Iron Making and Steel Making
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Module – 06
Lecture – 29
Dephosphorization of Liquid Steel

In this lecture, we will talk about the oxidation of phosphorus during steel making.

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CONCEPTS COVERED

- Thermodynamics for phosphorus removal
- Phosphorus capacity and its correlation

Topics to be covered are the thermodynamics of phosphorus removal and the phosphorous capacity and its correlation.

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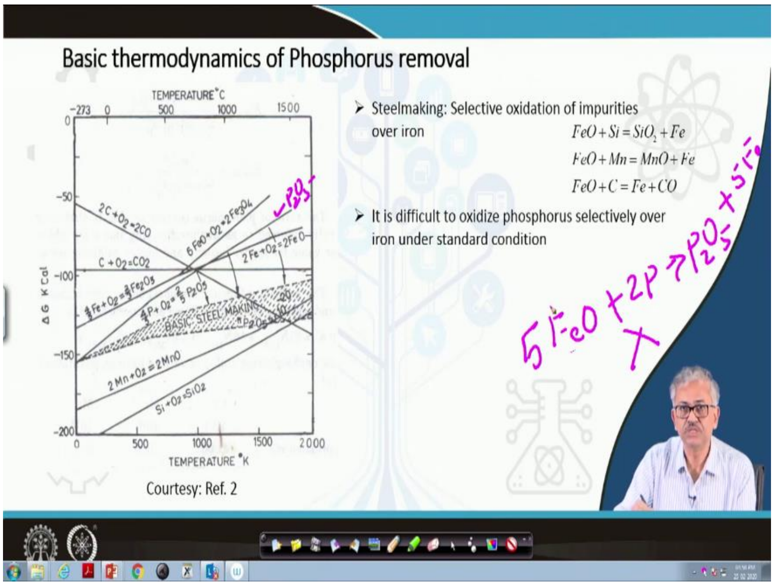

Basic thermodynamics of Phosphorus removal

- Steelmaking: Selective oxidation of impurities over iron $FeO + Si = SiO_2 + Fe$ $FeO + Mn = MnO + Fe$ $FeO + C = Fe + CO$
- It is difficult to oxidize phosphorus selectively over iron under standard condition

$5FeO + 2P \rightarrow P_2O_5 + 5Fe$

Courtesy: Ref. 2

In steelmaking, aim is to selectively oxidise of impurities over iron, such that impurities are removed by oxidation without losing much iron in the slag in the form of FeO. In Basic oxygen steel making like LD, oxygen is lanced from top and oxidation of iron is preferred kinetically, because it constitute 95% of the liquid iron. So, by law of mass action it is the iron that will get oxidized first; subsequently FeO will oxidize the impurities which forms more stable oxides. These reactions could be written as:

$$FeO + Si = SiO_2 + Fe$$

(29.1)

$$FeO + Mn = MnO + Fe$$

(29.2)

$$FeO + C = Fe + CO$$

(29.3)

If we examine the Ellingham diagram with oxides relevant to steelmaking (Figure 29.1), it may be observed that silicon oxide, manganese oxide are more stable oxides compared to the FeO, even at high steelmaking temperature. CO is also much more stable compared to the FeO at high temperature. So, all these right hand side impurity oxides that are more stable compared to the iron oxide. So, even though the iron oxide form first, the impurity will reduce the iron oxide to iron and they themselves will be oxidized to SiO_2, MnO and CO. Out of these oxides, CO is a gas gaseous product. So, CO will go away from the system; but SiO_2 and MnO have to be arrested into the slag, such that these reactions move in the forward direction.

