Iron Making and Steel Making

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Module – 07

Lecture – 33

LD Steelmaking: Evolution of Impurities in steel and slag Constituents during LD processing

In this lecture, I will discuss about the Evolution of impurities in steel as well as the slag constituents during LD processing.

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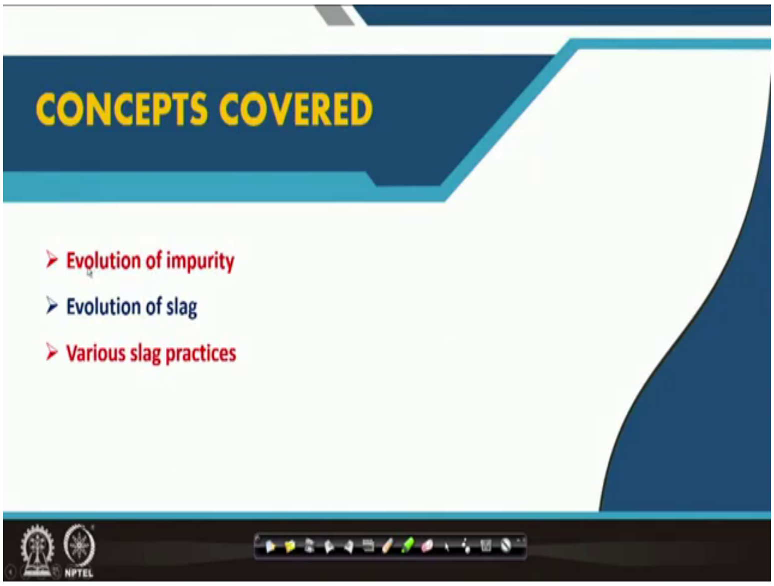

CONCEPTS COVERED

- Evolution of impurity
- Evolution of slag
- Various slag practices

So, the topics covered will include the evolution of impurity during LD steelmaking, followed by the evolution of various slag constituents and finally various slag practices to treat different hot metal of high and low phosphorus content.

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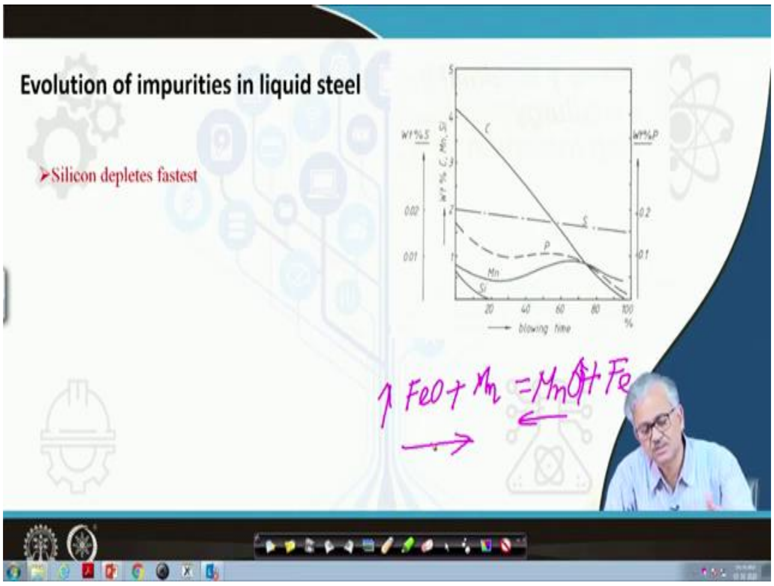

Evolution of impurities in liquid steel

- Silicon depletes fastest

↑ FeO + Mn = MnO + Fe

→ ←

Figure 33.1 depicts the evolution of impurities in liquid iron during LD steel making.

