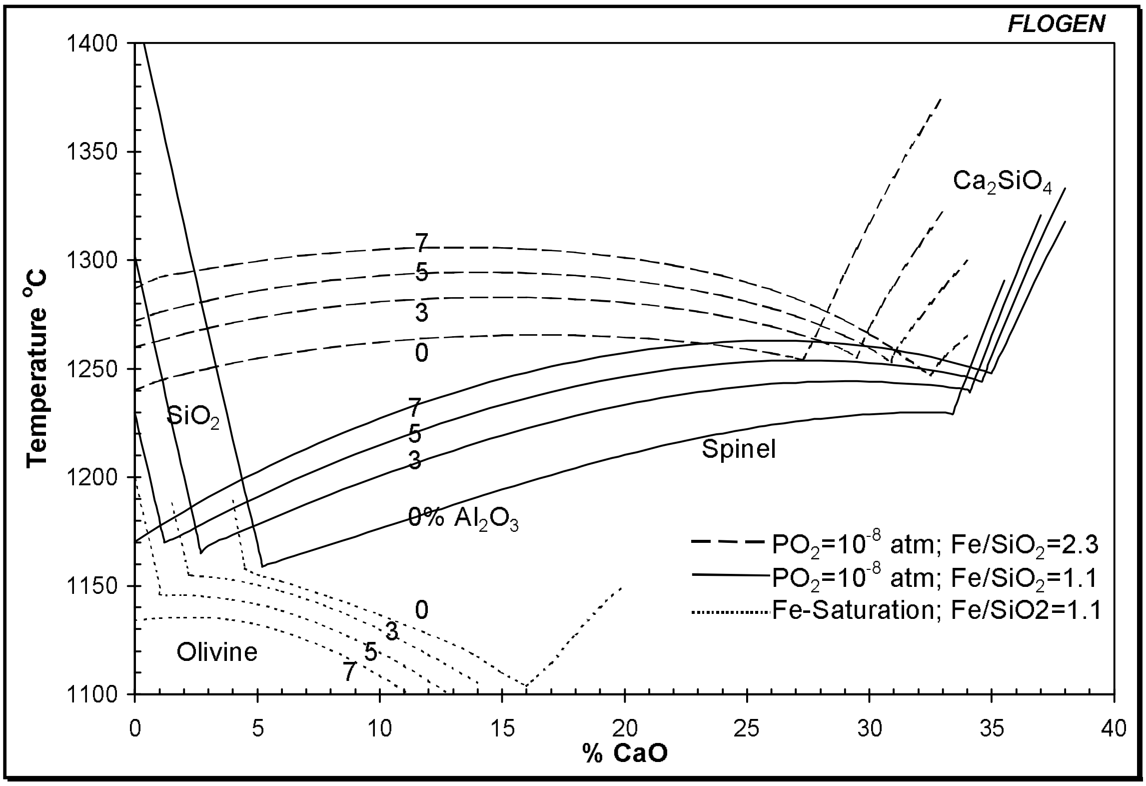

Figure 7 - Effect of Al_2O_3 on the liquidus temperature at $PO_2=10^{-8}$ atm and several Fe/SiO_2 ratios.