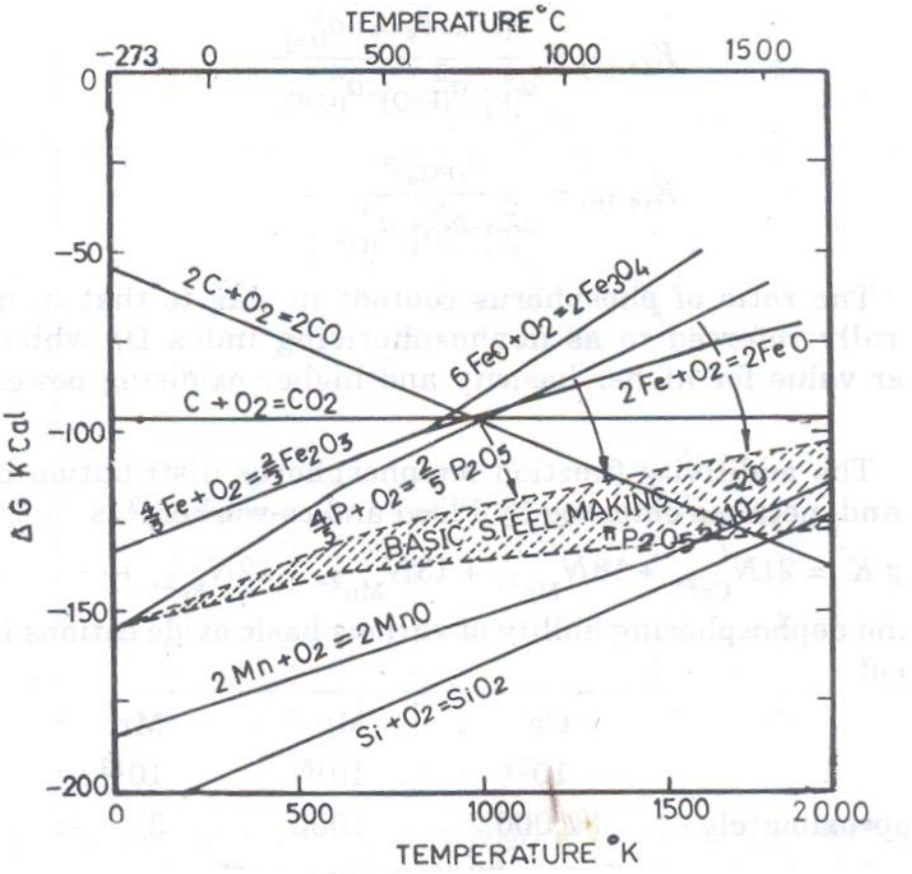

Figure 29.1: Ellingham diagram with relevant oxides in steelmaking [4]

From Figure 29.1, it may be observed that phosphorous line is very close to the FeO line and even cross the FeO line at higher temperature; so when both are pure, P_2O_5 becomes more stable compared to FeO. Therefore, unlike reactions represented by equations 29.1 to 29.3, the reaction given by equation (29.4) is not feasible when both FeO and P_2O_5 are in their standard state, or are in their pure state:

$$2P + 5FeO = P_2O_5 + 5Fe$$

(29.4)

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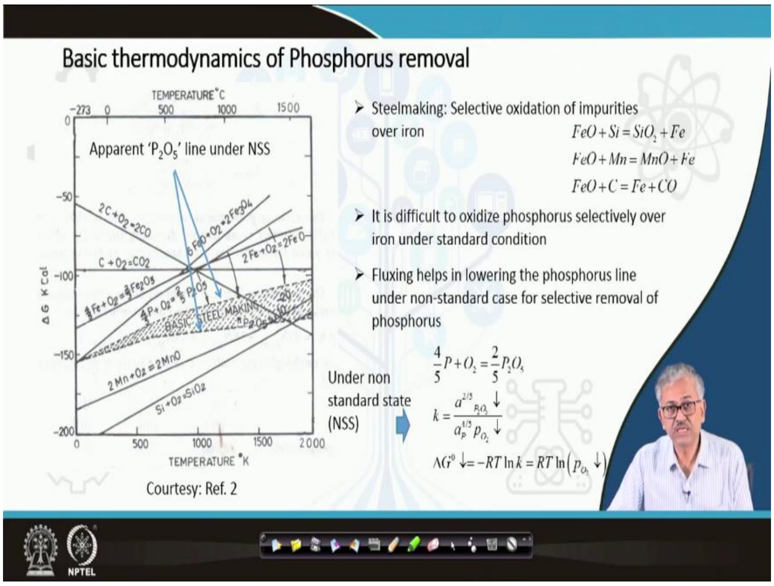

Basic thermodynamics of Phosphorus removal

Courtesy: Ref. 2

- Steelmaking: Selective oxidation of impurities over iron

$$FeO + Si = SiO_2 + Fe$$
$$FeO + Mn = MnO + Fe$$
$$FeO + C = Fe + CO$$

- It is difficult to oxidize phosphorus selectively over iron under standard condition
- Fluxing helps in lowering the phosphorus line under non-standard case for selective removal of phosphorus

Under non standard state (NSS)

$$\frac{4}{5}P + O_2 = \frac{2}{5}P_2O_5$$
$$k = \frac{a^{2/5}{}_{P_2O_5}\downarrow}{a_P^{4/5}\,p_{O_2}\downarrow}$$
$$\Delta G^0 \downarrow = -RT\ln k = RT\ln\left(p_{O_2}\downarrow\right)$$

So, that is why it is difficult to oxidize phosphorous selectively over iron under the standard state. Now, if the activity of P_2O_5 in the slag can be reduced significantly by fluxing it with lime, the reaction can move forward. The apparent phosphorus line (indicated by dotted line) will move down in the Ellingham diagram. To understand this, let us consider the phosphorus oxidation (equation 29.5) and its equilibrium constant (equation 29.6) and apparent standard free energy change (Equation 29.7).

$$\frac{4}{5}P + O_2 = \frac{2}{5}P_2O_5$$

(29.5)

$$k = \frac{a^{2/5}{}_{P_2O_5}\downarrow}{a_P^{4/5}\,p_{O_2}\downarrow}$$

(29.6)

$$\Delta G^0 \downarrow = -RT\ln k = RT\ln\left(p_{O_2}\downarrow\right)$$

(29.7)

Since, equilibrium constant (K) is constant at a particular temperature; a decrease in activity coefficient of P_2O_5, will cause the apparent partial pressure of oxygen in equilibrium with P-P_2O_5 to decrease following equation (29.6). Consequently, the apparent chemical potential of oxygen, or apparent standard free energy change will decrease, lowering the position of the line P-P_2O_5 in the Ellingham diagram. The "apparent" word is being used because Ellingham diagram is developed for metal and their oxides in standard state. So when we are using metal oxide in non-standard state, then modified partial pressure of oxygen and standard free energy does not represent the standard state, and termed as "apparent" to show the revised position of the line under non-standard condition of the oxide.

