Steel Making

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Module No. # 01

Lecture No. # 07

The Science Base of Iron and Steelmaking

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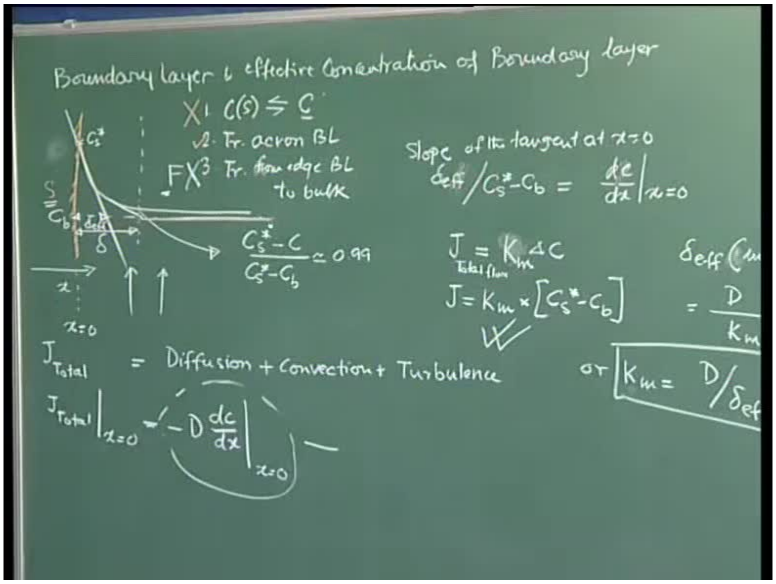

Boundary layer & effective Concentration of Boundary layer

X 1 $C(s) \rightleftharpoons \underline{C}$

2\. Tr. across BL

FX 3 Tr. from edge BL to bulk

Slope of the tangent at $x=0$

$\delta_{eff} / C_s^* - C_b = \frac{dc}{dx}\Big|_{x=0}$

$\frac{C_s^* - C}{C_s^* - C_b} \simeq 0.99$

$J_{\text{Total flux}} = K_m \Delta C$

$J = K_m \times [C_s^* - C_b]$

δ_{eff} (

$= \frac{D}{K_m}$

J_{Total} = Diffusion + Convection + Turbulence

or $\boxed{K_m = D / \delta_{ef}}$

$J_{Total}\Big|_{x=0} = -D \frac{dc}{dx}\Big|_{x=0}$ —

Let me now illustrate or introduce a few more concepts and the first that I want to talk in the context of mass transport, before I conclude my discussion, is the effective concentration boundary layer thickness and the boundary layer thickness.

So, it is a concentration boundary layer and effective concentration boundary layer. Now, we consider a solid say which is dissolving, so this is a solid here and this is the fluid, and the flow is in this direction, we are talking about convective mass transport and this is the direction x.

And if you plot the concentration versus distance in this particular system, the concentration goes like this; c b star s and then, it changes in this particular fashion and goes like this. And as I have indicated earlier that the distance, where suppose this, if at this distance, if we say C s star minus C divided by C s star minus C b, what is C b? C b is this for concentration. If it is proximately is equal to 0.99, so the location at which the concentration is such that this definition or this criteria is fulfilled, that particular location the distance from the interphase is the concentration.

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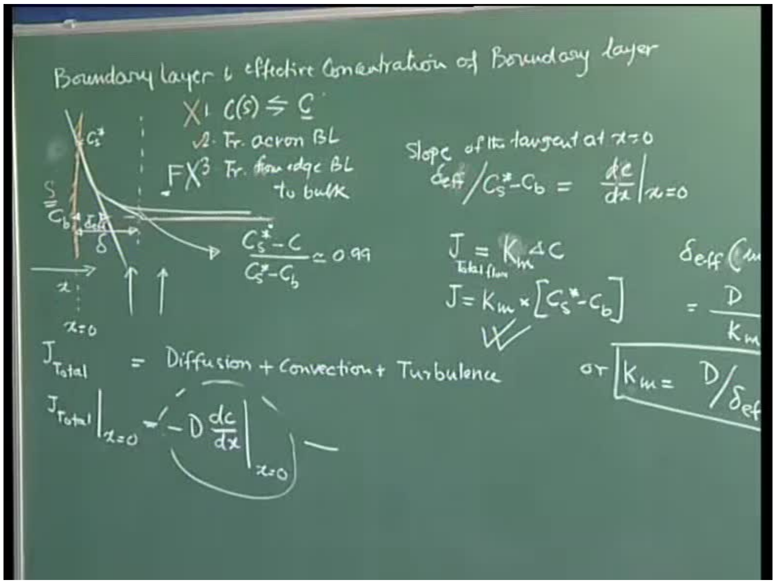

Now, if you draw a tangent to the surface at this particular point, suppose this is the tangent, then you see the slope of the tangent, the slope and this is at x is equal to 0 is nothing but I would say this is c s star minus c b perpendicular divided by so this and the delta this distance which is nothing but delta.

So, therefore, I can say that the slope of the distance actually this should be I would say this distance, suppose this is the distance and divided by this distance I name as delta equal.