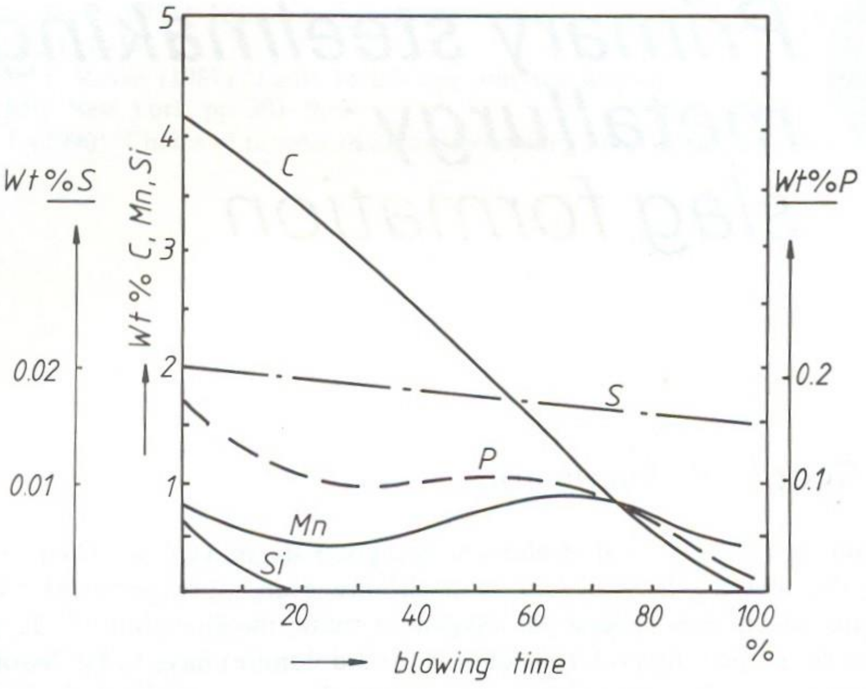

Figure 33.1 Typical evolution of various impurities in liquid iron during progress of oxygen blowing in the liquid bath [2]

x-axis represents the percentage of blowing, while total blowing time could be only 20 minutes. Weight percentage of phosphorus and Sulphur are given in two different y-scale. The main y-scale represents the percentage of C, Mn, and silicon.

The figure shows the typical evolution of the impurities during LD refining. It is found that silicon depletes the fastest and within 20 percent of blowing time (4 minutes) silicon goes down to zero almost; because silicon oxide is the most stable oxide and chemical potential for formation of the silicon oxide is very high. In fact, we showed by thermodynamic calculation that silicon can be reduced to less than 1 ppm into the steel under basic steel making condition; but because of kinetic limitation the silicon can be reduced to around 30 to 50 ppm; that means, 0.005 or 0.003 wt%.

Manganese decreases initially but it may also noted that at the later stage of blowing there is a reversion of manganese. Manganese is a unique impurity in the steel in the sense that it produces an oxide that is basic in nature. So, when the basic slag forms at later stage, activity of manganese oxide increases in the slag and it becomes unstable in the basic slag and reverts back to metal phase. As a result the manganese in the metal phase increases and shows a hump on its evolution curve. Thereafter, again manganese content in the metal bath decrease. At the later stage when most of the impurities have left the bath, the FeO content and the oxygen potential in the slag increases, which facilitates manganese oxidation, reducing the bath manganese content.

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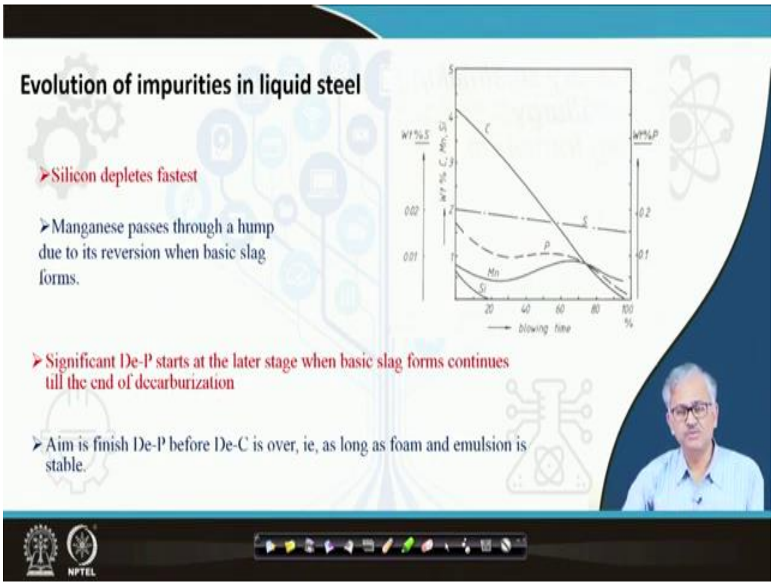