Under basic slag condition, activity of FeO, being a basic oxide, however will increase and therefore apparent Fe-FeO line will remain same or move up little. So, under basic slag condition, the apparent P-P_2O_5 line will move down w.r.t. Fe-FeO line making it feasible to oxidize phosphorus preferentially under basic slag condition, and the following the equation (29.5) will be feasible:

$$5(FeO) + 2[P] + 3(CaO) = (3CaO.P_2O_5) + 5Fe \tag{29.8}$$

The first and third parenthesis indicate that the constituents are in slag and metal phases, respectively.

So, it may be concluded that for de-phosphorization, a basic slag is a must. But for removing silicon, manganese, carbon basic slag is not a must; but obviously, the silicon removal will be facilitated in presence of basic slag because activity silica in basic slag decreases significantly. So, basic slag obviously helps the silicon oxidation or the silicon removal, but for preferential removal of silicon fluxing of slag is not a must because silica itself is more stable oxide compared to the iron oxide. In case of manganese, it is a basic oxide. So, basic slag does not help much. But manganese oxide itself is more stable oxide compared to the FeO. So, manganese also can be removed preferentially over iron under steel making condition. And, for carbon it is also not a problem because CO is a stabler oxide, especially at high temperature; and since it is a gas, its retention in the slag also not required; So preferential carbon removal is also not a problem. But for removal of phosphorus, a basic slag is a must; such that activity of P_2O_5 decreases, and it can be selectively removed over iron. Activity coefficient of P_2O_5 decreases significantly with increase in basicity of slag, as shown in Figure 29.2.

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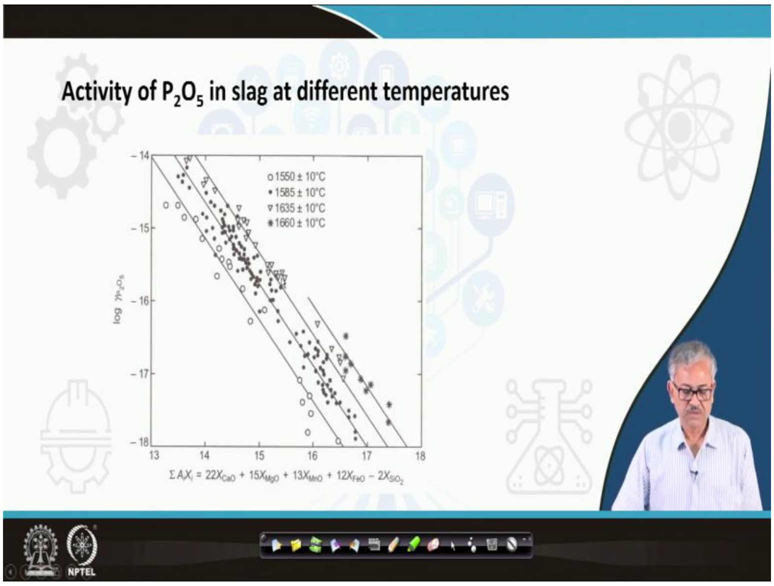

Activity of P_2O_5 in slag at different temperatures

Figure 29.2 shows the variation of activity coefficient of P_2O_5 in slag with basicity at three different temperatures. It may be found that activity coefficient decreases with decrease in temperature and increase in basicity. Basicity is defined as summation of various basic oxides with different weighting factors. CaO being the most influential, its weighting factor is 22, followed by MgO with weighting factor of 15, subsequently MnO with a factor of 13 and FeO with 12. Finally, twice the mole fraction of SiO_2 is substracted to account for annihilation of basic oxides in silicate melt.

