



THEORETICAL INVESTIGATION ON Si TRANSFER FROM INJECTED PULVERIZED COAL TO IRON¹

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Abstract

The quaternary Fe-Si-C-O system has been used in this thermodynamic analysis to investigate the Si transfer from ashes of the pulverized coal injected into the blast furnace into the molten pig iron inside the blast furnace. A new variable is introduced as the mole percent of SiO₂ along the "FeO-SiO₂-axis" of the quaternary composition tetrahedron. Using this variable as an input for the simulation, a series of equilibrium states were determined for X_c equal to 0.25, 0.35 and 0.5. These selected carbon mole fractions were chosen on the basis of the two other systems Fe-C-O and Si-C-O, preliminarily analyzed in the present work. Results show that, for high X_c values, there is an increase of Si in liquid iron proportional to an increase of the SiO₂ share on the SiO₂/FeO ratio.

Key words: PCI; Computation thermodynamics; Mineralogical composition.

INVESTIGAÇÃO TEÓRICA SOBRE A TRANSFERÊNCIA DE Si DO CARVÃO PULVERIZADO INJETADO AO FERRO

Resumo

O sistema quaternário Fe-Si-C-O foi utilizado, nesta análise termodinâmica, para se investigar a transferência de Si, das cinzas do carvão da injeção de carvão pulverizado no alto-forno, ao ferro gusa líquido. Uma nova variável foi introduzida como sendo a porcentagem molar de SiO₂ ao longo do "eixo FeO-SiO₂" do tetraedro da composição quaternária. Usando esta variável como uma entrada para a simulação, uma série de estados de equilíbrio foram determinados para X_c igual a 0,25, 0,35 e 0,5. Estas frações molares de carbono selecionadas foram escolhidas com base em dois outros sistemas Fe-C-O e Si-C-O, preliminarmente analisados no presente trabalho. Os resultados mostram que, para altos valores de X_c , há um aumento de Si no ferro gusa líquido, proporcional ao aumento da quota de SiO₂ na relação SiO₂/FeO.

Palavras-chave: ICP; Termodinâmica computacional; Composição mineralógica.

¹ Technical contribution to 65th ABM Annual Congress, July, 26th to 30th, 2010, Rio de Janeiro, RJ, Brazil.

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1 INTRODUCTION

1.1 PCI

Coke is simultaneously the raw material of higher cost in the production of pig iron and the item of greatest concern considering environmental damage generated by the steel industry.^(1,2)

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.⁽³⁾

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.⁽⁴⁾

Some research results indicate that it is possible to correlate this phenomenon to the remaining *inorganic 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.⁽⁵⁾

With the progress of shifting to operation of intensive coal injection, one of the peculiarities which were noticed is that Si in molten metal tends to increase, with consequences that are beyond the scope of the present work.⁽⁶⁾

The purpose of this study is a preliminary evaluation, based on the computational chemical thermodynamics, of the silicon transfer from mineral matter of coal used in PCI into the molten pig iron being produced by the blast furnace.

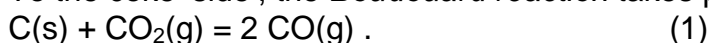
The advancement of knowledge in this subject aims, in addition, to objectively improve the selection of coals used for PCI in blast furnaces, so that it will be possible in a next future to establish a high rate of injection without the known operational difficulties.

1.2 Simulation Formulation

In order to analyze and to explain the modifications that PCI does in the blast furnace, under the point of view of the chemical thermodynamics, a systematically organized knowledge was devised and will be presented next.

The two simplest thermodynamic systems that can be used to understand the production of pig iron via the BF are: (i) a 'coke-based' system and (ii) an 'iron ore-based' system. The first can be expected to exist near a coke and the second near an iron ore particle. However, for the reason that the boundary between them is *open, matter* – the gas phase especially – can move freely from one to the other system. As it will be seen later, because of this, both systems compete to establish a single equilibrium state inside the furnace.

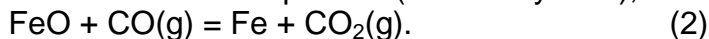
To the coke 'side', the *Boudouard reaction* takes place:



This happens to be the summation of other two reactions between solid carbon and oxygen – the first producing CO, the second CO₂. On the whole, it looks like the production of CO from CO₂ at the expenses of coke.



