2. Literature Review

2.1. Thermodynamic and Kinetic Review

The decarburization and iron oxide reduction in EAF operation take place in heterogeneous system. The liquid phase includes molten metal and slag, the gas phase basically contains C-O compounds and the solid phase is the carbonaceous source such as graphite, coke or anthracite, assuming that all ferrous materials are in liquid phase. For the sake of simplicity, volatile matter present in carbonaceous materials, and therefore hydrogen are omitted. Figure 1 presents a simplified diagram pointing out the most probable reactions and interfaces, which have been studied in the literature.



Figure 1 - Heterogeneous reactions in the system Fe-C-O interface

There are six binary interfaces: (i) MS Metal-Slag; (ii) MG Metal-Gas; (iii) MC_{gr} Metal-Graphite; (iv) SC_{gr} Slag-Graphite; (v) SG Slag-Gas; (vi) GC_{gr} Gas-Graphite. Additionally, there are three ternary interfaces: GSM Gas-Slag-Metal; MGC_{gr} Metal-Gas-Graphite; SGC_{gr} Slag-Gas-Graphite.

MS Metal-Slag is interface of the metal phase covered by slag, where most of reactions can occur. MG Metal-Gas occurs when metal droplets are ejected from the metal phase and interacts with the oxidant compounds present in the EAF atmosphere. MC_{gr} Metal-Graphite is expected to occur when the metal phase is submitted to deep carbon injection, the dissolution of solid carbon particles and their reaction with soluble or gaseous oxygen may take place in the metal phase bulk. SC_{gr} Slag-Graphite interface includes the iron oxide reduction kinetics, which is one of the more important investigation issues for EAF operation, because of its significant effect on the metallic mass yield. The SG Slag-Gas and GC_{gr} Gas-Graphite have a minor role on the possible and realistic interfaces for the mentioned reactions.

However, complex ternary interfaces are considered to occur more often than the binary interfaces. Experiments under laboratory conditions have been used to isolate some variables in order to study the binary interfaces or to suppress combined effects of different rate-controlling mechanisms. Some of those experiments will be approached to consolidate the most accepted set of fundamentals involving the reactions on Fe-C-O system. Nevertheless, decarburization and iron oxide formation and reduction are usually taking place simultaneously along the melting time in industrial scale, and therefore, reactions in series have been concluded to occur very often.

A short review is presented in the next sections, describing briefly the basis of thermodynamics and kinetics involved on the decarburization and iron oxide reduction processes.

Note: Equations notation including "AN" mean that the demonstration and complimentary data are available in Annexes 1 to 3.

2.1.1. Thermodynamics of the Decarburization

Kinetics models usually refer to driving forces, those of which in some conditions define the rate of reactions. Generally, the driving forces for mass transfer process or to move forward or reverse a chemical reaction, depend on the thermodynamic equilibrium at the interface of reactions. Hence, some particular conditions on the system Fe-C-O are reviewed, aiming to identify the equilibrium concentrations of carbon and iron oxide which are commonly used in the kinetics models.

System [C]-[O]-CO

Assuming the overall reaction as follows,

 $\underline{C} + \underline{O} \rightarrow CO_{(g)}$ $\Delta G^{0} = -18,544 - 40.76 \text{ T [J/mol]}$

eq.AN1 - 4

Liquid Phase: Solution Fe-C-O Gas Phase: CO (CO₂ and O₂ are neglected) The equilibrium relation in the system Fe-C-O resulting in a liquid solution in equilibrium with CO in the gas phase, where total pressure $p = p_{CO}$ can be written as

$$[\% O] = \left(\frac{P_{CO}}{f_C \cdot f_O}\right) \cdot EXP\left(-\frac{2,230}{T} - 4.90\right) \cdot \frac{1}{[\% C]} \qquad \text{eq.AN1 - 9}$$

where f_c and f_o are the Henryan coefficient of activity for carbon and oxygen, respectively. Figure 2 plots eq.AN1 - 9.



Figure 2 - Equilibrium curves for C-O dissolved in iron at 1873 K, according to eq.AN1 - 9 (solid line) and eq.AN1 - 18 (dashed line, alternative data base) demonstrated in Annex 1, for different CO partial pressures.

The effect of p_{CO} is significant on the solubility of carbon and oxygen in iron. This concept is well known in industry and has been used to develop OSM and EAF models. Secondary metallurgy through vacuum degassing, decrease the partial pressure of CO, allowing lower carbon concentrations equilibrated with lower soluble oxygen, as shown in Figure 3 (a). This technology allows the production of ductile materials due to low carbon content, as well lower inclusions index because of small amount of further deoxidation products. Nevertheless, in EAF operation, the carbon and oxygen data lies above the equilibrium curve for $p_{CO} = 1$ atm. Figure 3 (b) reports industrial data, indicating that the soluble oxygen is around 15 to 25% higher than the equilibrium at $p_{CO} = 1$ atm. According to the reaction $\underline{C} + \underline{O} \rightarrow CO_{(g)}$ and eq.AN1 - 5 at 1873 K, the equilibrium product should be $[\% \underline{C}].[ppm\underline{O}] \equiv 23$, instead of 24-28 as reported by industrial data [7-9]. As discussed in the next section, for low carbon contents kinetic constraints may explain this fact. The arriving oxygen does not react with carbon because of its slow mass transfer in this condition. Therefore oxygen could dissolve in the metal phase and precipitate iron oxide [1].



Figure 3 – Soluble oxygen (a) in a vacuum degasser; (b) Industrial data 1 [7], Industrial Data 2 and 3 [9]

System [C]-[O]-CO-CO₂

Assuming the overall reaction as follows,

$$CO_{2(g)} + \underline{C} \rightarrow 2CO_{(g)} \quad \Delta G^0 = 148.006 - 132,20T \qquad eq.AN1 - 22$$

Liquid Phase: Solution Fe-C-O Gas Phase: CO-CO₂ (O₂ neglected)

The equilibrium relation in the system Fe-C-O resulting in a liquid solution in equilibrium with CO in the gas phase, where total pressure $p_{CO} + p_{CO_2} = 1$, and allowing CO₂ to coexist, a thermodynamic relation can be written as

$$\frac{P_{CO}^2}{1 - P_{CO}} = EXP\left(\frac{-17,802}{T} + 15.90\right) f_C \cdot [\% C]$$
eq.AN1 - 27

Figure 4 presents the plot of p_{CO} as a function of carbon concentration in iron. It can be seen that $p_{CO_2} \approx 1\%$ when %C >0.15%. In the range of 0.04%< %C < 0.15%, $p_{CO_2} \approx 2\%$, and for %C <0.03% may reach $p_{CO_2} \approx 5-15\%$. For simplification purposes, p_{CO_2} is assumed to be zero at EAF operational conditions.



Figure 4 – Equilibrium of CO and CO₂ at 1873 K.

System [C]-[O]-(FeO)

Assuming the overall reaction as follows,

 $Fe_{(l)} + \underline{O} \rightarrow FeO_{(l)}$ $\Delta G^{0} = -140,250 + 58.31 \text{ T}$ eq.AN1 - 31

Liquid Phase: Solution Fe-C-O

Pure FeO (Slag)

Gas Phase: CO (CO₂ and O₂ are neglected)

The equilibrium relation in the system Fe-C-O as a liquid solution in equilibrium with CO, CO₂ and O₂ in the gas phase, where the activity of FeO is $a_{FeO} = 1$

$$K_{FO} = \frac{a_{FeO}}{h_O} = EXP\left(\frac{16,869}{T} - 7.01\right)$$
 eq.AN1 - 32

$$[\%C_{MIN}] = EXP\left(\frac{14,639}{T} - 11.91 + \ln\frac{P_{CO}}{f_C}\right)$$
eq.AN1 - 36

[% C_{MIN}] is the carbon concentration in equilibrium when the maximum oxygen solubility is achieved under $a_{FeO} = 1$. In Table 1, the [% C_{MIN}] could be estimated as 0.011% at $p_{CO} = 1$ atm.

fc	1,00		
fo	1,00		
Т	1873	К	
P _{CO}	[atm]	[atm]	[atm]
	0,5	1,0	1,5
[%C _{MIN}]	0,006%	0,011%	0,017%
[%O]	0,2171%	0,2171%	0,2171%
ppm [O]	2171	2171	2171

Table 1 – Minimum carbon concentration estimate [9].

On the other hand, with the presence of other oxides in the slag, the activity of FeO assumes values different than unity. Figure 5 presents a plot and regression of experimental data from wide slag sources such as silicates up to CaO saturated. The basicity B varied from 0 to 3, and this particular regression, the activity coefficient is valid only for slags containing CaO, SiO₂, FeO <40%, MnO<15%, MgO<20% and P₂O₅<20%.



Basicity B is defined as:

$$B = \frac{\% CaO + 1.4\% MgO}{\% SiO_2 + 0.84\% P_2O_5} \quad \text{eq. 1}$$

Figure 5 – Effect of slag basicity on the activity coefficient of iron oxide in simple and complex slags at 1600 $^\circ C$ [8]

Applying the activity coefficient of iron oxide in eq.AN1 - 38 (alternative data base) thus,

$$K_{FO} = \frac{a_{FeO}}{h_O} = \frac{\gamma_{FeO}(\% FeO)}{h_O} = EXP\left(\frac{13.200}{T} - 5,52\right)$$
 eq. 2

combining $a_{FeO} = \gamma_{FeO} \cdot \frac{\% w_{FeO}}{MW_{FeO} \cdot \sum \frac{\% w_i}{MW_i}}$

$$\ln h_o = -\frac{13,200}{T} + 5.52 + \ln(\gamma_{FeO}.0.00847 \cdot (\% FeO))$$
eq. 3

rearranging eq.AN1 - 7

$$\ln P_{CO} - \ln f_C . [\% C] - \ln f_O . [\% O] = \frac{2,555}{T} + 4.67$$
 eq. 4

Fe saturated with oxygen, precipitating pure FeO

 $\ln h_{Q} = \ln f_{Q}.[\% O] \qquad \qquad \text{eq.AN1 - 35}$

Combining eq. 3, eq. 4 and eq.AN1 - 35,

$$[\%C_{MIN}] = \\ = EXP\left(\frac{10,645}{T} - 10.19 + \ln\frac{P_{CO}}{f_C} - \ln(\gamma_{FeO}.0.00847 \cdot (\%FeO))\right) \qquad \text{eq. 5}$$

Then, $[%C_{MIN}]$ is now defined as a function of maximum solubility of oxygen in iron in the presence of FeO with activity smaller than unity.

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Table 2 considers typical EAF slag compositions (B = 2.7 to 3.3) and extreme compositions (B = 2.1 and 3.9). The FeO content is kept smaller than 40%, avoiding any extrapolation of the regression available in Figure 5.

Table 2 – Estimate for minimum carbon concentration taking into account FeO activity in the slag different than unity. Where, $B2 = CaO/SiO_2$.

	-		,	-
fc	1,00			
fo	1,00			
Т	1873	К		
m	0,00847			
P _{CO [atm]}	1,0	1,0	1,0	1,0
В	2,1	2,7	3,3	3,9
B2 (MgO 10%, SiO2 12-20%)	1,5	2,0	2,5	3,0
CaO+SiO ₂ +MgO+P ₂ O ₅	65%	66%	65%	65%
SiO ₂	20%	17%	14%	12%
CaO	29%	33%	35%	37%
MgO	10%	10%	10%	10%
P ₂ O ₅	1%	1%	1%	1%
MnO	5%	5%	5%	5%
FeO	35%	35%	35%	35%
γ́FeO	2,49	1,52	1,23	1,05
γ _{FeO} . (%FeO)	0,87	0,52	0,43	0,37
(%FeO).[%C]	0,52	0,86	1,06	1,24
γ _{FeO} . (%FeO).[%C]	1,30	1,30	1,30	1,30
[%C ^{eq}]=[%C _{MIN}]	0,015%	0,025%	0,030%	0,035%

Thus, according to the available data, it can be said that the minimum carbon [% C_{MIN}] expected during decarburization process in EAF may vary form 0.013% up to 0.030%.

2.1.2. Thermodynamics of the Iron Oxide Reduction

System [C]-CO-(FeO) and variable Slag Basicity

Assuming the overall reaction as follows,

 $FeO_{(1)} + C = Fe + CO$ $\Delta G^0 = 121.706 - 99,07 T$ eq.AN1 - 47

Liquid Phase: FeO-CaO-MgO-SiO₂-P₂O₅ (Slag) Solution Fe-C-O Gas Phase: CO (CO₂ and O₂ are neglected)

FeO as a liquid solution in equilibrium with CO in the gas phase. The activity of FeO a_{FeO} is a function of slag basicity. FeO activity is converted to %wt

FeO based on the regression available in Figure 5 and the slag molecular weight computed according to

Table AN1 - 9.

Thus, at 1873 K, assuming f_c=1 e P_{CO}=1 atm,

$$K_{FC} = \frac{1}{\gamma_{FeO} \cdot (0,00846) \cdot (\% FeO) \cdot [\% C]} = 59,99$$

$$(\% FeO) \cdot [\% C] = \frac{1}{\gamma_{FeO} \cdot (0,508)}$$
eq.AN1 - 54



Figure 6 – FeO in slag in equilibrium with Fe-C alloy. The FeO is computed assuming effect of the slag basicity on the FeO activity

In Figure 6, computing FeO content based on eq.AN1 - 54, it is shown significant influence of slag basicity for carbon concentrations below 0.10%C, and very high effect below 0.05 %C. In Figure 7 industrial data from oxygen steelmaking and EAF are compared in terms of resulting FeO content in the slag by the end of refining step. Although, iron oxide content of the slag is well above the slag-metal equilibrium values for low carbon contents just before tap for EAF conditions, the product [%C].[ppm O] = 26 ± 2 approximately corresponds to the C–O equilibrium value for gas bubble pressures of 1.3 ± 0.2 atm in the EAF steel melt [9].



