Iron Making
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Lecture - 34
Iron Making

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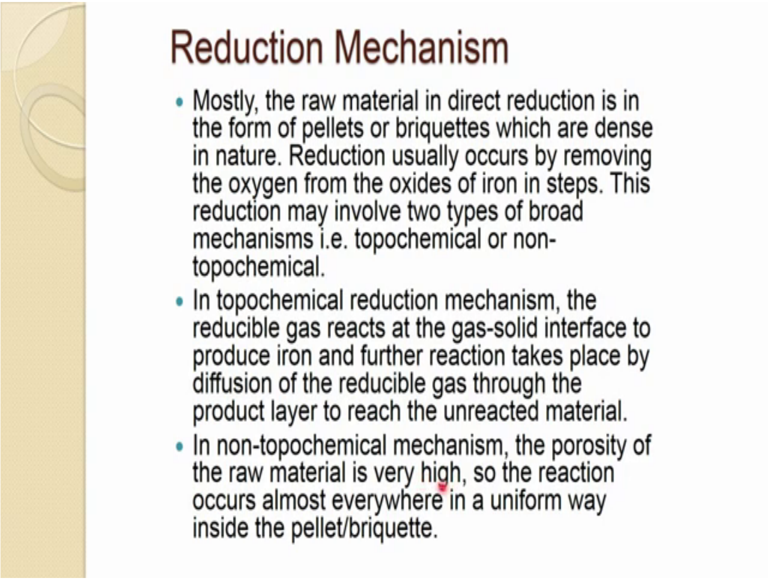

Reduction Mechanism

- Mostly, the raw material in direct reduction is in the form of pellets or briquettes which are dense in nature. Reduction usually occurs by removing the oxygen from the oxides of iron in steps. This reduction may involve two types of broad mechanisms i.e. topochemical or non-topochemical.
- In topochemical reduction mechanism, the reducible gas reacts at the gas-solid interface to produce iron and further reaction takes place by diffusion of the reducible gas through the product layer to reach the unreacted material.
- In non-topochemical mechanism, the porosity of the raw material is very high, so the reaction occurs almost everywhere in a uniform way inside the pellet/briquette.

So, now we will go a little bit about the reduction mechanism, though we did not talk this reduction mechanism, when we were discussing about the reduction in the stake region in the blast furnace, but in this direct direction would be discussing about this now. And this would be again point stake region also. So, mostly the raw material indirect reduction is in the form of pellets, or briquettes which are dense in nature.

So, in direct reduction we use or either in the form of pellets, or briquettes. So, these are actually sometime composite or not composite pellets, but as such raw material iron ore, or pellets in the briquettes form or, pellets form we use that 1 and many times they are dense in nature. So, reduction usually occurs by removing the oxygen from the oxide of the iron in steps.

So, this reduction may involve 2 types of broad mechanism one topochemical, and another is non topochemical. So, I am not going too much into the detail of these because, this symbol mode transport processes especially the mass transfer of the species and, which I am not sure how many of you who are taking this course and, I believe their undergraduate students are familiar with the transport phenomenon and those mass transfer and heat transfer. That is why I concise concisely avoid in the heat transfer, mentioning the heat transfer in this whole course because; again I am not sure how many of you are aware of it. So, the mechanism are mostly topochemical and non topochemical. So, in topochemical reduction mechanism, the reducible gas will reacts at the gas solid interface to produce iron and, further reaction takes place by diffusion of the reducible gas through the product layer to reach the unreacted material.

You will understand this mode in the next slide where the figure is there and, so, but remember in this the reducible gas will react at the gas solid interface to produce iron and, further reaction takes place only by diffusion of reducible gas through the product layer. To reach the unreacted material; however, in non topochemical mechanism the porosity of the raw material is very high, when the porosity is very high the reducing gas can reach almost everywhere, and in the pellets all briquette the reaction occur almost everywhere in a uniform way inside the pellets.