Around an iron ore particle (second system), the reaction is:



In opposition to the 'coke-based' system, here CO is transformed into CO₂ while iron ore is being reduced to Fe.

Metallurgists usually characterize the gas phase of each of these systems by its CO₂/CO mole ratio. From the two above mentioned stoichiometric reactions, and using the expression for equilibrium constant, this is equal to:

$$\frac{p\text{CO}_2}{p\text{CO}} = \frac{p\text{CO}}{K_1} \quad (3)$$

and

$$\frac{p\text{CO}_2}{p\text{CO}} = K_2, \quad (4)$$

respectively.

While for reaction (1) the mole ratio depends on the temperature *and* total pressure, for (2) it is purely a temperature-dependent function.

Fundamental knowledge on this subject says that, with the exception of a single temperature (for a fixed *total* pressure), these two values are equal, elsewhere the two ratios show different values – which means, 'local' gas phase compositions are different. As long as a finite *difference* persists between the CO₂/CO mole ratio of both systems (and recalling that the systems are 'connected' – as open systems – by the gas phase), there is driving force to keep the reactions going on (toward a *global* – or single – equilibrium). In simple terms, CO gas produced by reaction (1) is transported by convection to the next system. After iron oxide reduction (reaction (2)), CO₂ is transported 'back' to the first system and the cycle closes.

This is the same as to say, that giving the proper time only one equilibrium state will succeed. So, depending on the relative C and iron oxide contents, a critical C/FeO ratio exists, *above* that the iron oxide phase will be completely 'consumed' (reduced). This is, in fact, carefully *adjusted*, in order to achieve the goal of iron extraction from iron ore by carbothermic (coke) reduction.

Once all iron ore is reduced, system (ii) condenses to



with

$$\frac{p\text{CO}_2}{p\text{CO}} = \frac{p\text{CO}}{h_C \cdot K_5}; \quad (6)$$

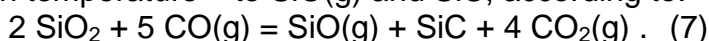
here, h_C stands for henrian activity of carbon dissolved in liquid iron.

Interesting to know, given that there is no 'solid carbon'-phase within this system, the liquid iron will be carburized sole by the gas. Once the gas composition is known, the content value can be determined with the help of Eq. (6).

A step further and the alluded *global* equilibrium resulting from the presence of graphite in equilibrium with liquid iron will establish. In the limit of the observed trend, when CO₂/CO mole ratio reaches that of the 'coal-based' system; hence, carbon content in iron will be at its highest value (see *results*, later).

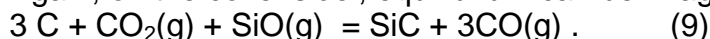
This is the same as having reaction (5) being controlled by the CO₂/CO mole ratio given by Eq.(3) – *i.e.*, value determined by Eq.(3) being inserted in Eq.(6).

In the presence of Si, a *third* system can be imagined which is composed mainly of SiO₂ particles. Similarly as with the iron ore, CO coming from the 'coke-based' system can reduce the SiO₂ – but only partially, as a consequence of the chosen temperature – to SiO(g) and SiC, according to:



$$\frac{pCO_2}{pCO} = \frac{K_7 \cdot p^4CO}{pSiO \cdot p^3CO_2} \quad (8)$$

Again, on the coke-'side', equilibrium can be imagined as composed of:



$$\frac{pCO_2}{pCO} = \frac{p^2CO}{K_9 \cdot pSiO} \quad (10)$$

As it can be seen from the CO₂/CO mole ratio expressions, Eq. (8) and (10), they both depend on the temperature *and* total pressure.

When all these systems are combined (system components are then: Fe-C-O-Si), a plain thermodynamic analysis of the Si transfer from injected pulverized coal to iron can be effected (see *results*).

