Iron Making and Steel Making
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Module – 09
Lecture – 42
Injection Metallurgy: Submerged injection of calcium powder

In this lecture we will discuss the Injection Metallurgy that is the submerged injection of the calcium powder.

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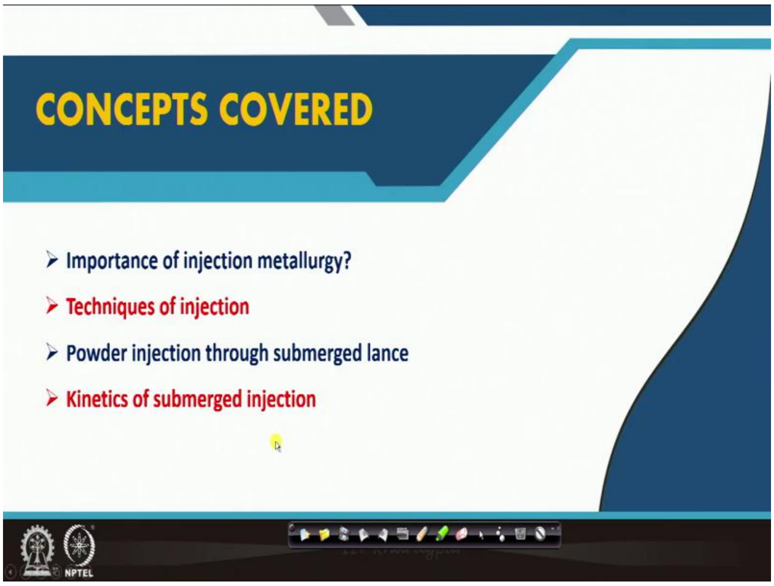

CONCEPTS COVERED

- Importance of injection metallurgy?
- Techniques of injection
- Powder injection through submerged lance
- Kinetics of submerged injection

The topics covered are importance of the powder injection, different techniques of powder injection, powder injection through submerged lance, and kinetics of submerged injection.

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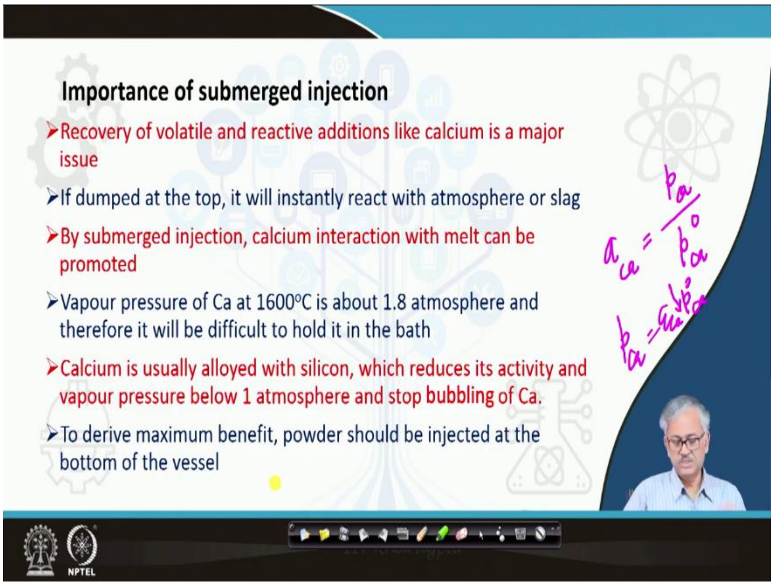

