Application of Gibbs Energy minimization to Oxygen Steelmaking Process

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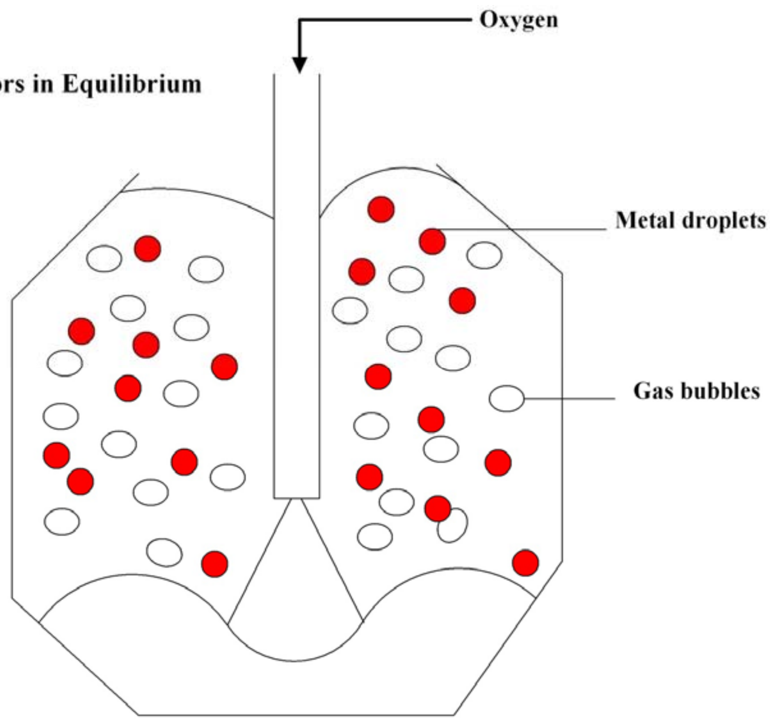
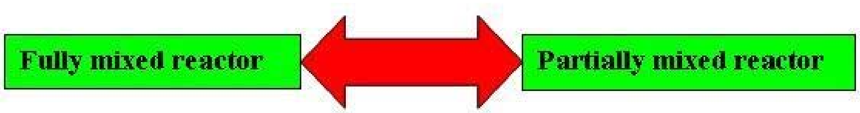
Different Reactors in Equilibrium Model



Metal Reactor : Under jet impact zone
Oxygen saturated metal droplets thrown in slag phase
Oxygen rich metal carried away by jet impact deep into metal bath

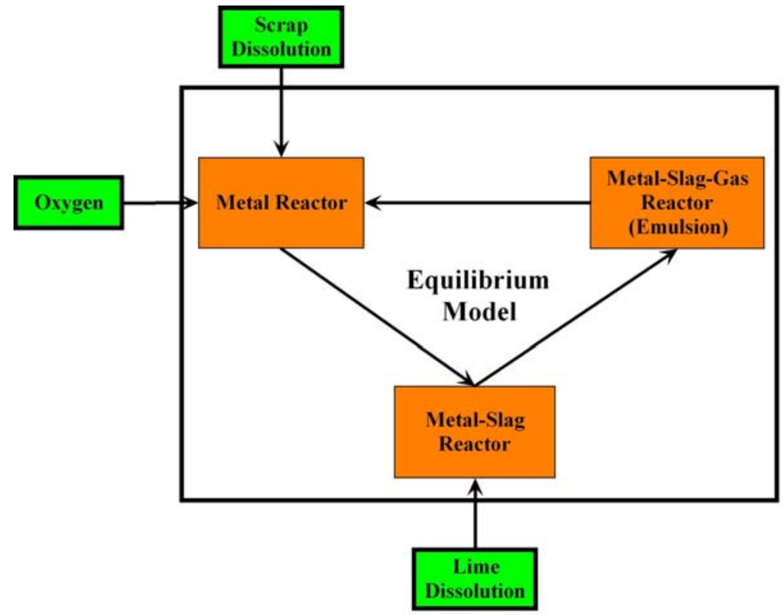
Metal Slag reactor : Metal droplet-slag interface
Bulk metal-slag interface

Metal-slag-gas reactor : Emulsion containing rising gas bubbles and liquid slag

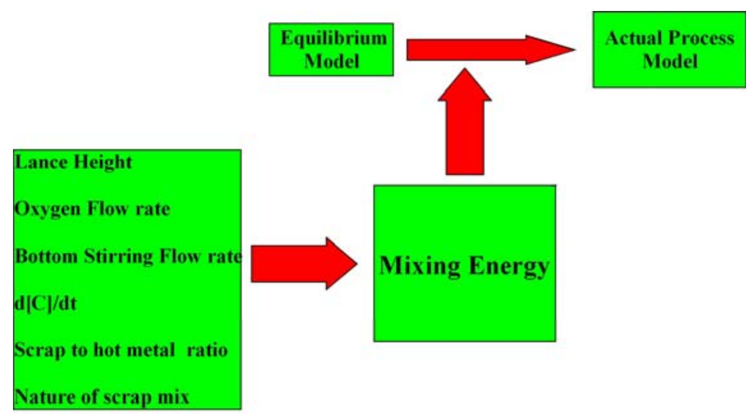


- Computational thermodynamics

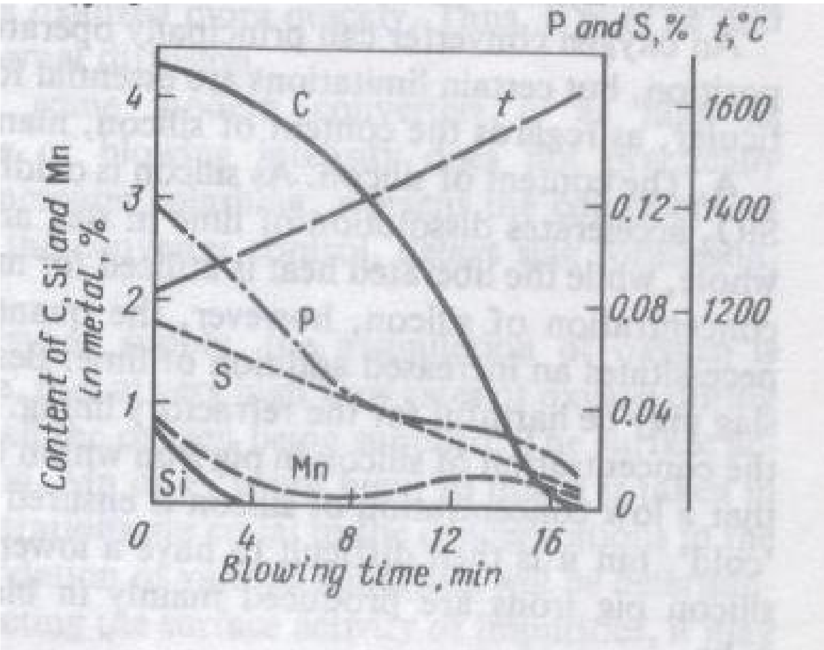
- Computational thermodynamics
- Computational kinetics
- Computational fluid dynamics



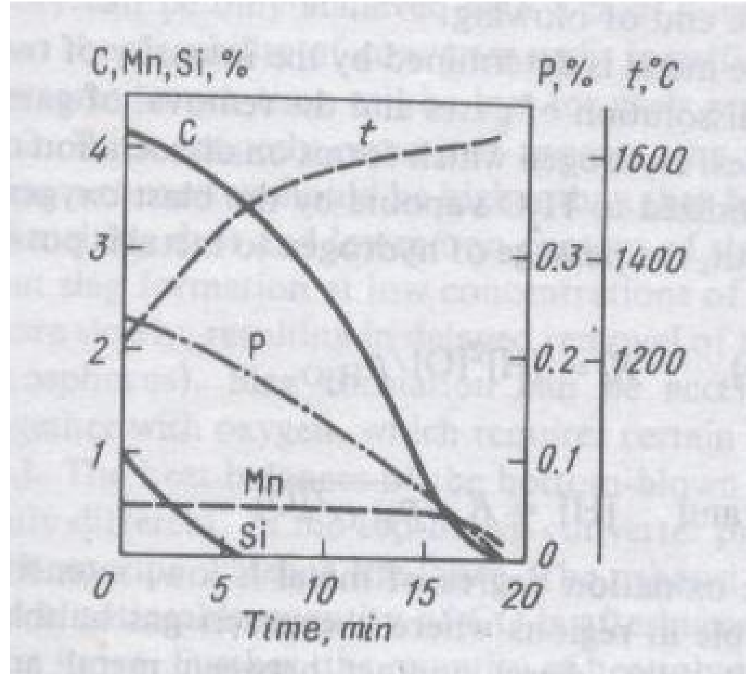
Interaction of different modules of Equilibrium Model



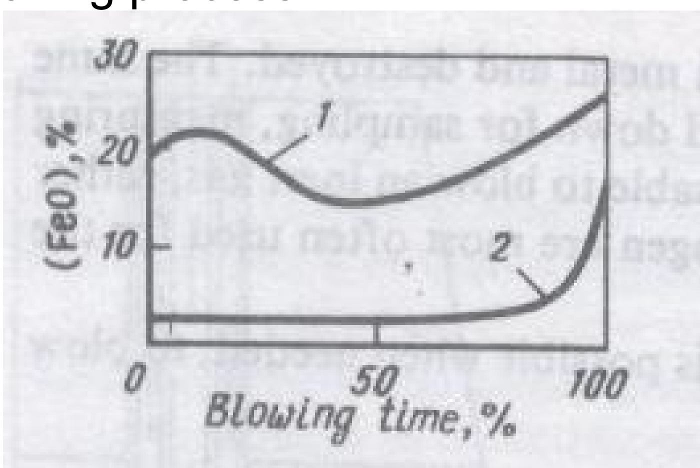
Relationship between Equilibrium Model and Actual Process Model