2 METHODOLOGY

2.1 Software and Databases

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 5.5) – software is described elsewhere by Bale *et al.*⁽⁷⁾

The following databases were employed:

- *FSstel*: the FSstel steel database is based on relevant steel sub-systems for metallurgy. The elements included in the FactSage FSstel steel database are: Al, B, Bi, C, Ca, Ce, Co, Cr, Cu, Fe, La, Mg, Mn, Mo, N, O, Nb, Ni, P, Pb, S, Sb, Si, Sn, Ti, V, W and Zr. The database contains approximately 115 completely assessed binary alloy systems, together with 85 ternary and 17 quaternary systems for which assessed parameters are available for phases of practical relevance. As such, the database is intended to provide a sound basis for calculations covering a wide range of steelmaking processes;
- *FToxid-solution*: contains oxide solutions evaluated and optimized by the FACT group; one of these is the molten slag phase (SLAGA), which contains the fully optimized common oxide systems. The molten slag phase is modeled accordingly to the modified quasichemical model;
- *FToxid-compound*: contains 247 stoichiometric solid and liquid oxide compounds evaluated and optimized by the FACT group to be thermodynamically consistent with the FToxid solution database; e
- *FACT53*: contains data for over 4500 compounds (pure substances). It contains data from standard compilations as well as most of the data for those compounds which have been evaluated and optimized to be thermodynamically consistent with the FACT FToxid solution database.

2.2 Other Parameters

For the sake of simplicity the analysis is conducted at 1500°C only.

In order to maintain the simplicity of analysis, the compositions were restricted to the quaternary system Fe-C-O-Si. Two ternary systems, namely: Fe-C-O and Si-C-O, are analyzed preliminarily in order to make the final analysis clearer.

For this analysis, introductory in nature, the chemical compositions used in the simulations were *carefully* calculated. An example of chemical composition used as input for a calculation can be seen in Table 1. There, the values utilized in the

Fe-C-O-Si system, for fixed 20 mole % SiO₂ (“FeO-SiO₂-axis” – line 3-4 in Fig. 1) and three X_c values are displayed (see later for details). The amount of matter contained in the system for any determination totalized always *one mol* (*unimolar system*).

Tabela 1: Example of chemical compositions used as *input* when SiO₂/(SiO₂+FeO) = 0.2 (SiO₂ mole fraction) or 20% SiO₂, as a function of X_c, – given both as *chemical* (SiO₂, FeO, C) and *atomic* (Fe-C-O-Si) species (note: ‘C’ denotes either *graphite* or the element *carbon*)

X _c	Amount [mole]					
	FeO	SiO ₂	Fe	C	O	Si
0.25	0.273	0.068	0.273	0.250	0.409	0.068
0.35	0.236	0.059	0.236	0.350	0.355	0.059
0.50	0.182	0.045	0.182	0.500	0.273	0.045

A schematic diagram displaying phases over the *composition tetrahedron* for the quaternary Fe-C-O-Si system can be seen in Figure 1 (see *results* for detailed explanations).