Importance of submerged injection

- Recovery of volatile and reactive additions like calcium is a major issue
- If dumped at the top, it will instantly react with atmosphere or slag
- By submerged injection, calcium interaction with melt can be promoted
- Vapour pressure of Ca at 1600°C is about 1.8 atmosphere and therefore it will be difficult to hold it in the bath
- Calcium is usually alloyed with silicon, which reduces its activity and vapour pressure below 1 atmosphere and stop bubbling of Ca.
- To derive maximum benefit, powder should be injected at the bottom of the vessel

$$a_{ca} = \frac{p_{ca}}{p^0_{ca}}$$

$$p_{ca} = a_{ca} p^0_{ca}$$

Importance of submerged injection: By this time we know that calcium powder injection in liquid steel serve several interesting purposes like deep deoxidation, desulphurization, inclusion removal and inclusion modification. And the recovery of the volatile and the reactive addition like calcium is a major issue. If calcium is dumped at the top of liquid metal, it will instantaneously react with the atmosphere and the slag as it is very reactive and its yield to metal phase will be zero. So, calcium need to be injected by submerged injection techniques.

Secondly, vapour pressure of calcium at 1600°C is around 1.8 atmosphere that is much above that 1 atmospheric pressure. So, pure calcium will form bubble in liquid steel, float to the top and then escape to the atmosphere. So, it is very difficult to retain the calcium even if pure calcium is injected through submerged injection. Therefore, calcium usually injected in the form of an alloy; either as the calcium silicide, or calcium ferrite. When calcium is alloyed, then activity of calcium in the alloy reduces, decreasing its vpour pressure (if activity of calcium in alloy is 0.5 then its vapour pressure will be 0.9 atm) and restricting its quick escape as bubble; subsequently, its assimilation in liquid will increase increasing its yield in metal. To derive the maximum benefit, powder should be injected at the bottom of the vessel, where the pressure is higher; besides calcium powder gets more residence time for its assimilation.

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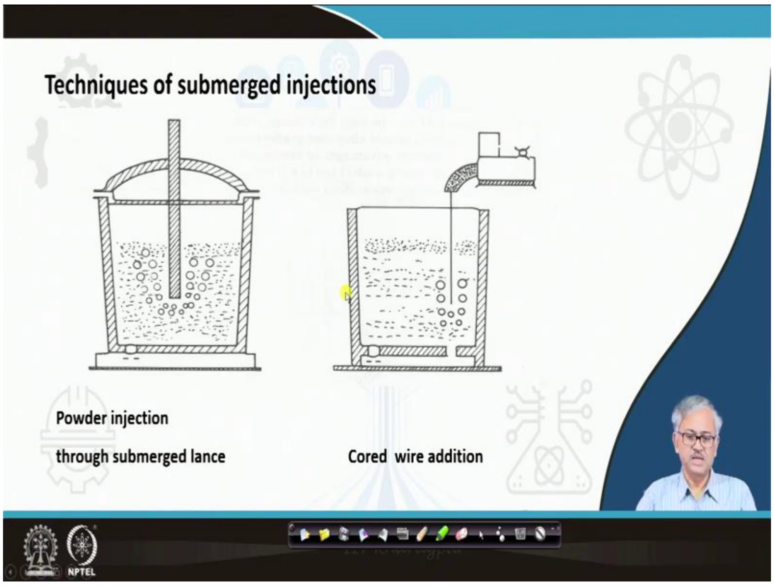

Techniques of submerged injections

Powder injection through submerged lance

Cored wire addition

There are two techniques of submerged injection: (i) powder injection through submerged lance, (ii) through cored wire injection. In case of former, calcium powder is injected deep in the bath through submerged lance and inert gas like argon is used as carrier gas for the powder. The powder during their rise through melt react with the liquid metal and finally joins the slag. In case of later, a hollow cylindrical mild steel wire packed with calcium powder, called the cored wire, is injected into steel melt and when the wire melts deep into the bath the powder get released.