So, this distance divided by this distance becomes equal to the slope of the tangent. So, this is I say delta defective or this is dt over dc over dx at x is equal to 0. So, now, if you have, for example, if you have seen the definition, the flux I have written is equal to J is equal to D into delta c.

So, therefore, the flux is also is equal to as I have seen this is not is equal to D this is mass transport coefficient So, this is j, the flux is equal to mass transport coefficient into delta c and if you look at it, the delta c remains same and J comes out to be is equal to J is equal to delta c is the same which is K m into C s star minus C b.

Having said so, I can now, on the basis of this you clearly show that, before I think I go and derive this part off, let us look what are the mechanisms of mass transport at the surface. So, mass is transported by diffusion, by convection and it is transported by turbulence.

So, this is the three different mechanisms of mass transport. Now, when you talk of mass transport, so this is the total flux J subtotal; now, if I say that the total mass transport from the surface J total at x is equal to 0, then obviously the convection part is equal to 0, because at the surface there is no fluid flow; at the surface there is no turbulence; therefore, the total flux is going to be is equal to the diffusion flux, which is nothing but dc by dx, but this is at x is equal to 0.

Now, you know that it tends to give you a picture that the mass transport at the surface is diffusion flux or the mass flux at the surface is so little to diffusion, but it is not so. Even though the expression looks like the diffusion flux, you must remember or you must note from this that the slope of the curve is related to the nature of the fluid flow; you can visualize possibly that if the flow pass the solid is very fast, this check is going to be very small .

So, the slope of the curve which is nothing but whatever I have done there; so the slope of the curve will depend on the nature of the fluid flow. So, therefore, even though the expression may look like diffusion, the fluid flow does have a role to play when mass transport in the fluid side is concerned.

So, therefore, if I can manipulate this equation total flux and this is also the total flux, which is mass transport coefficient into the concentration gradient. If I manipulate these two, then I can show that the delta effective comes out to be mass transport coefficients. So, delta effective is in distance, which is the slope which is say has a dimension of meter and this is equal to a mass transport coefficient or the diffusion coefficient which is D divided by or I can otherwise say also K m or K m the mass transport coefficient is equal to D right.

So, this as you can see that the mass transport coefficient when you talk about mass transport between a solid and the fluid is directly proportional to delta and is inversely proportional to delta effective so that means the delta effective is this distance.

So, therefore, as this distance becomes less and less, the mass transport coefficient becomes more and more, which essentially means these distance will become less and less provided the current of fluid is faster solid, which is more intensive and this is K m proportional to the power D to the power 1, when we are talking of mass transport between a solid and the fluid. But if we are talking of mass transport between the two fluids, in that case it is found out that the mass transport coefficient becomes proportional to D to the power half which one can show from in this model of post which we are not discussing here; if we have taken any kinetic scores or mass transport scores you know already.

Now, therefore, the effective concentration boundary layer is important for us and if you know the mass transport coefficient, we should be able to find out the effective concentration boundary layer thickness or vice versa.

Now, in this particular case, for example, as I have mentioned that how do you calculate the overall rate? So, therefore , either you know the delta effective or alternatively if you know the mass transport coefficient, in that case directly you should be able to use this equation and then, you should be able to calculate the rate.

Now, as I mentioned to you already that this C s star, the concentration of the species, which is there in the solid and which is going to the liquid phase is dictated by the loss of chemical equilibrium and thermodynamics, how?

This also I have mentioned and I will briefly reiterate that the transport of the species from the solid to the liquid phase depends on number 1, first is the interfacial chemical reaction once the interfacial chemical reaction takes place, then the transport across the boundary layer and number 3 is from the age of the boundary layer to the bulk.

So, the overall processes of dissolution we can visualize to be comprised of three different kinetic steps; interfacial chemical reaction, which is C at solid is going to C sub at this all that is what is happening and then, we have number 2 is the mass transport across boundary layer, then transport from edge of B L- boundary layer- to bulk. This step can be assumed to be very fast. So therefore, we will say that for the concentration really comes to here like this; end from here edge of the boundary layer.

So, this is really the simplified concentration profile, where I am saying that from this kinetic step number 3 does not exist; so within the bulk there is no difference in concentration; the concentration remains horizontal, whatever reaches here that same precise which is here almost instantaneous.

If I say that this chemical reaction or a interfacial reaction is also very fast related to this, that means, I am essentially saying that the dissolution is controlled by transport across the boundary layer or boundary layer mass transport is the rate limiting step, in that case this chemical reaction becomes… therefore, I can say that this is now I can complete the arrows and this is at equilibrium and therefore, I can say that this equilibrium essentially implies that we have reached the equilibrium solution, equilibrium concentration of the solid at the surface and what is the equilibrium concentration, equilibrium concentration, in this case is nothing but the saturation concentration of the species.

So, at that temperature, where I carry out the measurements I can say I can find out very easily that what is the concentration situation concentration level and therefore, the surface concentration can be this term can be now.

So, therefore, so where the surface concentration, interfacial concentration during boundary layer mass transport is calculated, is simply by the application of equilibrium concepts and in this case, it comes out to be that the saturation concentration is the surface concentration.

