Iron Making and Steel Making
Prof. Gour Gopal Roy
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Module – 06
Lecture - 30
Kinetics of slag metal reaction

In this lecture I will discuss about the Kinetics of slag metal reaction.

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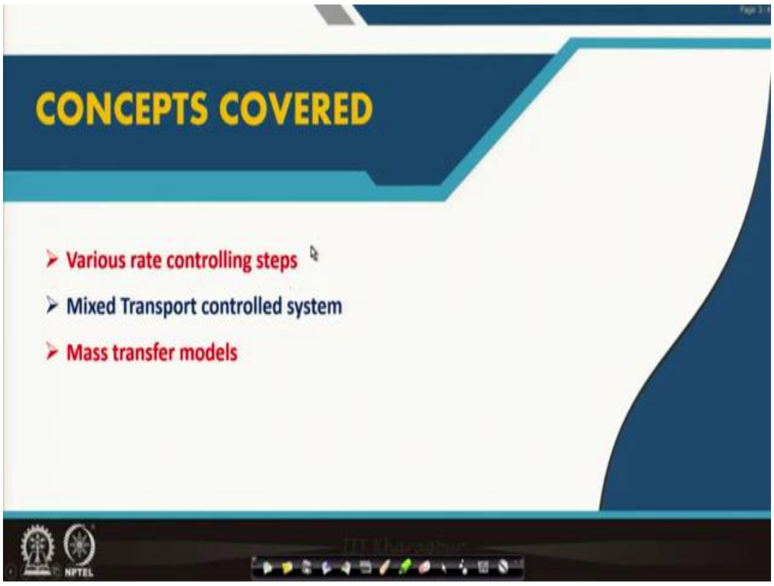

CONCEPTS COVERED

- Various rate controlling steps
- Mixed Transport controlled system
- Mass transfer models

Topics that will covered are various rate controlling steps of slag-metal reaction, mixed transport controlled system and some of the mass transfer models.

For heterogeneous slag metal reaction, the kinetics steps involved are: i) transport of the species through metal side concentration boundary layer, chemical reaction at the surface, transport of species through slag side concentration boundary layer.

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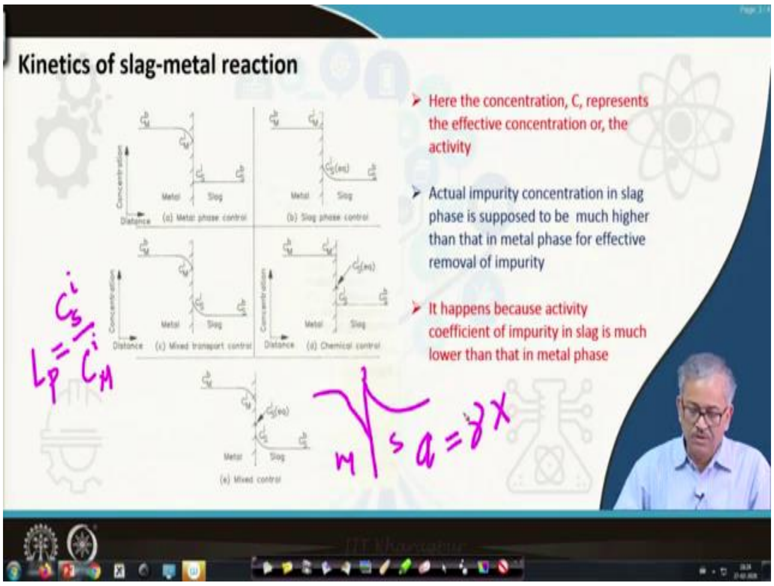

Kinetics of slag-metal reaction

- Here the concentration, C, represents the effective concentration or, the activity
- Actual impurity concentration in slag phase is supposed to be much higher than that in metal phase for effective removal of impurity
- It happens because activity coefficient of impurity in slag is much lower than that in metal phase

$L_p = C_S^i / C_M^i$

M | S $a = \gamma x$

Figure 30.1 shows the various concentration profiles under different rate controlling steps for slag-metal reaction.

