Iron Making and Steel Making

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Module – 02
Lecture - 09
Kinetics of gas solid reaction: iron oxide reaction part 01

Welcome. This is the model to lecture 9 and it is on kinetics of gas solid reaction of iron oxide reduction part 1. I will cover iron oxide reduction kinetics in two lectures. In first lecture I will talk about the model and different rate controlling mechanism. And in the second lecture we will talk about the mixed control system and we will also solve two problems.

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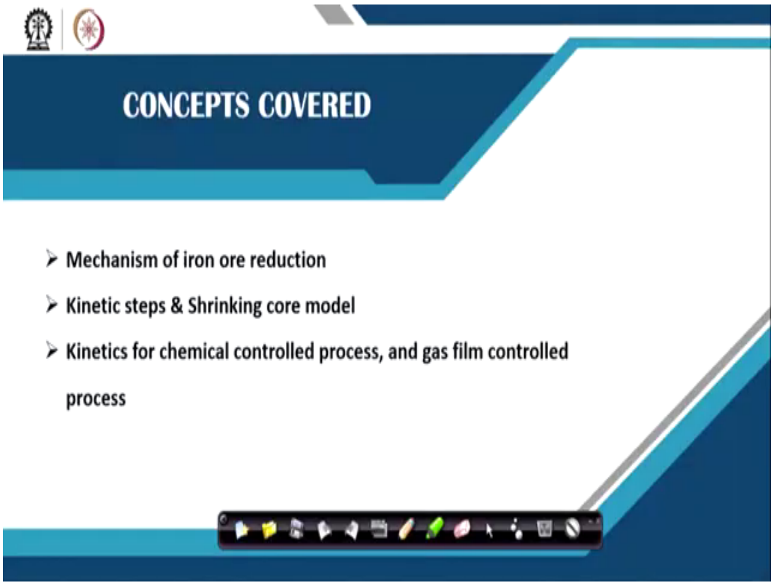

CONCEPTS COVERED

- Mechanism of iron ore reduction
- Kinetic steps & Shrinking core model
- Kinetics for chemical controlled process, and gas film controlled process

Concept covered in this lecture include the mechanism of iron oxide reduction and kinetic steps, quantification of chemical controlled process and gas film controlled process using shrinking core model.

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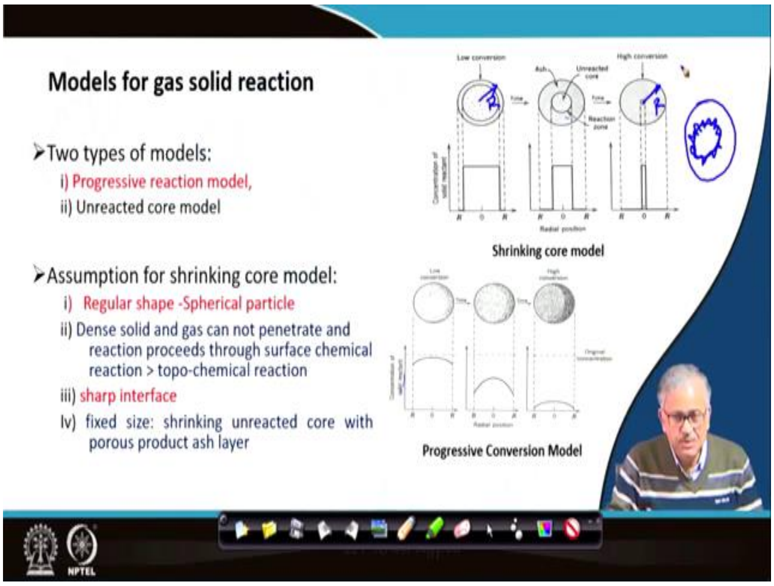

Models for gas solid reaction

- Two types of models:
  - i) Progressive reaction model,
  - ii) Unreacted core model