Figure 7 – Relation between %FeO in slag and %C in steel at tap in EAF steelmaking is compared with the relations in BOF (Basic Oxygen Furnace) and OBM(Q–BOP) steelmaking [9].

System [C]-CO-(FeO) and variable Slag Basicity

The gas bubble is presumed to be essentially composed by CO. However, assuming the overall reaction as follows,

 $FeO_{(l)} + CO = Fe + CO_2$ $\Delta G^0 = -55.400 + 44,0 \text{ T}$ eq.AN1 - 56

Liquid Phase: FeO-CaO-MgO-SiO₂-P₂O₅ (Slag) Gas Phase: CO and CO₂ (O₂ is neglected)

FeO as a liquid solution in equilibrium with CO and CO₂ in the gas phase,

$$K_{FCO_2} = \frac{P_{CO_2}}{a_{FeO}} = EXP\left(\frac{6,663}{T} - 5.29\right)$$
eq.AN1 - 57

Consequently, at 1873 K some CO₂ may be expected, according to the computed ratio p_{CO_2}/p_{CO} in Table 1, when the FeO activity is smaller than one.

Temperature	1873	К			
Basicity B	1,7	2,1	2,7	3,3	3,9
B2 (MgO 10%, SiO2 12-20%)	1,1	1,5	2,0	2,5	3,0
$CaO+SiO_2+MgO+P_2O_5$	64%	67%	68%	67%	67%
SiO ₂	22%	20%	17%	14%	12%
CaO	24%	29%	33%	35%	37%
MgO	10%	10%	10%	10%	10%
P_2O_5	1%	1%	1%	1%	1%
MnO	5%	5%	5%	5%	5%
Other	2%	2%	2%	2%	2%
FeO	36%	33%	33%	33%	33%
γ́FeO	2,79	2,49	1,52	1,23	1,05
γ_{FeO} . (%FeO)	1,00	0,82	0,49	0,41	0,35
P _{CO2} /P _{CO}	0,18	0,15	0,09	0,07	0,06

Table 3 – Estimate the ratio p_{CO_2}/p_{CO} taking into account FeO activity in the slag as a function of slag basicity. Where, $B_2 = CaO/SiO_2$

Many reports based on industrial data have proved that both oxygen and EAF steelmaking can be considered a non-equilibrium state. Several empirical relations in the system Fe-C-O have been proposed so far. Figure 8 presents examples valid for OSM.



(a) (b) Figure 8 – (a) Variation of product (FeO)[%C] with carbon content of steel at first turndown;(b) Variation of product [ppm O][%C] with carbon content of steel at first turndown [10].

2.1.3. Summary – Thermodynamics of System Fe-C-O

- It has been accepted that during the course of oxygen blowing, the C-O relation may departs significantly from the predicted equilibrium assuming the partial pressure of CO to be 1 atm. That behavior might be related to kinetics limitation mainly at lower carbon concentrations or even due to a higher CO pressure 1.3-1.5 atm. Consequently, empirical relations for % wt FeO in slag, soluble oxygen and carbon in iron melts have been proposed.
- The activity of FeO in complex slags maybe affected by slag basicity, and consequently, the C-O relations may be affected too. The minimum carbon concentration in equilibrium is expected to be around 0.01 to 0.03 %wt C.
- The composition of the gas bubbles in the metal phase is presumed to be predominantly filled by CO, or $p_{CO_2} \approx 2\%$ when %wt C reaches the usual tapping content of 0.05 to 0.10% in regular EAF operation. Nevertheless, when carbon concentration in iron melts decreases to values below 0.010 %wt C approximately, the ratio p_{CO_2}/p_{CO} can reach 5-15%.
- According to Boudouard reaction, CO₂ is very unstable at temperatures above 1300 K. However, a gas mixture CO-CO₂ equilibrated with Fe-FeO at 1873 K can accommodate P_{CO2}/P_{CO} ratio of 0.03 to 0.08 when iron oxide activity varies from 0.20 to 0.50, respectively.

2.2. Decarburization Kinetics

Decarburization of Fe-C melts occurs through the reaction of carbon dissolved in iron and oxidation agents, such as: i) gaseous species, ii) species dissolved in iron, or iii) liquid species.

Gaseous oxidation species:

$$\underline{C} + 1/2O_{2(g)} \rightarrow CO_{(g)} \qquad \qquad \text{eq. 6}$$

$$\underline{C} + CO_{2(g)} \rightarrow 2CO_{(g)} \qquad \qquad \text{eq. 7}$$

$$\underline{C} + H_2 O_{(g)} \rightarrow 2CO_{(g)} + H_{2(g)}$$
eq. 8

Dissolved oxidation species:

$$\underline{C} + \underline{O} \rightarrow CO_{(g)} \qquad \qquad \text{eq.AN1 - 4}$$

Liquid oxidation species:

$$\underline{yC} + (M_xO_y) \to yCO_{(g)} + xM$$
 eq. 9

For instance: $(M_x O_y) \Rightarrow FeO, MnO, SiO_2$

Results from laboratory experiments presented on Figure 9 (a) pointed out that: after a short start up time (Stage I), decarburization takes places at a rate which is not depending of carbon content (Stage II), but depending on the oxygen flow rate. The rate increases with the increase of the oxidant gas flow rate, as expected for a mass transfer control. If a chemical reaction was controlling the rate, the rate would be independent of blowing rate. After certain carbon content has been achieved (Stage III), called critical or transition carbon C^{Cr} , the decarburization rate becomes somehow dependent on the carbon content.



Figure 9 – Decarburization rates as function of carbon content of melts when top blowing at various oxygen flow rates onto 5 kg iron-carbon melts in an induction furnace [11];(b) Rate of decarburization vs. carbon content for two heats under identical lowing conditions.

Figure 10 (a) suggests a possible effect of desiliconization retarding decarburization and, (b) and (c) proposing a simultaneous reaction of carbon and silicon oxidation [12, 13]. Even though silicon has much higher affinity for oxygen than carbon, it has been shown that at low silicon content in hot metal around 0.6 %wt, silicon can not suppress nucleation of CO bubbles [14]. In addition, it was found that the critical carbon and critical silicon contents were connected somehow [13].



(c)

Figure 10 – (a) Decarburization profile in (a) low [9] and (b) high initial silicon content [12]; (c) Decarburization of Fe-C-Si alloys with a gas mixture of O_2 -He. Initial silicon content varied between 0.38 to 0.71% [13].

Figure 11 presents sketches of the most common behavior of the decarburization process, in respect to the decarburization rate and its dependence on carbon content and blowing time. In the Stage I, several oxidation reactions other than carbon oxidation take place and consume most of the available blown oxygen. These reactions are related mainly to silicon and manganese present in the hot metal charged to the BOF or in the scrap and pig iron charged to the EAF. According to former studies, the coexisting silicon tends to oxidize earlier than carbon, somewhat decreasing the decarburization rate in the very beginning. Nevertheless, depending on the initial silicon content and the blowing conditions, silicon removal may present different rates.



Figure 11 – Decarburization Stages. Schematic representation of (a) dC/dt vs. %C [1]; (b) dC/dt vs. blowing time [15]; (c) %C vs. blowing time.

Figure 12 presents the measured CO_2 concentration profile regarding former experiments with heterogeneous reaction of $CO-CO_2$ gas mixture and Fe-C melts [16].



Figure 12 – Distribution of CO_2 near the reaction surface of liquid Fe-C system. (modified figure)[16].

The suggested CO_2 mass balance according to eq.AN3 - 54 and eq. 51 can be written as follows,

$$N_{CO_2} = -\frac{p}{R.T} D_{CO_2} \frac{\partial X_{CO_2}}{\partial y} + X_{CO_2} \cdot (N_{CO_2} + N_{CO})$$
eq. 10

where $\frac{p}{R.T} \cdot D_{CO_2} \cdot \frac{\partial X_{CO_2}}{\partial y}$ is the diffusion portion and $X_{CO_2} \cdot (N_{CO_2} + N_{CO})$ is the convection portion of the transported mass of CO_2 through the boundary layer.

 N_{co_2} and N_{co} [moles/m².s] are the CO_2 and CO molar flow per unit of area in the concentration boundary layer, respectively; p is the pressure in gas phase; D_{co_2} is diffusion coefficient of CO_2 in the gas phase, X_{co_2} is the CO_2 molar fraction, $\frac{\partial X_{CO_2}}{\partial y}$ is the molar fraction gradient through the boundary layer. A concentration boundary layer δ_c can be estimated approximately as 20 mm from Figure 12 data. Considering $N_{co} = 2.N_{co_2}$, boundary conditions $X_{co_2} = X_{co_2}^{eq}$ at y = 0; $X_{co_2} = X_{co_2}^{\infty}$ at $y = \delta_c$, integrating eq. 10 from y = 0 to $y = \delta_c$,

$$N_{CO_2} = -\frac{p}{R.T} \frac{D_{CO_2}}{\delta_C} \ln\left(\frac{1 + X_{CO_2}^{\infty}}{1 + X_{CO_2}^{eq}}\right)$$
eq. 11

where $m_{CO_2} = \frac{D_{CO_2}}{\delta_C}$ is the mass transport coefficient of CO_2 in the boundary layer. Taking into account the carbon mass balance, $N_{CO_2}\Big|_{gas} = N_C\Big|_{Melt}$, the diffusion of carbon through the metal phase can be written as postulated by Newton's Law for the fluid (Mass Transfer by Convection), eq.AN3 - 50, it follows that,

$$N_C = m_C \cdot (C_C^{\infty} - C_C^{eq}) \qquad \text{eq. 12}$$

where C_{C}^{eq} is the carbon molar density in equilibrium with $X_{co_2}^{eq}$ and $X_{co_2}^{eq}$ at the interface liquid-gas. Therefore, considering steady-sate conditions, combining eq. 11 and eq. 12,

$$(C_{C}^{\infty} - C_{C}^{eq}) = -\frac{p}{R.T} \frac{m_{CO_{2}}}{m_{C}} \ln\left(\frac{1 + X_{CO_{2}}^{\infty}}{1 + X_{CO_{2}}^{eq}}\right)$$
eq. 13

The left side of eq. 13 is the driving force for carbon diffusion in the liquid phase and the right side means the drive force for CO_2 in diffusion the gaseous

phase. The overall resistance to the reaction depends on mass transfer kinetics on both phases. Other authors [1, 2, 4, 17] have proved that gas phase mass transfer (GPMT) represented by eq. 11 was valid for high carbon contents. It was concluded that (i) the apparent decarburization rates were independent on the carbon content in the high concentration ranges, (ii) but very much affected by the gas mixture flow rate, suggesting mass transport control.

$$CO_{2(g)} + \underline{C} \rightarrow 2CO_{(g)}$$
 eq.AN1 - 22

combing eq. 11, eq.AN2 - 21 and eq.AN2 - 26 [18, 19],

$$\frac{d[\%C]}{dt} = -\frac{MW_c.A}{\rho_m.V} \cdot \frac{p}{R.T} \frac{D_{CO_2}}{\delta_C} \ln\left(\frac{1+X_{CO_2}^{\infty}}{1+X_{CO_2}^{eq}}\right)$$
eq. 14

assuming $D_{CO_2}/\delta_C = m_{CO_2}$ as the mass transport coefficient of CO₂ in the gas phase, $X_{cO_2}^{eq}$ is small enough to be ignored, $X_{cO_2}^{\infty} = p_{CO_2}/p$ and p = 1 atm, then, eq. 14 can be written as follows

$$\frac{d[\%C]}{dt} = -\frac{MW_c.A}{\rho^{Melt}.V} \cdot \frac{m_{CO_2}}{R.T} \ln\left(1 + p_{CO_2}^{\infty}\right)$$
eq. 15

Similar experiments had been done, but blowing pure oxygen instead of $CO-CO_2$ mixtures [2, 3, 20-22]. Decarburization rates were also independent of carbon content in the Fe-C melts, considered in good agreement with the calculated oxygen diffusion rate through the gas boundary layer. Additionally, the decarburization rates with oxygen were 2.5 times higher when compared with CO_2 mixtures as the oxidizing agent. If mass transport in the gas phase is the controlling mechanism, eq. 16 can be written as follows,

$$N_{O_2} = -\frac{p}{R.T} \frac{D_{O_2}}{\delta_C} \ln\left(1 + X_{O_2}^{\infty}\right)$$
 eq. 16

assuming $X_{o_2}^{eq}$ at the liquid-gas interface is very small and can be neglected, according to the equilibrium of reaction described in the eq. 17,

$$2\underline{C} + O_{2_{(g)}} = 2CO_{(g)} \qquad \qquad \text{eq. 17}$$

combing eq. 16, eq.AN2 - 27 and eq.AN2 - 31 [18, 19],

$$\frac{d[\%C]}{dt} = \frac{2.MW_c.A}{\rho^{Melt}.V} \cdot \frac{1}{R.T} \frac{D_{O_2}}{\delta_c} \ln\left(1 + p_{O_2}^{\infty}\right)$$
eq. 18

$$\frac{d[\%C]}{dt} = \frac{2.MW_{c}.A}{\rho^{Melt}.V} \cdot \frac{m_{c}}{R.T} \ln\left(1 + p_{0_{2}}^{\infty}\right)$$
 eq. 19

Figure 13 presents the plot of the decarburization rates and their correlation with $\ln(1 + p_{co_2}^{\infty})$ and $\ln(1 + p_{o_2}^{\infty})$. The experimental data is in god agreement with the hypothesis of mass transfer of oxidant gases in the gas phase as the rate-controlling mechanism. Both experiments were carried out in Fe-C with high carbon content.