Variation of metal composition during BOF steelmaking process



Variation of metal composition during Q-BOP steelmaking process



Variations of Oxygen Steelmaking top vs Bottom blowing
Courtesy: Steelmaking by V. Kudrin

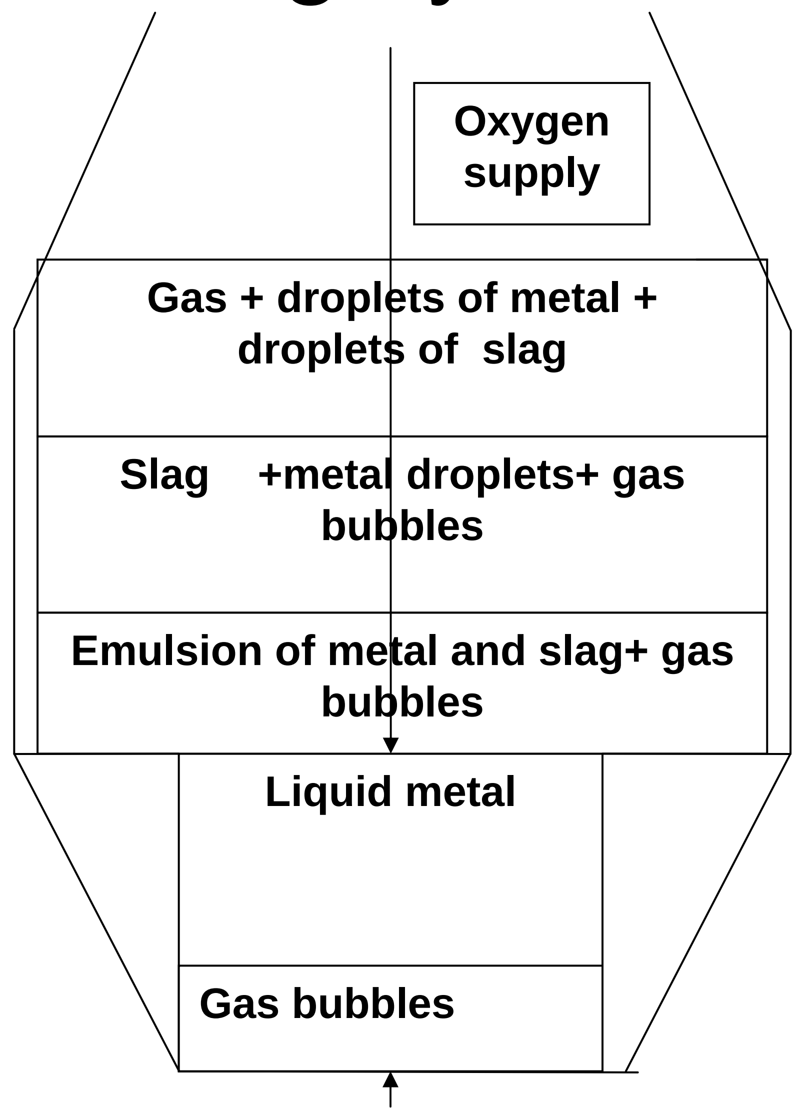
FeO level in the slag for (1) Top blown BOF steelmaking process and (2) blown Q-BOP steelmaking process

Sequence of reactions in an oxygen steelmaking system

Let the metal phase contain [C], [Si],[P] and [O] in dissolved state.

The slag phase contains CaO, FeO, SiO2 and P2O5.

The gas phase contains CO,CO2 and O2.



Representation of BOF steelmaking process as fully mixed free energy minimization system

Total Gibbs free energy of the system Is given as:

$$
\begin{aligned}
G = {} & n_C.\overline{G_C} + n_{Si}.\overline{G_{Si}} \\
& + n_{Fe}.\overline{G_{Fe}} + n_P.\overline{G_P} + n_O.\overline{G_O} \\
& + n_{SiO2}.\overline{G_{SiO2}} + n_{FeO}.\overline{G_{FeO}} \\
& + n_{P2O5}.\overline{G_{P2O5}} + n_{CaO}.\overline{G_{CaO}} \\
& + n_{CO2}.\overline{G_{CO2}} + n_{O2}.\overline{G_{O2}} \\
& + n_{CO}.\overline{G_{CO}} \qquad (1)
\end{aligned}
$$

It is subject to the following mass conservation constraints:

$$n_C + n_{CO} + n_{CO2} = A \qquad (2)$$

$$n_{Si} + n_{SiO2} = B \qquad (3)$$

$$n_{Fe} + n_{FeO} = C \qquad (4)$$

$$n_P + 2.n_{P2O5} = D \qquad (5)$$

$$n_{CaO} = E \qquad (6)$$

$$\frac{n_{CO}}{2} + n_{CO2} + n_{SiO2} + \frac{n_{FeO}}{2} + \frac{5.n_{P2O5}}{2} + \frac{n_O}{2} = N_{OXY} \qquad (7)$$

In a fully mixed system, the equation (1) has to be minimized subject to the constraints (2) – (7). Let a function G' be defined such that all the equality constraints are added to equation (1)by using Lagrange multipliers:

$$
\begin{aligned}
G' = {} & n_C.\overline{G_C} + n_{Si}.\overline{G_{Si}} + n_{Fe}.\overline{G_{Fe}} + n_P.\overline{G_P} + n_O.\overline{G_O} \\
& + n_{SiO2}.\overline{G_{SiO2}} + n_{FeO}.\overline{G_{FeO}} \\
& + n_{P2O5}.\overline{G_{P2O5}} + n_{CaO}.\overline{G_{CaO}} \\
& + n_{CO2}.\overline{G_{CO2}} + n_{O2}.\overline{G_{O2}} + n_{CO}.\overline{G_{CO}} \\
& + \lambda_1.(n_C + n_{CO} + n_{CO2} - A) \\
& + \lambda_2.(n_{Si} + n_{SiO2} - B) \\
& + \lambda_3.(n_{Fe} + n_{FeO} - C) \\
& + \lambda_4.(n_P + 2.n_{P2O5} - D) \\
& + \lambda_5.(n_{CaO} - E) \\
& + \lambda_6.\left(\frac{n_{CO}}{2} + n_{CO2} + n_{SiO2} + \frac{n_{FeO}}{2} + \frac{5.n_{P2O5}}{2} + \frac{n_O}{2} - N_{OXY} \right)
\end{aligned}
\qquad (8)
$$

In order to have minima for G, the following conditions should be satisfied:

$$\frac{\partial G'}{\partial n_i}=0 \qquad \frac{\partial G'}{\partial \lambda_i}=0$$

This, in turn, results in the following equations:

$$\overline{G_C}+\lambda_1=0 \quad (9)$$

$$\overline{G_{Fe}}+\lambda_3=0 \quad (10)$$

$$\overline{G_{Si}}+\lambda_2=0 \quad (11)$$

$$\overline{G_P}+\lambda_4=0 \quad (12)$$

$$\overline{G_{CaO}}+\lambda_5=0 \quad (13)$$

$$\overline{G_{SiO2}}+\lambda_2+\lambda_6=0 \quad (14)$$

$$\overline{G_{FeO}}+\lambda_3+\frac{\lambda_6}{2}=0 \quad (15)$$

$$\overline{G_{P2O5}}+2.\lambda_4+\frac{5.\lambda_6}{2}=0 \quad (16)$$

$$\overline{G_{CO}}+\lambda_1+\frac{\lambda_6}{2}=0 \quad (17)$$

$$\overline{G_{CO2}}+\lambda_1+\lambda_6=0 \quad (18)$$

$$\overline{G_O}+\frac{\lambda_6}{2}=0 \quad (19)$$

Equations (9) to (14) give:

$$\lambda_1=-\overline{G_C} \qquad \lambda_2=-\overline{G_{Si}}$$

$$\lambda_3=-\overline{G_{Fe}} \qquad \lambda_4=-\overline{G_P}$$

$$\lambda_5=-\overline{G_{CaO}} \qquad \lambda_6=\overline{G_{Si}}-\overline{G_{SiO2}}$$

Plugging these values in Equations (15)-(19),

$$\overline{G_{FeO}} - \overline{G_{Fe}} + \frac{1}{2}.\left(\overline{G_{Si}} - \overline{G_{SiO2}}\right) = 0 \qquad (20)$$

$$\overline{G_{P2O5}} - 2.\overline{G_{P}} + \frac{5}{2}.\left(\overline{G_{Si}} - \overline{G_{SiO2}}\right) = 0 \qquad (21)$$

$$\overline{G_{CO}} - \overline{G_{C}} + \frac{1}{2}.\left(\overline{G_{Si}} - \overline{G_{SiO2}}\right) = 0 \qquad (22)$$

$$\overline{G_{CO2}} - \overline{G_{C}} + \left(\overline{G_{Si}} - \overline{G_{SiO2}}\right) = 0 \qquad (23)$$

$$\overline{G_{O}} + \frac{1}{2}.\left(\overline{G_{Si}} - \overline{G_{SiO2}}\right) = 0 \qquad (24)$$

Equations (20)-(24) imply that ΔG →0 for the following chemical reactions while the system marches towards minimum free energy:

(FeO) + 0.5[Si] = 0.5 SiO2 + [Fe] (A)
(P2O5)+ 2.5[Si] = 2.5 SiO2 + 2 [P] (B)
{CO} + 0.5[Si] = 0.5 SiO2 + [C] (C)
{CO2} + [Si] = SiO2 + [C] (D)
0.5 [Si] + [O] = 0.5 (SiO2) (E)

Similarily ΔG →0 for the following reactions also:

[Fe] + [O] = (FeO) (F)
[C] + [O] = {CO} (G)
[C] + 2[O]={CO2} (H)
{CO2} + [C] = 2{CO} (I)
(FeO) + [C] = {CO} + [Fe] (J)
2.5 (FeO) + [P] = 0.5 P2O5 + 2.5 [Fe] (K)

Suppose that oxygen is added to the metal bath.
The free energy of reactions (E),(F) and (G) before supplying oxygen is given as:

$$\Delta G_{Si} = \Delta G^{o}_{Si} + RT \ln\left(\frac{(\gamma_{SiO2} . X_{SiO2})^{0.5}}{(f_{Si} .[Si])^{0.5} . f_{o} .[O]_{eq}} \right) = 0 \qquad (25)$$

After supply of little bit oxygen the free energy of reaction (E) becomes:

$$\Delta G_{Si} = \Delta G^{o}_{Si} + RT \ln\left(\frac{(\gamma_{SiO2} . X_{SiO2})^{0.5}}{(f_{Si} .[Si])^{0.5} . f_{o} .([O]_{eq} + \Delta[O]_{Si})} \right) \qquad (26)$$

From Equations (25) and (26), the following equation is derived:

$$\frac{[\Delta O]_{Si}}{[O]_{eq}} = \exp\left(-\frac{\Delta G_{Si}}{RT}\right) - 1 \qquad (27)$$

The oxygen dissolved in excess of equilibrium amount will be consumed and free energy of reaction (26) will tend towards zero.

