

# EVALUATION ON Si TRANSFER FROM INJECTED PULVERIZED COAL TO IRON INCORPORATING THE THERMODYNAMIC SYSTEM $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ <sup>1</sup>

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## Abstract

Another study was made by means of the computational thermodynamic, incorporating the  $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$  system, of the carbothermic reduction in the blast furnace which could lead to the Si transfer from the mineral matter of the pulverized coal (from the coal injection) into the hot metal. Pulverized coal injection technique, PCI, lowers the coke derived costs and decreases the emission of  $\text{CO}_2$  from coke ovens. Si content in molten metal, on the other hand, tends to increase with intensive coal injection and deteriorates the good steelmaking practice because it raises the slag amount in the refining shop. The extended Fe-C-O-Si-Al-Ca system has been used in this thermodynamic analysis which used selected carbon mass fractions and some amounts of  $\text{SiO}_2$  (later  $\text{Al}_2\text{O}_3$  and CaO), balance FeO, as input for simulations. Preliminary results show, using the percentage of  $\text{SiO}_2$  as variable, that, for the selected compositions, under strongly reducing conditions and in the presence of free carbon, minerals from the coal injected into blast furnace may have an important role in Si transfer from ash into the hot metal.

**Keywords:** PCI; Si transfer; Thermodynamics;  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ .

## ANÁLISE DA TRANSFERÊNCIA DE Si DA INJEÇÃO DE CARVÃO PULVERIZADO PARA O GUSA CONSIDERANDO O SISTEMA $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$

### Resumo

Outro estudo da redução carbotérmica no alto-forno, que pode resultar na transferência de Si, da matéria mineral do carvão pulverizado (da injeção de carvão pulverizado) ao ferro gusa, foi feito por meio da termodinâmica computacional, levando em conta o sistema  $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ . A técnica de injeção de carvão pulverizado, ICP, reduz os custos com o coque e diminui a emissão de  $\text{CO}_2$  da coqueria. O conteúdo de Si no metal fundido, por outro lado, tende a aumentar com a injeção intensiva de carvão e deteriora a boa prática na aciaria porque aumenta a quantidade de escória na ala de refino. O sistema estendido Fe-CO-Si-Al-Ca foi utilizado nesta análise termodinâmica que usou frações mássicas escolhidas de carbono e de  $\text{SiO}_2$  (e mais tarde  $\text{Al}_2\text{O}_3$  e CaO), balanço FeO, como dados de entrada para as simulações. Os resultados preliminares mostram que, tendo a porcentagem de  $\text{SiO}_2$  como variável, para as composições selecionadas, sob condições fortemente redutoras e na presença de carbono livre, minerais do carvão injetado no forno podem ter um papel importante na transferência de Si, das cinzas para o ferro gusa.

**Palavras-chave:** PCI; Transferência de Si; Termodinâmica,  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$

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## 1 INTRODUCTION

The practice of pulverized coal injection through the *tuyères* of the blast furnace – known as PCI –, consolidated worldwide, stands out as an alternative technology for a cleaner production of iron *via* the blast furnace. The basic feature of PCI technique can be found in the supplementary production of reducing gases to the process, allowing this way the partial replacement of coke.<sup>(1)</sup>

Type of coal and operating conditions, such as: pulverized coal diameter and injection method, influence the combustion behavior in the raceway zone and process efficiency. Nevertheless, operational difficulties can hinder the implementation of high PCI-rates in the blast furnace. Especially under these conditions, the unburned char presents a tendency to accumulate in the furnace causing the permeability through the coke bed to decrease.<sup>(2)</sup>

Some research results indicate that it is possible to correlate this phenomenon to the remaining *mineral matter* from coal combustion – the coal *ash*. The loss of permeability is therefore due, at least in part, to the influence of PCI ashes in the bed of coke ('dead man'), before being incorporated in the process slag.<sup>(3)</sup>

With the progress of shifting to operation of intensive coal injection, one of the peculiarities which were noticed is that Si content in molten metal tends to increase<sup>(4)</sup> – with consequences which are beyond the scope of the present work.

The purpose of this study is to set forth an evaluation described elsewhere<sup>(5)</sup> of some features which could lead or influence the silicon transfer from mineral matter of coal used in PCI into the molten pig iron being produced by the blast furnace. With the basis on the computational chemical thermodynamics, several subsystems of the Fe-O-C-Si-Al-Ca system were used in this analysis.

The advancement of the knowledge on this subject aims, in addition, to objectively improve the selection of coals used for PCI in blast furnaces, hoping that in a next future it will be possible to establish a high rate of injection with the known operational difficulties minimized or, even, eliminated.