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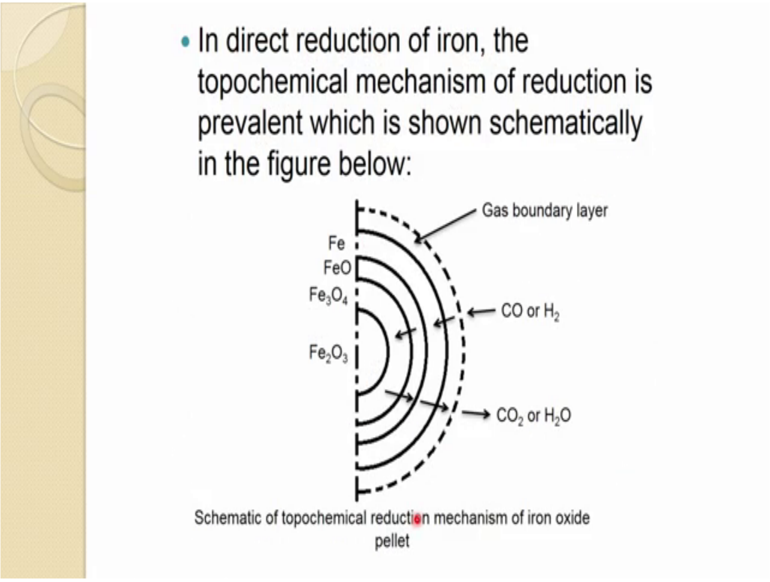

- In direct reduction of iron, the topochemical mechanism of reduction is prevalent which is shown schematically in the figure below:

Schematic of topochemical reduction mechanism of iron oxide pellet

So, diffusion is not there in that case and I know you must be familiar about this diffusion. And other things and so, that terminologies should not be a new one for you.

So, in direct reduction of iron the topochemical mechanism of reduction is prevalent, which is shown schematically in the figure below. So, usually this is the pallets solid line. So, it is showing the half cross section of that of that is spherical pallet to dense pellet iron oxide. So, it is like Fe 2 O 3 pellets and, when the reducing gas is coming into the contact is it CO or hydrogen, then at. So, when reducing gas is coming into contact, it is naturally makes near the solid a very thin film of the gas.

So, that is actually what we call the gas boundary layer. So, when reducing gases are flowing through this, surface of the particle. So, they form the gas actually stick to the surface of that and that sometime in very low velocity jet near the surface of the particle exist of the gas and usually you call that 1 is a boundary layer. And then at this because gas is having a CO or hydrogen, it is immediate reacts with a Fe O Fe O 2 O 3 to Fe, then covert Fe 3 O to Fe O 2 to Fe. So, after reduction of this is formed iron, or first it will form magnetite and some CO will come out.

When it will form magnetite so, oxygen CO will come out it will become bit more porous. So, now CO 2 will come outside sorry after CO CO 2 will come out CO will go in CO 2 will come out it, then more CO would replace the CO 2 which is coming out CO 2 now has to diffuse out, through this thin layer of the gas, which formed here. So, CO 2 diffuse out from that and CO also has to defuse into this thin layer of the gas. To reach further or to reduce this further. So, then it reduces to Fe O again CO 2 is from which comes out and, this CO again diffuse from that further more CO from the outer gas, through this gas boundary layer to this and it will reduce Fe O and make the from the iron. Now iron on the surface so, hematite addresses into the iron on the surface.

Now, CO has already reduced iron and there is no more oxygen left from which it can remove so, but still there is lots of part which is unreacted. So, what happened due to this removal of oxygen, this iron becomes porous whatever iron is formed. So, CO or hydrogen has to diffuse now, through this iron layer which is porous in nature to reach the lower oxides of iron and, it reduce them further and the product gas also has to come out through this porous iron thing layer and, then has to diffuse also through this gas boundary layer. So, this process continues till they all pellet pellet has reduced into iron. So, this sort of reaction whether a diffusion and then chemical reaction at the interface, of diffusion of the reactant gas, diffusion out of the product gases interface reaction formation of this boundary layer.

So, so this sort of reaction which occurs is know a topochemical reduction mechanism, it is not just on the associated with iron oxide it will be the other sort of reaction which are similar to that, it can be associated. So, this is a typical topochemical reaction and their many steps which are involved into this, and some important steps actually I have mentioned here.