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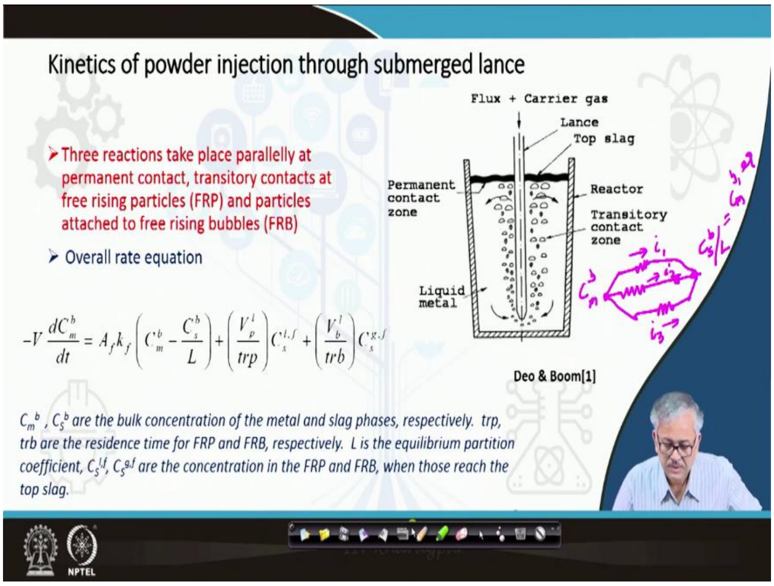

Kinetics of powder injection through submerged lance

- Three reactions take place parallelly at permanent contact, transitory contacts at free rising particles (FRP) and particles attached to free rising bubbles (FRB)
- Overall rate equation

$$-V\frac{dC_m^b}{dt} = A_f k_f\left(C_m^b - \frac{C_s^b}{L}\right) + \left(\frac{V_p^l}{trp}\right)C_s^{l.f} + \left(\frac{V_b^l}{trb}\right)C_s^{g.f}$$

Deo & Boom[1]

C_m^b, C_S^b are the bulk concentration of the metal and slag phases, respectively. trp, trb are the residence time for FRP and FRB, respectively. L is the equilibrium partition coefficient, $C_S^{l.f}$, $C_S^{g.f}$ are the concentration in the FRP and FRB, when those reach the top slag.

Kinetics of powder injection: There are three modes of reaction by which powder after being released in liquid metal will participate in impurity transfer. A fraction of powder after entering into liquid would melt, form liquid droplet and rise as free rising particles (FRP). Another fraction might attach with the spherical cap bubble as particle inside the bubble (PIB). Reaction kinetics at all interfaces are mass transfer controlled and will depend on the mass transfer coefficient at the powder/slag-liquid metal interfaces.

Reactions at FRP and PIB are called the transitory contacts because impurity transfer from metal to powder particle takes place during their ascent through the melt till particles join the top slag. Reaction at the top slag metal interface is called permanent contact. And these reactions take place simultaneously and parallelly. So, overall rate will be the summation of three rates at FRP, PIB and at top slag-metal interface. An electrical analogy is shown in the slide above. The overall mass balance may be expressed mathematically as:

$$-V\,\frac{dC_m^b}{dt} = A_f k_f\left(C_m^b - \frac{C_s^b}{L}\right) + \left(\frac{V_p^l}{trp}\right)C_s^{l,f} + \left(\frac{V_b^l}{trb}\right)C_s^{g,f} \tag{42.1}$$

The term of LHS represents the rate of transfer of impurity (kg/s) from metal to the slag phase. The three terms on RHS represents rate of impurity transfer through permanent contact, FRP and PIB, respectively. Where, V is the volume of the liquid bath, C_m^b, C_S^b are the bulk concentration of impurity in the metal and slag, respectively. $C_S^{l,f}, C_S^{g,f}$ are the concentration of impurity in slag phase when the FRP and PIB reaches the top slag, respectively. V_P^l, V_b^l are the volume of FRP and PIB, respectively. $\frac{C_S^b}{L}$ represent the equilibrium concentration in the metal phase corresponding to instantaneous slag bulk composition, C_S^b .