Evolution of impurities in liquid steel

- Silicon depletes fastest
- Manganese passes through a hump due to its reversion when basic slag forms.
- Significant De-P starts at the later stage when basic slag forms continues till the end of decarburization
- Aim is finish De-P before De-C is over, ie, as long as foam and emulsion is stable.

If you follow the evolution curve of phosphorus you may find an initial plateau and followed by a hill and then progressive decrease in its content in the liquid bath. Initial oxidation of phosphorus makes such plateau but phosphorus oxide does not become stable in absence of basic slag; temperature rise also makes it further unstable; and so phosphorus again reverts back to metal phase. But, by the time when FeO build-up in slag is high and temperature is also high; lime starts dissolving in the slag and form the basic slag. It may be noted that fine lime dissolves faster but lumpy lime stone dissolution is stopped in the initial period itself by the formation of solid adherent di-calcium silicate layer over the lumpy limestone. FeO helps in breaking the adherent silicate layer by forming low melting liquid product like $CaO\text{-}FeO\text{-}SiO_2$. Once basic slag forms de-phosphorization resumes in full potency and it continues progressively as long as emulsion is stable. The aim is to complete dephosphorization before emulsion collapse, or till decarburization continues; such that de-phosphorization could be carried out in emulsion phase most effectively.

Decarburization starts at the beginning and continues till the end of the refining. Therefore, to treat hot metal of different phosphorus content, blowing practice and slag evolution is tailored in such a way such that decarburization continues till all other impurities, especially phosphorus (which starts later in the process when basic slag forms) removal is complete.

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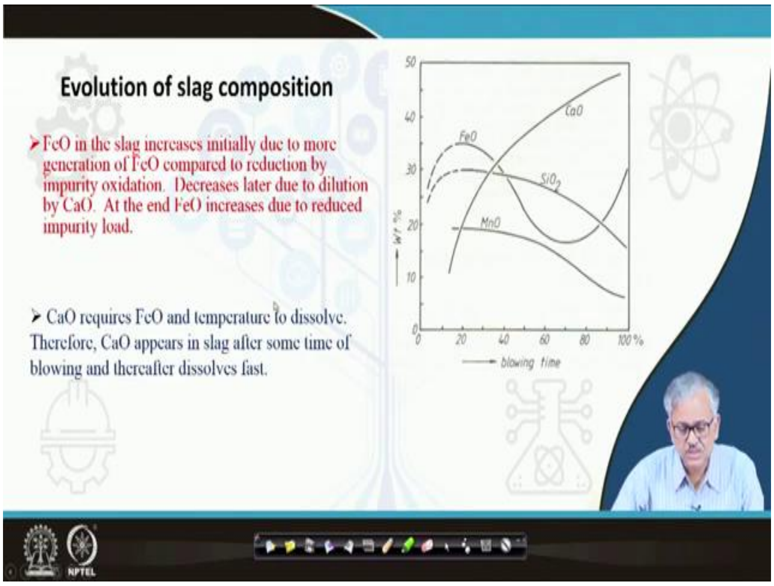


Evolution of slag composition

- FeO in the slag increases initially due to more generation of FeO compared to reduction by impurity oxidation. Decreases later due to dilution by CaO. At the end FeO increases due to reduced impurity load.

- CaO requires FeO and temperature to dissolve. Therefore, CaO appears in slag after some time of blowing and thereafter dissolves fast.

Figure 33.2 shows the evolution of the slag constituents with progress of blowing. As you can find that is the FeO initially increases and attains a maximum. As oxygen is charged in the bath, iron being the major constituents, by law of mass action, iron first get oxidized to FeO. Subsequently, impurity is transported from the bulk to the slag metal interface and it consumes FeO by forming more stable oxides. So initially FeO builds up in the slag. Since silicon is depletes first in the bath SiO_2 in the slag also increases in the bath initially.