- Assumption for shrinking core model:
  - i) Regular shape -Spherical particle
  - ii) Dense solid and gas can not penetrate and reaction proceeds through surface chemical reaction > topo-chemical reaction
  - iii) sharp interface
  - Iv) fixed size: shrinking unreacted core with porous product ash layer

Shrinking core model

Progressive Conversion Model

For predictive model of the iron oxide reduction, that there two types of models are available. One is called the progressive reaction model, another is called the unreacted core model. What is the progressive reactive model? In this model, the solid material that is being reduced is considered porous enough such that reductant can easily penetrate through the solid material. As a result what happens? The reaction takes place throughout the body from the start of the reaction because the material is porous to the gaseous reductant. Although truly speaking the reaction may not be a totally uniform throughout the body; surface reaction will be more compared to that in the core, because there exists some resistance for the gas to penetrate to the core. But, more or less reaction will take place throughout the body.

So, if you follow the concentration of the unreacted solid reactant in the radial direction at certain time-it is evident that unreacted solid concentration is more at the core than at the surface. Again, if you follow the unreacted solid concentration profile with time, you can see the average concentration of this concentration profile is decreasing with time and finally unreacted solid concentration become zero both at surface and center. So, although there exists a difference of unreacted solid concentration between surface and core; both these concentration diminishes with time – indicating reaction throughout the body.

But this is not the real situation; because in most of the practical cases, such progressive reaction pattern is not observed. If you take a partially reduced body and make a cross section, you will find at the core of the body there is an unreacted core. So, no reaction at the core of the body, although the surface region has been reacted completely. Why it happens? Because, in most of the cases, solid are very dense and gas can not permeate through the solid and react at the core, unless the reaction interface from surface reaches the core region. And the solid product formed that adhere to the unreacted core, called the ash layer, in most of the cases porous that paves the path for the reactant at the unreacted core-ash interface. This is called the shrinking core model-as the unreacted core shrink with time. It is also called topo (surface) chemical reaction. Topo-in Latin stands for surface. The model also makes some assumptions that makes the derivation simpler and handy. For example, it assumes regular shape of the object, say spherical. Second, the reaction interface is sharp-although in real situation the interface is likely to be diffused. If you follow the diagram for shrinking core model, you can find that unreacted core is shrinking following some concentric ring-indicating sharp reaction interface for spherical object. The model also assumes that the size of the particle undergoing reduction remains unchanged, in one version, called the model for unchanging particle size. It happens when the product of reaction is solid and that adhere to the surface of unreacted core and has sufficient porosity to transport gas to the reaction interface.

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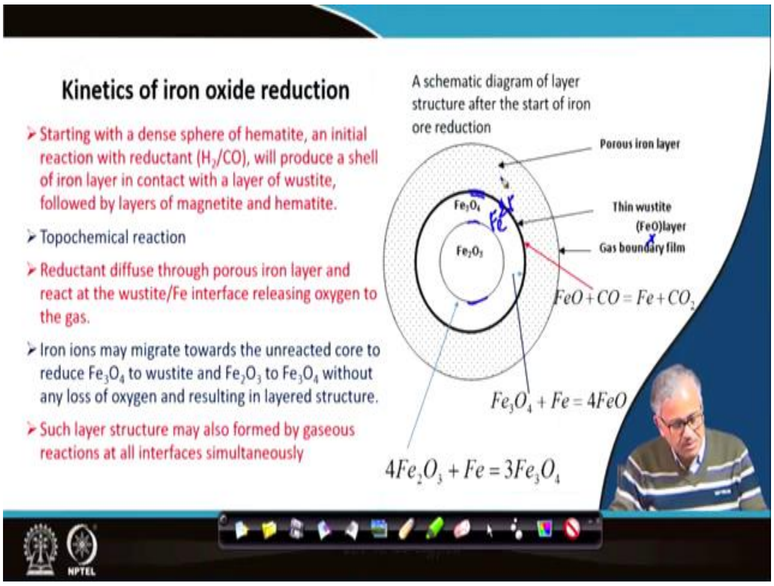