## 2 METHODOLOGY

The equilibrium state for every system under study in the present work was determined by the Gibbs energy minimization method using the *Equilib* module of the *FactSage* software (version 6.1) – software is described elsewhere by Bale et al.<sup>(6)</sup>

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].

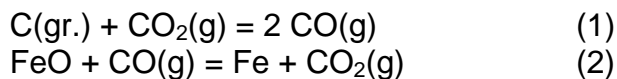
For the sake of simplicity, the analysis was mostly restricted to the temperature of 1550°C. Total pressure is 1atm but O<sub>2</sub> partial pressure varies.

## 3 RESULTS AND DISCUSSION

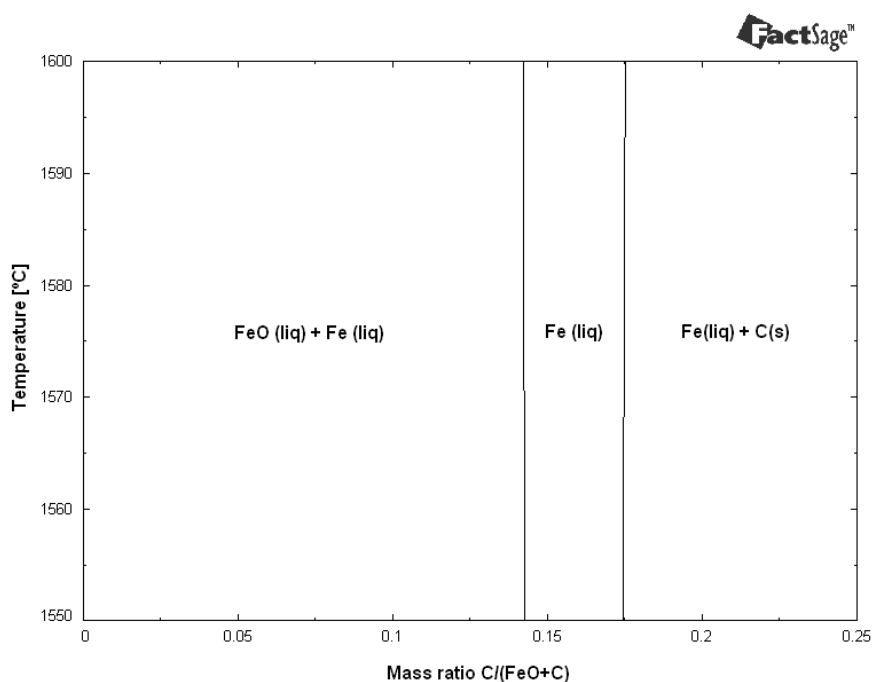
### 3.1 Fe-C-O system

The blast furnace (as any other reactor based on *carbothermic reduction*) established for the extraction of iron from its ore, should be thought of as a place where an overall equilibrium containing both phases: FeO (*l*) Fe (*l*), graphite and atmosphere will never be achieved. This is not easy to be understood, for the reason

that the equilibria suggested by the following stoichiometric reactions (CO and systems Fe-CO) seem to show otherwise:



However, it is precisely through them that it can be demonstrate that the statement is true. Analyzing the composition of each gas phase at the equilibrium state separately – both for a total pressure of 1 atm – one can see that they are identical only for the temperature of ~710 C (Baur-Glaessner diagram). Consequently, for the high temperatures in the base of the blast furnace, the equilibrium atmosphere of each of these reactions will always be dissimilar. Thus, the initial statement is fully justified by chemical thermodynamics.



**Figure 1:** Phase diagram, system FeO-C, 1 atm total pressure

The origin of this chimera is the known fact that the blast furnace is not a homogeneous reactor. There are ‘ore rich’ and other ‘coke rich’ areas so to speak. In each, there will be a local equilibrium – given by the abovementioned reactions. Nevertheless, because of a higher amount of solid carbon in the (Fe-CO) system relative to that of FeO, the overall composition of the atmosphere will tend to be close to that given by reaction (1) and, accordingly, among the liquid phases FeO and Fe, iron will be the only stable phase. By this way, the production of metallic iron from its ore – reactor’s final objective – will be reach.

The relative amount of reagent will therefore be decisive for determining the *global* equilibrium state (a fact which is not restricted to this system). This reasoning – one might say – rests on the concept of ‘excess amount of reagent’ or ‘excess reagent’. The phases and their quantities present in the state of *global* equilibrium will be directly dependent on it. The recognized existence of local equilibria – as limiting conditions –, as seen above, thought, does not oppose to the ‘*global* equilibrium’ concept.