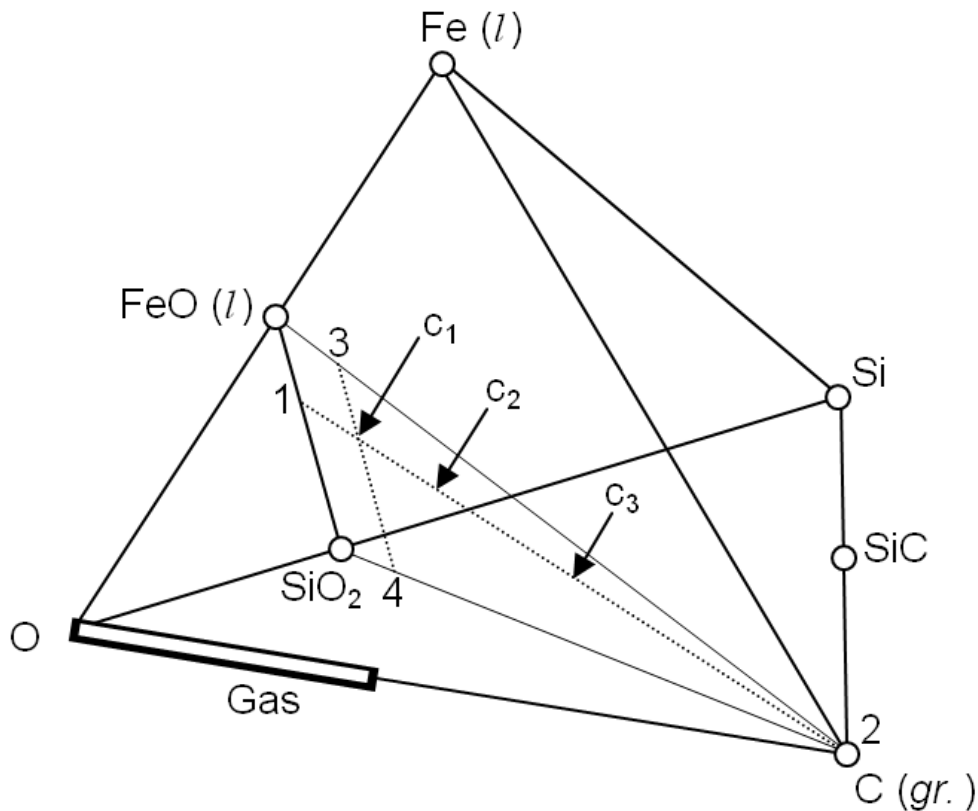


Figure 1: Schematic diagram displaying phases over the composition tetrahedron for the quaternary Fe-C-O-Si system; only positions of the analysis-related phases are presented; see *results* for details on compositions c₁, c₂ and c₃



3 RESULTS AND DISCUSSION

3.1 Fe-C-O System

The most relevant phases of the *ternary* system Fe-C-O at temperature of 1550°C *i.e.* liquid iron, liquid FeO (slag), gas and graphite – given on a mole basis – are displayed over the ‘frontal’ face of the composition tetrahedron (Figure 1).

As can be easily seen, along the line which connects FeO(*l*) to graphite the carbon mole fraction, X_c , increases from *zero* to *unity*. This is analogous to the increase of the coke fraction inside a reactor containing iron ore (FeO(*l*)) and coke. Taking a very simplified representation of the blast furnace as a model, this corresponds with some places located in the throat – where the ratio can be almost zero – and some other in bosh – where it tends to be unity.

Using the X_c variable as an input for simulation, a series of equilibrium states for this system were determined and the results can be seen in Figure 2.