And in this case, bulk concentration of course can be taken to be 0 or it can be taken to be changing with time depending on whether the reactor size is much bigger to the dissolving species or not. For example, if I am talking of a 150 tons steel bath and I have added 2 lumps of pirean IBM, I can consider that the bulk concentration of pirean IBM possibly respond 0 0 1 or 0.01 percentage and I can ignore it.

So, generally, we will calculate we will considered these to be approximately is equal to 0; this will be obtained from the concept of equilibrium concentration and the only job therefore, which remains to be addressed at this particular point is the mass transport coefficient.

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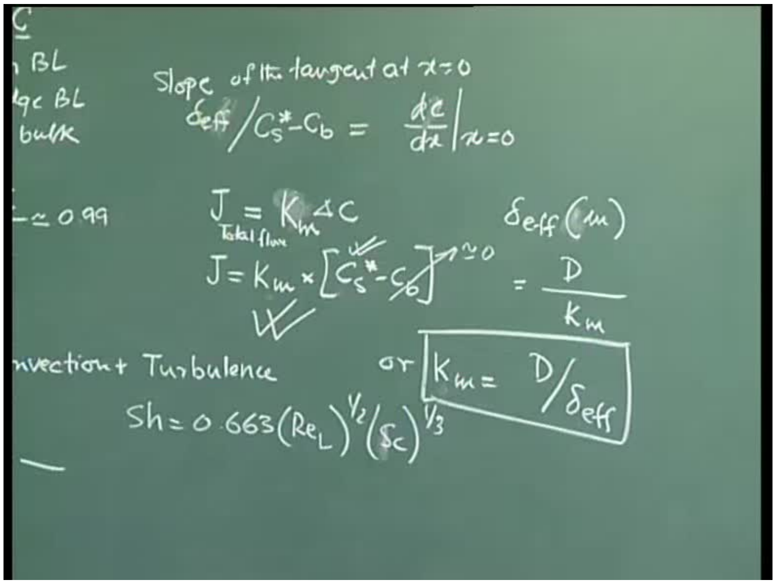

And if you consider the geometry to be a flat free, in that case we can say that Sherwood's is equal to 0.663 into Reynolds raise to the power half and Schmitz raise to the power one - third this can be used to calculate the mass transport coefficient, because this is nothing but K m then L.

So, having given the velocity, I should be able to calculate the Sherwood's number from this flat plate correlation so past a flat plate and use this correlation to predominant m and once I know K m, I can multiplied K m with the C s star and get the net rate of dissolution, which I am trying to know.

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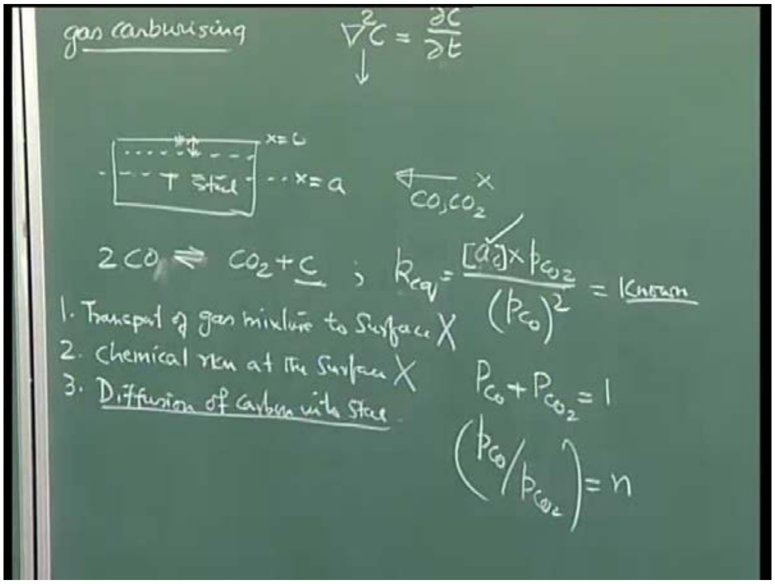

Now, we can say few more things about slag metal reactions and multiphase controls. So, let us I can also before I going to that, I can also tell you one more thing that how thermodynamic concepts are used to determine interfacial concentrations.

I will take the example of say gas carburizing and explain this concept to you and it will be certain to you that yes, in mass transport analysis, indeed the knowledge of thermodynamic is adequate and the knowledge of thermodynamics and consideration of equilibrium really gives us the avenue to you know fix concentrations, which are used to compute the rate of mass transport.

Now, suppose I have a solid and I am using a gas Co, Co 2 at a high temperature T and we have carburization taking place, which is known as gas carburization; so this is steel, which contains, and this Co 2 basically decomposes at the surface to produce 2 Co Co 2.

Now, in these cases what happens is, if you want to find out the rate at which carbon is diffusing or the rate at which the case depth means, the depth to which carbon is penetrating noticeable carbon penetrates.

If you want to calculate this rate, it is necessary for us to have the surface concentration. No, why it is necessary for us? Because if you remember, I have told you that we have to solve this equation in order to find out the concentration profile of carbon.

So, we have to solve the differential equation and in this particular case, we will require the boundary conditions that at x is equal to 0, suppose this is x is equal to 0 and this is x is equal to some constant a at x is equal to 0; we have known the boundary condition, because this is a second order derivative. So, we will require a boundary condition here.