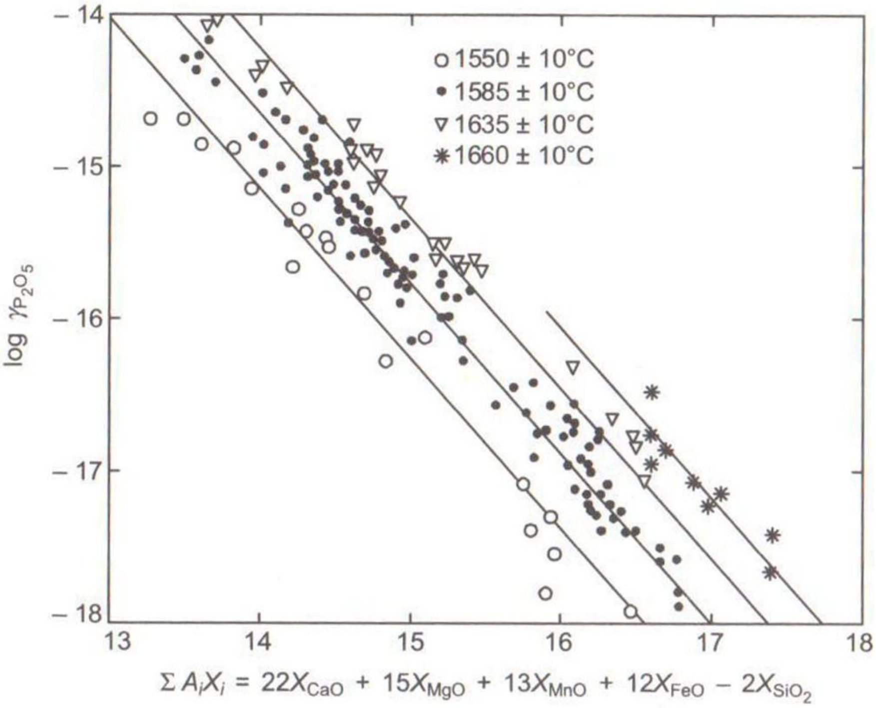

Figure 29.2 variation of activity coefficient with basicity and temperature [1,2].

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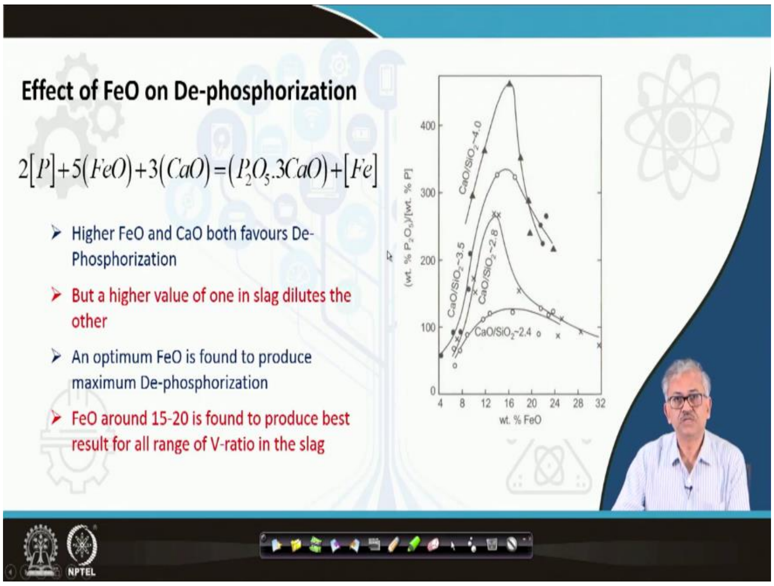

Effect of FeO on De-phosphorization

$$2[P]+5(FeO)+3(CaO)=(P_2O_5.3CaO)+[Fe]$$

- Higher FeO and CaO both favours De-Phosphorization
- But a higher value of one in slag dilutes the other
- An optimum FeO is found to produce maximum De-phosphorization
- FeO around 15-20 is found to produce best result for all range of V-ratio in the slag

According to ionic theory the reaction represented by equation 29.5 can be expressed as:

$$2[P]+5[O]+3(O^{2-})=2(PO_4)^{3-}$$

(29.9)

The equilibrium constant may be expressed as:

$$K = \frac{a^2{}_{(PO_4)^{3-}}}{a^2{}_{[P]} a_{[O]}{}^5 a^3{}_{(O^{2-})}}$$

(29.10)

The partition coefficient of phosphorus may be represented as:

$$D_P = \frac{(\%P)}{[\%P]} = \sqrt{K'} a_{[O]}{}^{5/2} a_{(O^{2-})}{}^{3/2}$$

(29.11)

So, partition coefficient of phosphorus depends on dissolved oxygen, basicity (represented by oxygen ion activity) and equilibrium constant or, temperature. The variation of phosphorus partition coefficient with wt% FeO is shown in Figure 29.3.