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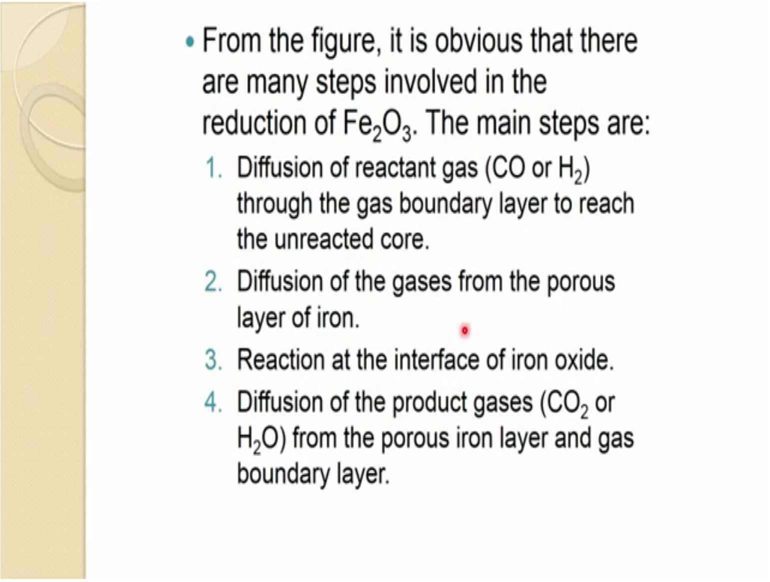

- From the figure, it is obvious that there are many steps involved in the reduction of Fe_2O_3. The main steps are:
  1. Diffusion of reactant gas (CO or H_2) through the gas boundary layer to reach the unreacted core.
  2. Diffusion of the gases from the porous layer of iron.
  3. Reaction at the interface of iron oxide.
  4. Diffusion of the product gases (CO_2 or H_2O) from the porous iron layer and gas boundary layer.

So, from the figure it is obvious that there are many steps in board in the reduction of hematite. The main steps are diffusion of reactant gas CO, or hydrogen through the gas boundary layer to reach the unreacted core, as you said diffusion of this to read unreacted core, diffusion of the gas from the porous layer of the iron. So, that porous layer of iron reaction at the interface of iron oxide, then it react at the interface diffusion of the product gas CO 2 or H 2 O from the porous iron layer and gas boundary layer so, diffusion of those gases. So, there are the major one, there few other we can offer karizma transfer and other things. So, I am giving a very simple view of this topochemical mechanism.

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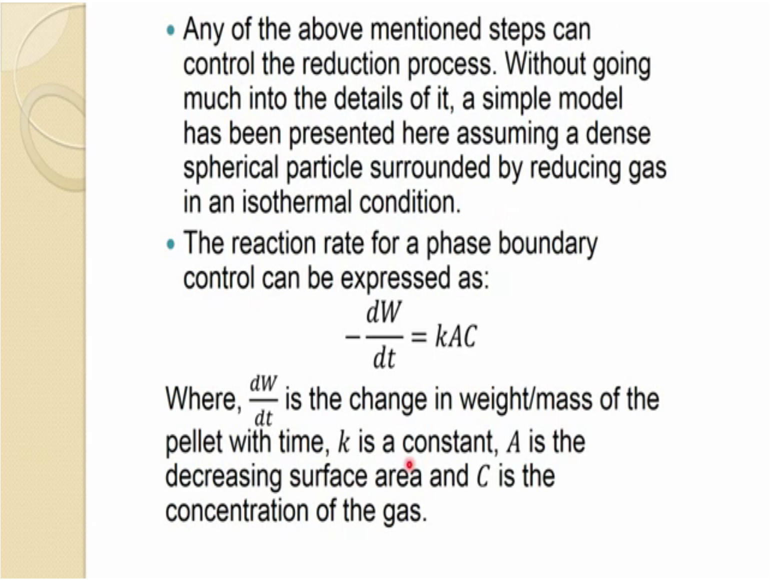

- Any of the above mentioned steps can control the reduction process. Without going much into the details of it, a simple model has been presented here assuming a dense spherical particle surrounded by reducing gas in an isothermal condition.
- The reaction rate for a phase boundary control can be expressed as:

$$-\frac{dW}{dt} = kAC$$

Where, $\frac{dW}{dt}$ is the change in weight/mass of the pellet with time, k is a constant, A is the decreasing surface area and C is the concentration of the gas.