Kinetics of iron oxide reduction

- Starting with a dense sphere of hematite, an initial reaction with reductant (H_2/CO), will produce a shell of iron layer in contact with a layer of wustite, followed by layers of magnetite and hematite.
- Topochemical reaction
- Reductant diffuse through porous iron layer and react at the wustite/Fe interface releasing oxygen to the gas.
- Iron ions may migrate towards the unreacted core to reduce Fe_3O_4 to wustite and Fe_2O_3 to Fe_3O_4 without any loss of oxygen and resulting in layered structure.
- Such layer structure may also formed by gaseous reactions at all interfaces simultaneously

A schematic diagram of layer structure after the start of iron ore reduction

$FeO + CO = Fe + CO_2$

$Fe_3O_4 + Fe = 4FeO$

$4Fe_2O_3 + Fe = 3Fe_3O_4$

If we consider a spherical hematite particle is being reduced; then what will be the situation after some time? It is shown in the above diagram.

When the reductant gas reduce the particle at surface, a shell of iron will form on the surface. And since the reduction will take place in three sequential steps, namely hematite to magnetite to wustite to iron, after some time of reduction; we will have first a iron layer on the surface followed by a thin wustite layer, magnetite layer and finally a unreacted hematite core. Gas solid reaction will take place at the wustite-iron interface. Magnetite to wustite may take place by migration of iron through the wustite layer to the wustite-magnetite inter face and hematite to magnetite conversion by migration of iron through magnetite layer to the hematite-magnetite interface by the following reactions:

$$4Fe_2O_3 + Fe = 3Fe_3O_4 \tag{1}$$

$$Fe_3O_4 + Fe = 4FeO \tag{2}$$

Wustite is non-stoichiometric iron deficient compound that allows migration of iron through it. Conversion of hematite to magnetite is also accompanied with volume change that introduces defects in magnetite promoting iron migration through it. Such conversions may take place also by gaseous reductant if wustite and magnetite layers are also permeable to gas.

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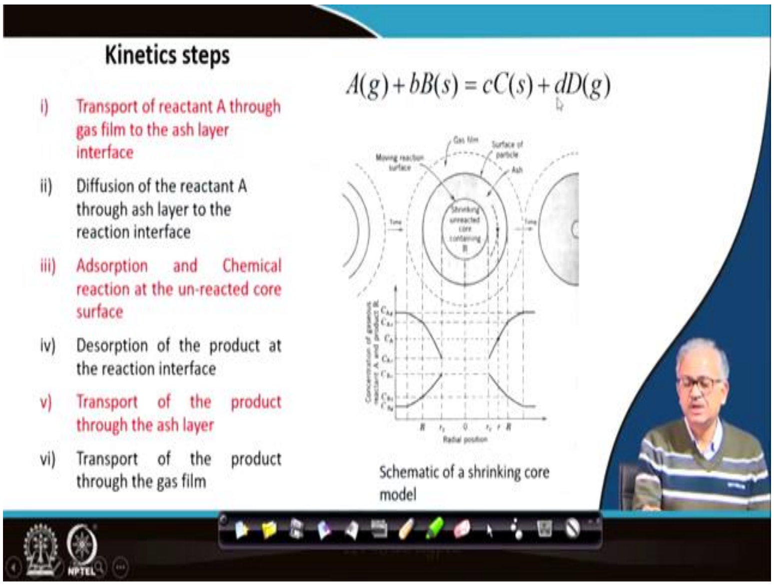

Kinetics steps

i) Transport of reactant A through gas film to the ash layer interface
ii) Diffusion of the reactant A through ash layer to the reaction interface
iii) Adsorption and Chemical reaction at the un-reacted core surface
iv) Desorption of the product at the reaction interface
v) Transport of the product through the ash layer
vi) Transport of the product through the gas film

$$A(g) + bB(s) = cC(s) + dD(g)$$

Schematic of a shrinking core model

So, let us see the kinetcs steps involved for a gas solid reaction based on shrinking core model. The involved reaction is:

$$A(g) + bB(s) = cC(s) + dD(g)$$

That is gas A is reacting with “b” mole of solid B solid producing “c” moles of solid C and “d” moles of gas D.