Figure 13 – (a) Rate of decarburization of Fe-C and Fe-C-S alloys and oxidation of graphite at 1800 K [23]; (b) Rate of decarburization as a function of in $(1+P_{O2})$ [2]

Therefore, the decarburization process brings about a well accepted sequence of steps, in summary:

Table 4 – Decarburizing process steps of Fe-C melt submitted to CO_2 as the oxidizing agent.

I.	Transport of CO ₂ from the bulk gas to the gas-metal interface	$N_{CO_{2}} = -\frac{p}{R.T} \frac{D_{CO_{2}}}{\delta_{C}} \ln \left(\frac{1 + X_{CO_{2}}^{\infty}}{1 + X_{CO_{2}}^{eq}} \right)$	eq. 11
II.	Transport of carbon from the bulk metal to the gas- metal interface	$N_C = m_C \cdot (\% C^\infty - \% C^{eq})$	eq. 12
111.	Chemical reaction at the gas-metal interface (including the chemisorption) [24]	$CO_{2(g)}$ Adsorption $CO_{2(g)} = CO_{2(ad)}$	eq. 20
		$CO_{2(ad)}$ Dissociation $CO_{2(ad)} \rightarrow O_{(ad)} + CO_{(ad)}$	eq. 21
		\underline{C} Adsorption of carbon from the metal $\underline{C} = C_{(ad)}$	eq. 22
		Chemical Reaction $C_{(ad)} + O_{(ad)} = CO_{(ad)}$	eq. 23
		$2CO_{(ad)} = 2CO_{(g)}$	eq. 24
IV.	Transport of oxygen from the gas-metal interface to the bulk metal	Oxygen diffusion	
V.	Transport of CO from the gas-metal interface to the bulk gas	$N_{CO} = \frac{p}{R.T} \frac{D_{CO}}{\delta_C} \ln \left(\frac{1 + X_{CO}^{\infty}}{1 + X_{CO}^{eq}} \right)$	eq. 25

The decarburization process steps performed by O_2 injection is somehow similar to the process conducted by blowing CO_2 as presented in Table 5:

Ι.	Transport of O ₂ from the bulk gas to the gas-metal interface	$N_{CO_{2}} = -\frac{p}{R.T} \frac{D_{CO_{2}}}{\delta_{C}} \ln \left(\frac{1 + X_{o_{2}}^{\infty}}{1 + X_{o_{2}}^{eq}}\right)$	eq. 11
II.	Transport of carbon from the bulk metal to the gas- metal interface	$N_C = m_C . (\% C^{\infty} - \% C^{eq})$	eq. 12
111.	Chemical reaction at the gas-metal interface (including the chemisorption) [18]	$O_{2(g)}$ Adsorption $O_{2(g)} = O_{2(ad)}$	eq. 26
		$O_{2(ad)}$ Dissociation $O_{2(ad)} \rightarrow 2O_{(ad)}$	eq. 27
		\underline{C} Adsorption of carbon from the metal $\underline{C} = C_{(ad)}$	eq. 28
		Chemical Reaction $C_{(ad)} + O_{(ad)} = CO_{(ad)}$	eq. 29
IV.	Transport of oxygen from	$CO_{(ad)} = CO_{(g)}$	eq. 30
	the gas-metal interface to the bulk metal		
V.	Transport of CO from the gas-metal interface to the bulk gas	$N_{CO} = \frac{p}{R.T} \frac{D_{CO}}{\delta_C} \ln \left(\frac{1 + X_{CO}^{\infty}}{1 + X_{CO}^{eq}} \right)$	eq. 31

Table 5 – Decarburizing process steps of Fe-C melt submitted to O_2 as the oxidizing agent

For experiments carried in induction furnaces, where the melt is strongly stirred by high-frequency induction, it is not realistic to assume a stagnant melt. Hence, if the diffusion in the metal is the rate-controlling, the decarburization rate should be independent on the gas composition when the equilibrium carbon contents are relatively small [16].

If mass transport is the rate controlling mechanism, the rate of reaction is expected to be directly proportional to the temperature, since the diffusion coefficient is linearly dependent on the temperature,

$$N_i \propto \frac{D_{O_2}}{\delta_C} . A \propto T$$
 eq. 32

where A is the interface available for reaction.

In the case of chemical reaction rate-controlling mechanism, the reaction rate constant is exponential temperature-dependent. The larger the activation energy, the more temperature-sensitive is the rate of reaction, according to eq. 33,

$$k = k_0 \cdot e^{-E/RT} \qquad \qquad \text{eq. 33}$$

where k is the rate constant of reaction, k_0 is the pre-exponential factor, and E is the activation energy.

Apparent activation energy was calculated for several experimental conditions as presented on Table 6. The experimental conditions considering metal phase stirred by magnetic field (induction furnaces) may decrease the role carbon diffusion as the rate-controlling mechanism, depending on how strong the stirring power was applied. The available data shows contradictory conclusions regarding the activation energy estimate, and consequently, the rate-controlling mechanisms. If mass transport in the metal phase is the rate-controlling mechanism, apparent activation energy is expected be in the range of 10-15 kcal (~ 42-63 kJ) [21]. In addition, surfactants species such as sulfur, came up as relevant agent on retarding the chemical reaction rate.

Moreover, for similar apparatus geometry, as higher the oxidant flow rate, higher the reaction rate, since D_{o_2}/δ_c increases because δ_c decreases. In consequence, if the rate control is determined by mass transfer, there maybe a change in the rate controlling mechanism to mixed control or even to interfacial chemical reaction. Under this hypothetic condition, the activation energy should increase.

Even though many experiments were conducted in similar apparatus, the decarburization rates and consequently the activation energy, were significantly different. For instance, the higher value of activation energy was calculated [1] because other investigators did not subtract the decarburization rate resulting from the reaction of the crucible wall from the total decarburization rate.

E				
Equipments	$CO-CO_2$ gas mixture and O_2 top blow - crucible Induction furnace	Gas flow rate Lpm (Liters per Minute)	Activation Energy kcal/mol (kJ/mol)	Ref
r=3 cm P ₀₂ = 0.02 to 0.2 atm High carbon melts		1.0	34.6 (~143)	[1]
r=3.5 cm		10.2	3.7 (~15)	
d=2.5 cm h=5 cm		8.4	6.1 (~26)	1
P ₀₂ = 0.17 atm		6.6	7.9 (~33)	[22]
High carbon mens		5.0	10.1 (~42)	
		3.0	13.4 (~56)	
		1.5	25.2 (~106)	1
r=4 cm d=0.4 mm $p_{co}/p_{co2}=0.10$ High carbon melts		1.5	5 (~21)	[4]
r=0.81 cm	~ 0 %S		23.4 (~98)	
$P_{CO2} = 0.1$ to 0.5 atm	0.0015 %S		24.2 (~101)	-
High carbon melts	0.0020 %S	30 - 40	26.4 (~111)	[24]
	0.0029 %S 4.5 ppm N		37.2 (~156)	
	0.0090 %S		41.6 (~174)	
r=9 cm h=10 cm	Gas Ar+O ₂		24 (~100)	
P_{O2} = 0.2 – 0.8 atm High carbon melts	Gas N ₂ +O ₂	6.0-8.3	32 (~134)	[2]
	Gas Ar+O ₂ Sulfur added		40 (~167)	
r=9 cm h=10 cm P_{02} = 0.2 - 0.8 atm Low carbon melts	Gas Ar+O ₂	8.3	12 (~50)	[3]

Table 6 – Apparent activation energy for decarburization process estimated from induction melting experiments.

Special experimental conditions were conducted emphasizing the study of the chemical reaction as the rate-limiting process. Mass transfer constraints were decreased by using an inductively stirred melt, very high gas flow rate and special geometry of lance-crucible arrangements, reducing the effects on liquid and gas transfer. Thus, the system was forced to behave under chemical control [24]. From Table 4, the step III describes the adsorption-dissociation-reaction processes.

The rate was found to be independent of the carbon concentration. Consequently, considering the overall reaction resulting from eq. 20 up to eq. 23,

$$CO_{2(g)} + \underline{C} \leftrightarrow 2CO_{(g)}$$

eq.AN1 - 22

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and according to eq.AN2 - 7

$$-r_{A,net} = k_A \cdot (C_A^a C_B^b - \frac{k_{-A}}{k_A} \cdot C_C^c \cdot C_D^d) \therefore K_C = \frac{k_A}{k_{-A}}$$
eq.AN2 - 7

$$-r_{C,net} = k_C \cdot (C_C \cdot C_{CO_2} - \frac{k_{-C}}{k_C} \cdot C_{CO}^2)$$
eq. 34

where k_{-C}/k_{c} refers to the rate constant of reaction, regarding the forward and reverse direction of reaction.

Assuming total pressure of 1 atm and the gas phase presenting ideal gas behavior, eq. 34 can expressed in respect to partial pressure of CO and CO₂,

$$K_{C} = \frac{k_{C}}{k_{-C}} = \frac{p_{CO}^{2}}{a_{C} \cdot p_{CO_{2}}}$$
 eq. 35

$$-r_{C,net} = k_C \cdot (C_C \cdot p_{CO_2} - \frac{k_{-C}}{k_C} \cdot p_{CO}^2)$$
eq. 36

as eq. 36 was found to be independent of C_c and p_{co} , eq. 37 represents the decarburization rate for the experimental condition,

$$-r_{C,net} = k_C \cdot p_{CO_2}$$
 eq. 37

The independence of the rate on the CO pressure, pointed out that back reaction of CO was concluded to be negligible and that CO chemisorption plays no major role. Consequently, under experimental conditions which force the mass transfer not to affect the rate of reaction (very high gas flow rates), the proposed chemical reaction control based on first-order relation with respect to CO₂ at high concentrations of carbon (carbon-saturated Fe-C) was in good agreement with eq. 37 and plot as presented in Figure 14.



Figure 14 – (a) Dependence of the decarburization rate of continuously carbon-saturated vs. p_{CO_2} at several temperatures. Flow rate 20-24 lpm [24]; (b) Initial rate of decarburization at 1580 °C as a function of p_{CO_2} [25].

In Figure 15 (a) the effect of sulfur on the rate constant of decarburization reaction is confirmed, and consequently its effect on the activation energy too. The increased activation energy from 20 to 30 kcal/mol (~84 to 126 kJ/mol), and from 30 to 40 kcal/mol (~126 to 167 kJ/mol), was concluded to be due to nitrogen and sulfur retarding effect, respectively. Figure 16 presents an example of how sulfur contamination may retard the decarburization rate. According to the authors, the results were conclusive in favor of chemisorption process as the rate controlling mechanism, which was supported by activation energy in the range of 20-30 kcal/mol (~84 to 126 kJ/mol) for low sulfur content. However, this experimental technique was said to be inaccurate [26] because of iron ejection from the crucible and iron vaporization losses at gas flow rates higher than 20 lpm. These experimental limitations may have overestimated the decarburization rate. Consequently, the calculated activation energy may have been over estimated as well.



Figure 15– (a) Temperature dependence of rate constants for several iron-melts.; (b) Comparison of the rate constants for the decarburization of solid and liquid iron [24]. A dashed line is added.

In Figure 15 (b), the activation energy for the metal phase decarburization with higher sulfur content is somehow high compared with pure iron and close to that found during the decarburization in solid state of Austenite. The sulfur concentration is suggested to account for the differences in the rates and for the higher activation energy, which was estimated around to 48 kcal/mol (~201 kJ/mol).



Figure 16 - Effect of sulfur in Fe-C_{saturated}-S on the rate constant of CO₂ reaction [26].

Sulfur cause depression of the surface tension of pure iron.

$$\sigma^{p} - \sigma = R.T.\Gamma_{i}^{0}\ln(1 + K_{s}.a_{s}) \qquad \text{eq. 38}$$

where σ^{p} is the surface tension for pure substance, $\sigma^{p} - \sigma$ is the surface tension depression, Γ_{i}^{0} is the saturation coverage by the solute, a_{s} is the activity of sulfur in the bulk and K_{s} is the adsorption coefficient for sulfur. If the dissociation of CO₂ is limited to take place only on the surface portion in which is not covered by sulfur, the adsorption of other substances is assumed to be weak. For instance, the rate constant in the equation $-r_{c,net} = k_{c} \cdot p_{CO_{2}}$ eq. 37, can be correct by the sulfur effect as follows [27].

$$-r_{C,net} = k_{C(app)} \cdot p_{CO_2}$$
eq. 39

where
$$k_{C(app)} = \frac{k_C}{1 + K_s . a_s}$$
 is the apparent rate constant eq. 40

Assuming Henryan behavior of sulfur in respect to iron

where
$$-r_{C,net} = \left(\frac{k_C}{1 + K_S . a_S}\right) p_{CO_2}$$
 eq. 41

In similar way, the activation energy can be correct by

$$E_{(app)} = E - \theta \Delta H_{ad}$$
 eq. 42

where $E_{(app)}$ is the apparent activation energy, θ is the fraction of surface which is covered by sulfur and ΔH_{ad} is the heat of adsorption of sulfur, which is about -17 kcal/mol (~71 kJ/mol) [27].

