# Iron Making and Steel Making
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## Module – 06
## Lecture – 28
## The reaction equilibria in steelmaking

In this lecture, I will talk about some very important reactions that are relevant for the steelmaking and their reaction equilibria.

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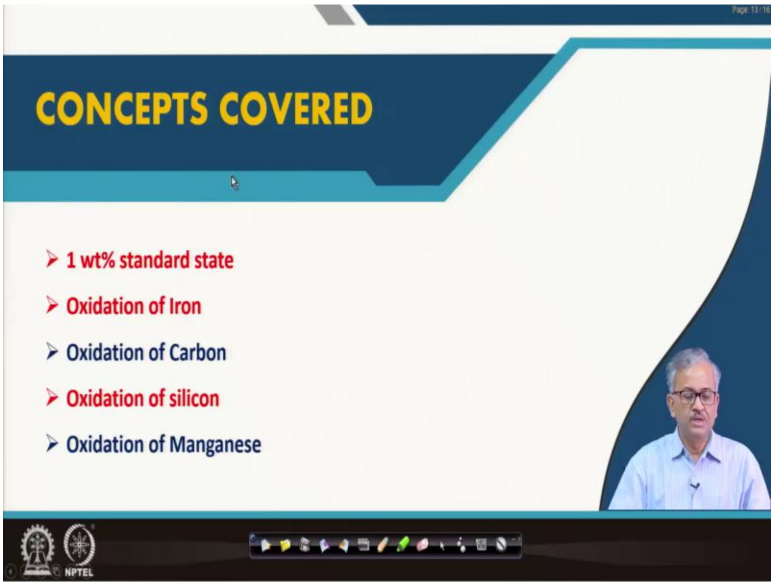

CONCEPTS COVERED

- 1 wt% standard state
- Oxidation of Iron
- Oxidation of Carbon
- Oxidation of silicon
- Oxidation of Manganese

Since concentration of impurities in liquid iron is very small, amounting to a total of 5% maximum and rest 95% is iron, so impurities form a dilute solution in iron. Therefore, for calculation of chemical equilibria, the activities of impurities should conveniently be addressed with respect to a different standard state, called the 1 wt% standard state. So, 1 wt% standard state will be discussed first followed by reaction equilibria like oxidation of iron, carbon, silicon and manganese.

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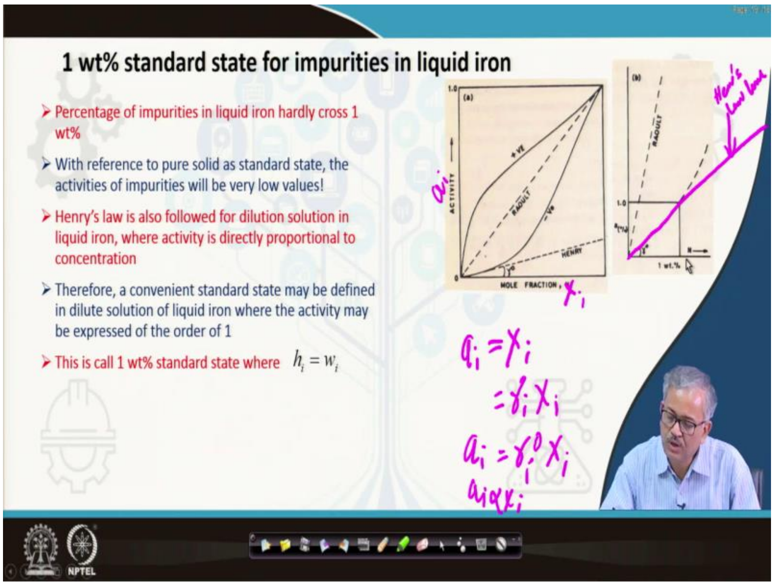

1 wt% standard state for impurities in liquid iron

- Percentage of impurities in liquid iron hardly cross 1 wt%
- With reference to pure solid as standard state, the activities of impurities will be very low values!
- Henry's law is also followed for dilution solution in liquid iron, where activity is directly proportional to concentration
- Therefore, a convenient standard state may be defined in dilute solution of liquid iron where the activity may be expressed of the order of 1
- This is call 1 wt% standard state where $h_i = w_i$

$a_i = X_i$

$= \gamma_i X_i$

$a_i = \gamma_i^0 X_i$

$a_i \propto X_i$

Percentage of impurities in liquid iron hardly cross 1 weight percent, most of them are much less than 1 weight percent and silicon can be little bit higher than 1wt% and carbon being the maximum around 4%. So, with reference to pure solid as the standard state (Raoult's law), the activity of impurities will be very low values. Besides, such value will be physically meaningless and inconvenient.