Similarly, if we consider reactions (F) and (G),

$$\frac{[\Delta O]_{Fe}}{[O]_{eq}} = \exp\left(-\frac{\Delta G_{Fe}}{RT}\right) - 1 \qquad (28)$$

$$\frac{[\Delta O]_{C}}{[O]_{eq}} = \exp\left(-\frac{\Delta G_{C}}{RT}\right) - 1 \qquad (29)$$

From equations (27),(28) and (29) it turns out that supplied oxygen Will distribute itself in the ratio of :

$$\left(\exp\left(-\frac{\Delta G_{reac}}{RT}\right) - 1\right)$$

Or,

$$\left(\frac{\Delta G_{reac}}{RT}\right) \qquad if\ \Delta G_{reac} < RT$$

Steps of calculations in partially mixed reactor

Metal Reactor

Reactions occurs under jet impact zone:

(a) Dissolution of oxygen under jet impact zone

$O_2 = 2\ [O]$ [A]

(b) Oxidation of impurities by dissolved oxygen in previous step

$[C] + [O] = \{CO\}$ [B]

$[Fe] + [O] = (FeO)$ [C]

$[Si] + 2\ [O] = (SiO_2)$ [D]

Free energies of reactions B,C and D are defined as:

$$\Delta GC1 = \Delta \overset{o}{G} C1 + RT.\ln\left[\frac{PCO}{a_C . a_O}\right]$$

$$\Delta GFe1 = \Delta \overset{o}{G} Fe1 + RT.\ln\left[\frac{a_{FeO}}{a_O}\right]$$

$$\Delta GSi1 = \Delta \overset{o}{G} Si1 + RT.\ln\left[\frac{a_{SiO2}}{a_{Si} . a_O^2}\right]$$

Distribution of oxygen occurs in the ratio of the free energies:

$$x_{C1} = \frac{\Delta GC1}{\Delta GC1 + \Delta GFe1 + \frac{1}{2}\Delta GSi1} \qquad x_{Si1} = \frac{\frac{1}{2}\Delta GSi1}{\Delta GC1 + \Delta GFe1 + \frac{1}{2}\Delta GSi1}$$

Finally rate equations for the removal of [C] and [Si] become as:

$$-\frac{d[C]}{dt}\frac{Wt\_HM}{100.M_C} = \frac{2.\eta_C .FO2}{22400}.x_{C1} \qquad -2\frac{d[Si]}{dt}\frac{Wt\_HM}{100.M_{Si}} = \frac{2.\eta_{Si} .FO2}{22400}.x_{Si1}$$

Slag-metal Reactor

Iron oxide in slag is reduced by following reactions:

[C] + (FeO) = {CO} + [Fe] [E]
[Si] + 2(FeO) = (SiO2) + 2[Fe] [F]

Free energies of reactions E and F are defined as:

$$\Delta GC2 = \Delta \overset{o}{G} C2 + RT.\ln \frac{PCO}{a_C . a_{FeO}} \qquad \Delta GSi2 = \Delta \overset{o}{G} Si2 + RT.\ln \left[\frac{a_{SiO2}}{a_{Si} . a_{FeO}^2} \right]$$

Distribution of FeO occurs in the ratio of the free energies:

$$x_{C2} = \frac{\Delta GC2}{\Delta GC2 + \frac{1}{2}\Delta GSi2} \qquad x_{Si2} = \frac{\frac{1}{2}\Delta GSi2}{\Delta GC2 + \frac{1}{2}\Delta GSi2}$$

Rate equations for the removal of [C] and [Si] by above mechanism:

$$-\frac{d[C]}{dt}\frac{Wt\_HM}{100.M_C} = \frac{2.\eta_C .FO2}{22400}.x_{C2} \qquad -2\frac{d[Si]}{dt}\frac{Wt\_HM}{100.M_{Si}} = \frac{2.\eta_{Si} .FO2}{22400}.x_{Si2}$$

Efficiency factors (η_C, η_{Si}) are assumed to vary as a function of total mixing energy of the bath as follows:

$$efficiency\ factor(\eta_C, \eta_{Si})\ \alpha\ \left(E_{total}^{o}\right)^n$$

Slag-metal-gas (emulsion) Reactor

Formed by metal droplets, rising gas bubbles and liquid slag:

{CO} + (FeO) = [Fe] + {CO2} [G]

Post combustion ratio (PCR) inside the vessel is defined as:

$$K_{CO-FeO} = \frac{P_{CO_2}}{P_{CO}.a_{FeO}}$$

Lime dissolution

Rate of lime dissolution depends upon activity of FeO in slag:

$$-\frac{dCaO}{dt} = k_{cao}.A_{CaO}.a_{FeO}$$

Scrap dissolution

Solves coupled heat transfer and mass transfer (of carbon) to predict the velocity of moving boundary

Figure 1.2 :Schematic diagram of temperature and composition profile in scrap and metal

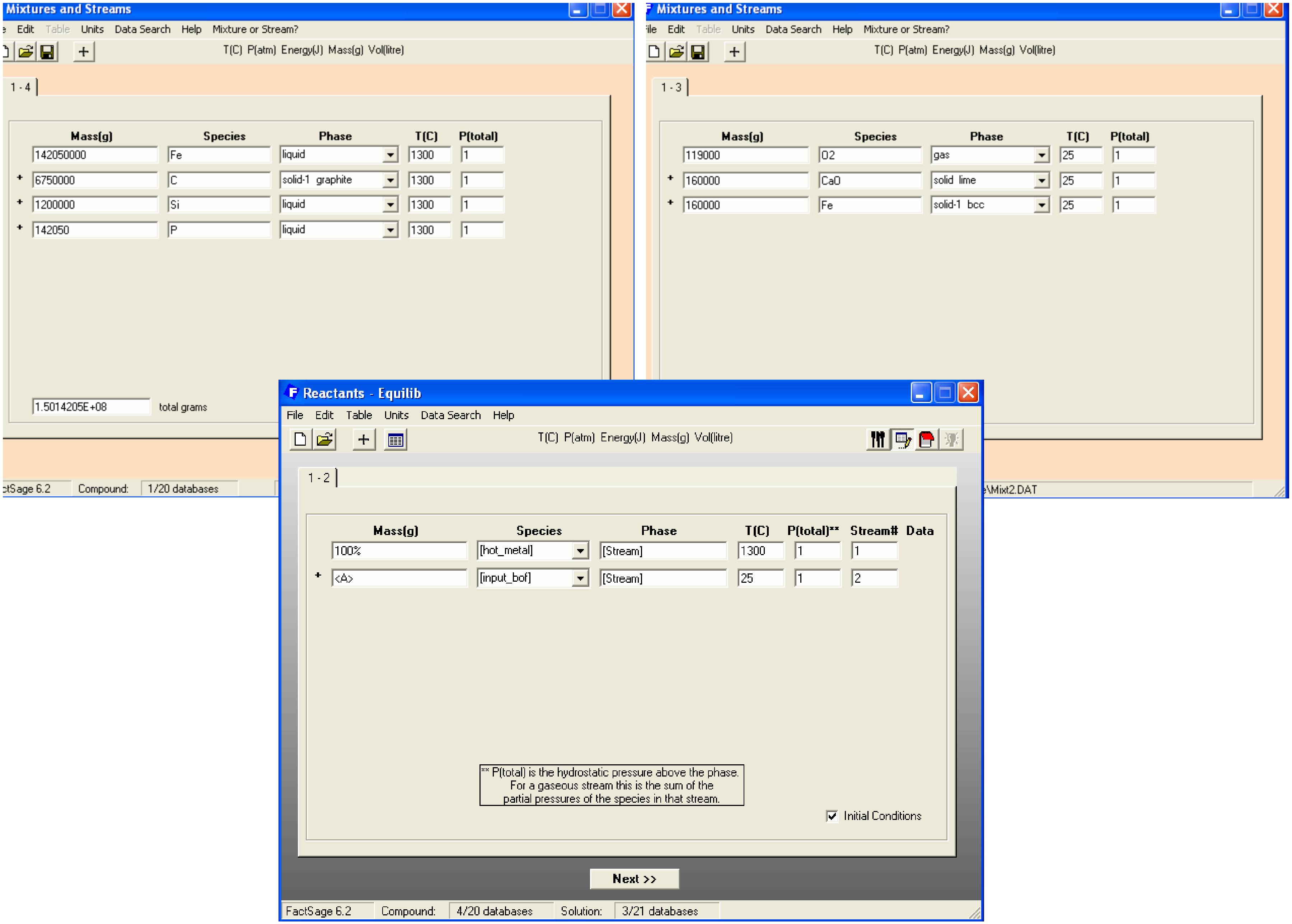
$$\rho H v + h(Tb - Ti) = \lambda \left. \frac{dT}{dX} \right|_{x=0}$$