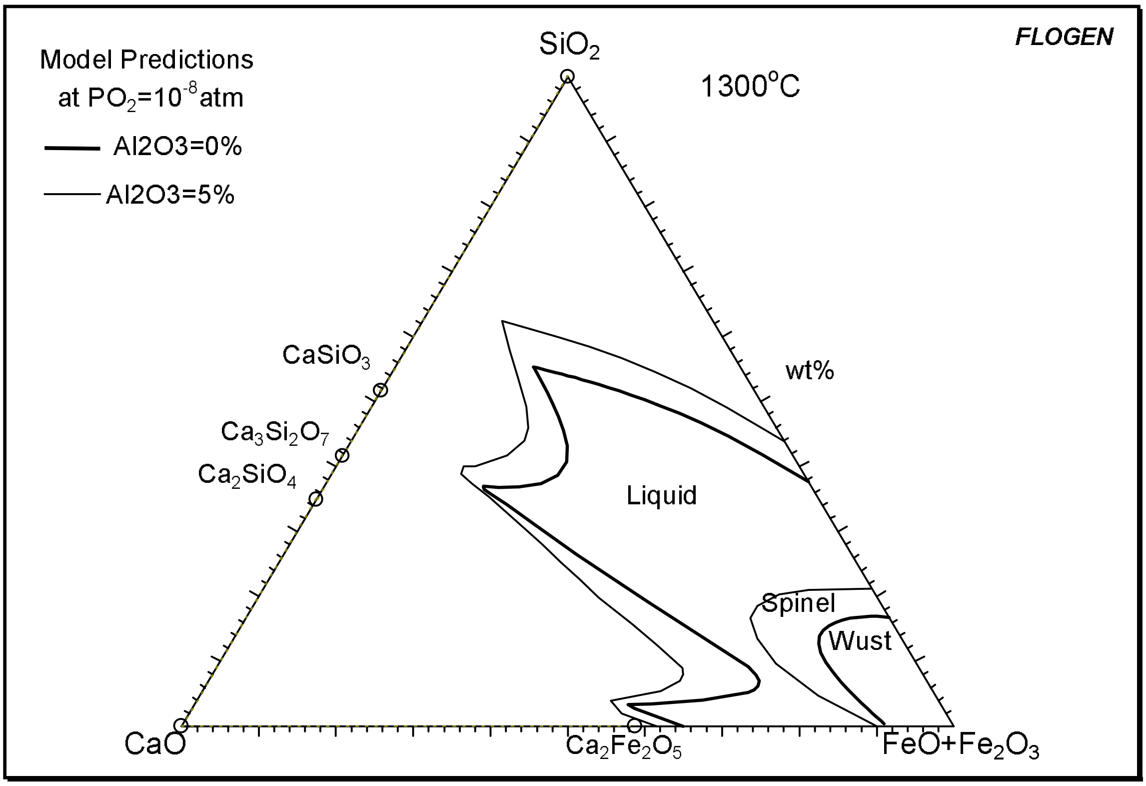

Figure 8 - Effect of Al_2O_3 on the liquid region at 1300°C and $PO_2=10^{-8}$ atm.