And, very simple gas we are going to consider in order to get some reaction rate or rate of change order in the weight of the pellet. So, any of the above mentioned steps can control the reduction process. So, when we say any of these steps can control the reduction process, the meaning of it if CO is not reaching properly, or proper amount of CO is not reaching due to the very low diffusion, then this process diffusion of gases from their layer let say the from the gas it difficult for CO to reduce. .

Then this then this is sort of trial controlling mechanism because, when you are not able to get more CO due to this limitation, other though other reaction may be faster and, can react and form, but this could be like a limiting is that. Similarly if diffusion of CO is quite easily can diffuse through the boundary layer, then diffuse porous layer of iron supposed is quite difficult gases to diffuse through that, then this may become a rate controlling steps.

So, the most resistance offering step usually is known as the rate controlling steps. So, any of the above mentioned steps can control the reduction process that is the meaning of it, without going much into the details of it a simple model has been presented here, assuming a dense spherical particle, surrounded I did it using cases in an isothermal condition. So, assuming isothermal and particle surrounded by the reducing gas. So, so, considering that and reaction rate is like a phase boundary control, if we considered that then it can be expressed the weight loss with the time. So, that is why the negative is equal to kAC.

So, dW by dt is the change in weight mass of the pellet with time, k is a constant, A is the decreasing surface yeah and C is the concentration of the gas, when we visit decreasing surface area and C is the concentration of the gas when we said decreasing surface area that is remind me, this topochemical reduction mechanism is also known as shrinking core model, though we are not a assuming in that one this pellet is shrinking what we are still a assuming pellet is having the same size what it has before, it might become porous, but size is not has not changed, but in shrinking core model usually that is that is shrinking.

So, this boundary also the interface shrink and that is why we said the shrinking core model. So, C is the concentration of the gas.

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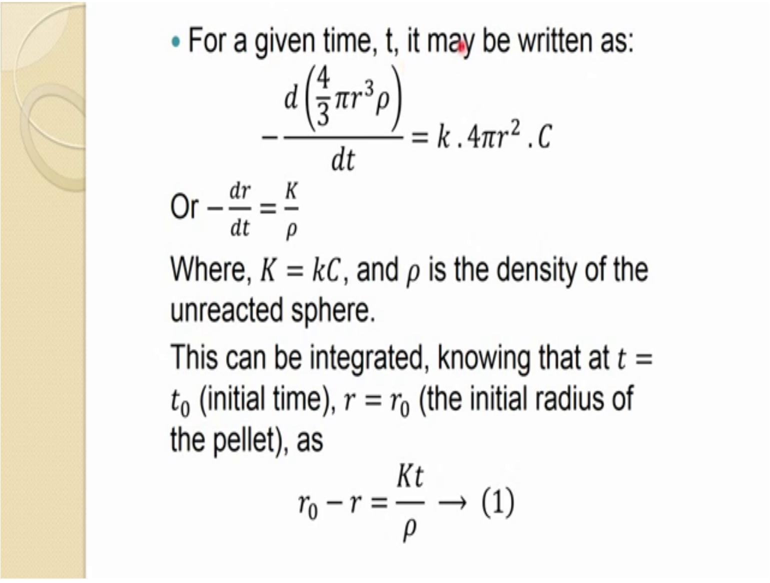

- For a given time, t, it may be written as:

$$-\frac{d\left(\frac{4}{3}\pi r^3\rho\right)}{dt} = k\,.4\pi r^2\,.C$$

Or $-\frac{dr}{dt} = \frac{K}{\rho}$

Where, $K = kC$, and ρ is the density of the unreacted sphere.