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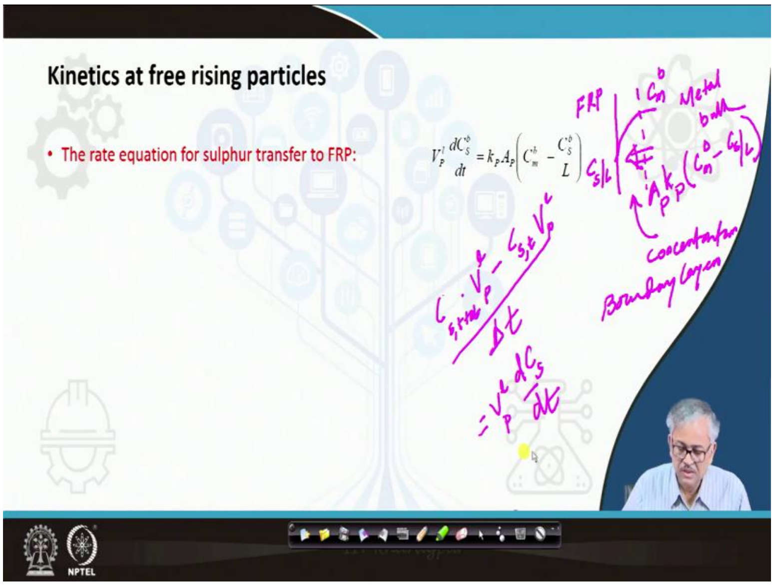

Kinetics at free rising particles

- The rate equation for sulphur transfer to FRP:

$$V_P^l \frac{dC_S^b}{dt} = k_P A_P \left(C_m^b - \frac{C_S^b}{L} \right)$$

FRP

C_m^b Metal bath

$C_{S|L}$

$A_P k_P (C_m^b - C_{S|L})$

concentration Boundary layer

$$\frac{C_{S,t+\Delta t} V_P^l - C_{S,t} V_P^l}{\Delta t} = V_P^l \frac{dC_S}{dt}$$

Calculation of $C_S^{l,f}$, and $C_S^{g,f}$:

First consider the concentration of impurity in FRP as it reaches the top slag, $C_C^{l,f}$.

The mass balance equation in FRP may be written as:

$$V_P^l \frac{dC_S^b}{dt} = k_P A_P \left(C_m^b - \frac{C_S^b}{L} \right) \tag{42.2}$$

The LHS term indicate the amount of impurity transferred to FRP per unit time. The RHS represent the amount of impurity that crosses the concentration boundary layer around FRP per unit time. k_P, A_P represent the first order mass transfer coefficient and the area at the FRP and liquid interface, respectively. L represent the equilibrium partition coefficient of the impurity between metal and slag.

The equation (42.2) may be integrated over the time of rise of FRP (trp):

$$\int_{0}^{C_S^{l,f}} \frac{dC_S^b}{\left(C_m^b - \frac{C_S^b}{L}\right)} = \frac{k_P A_P}{V_P^l} \int_{0}^{trp} dt$$

(42.3)

Assuming concentration of impurity in metal bulk does not change during the rise of FRP through it (as FRP is a miniscule amount considering the large metal mass), the final integral of this equation may be given as:

$$C_S^{l.f} = LC_m^b \left[1 - e^{\left(-\frac{A_P k_P}{L V_P^l} trp \right)} \right]$$

(42.4)

Similarly, the concentration of impurity in PIB as it joins the final slag at top, $C_S^{g,f}$, may be given as:

$$C_S^{g.f} = LC_m^b \left[1 - e^{\left(-\frac{A_g k_g}{L V_P^g} trb \right)} \right]$$

(42.5)

Where, k_g, A_g represent the mass transfer coefficient and area at the PIB liquid interface, respectively.