The concentration profile of A is shown in the figure above. $C_{A,g}$ is the concentration at the bulk gas-gas film interface. When we put a particle in a moving gas, a gas film envelops the particle, where a gradient of velocity, concentration develops indicating the mass transfer resistance across the film. So, the concentration then drops to $C_{A,S}$, the concentration at the film-ash layer interface. Then the gas need to be diffused through the ash layer setting up a gradient across the ash layer and the concentration $C_{A,S}$ drops to $C_{A,C}$, the concentration at the ash layer-unreacted core interface. Finally, the chemical reaction at the reaction interface calls for a drop in concentration from $C_{A,C}$ to the equilibrium concentration, $C_{A,e}$, representing the resistance due to chemical reaction. Similarly, the product gas moves in opposite direction through all steps as mentioned above. Therefore, there are six steps involved for the gas solid reaction as mentioned explicitly in the slide above.

Now, out of these six steps, there may be one slowest step, the rate for which too slow to be comparable with other steps and may be declared rate controlling step. Sometimes rates of two or more steps might be comparable and control the overall reaction together-the situation is called the mixed controlled.

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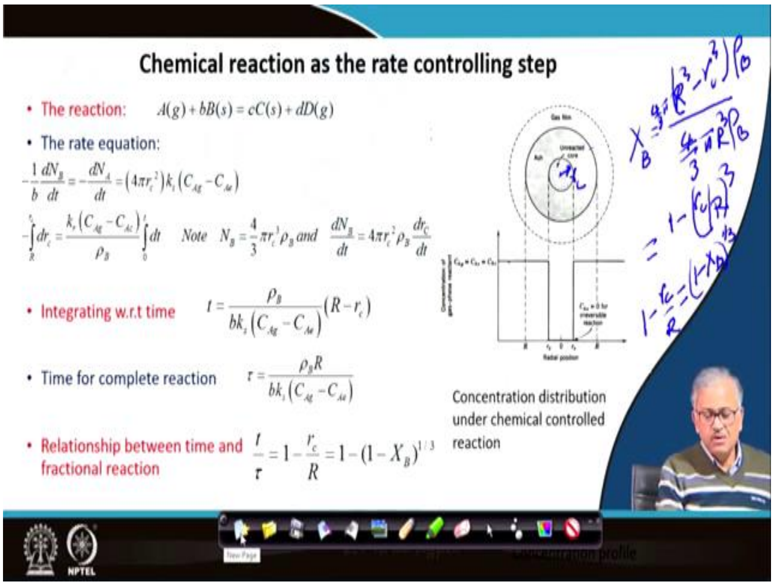

Chemical reaction as the rate controlling step

- The reaction: $A(g) + bB(s) = cC(s) + dD(g)$
- The rate equation:

$$-\frac{1}{b}\frac{dN_B}{dt} = -\frac{dN_A}{dt} = \left(4\pi r_c^2\right)k_s\left(C_{Ag} - C_{Ae}\right)$$

$$-\int_R^{r_c} dr_c = \frac{k_s\left(C_{Ag} - C_{Ae}\right)}{\rho_B}\int_0^t dt \quad Note \quad N_B = \frac{4}{3}\pi r_c^3\rho_B \, and \, \frac{dN_B}{dt} = 4\pi r_c^2\rho_B\frac{dr_C}{dt}$$

- Integrating w.r.t time $t = \frac{\rho_B}{bk_s\left(C_{Ag} - C_{Ae}\right)}\left(R - r_c\right)$
- Time for complete reaction $\tau = \frac{\rho_B R}{bk_s\left(C_{Ag} - C_{Ae}\right)}$
- Relationship between time and fractional reaction $\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3}$