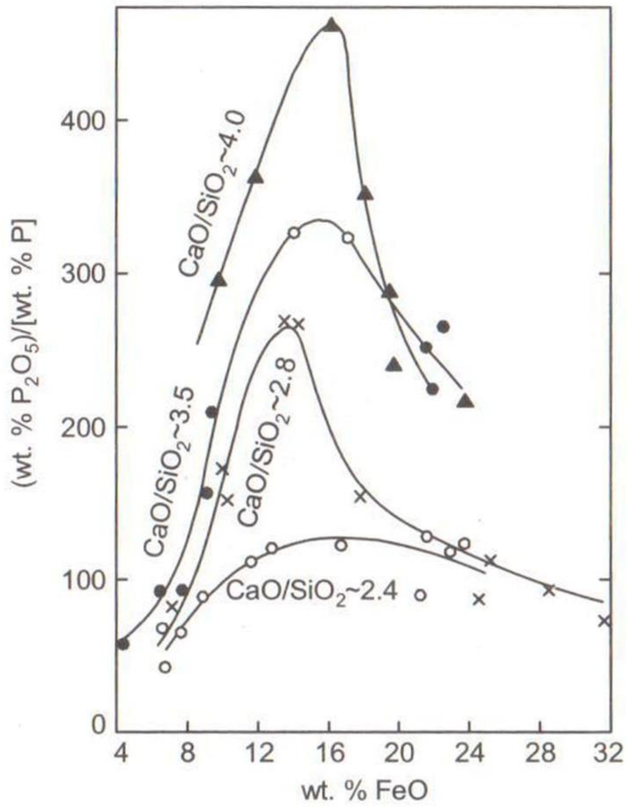

Figure 29.3: Variation of Phosphorus partitioning with wt% of FeO in slag [1,2]

With reference to the equations (29.4) and (29.5), it may be seen that the de-phosphorization reaction is favoured when FeO in slag increases (increasing oxidation potential of the slag) , or CaO increases (increasing the basicity of the slag), or, both increases. But, if you go on increasing the FeO progressively, then CaO in slag get diluted; similarly, if you increase the amount of CaO progressively in the slag, then FeO get diluted. So, a higher value of one in the slag dilutes the other. An optimum amount of FeO should be required that does not dilute the CaO, maintaining proper slag basicity. From Figure 29.4, it is seen that optimum FeO in the slag is around 15% and it is found to be true at various basicity values; and partitioning being maximum at basicity (V-ratio) of 4.

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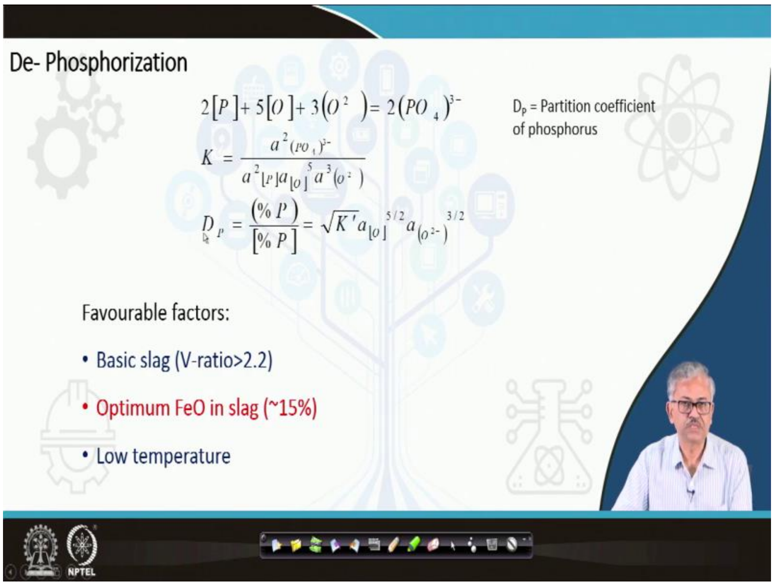

De- Phosphorization

$$2[P]+5[O]+3(O^{2-})=2(PO_4)^{3-}$$

$$K=\frac{a^2_{(PO_4)^{3-}}}{a^2_{[P]}a^5_{[O]}a^3_{(O^{2-})}}$$

$$D_P=\frac{(\%P)}{[\%P]}=\sqrt{K'}a_{[O]}^{5/2}a_{(O^{2-})}^{3/2}$$

D_P = Partition coefficient of phosphorus

Favourable factors:

- Basic slag (V-ratio>2.2)
- Optimum FeO in slag (~15%)
- Low temperature

It may be noted that K (equilibrium constant) is inversely proportional to the temperature. So, if temperature is low, K is high; so Dp is high. Therefore, at lower temperature, phosphorus partitioning will be favoured. To understand physically, you know that phosphorus oxidation is exothermic, so the reaction will be favoured at lower temperature.

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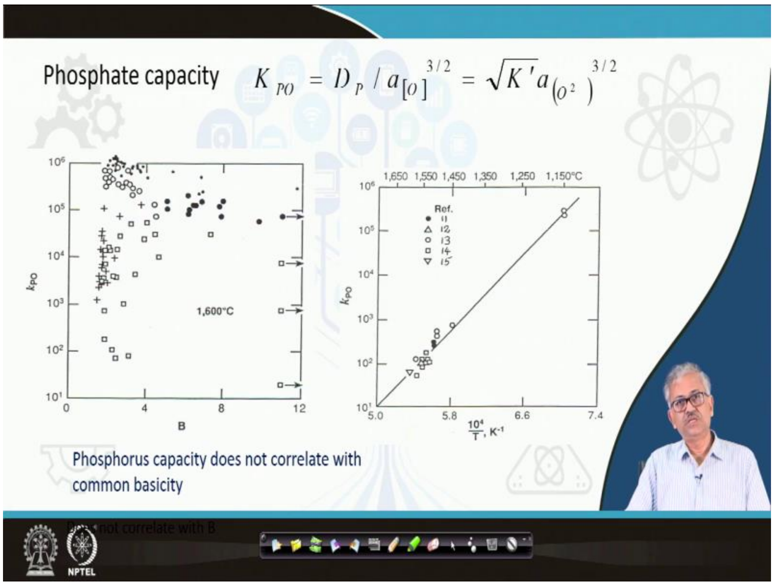