Similarly, at x is equal to a, where carbon is not able to penetrate the concentration for all time remains equivalent to the original concentration level at t is equal to 0. We need another condition, which essentially tells us, which essentially gives us that time t is equal to 0; the concentration everywhere is equal to the homogeneous from concentration.

So, we need the surface concentration to calculate the rate at which carbon is defusing to calculate that is the k th depth here. Now, how do we determine this surface concentration here? So, surface concentration here which determine on the basis of… So, we have how the process goes on the carbon monoxide; carbon dioxide mixture comes into the furnace, enters into the furnace, then the carbon monoxide reaches the surface; at the surface these chemical reaction takes place and thereafter, this carbon which dissolves into the solid starts diffusing. So, therefore, there are we can visualize it; the whole process to be made up of several kinetic steps.

The first kinetic step is transport of gas mixture to surface; number 2, chemical reaction of the surface and number 3 diffusion of carbon. So, the rate at which carbon or the case depth is growing is a function of the rate of these three processes.

So, therefore, I can now make an assumption to say that look the gas, whatever I inject here, reaches immediately here; so this is not the rate limiting step. Similarly, this is a high temperature process; so I can say the chemical reaction is not rate limiting; it is the diffusion of carbon that determines the rate of growth of the oxide layer.

So, I can therefore, say that well this equation, which I have written like this, I can represent this equation. This is operating close to equilibrium and if I write the k equilibrium for this situation therefore, I will say the activity of carbon into pc o 2 divided by pc o square.

The equilibrium concept is known to me from thermodynamics; from delta g naught known. Now, suppose is the total pressure, so I have this is known; I have one unknown, two unknown and three unknowns.

So, I have to have three equations in order to find out what is the value of such c or the concentration of carbon at the surface that is what this activity of carbon and the surface is. So, I can write it like this; you can take it to be weight percentage of carbon, but no matter what you take, it turns out looking at this equation we need three equations in order to find out.

If the whole experiment is conducted at one atmosphere pressure, then I can say pc o plus pc o 2 this is equal to 1; this has to be fulfilled and finally, I can say that the gas mixture that I have been producing, if it is has pc o, pc o 2 the ratio of composition is known to me, in that case the whole purpose is fulfilled. So, I have now three equations and based on this equation, I can calculate this surface concentration and this forms the basis of rate calculation.

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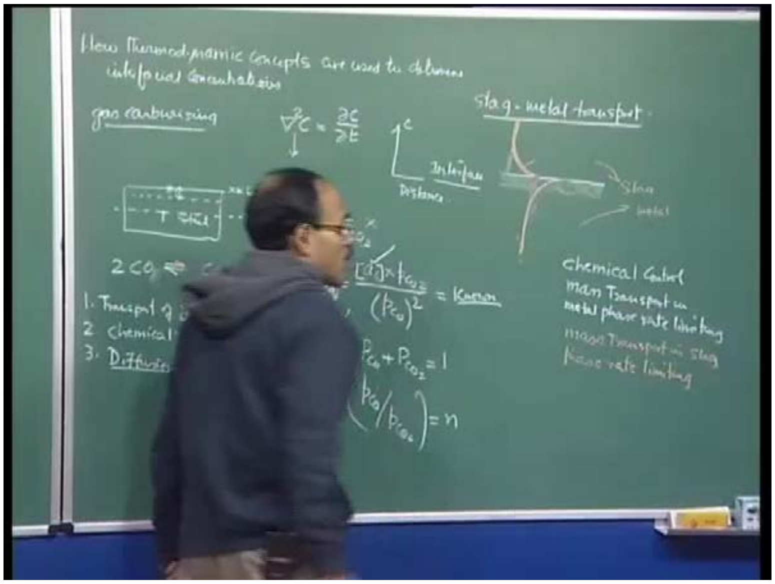

Finally, before I conclude, I want to show you the slag metal reaction; just show you some figure and explain slag metal transport so that you understand. If I have a species, which is transferring between slag and metal, so this is the interphase and this is metal. Basically if a species is transported as I said, that we have slag phase, metal phase transport, slag phase transport and chemical reaction.

So, I can say that, if there is only metal phase transport is rate limiting; slag phase transport is not rate limiting, in that case the mixing or the mass transport in the slag is instantaneous and the concentration profile looks like this.

If I say that both metal and slag transport are rate limiting, then I can say that well, this chemical like this, you must remember that this is the interphase; if you plot temperature there, you find at the interphase, you have a constant temperature, but this does not have been produced plot concentration.

So, this is what we are doing is, this is basically concentration and this is basically distance that is what we are trying to plot. So, the red line that I have shown here basically represents the slag metal phase controlled. So, there is some difference in interphase; there is a boundary layer development.

So, there is some resistance across the boundary layer in the transport is rate limiting and corresponding red line is horizontal, which essentially means that there is no concentration gradient here and therefore, the transport in the metal phases is not gradient.

We have three possibilities here; either one is species transported in the from the metal to the slag or vice versa. We can have either the metal phase rate limiting or the slag phase transport rate limiting; firstly I would say we can have firstly transport processes as the rate limiting or chemical reaction as the rate limiting.