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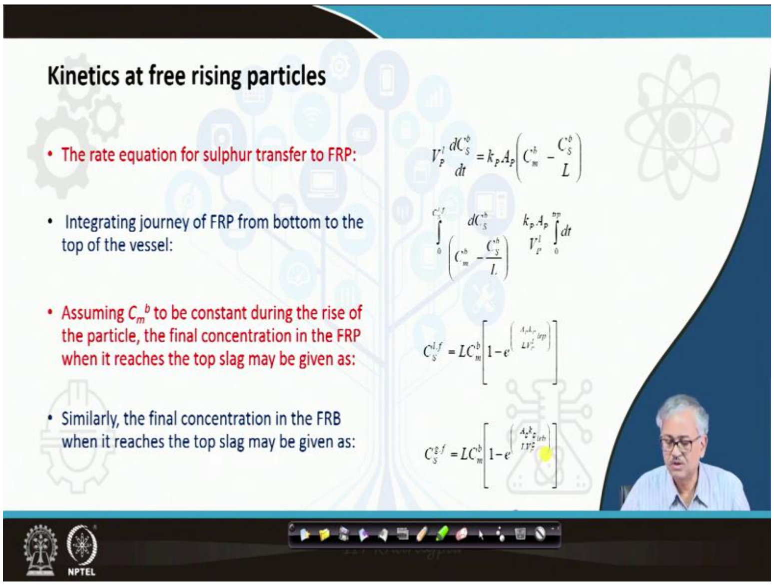

Kinetics at free rising particles

- The rate equation for sulphur transfer to FRP: $V_P^l \frac{dC_S^b}{dt} = k_p A_p \left(C_m^b - \frac{C_S^b}{L} \right)$
- Integrating journey of FRP from bottom to the top of the vessel: $\int_0^{C_S^{l,f}} \frac{dC_S^b}{\left(C_m^b - \frac{C_S^b}{L} \right)} \quad \frac{k_p A_p}{V_P^l} \int_0^{trp} dt$
- Assuming C_m^b to be constant during the rise of the particle, the final concentration in the FRP when it reaches the top slag may be given as: $C_S^{l,f} = LC_m^b \left[1 - e^{\left(\frac{A_p k_p \, trp}{LV_P^l} \right)} \right]$
- Similarly, the final concentration in the FRB when it reaches the top slag may be given as: $C_S^{g,f} = LC_m^b \left[1 - e^{\left(\frac{A_g k_g \, trb}{LV_P^g} \right)} \right]$

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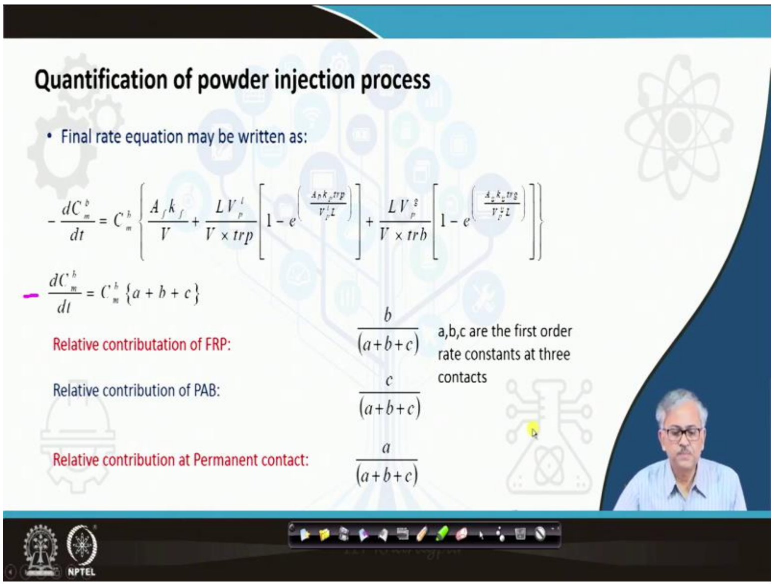

Quantification of powder injection process

- Final rate equation may be written as:

$$-\frac{dC_m^b}{dt} = C_m^b \left\{ \frac{A_f k_f}{V} + \frac{LV_p^l}{V \times trp} \left[1 - e^{\left(\frac{A_P k_p trp}{V_p^l L} \right)} \right] + \frac{LV_p^g}{V \times trb} \left[1 - e^{\left(\frac{A_g k_g trg}{V_p^g L} \right)} \right] \right\}$$