Importantly, the global equilibrium – within the notion of ‘excess reagent’ – is achieved through the interaction provided by the *gas* phase.

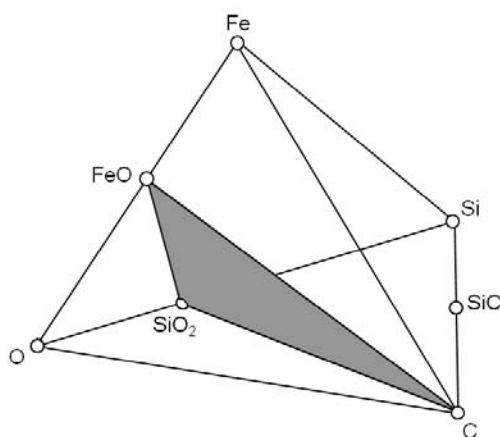
The equilibrium state of the system suggested at the outset was calculated varying the relative amounts of carbon and iron oxide. The result, a condensed overview of the phases present at equilibrium for a temperature range from 1550 °C to 1600 °C can be seen in Figure 1.

It can be observed that, starting from a value of  $C/(FeO+C)$  close to 0.15, because of excess solid carbon (and under highly reducing conditions), there is no more free iron oxide in the system at the equilibrium state. The addition of some more carbon produces no modification because there is no solid phase present in equilibrium in an intermediate region of the ratio  $C/(FeO+C)$ . That is to say that the solid carbon is *unstable* in liquid iron, which dissolves it until saturation. After saturation, the graphite phase is to participate in the equilibrium state.

Because of this behavior, the carbon content of liquid iron in equilibrium with the liquid oxide (Fe-C system) will be very different from that in equilibrium with the solid carbon, increasing from ~0 wt.% (in equilibrium with FeO) up to the saturation value of 5.36 wt.%. The lower end of the blast furnace has similarity with the last of these situations. Because of this, the carbon content of the molten metal produced in blast furnace tends to be high. Nevertheless, the actual solubility limit achieved by the C in hot metal will be given by an equilibrium in which other elements present in liquid iron – e.g. Si and Mn – have to be taken into account.

### 3.2 Fe-C-O-Si system

The system Fe-C-O-Si can adequately represent the presence of silica in the carbothermic reduction of iron in the blast furnace. The previous analysis was done considering the ternary Fe-C-O, and the system composition used in the simulation of the ore reduction was restricted to a single line (‘FeO-C’) on the composition tetrahedron of the quaternary system (Figure 2).



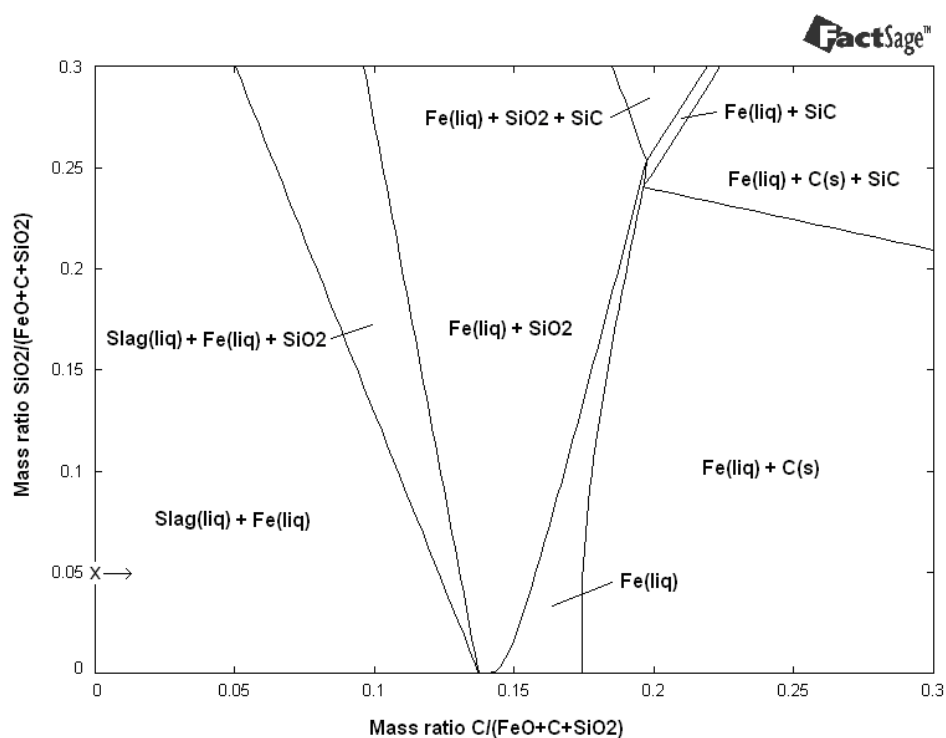
**Figure 2:** Fe-C-O-Si system, composition tetrahedron (schematic, molar basis), FeO-SiO<sub>2</sub>-C pseudoternary system can be seen as a gray triangle.