Table 7 and Table 8 present a summary of the main variables affecting the decarburization rate and the possible rate-controlling mechanisms as a function of the carbon concentration ranges for different experiment conditions. Table 7 suggests a brief recapitulation of the main investigations in the last forty years:

- (i) The oxidant flow rate has been proved to be significant for high carbon contents, and it is expected to decrease the boundary layer thickness, decreasing the mass transfer resistance in the gas phase.
- (ii) The activation energy ranges are presented according to the rate mechanism.
- (iii) The surface active elements interferes in the interfacial reactions, particularly in chemisorption kinetics,

- (iv) The stirring intensity of the metal phase may significantly affect the diffusion of carbon to the metal-gas interface, specially for lower carbon concentration.
- (v) The temperature sensitivity supports the hypothesis of mixed or chemical reaction control in certain experimental conditions.

		MASS TRANSFER		CHEMICAL
PROCESS VARIABLES		CONTROL		REACTION
		GAS PHASE	LIQUID PHASE	CONTROL
i.	Effect of oxidant flow rate	High		None
			Low (iron) 10-15	
	Apparent activation anarray	Low 1-4 [2]	[21]	High 20-100
ii. Apparent activation energy		kcal/mol	Low (slag) 7 [28]	kcal/mol
			kcal/mol	
	Effect of surface active elements (S. P.)	None		Retarding the
		NONE		rate
iv.	Effect of molten melt stirring (forced		High	
	convection)			
٧.	Effect of temperature	Low	Low	High

Table 7 – Process variables affecting the decarburization rate-controlling mechanism.

Table 8 shows distinct controlling mechanisms according to carbon content. There are several controversies regarding the predominant mechanisms. Both rate equations for mass transfer and chemisorption models under some experimental conditions, present good agreement in terms of the effect of the oxidant partial pressure. Nevertheless, the activation energy is higher than expected to support only mass transfer in the gas phase, indicating the possibility of mixed control. Table 8 – decarburization rate-controlling mechanism and transition carbon content (critical carbon).

GPMT: Gas phase mass transfer of gas oxidizing agent through the gas phase LPMT: Liquid phase mass transfer of carbon in the Fe-C melt to the metal-gas interface MIXED: Mixed control mechanism, GPMT and LPMT, or chemical reaction CHEMICAL REACTION: CO_2 dissociation or O_2 adsorption in the metal-gas interface

Experiment Condition	%wt C in the Fe-C		Rate-Controlling Mechanism				Ref
melt		GPMT	MIXED/ OTHERS	LPMT	CHEMICAL REACTION		
$CO-CO_2$ gas mixture top blow - crucible Induction furnace 1600 °C	0.5%	p _{CO2} <= 1/4 p _{CO2} <= 7/3	%C>0.10-0.15	0.05<%C<0.10- 0.15	%C<0.05 carbon diffusion	%C<0.05 %C<0.05	[5]
		p _{CO2} >= 7/3			%C<0.05 carbon diffusion		
Oxygen top blowing Lab Induction furnace 1650 °C	0.04	4-4.5%		%C>0.20 Oxygen supply rate			[29]
CO-CO ₂ gas mixture top blow - crucible Lab Induction furnace 1580 °C		1%				%C<0.05 CO ₂ dissociation	[25]
CO-CO ₂ gas mixture top blow - crucible Lab Induction furnace 1600 °C		4%	%C>0.5 GPMT	0.1<%C<0.5 GPMT LPMT carbon diffusion	%C<0.1 carbon diffusion		[23]
Oxygen top blowing Lab Induction furnace 1550-1650 °C	0.2	-4.0%	%C>0.1 GPMT		0.07<%C<0.1 carbon diffusion		[3]
Industrial EAF 40-100 ton 1550-1620 °C	1	.5%		%C>0.1 Oxygen supply rate	%C<0.10 carbon diffusion		[30]
Industrial EAF 100 ton 1540-1660 °C	C	.6%		%C>0.075 Oxygen supply rate	%C>0.075 carbon diffusion		[31]

According to the data listed above the critical carbon estimates seem to vary over the in the range of 0.05-0.15%C, depending on the experimental conditions. More recent work has found the same range [13]. Considering industrial data in oxygen steel making (OSM) according to Figure 17, even though the curves vary from mill to mill, perhaps due to differences in the operational conditions of oxygen blowing and vessel geometry, most of the curves presented the same tendency. The transition carbon content, which defines the linear to non-linear decarburization rate vs. carbon content, also called, critical carbon, varies significantly among the industrial facilities instead. The critical carbon lies in a very wide range of 0.1-1.2 %wt C.



Figure 17 –Decarburization rate vs. carbon content in various open hearth furnaces in Japan [1]

Under laboratory conditions with top blow oxidant gas mixture, the jet momentum is low when compared to the industrial scale. Therefore, the gasmetal interface in laboratory conditions is not disturbed and FeO production is somehow very little. If counter diffusion of CO-CO₂ occurs in the gas phase boundary layer, as the oxidant gas flow rate increases, the amount of resultant CO increases also, keeping or enhancing the resistance of gas-phase mass transfer. In actual steelmaking environment, very high oxygen flow rate practices provide high jet momentum. If intense boiling due to CO evolution is considered, in this extreme mixing condition, slag and molten Fe-C form an emulsion, dispersing FeO particles in the metal phase where the decarburization progress may take place. The oxygen flow rate, the distribution and characteristics of the oxygen injection technology, slag chemical composition and other conditions may change from furnace to furnace, which together can result in different level of emulsification intensity. All these reasons can produce distinct critical carbon. Actually the critical carbon is achieved when the oxygen supply rate is equal to the carbon supply rate at the interface of reaction. The emulsification intensity affects the free surface area for reaction and stirring by boiling increases the mass transfer of carbon by enhanced convection.

Commonly accepted, a former model postulated that carbon and oxygen react at the surface of CO bubbles, which provide suitable nucleation sites. However, this model can not account for the very high oxidation level per unit melt area. A mathematical model was developed to quantify the additional area from the emulsion phase, and how it could affect the decarburization rate [6]. It is proposed that the interaction between CO bubbles and emulsion consist of molten iron and molten iron oxide particles in a region near the slag-metal interface. According to Figure 18, the reaction of carbon oxidation occurs at the metal-gas interface (x=a plane) in the three-phase volume FeO-Fe-CO. The path for oxygen and carbon are in x-direction and y-direction respectively. No diffusion of carbon occurs in the plane y=L. The equilibrium condition is assumed at the interface gas-metal, and the curves for decarburization rates are plotted in Figure 19 vs. carbon concentration in the metal phase. A geometry factor is defined as $F_{g} \propto L^{2}/a^{2}$, which accounts for the area available for simultaneous diffusion of oxygen from FeO particles and carbon from the metal phase to the CO bubbles interface.



Figure 18 - (a) Possible diffusion paths of carbon and oxygen toward the surface of a CO bubble in an emulsion of molten iron and FeO particles; (b) Schematic representation of the three-phase region shown in (a) [6].



Figure 19 - Calculated carbon oxidation rate vs. the carbon concentration for various values of F_q (geometry factor, proportional to the emulsification intensity) [6]

According to this model proposition, diffusion of carbon maybe the ratecontrolling mechanism, occurring at a wide carbon concentration. The dependence on the geometry of the three-phase volume is the effect of the emulsion intensity. Moreover, the large interfacial area present in this emulsion could explain the very high decarburization rates in oxygen steel making. Additionally, it can also be seen from Figure 19 that as more intense the emulsification degree, higher the critical carbon will be. The three-phase FeO-Fe-CO model will be applied for kinetics of iron oxide reduction in the next chapter.

Investigations performed in industrial scale for EAF of 40 and 100 ton capacity, reported zero-order and first-order reactions for initial carbon concentrations of 1.5-0.1 %wt C and 0.10-0.07 %wt C, respectively. It was concluded that above 0.1 %wt C, the rate depends on the oxygen supply flow rate, below 0.1 %wt C the predominant mechanism for carbon oxidation is controlled by mass transfer of carbon through the metal phase [30].

Table 9 summarizes the most accepted decarburization rates for stages I and II according to Figure 11 definitions.

Stage IIDirect dependence on oxygen supply (zero-order)eq.AN2 - 31 $\frac{d[\% C]}{dt} = -\frac{2.MW_C.A}{W^{Melt}}.N_{O_2}$ eq.AN2 - 43Stage IIIAssuming mass transfer of carbon in the metal
phase as the rate controlling-mechanismeq.AN2 - 43 $\frac{d[\% C]}{dt} = -\frac{\rho_{Melt}m_C.A}{W^{Melt}}([\% C]^{\infty} - [\% C]^{eq})$ eq.AN2 - 43

Table 9 – Most accepted decarburization rate equations for stage II and III.

2.2.1. Decarburization Kinetics Summary

Former studies on decarburization kinetics pointed out contradictory conclusions regarding the rate-controlling mechanisms, particularly in regards to low carbon contents. Nevertheless, today it is generally accepted that:

- For high carbon content in Fe-C melts, the decarburization rates are independent of carbon content and are very much affected by the oxidant gas flow rate. It follows zero-order reaction in respect to carbon and oxygen;
- For low carbon content in Fe-C melts, the decarburization rates are dependent of carbon content and are not affected by the oxidant gas flow rate. The mass transfer of carbon in the metal phase is the most accepted rate-controlling mechanism. It follows a first-order reaction in respect to carbon;
- Surface active elements such as sulfur and nitrogen present a retarding effect on decarburization rate. The higher activation energy found maybe explained by the effect of surface active elements;
- The emulsion intensity, related to the complex reacting area available from the three phase volume consisting of molten iron, molten slag and CO bubbles, determines the decarburization area. In oxygen steel making the emulsion intensity is expected to be higher than in electric arc furnace processing;
- In industrial scale, the critical carbon content varies significantly in a wide range of 0.1-1.2 %wt C, depending on the oxygen blowing practice and the available technology.

2.3. Kinetics of Iron Oxide Reduction

Iron oxide reduction is a heterogeneous reaction type, and therefore, it may imply mass transfer as well as interfacial chemical reactions as possible rate-controlling mechanisms. As mentioned in the item 2.2, the reduction of iron oxide involves the formation of a CO-CO₂ gas phase when particles of slag are in contact with carbon sources. Figure 20 presents three ways in which iron oxide may be reacting with carbon sources: (a) Fe-C droplet in slag phase; (b) slag droplets in the Fe-C melt bulk; (c) carbonaceous source represented by a graphite particle in the slag phase. The cases (a) and (b) are typically the macrostructures of the emulsions which are developed as a mixture of slag and the molten metal and can be simplified in the system (d) with the constituents Fe-<u>C</u>-Gas-Slag and the condition (c) C_{gr} -Gas-Slag is related to the system (e).



Figure 20 – Possible cases of iron oxide reaction with different sources of carbon in steelmaking facilities.

The Wustite $FeO_{1.076}$ is denoted as FeO for convenience is this review. As presented earlier, the iron oxide reduction by carbon dissolved in the metal phase bulk is the expected mechanism for decarburization [6] and this overall reaction can be expressed by the overall reactions (Figure 20(a) and (b)),

$$FeO_{(l)} + \underline{C} = Fe + CO$$
 eq.AN1 - 47

In addition to the decarburization, iron oxide reduction occurs very often by means of a solid graphite injection or a charge in EAF or smelting process, as the overall reaction is expressed in eq.AN1 - 43. The carbon source can also be

composed of coke, anthracite, charcoal or other source of carbon commonly used in steelmaking.

$$FeO_{(l)} + C_{gr} = Fe + CO$$
 eq.AN1 - 43

However these overall reactions are otherwise considered to proceed in two steps, regarding the gaseous reactions at both metal-gas and slag-gas interfaces.

The proposed and well accepted mechanisms for FeO reduction by carbon dissolved in Fe-C melts [32-35] and by solid carbon [33, 36-40] are presented in Figure 21. The common steps are the mass transfer of FeO in slag, the gaseous containing species CO and CO_2 in the gas halo which is formed immediately when FeO is in contact with a carbon source. The main differences lie in the mass transfer of carbon in the Fe-C melt and the nature of the chemical reaction in the (metal or carbon)-gas interface.



Figure 21 – Schematic diagrams of reduction of FeO containing slag by (a) carbon dissolved in Fe-C melts [34] and (b) solid carbon [36].

Table 10 summarizes the possible rate-controlling steps for reduction of liquid FeO in slag. The mass transfer of CO_2 produced at slag-gas interface occurs through the gas halo up to the metal-gas interface. Then, CO_2 dissociates, resulting in CO and an adsorbed oxygen atom which reacts with dissolved carbon present in Fe-C melts or reacts directly with a carbon solid particle. At steelmaking temperature, CO_2 is unstable at the metal-gas or carbon-gas

interface in presence of graphite, tending to be completely consumed and presenting negligible concentration. Consequently, a CO₂ gradient occurs, driving its diffusion through the gas halo in the direction of the carbon source, until the source of oxygen at the slag-metal interface is approaching to the equilibrium state or the source of carbon is exhausted. The source of oxygen in slag-gas interface is simplified to be proportional to FeO concentration in the slag phase.

Table 10 – Process steps for iron oxide reduction by dissolved carbon in Fe-C melts and by a generic solid carbon source.