Accordingly to Raoult's law, activity of pure solid or pure liquid is assigned a value of 1. Raoult's law states that for a binary ideal system when there is no interaction between the impurity and the solvent, activity is equal to the mole fraction, and when mole fraction is one, activity is also one. Now, in actual system, or in non-ideal system, activity is defined by equation 28.1.

$$a_i = \gamma_i X_i \tag{28.1}$$

where, $\gamma_i$ represents the activity coefficient of the solute. If $\gamma$ is greater than 1 (repulsive interaction between solute and solvent), it gives the positive deviation and if it is less than 1(attractive interaction between solute and solvent), it gives the negative deviation from Raoult's law (Figure 28.1). Besides, the activity coefficient also changes with change in concentration of the solute. However at very dilute solution, the slope on the curve becomes constant, yielding a relationship, given by equation (28.2), called the Henry's law.

$$a_i = {\gamma_i}^0 X_i$$

(28.2)

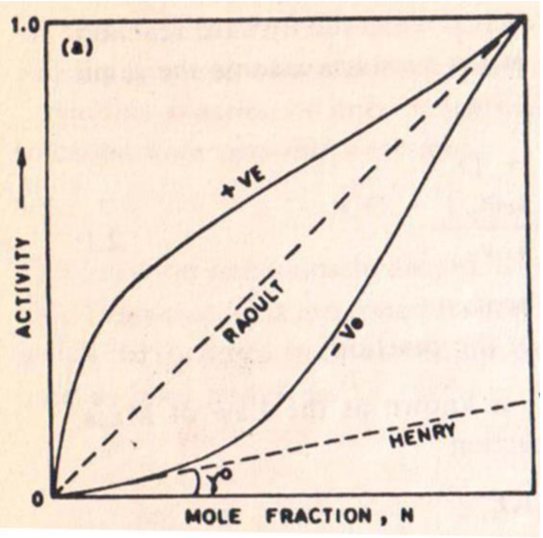

Figure 28.1 Activity of solute with respect to pure solid as the standard state in binary system[2]

The constant activity coefficient at infinite dilute solution, ${\gamma_i}^0$, is called the Henry's activity coefficient. Since at dilute solution, activity coefficient becomes constant; or activity becomes directly proportional to the solute concentration; therefore, at infinite dilution, it is possible to define another standard where activity is 1 when the concentration of solute in solvent is 1 wt%, called the 1wt% standard state. Any deviation from Henry's law is taken care of by introducing a new activity coefficient, called the Hernian activity coefficient, $f_i$ (equation 28.3).

$$h_i = f_i W_i$$

(28.3)

Where, $h_i$ represent the hernian activity with respect to 1wt% standard state. $W_i$ is the weight percentage of the solute i.

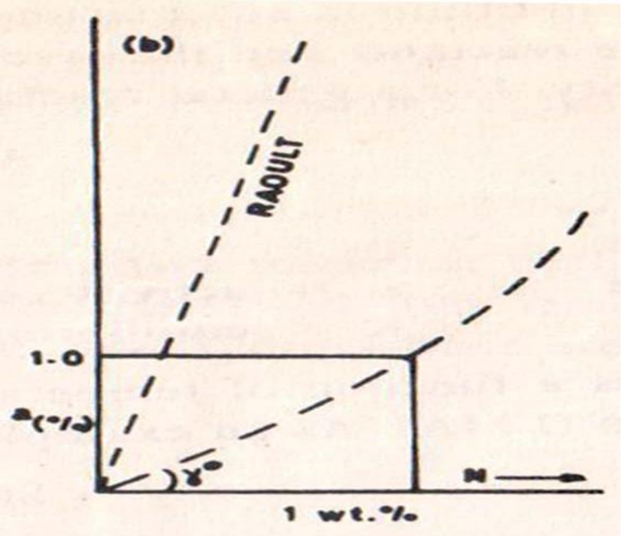

Figure 28.2: Activity concentration relationship in 1 wt% standard state[2]

The activity of solute i on Raoultian scale may be correlated to that on Henrian scale by the following relationship (equation 28.3).

$$h_i = \frac{100M_i}{56}\frac{a_i}{\gamma_i^0}$$

(28.3)

The corresponding free energy change for changing the activity between these two scales may be given by equation (28.4).

$$\Delta G_{P-wp} = RT\ln\left(\frac{0.56}{M_i}\gamma_i^0\right)$$

(28.4)

Hernia activity coefficient of solute ‘i’ in multicomponent dilute liquid solution can also be calculated as (Equation 28.5):

$$\log(f_i) = \sum_{j=1}^{n} e_i^j w_j$$

(28.5)

Where, $e_i^j$ represent the interaction coefficient of j-th solute on the i-th solute.