Concentration distribution under chemical controlled reaction

$$X_B = \frac{\left(R^3 - r_c^3\right)\rho_B}{\frac{4}{3}\pi R^3\rho_B}$$

$$= 1 - \left(r_c/R\right)^3$$

$$1 - \frac{r_c}{R} = \left(1 - X_B\right)^{1/3}$$

Now let us develop some handy correlation between fractional reduction versus time using shrinking core model under different rate controlling situation. First let us let us develop such correlation when chemical reaction is the rate controlling step. Under this condition, the concentration profile of the gaseous reductant will look like as shown in the concentration profile above. In that case what happens? There will be no concentration gradient across the transport layers like ash and film layer and $C_{A,g}$ should be equal $C_{A,C}$ and the reaction will continue till $C_{A,C}$ becomes equal to $C_{A,e}$. There would be no concentration gradient across ash and film layer because diffusion mass transport through the film layer and diffusion through the ash layer are comparatively much faster than the rate of chemical reaction at the interface.

The mass balance equation for chemically controlled process considering first order kinetics, may be written as:

$$-\frac{1}{b}\frac{dN_B}{dt} = -\frac{dN_A}{dt} = \left(4\pi r_c^2\right)k_s\left(C_{Ag} - C_{Ae}\right) \tag{1}$$

The LHS represents that rate at which molar concentration of B in terms of A are changing and the RHS represents the rate at which A is comsuming at the interface by chemical reaction. Where, k_s is called the chemical rate constant (1/sec). r_c is the radius of the unreacted core. N_A, N_B represent the number of moles of A and B at certain time t, respectively. The minus sign indicates that both A and B are consuming in the process.

Now rearranging and integrating the equation, we get:

$$-\int_{R}^{r_c} dr_c = \frac{k_r\left(C_{Ag} - C_{Ac}\right)}{\rho_B}\int_{0}^{t} dt \qquad Note \quad N_B = \frac{4}{3}\pi r_c^{\ 3}\rho_B \ and \quad \frac{dN_B}{dt} = 4\pi r_c^{\ 2}\rho_B\frac{dr_C}{dt}$$

$$t = \frac{\rho_B}{bk_s\left(C_{Ag} - C_{Ae}\right)}\left(R - r_c\right) \tag{2}$$

Now the time for complete conversion (τ) can be achieved by putting r_c=0.

$$\tau = \frac{\rho_B R}{bk_s\left(C_{Ag} - C_{Ae}\right)} \tag{3}$$

Keeping in mind, that fractional conversion of B (X_B) can be written in terms of R and r_c as follows: $X_B = 1 - \left(\frac{r_c}{R}\right)^3$, the relationship between the dimensionless time and fractional conversion of B, can be written as:

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3} \tag{4}$$

So, if you plot experimental data as $1 - (1 - X_B)^{1/3}$ against the dimensionless time $\left(\frac{t}{\tau}\right)$, and if you find the data follows the straight line passing through the origin, then you can say that this is a chemical control process.

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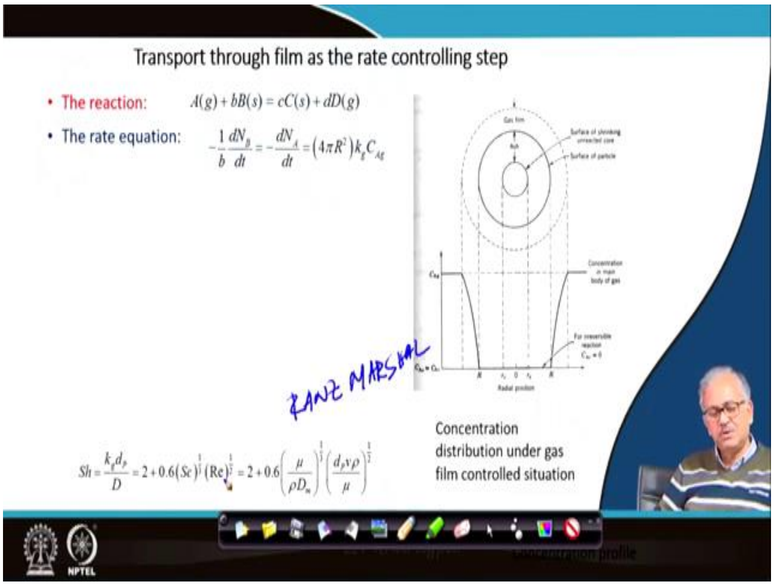