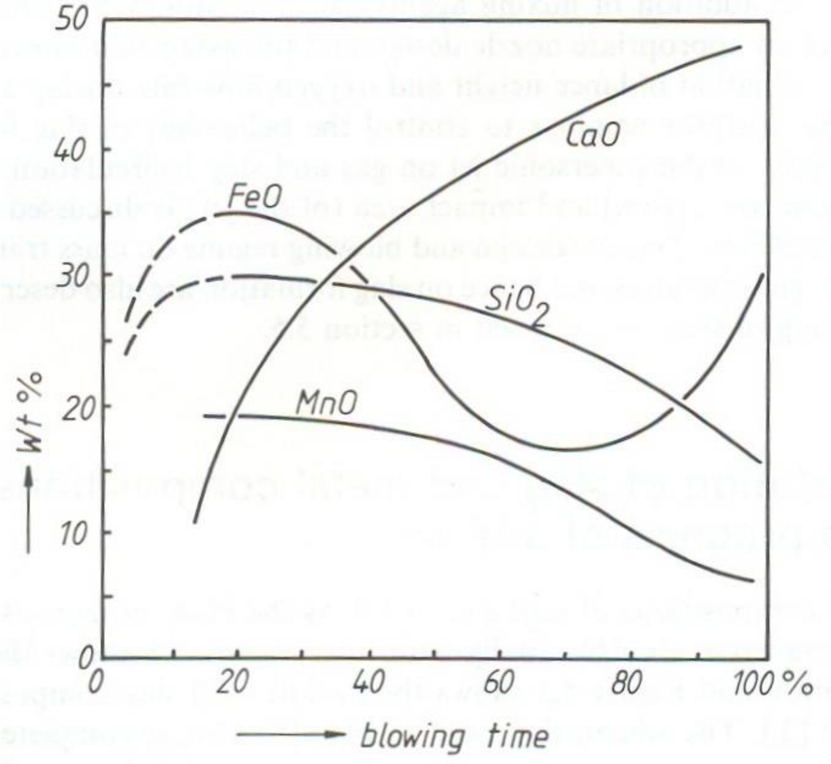
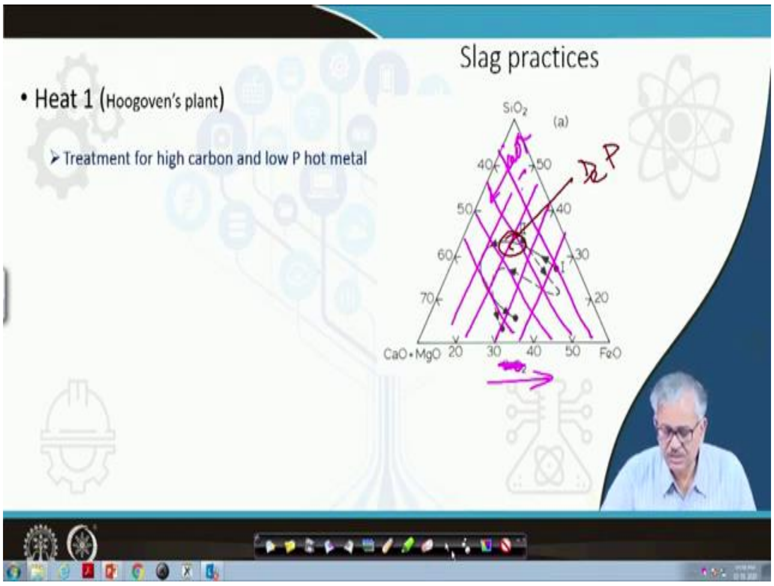


Figure 33.2: Evolution of slag constituents with progress of blowing[2]

After certain blowing of oxygen, when FeO is sufficient in the slag and temperature also high in the slag due to exothermic Si/Mn/C oxidation, then CaO start dissolving and its amount progressively increases. Then the other constituents of the slag like FeO, SiO_2, MnO starts decreasing due to dilution effect of CaO. Another reason for FeO decrease in the slag is due to addition of phosphorus load (in addition to the carbon load) as soon as basic slag forms and phosphorus starts transporting to the slag phase. In this period, rate of generation of FeO by oxygen charging fall short of the combined effect of phosphorus oxidation and dilution effect of lime dissolution, which results in FeO decrease in slag.