This can be integrated, knowing that at $t = t_0$ (initial time), $r = r_0$ (the initial radius of the pellet), as

$$r_0 - r = \frac{Kt}{\rho} \rightarrow (1)$$

For a given time t, it may be written as. So, W you know it is a weight of the particle of pellet and we are considering spherical pellet. So, this can be written in a volume of the particle multiplied by the density is going to give you the weight. So, this is the weight of the particle at a particular time at that time at that instant.

So, r is a variable equal to k which is coming from here, A is the area what we are talking for A phi r square particle for a spherical part and C is the concentration that is over here.

Now there are usually constant gas concentration these so, what we will do we will combine this one into another constant k. So, and this when you differentiate it with respect to r so, 3 three will constant pi r square will come and for 4 phi 4 phi will get constant through this. So, you will get minus dr by dt equal to k by rho.

So, now this rho is the density of the unreacted sphere. Now this a very simple equation which you can integrate it and, knowing that at time t equal to 0 that before starting the reaction, the radius of the pellet is the initial radius. So, t equal t naught that is a initial time radius of the palate is equal to the initial radius of the pellet. So, you integrated between these limit, then essentially so, dr a 0 to r naught and this is a constant dt t so, it will get r naught minus r equal to K t by rho. .

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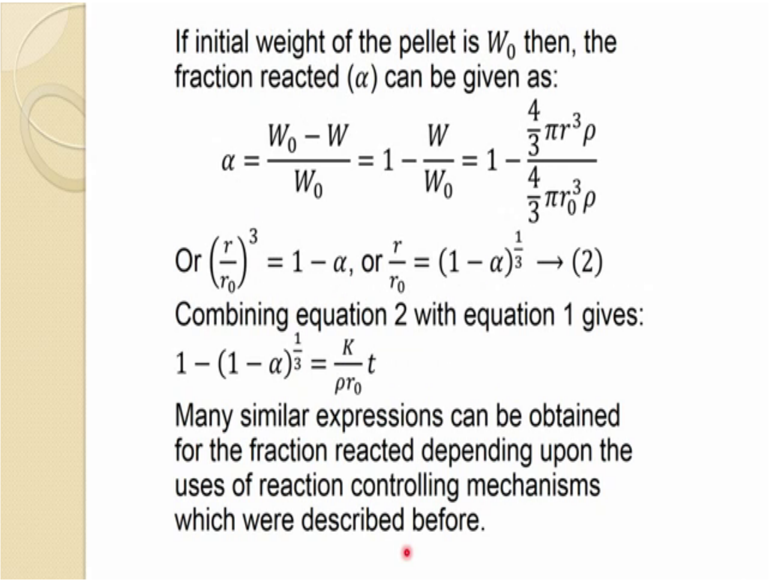

If initial weight of the pellet is W_0 then, the fraction reacted (α) can be given as:

$$\alpha = \frac{W_0 - W}{W_0} = 1 - \frac{W}{W_0} = 1 - \frac{\frac{4}{3}\pi r^3 \rho}{\frac{4}{3}\pi r_0^3 \rho}$$

Or $\left(\frac{r}{r_0}\right)^3 = 1 - \alpha$, or $\frac{r}{r_0} = (1-\alpha)^{\frac{1}{3}} \rightarrow (2)$

Combining equation 2 with equation 1 gives:

$1 - (1-\alpha)^{\frac{1}{3}} = \frac{K}{\rho r_0} t$

Many similar expressions can be obtained for the fraction reacted depending upon the uses of reaction controlling mechanisms which were described before.

So, this is the equation which can be simplified further so, in if initial weight of the palate is W naught, then the fraction reacted alpha can be given as so now, here we are introducing the definition of fraction reacted, how much fraction has been reacted of the pellet by the gas.

ah So, fraction it can be given by then. So, initial weight of the pellet minus weight of the palette at that time at an intermediate time divide by W naught initial weight of the palette, is going to gives you the fraction reacted that the ways you define the fraction reacted, which is nothing 1 minus W over W naught which is nothing 1 minus W h we said the weight of the particle at that instant. So, it is a 4 by 3 pi r cube rho divided by way initial weight of the particle.

