

3. Reaction of chromium is dealt with in Chapter 21 (stainless steelmaking). Oxidation of iron, carbon, phosphorus and manganese takes place throughout the blow and precise control is required to obtain the required steel quality.

Since gaseous oxygen reacts with liquid iron very rapidly, for all practical purposes, only reaction with oxygen dissolved in the liquid metal bath rather than gaseous oxygen needs to be considered. This is what is done in the following section.

15.4.2 Oxidation of Iron

For the slag–metal reaction:



the equilibrium constant is given as:

$$K_{\text{Fe}} = \left\{ \frac{(a_{\text{FeO}})}{[a_{\text{Fe}}][h_{\text{O}}]} \right\}_{\text{eq.}} \quad (15.12)$$

$$\log K_{\text{Fe}} = \frac{6150}{T} - 2.604 \quad (15.13)$$

Since Fe in steel is almost pure, $a_{\text{Fe}} \sim 1 \cdot h_{\text{O}} = f_{\text{O}} \cdot w_{\text{O}}$, where w_{O} is wt. % oxygen in liquid steel. Also, $\log f_{\text{O}} = -0.17[w_{\text{O}}]$ for Fe–O binary. For pure FeO, calculations yield equilibrium (i.e. saturation) concentration of oxygen in liquid iron as 0.18 wt. %, 0.227 wt. % and 0.252 wt. % respectively at 1550°C, 1600°C and 1650°C. From Figures 15.1 and 15.3, a_{FeO} for BOF type slags may be taken as 0.5 approximately. Accordingly, saturation concentrations would be about half of the above values. It may be mentioned here that the turndown oxygen level ranges from 600 to 1000 ppm (0.06 to 0.1%), which is lower than the saturation value at normal BOF steelmaking temperature of 1600–1650°C.

15.4.3 Reactions of Carbon

For the reaction



the equilibrium constant is given as

$$K_{\text{CO}} = \left\{ \frac{p_{\text{CO}}}{[h_{\text{C}}][h_{\text{O}}]} \right\}_{\text{eq.}} \quad (15.15)$$

$$\log K_{\text{CO}} = \frac{1160}{T} + 2.003 \quad (15.16)$$

As a first approximation, it may be noted that $h_{\text{C}} = w_{\text{C}}$ and $h_{\text{O}} = w_{\text{O}}$. It has been shown that the error is small if these assumptions are made.

Figure 15.4 (T. Saeki et al. 1978) shows the relationship between dissolved carbon and dissolved oxygen in a molten iron bath in a 100 kVA induction furnace at 1600°C. The line corresponds to equilibrium with $p_{\text{CO}} = 1 \text{ atm}$. The dissolved oxygen contents were measured by a solid electrolyte oxygen sensor with two types of reference electrode.

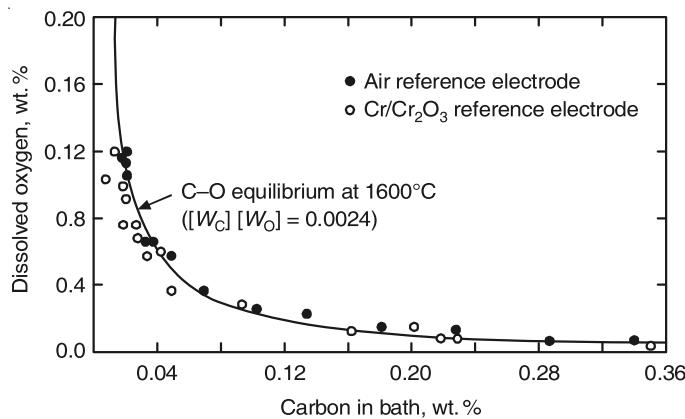
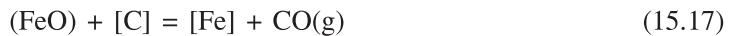


Figure 15.4 Dissolved oxygen content of liquid iron as a function of bath carbon at 1600°C (1873 K) in a 100 kVA induction furnace.