And, at the end of blowing period, FeO again starts increasing when the impurity load diminishes. (Refer Slide Time: 13:30)



Slag practices

- Heat 1 (Hoogoven's plant)
  - ➤ Treatment for high carbon and low P hot metal

So, now I will discuss about the slag practices used for treating hot metal of different composition. Figure 33.3 shows the evolution of slag composition in a ternary CaO-FeO-SiO_2 diagram, for two heats treating low and high phosphorus hot metal. Heat 1 represents a heat in Hoogoven's plant for treating low phosphorus hot metal (<0.1wt% P); while heat II represents a heat in Mannesmann plant for treating hot metal of high phosphorus (>1wt%) hot metal.

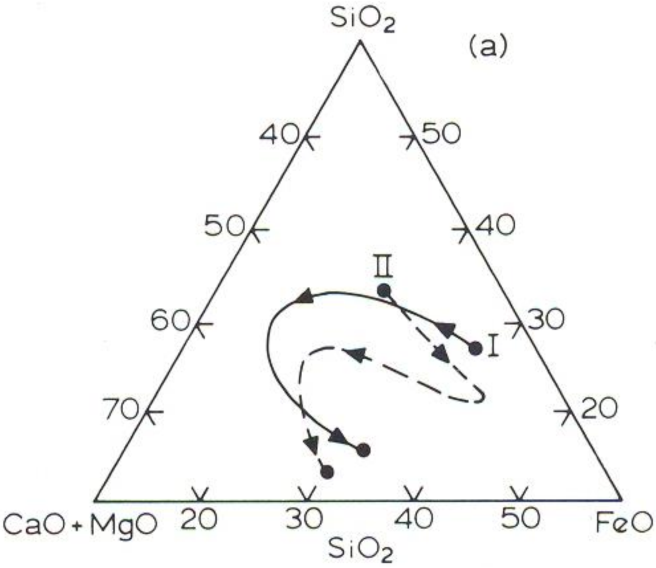


Figure 33.3: Evolution of slag constituents during two heats treating low and high phosphorus hot metal[1]

For low phosphorus hot metal we have lot of carbon in to the hot metal (~4wt%), but we have phosphorus at a very low level (<0.1 wt%). In this case, the slag practice represented by heat I is used. Since, phosphorus is very low and comparatively large carbon is available, we need not to bother about preservation of the carbon; rather we need to concern about removing the carbon from the beginning such that refining time does not prolong for carbon removal. So, we should start removing carbon from the beginning at moderate rate. After certain blowing period, when the basic slag forms, phosphorus will be removed in a short span of decarburization period, which will still persists even after all phosphorus is removed.

If you follow the slag evolution for heat-I, it is seen that the slag starts with large FeO, which can be achieved by adding mill scale. Large FeO at the start ensures faster decarburization from the beginning. Thereafter, along the slag curve, FeO decreases and both CaO, and SiO_2 in the slag increases, so also the basicity increases. Then dephosphorization starts. Subsequently again the FeO in the slag starts increasing as the phosphorus and carbon load is removed.