Phosphate capacity $K_{PO} = D_P / a_{[O]}^{3/2} = \sqrt{K'} a_{(O^{2-})}^{3/2}$

Phosphorus capacity does not correlate with common basicity

Using equation (29.7), phosphate capacity of slag, or the holding capacity for phosphorus in the slag, may be defined as follows:

$$K_{PO} = D_P / a_{[O]}^{3/2} = \sqrt{K'} a_{(O^{2-})}^{3/2}$$

(29.12)

It may be noted that that phosphate capacity is defined by normalizing D_P with respect to the dissolved oxygen in steel or oxidizing power of the bath, such that phosphate capacity become function of oxygen ion activity (composition of slag) and temperature (equilibrium constant), irrespective of oxidizing power of the bath. Figure 29.4 shows the variation of phosphate capacity with common basicity at 1600^{o}C. No correlation is observed. As mentioned earlier also that common basicity, which is defined as the ratio of summation of all basic oxides to the summation of all acidic oxides, does not represent the basicity properly, because all basic oxides are not equally effective in retaining impurities in slag. Therefore, when basicity is redefined in a proper way considering only the relevant basic oxides, it gives an excellent correlation of phosphate capacity with modified basicity (Figure 29.5). Where, basic constituents like CaO and CaF_2 are given full weightage and MgO with 30% weightage, are considered.

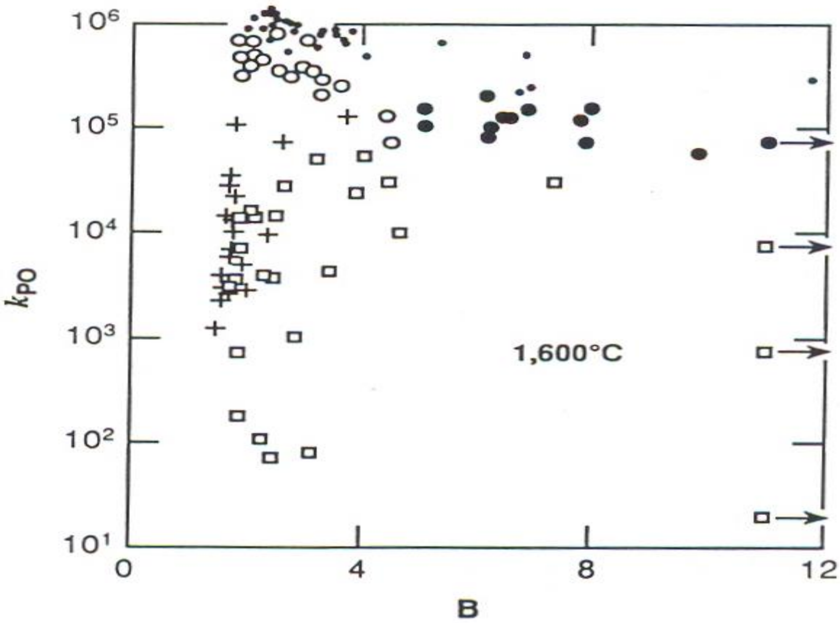

Figure 29.4: Correlation of K_{PO} of slag with common basicity at 1600^{o}C [2]

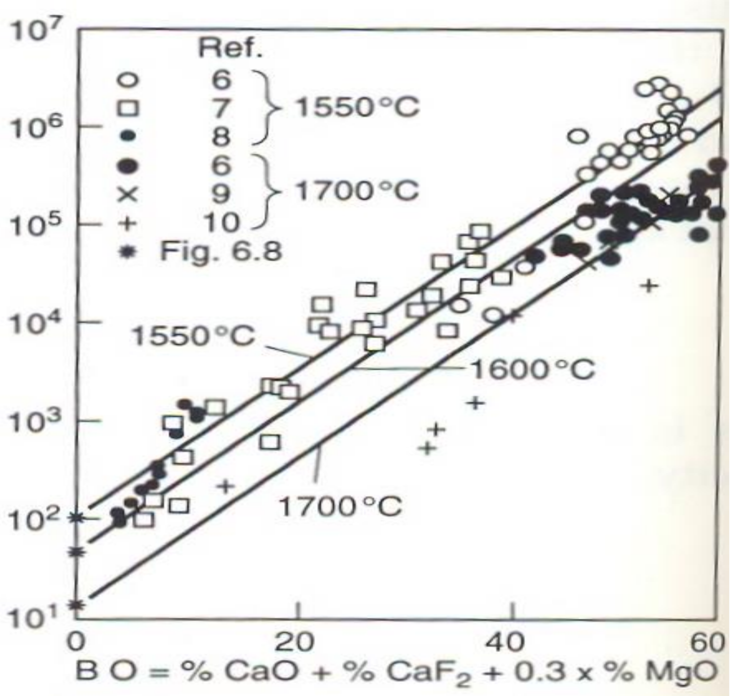

Figure 29.5: Phosphate capacity correlated against modified basicity [2]