So, this is 4 3 pi r naught cube, that is a initial radius of the pellet provided by rho. So, essentially this would be get cancelled out, or these y are not cube equal to and you bring that 1 here, then this could there. So, that becomes this if you bring this 1 here this is there 1 minus alpha and r by r naught equal to 1 minus alpha to the power 1 by 3 and this, we did it because we are having our relation here like this so, this also if you divide by r r naught because that is known.

So, we combine this equation this equation, then we can get 1 minus 1 minus alpha to the power 1 by 3 equal to k rho r naught t. So, this gives us a relation about an from using this relation 1 1 can calculate the fraction reacted in a given time. So, many similar expressions can be obtained for the fraction reacted depending upon the uses of reaction controlling mechanisms, which were described before. So, as we say they are many mechanism which can control the reaction and, depending which mechanism you used, you have to start or reaction equation this accordingly that will change and, then you will follow with that 1 and you can get a little different expression for that. So, now I and this is actually more about the topochemical reactions.

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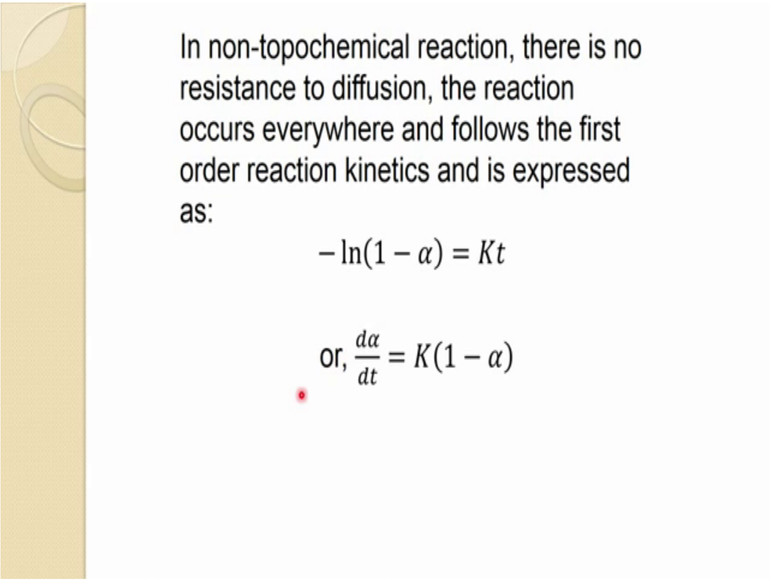

In non-topochemical reaction, there is no resistance to diffusion, the reaction occurs everywhere and follows the first order reaction kinetics and is expressed as:

$$-\ln(1-\alpha) = Kt$$

$$\text{or, } \frac{d\alpha}{dt} = K(1-\alpha)$$

And if it is non topochemical reaction which where we said, there is no resistance diffusion on reaction the reaction occurs everywhere.

So, it follows the first order reaction kinetics especially for iron oxide reduction and, in that way it is expressed in this form which gives you I this fraction reacted things and can be convert it again to that form are way r naught. So, this is for the non topochemical reaction, the reaction kinetics is.

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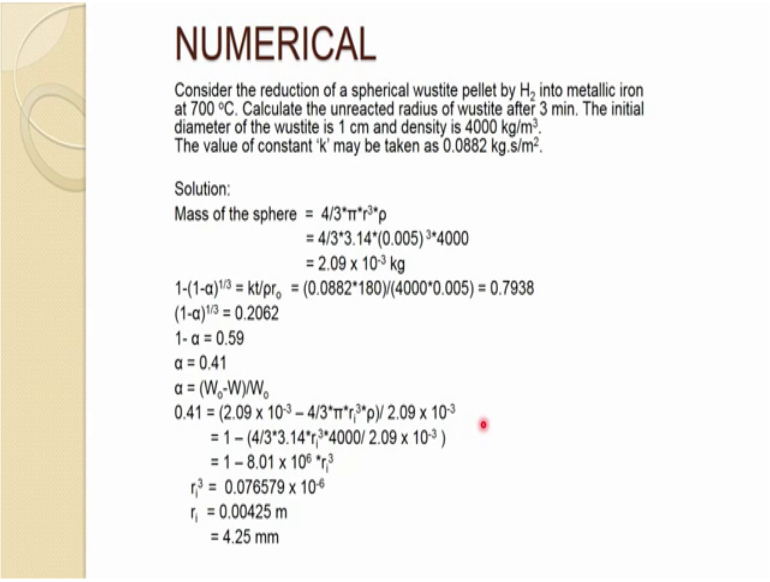