Carbon also reacts with FeO and MnO in slag. The reaction with FeO is



for which the equilibrium constant is

$$K_{FC} = \left\{ \frac{[a_{Fe}] \cdot p_{CO}}{[h_C](a_{FeO})} \right\}_{eq.} \cong \left\{ \frac{p_{CO}}{[w_C](a_{FeO})} \right\}_{eq.} \quad (15.18)$$

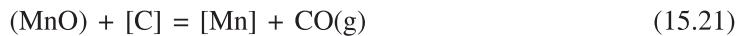
Combining Eqs. (15.13) and (15.16),

$$\log K_{FC} = -\frac{4990}{T} + 4.607 \quad (15.19)$$

Turkdogan (1996) has proposed several simplified correlations for reactions in steelmaking for the convenience of users. He assumed a slag basicity of 3.2 and the average pressure of CO in BOF vessels as 1.5 atm. Noting that $\gamma_{FeO} = 1.3$ at this basicity, at 1600°C his equilibrium correlation turns out to be

$$(w_{FeO})[w_C] \cong 1.0 \quad (15.20)$$

Similarly, for the reaction:



$$K_{MC} = \left\{ \frac{[w_{Mn}] \cdot p_{CO}}{[w_C](a_{MnO})} \right\}_{eq.} \quad (15.22)$$

and

$$\log K_{MC} = -\frac{13182}{T} + 8.574 \quad (15.23)$$

Again simplification, assuming γ_{MnO} in slag = 2.05, leads to the equilibrium correlation:

$$\frac{[w_{Mn}]}{(w_{MnO})} = 0.4 [w_C] \text{ at } 1600^\circ C \quad (15.24)$$

15.4.4 Oxidation of Silicon

The reaction is



for which the equilibrium constant is

$$K_{\text{Si}} = \left\{ \frac{(a_{\text{SiO}_2})}{[h_{\text{Si}}][h_{\text{O}}]^2} \right\}_{\text{eq.}} \cong \left\{ \frac{(a_{\text{SiO}_2})}{[w_{\text{Si}}][w_{\text{O}}]^2} \right\}_{\text{eq.}} \quad (15.26)$$

and,

$$\log K_{\text{Si}} = \frac{30110}{T} - 11.4 \quad (15.27)$$

From Figures (15.1) and (15.3), for a typical BOF slag, a_{SiO_2} may be taken as 5×10^{-4} . Calculations at 1600°C yield

$$\{[w_{\text{Si}}][w_{\text{O}}]^2\}_{\text{eq.}} = \frac{5 \times 10^{-4}}{4.74 \times 10^4} \cong 10^{-8} \quad (15.28)$$

Assuming $w_{\text{O}} = 0.08$ wt. % at turndown, wt. % Si at equilibrium becomes 1.6×10^{-6} , which is extremely low. Hence, this equilibrium is not of any importance and it only confirms that all the silicon present should get oxidised in primary steelmaking.

15.4.5 Reaction of Phosphorus

As mentioned earlier, the removal of phosphorus from liquid steel is of major interest. It can be effectively carried out only in primary steelmaking operations to achieve phosphorus contents of around 0.025–0.030 wt. % in steel. With increasing demand for ultra-low phosphorus steel (wt. % P < 0.005) for some special grades (like steel used in automobiles), removal of phosphorus has become of even greater significance. Therefore, there have been extensive investigations on slag–metal phosphorus reaction for over 60 years, the salient features of which will now be presented briefly.

The earliest systematic documentation was done by Ward (1962). At steelmaking temperatures, the stable state of phosphorus is gaseous P_2 . P_2O_5 is also a gas. Phosphorus has a very high solubility in liquid iron as well. Tables 4.1, 4.2 and 15.1 contain free energy, enthalpy and entropy data. Hence, they will not be repeated here.

From Table 4.1, for



$$\Delta G_{29}^0 = -3140929 + 964.83T \text{ J} \cdot \text{mol}^{-1} \quad (15.30)$$

From Table 4.2,

$$\frac{1}{2}\text{O}_2(\text{g}) = [\text{O}]_1 \text{ wt\%} \quad (15.31)$$

$$\Delta G_{31}^0 = -117150 - 2.89T \text{ J} \cdot \text{mol}^{-1} \quad (15.32)$$

and

$$\frac{1}{2}\text{P}_2(\text{g}) = [\text{P}]_1 \text{ wt\%} \quad (15.33)$$

$$\Delta G_{33}^0 = -122170 - 19.25T \text{ J} \cdot \text{mol}^{-1} \quad (15.34)$$