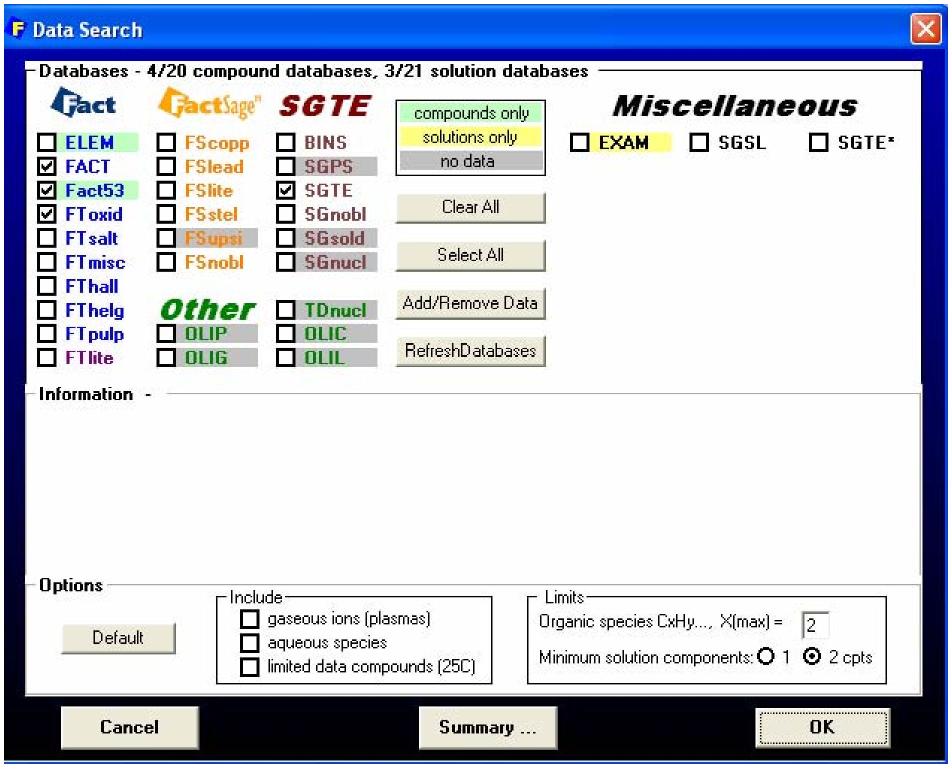
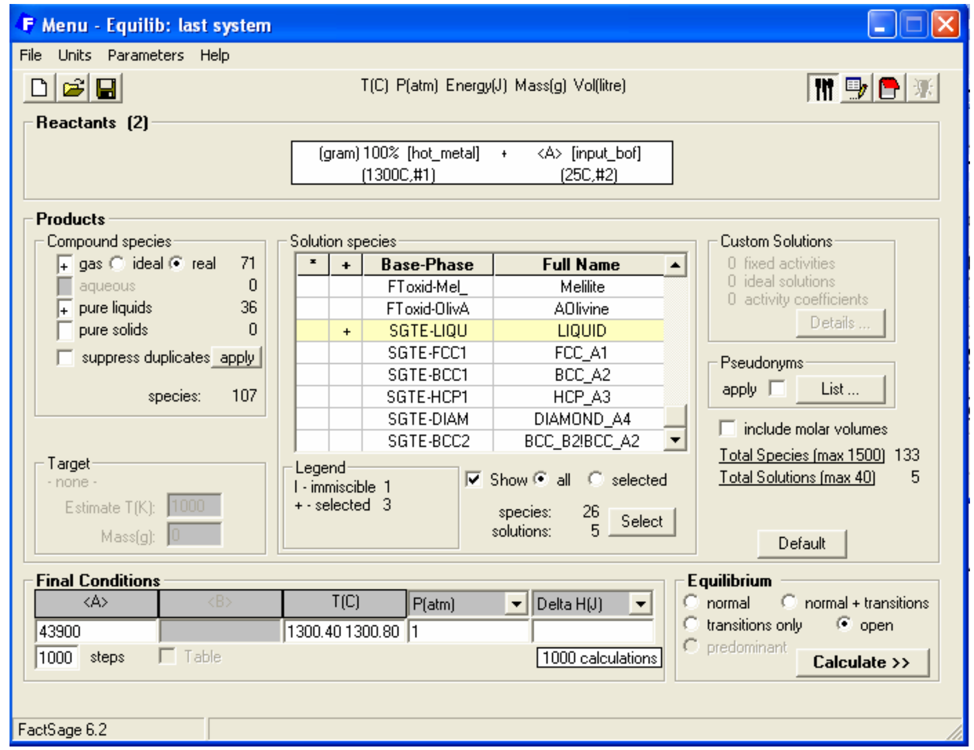
$$\alpha \frac{\partial^2 T_{sc}(x,t)}{\partial x^2} = \frac{\partial T_{sc}(x,t)}{\partial t}$$

v(Ci-Cs)=k(Ci-Cb)

Accuracy of the model is validated by fundamental Green's function approach

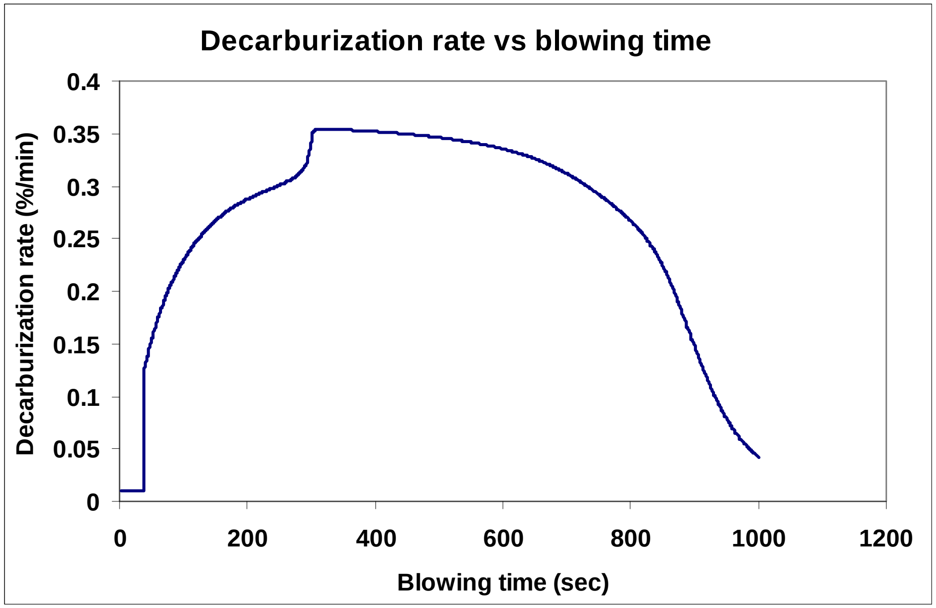
Calculations steps using FactSage

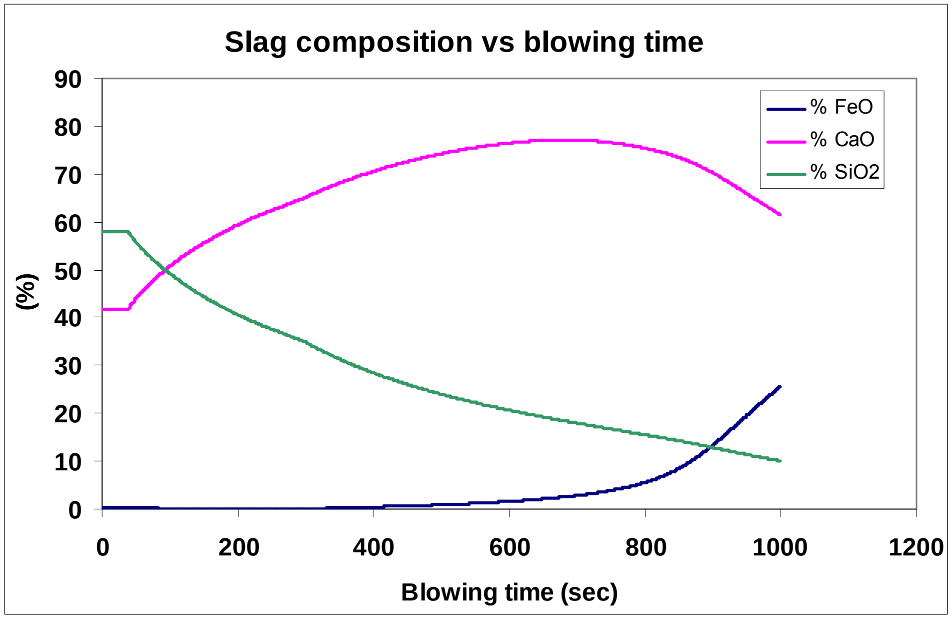



Data Search
Databases - 4/20 compound databases, 3/21 solution databases
Fact
FactSage
SGTE
compounds only
solutions only
no data
Miscellaneous
ELEM
FACT
Fact53
FToxid
FTsalt
FTmisc
FThall
FThelg
FTpulp
FTlite
FScopp
FSlead
FSlite
FSstel
FSupsi
FSnobl
Other
OLIP
OLIG
BINS
SGPS
SGTE
SGnobl
SGsold
SGnucl
TDnucl
OLIC
OLIL
Clear All
Select All
Add/Remove Data
RefreshDatabases
EXAM
SGSL
SGTE*
Information -
Options
Default
Include
gaseous ions (plasmas)
aqueous species
limited data compounds (25C)
Limits
Organic species CxHy..., X(max) = 2
Minimum solution components: 1 2 cpts
Cancel
Summary ...
OK