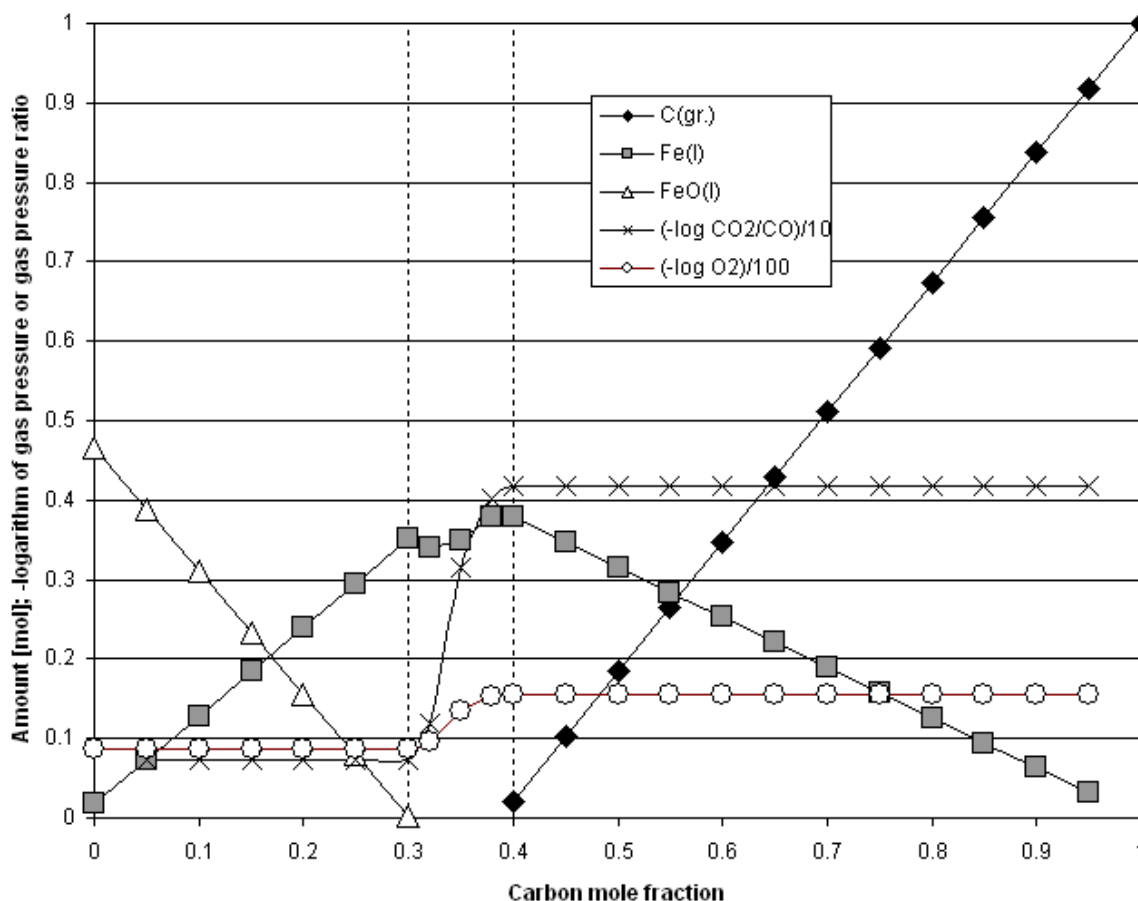


Figure 2: Amount of phases [mol] present at equilibrium state for system Fe-O-C at 1550°C, along the FeO(*l*)-C(*gr.*) line of Fig.1, as a function of carbon mole fraction, X_c ; see text for explanation on sections **A**, **B** and **C**

The *Boudouard reaction* (1) – even though very important – is only approximately represented at the extreme right of Section **C** of Figure 2, close to $X_c = 1$, where no more iron is present in the system (actually it belongs to the binary C-O subsystem).

Section **A** corresponds to equilibrium depicted by Reaction (2) where the reduction of the iron ore takes place and composition of the gas phase is set by Eq.(3) and section **B** corresponds to Reaction (5) with gas phase (Eq.6) setting the carbon content of liquid iron.