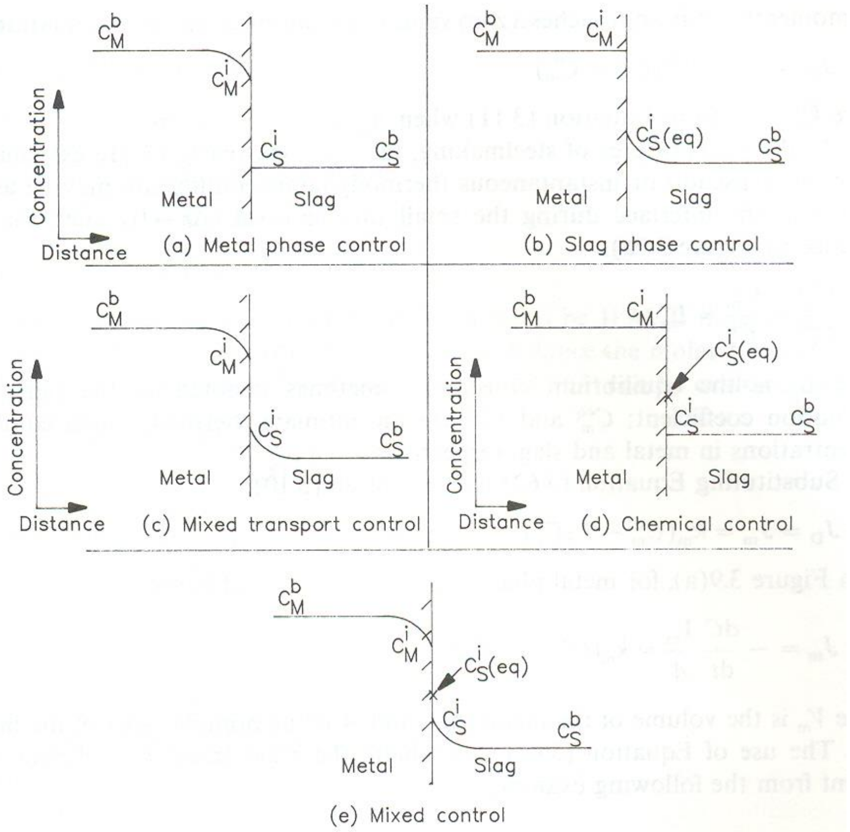

Figure 30.1: Concentration profile under different rate controlling steps for slag metal reaction

"C" represents the effective concentration, or the activity of the transporting species. Figure 30.1(a) depicts the concentration profile for metal phase mass transfer control. It is observed that there exists concentration gradient on the metal side boundary layer only; in other words, major resistance for the overall reaction lies on the metal side mass transfer. All other kinetic steps like chemical reaction at the slag-metal interface and slag phase mass transfer are quite fast. As a result the interface attains equilibrium partitioning instantaneously and no concentration gradient on the slag phase. The overall reaction rate may be calculated by the rate at which species is transported through the concentration boundary layer on the metal side.

Similarly, if the reaction is slag phase mass transfer controlled (figure 30.1(b)), there exists concentration gradient only on the slag side concentration boundary layer; and the overall slag metal reaction may be calculated by the rate at which species gets transported through the slag side boundary layer.

Figure 30.1(c) represents a mixed transport controlled reaction, where resistance lies both in the metal as well as in the slag phase, as indicated by the existence of concentration boundary layers both on the metal and slag side.

Figure 30.1(d) represents a case when the overall reaction is controlled by chemical reaction at the interface. All transport steps on the metal and slag sides are comparatively faster as indicated by absence of concentration gradients on the metal and slag side.

Figure 30.1(e) represents a case when the reaction is mixed controlled. It may be noted that concentration gradients exists both on the metal as well as on the slag side. Also equilibrium is not attained at the interface. The slag phase concentration at the interface$\left(C_S^i\right)$ remains much below it equilibrium value$\left(C_{S,eq}^i\right)$. Here the rate of reaction can be obtained by adding all resistance in series.

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It may be noted that all the concentrations shown in the figure (30.1) represent the effective concentration or activity of the species. Species transport always takes place downhill the chemical potential gradient or the activity gradient. However, transport of species uphill the concentration gradient is also possible. For example, in slag metal reaction, where the species concentration is higher on slag side compared to that on the metal side; but species transport takes place from metal side to slag side. It could be realized from the fact that the equilibrium partition coefficient of species (ratio of the concentration of species in the slag phase to that in the metal phase) could be as high as 100, during slag metal reaction in steelmaking. This is due to the fact that the activity coefficient of the species in the slag phase is lowered significantly by forming strong compounds with flux, which reduces its activity much below that of the metal phase, as indicated in the figure (30.1).

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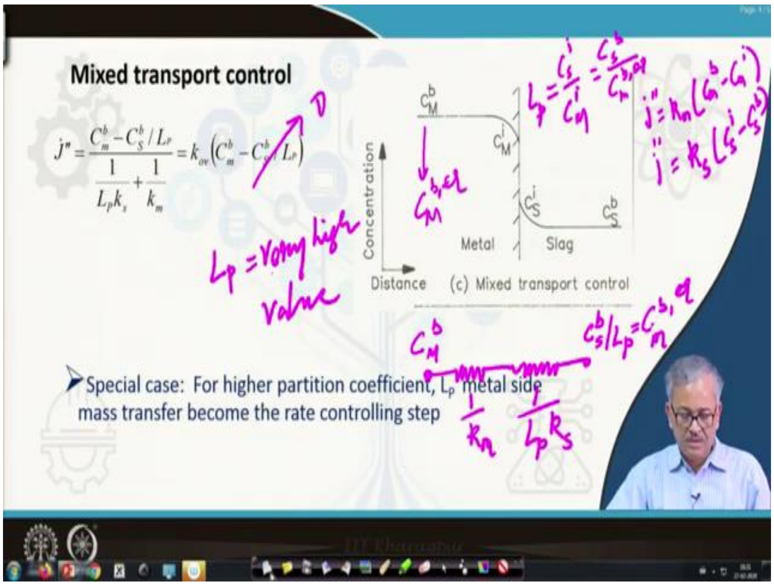