Ι.	Mass transfer of FeO (or Fe^{+2} and O^{-2} ions) through the slag to gas-slag interface	$N_{FeO} = m_{FeO} \cdot (C_{FeO}^{\infty} - C_{FeO}^{sg})$	eq.AN2 - 44
II.	Chemical reaction at the slag-gas interface	$FeO_{(l)} + CO = Fe + CO_2$	eq.AN1 - 56
111.	Diffusion of gaseous species in the gas halo surrounding the Fe-C droplet or the carbon particle	$N_{CO_{2}} = -\frac{p}{R.T} \frac{D_{CO_{2}}}{\delta_{C}} \ln \left(\frac{1 + X_{CO_{2}}^{\infty}}{1 + X_{CO_{2}}^{eq}} \right)$	eq. 11
IV.	Mass transfer of the carbon in the Fe-C melt	$N_C = m_C . (\% C^{\infty} - \% C^{eq})$	eq. 12
V.	Chemical reaction at the	$CO_{2(g)}$ Adsorption and Dissociation	eq. 26
	(including the chemisorption)		to eq. 28
	[18] or at the carbon-gas interface	Chemical Reaction (metal-gas interface) $CO_{2(g)} + \underline{C} \rightarrow 2CO_{(g)}$	eq.AN1 - 22
		Chemical Reaction (carbon-gas interface)	eq.AN1 - 59
		$C_{gr} + CO_2 = 2CO$	
VI.	Transport of CO from the gas-metal interface or gas- carbon interface to the bulk gas	$N_{CO} = \frac{p}{R.T} \frac{D_{CO}}{\delta_C} \ln \left(\frac{1 + X_{CO}^{\infty}}{1 + X_{CO}^{eq}} \right)$	eq. 31

Many times the rate-controlling step is not a trivial equation to be determined, because the rate of the individual step cannot be measured independently. Investigators usually compare the experimental results with theoretical rate equations associated to an assumed rate-controlling mechanism.

It is well known that diffusivity and viscosity follow the Arrhenius type equation [41]. For liquids, eq.AN3 - 36 and eq.AN3 - 39 represents the dependence of diffusion and viscosity on temperature, respectively.
$$D = D_0 \cdot e^{-E/RT} \qquad \qquad \text{eq.AN3 - 36}$$

$$\mu = A.e^{(1000.B/T)}$$
 eq.AN3 - 39

It is expected the increasing effect of the temperature on increasing the reaction rate (eq.AN3 - 38), if the rate-controlling mechanism is related to diffusion.

$$D = \frac{k_B T}{2.R.\mu}$$
 eq.AN3 - 38

It is accepted that the diffusivity in iron is twice as much as in the slag phase [28], and the activation energies for diffusion in slag are larger those in iron

 $D_{Melt} \propto 2D_{Slag}$ eq. 43

where D_{Melt} is the diffusivity in iron melts and D_{Slag} the diffusivity in slag.

Hence, if the rate-controlling of the reduction of iron oxide is limited by the diffusion of iron oxide in the slag phase, the activation energy is expected to be higher than if the reaction was controlled by diffusion of carbon in Fe-C melts. From eq.AN3 - 36, the higher the activation energy for diffusion, the lower is the diffusivity.

In general, the overall rate is controlled by various mechanisms in series, as illustrated in Figure 21 for both carbon sources cases: carbon and Fe-C melts. The terms refer to resistances to R_s FeO mass transfer in slag, R_{sg} chemical reaction at the slag-gas interface, R_g gaseous species diffusion in the gas phase, R_{cg} chemical reaction at the carbon-gas interface, R_{mg} chemical reaction at the metal-gas interface and R_{cm} carbon diffusion from the metal phase bulk to the metal-gas interface.



Figure 22 – Diagram representing resistance series circuit for reduction of iron oxide in slag.

The resistances represented by R for each one of the steps suggested in Table 10 and Figure 22 can be derived by equating the rates or mass fluxes from the individual process steps [35], as follows

Mass transfer of FeO in the slag

It was found that reduction of iron oxide rate increases when the iron oxide content in the slag increases. Furthermore, the function correlating the rate and the FeO content was not linear, according to experiments presented in Figure 23.



Figure 23 – Reaction rate vs. slag FeO content for reduction by stationary and rotating rods [38]

Considering,

$$N_{FeO} = \frac{\rho_{Slag} \cdot m_{FeO}}{100 \cdot MW_{FeO}} \cdot ((\% FeO)^{\infty} - (\% FeO)^{sg})$$

$$m_{Slag} = \frac{\rho_{Slag} \cdot m_{FeO} \cdot A^{sg}}{100 \cdot MW_{FeO}} \Longrightarrow R_{S} = \frac{1}{k_{Slag}}$$
eq. 44

where m_{FeO} is the mass transfer coefficient of FeO in slag, MW_{FeO} is the FeO molecular weight, A^{sg} is the slag-gas interface area, m_{Slag} is the overall mass transfer coefficient in slag and ρ_{Slag} is the mass density of slag.

Chemical reaction control at the metal-gas interface

 $CO_{2(g)} + \underline{C} \rightarrow 2CO_{(g)}$

If the metal-gas reaction is rate-controlling, it can be assumed that slag-gas reaction $FeO_{(l)} + CO = Fe + CO_2$ is at equilibrium, $p_{CO_2}^{mg} \approx 0$, $p_{CO}^{sg} \approx 1$

$$N_{FeO} = -r_{CO_2} = \frac{k_{CO_2} \cdot K_{FCO_2} \cdot \gamma_{FeO} \cdot \rho_{Slag}}{100 \cdot C_{Slag} \cdot MW_{FeO}} [\% FeO]^{sg}$$
eq.AN2 - 51

$$k_{mg} = \frac{k_{CO_2} \cdot K_{FCO_2} \cdot \gamma_{FeO} \cdot \rho_{Slag} \cdot A^{sg}}{100.C_{Slag} \cdot MW_{FeO}} \Longrightarrow R_{mg} = \frac{1}{k_{mg}}$$
eq. 45

where k_{mg} is the overall rate constant of the reaction at the metal-gas interface, K_{FCO_2} is the equilibrium constant and k_{CO_2} is the rate constant, both for the slag-gas reaction, C_{Slag} is molar density of slag, γ_{FeO} is the FeO coefficient of activity in the slag.

Diffusion of gaseous species in the gas halo

From eq. 11, presuming $m_{CO_2} = D_{CO_2} / \delta_C$, p = 1 atm, $X_{CO_2}^{\infty} = p_{CO_2} / p$, $p_{CO_2}^{eq} \equiv 0$ $N_{CO_2} = \frac{m_{CO_2} \cdot (A^{sg} + A^{mg})/2}{R.T} \ln p_{CO_2}$ $m_g = \frac{m_{CO_2} \cdot (A^{sg} + A^{mg})/2}{R.T} \Rightarrow R_g = \frac{1}{m_a}$ eq. 47

where $(A^{sg} + A^{mg})/2$ is the approximate area for slag-gas and metal-gas interfaces, respectively m_{CO_2} is the mass transfer coefficient of CO₂ in the gas phase and m_g is the overall mass transfer coefficient in the gas phase

Mass transfer of the carbon in the Fe-C melts

This mechanism is discarded since the rates have been proved to be strongly dependent on sulfur content because of the surface active nature of sulfur and iron interaction. Besides, the rates of FeO reduction were found to be independent of the carbon content when sulfur is higher than 0,01%. At high sulfur contents (0.20%) it is suggested to be controlled mainly by the metal-gas reaction. In very low sulfur contents (0.003%) the rate should be mixed controlled by rate at the metal-gas interface, slag-gas reaction rate and mass transfer of FeO in the slag [35].

Chemical reaction control at the slag-gas interface

 $FeO_{(l)} + CO = Fe + CO_2$

Similarly, If the slag-gas reaction is rate-controlling, it can be assumed that the metal-gas reaction $CO_{2(g)} + \underline{C} \rightarrow 2CO_{(g)}$ is at equilibrium.

$$r_{FeO} = k_{CO} \cdot (1 - \frac{1}{K_{FCO_2}} \frac{p_{CO_2}^{sg}}{a_{FeO}}) \cdot a_{FeO}$$

$$k_{sg} = k_{CO} = (1 - \frac{1}{K_{FCO_2}} \frac{p_{CO_2}^{sg}}{a_{FeO}}) \implies R_{mg} = \frac{1}{k_{mg}}$$
eq. 48

where k_{sg} is the overall rate constant at the slag-gas interface, K_{FCO_2} is the equilibrium constant slag-gas reaction and k_{CO} is the rate constant, both for the metal-gas reaction. The equilibrium governed by Boudouard reaction at metalgas interface implies in $p_{CO_2}^{sg} \approx 0 - 0.05$ and $p_{CO}^{mg} \approx 1$. Actually, the slag-gas reaction is reported to be very fast, and probably not the predominant rate controlling mechanism, except for very low FeO contents [40].

The overall rate of iron reduction reaction can be written according to eq.AN2 - 60 and eq. 49,

> eq.AN2 - 60 $N_{FeO} = k_0 \cdot [\% FeO]^{sg}$

 $k_0 = \frac{1}{\frac{1}{m_{Slag}} + \frac{1}{k_{sg}} + \frac{1}{m_g} + \frac{1}{m_C} + \frac{1}{k_{mg}}}$ where N_{FeO} is the net FeO reduction rate and k_0 is the overall rate constant of the series reaction.

eq. 49



Figure 24 – Comparison of experimental measurements with the rate model predictions for 1 cm diameter graphite rods (a) stationary rod and (b) rotating rod at 1050 rpm [39]

According to Figure 24 (a), the experiments with graphite rods show the predictions of the kinetic mechanisms possibly involved and the experimental results, based on equations eq.AN2 - 60 and eq. 49 [39]. It can be seen that the gas-carbon reaction presents a minor effect when compared with the significant influence of the FeO mass transfer in slag (LPMT), specially at low FeO contents. At higher FeO contents, the slag-gas reaction increases with greater influence on the rate. It is suggested that the higher the FeO, the higher the CO gas evolution resulting in enhancement on the slag stirring by boiling effect. In Figure 24 (b), the effect of a rotating device changes the rate-controlling to a mixed control set of mechanisms, composed by LPMT, GPMT and slag-gas at lower FeO contents and definitely to slag-gas reaction as the FeO increases. Despite the fact that there were a lot of assumptions made and uncertainties, the experimental results were in good agreement with the proposed model.

There are still controversies about the effect of the FeO activity on its reduction rate. Considering the reaction $FeO_{(l)} + CO = Fe + CO_2$ at the slag-gas interface (eq.AN1 - 56), the rate of reaction can be rewritten as presented in eq.AN2 - 55, assuming the rate is proportional to the activities of reactants,

$$r_{FeO} = k \cdot a_{FeO} \cdot p_{CO} = k_{CO} \cdot p_{CO} \cdot \left(1 - \frac{1}{K_{FCO_2}} \frac{p_{CO_2}}{a_{FeO} \cdot p_{CO}}\right)$$
eq.AN2 - 55

where $\left(1 - \frac{1}{K_{FCO_2}} \frac{p_{CO_2}}{a_{FeO} \cdot p_{CO}}\right)$ indicates the departure from equilibrium and $\frac{1}{K_{FCO_2}} \frac{p_{CO_2}}{a_{FeO} \cdot p_{CO}}$ is virtually zero at high temperatures, because $p_{CO_2} \approx 0$ and $p_{CO} \approx 1$.

The apparent first-order reaction rate $k_A \propto k \cdot a_{FeO}$ in respect to p_{CO} would be proportional to the a_{FeO} . However, experiments forcing the decreasing of the FeO activity through addition of basic oxides in FeO-CaO slags, resulted in the opposite direction response, because the reduction rate was increased. Thus, it was concluded that there is no simple rate law such as the slag-gas reaction described in $FeO_{(l)} + CO = Fe + CO_2$ eq.AN1 - 56 which could explain the effect of iron oxide content on the reaction rate [33]. The apparent first order rate constant k_a calculated from eq. 50, indicated a dependence of FeO content only above FeO 20%. The rate constant k_A was constant in the range of 5-20% of FeO content in slag, as shown in Figure 25 (a),

$$r_{FeO} = k_A \left(p_{CO} - p_{CO_2} \left(\frac{p_{CO_2}^{eq}}{p_{CO}^{eq}} \right)^{-1} \right)$$
eq. 50



Figure 25 – (a) dependence of the apparent rate constant for the reduction of iron oxide by CO on iron oxide content in slags [33]; (b) Iron oxide reduction rate by solid carbon change with FeO activity (CaO/SiO₂ mass 1.15) [36]

On the other hand, other investigators found good correlation between a_{FeO} and FeO reduction rate constant in experiments with solid carbon, as shown in Figure 25 (b). Furthermore, a qualitative model was suggested, indicating a strong dependence of the reduction mechanism on the FeO content in the slag [36] : at low FeO content, LPMT of FeO in slag; increasing FeO, Boudouard chemical reaction could be governing the reaction rate. Mixed rate control would be expected in intermediary FeO contents (Figure 26).



Figure 26 – Schematic diagram of the rate-limiting step vs. FeO content in slag [36].