Menu - Equilib: last system
File Units Parameters Help
T(C) P(atm) Energy(J) Mass(g) Vol(litre)
Reactants (2)
(gram) 100% [hot_metal] + <A> [input_bof]
(1300C,#1) (25C,#2)
Products
Compound species
gas ideal real 71
aqueous 0
pure liquids 36
pure solids 0
suppress duplicates apply
species: 107
Solution species
* + Base-Phase Full Name
FToxid-Mel_ Melilite
FToxid-OlivA AOlivine
+ SGTE-LIQU LIQUID
SGTE-FCC1 FCC_A1
SGTE-BCC1 BCC_A2
SGTE-HCP1 HCP_A3
SGTE-DIAM DIAMOND_A4
SGTE-BCC2 BCC_B2!BCC_A2
Custom Solutions
0 fixed activities
0 ideal solutions
0 activity coefficients
Details ...
Pseudonyms
apply List ...
include molar volumes
Total Species (max 1500) 133
Total Solutions (max 40) 5
Target
- none -
Estimate T(K): 1000
Mass(g): 0
Legend
I - immiscible 1
+ - selected 3
Show all selected
species: 26
solutions: 5
Select
Default
Final Conditions
<A> <B> T(C) P(atm) Delta H(J)
43900 1300.40 1300.80 1
1000 steps Table 1000 calculations
Equilibrium
normal normal + transitions
transitions only open
predominant
Calculate >>
FactSage 6.2

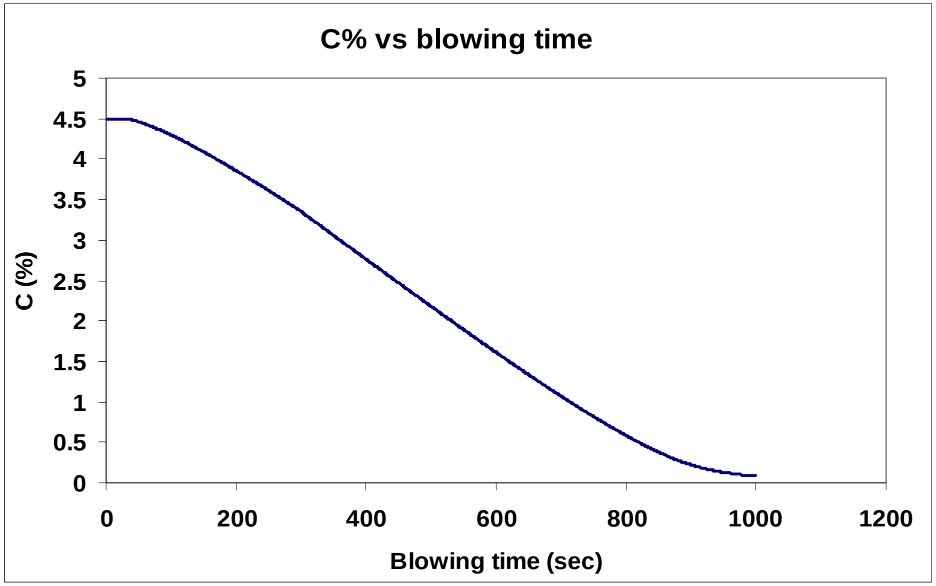
Calculation results using FactSage 6.2

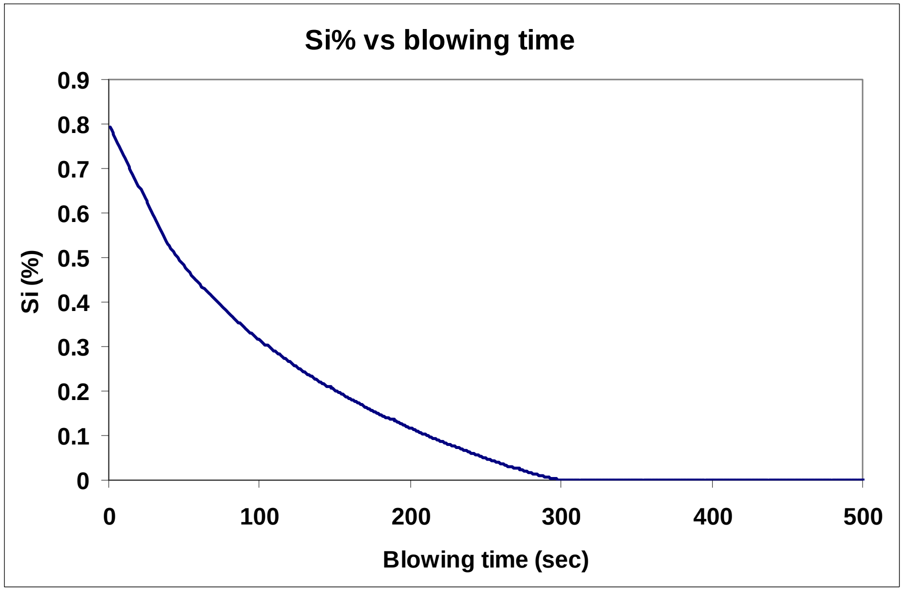
The Equilibrium module was used for the open system where a feed equivalent to the **oxygen, lime and scrap** equivalent to one second is given for **1000 steps**. **FTOxid** database was used for slag solution, **FTmisc** was used for liquid metal and Fact53 was used for gaseous phase.

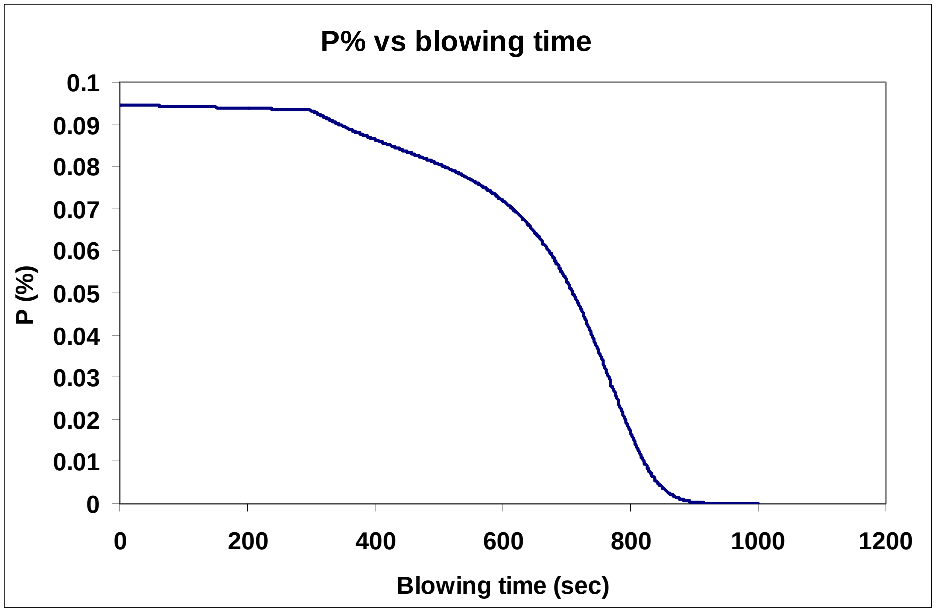


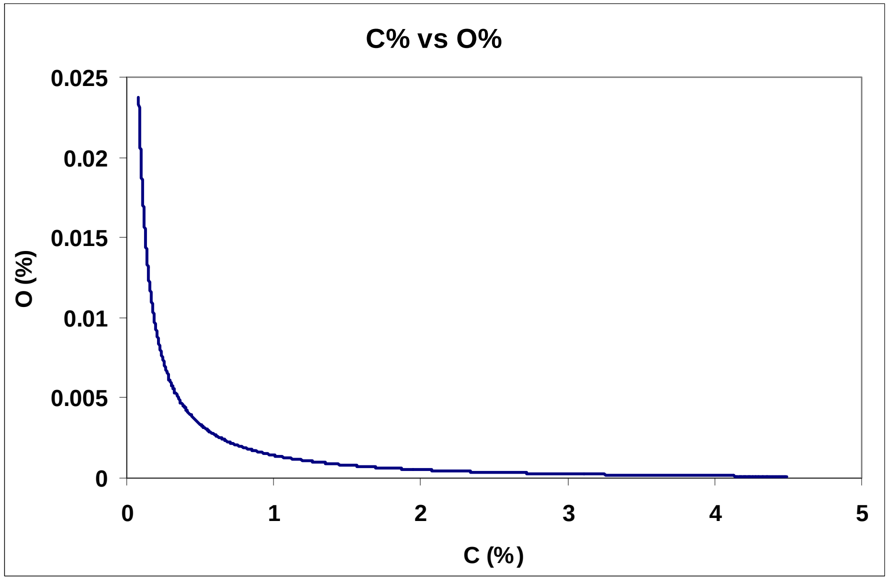


Calculation Results using FactSage 6.2 (continued)