Mixed transport control

$$j'' = \frac{C_m^b - C_S^b / L_P}{\frac{1}{L_p k_s} + \frac{1}{k_m}} = k_{ov}\left(C_m^b - C_S^b / L_P\right)$$

L_p = very high value

$L_p = \frac{C_S^i}{C_M^i} = \frac{C_S^b}{C_m^{b,eq}}$

$j'' = k_m(C_m^b - C_m^i)$

$j'' = k_s(C_S^i - C_S^b)$

$C_S^b / L_p = C_m^{b,eq}$

➤ Special case: For higher partition coefficient, L_P metal side mass transfer become the rate controlling step

Due to high temperature during steelmaking, chemical reaction at the interface may be considered fast and the reaction is likely to be influenced by species transport through the concentration boundary layers either on the metal or, on the slag side, ot both. For a situation where mass transfer both of the metal side as well as slag side control the overall reaction is represented by figure 30.1(c).

In this situation, under steady state, the species flux crossing the metal side boundary layer (J''_m) should be equal to the flux on the slag side boundary layer (J''_S). Such fluxes could be expressed by equations (30.1) & (30.2).

$$J''_m = k_m\left(C_m^b - C_m^i\right)$$

(30.1)

$$J''_S = k_S\left(C_S^b - C_S^i\right)$$

(30.2)

Where, k_m and k_S represent the mass transfer coefficients on the metal side and slag side boundary layers, respectively. C represent the concentration of the species in metal/slag phases. Subscripts m and S represent the metal and slag phases, respectively. Superscripts b and i represent the bulk phase and slag-metal interface, respectively.

Noting the partition coefficient (L_P), defined by equation (30.3), and equating the fluxes given by (30.1) and (30.2), the overall rate of the reaction may be expressed as two resistance in series, as shown by equation (30.4).

$$L_P = \frac{C_m^i}{C_S^i}$$

(30.3)

$$J'' = \frac{\left(C_m^b - \frac{C_S^b}{L_P}\right)}{\left(\frac{1}{L_P.k_S} + \frac{1}{k_m}\right)}$$

(30.4)

Usually, L_P is quite high for impurities during steel making. Therefore, the first term on the denominator, representing the resistance in the slag phase concentration boundary layer may be ignored. Then the overall reaction is controlled by mass transfer on the metal side. Now making a mass balance on the metal phase (i.e., the equating the rate of transfer of impurity from metal phase to the rate of transfer of impurity crossing the slag metal interface, as represented by equation (30.5)), the mass balance equation may be represented by the equation (30.6):

$$V_m \frac{dC_m^b}{dt} = k_m A\left(C_m^b - \frac{C_S^b}{L_P}\right)$$

(30.5)

Where, *V_m* and *A* represents the metal volume and slag metal interfacial area, respectively.

Integrating the equation (30.6), with respect to time, we get,

$$ln\left(\frac{\left(C_m^b - \frac{C_S^b}{L_P}\right)}{\left(C_m^0 - \frac{C_S^b}{L_P}\right)}\right) = k't$$

(30.6)

Where, k'represent the volumetric mass transfer coefficient, or the mass transfer rate constant (/s), defined as equation (30.7)

$$k' = \frac{k_m A}{V_m}$$

(30.7)

The volumetric mass transfer coefficient can be estimated from experimental data by plotting LHS of equation (30.6) against time. It is to be noted that estimating mass transfer coefficient from k' is difficult because calculating the slag metal interfacial area (A) is very tough. Because, under bath agitation the slag phase disintegrates and emulsify into metal phase increasing the tremendous surface area; but quantifying such slag-metal interfaces in the emulsion is very difficult. Mass transfer coefficient however may be calculated from various dimensionless correlations given in literature (Sherwood number as a function of Reynolds number and Scmidth number). One of the most well known correlation for mass transfer from a spherical particle to liquid is given by Ranz Marshall correlation, given by equation (30.9)

$$Sh = 2 + 0.6Re^{0.5}Sc^{0.33}$$

(30.9)

Where, Sherwood number= $Sh = \left(\frac{K_m L}{D}\right)$ K_m, L, D are the mass transfer coefficient, characteristics length and diffusivity of the species in liquid. Re is the Reynolds number $= \frac{\rho U L}{\mu}$, and $Sc = \frac{\mu}{\rho D}$, where U, ρ, μ are characteristics velocity, density and viscosity of liquid.