Likewise, taking compositions restricted to the (gray) triangle ‘FeO-SiO<sub>2</sub>-C’ in Figure 2, one can simulate the carbothermic reduction of iron oxide in the presence of silica, given that the burden on the lower portion of the reactor can be adequately represented by simple substances. They are: ore (FeO), silica and coke (graphite), whose compositions are identical to those of the pseudoternary *components*.

The concept of 'excess reagent' still applies here. The possibility of having a site in the furnace containing only silica is covered, and joins to the other two limiting compositions previously mentioned.

A determination of the phases at the equilibrium state in this system was made considering only the isotherm of 1550 °C, assuming that this temperature is the appropriate temperature for this region of interest in the blast furnace.

The phases of the equilibrium state in the region corresponding to the 'FeO-rich' corner – the region where the ore is dominant – can be seen in Figure 3.



**Figure 3:** Phase diagram, syst. FeO-C-SiO<sub>2</sub>, 1550 °C 1 atm, FeO-rich corner ('x' and arrow: see text).

Based on the results it can be stated that for a system containing only FeO and some SiO<sub>2</sub> – as, for example, SiO<sub>2</sub>/(FeO+SiO<sub>2</sub>)=0.05 (or 5 wt.% SiO<sub>2</sub>) marked by an 'x' on Figure 3 – there is no condensed phase at the equilibrium state whose composition exactly matches one of these 'pure' substances. Thus, given the time, FeO and SiO<sub>2</sub> will 'reduce' into a *single* liquid slag. Adding C(s) into the system (see arrow), increasingly reducing conditions are generated and iron in the liquid state comes out – reproducing the behavior of the previous system. The addition of more carbon to the system will reduce all the iron oxide from the slag into liquid Fe, leaving in equilibrium the phases SiO<sub>2</sub> (cristobalite) – *solid* at this temperature – and liquid Fe. Between these two regions (of the diagram), there is an intermediate zone, where SiO<sub>2</sub> is in equilibrium with the slag and with liquid iron. This sequence of events shows that, with a median amount of carbon, silica dissolves only partially in FeO (forming a slag), remaining in equilibrium sometimes with it, sometimes with the liquid iron phase.

If there is an excess of solid carbon in the system, SiO<sub>2</sub> also happens to be reduced, leaving only the target phase: the liquid iron. Thereafter, the system behaves as in the previous case, *i.e.*, solid graphite is an *unstable* phase, and C dissolves into liquid iron up to saturation. While saturated, besides the atmosphere, only the liquid metal and the graphite phases are present.



### 3.3 PCI and its Relationship with the Silicon

The SiO<sub>2</sub>-rich corner may represent regions of the blast furnace where there are silica or silicate particles. In relationship to the PCI, this is very relevant – as some coals have very high levels of silica and are introduced into the furnace directly in the *tuyère* zone. It must be emphasized: this route is completely different from that followed by the silicates introduced *within* the charge.

To clarify this point, the phases in equilibrium for the complete FeO-SiO<sub>2</sub>-C system were determined at a temperature of 1550 °C, 1 atm, and can be seen in the phase diagram of Figure 4.