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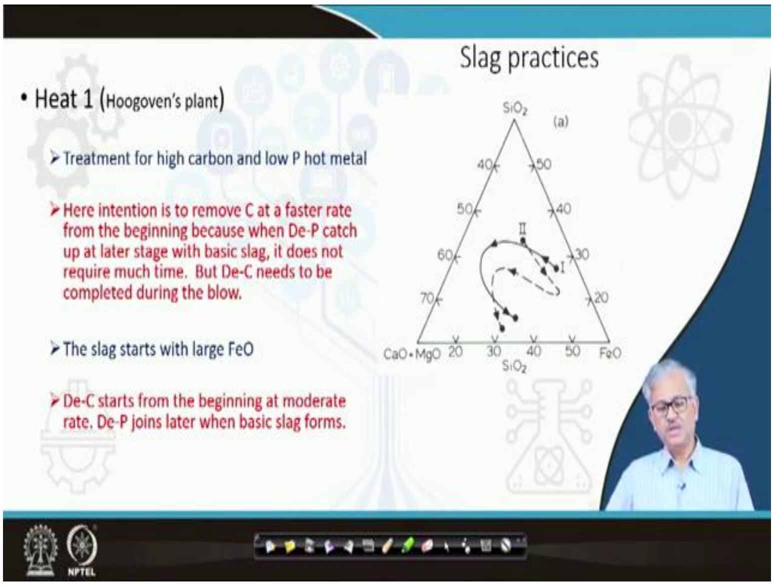

Slag practices

- Heat 1 (Hoogoven's plant)
  - Treatment for high carbon and low P hot metal
  - Here intention is to remove C at a faster rate from the beginning because when De-P catch up at later stage with basic slag, it does not require much time. But De-C needs to be completed during the blow.
  - The slag starts with large FeO
  - De-C starts from the beginning at moderate rate. De-P joins later when basic slag forms.

So, for heat I, the intention is to remove the carbon at a faster rate from the beginning because when dephosphorization catch up at the later stage with basic slag, it does not require much time; but decarburization needs to be completed simultaneously with the end phosphorus removal; otherwise it will prolong the refining period. So, heat I represents the standard slag practice when you have a low phosphorus in hot metal. Here we should not be concerned about the preserving the carbon because carbon is already very high and the phosphorus is very low.

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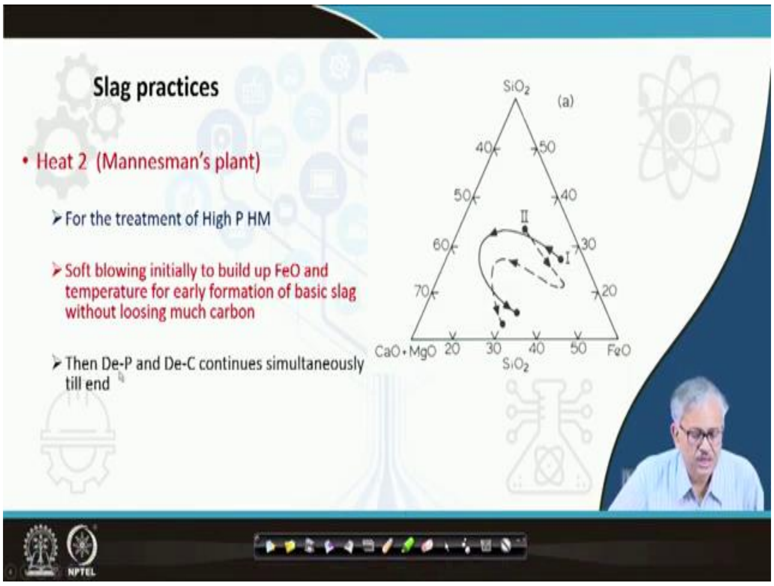

Slag practices

- Heat 2 (Mannesman's plant)
  - ➢ For the treatment of High P HM
  - ➢ Soft blowing initially to build up FeO and temperature for early formation of basic slag without loosing much carbon
  - ➢ Then De-P and De-C continues simultaneously till end

The heat 2 that is used in Mannesman's plant to treat hot metal hot metal with higher phosphorus (>1wt%). Since in this case phosphorus is very high from the beginning, then plant operator has to be very economic in consuming the carbon from the beginning of the heat.