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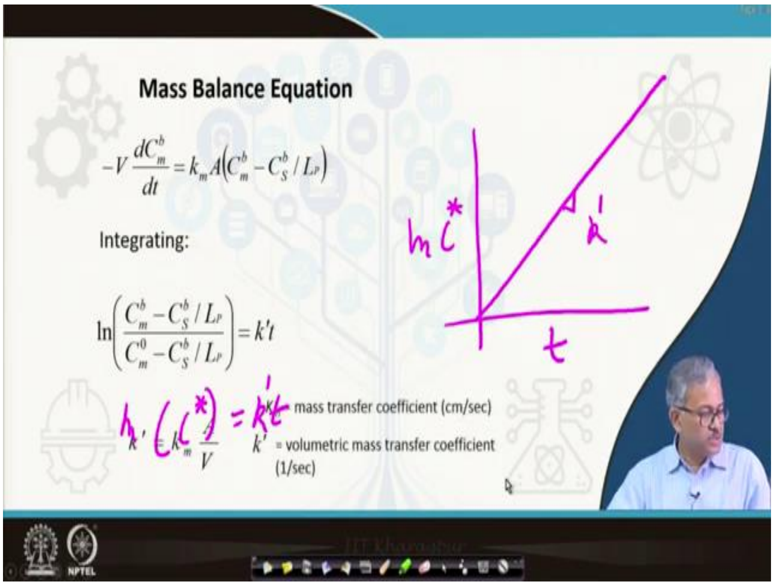

Mass Balance Equation

$$-V\frac{dC_m^b}{dt} = k_m A\left(C_m^b - C_S^b / L_P\right)$$

Integrating:

$$\ln\left(\frac{C_m^b - C_S^b / L_P}{C_m^0 - C_S^b / L_P}\right) = k't$$

$$\ln\left(C^*\right) = k't$$

$$k' = k_m \frac{A}{V}$$

k_m = mass transfer coefficient (cm/sec)

k' = volumetric mass transfer coefficient (1/sec)

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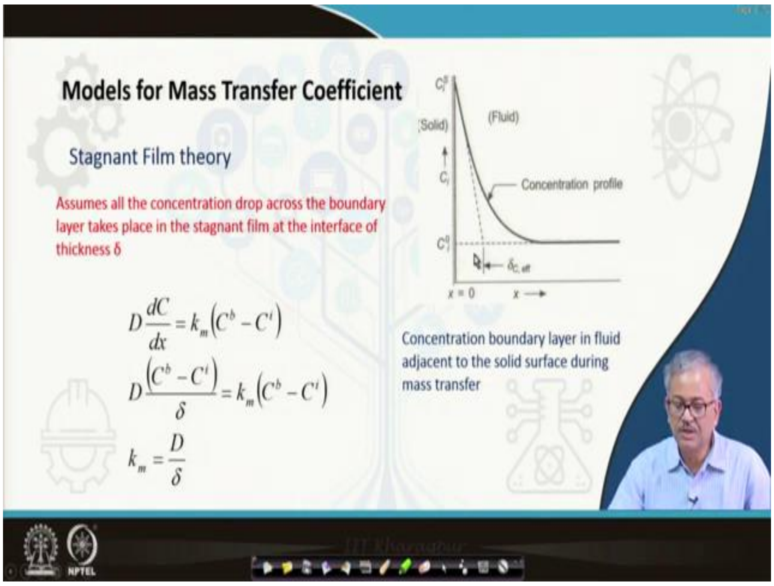

Models for Mass Transfer Coefficient

Stagnant Film theory

Assumes all the concentration drop across the boundary layer takes place in the stagnant film at the interface of thickness δ

$$D\frac{dC}{dx} = k_m\left(C^b - C^i\right)$$

$$D\frac{\left(C^b - C^i\right)}{\delta} = k_m\left(C^b - C^i\right)$$

$$k_m = \frac{D}{\delta}$$

Concentration boundary layer in fluid adjacent to the solid surface during mass transfer

There also exists some theoretical models from which mass transfer coefficient can also be calculated. First model is called the stagnant film model. Here the actual concentration profile in the concentration boundary layer is approximated by a straight line, assuming the concentration boundary layer is stagnant (Figure 30.1).