From Eqs. (15.30), (15.32), (15.34), for



$$\begin{aligned} \Delta G_{35}^0 &= \frac{1}{2} \Delta G_{29}^0 - 5\Delta G_{31}^0 - 2\Delta G_{33}^0 \\ &= -740375 + 535.365T \text{ J} \cdot \text{mol}^{-1} \end{aligned} \quad (15.36)$$

for reaction (15.35),

$$K_p = \left\{ \frac{(a_{\text{P}_2\text{O}_5})}{[h_{\text{P}}]^2 [h_{\text{O}}]^5} \right\}_{\text{eq.}} \quad (15.37)$$

$$\log K_p = -\frac{\Delta G_{35}^0}{2.303 RT} = \frac{38668}{T} - 27.96 \quad (15.38)$$

Assuming $h_{\text{P}} = w_{\text{P}}$ and $h_{\text{O}} = w_{\text{O}}$, at 1600°C (i.e. 1873 K), and at equilibrium

$$\frac{(a_{\text{P}_2\text{O}_5})}{[w_{\text{P}}]^2 [w_{\text{O}}]^5} = 4.0 \times 10^{-8} \quad (15.39)$$

Assuming wt. % P and wt. % O in steel at turndown to be 0.01 and 0.08% respectively, $a_{\text{P}_2\text{O}_5}$ in slag at equilibrium (with respect to gaseous P_2O_5 as standard state) is 1.57×10^{-17} . If wt. % $\text{P}_2\text{O}_5 = 2$, then mole fraction of P_2O_5 in slag ($X_{\text{P}_2\text{O}_5}$) is about 0.01. Since, $a_{\text{P}_2\text{O}_5} = X_{\text{P}_2\text{O}_5} \cdot \gamma_{\text{P}_2\text{O}_5}$, $\gamma_{\text{P}_2\text{O}_5}$ (i.e. activity coefficient of P_2O_5) in slag at equilibrium should be 1.31×10^{-15} .

This is indeed a very low value. Such a low $\gamma_{\text{P}_2\text{O}_5}$ is possible only in a highly basic slag since P_2O_5 is an acidic oxide. Correlations based on experimental data have been proposed. One of the earliest by Turkdogan and Pearson (1953) is reproduced below:

$$\log \gamma_{\text{P}_2\text{O}_5} = -1.12[22X_{\text{CaO}} + 15X_{\text{MgO}} + 13X_{\text{MnO}} + 12X_{\text{FeO}} - 2X_{\text{SiO}_2}] - \frac{42000}{T} + 23.58 \quad (15.40)$$

where X is mole fraction in slag.

Figure 15.5 (Turkdogan and Pearson, 1953) presents this relationship. It may be noted from Eq. (15.40) that CaO is the most powerful deporphoriser. Of course, Na_2O , BaO are more powerful than CaO , but they cannot be used in steelmaking owing to their tendency to attack the lining of the furnace. The approximate deporphorisation power ratio for some cations in slag has been estimated as (Ward 1962):

$$\begin{array}{cccc} \text{Ca}^{2+} & \text{Mg}^{2+} & \text{Mn}^{2+} & \text{Fe}^{2+} \\ 30,000 : 1000 : 3 : 1 \end{array}$$

Coming back to the issue of $\gamma_{\text{P}_2\text{O}_5}$, from Eq. (15.40) at $X_{\text{CaO}} = 0.6$ and $T = 1873$ K, $\gamma_{\text{P}_2\text{O}_5} = 2.36 \times 10^{-14}$. Ward proposed a temperature correction for Eq. (15.40), which was $-44600/T + 23.80$. Accepting this suggestion, $\gamma_{\text{P}_2\text{O}_5} = 1.6 \times 10^{-15}$. This shows that for highly basic, limey slags it is possible to obtain sufficiently low $\gamma_{\text{P}_2\text{O}_5}$ for effective deporphorisation.