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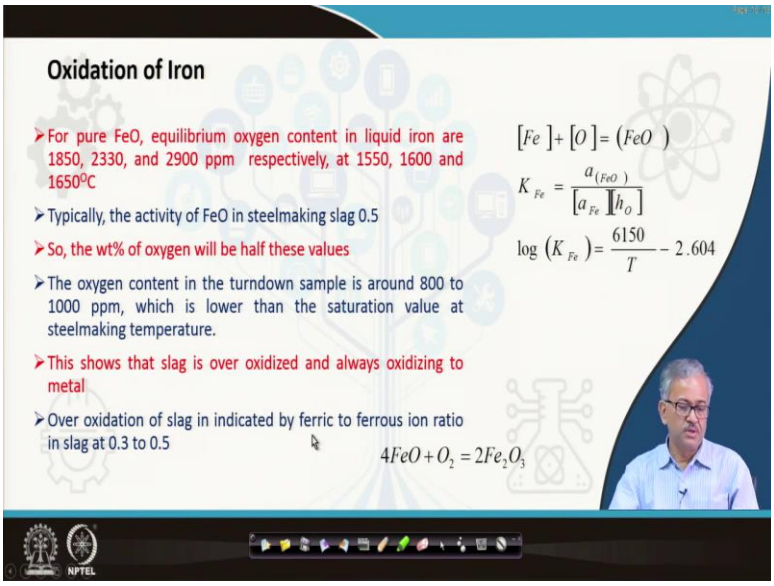

## Oxidation of Iron

- For pure FeO, equilibrium oxygen content in liquid iron are 1850, 2330, and 2900 ppm respectively, at 1550, 1600 and 1650$^0$C
- Typically, the activity of FeO in steelmaking slag 0.5
- So, the wt% of oxygen will be half these values
- The oxygen content in the turndown sample is around 800 to 1000 ppm, which is lower than the saturation value at steelmaking temperature.
- This shows that slag is over oxidized and always oxidizing to metal
- Over oxidation of slag in indicated by ferric to ferrous ion ratio in slag at 0.3 to 0.5

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

$$K_{Fe}=\frac{a_{(FeO)}}{[a_{Fe}][h_O]}$$

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

$$4FeO+O_2=2Fe_2O_3$$

Now, let us now consider the reactions elevant to steel making.  Firs, consider the equilibrium of iron oxidation. Since iron forms the 95% of the total liquid iron bath, during oxygen purification of liquid iron, the oxidation of iron will be favoured kinetically; iron oxide in turn will supply the oxygen for forming more stable impurity oxides.  So, Fe-O-FeO equilibria (equation 28.6) is of importance.

$$[Fe]+[O]=(FeO) \tag{28.6}$$

The equilibrium constant ($K_{Fe}$) for the above reaction may be represented as the ratio of activities of the product to that of the reactants (equation 28.7)

$$K_{Fe}=\frac{a_{(FeO)}}{[a_{Fe}][h_O]} \tag{28.7}$$

It may be noted that the activity of dissolved oxygen has been represented in Henrian scale w.r.t. 1 wt% standard state; while activities of FeO and Fe has been represented in Raoultian scale.

Accordingly, the relationship of equilibrium constant and temperature (Equation 28.8) has been derived considering the activity scale conversion for the solute.

$$\log\left(K_{Fe}\right)=\frac{6150}{T}-2.604$$

(28.8)

One immediate advantage of such scale conversion is that we can directly get the concentration of dissolved oxygen in steel in wt%, even considering interaction among solute in multicomponent system.

For simplicity, without considering any solute interaction ($h_O = W_O$) and considering FeO as pure, the saturation level of oxygen in the bath at various temperatures namely 1550, 1600 and 1650 can be calculated as 1850, 2330 and 2900 ppm, respectively.  Activity of FeO in slag typically is 0.5(w.r.t. pure solid as standard state, or Raoultian scale). Then the saturation level in the bath will be just be half the values than what we have calculated considering pure FeO, i.e. 925, 1115 and 1450 ppm, respectively.  However, in turndown sample the dissolved oxygen is found in the range 800-1000 ppm, much lower than calculated equilibrium saturation level.   This indicates that oxygen accumulates in slag, which may be attributed to mass transport limitation of oxygen from slag to the bath. Such accumulation of oxygen in slag leads to oxidation of FeO to higher oxide $Fe_2O_3$.  In fact the BOF slag shows the presence of both ferrous and ferric ion and the ratio $Fe^{3+}/Fe^{2+}$ in the range 0.3 to 0.5.  Therefore oxidation potential of the slag may also be determined by considering the following reaction (equation 28.9). Another inference of these calculation is that the steelmaking slag always remain oxidizing to the metal bath.

$$4FeO+O_2=2Fe_2O_3$$

(28.9)