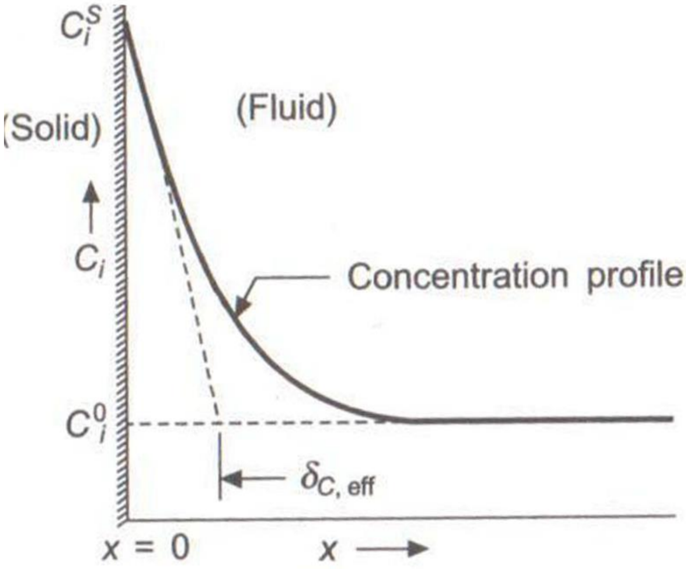

Figure 30.2: Approximation of the concentration profile in the boundary layer by a straight line

Under this condition, the mass balance on the metal phase yields:

$$D\frac{dC}{dx} = k_m\left(C_i^S - C_i^0\right)$$

(30.10)

Where, D is the mass diffusivity of the species through the concentration boundary layer. Integrating equation (30.10) yields:

$$D\frac{\left(C_i^S - C_i^0\right)}{\delta_{C,eff}} = k_m\left(C_i^S - C_i^0\right)$$

(30.11)

Where, $\delta_{C,eff}$ represents the effective boundary layer coefficient, as indicated in the Figure 30.2. It means that total concentration difference across the actual boundary layer, $\left(C_i^S - C_i^0\right)$, takes place under effective concentration boundary layer thickness.

Equation (30.11), yields the following expression from which mass transfer coefficient can be calculated:

$$k_m = \frac{D}{\delta_{C,eff}}$$

There are some empirical correlations available in literature from which the boundary layer thickness may be calculated.

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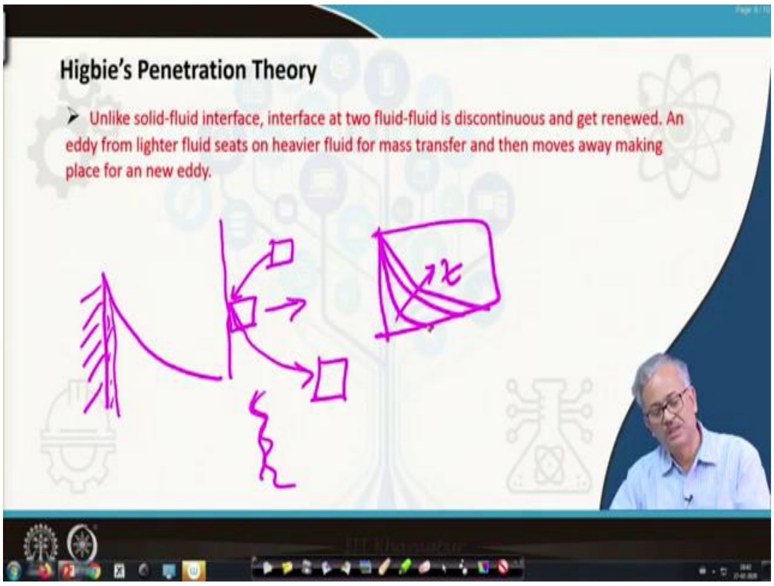

Higbie's Penetration Theory

- Unlike solid-fluid interface, interface at two fluid-fluid is discontinuous and get renewed. An eddy from lighter fluid seats on heavier fluid for mass transfer and then moves away making place for an new eddy.

Stagnant film theory is more appropriate for solid-liquid interface where boundary layer remain attached to the solid surface. Under mild flow assumption, of stagnant film layer may also be justified. However, in case of slag-metal reaction, which forms a liquid liquid interface, it is unlikely that two liquid will remain in contact through a fixed boundary layer for all time. Under bath agitation the lighter liquid phase may emulsify into heavier phase and under that condition lighter phase will come in contact with heavier phase for some time before it floats up to join the parent phase at the top. To deal with liquid-liquid mass transfer, another popular mass transfer model exists that is based on Higbie's penetration theory. Here, interaction of two fluids is considered as a transient phenomenon for a small duration of time, before the surface get renewed. During this short interaction transient mass transfer takes place. It is more realistic, especially under turbulent condition, when fluid interfaces are likely to be renewed frequently. As shown in Figure 30.3, fluid element of fluid-1 comes in contact with fluid-2 for a small duration of time; transient species transfer takes place from fluid-2 to fluid-1 in a transient manner and transient concentration profiles develops in fluid 2, as shown.