If we follow the slag evolution for heat II, slag starts with comparatively low FeO (say 25%), where decarburization is comparatively low. It may be noted lime and silica are also present in the slag both to the tune of 40%. Subsequently, the slag enriches in FeO, with decrease in SiO_2 and CaO (due to dilution effect of FeO increase). FeO build up in the slag can be achieved by soft blow practice, where JFN is decreased or, lance is moved up to reduce the partial pressure of oxygen on the bath that decreases decarburization rate and allows smooth build-up of FeO in the slag, and temperature through impurity oxidation. Thereafter, CaO starts dissolving in the slag with a corresponding decrease in FeO (due to dilution effect of CaO and impurity oxidation). Slight increase in SiO_2 might be due to fresh silicon oxidation under basic slag. When the basic slag forms, the lance is lowered, to carry out both decarburization and dephosphorization simultaneously at moderate rate and FeO further decreases. At the end of blow again the curve turns showing increase in FeO in slag when the impurity load diminishes. (Refer Slide Time: 29:52)

REFERENCES

1) E. T. Turkdagon: Fundamental of Steelmaking, Institute of Materials, London, 1996, 188
2) Ghosh & Chatterjee: Ironmaking & Steelmaking PHI, New Delhi, 2008.
3) H. S. ray: Introduction to melts, molten salts, slag & glasses, Allied publishes Pvt. Ltd., Kolkata, 2006

References are marked in the slide above. Please ignore reference 3 for this lecture.

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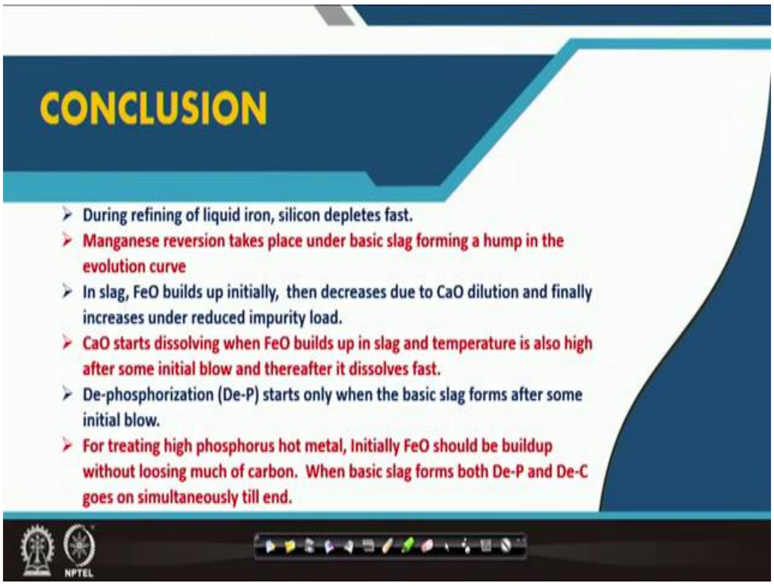

CONCLUSION

- During refining of liquid iron, silicon depletes fast.
- Manganese reversion takes place under basic slag forming a hump in the evolution curve
- In slag, FeO builds up initially, then decreases due to CaO dilution and finally increases under reduced impurity load.
- CaO starts dissolving when FeO builds up in slag and temperature is also high after some initial blow and thereafter it dissolves fast.
- De-phosphorization (De-P) starts only when the basic slag forms after some initial blow.
- For treating high phosphorus hot metal, Initially FeO should be buildup without loosing much of carbon. When basic slag forms both De-P and De-C goes on simultaneously till end.

Conclusion: During the refining of liquid iron, silicon depletes at fastest rate within first 4-5 minutes. Manganese evolution curve shows a hump of manganese reversion when basic slag forms. Reasonable phosphorus removal only starts when the basic slag forms after certain period of blowing. Decarburization starts from the beginning and continues till the end of refining.

In slag, FeO builds up initially and then decreases due to CaO dilution and finally, again increases when impurities in the bath is reduced significantly. And, CaO start dissolving after certain period of blowing when when temperature and FeO in the slag is high.

Dephosphorization is delayed due delay in formation of basic slag. Since decarburization need to continue till the end of the refining to ensure emulsion; for treating the high phosphorus hot metal, judicious and economic use of carbon from the beginning is essential. The slag evolution and blowing practice should ensure carbon conservation till end of refining. When phosphorus load in hot metal is low then care should be taken such that refining period is not prolonged for carbon removal.