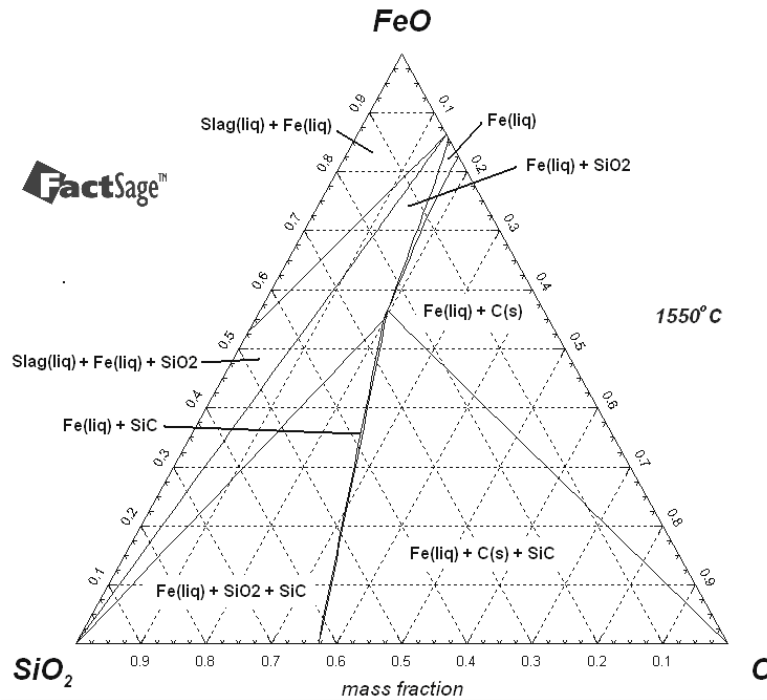


Figure 4: Phase diagram, system FeO-C-SiO<sub>2</sub>, 1550 °C 1 atm.

It is apparent from the observation of the entire phase diagram: the area where the SiC phase participates in the equilibrium state is very wide, located mainly between SiO<sub>2</sub> and C (as expected). This can be attributed to the relative stability of the SiC phase (at the expense of the silicon phase) at this temperature and reducing conditions – a fact that favors its formation during the silica reduction.

It was also noted that in areas where solid carbon (graphite) is in the equilibrium state, the ratio FeO/(FeO+SiO<sub>2</sub>)≈0.7 sets the upper limit for the formation of SiC. Where the ratio has a higher value (this corresponds to a 'normal' charge of a blast furnace) the phase SiC will not establish itself in the equilibrium state.

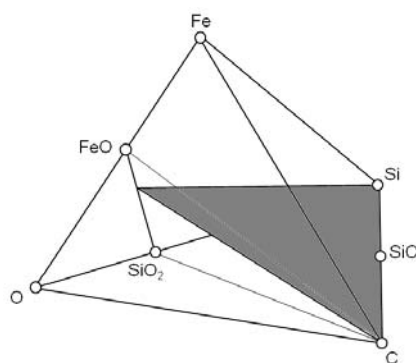
An analysis of these two aspects together reveals an interesting and novel possibility for interaction and transfer of silicon, from the mineral matter to the liquid metal. Its effect would add to that provided by the exchange of Si and C that occur through the *gaseous* phase (by means of CO, CO<sub>2</sub> and SiO). This hypothesis is based on two facts highlighted above: (i) the great chance for SiC formation in 'silica rich' regions of the blast furnace (due to some reasons; among them the PCI itself) and (ii) its instability in places where liquid iron is present as a stable phase.

In this case, direct contact of the SiC phase with the melt is essential to the idea and admitted as highly probable. Based on the phase diagram, the SiC phase

would be unstable, dissolving itself in the bath, causing, therefore, an increase in the silicon content (or Si and C – if the liquid Fe is not saturated in C).

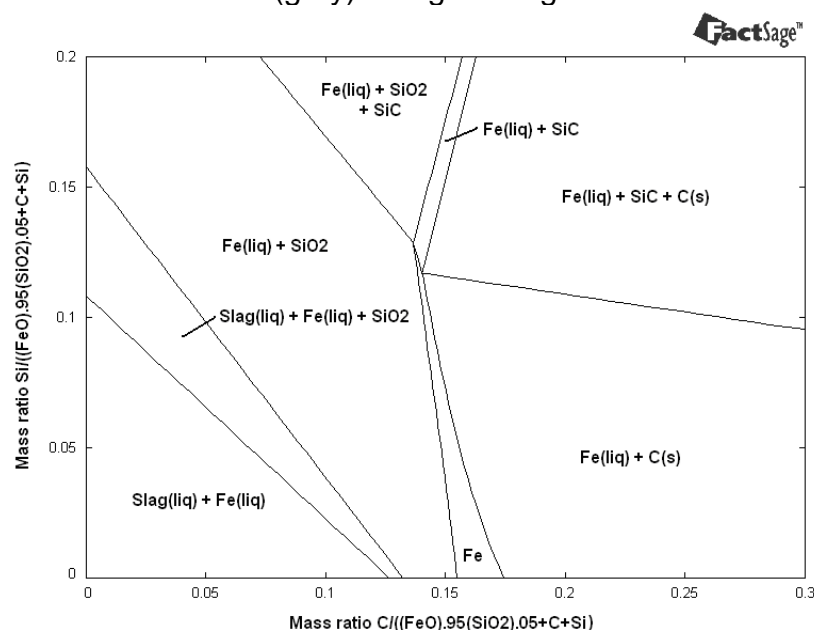
Two examples where this interaction may occur can be cited: first, a drop of iron touches a particle of SiC placed in its path while descending towards the crucible of the blast furnace; in the second, a SiC particle, formed in a region located above the bath, falls by gravity directly on it.