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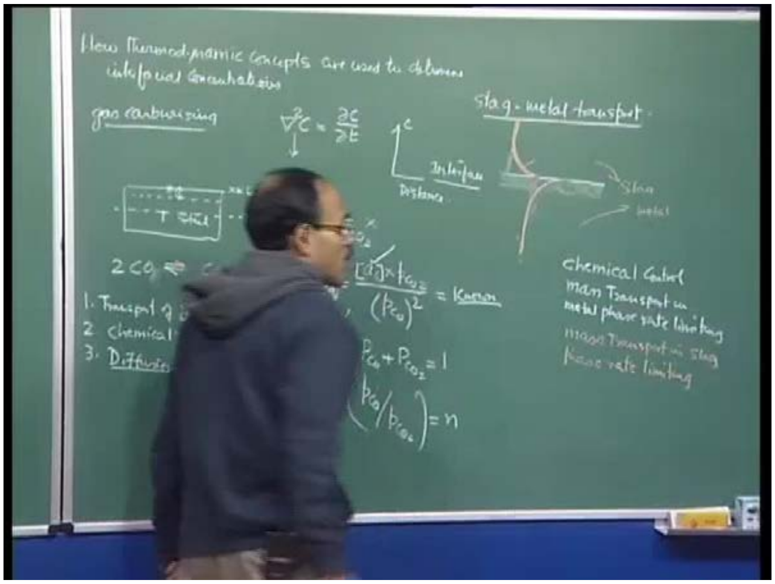

Now, of the transport processes being rate limiting or if the transport processes are rate limiting, then I can say transport in the metal phase can be rate limiting or transport in the slag phase can be rate limiting.

So, there is possibility of one phase controlling and there is possibility of mass transport being controlled by transport in the phases. So, therefore, I can say that it could be there is a possibility of purely chemical control this is one possibility that means the reaction controls are, in that case I will draw this particular line.

If it is chemical control, then I will see that well, there is no boundary layer neither in the metal phase or in the slag phase the lines are completely horizontal and this is an indication of chemical control, that means, the rate of the chemical reaction is rate limiting. Pure chemical control, other hand if I say that mass transport is rate limiting in the metal phase, I will say that well this goes like this; this is case 2, which I would say mass transport. In metal phase rate limiting and if I say that this is also like this, that the line goes like this, then I would say this is also case of mix transport control; I would say this essentially represents mass transport in slag phase rate limiting.

Now, we can have various permutation and combinations. So, if I now draw these two lines simultaneously, this line as well as this line, if I draw them simultaneously, then I would say that well, this essentially represents that transport in both metal and the slag phases is rate limiting.

If I draw only one line out of the two, then I will say transport in metal phases rate limiting or slag phases rate limiting. On the other hand, if I draw these two lines as horizontal vertical lines here, then I will say chemical reaction as the rate limiting.

This essentially also tells us that well, this could be mixed transport control and this nevertheless that is not only tell us that there is you know that chemical reaction is not rate limiting is similar kind of plots can also be. So, this is a scenario which I would say that when this sort of a condition exists and this I would say is what is known as mixed control.

Mixed control basically implies that more than one kinetic steps are rate limiting; mix control also does not tell us that it is whether mass transport it rate limiting or cubic mass transport for chemical reaction is rate limiting, it tells us that more than one kinetic steps are involved in the whole process.

These two steps could be mass transport in the both phases rate limiting or these two processes be such that mass transport t in the both phases as well as chemical reaction at the interface these responsible for governing the rate of the process.

So, enough is said about mass transport. Now, let us concentrate on the situation when chemical reaction is the rate limiting step. So, I have shown you that if mass transport is the rate limiting step, how to calculate? If it is a diffusion mass transport, you calculate the diffusion fluxes solving the relevant equations; if it is convective mass transport, you know the mass transport coefficient.

So, theoretical frame work do exists as we understand based on which the rates of the mass transport controlled processes can be calculated. Now, in those situations, where chemical reaction controls the rate and as I have mentioned to you that, by the by how do you find out for example whether mass transport is the rate limiting step or chemical reaction is the rate limiting step?

You will have some acid tests and what are those steps? Suppose you take a reaction and you increase the gas velocity or the intensity of stirring in the system and if you find that the intensity of stirring does not have any significant influence on the rate of the process reaction, in that case you will conclude rate is not chemical control and if the stirring has no effect, it essentially implies that the rate of the chemical reaction process is controlled by chemical reaction.

So, it is chemical kinetics control and not mass transport control. On the other hand, if you say that the temperature if you increase the temperature, the second test would be if you increase the temperature and you find out that if I increasing temperature the rate of the process is not changing in significantly, in that case you can say that well this process must be mass transport control.

Because the rate of chemical reaction is strongly dependent on temperature and we should expect that if you increase the rate, if you increase the temperature, the rate of the process particularly for those, where chemical reaction is rate limiting is controlled extensively.

So, we have catalyst, for example, you introduce a catalyst and the catalyst will have no role as per as the rate of mass transport is concerned, but the catalyst has some role as far as chemical reaction rate is concerned.

So, catalyst can influence the rate of a chemical reaction, but not mass transport. So, using a catalyst, you should be able to find out a nature of the rate limiting step. So, coming back to the question of, calculation of rate when chemical reactions are rate limiting?