Section **B** of the figure can be identified with the point in time where iron ore 'vanishes' and the remaining liquid iron reaches the 'coke-based' system. The presence of graphite in equilibrium with liquid iron (section **C**) was referred earlier as 'global equilibrium'. This will cause the saturation of liquid iron with carbon, Figure 3.

For the Fe-C-O system, above $X_c = 0.3$ there is no more iron ore phase left.

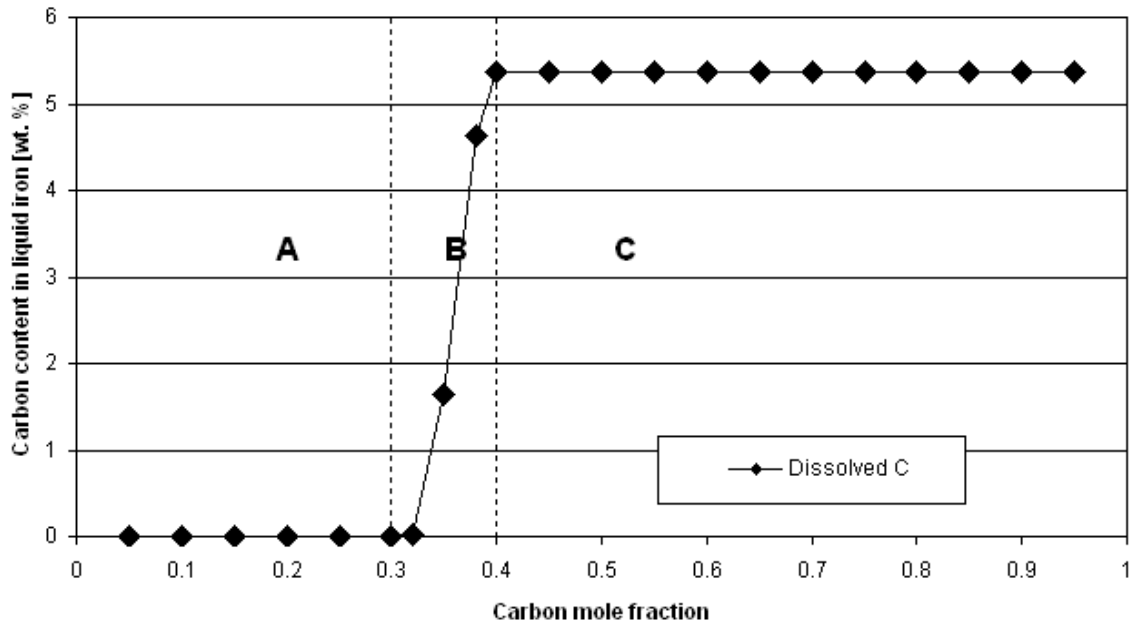


Figure 3: Carbon content in liquid iron at equilibrium state for system Fe-O-C at 1550°C, along the line FeO(l)-C(gr.) of Fig.1, as a function of carbon mole fraction, X_c ; see text for explanation on sections **A**, **B** and **C**