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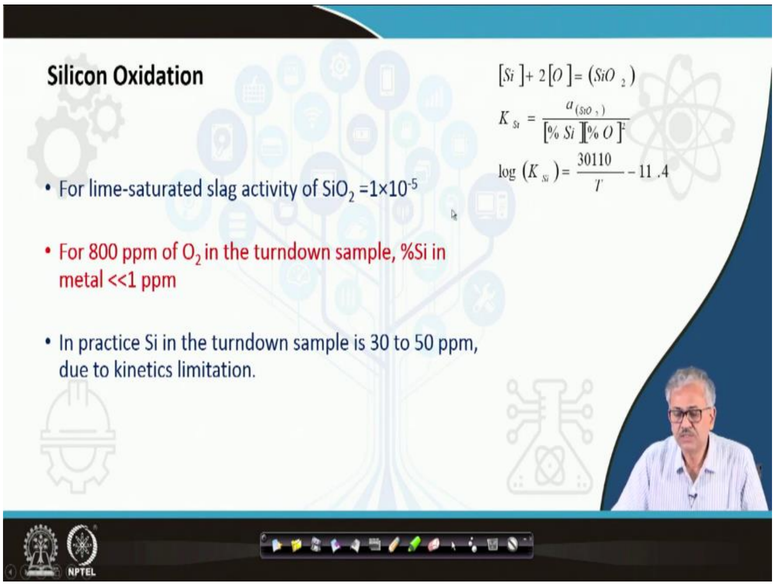

**Silicon Oxidation**

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

$K_{Si}=\frac{a_{(SiO_2)}}{[\%Si][\%O]^2}$

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

- For lime-saturated slag activity of $SiO_2 = 1\times10^{-5}$
- For 800 ppm of $O_2$ in the turndown sample, %Si in metal <<1 ppm
- In practice Si in the turndown sample is 30 to 50 ppm, due to kinetics limitation.

Silicon reaction (Equation 28.10), equilibrium constant (Equation 28.11) and its relationship with temperature (Equation 28.12) can be given as follows:

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

(28.10)

$$K_{Si}=\frac{a_{(SiO_2)}}{[\%Si][\%O]^2}$$

(28.11)

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

(28.12)

Activities of impurities have been expressed on Henrian scale wrt 1wt% standard state and Henry’s law has been assumed to be valid for impurities.

Applying these relationship, the saturation concentration of silicon in the bath can be calculated. Activity of silica in lime saturated slag may be taken as $10^{-5}$. Using this value and assuming dissolved oxygen in turndown sample as 800 ppm, percentage of silicon into the metal bath may be calculated to be less than 1 ppm. So, thermodynamically it is possible to reduce the silicon in liquid iron to a very low level, but bringing it down below 50 ppm appears to be difficult due to kinetic limitation.

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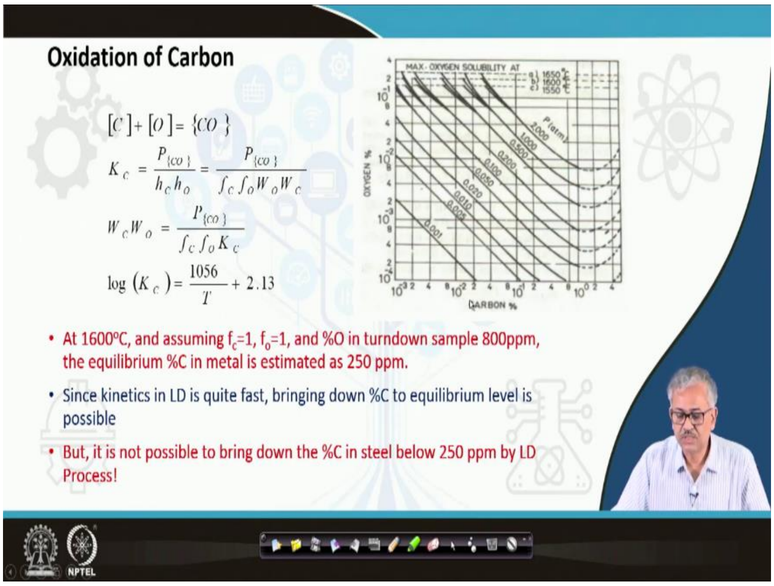

**Oxidation of Carbon**

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

$$K_C = \frac{P_{\{CO\}}}{h_C h_O} = \frac{P_{\{CO\}}}{f_C f_O W_O W_C}$$

$$W_C W_O = \frac{P_{\{CO\}}}{f_C f_O K_C}$$

$$\log(K_C) = \frac{1056}{T} + 2.13$$

- At 1600°C, and assuming $f_c=1$, $f_o=1$, and %O in turndown sample 800ppm, the equilibrium %C in metal is estimated as 250 ppm.
- Since kinetics in LD is quite fast, bringing down %C to equilibrium level is possible
- But, it is not possible to bring down the %C in steel below 250 ppm by LD Process!