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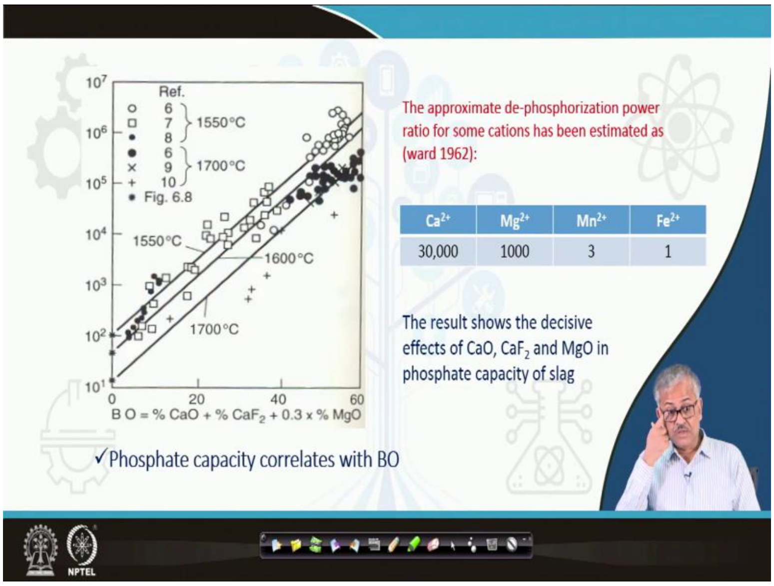

✓Phosphate capacity correlates with BO

The approximate de-phosphorization power ratio for some cations has been estimated as (ward 1962):

Ca^{2+}	Mg^{2+}	Mn^{2+}	Fe^{2+}
30,000	1000	3	1

The result shows the decisive effects of CaO, CaF_2 and MgO in phosphate capacity of slag

The approximate de-phosphorization power for some cations has been estimated by ward 1962, by separately equilibriating phosphorus oxidation reaction in presence of various cations, calculating their equilibrium constants and comparing those. This is presented in Table 29.1.

Table 29.1: Influence of various cations on De-phosphorization [3]

Ca^{2+}	Mg^{2+}	Mn^{2+}	Fe^{2+}
30,000	1000	3	1

The result shows the decisive effects of CaO, CaF_2 and MgO in phosphate capacity of the slag. The effect of MnO and FeO is also found to be negligible.

K_{PO} also holds a nice correlation with inverse of temperature (Figure 29.6).

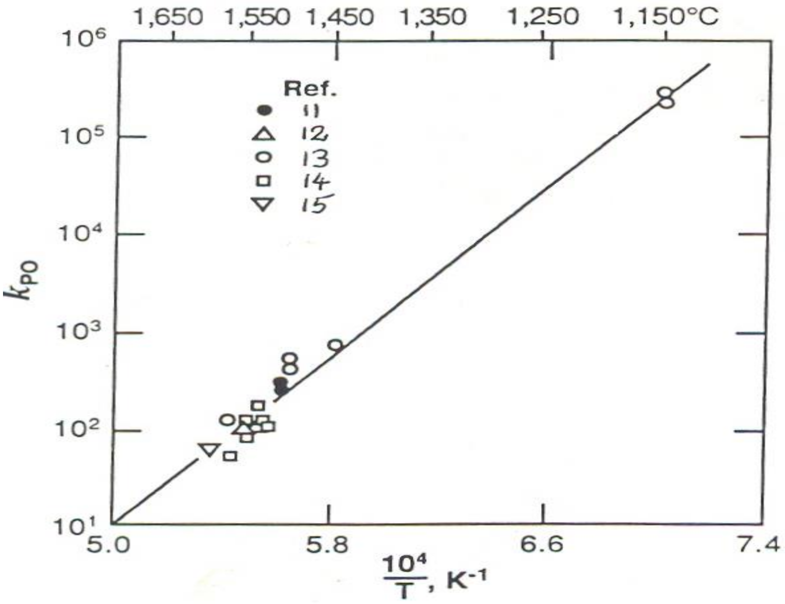

Figure 29.6: Variation of phosphate capacity with temperature [2]