$$-\frac{dC_m^b}{dt} = C_m^b \{a + b + c\}$$

Relative contributation of FRP: $\frac{b}{(a+b+c)}$

Relative contribution of PAB: $\frac{c}{(a+b+c)}$

Relative contribution at Permanent contact: $\frac{a}{(a+b+c)}$

a,b,c are the first order rate constants at three contacts

The final rate equation may be given as:

$$-V\frac{dC_m^b}{dt} = C_m^b \left\{ A_f k_f + \frac{LV_p^l}{trp} \left[1 - e^{\left(-\frac{A_P k_p trp}{V_p^l L} \right)} \right] + \frac{LV_p^g}{trb} \left[1 - e^{\left(-\frac{A_g k_g trg}{V_p^g L} \right)} \right] \right\}$$
$$= C_m^b \{a + b + c\}$$

(42.6)

Where, k_f, and A_f represent the mass transfer coefficient and the reaction area at the top slag metal interface, respectively. It may be also noted that the equation gas been written in terms of three first order rate constants at three interfaces, where “a” represent the first order rate constant at the permanent contact zone (top slag/metal interface) and “b”, “c” represent the first order mass transfer rate constants at FRP and PIB interface (transitory contacts), respectively.

Therefore, $\frac{a}{(a+b+c)}$ represents the relative contribution of permanent contact zone to the overall reaction. Similarly, $\frac{b}{(a+b+c)}$ and $\frac{c}{(a+b+c)}$ represent the relative contribution of FRP and PIB, respectively.

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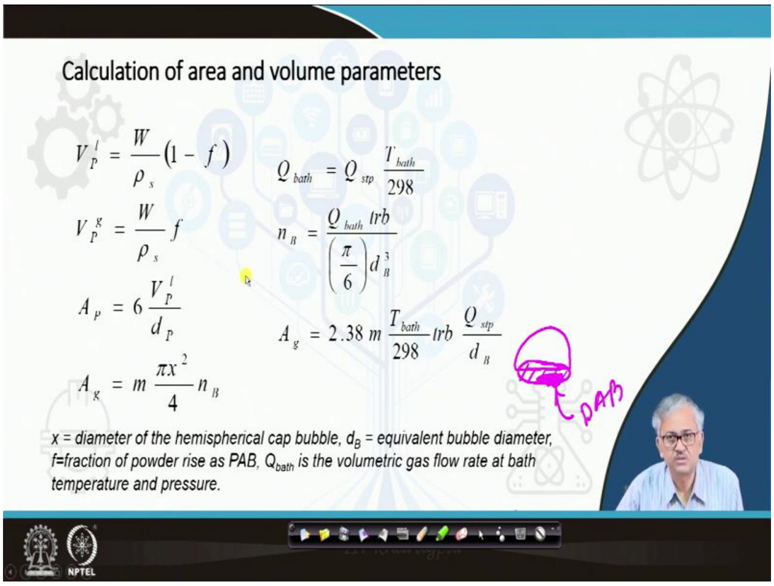

Calculation of area and volume parameters

$$V_P^l = \frac{W}{\rho_s}(1-f)$$

$$V_P^g = \frac{W}{\rho_s} f$$

$$A_P = 6\frac{V_P^l}{d_P}$$

$$A_g = m\frac{\pi x^2}{4} n_B$$

$$Q_{bath} = Q_{stp}\frac{T_{bath}}{298}$$

$$n_B = \frac{Q_{bath}\, trb}{\left(\frac{\pi}{6}\right) d_B^3}$$

$$A_g = 2.38\, m \frac{T_{bath}}{298} trb \frac{Q_{stp}}{d_B}$$

PAB

x = diameter of the hemispherical cap bubble, d_B = equivalent bubble diameter, f=fraction of powder rise as PAB, Q_{bath} is the volumetric gas flow rate at bath temperature and pressure.