In that case, we must understand that there is no theoretical basis based on which like mass transport, we should be able to calculate the rate of the chemical reaction; the rate of the chemical reaction has to be predominantly determine by knowing the rate constant or experimentally determine the order of the reaction and rate constant.

So, it is totally experimentally determine rate that is to be obtained when chemical reaction is the rate limiting step. There is of course some theoretical considerations to go in order to find out the concentration driving force for the chemical process, but apart from that, the subject is going to be only based on experimental measurements.

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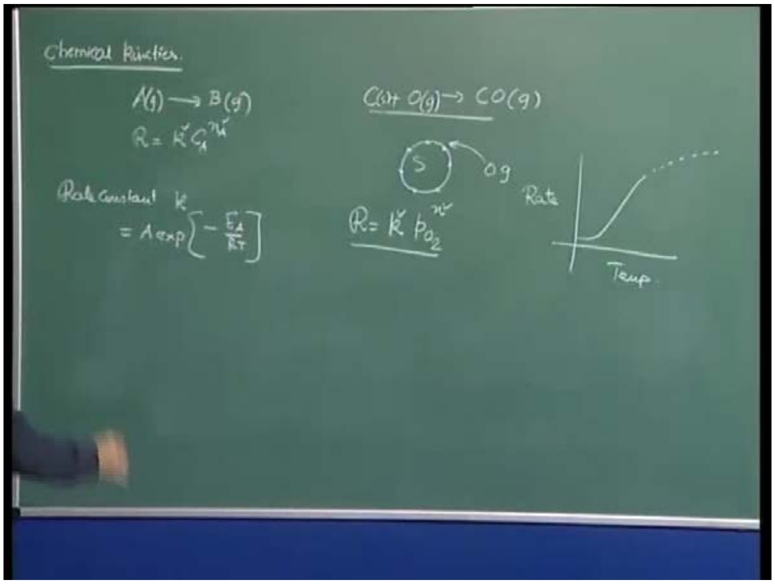

Now, suppose we have chemical kinetics, I will very briefly just mention some of the key concepts. Suppose we have this is the forward reaction and suppose both of these- a gaseous product A is being converted in to gaseous product B and I can say that the rate of the reaction is equal to the rate constant into concentration of A raise to the power n A, in which n A represents the order of the reaction; n A could be 1, 1.52 depending on the process; this is the rate constant and this is the overall rate and this concentration, is the concentration per unit volume; this is a homogeneous reaction A is a gaseous product and B is the gaseous, R product gaseous reactant and B is a gaseous reactant.

Consider this situation, we have carbon plus oxygen and producing carbon monoxide or we can say that in this case, for example, we have a gas solid reaction, this is again the forward reaction; so this is now a hydrogenous reaction; this is the homogeneous reaction A is gaseous B is gaseous; here we have oxygen and this gas carbon is a solid and carbon monoxide is a gas so this is a hydrogenous reaction.

And hydrogenous reaction as you all know so you have the solid here and you have the gas here, so the site of the reaction is actually like this; so these are the sites of reactions.

And as we can see if we write down the rate in this particular case, I can say that well, the rates are always to be you, know I have written the concentration, but because as I have had mentioned also that apart from concentration, perhaps activity of you know chemical potential is for more important, because that represents the driving force. And if I assume that well, the gases behaves ideally; the activity of carbon is in pure phase and carbon is equal to 1;so I can then say that it is going to be is equal to po 2 and this is based on this opposition, that the activity of carbon is equal to 1; oxygen is behaving like an ideal gas and which n represents the order of the And this specific rate constants, this order of the reactions there is no way that for hydrogenous chemical reactions, one can determine experimentally or theoretically.

So, therefore, that overall rate calculation has to be… Now, when I have shown this equation, which is going from left, it is a continuous oxidation of carbon to carbon monoxide. However, when as this equation, if this equation approaches equilibrium or it is not at equilibrium; it is approaching equilibrium, that means, there is a reverse reaction rate also, in that case the overall rate of the reaction is going to be the forward reaction and minus the backward reaction.

So, the net rate of the reaction is the rate of the forward reaction minus the backward reaction and in that context, the expression becomes a far more a little bit more complicated that we have to deal with two different rate constants- forward rate constant and a back ward rate constants.

Now, the rate of a chemical reaction basically, where is suppose, for example in order to the hydrogenous rate constant, so we can say this is k and this where is A exponential minus E sub A divided by R T.

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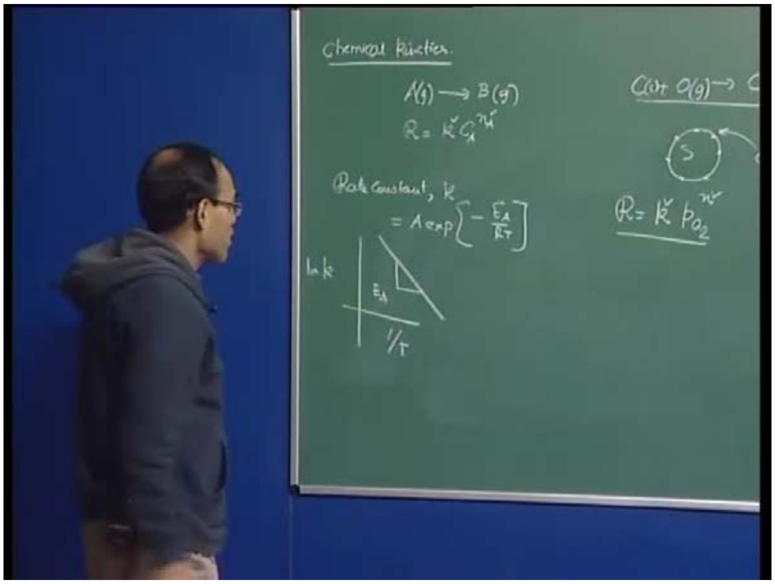