Now, come to the oxidation of carbon. Similarly, carbon oxidation reaction, equilibrium relationship, solubility product of dissolved carbon and oxygen, and the equilibrium constant-temperature relationship may be given by equations (28.13) to (28.16), respectively.

$$[C]+[O]=\{CO\} \tag{28.13}$$

$$K_C = \frac{P_{\{CO\}}}{h_C h_O} = \frac{P_{\{CO\}}}{f_C f_O W_O W_C} \tag{28.14}$$

$$W_C W_O = \frac{P_{\{CO\}}}{f_C\, f_O K_C}$$

(28.15)

$$\log\left(K_C\right) = \frac{1056}{T} + 2.13$$

(28.16)

The second bracket in the above expressions represent gaseous product. It is to be noted that among the impurities in liquid iron, carbon only produces the oxidation product in the gaseous state. Therefore, retaining the impurity oxide in the slag is not an issue. It has another advantage also; this is the only reaction (equation 28.13) that can be influenced significantly by the pressure, because the right hand side is a gas. Carbon oxidation can preferential be carried out under vacuum.

The solubility product of dissolved carbon and oxygen is a function of ambient pressure, and equilibrium constant, which in turn is a function of temperature. Therefore the relationship between dissolved oxygen and carbon can be mapped at various pressure temperature, which is presented by the Figure 28.3. The Hernia activity coefficient $f_c$ and $f_o$ have been assumed to be 1.

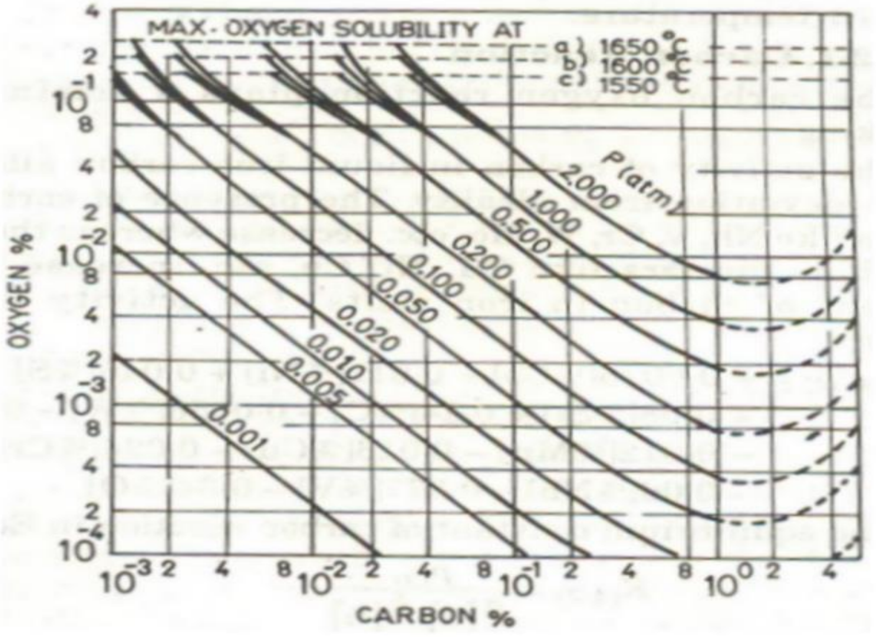

Figure 28.3 Equilibrium relationship between dissolved oxygen and carbon at various pressure at three different temperature [1]

At 1600$^{o}$C, and if we assume $f_c$, and $f_o$ is equal to 1, wt% oxygen in the turndown sample to be 800 ppm, the equilibrium amount of carbon in the metal is estimated as 250 ppm (Equation 28.14). So, carbon can be lowered to a minimum level of 250ppm under 1 atmospheric pressure. Since BOF operate at 1 atmospheric pressure, lowering carbon in the bath below 250 ppm is not possible. Therefore, to produce ultra low carbon steel, it can only be done under vacuum during secondary steelmaking.

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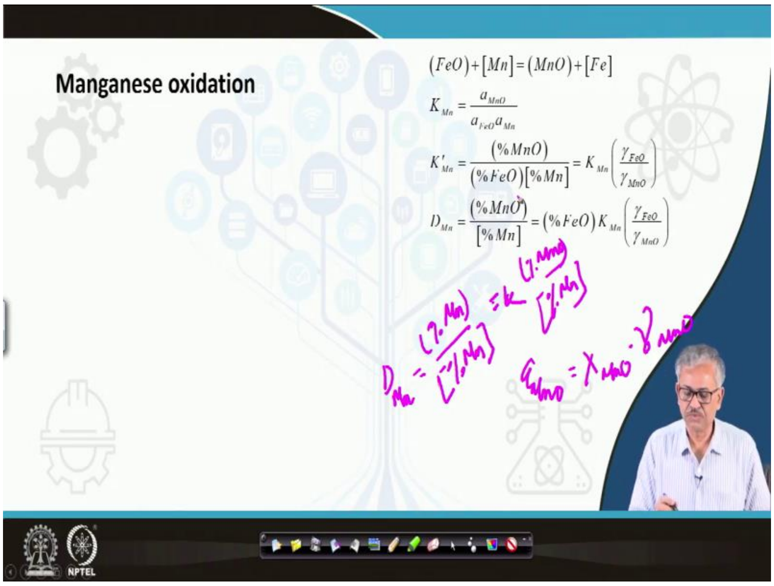