3.2 Si-C-O System

The 'base' face of the composition tetrahedron of Figure. 1 shows the positions for the most relevant phases of system Si-C-O at the temperature of 1550°C: silicon, silicon oxide (SiO_2 – cristobalite), SiC, gas and graphite in a molar basis.

Going along the line which connects SiO_2 to graphite, the carbon mole fraction of this system increases, from zero to unity. This is comparable to the introduction of coke into a reactor containing initially silicon oxide only.

Using this variable as an input for the simulation, a series of equilibrium states for this system were determined and the results can be seen in Figure 4.

Sections **A** and **B** correspond to equilibria depicted by Reactions (7), and (9), respectively, with the gas phase given by Eq.(8) and (10).

As can be easily noticed, for this system, above $X_c = 0.5$ there is no more silicon oxide phase left in the equilibrium state.

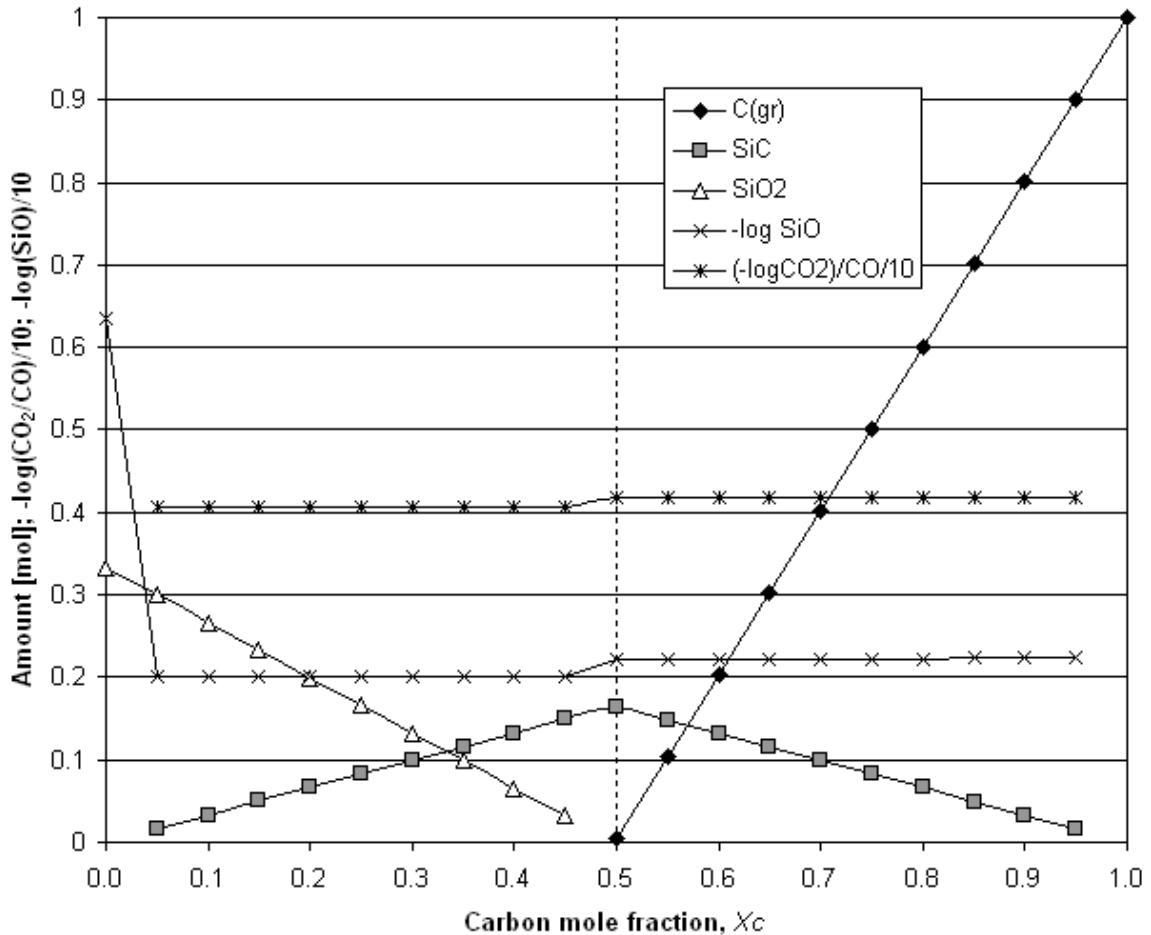


Figure 4: Amount of phases present at equilibrium state for system Si-C-O at 1550°C, along the SiO₂-C(gr.) line of Fig.1, as a function of carbon mole fraction, X_c ; see text for explanation on sections A and B.

3.3 Fe-C-O-Si System

The last system to be analyzed is the quaternary Fe-Si-C-O system. All compositions used in this analysis will belong to the triangle FeO(l)-SiO₂-C. Taking the point C₁ as an example, it can easily be seen that X_c (given along the line 1-2) varies from zero to unity and as a fixed value at C₁. A new variable is introduced and is given as the mass percent of SiO₂ along the “FeO-SiO₂-axis”. Along the line 3-4 it varies from 0 to 100 mole % and has a fixed value at C₁. As can be easily seen, points C₂ and C₃ have the same mole %SiO₂ but show increasingly X_c values.

Using this variable as an input for the simulation, a series of equilibrium states for this system were determined for X_c equal to 0.25, 0.35 and 0.5 and the results can be seen in Figure 5. These selected carbon mole fractions were chosen on the basis of the two predecessor systems Fe-C-O and Si-C-O and justify the former analyses.

As can be seen, the increase on SiO₂ proportion alone does not reflect necessarily an effective increase of %Si in liquid iron. To be successful, a high X_c value is also necessary – additionally, X_c values will control the \underline{C} in liquid iron. Once that requisite is satisfied, the relative amount of SiO₂ in the system does promote a clear effect on \underline{Si} , with a steep increase for a growing mole %SiO₂ proportion.