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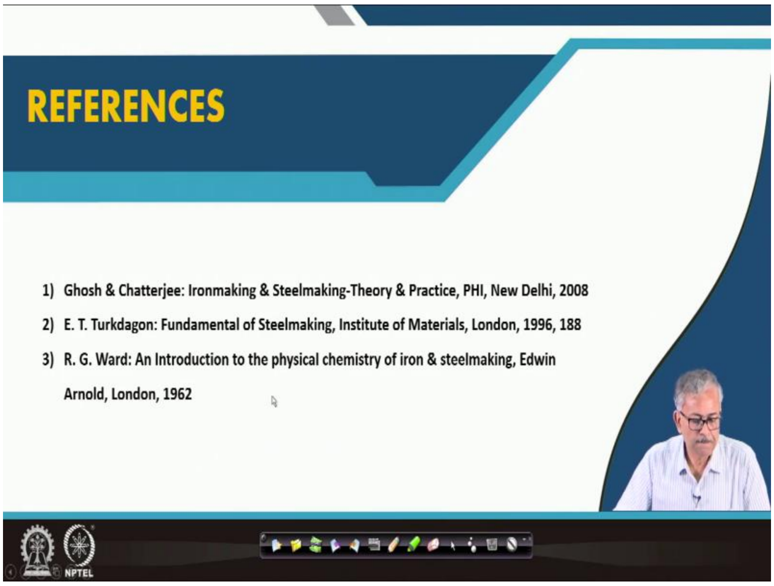

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1) Ghosh & Chatterjee: Ironmaking & Steelmaking-Theory & Practice, PHI, New Delhi, 2008
2) E. T. Turkdagon: Fundamental of Steelmaking, Institute of Materials, London, 1996, 188
3) R. G. Ward: An Introduction to the physical chemistry of iron & steelmaking, Edwin Arnold, London, 1962

Reference are given in the slide above. Another reference is missed that is given here: (4) R. H. Tupkary, An Introduction to Modern Steelmaking, Khanna Publishers, 1998, New Delhi

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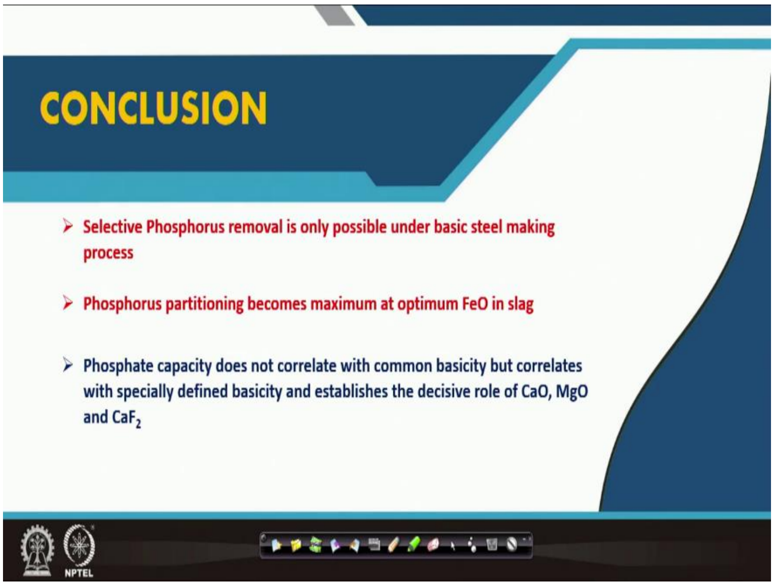

CONCLUSION

- Selective Phosphorus removal is only possible under basic steel making process
- Phosphorus partitioning becomes maximum at optimum FeO in slag
- Phosphate capacity does not correlate with common basicity but correlates with specially defined basicity and establishes the decisive role of CaO, MgO and CaF_2

Conclusion: Selective phosphorous removable is only possible under basic steel making condition. Selective removal carbon, manganese, and silicon is possible under acid making condition (without adding any external flux). Although, the basic slag favours the silicon removal that is different thing. But, removal of phosphorous in preference to iron is only possible using basic slag with flux (CaO) addition only.

Dephosphorization is favoured at high oxidation potential of the bath, higher basicity of slag and at lower temperature. Since FeO and CaO represent the oxidizing powder and basicity of the slag, and higher presence of one, dilutes the other; an optimum amount of FeO (15 wt% FeO in slag) has been found to maximize the phosphorus partitioning. A V-ratio of 4 maximize de-phosphorization at 15 wt% FeO in slag.

Phosphate capacity of slag that represents the holding capacity of phosphorus in slag, is normalized with respect to oxidizing power of the bath and is a function of slag composition and temperature. Phosphate capacity does not correlate with the common basicity, where all the basic oxides are considered to contribute equally to the basicity of the slag.

While, phosphate capacity perfectly correlates with a modified definition of basicity, where slag constituents like CaO and CaF_2 are given full weightage and MgO is also considered with 30% weightage; other basic oxides like MnO and FeO are not considered.

This follows from work of the Ward, who estimated the power of cations in slag, those are responsible for holding phosphorus in slag.