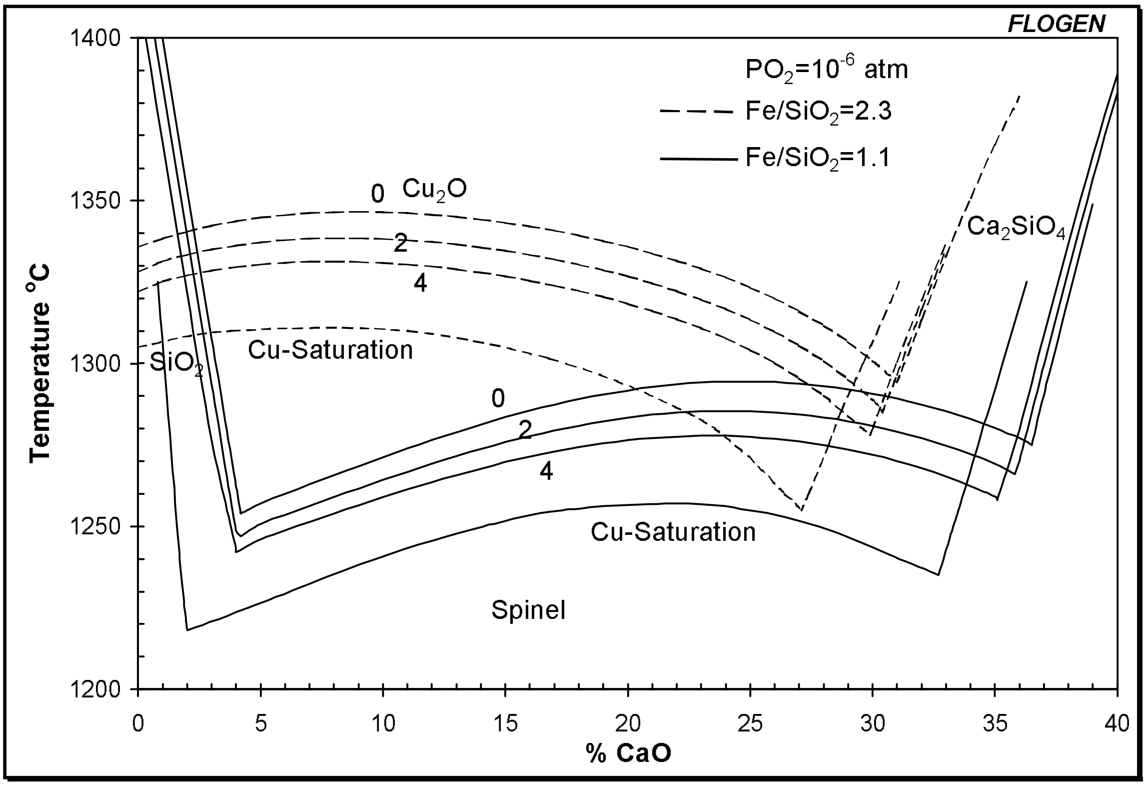

Figure 9 – Effeft of Cu_2O on the liquidus temperature at $PO_2=10^{-6}$ atm and several constant Fe/SiO_2 ratios.