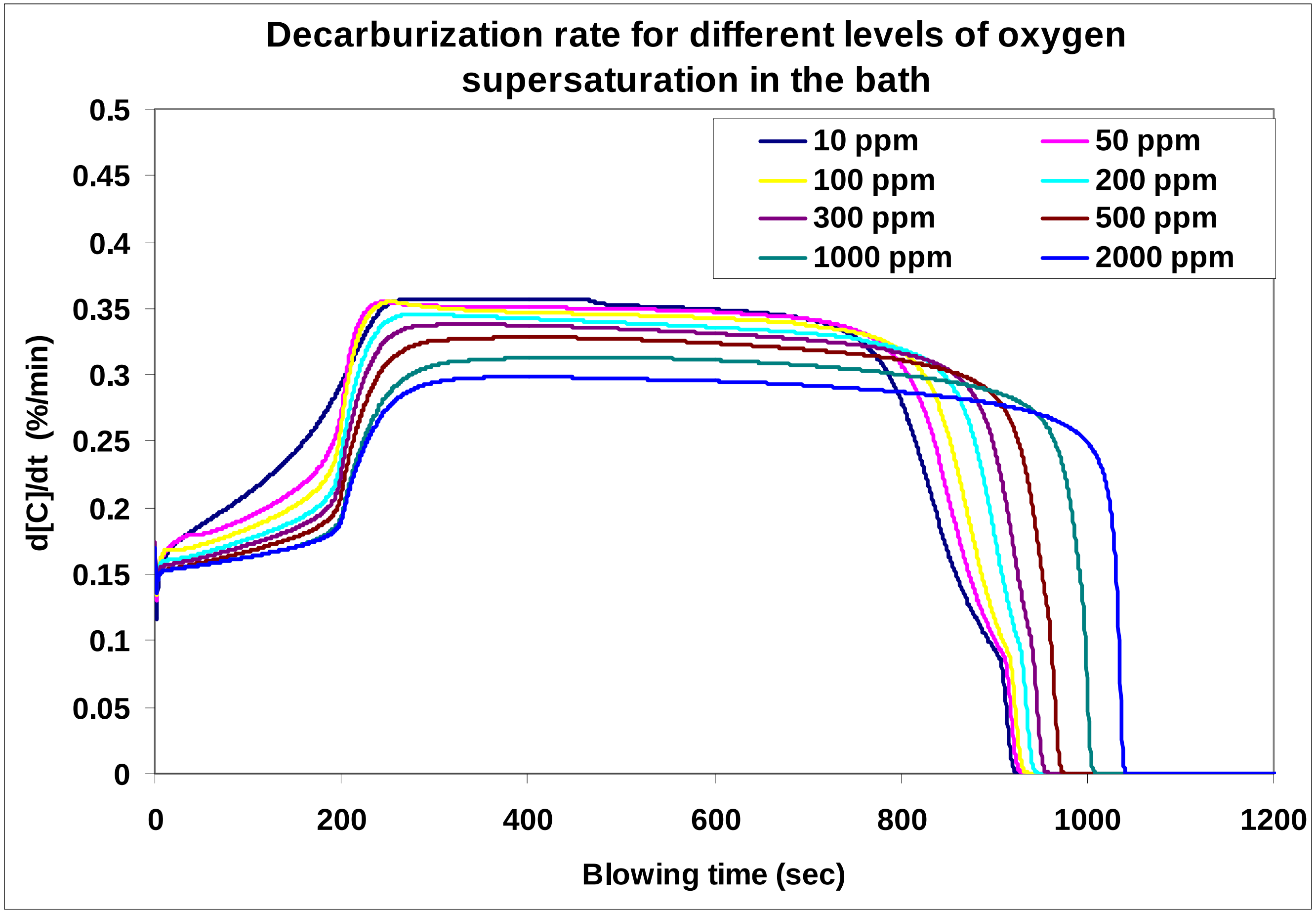




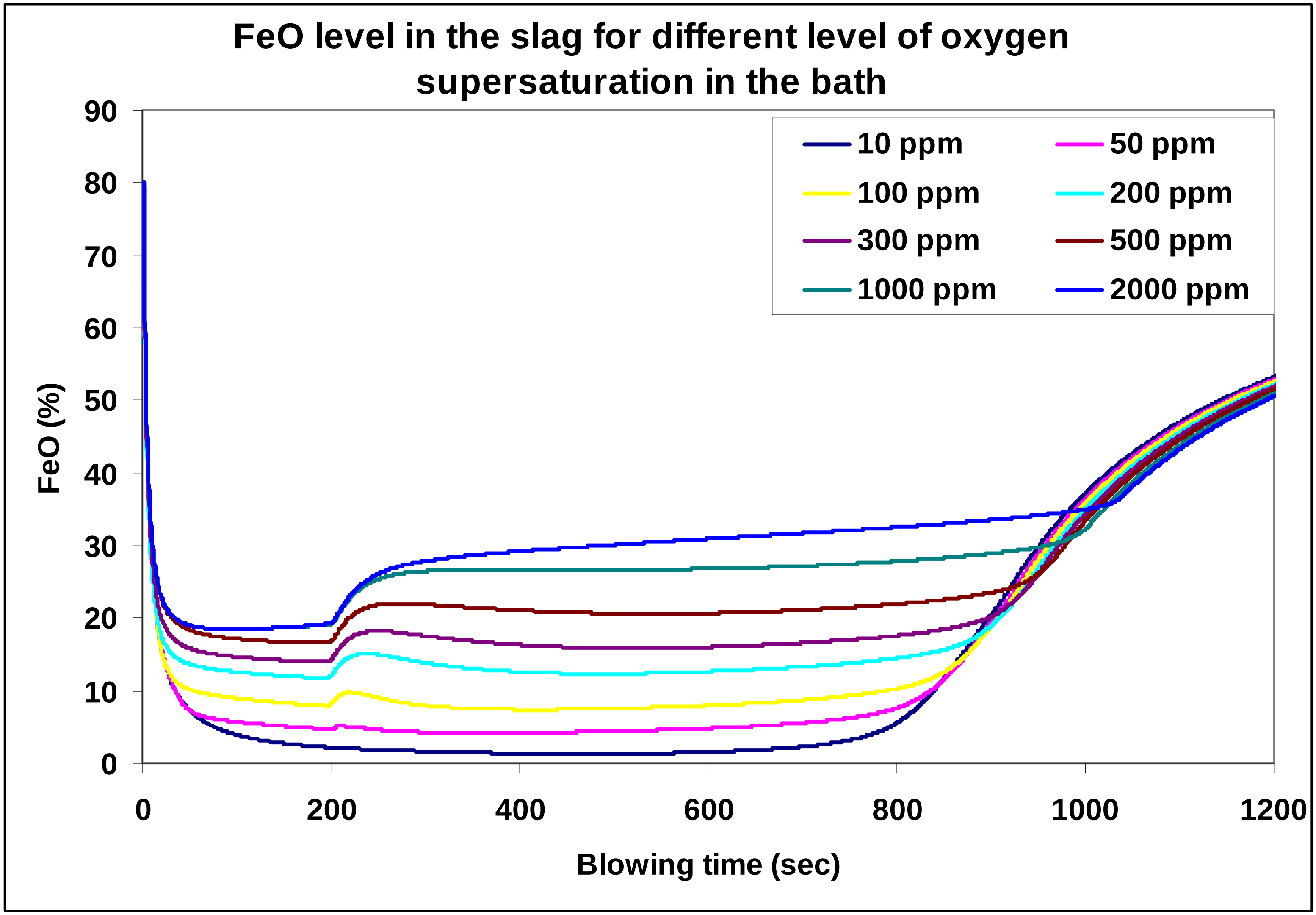


Results of partially mixed reactor

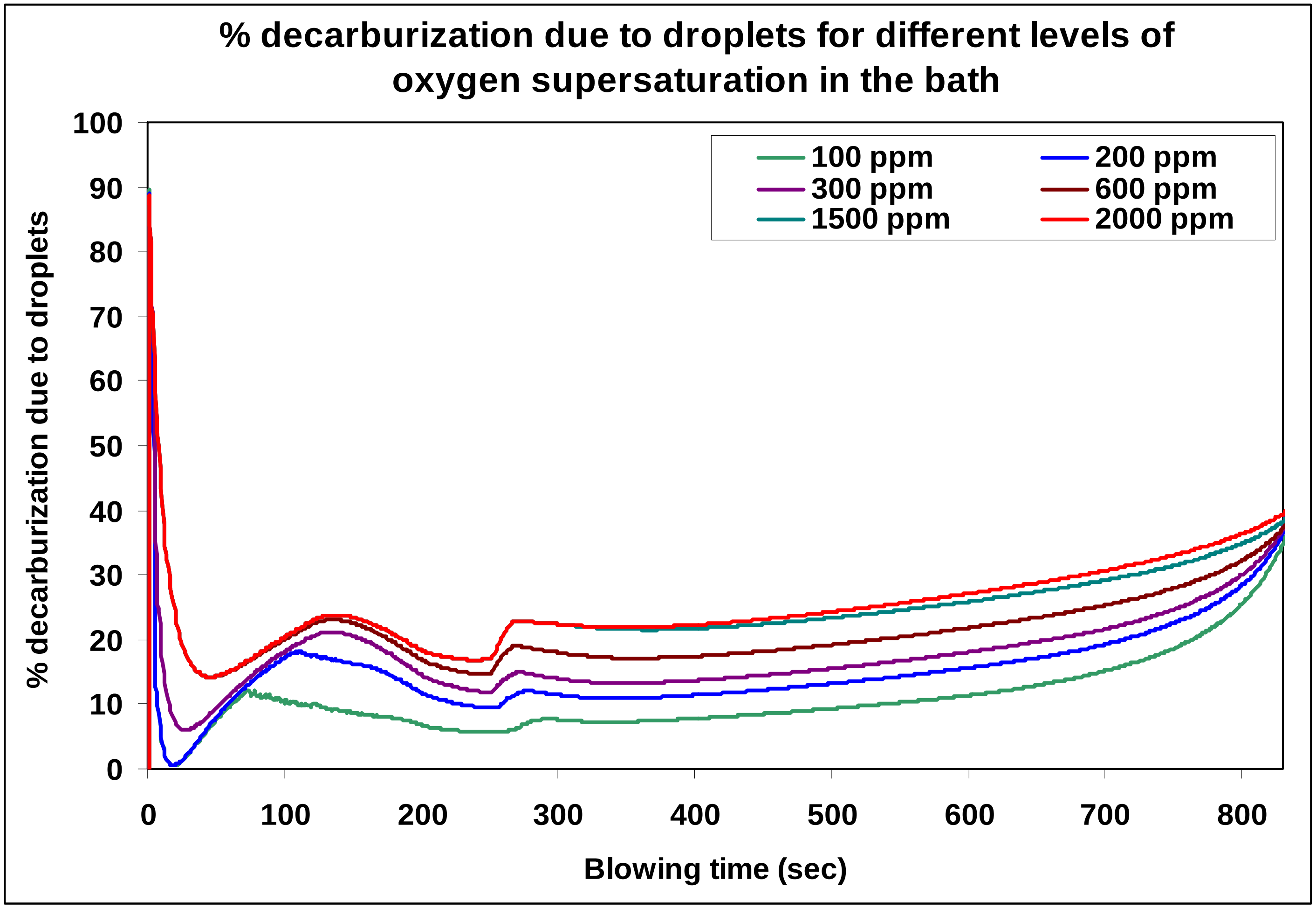
The calculations are done for a fully mixed system with the following initial conditions:
Hot metal = 150 tons, Si_HM = 0.8%, C_HM=4.5%, P_HM = 0.1%,
Temperature of hot metal = 1300 C. Oxygen flow rate = 500 NM3/min,
Lime dissolution rate = 1 ton/min and scrap dissolution rate = 1 ton/min.