2.3.1. Kinetics of Iron Oxide Reduction Summary

- The rate of iron oxide reduction increases when the iron oxide content or its activity in the slag increases. The non linear dependence of the rate with increasing FeO content may be associated to CO evolution. The CO evolution may enhance the FeO mass transport. (the boundary layer thickness is inversely proportional to the CO flow rate);
- The slag basicity may influence the iron oxide activity and, consequently, its reduction rate;
- The carbonaceous materials size and the injection flow rate effect the of iron oxide reduction rate. The higher the available area and the media flow rate, the higher the iron oxide reduction rate will be;
- FeO range 3%-10%
 - At very low sulfur content (0.003%), the rate of reduction of iron oxide seems to be under mixed control of FeO mass transfer, slag-gas and slag-metal reactions rates;
 - At high sulfur content 0.20% the rate is supposed to be controlled by metal-gas chemical reaction rate;

2.4. Melting Kinetics

Melting of ferrous materials is a dissolution phenomenon in which heat and mass transfer mechanisms are taking place. Regarding the chemical composition of co-existing melts (liquid phases) and solids, two main conditions may be described under the perspective of industrial steelmaking applications:

i) High carbon melt – Low carbon solid charge (BOF conditions): involves mass transfer of carbon from liquid phase to dissolution interface and subsequent diffusion into the solid, decreasing its melting temperature. Thus, heat and mass transfer significantly affect the melting rates;

ii) Low carbon melt – (Low and) High carbon solid charge (EAF conditions): The lower melting point of the pig iron suggests that the superheat should be available mostly for heat transfer, resulting in the predominant melting mechanism;

Many studies have been done in the last decades [42-51], most of them related to High carbon melt – Low carbon solid condition, applied to BOF process when solid scrap is used for temperature control of the hot metal (melt coolant). The scrap melting rate was concluded to be dependent on heat and mass transfer, hence, dependent on:

- superheat;
- carbon gradient at the liquid-solid interface;
- metal phase convective conditions

A short literature review is presented on Appendices 1. Experimental apparatus, testing conditions, principal assumptions and conclusions are summarized. Figure 27 presents the distribution of the several experiments performed and their results published in the relevant literature. Less than 5% of the studies evaluated the condition Low carbon melt – High carbon solid, a typical industrial reality in countries like Brazil, where the scrap shortage implies in charging significant amount of solid pig iron in the electric arc furnaces.



Figure 27 – Laboratory experiments map as a function of %C in the liquid metal phase, %C in the solid samples and convective conditions.

Former [42, 43, 52] and more recent [53] analysis of melting rates of individual scrap grades have proved to be limited, because different scrap arrangements in the charge may significantly influence the melting rates, being not only a matter of weighting individual separated behaviors.

Experimental data have lead to conclusions that pig iron should melt almost in the same behavior of low-C scrap [42]. However, most recently, mills where pig iron have a significant role on the EAF charge, have reported indications that pig iron melts at lower rates than regular scrap grades. Latest trials have shown that higher pig iron charge came up as a real limiting factor for ultra-high power EAF applications [54].

Table 11 presents a simplified parameter deployment for a conventional EAF production process. As it can be seen, the melting process in an EAF is a complex phenomenon, being affected by simultaneous variables and presenting remarkable transient steps.

CHARGING		Size and Geometry (Area/Volume)	
	Scrap and Substitutes	Distribution in the EAF volume	
		Chemistry of impurities	
		Distribution in the EAF volume	
	Fluxes	Dissolution rates	
			Power losses rate
	Scrap and Pig Iron Melting Rates	Electrical Power input	Bath superheat
			Induction stirring
MELTING		Poth stirring	Bottom blowing (inert gas)
		Datri stirning	CO generation (pig iron)
		Hot heel practices	
		Scrap and Pig Iron clustering	
		Off-gas heat losses	
	Decarburizing and FeO Generation	Oxygen Injection	Efficiency of burners
			Efficiency of decarburizing jets
			Efficiency of postcombustion
		EaO Raduction Poto	Efficiency carbon Injection
			Slag foaming

Table 11 - Typical variables affecting the melting of ferrous charge in EAF.

The first premise for melting a solid body is that the environmental temperature must be higher than its melting temperature. The simplest phase change problem is one-phase type, meaning that only one of the phases is active (liquid), and the other phase stays at its melting temperature T_m at the melting interface. The solution with constant thermo physical properties shows that the rate of melting or solidification in a semi-infinite body is determined by a dimensionless number, known as the Stefan number (St) [55]:

$$St = \frac{c_{P_L} \cdot (T_L - T_m)}{\Delta H_m}$$
 eq. 51

or also represented by Phase transition number (Ph)

$$Ph = \frac{\Delta H_m}{c_{P_L} \cdot (T_L - T_m)}$$
 eq. 52

Practical melting problems are not usually one-dimensional, initial and boundary conditions are complex, the thermo physical properties can vary with phases, temperature, species chemical activity and mass concentration. Furthermore, transport mechanisms such as convection, conduction, radiation, and diffusion may occur simultaneously.

For introductory energy balance purposes, a simple case is presented below, using analytical solutions for a one-dimensional approach to an infinite region with simple boundary conditions. A solid is immersed in a melt with the same chemical composition with a volume large enough to keep its bulk temperature constant, neglecting any effect of solute content, which means that complete and instantaneous solute mixing process occurs, and the liquid immediately flows off the solid. No chemical potential is affecting the mass flow and the temperature at the interface liquid-solid remains at the melting temperature when the melting began. Some equations aiming to describe the heat balance are derived and presented below.

Figure 28 shows a general enthalpy balance at the interface of a solid cylinder and a liquid melt. A temperature boundary layer is assumed to be developed and eq. 53 describes a general enthalpy balance [56]:



Figure 28 - Heat flux on a solid immersed in its own melt

$$-\Delta H_{R} = \Delta H_{S} + \Delta H_{m} + \Delta H_{L} + \Delta H_{R}$$
eq. 53

Presuming that heat balance is not affected by C and Si dissolution and chemical reaction enthalpies from CO and SiO_2 formation are not taking place (i)

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 $\Delta H_R = 0$, the enthalpy ΔH_B transferred from the liquid melt is consumed to: (ii) preheat the solid (ΔH_S) from T_{S0} up to T_m ; (iii) to melt fraction of the solid (ΔH_m) ; (iv) and raise the temperature of the melt fraction from T_m to the melt temperature $T_L (\Delta H_L)$. The properties c_p and ρ of all materials are considered temperature-independent. The film theory applied to heat transfer assumes a liquid layer surrounding the solid surface through which the heat is transferred by conduction only [52]. At the outer boundary layer interface, assuming an isothermal process $\partial T_L / \partial t = 0$ and T_{δ} is constant, thus, eq. 54 is null.

$$\rho_L c_{p_L} \frac{V_L}{A^i} \frac{dT_L}{dt} = -k_{\delta} \frac{dT_{\delta}}{dr} \bigg|_{r+\delta_r} \quad \left[W/m^2 \right]$$
eq. 54

where V_L is the liquid phase volume, A^i is the boundary layer-liquid interface, and k_{δ} is the heat conductivity in the boundary layer. The boundary layer is expected to move towards the center of the solid as the melting process proceeds. The temperature at the outer boundary layer tends to reach T_m , and the heat transfer by conduction across the boundary layer can be expressed by eq. 55:

$$k_{\delta} \cdot \frac{dT_{\delta}}{dr}\Big|_{r+\delta_r} = -\rho_L \cdot c_{p_L} \cdot (T_L - T_m) \cdot \frac{dr}{dt} + k_{\delta} \cdot \frac{dT_{\delta}}{dr}\Big|_r \quad [W/m^2] \qquad \text{eq. 55}$$

If $\delta_r \ll r$, then, $k_{\delta} \cdot \frac{dT_{\delta}}{dr}\Big|_{r+\delta_r} \cong k_{\delta} \cdot \frac{dT_{\delta}}{dr}\Big|_r$ and $\rho_L \cdot c_{p_L} \cdot (T_L - T_m)$ could be considered

negligible. Consequently, the temperature gradient in the boundary layer could be considered constant.

$$k_{\delta} \cdot \frac{dT_{\delta}}{dr}\Big|_{r+\delta_{r}} \cong k_{\delta} \cdot \frac{dT_{\delta}}{dr}\Big|_{r} = \frac{k_{L}}{\delta_{r}} \cdot (T_{L} - T_{m}) = h \cdot (T_{L} - T_{m}) \quad \left[W/m^{2}\right] \qquad \text{eq. 56}$$

Thus, at the inner limit of the temperature boundary layer is the heat transfer balance results in heat consumption for solid pre-heating $k_s dT_s/dr|_r$ and $\rho_s \Delta H_m dr/dt$ the melting latent heat for melting:

$$k_{\delta} \cdot \frac{dT_{\delta}}{dr}\Big|_{r} = -\rho_{S} \cdot \Delta H_{m} \cdot \frac{dr}{dt} + k_{S} \cdot \frac{dT_{S}}{dr}\Big|_{r} \quad \left[W/m^{2}\right]$$
eq. 57

combining eq. 56 and eq. 57, heat transfer convection

$$k_{\delta} \cdot \frac{dT_{\delta}}{dr}\Big|_{r} = h \cdot (T_{L} - T_{m}) = -\rho_{S} \cdot \Delta H_{m} \cdot \frac{dr}{dt} + k_{S} \cdot \frac{dT_{S}}{dr}\Big|_{r} \qquad \left[W/m^{2}\right] \qquad \text{eq. 58}$$

therefore,

If
$$h(T_L - T_m) < -k_s \cdot \frac{\partial T_s}{\partial r}$$
, then $-\rho_s \cdot (\Delta H_m) \cdot \frac{\partial r}{\partial t} < 0$, $\frac{\partial r}{\partial t} > 0$, solidification of

a shell occurs when the enthalpy flow from the melt is lower than the enthalpy flow to heat the solid;

If
$$h(T_L - T_m) = -k_s \cdot \frac{\partial T_s}{\partial r}$$
, then $-\rho_s \cdot (\Delta H_m) \frac{\partial r}{\partial t} = 0$, $\frac{\partial r}{\partial t} = 0$, no solidification

or melting occur when the enthalpy flow from the melt is equal to the enthalpy flow to preheat the solid up to T_m ;

If
$$h(T_L - T_m) > -k_s \cdot \frac{\partial T_s}{\partial r}$$
, then $-\rho_s \cdot (\Delta H_m) \frac{\partial r}{\partial t} > 0$ and $\frac{\partial r}{\partial t} < 0$, melting

occurs when the enthalpy flow from the melt is higher than the enthalpy flow to heat the solid;

The heat conduction within the solid obeys the Fourier's second law. The differential equation eq. 59 is,

$$\frac{\partial T}{\partial t} = \frac{k_s}{\rho_s.c_{p_s}} \cdot \left(\frac{\partial^2 T}{\partial r^2} + \frac{(n-1)}{r} \cdot \frac{\partial T}{\partial r} \right)$$
eq. 59

where *n* is the symmetry number: n=1 for a plate; n=2 for a cylinder n=3 for a sphere [57, 58]. Solutions can be found in the literature for different boundary conditions, and some of them are presented on

Table 12 considers that the heat conduction in the solid is not taken into account when the solid is preheated close to the its melting temperature (conditions I and II). The condition III considers the limiting cases when the solid thermal conductivity is null or infinite.

		I	II		III	
NO	preheat scrap charged		preheat scrap		cold scrap charged in a	
ΠΠ	in a huge hot heel		charged in a limited		huge hot heel volume	
CON	volu	ume	hot heel volume			
	ISOTHERMAL		ADIABATIC		ISOTHERMAL	
F	$T_L \approx T_m$		$T_L(t) \approx T_m$		$T_L \approx T_m$	
MEL	$\Delta H_B = 0$	$\Delta H_L = 0$	$\Delta H_B \neq 0$	$\Delta H_L = 0$	$\Delta H_B = 0$	$\Delta H_L = 0$
	$\frac{\partial T_L}{\partial t} = 0$	$\frac{\partial T_L}{\partial r} = \frac{T_L}{\delta_r}$	$\frac{\partial T_L}{\partial t} \neq 0$	$\frac{\partial T_L}{\partial r} = \frac{T_L}{\delta_r}$	$\frac{\partial T_L}{\partial t} = 0$	$\frac{\partial T_L}{\partial r} = \frac{T_L}{\delta_r}$
	НОТ		НОТ		COLD	
SOLID	$T_{s} \approx T_{m}$		$T_{s} \approx T_{m}$		$T_s \ll T_m$	
		∂T_{c}		∂T_{a}	ΔH_s	$f \neq 0$
	$\Delta H_s \cong 0 \Longrightarrow \frac{\partial F_s}{\partial r} \cong 0$		$\Delta H_s \cong 0 \Longrightarrow \frac{\partial F_s}{\partial r} \cong 0$		$\frac{\partial T_s}{\partial r} < 0$	
	$h.(T_L - T_m) = -\rho_S.\Delta H_m.\frac{dr}{dt}$		$-\frac{\rho_L c_{p_L} V_L}{A} \cdot \frac{d}{d}$	$\frac{dT}{dt}h.(T_L - T_m) =$	$(V_{\max} - V_0) \cdot \left[\Delta H_m + \right]$	$+c_{p_L}\cdot\frac{\rho_L}{\rho_s}\cdot(T_L-T_m)$
ODE			$= -\rho_s . \Delta H_m . \frac{dr}{dt}$		$=V_0.c_{p_s}.(T_m-T_I)$	
2	(eq. 60)		(eq. 61)		(eq. 62)	
MELTDOWN TIME	$t_m = \frac{\rho_s . \Delta H_m . R_0}{h . (T_L - T_m)}$		$t_m = \frac{\rho_L \cdot c_p}{h \cdot A}$	$\frac{V_L}{A_0} \cdot f(\varphi)$	$t_m = \frac{\rho_s \cdot \Delta H_m \cdot R_0}{h \cdot (T_L - T_m)} \cdot \left[1 \\ k_s = 0 \right]$	$+\frac{c_{p_s}.(T_m-T_l)}{\Delta H_m}\right]$
	(eq. 63)		(eq. 64)		(eq. 65)	
					$t_m = \frac{\rho_s . \Delta H_m . R_0}{h . (T_L - T_m)} . \left[1 \right]$	$\left[+\frac{c_{p_s}.(T_m-T_I)}{\Delta H_m}\right]^{1/n}$
					$k_s = \infty$	-
					(eq. 66)	

Table 12 – Heat transfer equations for special cases applied to meltdown a solid in its own melt [56, 58].

where V_{s0} is the volume and A_0 is the initial area of the solid just before immersing. V_L is the volume of liquid. T_I is the initial temperature of the solidified shell in the case III. Hot heel means a pool of molten metal. τ_m and t_m are the dimensionless time and time for complete melting, respectively. Particularly, the condition named II is shown on Figure 29.