Transport through film as the rate controlling step

- The reaction: $A(g) + bB(s) = cC(s) + dD(g)$
- The rate equation: $-\frac{1}{b}\frac{dN_B}{dt} = -\frac{dN_A}{dt} = \left(4\pi R^2\right)k_g C_{Ag}$

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$$Sh = \frac{k_g d_p}{D} = 2 + 0.6(Sc)^{\frac{1}{3}}(Re)^{\frac{1}{2}} = 2 + 0.6\left(\frac{\mu}{\rho D_m}\right)^{\frac{1}{3}}\left(\frac{d_p v \rho}{\mu}\right)^{\frac{1}{2}}$$

Concentration distribution under gas film controlled situation

Let us derive a similar dimensionless correlation for the case of gas film controlled situation. Now, if we see the concentration profile, we see all the concentration gradient exists across the film layer, because diffusion through ash layer and chemical reaction are much faster not allowing any gradient to develop there.

The mass balance equation across the gas film can be written as:

$$-\frac{1}{b}\frac{dN_B}{dt} = -\frac{dN_A}{dt} = \left(4\pi R^2\right)k_g C_{Ag}$$

(5)

The RHS here represent the rate at which reactant A is being transported through the film. So the above mass balance equation states that the rate at which B is consuming is equal to the rate at which A is transporting through the film multiplied by the stoichiometric factor “b”. Here, k_g represents the mass transfer coefficient in the film, which quantifies the mass transfer conductance through the film and when it is multiplied by concentration difference across the film, it gives the mass flux. And this flux multiplied by the external area, provides the rate at which A is transporting through the film (moles/sec) and it is equated to the rate at which B is being consumed by the stoichiometric factor “b”. .

The mass transfer conductance of the gas film, or the mass transfer coefficient, k_g, depends on the hydrodynamic condition of the gas film. If the film is very turbulent or then mass transfer efficacy is very fast then $k_g$is also very high; if the film is stagnant then $k_g$is very small. For calculating k_g, various dimensionless correlation are available in literature for various flow system lencompassing almost all practical situations. For fluid flow over a sphere (as in the present case), the well known dimensionless correlation is called the Ranz Marshall correlation, given as follows:

$$Sh = \frac{k_g d_P}{D} = 2 + 0.6(Sc)^{\frac{1}{3}} (\mathrm{Re})^{\frac{1}{2}} = 2 + 0.6\left(\frac{\mu}{\rho D_m}\right)^{\frac{1}{3}} \left(\frac{d_P v \rho}{\mu}\right)^{\frac{1}{2}} \tag{6}$$

Sh, called the Sherwood number, represents dimensionless mass transfer coefficient. Sc is the Smidth number and Re the Reynolds number. Here, D, d_P, μ, ρ, v represent mass diffusivity, particle diameter, viscosity, density, velocity of the fluid, respectively.

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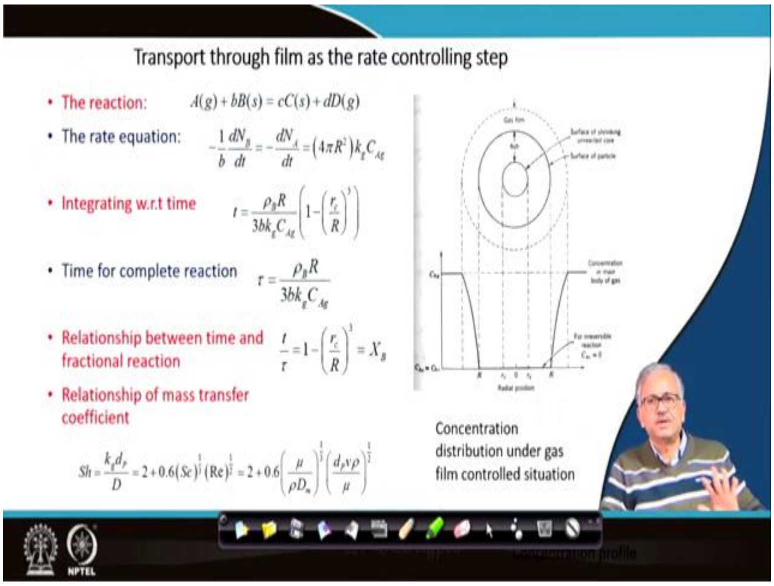