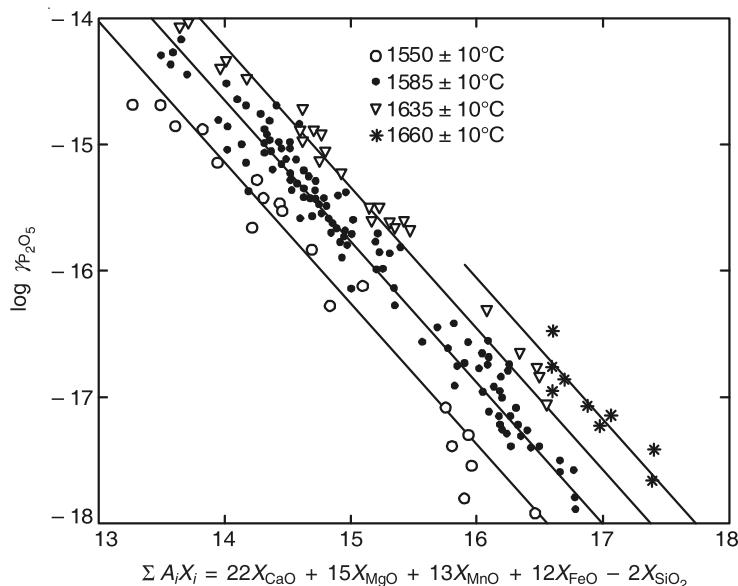


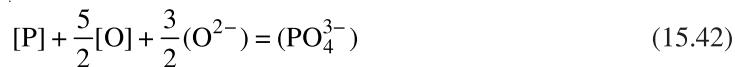
Figure 15.5 Log $\gamma_{\text{P}_2\text{O}_5}$ versus $\Sigma \text{X}_{\text{MO}}$ in slag at different temperatures.

Again, the dissolved oxygen content of steel is approximately proportional to a_{FeO} in slag. Therefore, an alternative way of writing the phosphorus reaction is



Hence, removal of phosphorus also requires a high concentration of FeO in the slag, besides high CaO. However, higher is the wt. % FeO, lower will be the wt. % CaO, and this will adversely affect the dephosphorising ability of the slag. Balajiva et al. (1946), in their pioneering study found that extensive dephosphorisation requires an optimum FeO content in steelmaking slags as shown in Figure 15.6.

This leads to the concept of phosphate capacity of slags (Eq. (4.54), Chapter 4). It was first employed by Healy (1970). Turkdogan (1996) has recently critically analysed and assessed the phosphorus reaction. He expressed the reaction as:



and the *phosphate capacity of slag* as:

$$\begin{aligned} K_{\text{PO}} &= \frac{(w_{\text{P}})}{[w_{\text{P}}]} [w_{\text{O}}]^{-2.5} \\ &= L_{\text{P,e}} [w_{\text{O}}]^{-2.5} \end{aligned} \quad (15.43)$$

where $L_{\text{P,e}}$ is the *slag–metal phosphorus partition ratio at equilibrium*.

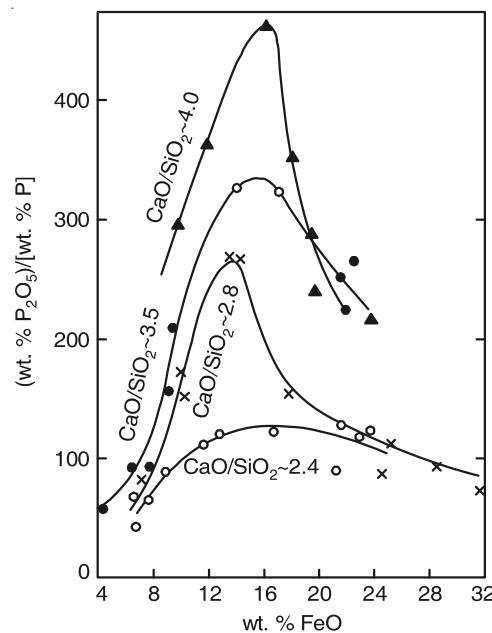


Figure 15.6 Dependence of the ratio, $(\text{wt. \% P}_2\text{O}_5)/[\text{wt. \% P}]$, on the iron oxide content of slags at different CaO/SiO_2 ratios in laboratory experiments at 1685°C .

Figure 15.7 (Turkdogan 1996) shows the dependence of K_{PO} on slag composition for BOF type slags. The correlation is based on data for widely differing slag compositions. The master correlation including temperature variation can be written as

$$\log L_{\text{P,e}} = \frac{21740}{T} - 9.87 + 0.071\text{BO} + 2.5 \log [w_{\text{O}}] \quad (15.44)$$

The relationship of $[w_{\text{O}}]$ with wt. % FeO in slag was estimated as:

$$\frac{[w_{\text{O}}]}{(w_{\text{FeO}})} = (0.1T - 155.3) \times 10^{-4} \quad (15.45)$$

In a recent study (Choudhary et al. 2005), the important correlations proposed in literature were critically examined, and the semi-empirical correlation of Turkdogan (Eq. (15.44)) was accepted as the most reliable. However, not all the lime added dissolves in slag; some of it remains undissolved as free CaO particles or free calcium disilicate in slag. These particles do not, by and large, absorb P_2O_5 owing to the slow kinetics. Therefore, they should be subtracted, and the overall slag composition should be corrected for the calculation of equilibrium $L_{\text{P,e}}$. Since free lime is not determined during routine slag analysis, it poses some uncertainty. Choudhary et al. assumed 0% and 10% free lime in their calculations.