Figure 29 – Adiabatic melting of a plate, cylinder or sphere. Theoretical estimate of dimensionless melting time for solids with the same volume, preheated to close to the their melting temperature and immersed in their own melt [56] (condition II, Table 12).

The equations from eq. 67 to eq. 73 are related to the condition named II shown on Table 12. The φ function is related to the ratio of the heat required for melting the solid to the heat content available in the liquid phase. Function $f(\varphi)$ varies according to the solid geometry.

$$\varphi = \frac{\rho_{s} \cdot \Delta H_{m}}{c_{p_{L}} \cdot \rho_{L} \cdot (T_{L} - T_{m})} \cdot \frac{V_{s0}}{V_{L}} \qquad \text{eq. 67}$$
$$\varphi \le 1$$

For Plates

$$f(\varphi) = -\ln(1-\varphi)$$

For Cylinders

 $f(\varphi) = 2 \cdot \left(\frac{\varphi}{1-\varphi}\right)^{1/2} \arctan\left(\frac{\varphi}{1-\varphi}\right)^{1/2}$

For Spheres

$$f(\varphi) = \left(\frac{\varphi}{1-\varphi}\right)^{2/3} \cdot \left[\frac{1}{2} \cdot \ln \frac{\left[1+\left(\frac{\varphi}{1-\varphi}\right)^{1/3}\right]^{3}}{1+\frac{\varphi}{1-\varphi}} - \sqrt{3} \cdot \arctan \left(\frac{1-2 \cdot \left(\frac{\varphi}{1-\varphi}\right)^{1/3}}{\sqrt{3}}\right) + \sqrt{3} \cdot \frac{\pi}{6}\right]$$
eq. 70

eq. 68

eq. 69

$$f(\varphi) = \tau_m = \frac{A_0 \cdot \alpha_L}{V_L \cdot \delta_T} \cdot t_m$$
 eq. 71

$$f(\varphi) = \frac{A_0}{V_L . \delta_T} . \frac{k_L}{\rho_L . C_{p_l}} . t_m$$
 eq. 72

$$t_m = \frac{C_{p_L} \rho_L V_L}{(\frac{k_L}{\delta_T}) \cdot A_0} \cdot f(\varphi) = \frac{C_{p_L} \rho_L V_L}{h \cdot A_0} \cdot f(\varphi)$$
eq. 73

The models proposed above point out the significant effect of the geometry of solids and the availability of energy in the liquid phase on melting rates.

In all cases presented in

Table 12, the thermal conductivity of the solid k_s was not taken into account because the body is pre-heated close to T_m (Conditions I and II) or a hypothetical limiting case is presumed (Condition III), meaning that the heat transfer predominant resistance is governed by heat transfer in the liquid-solid interface. Nevertheless, it is reasonable to admit that the thermal conductivity in the solid phase (iron alloys) is not so high (40 W/m.K) compared to the heat transfer coefficient (20,000 W/m².K), resulting in a Biot number higher than 0.1, $Bi = h.(V_s/A_s)/k_s$, eq.AN3 - 71 specially for heavy bodies. Actually, when cold ferrous material is charged, the process of fusion and heating the solid to melting temperature should occur simultaneously. Hence, the thermal conductivity in the solid phase has to be taken into account as well a non-isothermal process in the very beginning of the solid immersion in the liquid pool. In addition, there is a possibility that the enthalpy ratio φ available in the hot heel may be not enough to provide the preheating energy rate demanded by the solid to raise the interface temperature to its melting temperature. Consequently, it can cause solidification of a shell around the solid surface, whose mass is provided by the metal phase. Hence, this becomes a boundary-moving problem, and usually the calculations must be performed numerically.

Figure 10 shows a sketch for heat flow and qualitative temperature profiles in a unidirectional approach, considering samples of cylindrical shape. For simplification purposes, heat flow in the length direction (z-axis) is omitted at this point.



Figure 30 - Cylindrical sample immersed in its own melt pool, submitted to a constant external heat source.

For simplification purposes, heat flow in the length direction (z-axis) is omitted at this point. (a) immediately after the sample immersion; (b) heat transfer from the melt through a temperature boundary layer; (c) the possibility of solidified shell over the former solid surface;(d) the solidified shell is re-melted and the melting interface advances toward r=0

(a) at t=0, the fluid is at a constant temperature T_{Lo} and the solid at T_{So} . In (b) at $t_1 > t_0$, a heat resistance at the solid-liquid interface may occur and the heat is transferred to the solid through a temperature boundary layer δ_T The solid temperature $T_s^i(t)$ at the interface may be equal to the solid melting temperature (dashed line), hence, the melting process at the interface starts meanwhile the solid by bulk is heated conduction. However, if the heat flow from the surrounding liquid is not enough to support the heat demands to heat the

solid and keep the liquid temperature higher than liquidus temperature as shown in (c), consequently, a solidified shell can be formed (solid line). Furthermore, a gap between the former solid and the new solidified shell may occur and become a significant contribution for heat flow resistance through the solid.

More complex scenarios have been studied for different melting conditions [45, 52, 59-64]. Figure 31 presents the premises adopted in the case of sponge iron pellets immersed in a pure iron melt [59]. In this case, the pellet is initially

preheated and a solid shell freezes, grows (time $t_0 \rightarrow t_1$) and melts later ($t_1 \rightarrow t_2$). The thermal conductivity in the solids is taken into account, and the temperature of the sponge iron pellet is equal to the melting temperature after the shell is remelted. T_m is considered constant, the thermal properties are temperature-independent. The formation of a mushy zone and mass transfer are not considered. Figure 32 shows the effect of liquid temperature on the radius variation of sponge iron pellets versus immersion time.



Figure 31 – Temperature profile through the sponge iron pellet and frozen shell [59].



Figure 32 – (a) Melting behavior of sponge iron pellets with initial radius $R_0 = 1$ cm [59]

As the immersion time moves forward, the melting rate increases because the interior of the solid is increasingly hot, thus $\frac{dT_s}{dr}$ decreases, permitting a larger amount of energy of the arriving heat from the melt $h.(T_L - T_m)$ to be used in the melting process $\rho_s.\Delta H_m.\frac{dr}{dt}$, according to eq. 58.

The effects of the thermal diffusivity and the density of the solid are shown on Figure 33. When $k_s \rightarrow 0$, although there is no frozen shell formed onto the surface of the solid. the melting time is its longest at $\left(\left[k_{s}\downarrow\frac{dT_{s}}{dr}\uparrow\right]\uparrow \therefore \rho_{s}.\Delta H_{m}.\frac{dr}{dt}\downarrow \therefore t_{m}\uparrow\right)$. Unlikeness, when $k_{s}\rightarrow\infty$, the portion of the frozen shell is at its largest, while the total melting time is at its shortest $\left(\left[k_{s}\uparrow\frac{dT_{s}}{dr}\downarrow\right]\downarrow::\rho_{s}.\Delta H_{m}.\frac{dr}{dt}\uparrow::t_{m}\downarrow\right)$. From Figure 33 (b), even though the sponge iron has the lower thermal conductivity, its melting time is shorter than materials with higher conductivities. Nevertheless, the melting time decreases meanwhile the density decreases, pointing out that the solid density is the predominant factor (see (eq. 65)).





(a) Radius of iron spheres with density of sponge iron submerged into liquid iron as a function of time and thermal diffusivity (k_c) of

the sphere

(b) Total melting time of iron spheres as function initial radius of the sphere. $k_{\scriptscriptstyle S}=\lambda$

Figure 33 - Initial Melt temperature (T_{OM})=1600 °C. Initial pellet temperature (T_{OS})=25 °C [60]

The proposed model could explain the melting rate increase when both the solid preheating temperature and the metal phase superheating increase. The same behavior was observed for larger spheres of iron immersed in iron melt [61].

Experimental and modeling program were developed to study the rate and mechanism for melting of HBI [64]. Thermocouples were inserted at a known radius location in the briquettes with cylinder shape, and later the samples were immersed in melt with low and high carbon content. During the immersion in melts, a heat transfer model was applied to estimate the melting rate and the heat flux from the melt to the briquette interface. Figure 34 presents the meltdown progress.



Figure 34 – (a) Radius variation and (b) Melting rate for a 1.22 %wtC HBI cylinder immersed in a 0.03 %wt C Melt [64].

Figure 35 shows that carbon content in the liquid phase is influencing the melting rates of HBI cylinders. The higher it is, the higher the expected CO generation caused by internal reaction of C and residual iron oxide. The coefficient of heat transfer is presumed to increase by the additional stirring effect.



Figure 35 – Predicted and experimental melting times for HBI cylinders [64].

Some studies conducted at BOF have suggested that the dissolution of low carbon scrap depends significantly on the scrap size distribution, being even more important than oxygen blowing rate [52] [43] [42]. At BOF conditions, the dissolution of heavy scrap starts after the light scrap is almost completely dissolved. Consequently, the rapid heat removed from the melt may cause the solidification of a shell over the remaining heavy scrap pieces.

Other observations have shown that a gap between the pig iron and the solidified shell may control the heat transfer and the further melting rate of heavy pieces [62]. Furthermore, in laboratory experiments using immersion of cylinders technique, it was concluded that the results could only be reproduced accordingly to the model if the heat conductivity of the solid was not assumed constant [65], which was associated to the effect of heat transfer resistance in the gap scrapsolidified shell. In the EAF conditions, this mechanism maybe occurring with pig iron mixed with light scrap such as shredder or turnings, and also non-dissolved lime may enhance this chilling trend.

Industrial experiments were performed with big pieces of pig iron and several different scrap sizes utilizing tracer elements. It was concluded that the melting of heavy scrap can only occur when substantial superheat can be created. Also, if this condition is not met, there should be no melting rates differences between low carbon heavy scrap and pig iron of similar size [42], which was confirmed on experiments in a industrial EAF facility.



Samples: Cylinder O 100 mm diameter Low-C ☆ 200 mm diameter low-C △ 200 mm diameter pig-iron

200 mm diameter pig-iron

The filled symbols correspond to samples charged in the first basket, and open symbols to samples charged in the third basket

Figure 36 – Experimental scrap melting time in EAF. Time 0 corresponds to power-on for the third basket [42].

According to Figure 36, there should be no benefits in charging heavy scrap pieces in the first basket, but on contrary, it is preferable to charge the heavier pieces after the lighter scrap is melted completely.

Recent studies have been conducted on a laboratory scale, using the multiple sample design in contrast to cylinder single sample design (Figure 37). This experimental innovation helped to simulate a direct immersion of several ferrous bodies in sizes together in a small volume of hot heel [63]. In practice, after the first bucket charge, the hot heel is actually spread in different small pools of liquid steel, delimited by surrounding solid charge.



(b)

Figure 37 – (a) Final melting vs. porosity for multi-bar sample (initial temperature of all samples T_{S0} = 25 °C an initial liquid melt temperature T_L = 1650 °C; (b) Cross sections after immersion for approximately 10 s.

2.4.1. Mass And Heat Transfer During Dissolution Of Low Carbon Steel In High Carbon Melt

The general mechanisms for low-carbon scrap dissolution in high-carbon melts are accepted as presented in the sequence below:

- heat transfer occurs from the melt to the solid depending on the superheat gradient and the fluid flow regime: natural convection, turbulent convective stirring and others;
- liquid phase mass transfer (LPMT) is predominant;
- carbon diffusion takes place through the boundary layer into the solidliquid interface;
- carbon diffusion in the solid surface decreases the solid melting point. The melting interface is considered to be a very thin layer. The carbon content in scrap is usually low, and in the beginning, the melting process produces a low carbon melt into which carbon diffuses from the bulk of carbon-rich melt [58]. The ratio between the dissolution rate and the carbon diffusion from the melt to solid interface determines the carbon content in the liquid phase at the interface liquid-solid [58];
- counter diffusion of Fe into the liquid phase can also occur [48];

Figure 38 presents a general sketch for the temperature and composition profiles at a certain moment of the dissolution process.



Figure 38 - Temperature and carbon distribution through the interface of high carbon melt – low carbon solid sample [43], [66], [45].

It is a moving boundary problem. The general equation for velocity of the melting interface adopted for a cylindrical sample submitted to an isothermal dissolution was first proposed as described in eq. 74 [46]:

$$\mathcal{G} = \frac{dr}{dt} = m . \ln(1 + \frac{C_L^0 - C_L^i}{C_L^i - C_S^0}) \qquad [m/s]$$
 eq. 74

where $\mathcal{G} = \frac{\partial r}{\partial t}$ is the moving interface rate

$$m = \frac{D_{C_L}}{\delta}$$
 [m/s] see also eq.AN3 - 51 eq. 75

where *m* is the carbon mass transfer coefficient defined as D_{C_L}/δ , the ratio of the diffusion coefficient to the boundary layer thickness, C_L^0, C_L^i, C_S^0 are the solute content in the liquid phase, interface liquid-solid and in the solid phase, respectively.