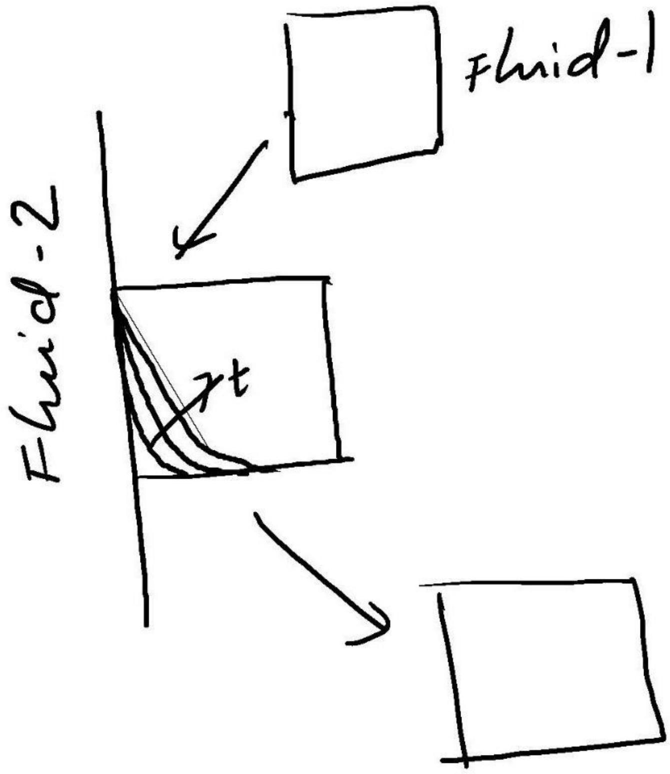

Fig.30.3 Transient interaction of two fluid elements according to Higbie's penetration theory

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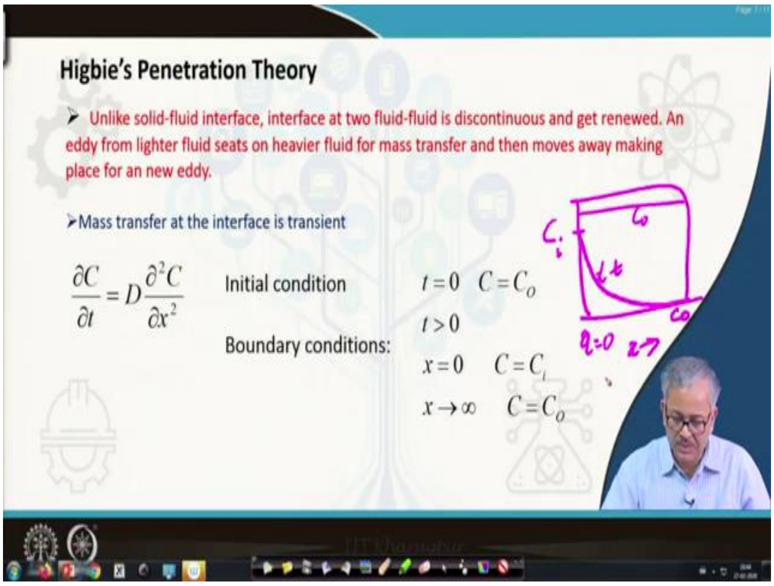

Higbie's Penetration Theory

- Unlike solid-fluid interface, interface at two fluid-fluid is discontinuous and get renewed. An eddy from lighter fluid seats on heavier fluid for mass transfer and then moves away making place for an new eddy.
- Mass transfer at the interface is transient

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Initial condition $t=0 \quad C=C_0$

$t>0$

Boundary conditions:

$x=0 \quad C=C_i$

$x\to\infty \quad C=C_0$

The transient mass transfer in fluid-1, may be represented by the following governing equation and initial and boundary conditions.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

(30.12)

Initial condition:

At $t=0$, $C(x,0) = C_0$

Boundary conditions:

At $t>0$,

At $x=0$, $C(0,t) = C_S$

at x trends to infinity, $C(\alpha,t)=C_0$

Please note that during this short period of time, species will not be able to penetrate much distance from the surface and concentration a few distance away from the surface may be considered at initial concentration. So distance along mass transfer may be considered semi-infinite.