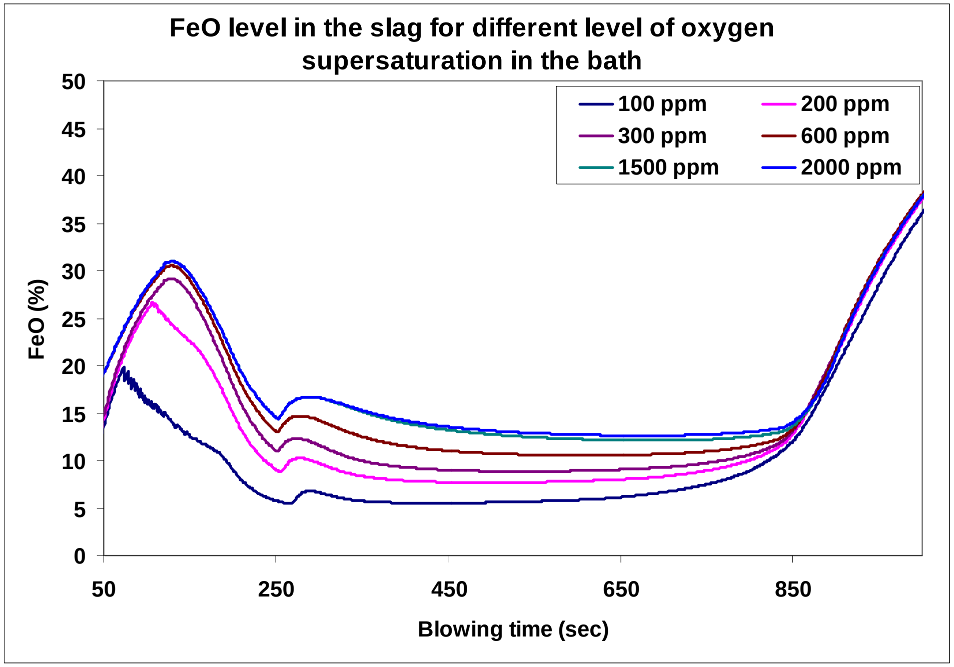


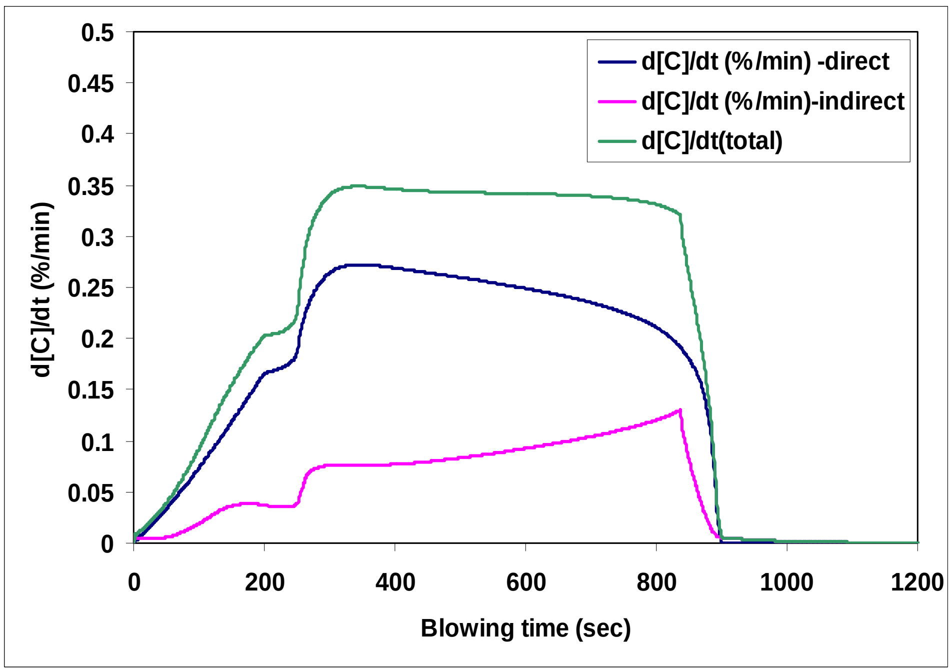
FeO level in the slag for different levels of oxygen super saturation for fully mixed system



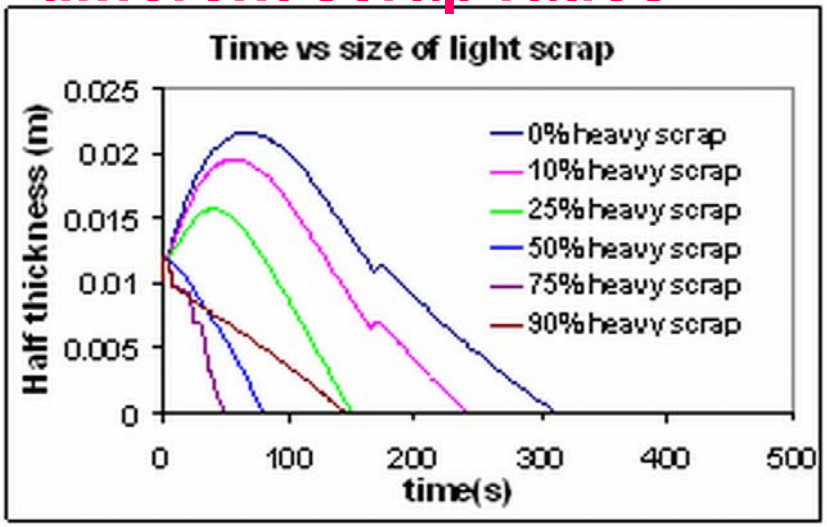
Predictions for a partially mixed oxygen steelmaking reactor



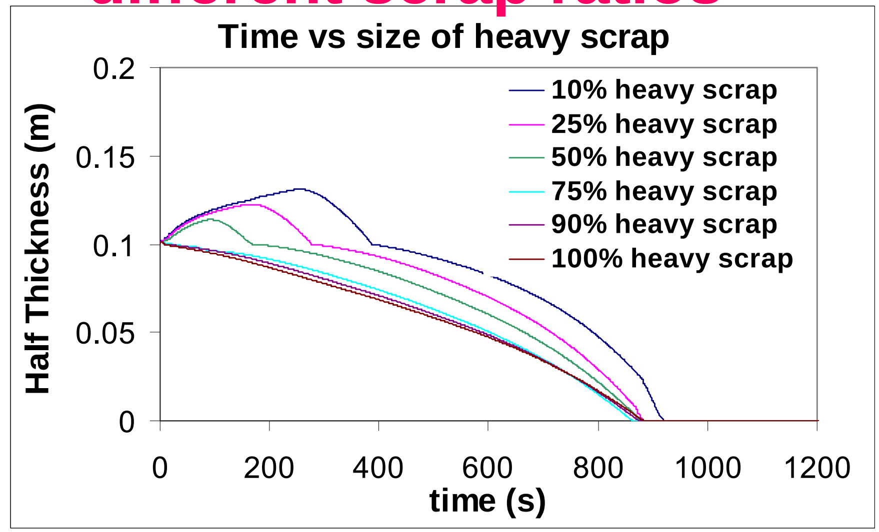

FeO level in the slag for different level of oxygen supersaturation in the bath
FeO (%)
Blowing time (sec)
100 ppm
200 ppm
300 ppm
600 ppm
1500 ppm
2000 ppm
0
5
10
15
20
25
30
35
40
45
50
50
250
450
650
850


d[C]/dt (%/min)
Blowing time (sec)
d[C]/dt (%/min) -direct
d[C]/dt (%/min)-indirect
d[C]/dt(total)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0
200
400
600
800
1000
1200

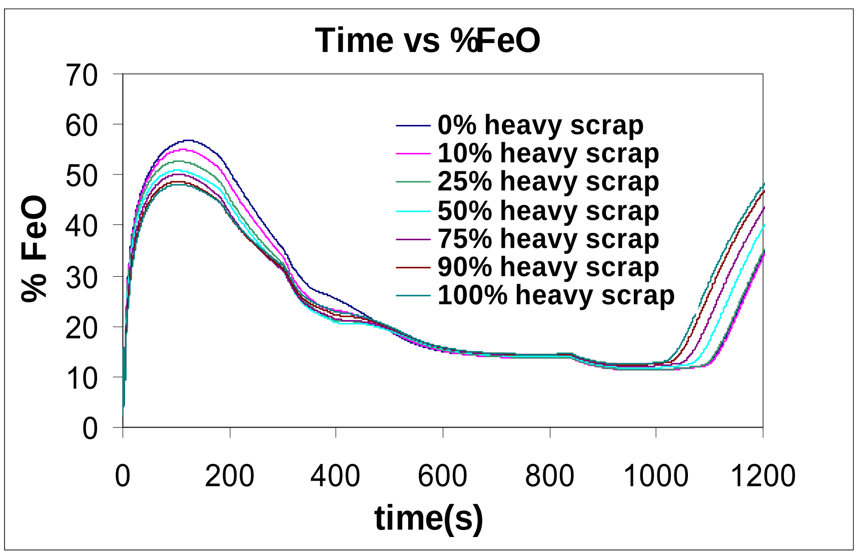
Light scrap size for different scrap ratios