In general, the mass transfer coefficient is a function of the bodies' geometry, Reynolds number R_e eq.AN3 - 64, Schmidt number Sc eq.AN3 - 68, which means: materials thermo physical properties: diffusivity, viscosity, density, and media velocity are independent of mass transfer and the concentration driving forces.

Nevertheless, modifications of eq. 74 have also been used [43], based on mass balance:

$$m.(C_L^0 - C_L^i) = (C_L^i - C_S^0).\vartheta - D_{C_S}.\frac{\partial C_S}{\partial r}$$
eq. 76

. .

The diffusivity in the solid phase $D_{C_{s.}}$ is neglected, because it is very much slower than in the liquid phase $D_{C_{L.}}$ The term $m.(C_L^0 - C_L^i)$ is the mass transfer rate from the liquid bulk to the melting interface, $(C_L^i - C_s^0).\mathcal{G}$ is the mass transfer rate through the boundary layer:

$$\Delta C = (C_L^0 - C_L^i) \qquad \text{eq. 77}$$

$$\mathcal{G} = \frac{dr}{dt} = m \cdot \frac{C_L^0 - C_L^i}{C_L^i - C_S^0} \qquad \text{eq. 78}$$

Thus far, ΔC is the driving force for mass transfer.

A correction for different liquid and solid densities is also proposed [45],

$$\mathcal{G} = \frac{dr}{dt} = m \cdot \frac{C_L^0 - C_L^i}{\frac{\rho_s}{\rho_L} C_L^i - C_s^0}$$
eq. 79

Regarding the heat balance in the interface, the following eq. 80 has been used [42, 43, 45, 50, 52, 55, 62]. The heat flux delivered by the liquid $h.(T_L - T_m)$ is consumed for melting a layer-surface $\rho_s \Delta H_M . 9$ and dissipated into the solid

 $k_S \left. \frac{\partial T}{\partial x} \right|_{\text{int erface}},$

$$h.(T_L - T_m) = \rho_S \Delta H_M \cdot \vartheta - k_S \left. \frac{\partial T}{\partial x} \right|_{\text{interface}}$$
eq. 80

Similar to eq. 58

$$\Delta T = (T_L - T_m)$$
 eq. 81

thus, ΔT is the driving force for heat transfer

Assumptions:

- Steady-state condition;
- Isothermal condition;
- D_L does not vary with carbon content;
- The densities of the solid and the liquid are equal, and all diffusion resistance occurs in the liquid boundary layer.
- Dissolution rates are controlled by the solute concentration, which is governed by the carbon content. In the case of a Fe-C system Si content is not taken into account.
- The interface temperature is close to the melt bulk temperature, and the liquid and solid at the interface will have the liquidus composition [51].

To compute the unknown terms:

$$T_i, C_L^i, C_S^i, \vartheta$$

Two additional equations from the Fe-C diagram are added to eq. 82 and eq. 84

$$C_L^i = f_1(T_i)$$

$$\begin{split} T_{Liquidus} &= 1536 - 90.\% C \quad \text{for} \quad 0\% \leq \% C \leq 4.26\% \ [67] & \text{eq. 83} \\ \text{Solidus curve} & \text{eq. 84} \\ C_S^i &= f_2(T_i) \\ T_{Solidus} &= 1585 - 202.\% C \quad \text{for} \quad 0.17\% \leq \% C \leq 2.04\% & \text{eq. 85} \end{split}$$

Consequently, the mass transfer coefficient can be computed.

Mass transfer coefficients estimates:

- After compiling the mass transfer coefficient for several different experimental conditions, a summary is presented below:

Stationary sample and non forced melt stirring:

1200 °C ~ 1 x 10⁻³ [cm/s] [45]

1450 °C ~ 5 x 10^{-3} [cm/s]

Rotary sample (depends on the rpm applied)

1200 °C ~ 8 x 10⁻³ - 2 x 10⁻² [cm/s] [48]

1450 °C ~ 3 x 10⁻³ - 2 x 10⁻² [cm/s]

Stationary Sample and forced gas stirring (depends on gas stirring)

 $1400 \,^{\circ}\text{C} \sim 1.0 \times 10^{-2} - 2.5 \times 10^{-2} \,[\text{cm/s}] \,[51]$

Stationary Sample and CO evolution as stirring gas (depends on ppm O in the sample)

 $1200 \ ^{\circ}\text{C} \sim 2.0 \ \text{x} \ 10^{-3} - 1.0 \ \text{x} \ 10^{-2} \ [\text{cm/s}] \ [47]$ $1400 \ ^{\circ}\text{C} \sim 8.0 \ \text{x} \ 10^{-3} - 8.0 \ \text{x} \ 10^{-1} \ [\text{cm/s}] \ [47]$

- Therefore, accordingly to the data base, depending on the experimental conditions, the mass transfer coefficient varied in almost 1000 order of magnitude ;

Figure 39 [45] presents the effect of the carbon content in the melt on the melting rates of low carbon samples at temperatures below the melting temperature expected for Fe-0.10%C alloys. The melting times are slightly affected by high bulk carbon contents. The sensitivity of melting times on the melt temperature is high, particularly at 2 and 1.5 wt% C.



Figure 39 – Predicted melting times for vertical steel plates and cylinders, 0.1" thickness immersed in stagnant pig iron melts versus melt temperature ($^{\circ}F$) for various melt carbon content [45].

Table 13 and Table 14 summarize some estimates for heat transfer coefficient and mixing power for several BOF converters and small scale experiment.

Equipment	Operational Conditions	Reference	Heat Transfer Coefficient [W/m ² .K]
LD Converter	Top blow	[43]	17,000
LD Converter	Top blow	[67]	50,196
LD Converter	Top blow	[52]	47,500
LET Converter	Bottom blow 0.05 m ³ .min ⁻¹ .t ⁻¹	[43]	25,000
LWS Converter	Bottom blow	[43]	50,000
LD Converter	Top blow	[52]	47,500
Small Scale Experiment	Induction Fnce	[50]	3,400 - 11,450
Small Scale Experiment	Induction Fnce	[68]	10,000 – 17,000
Small Scale Experiment	Induction Fnce	[69]	13,400
Small Scale Experiment	Induction Fnce	[59]	25120

Table 13 – I	Mass and h	eat transfer	coefficients	estimates
	111255 2110 11		COEIIICIEIIIS	countateo

Some authors have suggested the relation for heat mass transfer in converters [43, 67] as in eq. 86:

$$h = 5,000 * \varepsilon$$
 eq. 86

where ε is the average mixing power due to turbulent regime W/m³. Hence, ε can be estimated for different operational conditions, indicating huge effect on h.

Table 14 – Average mixing power versus heat transfer coefficient in converters

h	• E
[W/m ² .K]	[W/m ³]
17,000	454
25,000	3.125
50,000	100.000

Studies made on the rates of dissolution of stationary and rotating samples of cylindrical iron containing different amounts of oxygen immersed in high carbon melt pointed out that CO evolution accelerates the dissolution rate. The CO evolution caused a drastic change in the shape of the specimen. The CO bubbles tend to move upward, affecting the heat and mass transfer coefficients. Figure 40 shows that the mass transfer coefficient *m* for dissolution of iron containing about 1% oxygen, is ten times higher than Al-killed sample. The mass transfer coefficient was found to be proportional to the CO flow rate Q_{CO} :

$$m = Q_{CO}^{0.3}$$
 eq. 87

However, m decreased in the case of Al-killed samples even for lower temperatures, as shown in Figure 41 (dashed area). This phenomenon was concluded to be related to bubbles coalescence on the sample surface. If the

bubbles do not detach quickly and coalesce, a blanketing layer may be produced on the surface, resulting in the decrease of the mass transfer coefficient.



Figure 40 – Mass transfer coefficient vs. CO evolution rate for stationary dissolution at various temperatures [47].



Figure 41 – Mass transfer coefficient vs. oxygen concentration for stationary dissolution at different temperatures [47].

Figure 42 shows that the heavy scrap dissolution in converters charged with high carbon melts is significantly affected by the presence of lighter scrap. The dissolution of heavy scraps starts after the light scrap is almost completely dissolved.



Figure 42 – Simultaneous dissolution of different scrap blend [52].

2.4.1.1. Melting Kinetics Summary

The melting rate of solids in their own melt increases $(m \uparrow)$ when :

- melt superheat increases ($\Delta H_B \uparrow, T_L >> T_m$)
- Enthalpy Ratio decreases ($\varphi \approx \frac{(\Delta H_m + \Delta H_s)}{\Delta H_B}$. $\frac{V_{s0}}{V_B} \downarrow$)
- Solid preheat increases $(h.(T_L T_m) = -\rho_s.\Delta H_m.\frac{dr}{dt} \uparrow +k_s.\frac{dT_s}{dr} \downarrow \Big|_r$
- Solid Area to volume ratio increases. The heat flux (q [W]) is proportional to the interface liquid-solid area ($q = h.A.(T_L T_m)$)
- Solid heat conductivity increases $(k_s \uparrow)$. When $k_s \to \infty$, the portion of the frozen shell is at its largest, while the total melting time is at its shortest $\left(\left[k_s \uparrow \frac{dT_s}{dr} \downarrow\right] \downarrow \therefore \rho_s . \Delta H_m . \frac{dr}{dt} \uparrow \therefore t_m \downarrow\right)$
- Solid density decreases. The density factor is predominant compared to the thermal conductivity effect. $(t_m \propto \frac{\rho_s . \Delta H_m . R_0}{h.(T_L T_m)})$
- The convective heat transfer coefficient *h* ↑ increases in case of vigorous stirring from CO evolution. Single HBI briquettes were observed to melt quickly relative to the scrap;
- The high heat rate consumed by light scrap results in decrease in the melt temperature to a level that solidification takes place on the relatively colder and heavy scrap grades;
- The rate of dissolution of steel in molten pig iron is raised by increased temperature, increased composition gradients and increased stirring;
- The rate of heating the solid steel is a limiting factor. Steel rods and spheres showed the build up of a frozen layer of solidified portion from the former melt;

- The evolution of CO increases the rate of dissolution. However, at lower temperatures, CO bubbles may not detach rapidly, forming a blanketing layer and decreasing the mass transfer coefficient;
- In the EAF the melting energy is directly transmitted to light scrap by radiation of the arcs and through the fumes. For heavy scrap or large pieces of pig iron, most of the energy is transmitted through the liquid metal;
- The conditions prevailing during the melting of heavy scrap might be closer to scrap or Fe-alloys melting in ladle than to converter conditions [42];
- At EAF facilities, the melting of heavy scrap can only occur when substantial superheat can be created. If this condition is not met, there should be no melting rates differences between low carbon heavy scrap and pig iron of similar size [42].

2.5. Meltdown at Electric Arc Furnace

The electric arc furnace technology has improved over the decades becoming a competitive route for almost 40% of steelmaking production in the world today. In contrast to OSM, the majority of EAF charges 100% solid ferrous materials, even though hot metal has been loaded at some facilities.

Figure 43 presents typical conventional EAF facilities. Usually, the installations are much more compact than integrated mills, focused on recycling ferrous scrap.



Figure 43 – Typical conventional EAF facilities, including auxiliary equipments: scrap bucket, slag pots; steel ladles; overhead cranes and off-gas system [70].

Figure 44 shows the top and cross section views of an eccentric bottom tapping EAF. The swinging roof covers the vessel, which consist of upper and lower shells. Refractory lining determine the lower shell profile and the upper shell are usually equipped with water cooled panels and gas injection technologies.



Figure 44 – Typical EAF lower and upper shell. (a) Eccentric bottom tapping design – EBT; refractory line in the lower shell suitable for high melt temperatures; (b) Water cooled parts and oxygen injectors at upper shell.

Conventional EAF is planned for batch charge of non-preheated materials and batch tapping of hot melt. The processing steps of this EAF category is presented in Figure 45: (a) solid charge through buckets; (b) meltdown energy supplied from fossil fuel via burners, electricity and exothermic reactions from solute oxidation; (c) oxygen injection for decarburization and slag formation purposes; (d) combined carbon and oxygen injection for foaming slag to cover the electric arc, increasing the energy efficiency, protecting refractory lining and water cooled parts against damage; (e) slag-off to avoid phosphorus reversion, to provide room for the next charge and avoid slag carry over to the ladle furnace (secondary metallurgy); (f) all charge is molten and the melt is overheat up to 1620-1680 °C for tapping.



Figure 45 – Meltdown and primary refining in conventional EAF [71]

There are many other alternate technologies innovating mainly the preheating of raw materials by re-using the available sensible heat of the exhausted gas. Two examples of such new technologies, which are available in industrial scale, are presented in Figure 46 and Figure 47. Both include continuous or semi-continuous charging of raw materials and batch tapping.


Figure 46 - Consteel process by Techint



Figure 47 – Shaft Furnace by Fuchs

Therefore, the heat transfer and mass transfer processes in EAF could be described in a simplified way such as:

- Charge Preheating
 - Forced preheating using the off-gas sensible heat out side the furnace vessel. Solid-gas interface;
 - Preheating by gas phase convection provided by burners and arc irradiation inside the furnace vessel, before cave in into the available hot heel (liquid metal pool). Solid-gas interface;
 - Preheating by immersion in the available hot heel. Solidliquid interface;
- Melting and Refining
 - Oxygen and carbon injection for decarburization reactions in the metal bulk and iron oxide reduction in the slag phase;
 - Energy input mainly from electricity.

Hence, EAF processing implies in relevant transient period.

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