The solution of above transient one-dimensional mass transfer in semi-infinite medium is the well-known error function solution, as given below:

$$\frac{C - C_i}{C_O - C_i} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

(30.13)

With the concentration boundary layer available, the mass transfer coefficient may be defined as:

$$-D\left.\frac{\partial C}{\partial x}\right|_i = k_m\left(C_i - C_O\right)$$

(30.14)

After evaluating the concentration gradient at the interface using the concentration profile given by equation (30.13), the expression of mass transfer coefficient may be evaluated as:

$$k_m = \sqrt{\frac{D}{\pi t}}$$

(30.15)

The time average mass transfer coefficient can be given by:

$$\bar{k}_m = 2\sqrt{\frac{D}{\pi t_0}}$$

(30.16)

t_0 is the exposure time between two fluids. Now, defining a new factor, called S, the surface renewal factor, which is inverse of t_0, the mass transfer coefficient may be defined as a square root of the product of diffusivity and surface renewal factor.

$$\bar{k}_m = 2\sqrt{\frac{D}{\pi t_0}} = \sqrt{DS}$$

S is called the surface renewal factor defined as inverse of exposure time. Approximate range of S is from 10/sec for mild turbulence to 300/s for violent turbulence. Boundary layer theory over-predicts the effect of diffusivity on mass transfer coefficient (α D) compared to penetration theory where mass transfer coefficient is proportional to square root of diffusivity. It was observed that for hydrogen transfer to liquid iron, there is a transition from boundary layer theory to penetration theory as the bath changes from quiescent to turbulent.

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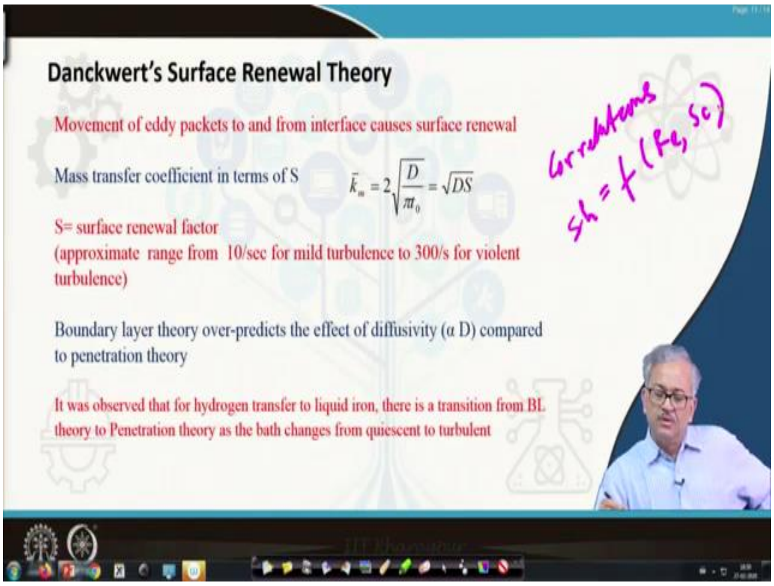

Danckwert's Surface Renewal Theory

Movement of eddy packets to and from interface causes surface renewal

Mass transfer coefficient in terms of S $\bar{k}_m = 2\sqrt{\frac{D}{\pi t_0}} = \sqrt{DS}$

S= surface renewal factor
(approximate range from 10/sec for mild turbulence to 300/s for violent turbulence)

Boundary layer theory over-predicts the effect of diffusivity (α D) compared to penetration theory

It was observed that for hydrogen transfer to liquid iron, there is a transition from BL theory to Penetration theory as the bath changes from quiescent to turbulent

Correlations
$Sh = f(Re, Sc)$

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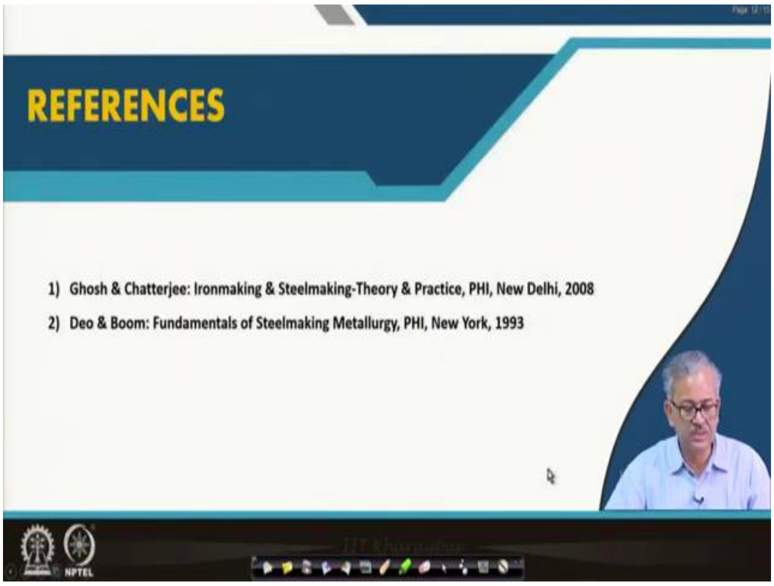

REFERENCES

1) Ghosh & Chatterjee: Ironmaking & Steelmaking-Theory & Practice, PHI, New Delhi, 2008
2) Deo & Boom: Fundamentals of Steelmaking Metallurgy, PHI, New York, 1993