## Manganese oxidation

$$(FeO)+[Mn]=(MnO)+[Fe]$$

$$K_{Mn}=\frac{a_{MnO}}{a_{FeO}a_{Mn}}$$

$$K'_{Mn}=\frac{(\%MnO)}{(\%FeO)[\%Mn]}=K_{Mn}\left(\frac{\gamma_{FeO}}{\gamma_{MnO}}\right)$$

$$D_{Mn}=\frac{(\%MnO)}{[\%Mn]}=(\%FeO)K_{Mn}\left(\frac{\gamma_{FeO}}{\gamma_{MnO}}\right)$$

$$D_{Mn}=\frac{(\%Mn)}{[\%Mn]}=k\frac{(\%MnO)}{[\%Mn]}$$

$$a_{MnO}=X_{MnO}\cdot\gamma_{MnO}$$

Now, I will come to the manganese oxidation.

Manganese is also a unique impurity because its oxide product is a basic oxide unlike silicon and the phosphorus, which form acidic oxide. Acidic oxides can be easily retained into the slag by using the basic slag; while manganese becomes uncomfortable in basic slag and tries to revert back to steel.

Manganese equilibria can be expressed by the following equations:

$$(FeO)+[Mn]=(MnO)+[Fe]$$

(28.17)

$$K_{Mn}=\frac{a_{MnO}}{a_{FeO}a_{Mn}}$$

(28.18)

$$K'_{Mn}=\frac{(\%MnO)}{(\%FeO)[\%Mn]}=K_{Mn}\left(\frac{\gamma_{FeO}}{\gamma_{MnO}}\right)$$

(28.19)

$$D_{Mn} = \frac{(\%MnO)}{[\%Mn]} = (\%FeO)\,K_{Mn}\left(\frac{\gamma_{FeO}}{\gamma_{MnO}}\right)$$

(28.20)

The LHS of (28.20), represents the manganese partition coefficient, which is shown to be function of wt% of FeO in slag, equilibrium constant, $K_{Mn}$, which is a function of temperature; and it also depends on the ratio of activity coefficients of FeO to activity coefficient of MnO. Both FeO and MnO possesses higher activity in basis slag but ratio of their activity coefficients vary significantly with increase in basicity, as shown in the Figure 28.4. It is obvious that with increase in basicity, the increase in $\gamma_{MnO}$ is much higher than $\gamma_{FeO}$ and consequently the said ratio decreases significantly. This reflects more basic nature of MnO compared to FeO.

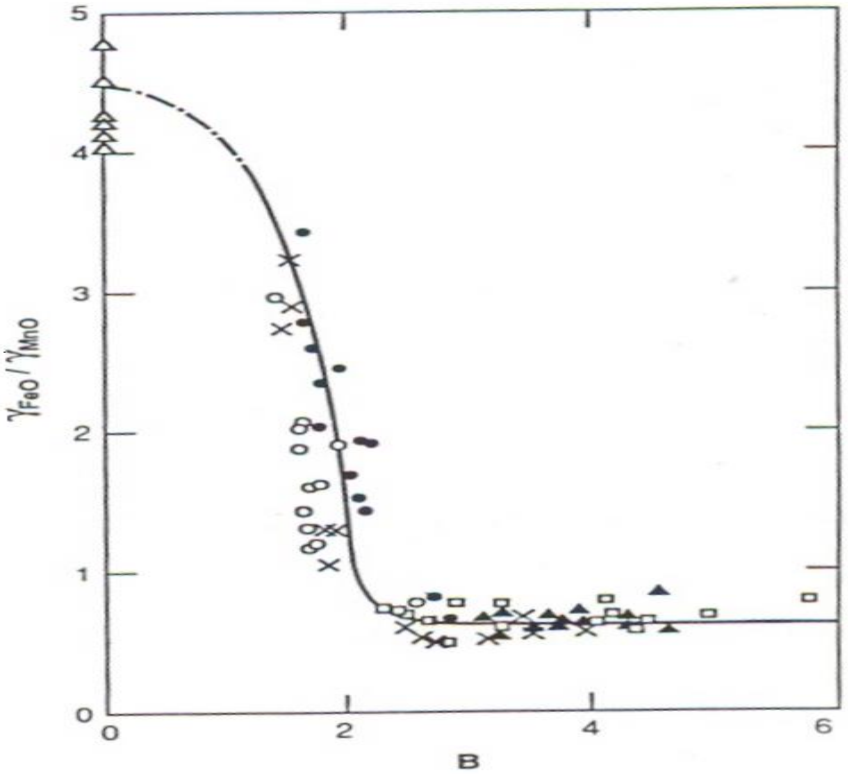

Figure 28.4: Variation of the ratio of activity coefficients of FeO to MnO with basicity[1].