Transport through film as the rate controlling step

- The reaction: $A(g) + bB(s) = cC(s) + dD(g)$
- The rate equation: $-\frac{1}{b}\frac{dN_B}{dt} = -\frac{dN_A}{dt} = (4\pi R^2) k_g C_{Ag}$
- Integrating w.r.t time $t = \frac{\rho_B R}{3bk_g C_{Ag}}\left(1 - \left(\frac{r_c}{R}\right)^3\right)$
- Time for complete reaction $\tau = \frac{\rho_B R}{3bk_g C_{Ag}}$
- Relationship between time and fractional reaction $\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3 = X_B$
- Relationship of mass transfer coefficient

$$Sh = \frac{k_g d_P}{D} = 2 + 0.6(Sc)^{\frac{1}{3}} (\mathrm{Re})^{\frac{1}{2}} = 2 + 0.6\left(\frac{\mu}{\rho D_m}\right)^{\frac{1}{3}} \left(\frac{d_P v \rho}{\mu}\right)^{\frac{1}{2}}$$

Concentration distribution under gas film controlled situation

Now, integrating equation (5), the following correlation is obtained:

$$t = \frac{\rho_B R}{3bk_g C_{Ag}}\left(1 - \left(\frac{r_c}{R}\right)^3\right) \tag{6}$$

Now, the time for complete conversion may be obtained as:

$$\tau = \frac{\rho_B R}{3bk_g C_{Ag}} \tag{7}$$

Finally dimensionless correlation between fraction reaction of solid B and the dimensionless time, may be obtained as:

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3 = X_B \tag{8}$$

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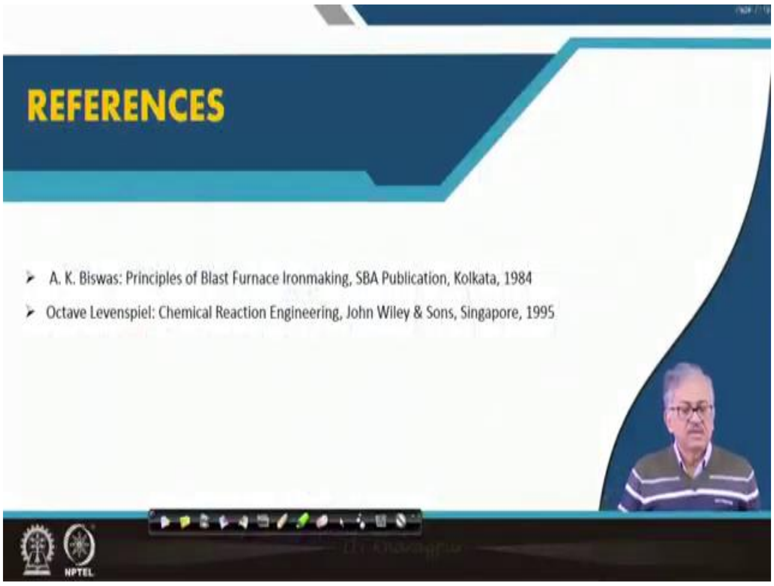

REFERENCES

- A. K. Biswas: Principles of Blast Furnace Ironmaking, SBA Publication, Kolkata, 1984
- Octave Levenspiel: Chemical Reaction Engineering, John Wiley & Sons, Singapore, 1995

The major reference of this lecture Octave Levenspiel: The Chemical Reaction Engineering, John Wiley and Sons Singapore 1995; this is a very good book on shrinking core model.