To elucidate the effect of SiC addition into this particular region of the furnace, new determinations of the phases in equilibrium were effected. To satisfy the hypothesis, any composition used in the determinations must be located in another subsystem of the quaternary system Fe-Si-C-O. A subsystem that can satisfy the necessary conditions is one which departs from a fixed FeO/(FeO+SiO<sub>2</sub>) ratio – for example, a system already studied, with 5 wt.% SiO<sub>2</sub> – and allows both the addition of carbon as well as that of SiC. This new system can be viewed as a gray triangle in Figure 5.



**Figure 5:** Fe-C-O-Si system, composition tetrahedron (schematic, molar basis), (FeO)<sub>0.95</sub>(SiO<sub>2</sub>)<sub>0.05</sub>-SiO<sub>2</sub>-C-Si subsystem.

It can be stated, based on results for a system containing only Fe or Fe and graphite in equilibrium – the two most interesting fields for the hypothesis – that the SiC added to the Si/((FeO)<sub>0.95</sub>(SiO<sub>2</sub>)<sub>0.05</sub>-Si-C) ≈ 0.1 is completely dissolved. This certainly leads to an increase in silicon content in the bath. carbon as that of SiC This new system can be viewed as a (gray) triangle in Figure 5.



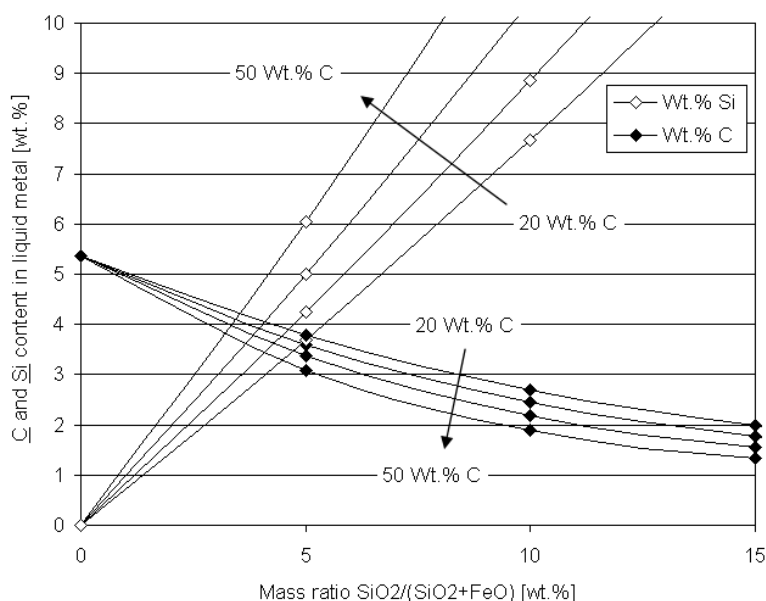
**Figure 6:** Phase diagram, system (FeO)<sub>0.95</sub>(SiO<sub>2</sub>)<sub>0.05</sub>-Si-C 1550 °C 1 atm, FeO-rich corner.

### 3.4 Analysis of Metal Produced

The contents of C and Si in the liquid phase for the region where the graphite phase is in equilibrium with liquid iron – similar to the region of the crucible furnace – for the system FeO-SiO<sub>2</sub>-C, were determined for an analysis.

For this a fixed value for  $C/(FeO+SiO_2+C) = 0.2$  was adopted – denoted, from now on, as 20 wt.% C – varying complementarily the values of FeO and SiO<sub>2</sub>. These values, taken as input, fall within the field Fe(l) + C(s) in that system (Figure 4).

The results can be seen in Figure 7. When the SiO<sub>2</sub> content of the charge increases, we observe a decrease in carbon content of the bath while the silicon content increases. The amount of carbon in the system, moreover, can not be neglected as it affects these values significantly.



**Figure 7.** Carbon and silicon content in liquid iron inside the Fe(l) + C(s) field of Figure 4, for 20-50 wt% C as function of wt.% SiO<sub>2</sub>, at 1550 °C 1 atm.