Calculation of area and volume parameters:

The volume of FRP $\left(V_P^l\right)$, PIB $\left(V_P^g\right)$, reaction area around FRP (A_P) and PIB (A_g) may be calculated as follows:

$$V_P^l = \frac{W}{\rho_s}(1 - f)$$

$$V_P^g = \frac{W}{\rho_s} f$$

$$A_P = 6\frac{V_P^l}{d_P}$$

$$A_g = m\frac{\pi x^2}{4} n_B$$

$$Q_{bath} = Q_{stp}\frac{T_{bath}}{298}$$

$$n_B = \frac{Q_{bath} trb}{\left(\frac{\pi}{6}\right) d_B^3}$$

$$A_g = 2.38m\frac{T_{bath}}{298} trb \frac{Q_{stp}}{d_B}$$

(42.7)

Where, W is the mass of powder injected. F represents the fraction of particle at rises as PIB. ρ_S represents the powder density, dp represents the FRP diameter, x is the diameter of spherical cap bubble at the base, m is the fraction of the base area of spherical cap bubble occupied by the powder particles, and n_B is the number of bubbles. T_{bath} represents the liquid bath temperature.

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REFERENCES

1) Deo & Boom: Fundamental of steelmaking metallurgy, PHI, NY, 1993

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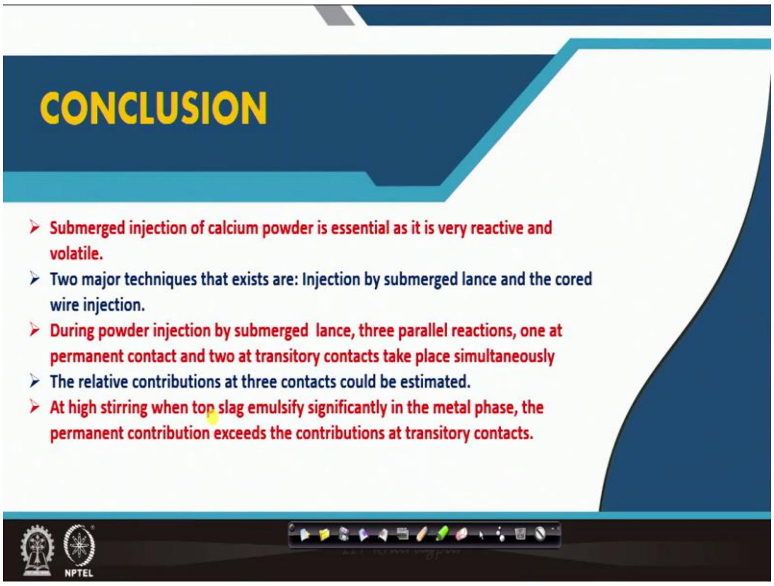

CONCLUSION

- Submerged injection of calcium powder is essential as it is very reactive and volatile.
- Two major techniques that exists are: Injection by submerged lance and the cored wire injection.
- During powder injection by submerged lance, three parallel reactions, one at permanent contact and two at transitory contacts take place simultaneously
- The relative contributions at three contacts could be estimated.
- At high stirring when top slag emulsify significantly in the metal phase, the permanent contribution exceeds the contributions at transitory contacts.

Conclusions: Submerged injection of calcium powder is essential, which is very reactive and volatile.

Two major techniques: powder injection by submerged lance using inert carrier gas and the cored wire injection. In cored wire injection, a hollow cylindrical wire packed with calcium powder is injected into liquid melt, which subsequently release the powder deep in the bath after the wire melts. .

During the powder injection by submerged lance, three parallel reaction take place simultaneously. First is at the permanent contact of top slag metal interface and two in the transitory contacts; one is at the FRP(free rising particle)-liquid interface and the other is at the PIB (particle inside the bubble)-liquid interface, parallelly. So, the total rate of the reaction is a combination of these three rates. The overall reaction rate may be expressed as in terms of first order mass transfer rate constants at FRP, PIB and top slag-liquid metal interfaces.

At mild stirring the transitory contact contribution become more than that of the permanent contact contribution, but when the intensity stirring is high when the top slag get emulsified into the metal and permanent contribution could be far exceeds the transitory contribution. But strong stirring as discussed in previous lecture, may contaminate the bath through slag eye opening.