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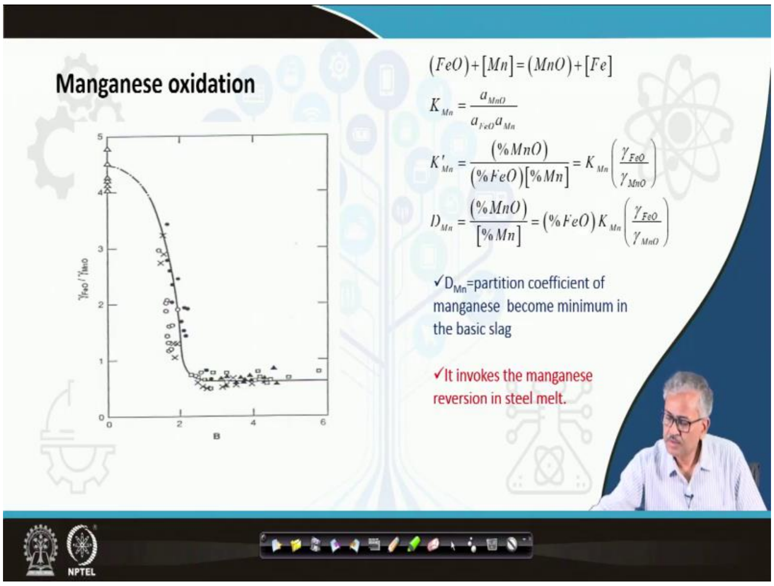

Manganese oxidation

$$(FeO)+[Mn]=(MnO)+[Fe]$$

$$K_{Mn}=\frac{a_{MnO}}{a_{FeO}a_{Mn}}$$

$$K'_{Mn}=\frac{(\%MnO)}{(\%FeO)[\%Mn]}=K_{Mn}\left(\frac{\gamma_{FeO}}{\gamma_{MnO}}\right)$$

$$D_{Mn}=\frac{(\%MnO)}{[\%Mn]}=(\%FeO)K_{Mn}\left(\frac{\gamma_{FeO}}{\gamma_{MnO}}\right)$$

✓$D_{Mn}$=partition coefficient of manganese become minimum in the basic slag

✓It invokes the manganese reversion in steel melt.

$\left(\frac{\gamma_{FeO}}{\gamma_{MnO}}\right)$ is quite high (>4) in acidic slag which subsequently decreased with increase in basicity and stabilizes to a value around 1 beyond basicity of 2. Therefore, as defined by equation (28.20), partition coefficient of manganese will decrease with increase in basicity.

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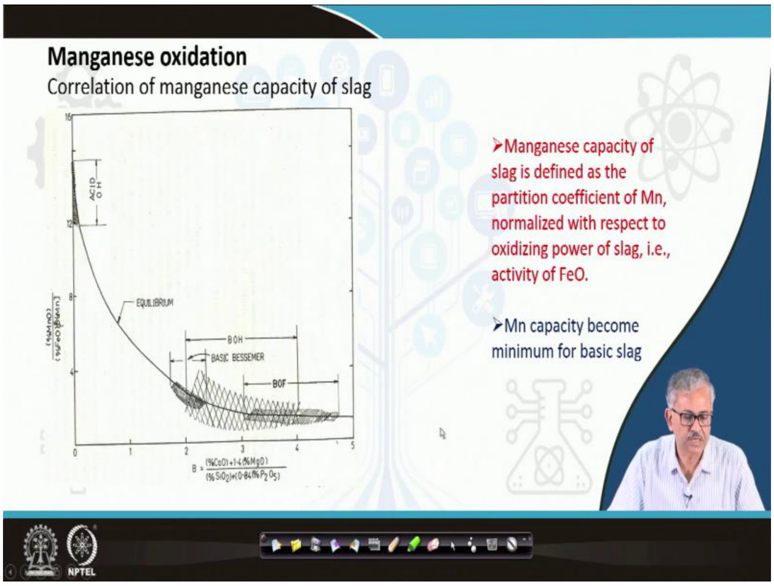

Manganese oxidation

Correlation of manganese capacity of slag

- Manganese capacity of slag is defined as the partition coefficient of Mn, normalized with respect to oxidizing power of slag, i.e., activity of FeO.
- Mn capacity become minimum for basic slag

The LHS of equation 28.19, represents the manganese capacity of slag ($K'_{Mn}$). It may be noted that it is partition coefficient of manganese normalized by the oxidizing power of slag (% FeO in slag); and it also becomes only function of slag composition and temperature and becomes independent of oxidizing power of slag. In other words it means that manganese capacity represents the holding capacity of the slag for manganese irrespective of oxidation potential of the slag and it is only a function of slag composition and temperature. So, it is obvious that manganese capacity will decrease with increase in basicity and will stabilize beyond basicity of 2. The variation of manganese capacity with basicity is shown in the figure below (Figure 28.5).