When the carbon content is presented as a function of silicon content of the bath there is a clear inverse relationship between them, Figure 8. This is a well known correlation between these two elements – see, e.g., Rosenqvist<sup>(7)</sup> – and has application in industry, ferroalloy production of low carbon content.

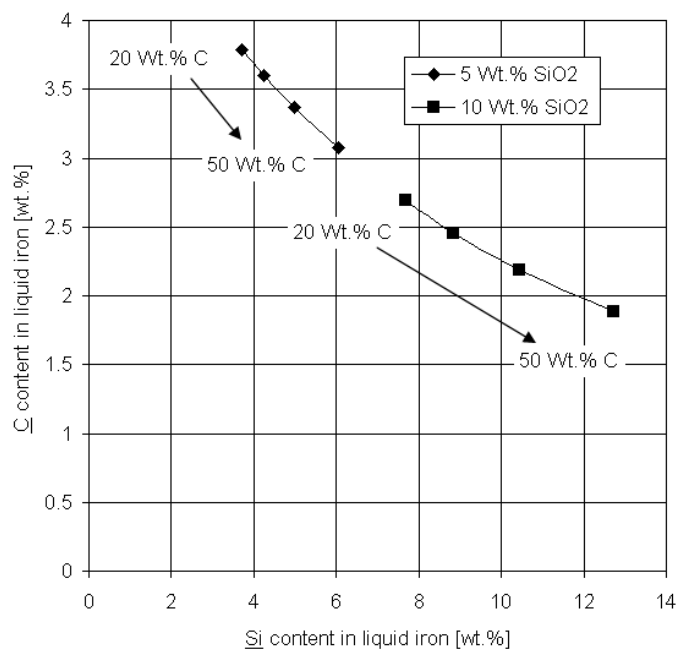
### 3.5 Systems of Higher Order

The systems of higher order: Fe-CO-Si-Al and Fe-CO-Si-Al-Ca were also studied in this work. In this case, however, a different methodology was adopted: instead of phase diagrams, equilibrium states based on some punctual trains were determined.

Basically, the mineral matter compositions from some of the coals used in PCI were cautiously simplified in order to study their product in the reducing environment of the blast furnace.

Four mineral compositions were chosen (Table 1). They represent, in a simplified way, the mineral matter found in some coals from South America and can be found in a ternary diagram CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.





**Figure 8.** Carbon-silicon relationship in liquid iron inside the Fe(l) + C(s) field of Figure 4, at 5 and 10 wt.% SiO<sub>2</sub>, for 20-50 wt% C, at 1550 °C 1 atm.

Each of these four samples was taken for a system containing 20 wt.% C – to keep track with the former results. The values of FeO and mineral matter (SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>+CaO) were varied complementarily, Tables 2 and 3 (first columns).

Determinations were always performed in the FeO-rich corner, following the concept of ‘excess reagent’.

**Table 1:** Composition of the synthetic mineral matter [wt.%], Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> mass ratio and binary basicity, CaO/SiO<sub>2</sub>

‘Coal’	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	Bas. C/S
A	80	20	0	0.25	-
B	60	40	0	0.67	-
C	76	19	5	0.25	0.07
D	57	38	5	0.67	0.09

**Table 2.** Input compositions for 20 wt.% C – (SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>) complementary to FeO content – and C and Si content in liquid iron (all figures are in wt.%)