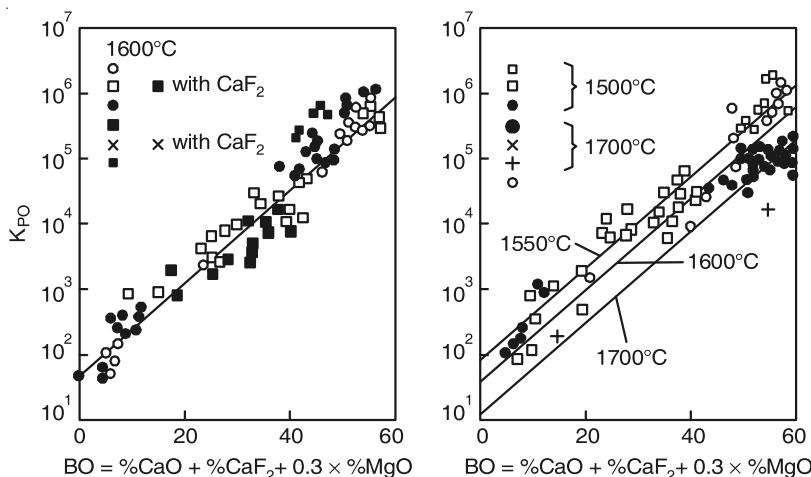


Figure 15.7 Equilibrium data from several investigations showing the decisive effects of CaO, CaF₂ and MgO on phosphate capacities of simple and complex slags.

The best conditions for phosphorus removal from liquid steel from a thermodynamic viewpoint can be summarised as:

- A highly basic, lime-rich slag
- A satisfactorily high level of oxidation of iron
- The lowest possible temperature
- The lowest possible amount of undissolved free lime in slag.

EXAMPLE 15.4

For the BOF heat, as in Examples 15.1 and 15.2,

- Calculate the equilibrium slag–metal phosphorus partition coefficient ($L_{P,e}$) at 1650°C. Assume 0% and 10% free lime in slag.
- Calculate the activity coefficient of P₂O₅ (i.e. $\gamma_{P_2O_5}$) in slag at 0% free lime.
- Calculate the wt. % P in metal and slag at slag–metal equilibrium as well as for $R_P = 0.4$. R_P is the ratio of actual L_P and equilibrium L_P (see Eq. (17.4)).

Solution: (a) $L_{P,e}$ can be calculated by using Eqs. (15.44) and (15.45). From Figure 15.7,

$$\begin{aligned} \text{BO} &= \text{wt. \% CaO} + \text{wt. \% CaF}_2 + 0.3 \text{ wt. \% MgO, in slag} & (\text{Ex. 15.6}) \\ &= 54 + 0 + 0.3 \times 2.5 = 54.75 \end{aligned}$$

From Eq. (15.45), $[W_O] = 0.0666\%$.

Noting that wt. % FeO in slag = 18 wt. % and $T = 1923$ K,

From Eq. (15.44), $\log L_{P,e} = 2.385$, giving $L_{P,e} = 242.7$ at 0% free lime.

Since, free lime does not appreciably react with P_2O_5 owing to very slow kinetics, it is assumed that only the liquid part of the slag participates in the phosphorus reaction at 10% free lime. This requires calculation of the liquid slag composition in the following manner.

Since, liquid slag is 90% of total slag, wt. % FeO = $18 \times 100/90 = 20\%$, wt. % MgO = $2.5 \times 100/90 = 2.78\%$, wt. % CaO = $(54 - 10) \times 100/90 = 48.9\%$, and $[W_O] = 0.074\%$.

Substituting these values in Eqs. (Ex 15.4) and (15.44), $\log L_{P,e} = 2.14$, giving $L_{P,e} = 138$.

(b) Equation (15.40) provides the relationship of $\gamma_{P_2O_5}$ with mole fractions of slag components and temperature. This requires conversion of weight percent into mole fraction (X). It can be done on the basis of Eq. (4.26) in Chapter 4. Calculation gives mole fractions of CaO, MgO, MnO, FeO, SiO_2 as 0.577, 0.0374, 0.022, 0.15 and 0.169 respectively.