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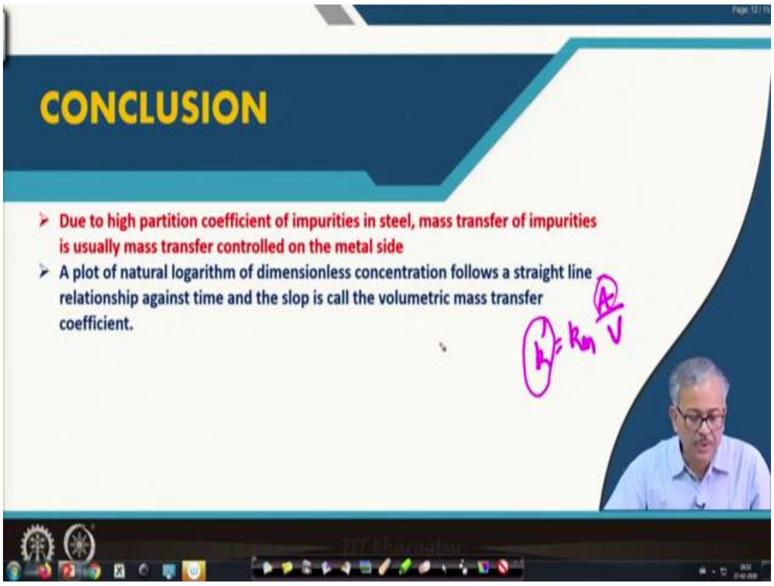

CONCLUSION

- Due to high partition coefficient of impurities in steel, mass transfer of impurities is usually mass transfer controlled on the metal side
- A plot of natural logarithm of dimensionless concentration follows a straight line relationship against time and the slop is call the volumetric mass transfer coefficient.

$\boxed{k'} = k_m \frac{\boxed{A}}{V}$

Conclusion:

Slag metal reaction during steelmaking is usually mass transfer controlled on the metal side, due to high partition coefficient of impurities in slag.

The mass transfer rate constant can be calculated from experimental data by plotting dimensionless concentration against time, as defined by equation (30.7). However, estimating mass transfer coefficient (k_m, cm/s) is difficult as it is tough to estimate the emulsified slag-metal interfacial area under bath agitation.

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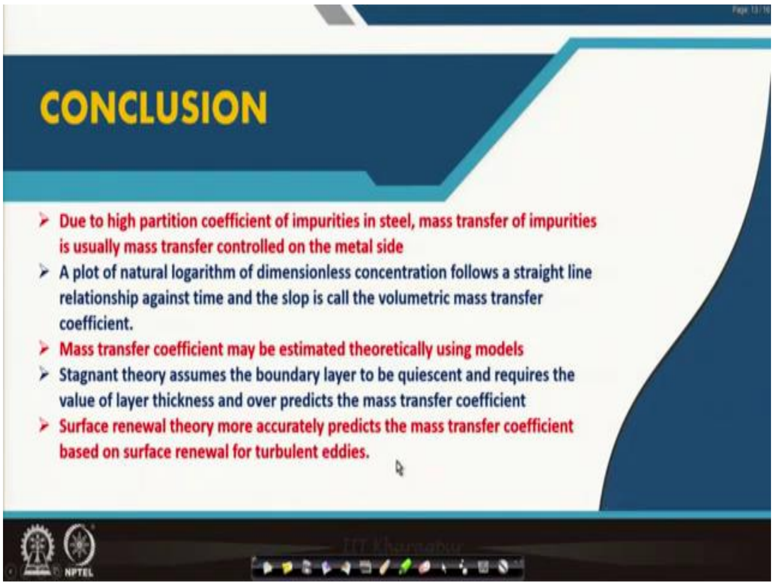

CONCLUSION

- Due to high partition coefficient of impurities in steel, mass transfer of impurities is usually mass transfer controlled on the metal side
- A plot of natural logarithm of dimensionless concentration follows a straight line relationship against time and the slop is call the volumetric mass transfer coefficient.
- Mass transfer coefficient may be estimated theoretically using models
- Stagnant theory assumes the boundary layer to be quiescent and requires the value of layer thickness and over predicts the mass transfer coefficient
- Surface renewal theory more accurately predicts the mass transfer coefficient based on surface renewal for turbulent eddies.

However, mass transfer coefficient may be estimated using correlations available in literature. There also exists theoretical model that provide mass transfer coefficient. More pragmatic and popular model to deal with slag-metal reaction is the surface renewal theory, where mass transfer coefficient is estimated as square root of the product of surface renewal factor and diffusivity. Surface renewal factor is defined as the frequency at which lighter liquid phase renews its surface over the second fluid phase under bath agitation. This value approximately ranges from 10/sec for mild turbulence to 300/s for violent turbulence.