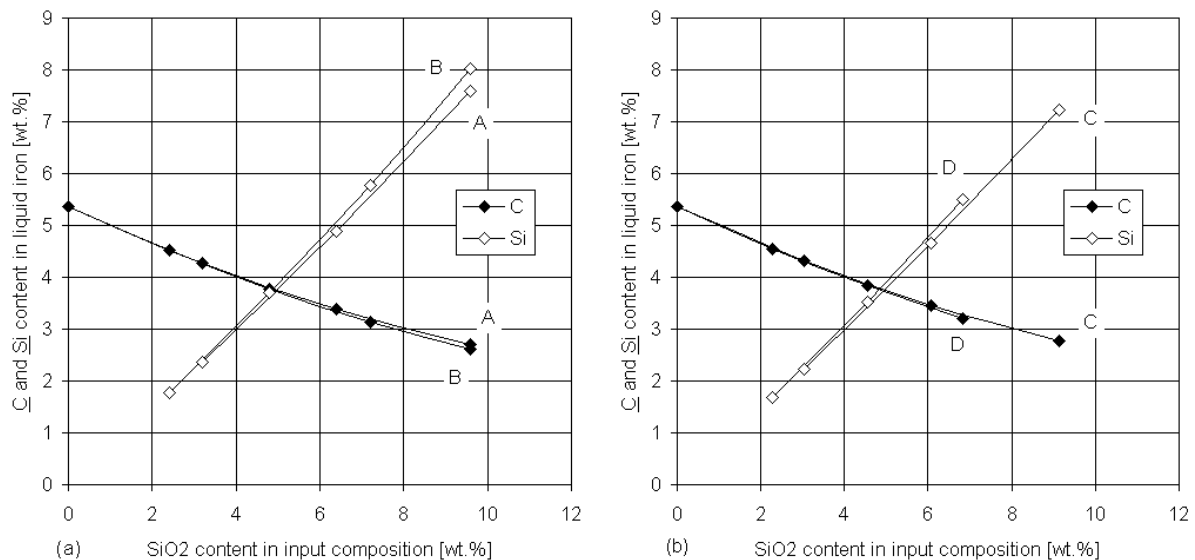
‘Coal’	FeO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	C	Si
<b>A</b>	<b>80</b>	0	0	5.36	-
(20 wt.% Al <sub>2</sub> O <sub>3</sub> )	76	3.2	0.8	4.27	2.36
	72	6.4	1.6	3.39	4.89
	68	9.6	2.4	2.70	7.58
<b>B</b>	<b>80</b>	0	0	5.36	-
(40 wt.% Al <sub>2</sub> O <sub>3</sub> )	76	2.4	1.6	4.52	1.77
	72	4.8	3.2	3.77	3.70
	68	7.2	4.8	3.14	5.78
	64	9.6	6.4	2.61	8.02

**Table 3** Input compositions for 20 wt.% C – (SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>+CaO) complementary to FeO content – and C and Si content in liquid iron (all figures are in wt.%)

'Coal'	FeO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	C	Si
<b>C</b>	<b>80</b>	0	0	0	5.36	-
(19 wt.% Al <sub>2</sub> O <sub>3</sub> )	76	3.0	0.8	0.2	4.32	2.24
	72	6.1	1.5	0.4	3.46	4.65
	68	9.1	2.3	0.6	2.78	7.23
<b>D</b>	<b>80</b>	0	0	0	5.36	-
(38 wt.% Al <sub>2</sub> O <sub>3</sub> )	76	2.3	1.5	0.2	4.55	1.69
	72	4.6	3.0	0.4	3.84	3.52
	68	6.8	4.6	0.6	3.21	5.50

The results can be seen in Tables 2 and 3 (last columns) and Figure 8 (a) and (b).

In general, the results follow the same trends as seen in Figure 7: when the SiO<sub>2</sub> content of the load increases, a decrease in carbon content of the bath is observed, while the silicon content increases. The compositions A, B, C and D affect very little this pattern.



**Figure 8.** Carbon and silicon content in liquid iron for 20 wt% C as function of wt.% SiO<sub>2</sub>, at 1550 °C 1 atm, coals A and B (a) and C and D (b)

#### 4 CONCLUSIONS

Several subsystems of the Fe-O-C-Si-Al-Ca system were used in this analysis to investigate the carbothermic reduction inside the blast furnace that could lead to the transfer of Si from the mineral matter of the injected pulverized coal (process known as PCI) into the liquid iron (hot metal).

It was shown using the amount of SiO<sub>2</sub> as variable, with or without other Al and Ca-oxides (balance FeO), as input for the simulation – under a carbon content equal or greater than 20 wt.% – that silicon oxide will exert a great influence on the Si content in liquid iron. The relative amount of SiO<sub>2</sub> (using a 'SiO<sub>2</sub>-FeO' or other, similar, axis) influences the Si content, which shows a steep increase for a growing %SiO<sub>2</sub> fraction.

Consequently, if the SiO<sub>2</sub>/FeO ratio in the bosh of the blast furnace increases – due to the silicate minerals which are arriving with the pulverized coal –, on the

basis of these results, it is reasonable to admit that silicon content in liquid iron will increase as well.

These preliminary results also suggest that, under strongly reducing conditions and in the presence of free carbon, the mineral content of the pulverized coal injected into the blast furnace could lead, in some areas of the furnace, to the production of SiC. This compound, hypothetically, along with the gas phase, could also give a contribution to aforementioned Si transfer.

Other elements, like Ca and Al (which can give origin to several mineral phases), normally present in the mineral matter of the injected coal, were also included in the analysis, but they seem not to interfere with the cited process.

## Aknowledgement

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