How does the rate changes with temperature? And as I mentioned to you repeatedly that the rate will change considerably significantly with temperature, because the temperature increases energy of the system and chemical reactions require bond formation and bond breakage; so they are associated with high activation energy.

So, you have to supply lot of energy in order to found new breaks break few bonds and found new once, because only when you break bonds, you will be able to form new once and at the whole process requires large and therefore, the rate is dependent on so that is how the rate change increases and if you look at the rate constant k versus l n k versus one by T and then, you will see, you will get a straight line with a negative slope.

So, rate constant k is equal to a exponentially minus E A by R T. So, if the l n k is equal to A l n A plus minus A exponential and l n A will nullify and therefore, we going to have E A by 1 over R T, which essentially tells us that if you plot l n k versus 1 by T, you should get a straight line and the slope of the straight line is a measure of E sub A; I am not saying it is equal to E sub A it is a measure of E sub A or the activation in order to process.

But looking at the activation energy also, we should be able to find out that, whether the reaction process is chemical control or mass transport control. Mass transport control processes, where there is no breakage of bound involve we will require we will know that this the mass transport processes are characterized by small activation energy; on the other hand, chemically controlled processes are characterized by high activation energy or more steeper line when you make an l n A k versus 1 by T plot.

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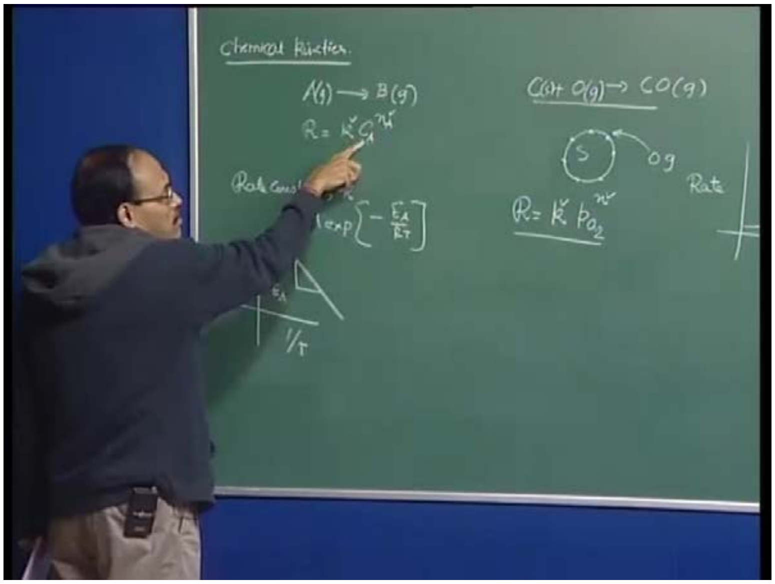

Now, one important thing here is that this concentration that we have introduced here what is this concentration? In this particular case, the concentration that I have written here is the bulk concentration.

So, everywhere there is A, it is a homogeneous chemical reaction, but now the concentration that I am talking about is that not the concentration at this particular location, but it is the concentration at the surface.

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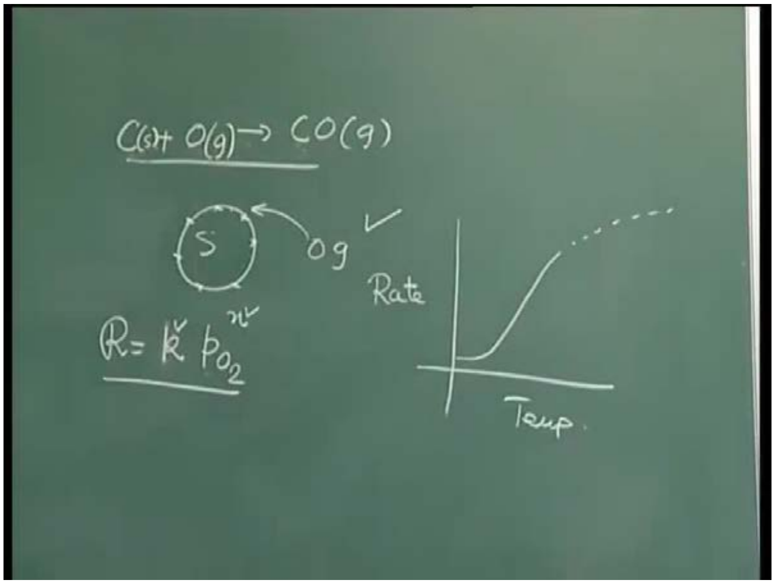

So, if it is the concentration of the surface, we must understand that the area of the surface will matter or the size of the particle is going to matter. So, bigger is the size of the particle, more is going to be the effect area and therefore, the concentration is going to be effected; therefore, the rate of the reaction it is going to be effected.