NUMERICAL

Consider the reduction of a spherical wustite pellet by H_2 into metallic iron at 700 °C. Calculate the unreacted radius of wustite after 3 min. The initial diameter of the wustite is 1 cm and density is 4000 kg/m^3.
The value of constant 'k' may be taken as 0.0882 kg.s/m^2.

Solution:

Mass of the sphere $= 4/3 * \pi * r^3 * \rho$

$= 4/3 * 3.14 * (0.005)^3 * 4000$

$= 2.09 \times 10^{-3}$ kg

$1-(1-\alpha)^{1/3} = kt/\rho r_o = (0.0882*180)/(4000*0.005) = 0.7938$

$(1-\alpha)^{1/3} = 0.2062$

$1-\alpha = 0.59$

$\alpha = 0.41$

$\alpha = (W_o - W)/W_o$

$0.41 = (2.09 \times 10^{-3} - 4/3 * \pi * r_i^3 * \rho)/ 2.09 \times 10^{-3}$

$= 1 - (4/3 * 3.14 * r_i^3 * 4000 / 2.09 \times 10^{-3})$

$= 1 - 8.01 \times 10^6 * r_i^3$

$r_i^3 = 0.076579 \times 10^{-6}$

$r_i = 0.00425$ m

$= 4.25$ mm

So, I think now it is a time to and for our numerical by which you can understand, how this reaction kinetics works and, how 1 can calculate the various parameter and other things. So, this example shows consider consider the reduction of a spherical wustite pellet by hydrogen into the metallic iron at 700 degree Celsius, calculate the un reacted radius of wustite after 3 minutes. The initial diameter of the wustite is 1 centimeter and density is 4000 k g per meter cube. The value of constant K may be taken as 0.0882 k g second per meter square.

So, these are the parameter which is given and what is needed to calculate the radius of the unreacted wustite after 3 minute. So, what we need we need actually first the fraction, if you look at this 1 that fraction reacted is needed. So, first so, mass of these sphere we know 4 pi 4 by 3 pi r cube rho. So, density is given radius is given. So, you substitute these values, we get the mass of the pellet wise sphere 2.09 into 10 to the power minus 3 k g. Now we know 1 from the reaction kinetin considering it is a phase boundary control, 1 minus 1 minus alpha this equal to k t rho r naught. So, here now everything is known k is given time is given 3 minutes rho is given r naught is given.

So, if we substitute that value k t you can convert it into second 3 into 60 180 second divided by density and the radius of the particle, that keeps you 1.7938 and which of course, will give you when you bring this one to this sides are subtract from 1 it will give to you 0.2062 as and finally, 1 minus alpha will gives you 0.59 and alpha will gives you 0.41. So, the fraction reacted would be 0.41 really. So, alpha now you know fraction reacted r can be represented by this W naught W that is the radius at that time. So, here in this case the radius of the pellet after 3 minutes W naught, if the initial 1 weight.

So, from this we can calculate. So, we not the initial weight or mass of the particles is given this minus 4 by 3 pi r cube r i 3 so, r i is the instantaneous radius so, radius at that time which here is 3 minutes after that. So, divided by W naught initial weight of the pellet and so, that gives you 1 minus then after some manipulation of this 1 minus 8.01 into 10 to the power 6 r i cube, now reacted we know we already calculated 0.41. .

Now everything is known so, r i cube would be this 1 and r I would be this one which means about 4.25 millimeter. So, 4.2 point millimeter radius would be there of the unreacted wustite after 3 minutes. So, which means almost 1.5 millimeter diameter has been reacted and formed iron. So, this keeps you an idea, how 1 can calculate the various parameters, or can obtain the unreacted radius of the pallets and thing.