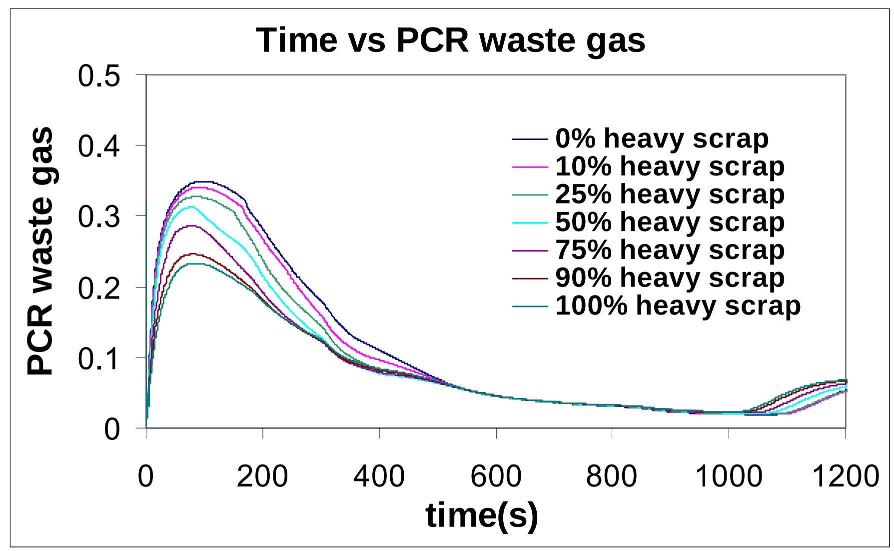
Heavy scrap size for different scrap ratios



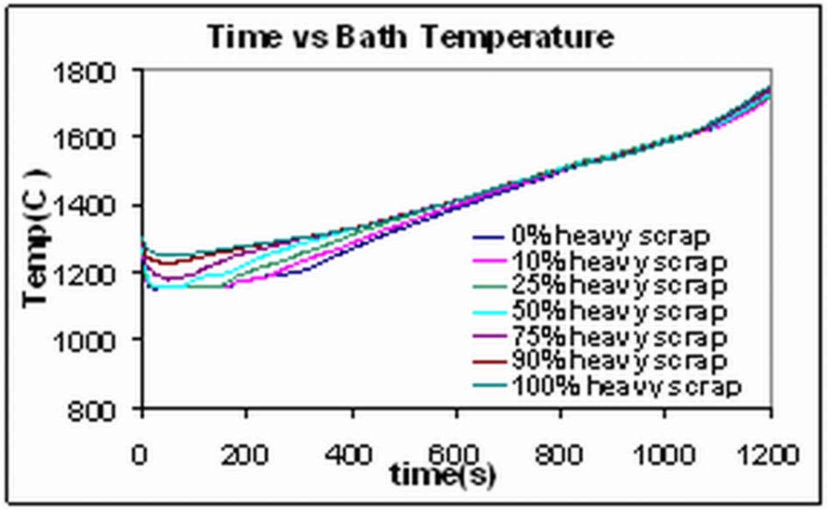
%FeO for different scrap ratios



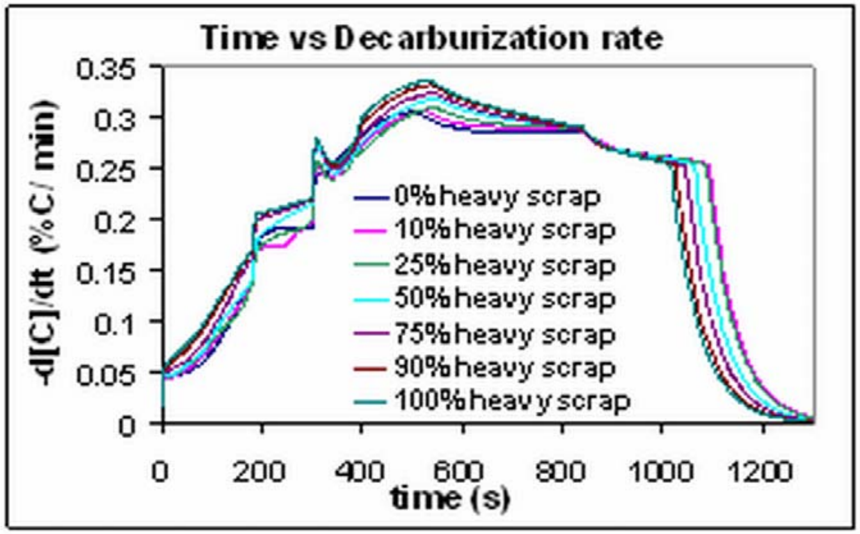
PCR for different scrap ratios



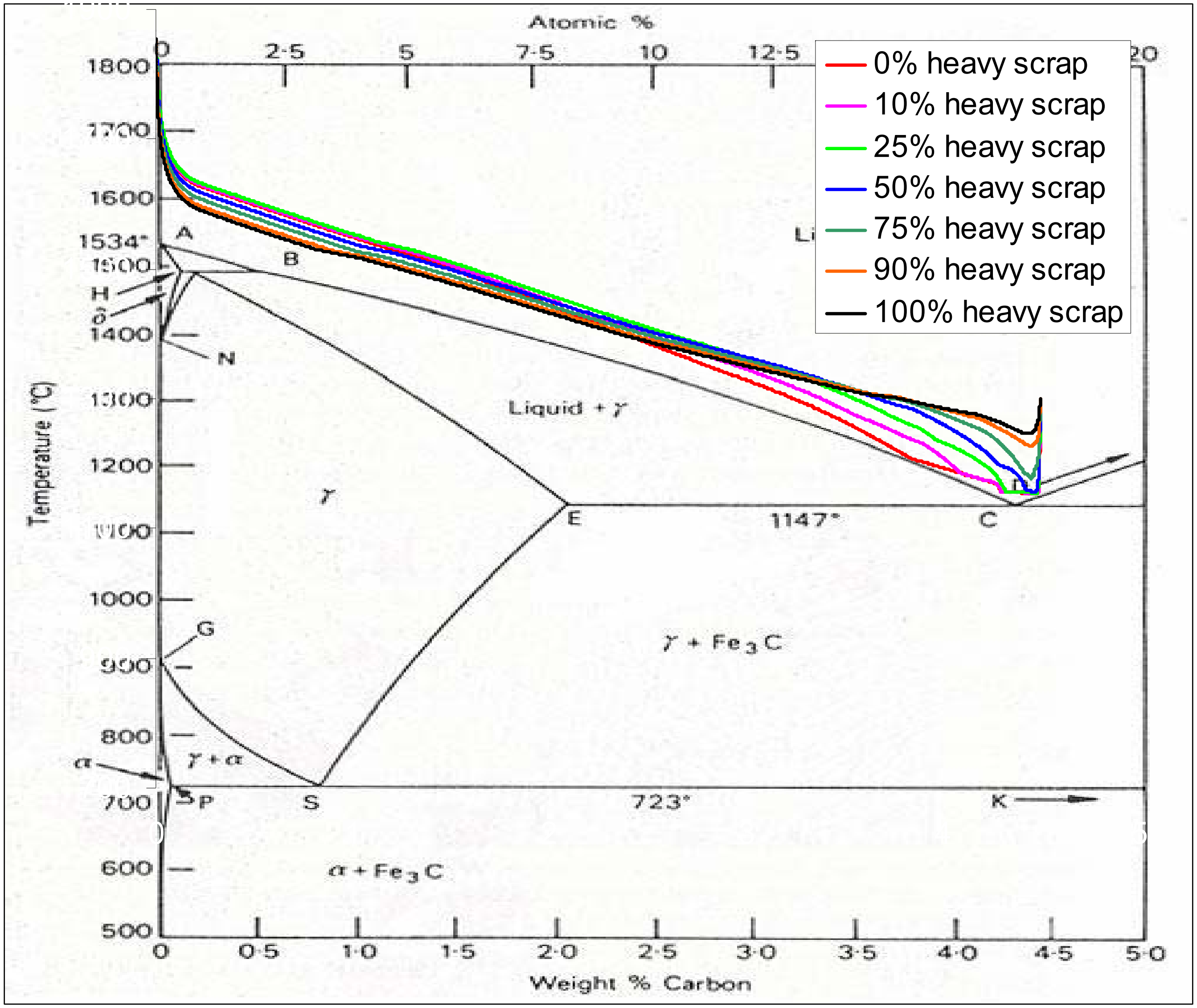
Temperature for different scrap ratios



Decarburization rate for different Scrap ratios



C-T trajectory for different ratios of heavy vs light scrap.



CONCLUSIONS

- A fundamental study of oxygen steelmaking process based upon Gibb's energy minimization technique, and also through FactSage, has been done for the case of a fully mixed reactor.

- The trend of results of free energy minimization are similar to an actual process in the middle blow period, implying that both BOF and OBM processes are close to equilibrium during the middle part of blow.

- The difference of results (based upon Gibb's energy minimization) and the actual process can be attributed to the lack of mixing and gradual change in extent of mixing during initial and final part of the process.

- The predicted indirect decarburization (due to droplets) is of the order of 10-25% during middle blow period and approximately 30% during end blow period.

- **Dephosphorization process cannot be explained adequately by free energy calculations because mass transfer in slag phase is important in that case. Mixing in metal phase cannot do much however extended surface area of slag-metal due to droplets thrown in slag phase help this to a great extent.**

- **Good agreement with the practical observations on the shopfloor. The model is integrated with the scrap dissolution model which is based upon coupled heat and mass transfer. The computed results are similar to the practical observations.**

- **The model can be used as a simulation tool to study the effect of various parameters. Further testing on extensive plant data required.**

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