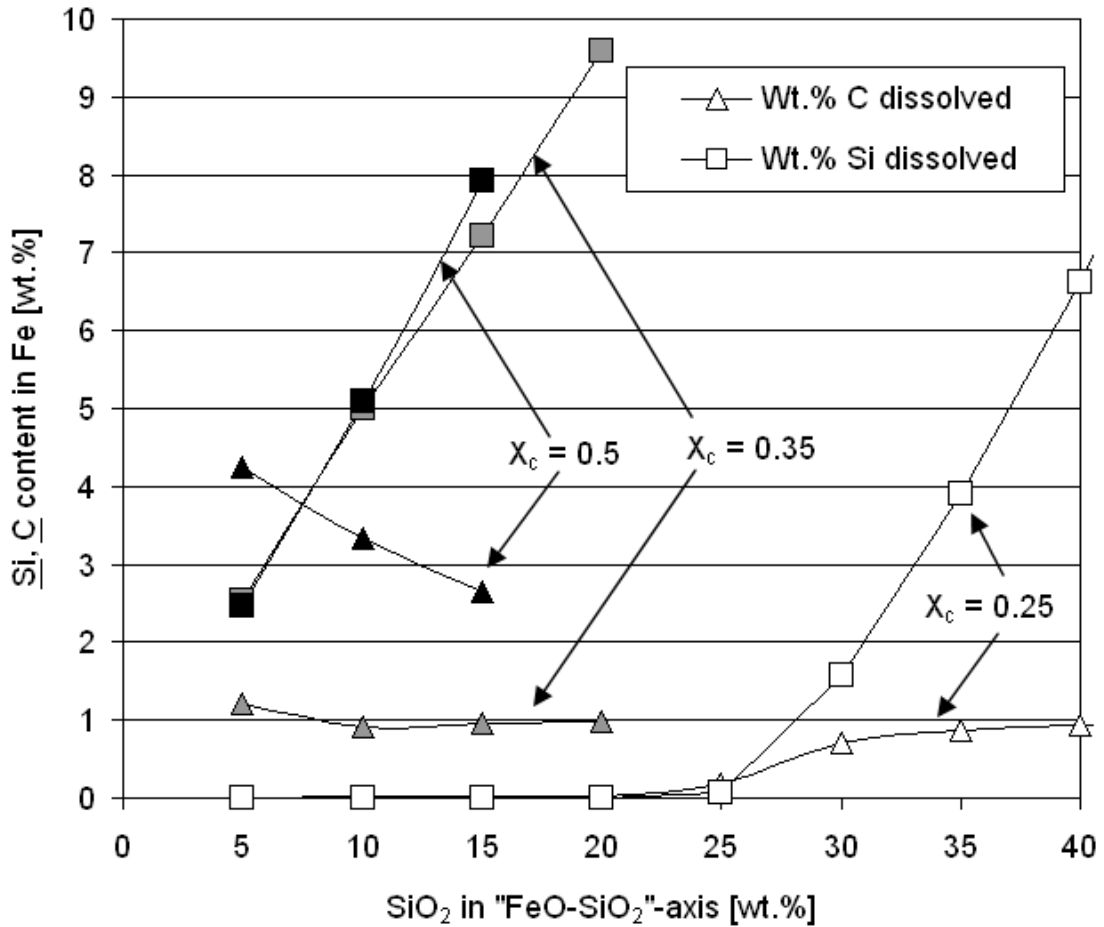


Figure 5: Silicon and carbon content in liquid iron as a function of %SiO₂ in the “FeO-SiO₂-axis”.

Therefore, if PCI alters the FeO/SiO₂ proportion, enlarging the SiO₂ share, among the consequences there is a direct increase of the silicon content in liquid iron.

The higher Si content in liquid iron is associated in the literature to presence of SiO(g) in the BF atmosphere.⁽⁶⁾

The SiO(g) content (or partial pressure) in gas phase determined within the present work appears to be directly proportional to the amount of SiO₂ – the higher the share, the greater the content in gas product. SiO(g) content, however, does not follow a direct proportion with X_c (Figure 6).

4 CONCLUSIONS

The quaternary Fe-Si-C-O system was used in this analysis to investigate the Si transfer from pulverized coal injection to iron in the blast furnace.

Using the variable mole percent of SiO₂ (along the “FeO-SiO₂-axis”) as input for the simulation – under X_c equal or greater than 0.35 – it was shown that it will control the S_i in liquid iron. The relative amount of SiO₂ in the system *does* promote a clear effect on S_i, with a steep increase for a growing mole %SiO₂ proportion.

These preliminary results show that, under strongly reducing conditions and in the presence of free carbon, the mineral content of pulverized coal injected into the blast furnace appears to have an important role in reactor conditions.

Therefore, if the SiO_2/FeO ratio in the bosh of the blast furnace increases due to the contribution of silica incoming 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.

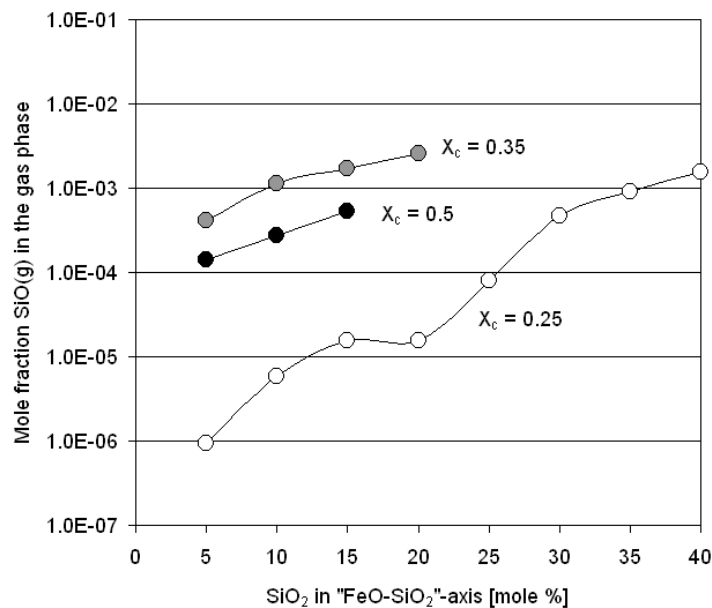


Figure 6: SiO(g) content in the gas phase as a function of %SiO₂ in the "FeO-SiO₂-axis"

Acknowledgement

The author is grateful for the support of this work by the National Research Council, CNPq.

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