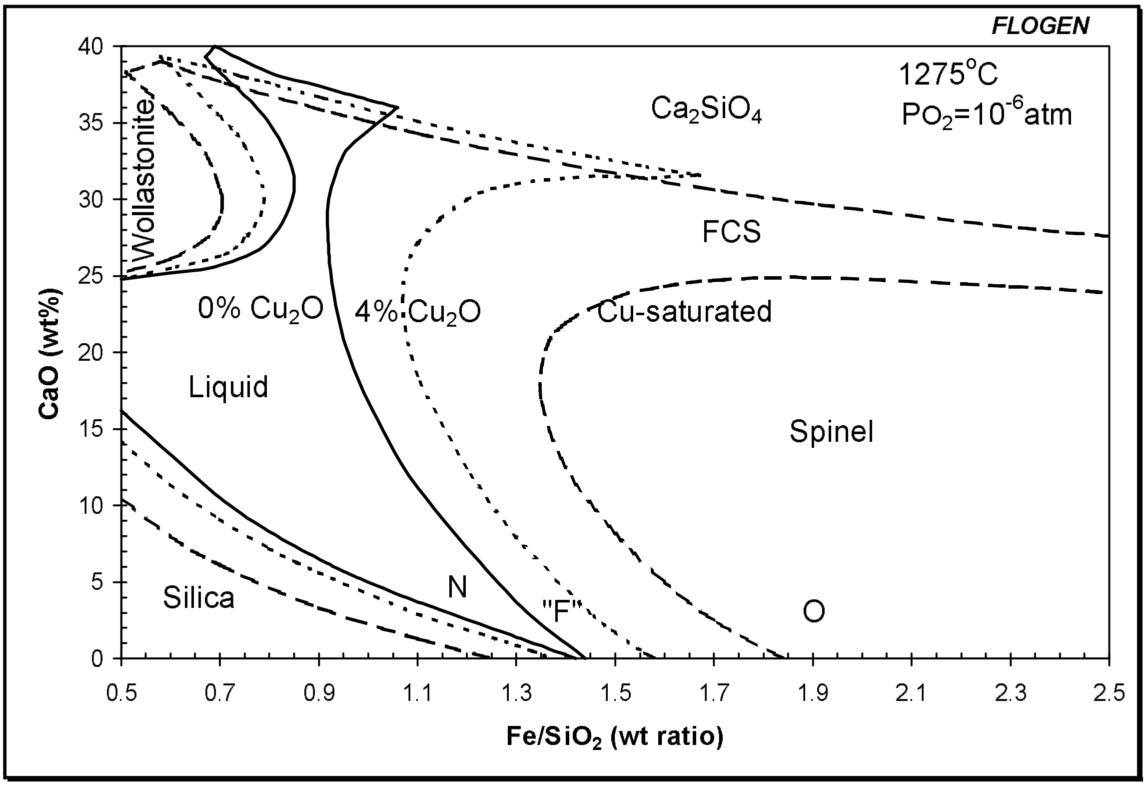

Figure 10 – Variation of liquid region of FeOx-SiO_2-CaO slag by addition of Cu_2O at 1275°C and $PO_2=10^{-6}$ atm. "F": region of "fayalite" slag; FCS: Region of ferrous calcium silicate slag.

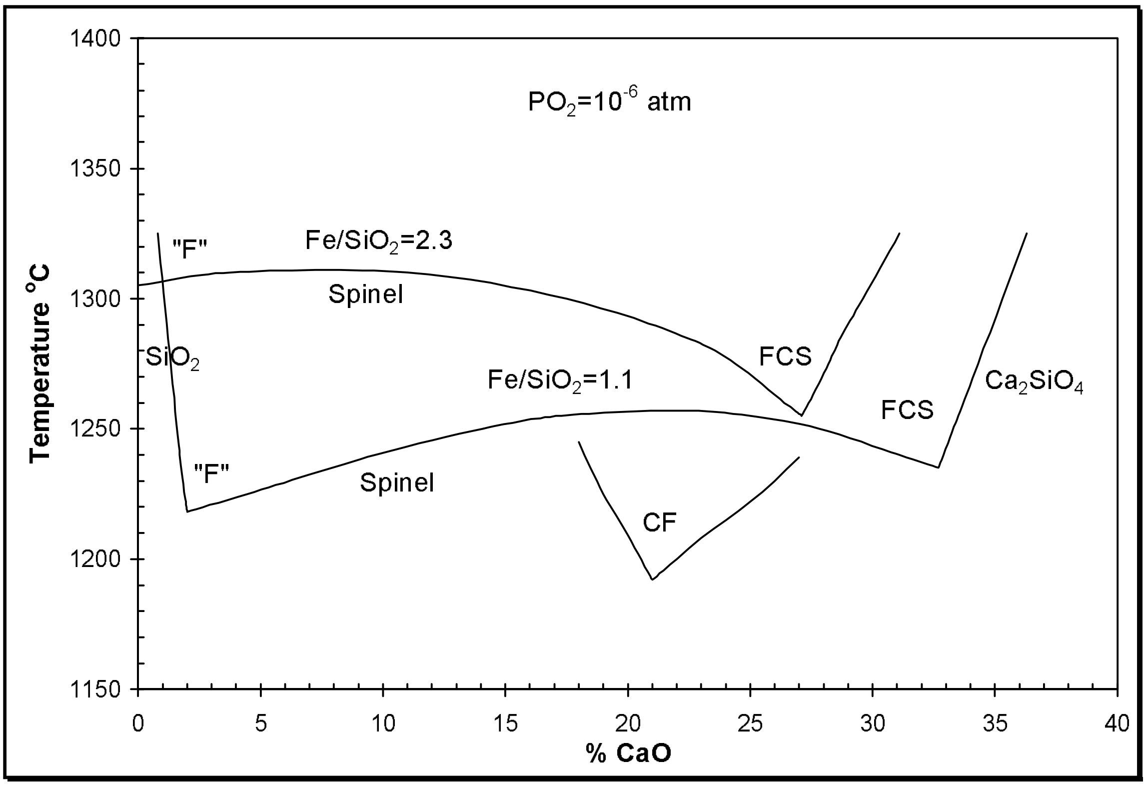

Figure 11 – Comparison of melting temperature of continuous converting slags at $PO_2=10^{-6}$ atm. "F": "fayalite" slag; FCS: ferrous calcium silicate slag; CF: calcium ferrite slag.