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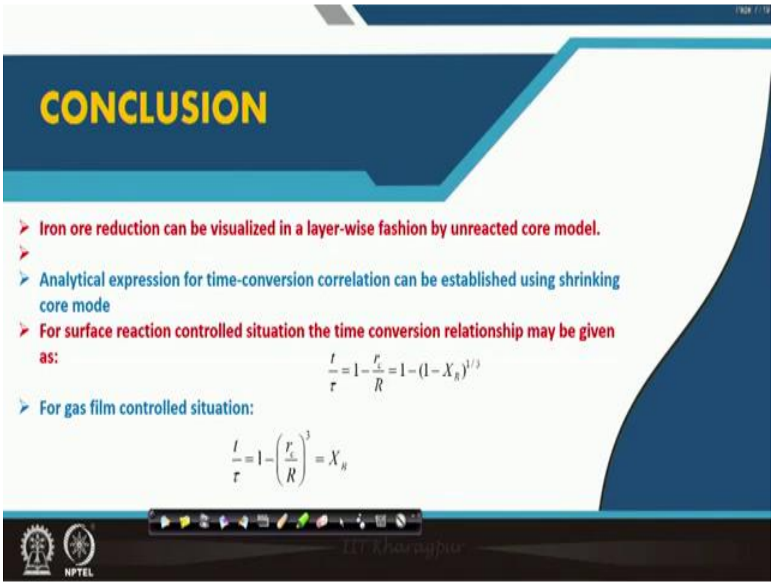

CONCLUSION

- Iron ore reduction can be visualized in a layer-wise fashion by unreacted core model.
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- Analytical expression for time-conversion correlation can be established using shrinking core mode
- For surface reaction controlled situation the time conversion relationship may be given as:

$$\frac{t}{\tau}=1-\frac{r_c}{R}=1-(1-X_B)^{1/3}$$

- For gas film controlled situation:

$$\frac{t}{\tau}=1-\left(\frac{r_c}{R}\right)^3=X_B$$

In conclusion, we can note the followings:

1. There are two models for gas-solid reduction. In progressive reaction model, the unreacted solid is assumed to be porous and reaction takes place throughout the body. In shrinking core model, unreacted solid is assumed to be dense and not permeable by gas. Reaction takes place at the surface and the reaction interface progressively moves inward. The adherent solid product layer is assumed permeable to gas and gas reaches the reaction interface through ash layer diffusion. Shrinking core model is found to be more realistic.
2. Iron reduction can be visualized in a layer wise fashion by unreacted core model. That means, the reduction of iron oxide can be nicely described by the shrinking core model and with an unreacted core of Fe_2O_3 at the center and followed by a Fe_3O_4 layer and a thin wustite layer and beyond which there is an ash iron layer, product iron layer.
3. The reactant gas will be transported through the gas film, and then diffuse through the ash layer to reach the wustite-iron interface and reduce wustite to iron at the interface and subsequently, the relieved oxygen in the form of CO_2 will leave the system.
4. The layer wise reduction of hematite to magnetite to wustite will progress through the diffusion of iron through the wustite and magnetite layer to the respective

interfaces. Such layerwise reduction may also be carried out by gaseous reductant if wustite and magnetite layers are also permeable to gaseous reductant.

5. For a gas solid reduction there are five kinetic steps that include transport of the gaseous reductant through the gas film, diffusion of gaseous reductant through ash layer, chemical reaction at the interface, diffusion of the product gas through the ash layer, transport of the product gas through gas film. The slowest step may be considered as rate controlling step if the resistance of the slowest step is much smaller that of other steps. If resistance two or more steps are comparable, the reaction may be rate mixed controlled.
6. Using shrinking core model, the time evolution fractional reduction of an unchanging spherical particle, under chemical reaction at the interface as rate controlling step, may be given as:

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3}$$

7. For gas film diffusion controlled situation, the similar expression may be give as:

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3 = X_B$$