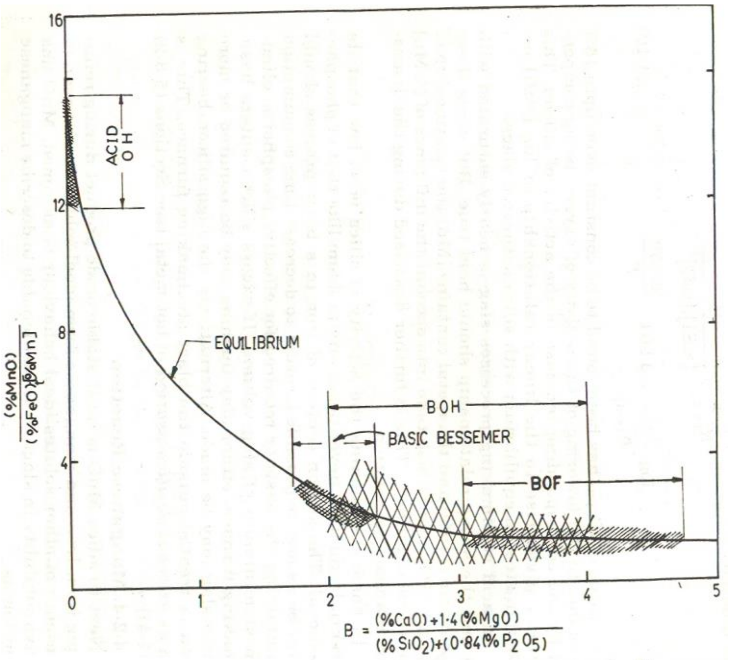

Figure 28.5: Variation of manganese capacity of slag with basicity[1].

In BOF process, as the slag become progressively limy, the MnO becomes unstable in slag and it reverts back to metal phase, called the manganese reversion.

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REFERENCES

1) E. T. Turkdagon: Fundamental of Steelmaking, Institute of Materials, London, 1996, 188
2) Ghosh & Chatterjee: Ironmaking & Steelmaking PHI, New Delhi, 2008.

References are mentioned in the slide above.

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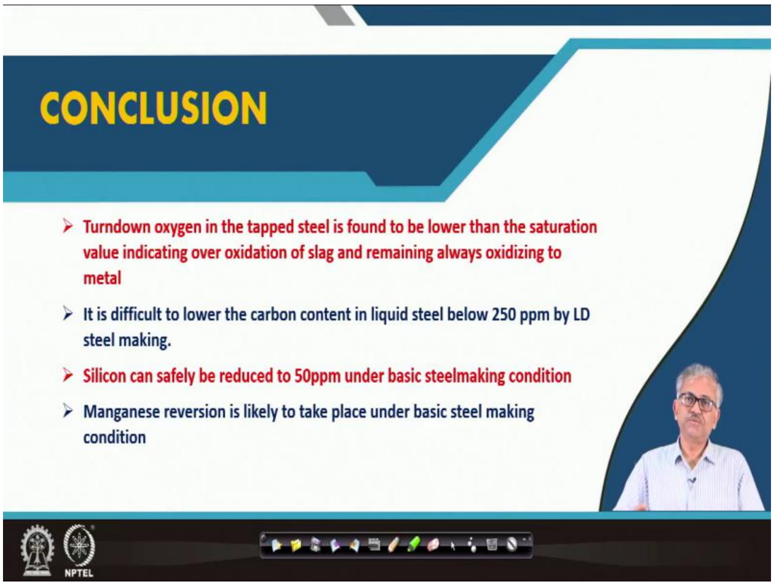

CONCLUSION

- Turndown oxygen in the tapped steel is found to be lower than the saturation value indicating over oxidation of slag and remaining always oxidizing to metal
- It is difficult to lower the carbon content in liquid steel below 250 ppm by LD steel making.
- Silicon can safely be reduced to 50ppm under basic steelmaking condition
- Manganese reversion is likely to take place under basic steel making condition

Conclusion: Turndown oxygen in the tapped steel form LD is found to be much lower than its saturation value. It indicates accumulation of oxygen in slag leading to over oxidation of slag to ferric oxide. As a result slag remain always oxidizing to the metal.

It is difficult to lower the carbon content in liquid steel below 250 ppm by the BOF steel making, which take place under one atmospheric condition. To produce ultra-low carbon steel, ladle treatment under vacuum is essential.

Silicon can safely be reduced to 50 ppm under basic steel making condition.

Manganese reversion is likely to take place under basic slag.