At 1923 K, putting in values in Eq. (15.40) gives $\log \gamma_{P_2O_5} = -15.06$, i.e. $\gamma_{P_2O_5} = 8.6 \times 10^{-16}$.

(c) P-balance: Initial P in HM = (P in steel + P in slag) at tap (Ex. 15.7)

$$\text{i.e. } \frac{W_{HM} \times \text{wt. \% P in HM}}{100} = \frac{1}{100} \times [W_P] \times (W_{steel} + W_{slag} \times L_{P,e})$$

where $[W_P]$ is wt. % P in steel at tapping.

$$\text{i.e. } 973 \times \frac{0.15}{100} = [W_P] \times (1000 + 242.7 \times 130) \times \frac{1}{100}$$

This gives $[W_P] = 0.00448\%$.

$$(W_P) = L_{P,e} \times [W_P] = 242.7 \times 0.00448 = 1.088\%$$

If $R_P = 0.4$, then $L_P = 0.4 \times 242.7 = 97.08$.

Calculations in a similar manner give $[W_P] = 0.0107\%$, and $(W_P) = 1.040\%$.

15.5 MASS TRANSFER AND KINETICS IN STEELMAKING

In Chapter 4, Section 4.5 some fundamental features of kinetics, mixing and mass transfer were briefly presented. These will be used in connection with process description, kinetics and process control in the later chapters, as and when required. Here, only some data on density (ρ), viscosity (η), kinematic viscosity ($\nu = \eta/\rho$), surface/interface tension (σ) and diffusion coefficient (D) of molten steel and slag are presented in Table 15.4 (*Slag Atlas*, 1981; Elliott, Gleiser and Ramakrishna, 1963).

Table 15.4(a) Viscosity (η), density (ρ), kinematic viscosity (ν) and interfacial tension (σ) of some steel and slag melts

Liquid (Composition, wt. %)	Temperature, K	η , $N \cdot m^{-2} \cdot s^{-1} \times 10^3$	ρ , $kg \cdot m^{-3} \times 10^{-3}$	ν , $m^2 \cdot s^{-1} \times 10^6$
Iron	1809	5.51	7.1	0.78
	1900	4.76	7.1	0.67
	2000	4.12	7.1	0.58
Iron, 4% Carbon	1800	5.0	6.4	0.78
CaO-Al ₂ O ₃ (45% CaO)	1873 1973	110 75	2.75 2.75	40.0 27.3
CaO-Al ₂ O ₃ -CaF ₂ (55% CaO, 35% Al ₂ O ₃)	1873	75	2.7	27.8
CaO-Al ₂ O ₃ -SiO ₂ (60% CaO, 35% Al ₂ O ₃)	1773	3500	2.5	1400
CaO-Al ₂ O ₃ -CaF ₂ -SiO ₂ (49% CaO, 41% Al ₂ O ₃ , 2.5% CaF ₂ , 7.5% SiO ₂) (assumed)	1873	110	2.5	44.0

Interfacial tensions of some slags with liquid iron at 1850 to 1950 K (approximate)—from *Slag Atlas*, 1981

Slag	σ , $Nm^{-1} \times 10^3$
CaO-45%, Al ₂ O ₃ -55%	1300
CaO-55%, Al ₂ O ₃ -35%, CaF ₂ -10%	1400
CaO-60%, Al ₂ O ₃ -35%, SiO ₂ -5%	1000-1100

Table 15.4(b) Some diffusion coefficient values in liquid iron and iron alloys

Medium (composition in wt. %)	Diffusing species	Temperature, K	D , $m^2 \cdot s^{-1} \times 10^9$
Iron	C	1863	7.2
	H	1873	90.0-140.0
	Mn	1953	63.0
	N	1873	3.8
	O	1833	2.3
	P	1823	4.7
	S	1873	4.8
Fe, 3.5% C	Si	1833	10.8
Fe, 2.5% Mn (C-saturated)	C	1823	6.7
Fe, 2.2% Si (C-saturated)	Mn	1773	3.7
Fe, 2.2% Si (C-saturated)	S	1658	3.0
Fe, 1.5% Si (C-saturated)	S	1843	3.8
Fe, 1.5% Si (C-saturated)	Si	1773	2.3

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