So, this shows us that when it creates some problem measuring specifying the concentration in terms of concentration per unit volume or amount per unit volume is a very easy task. But how do you know that what is a concentration per unit surface, particularly when the reaction front is changing as a function of time at ten o' clock, the size of the carbon particle is this; at 10: 15, the size of the carbon particle become smaller.

So, the area is continuously changing; so, therefore, there is some issues some problem as far as specifying this concentration at the surface is concerned. But we must understand what I am trying to say here that the rate of the reaction will depend on the size of the particles; if you change the size of the particle, the concentration also changes because this is the concentration at the surface of the solid.

Now, in most of the analysis and this is the parameter, which poses problem what is known to us is the bulk concentration. So, somehow this equation is to be converted in terms of the bulk concentration by applying of you know relevant theories and then, you know this po 2 the surface concentration is to be replaced by the bulk concentration.

So, some analyze, some application, some thermodynamics, some additional concepts are necessary in order to convert this equation in a form which we can tackle, because we do not know what is the surface concentration at an instant; what we know is the bulk concentration. So, convert this equation, which contains surface concentration in purely corresponding equation, which contains the bulk concentration.

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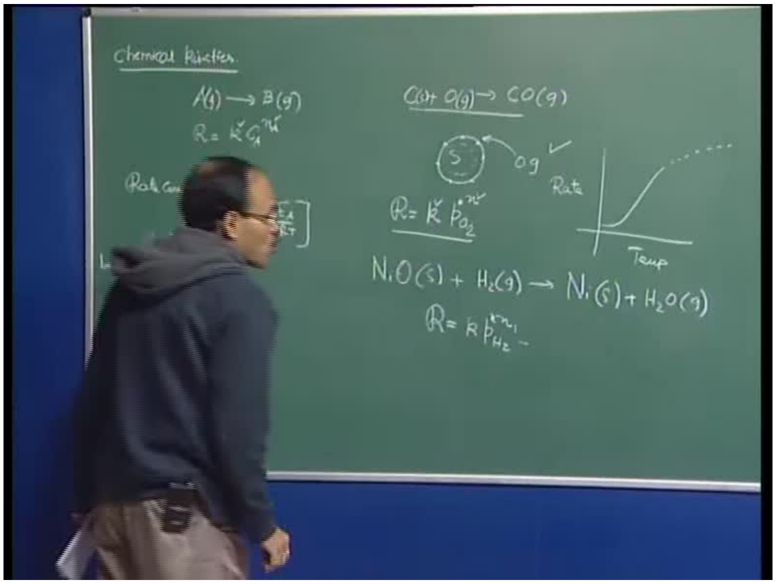

Let us look this particular equation say nickel oxide, which is solid, I will just explain this particular point, and then, we have hydrogen, which is gas, and then they we nickel, which is solid and H 2 O.

So, similarly, the rate of the reaction is going to be proportional to the forward reaction. Nickel oxide is solid activity is equal to 1; so, I can say that the rate of the reaction is going to be proportional to the concentration of hydrogen in the system.

Now, if we consider this, similar kind of an expression will come and therefore, we will encounter that well, you know the reaction rate will come out to be partial hydrogen and this is going to be… so this is the surface concentration; so this is n 1 and that is the rate.

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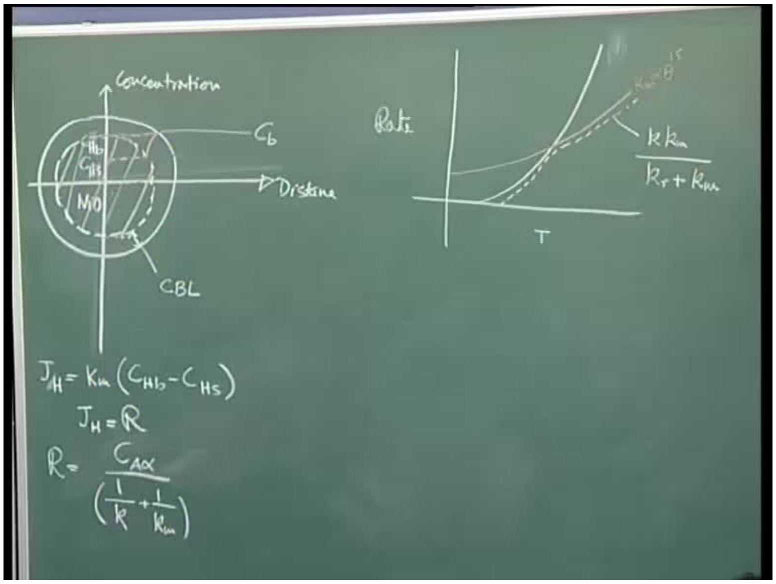

So, how to determine the rate of this particular the overall rate by converting this into a bulk concentration? So, if you look at the profile, how does the profile looks like? So, we have this is the nickel oxide and then, we have this is a residing interphase; this is a topo-chemical reaction model.

So, we draw this line; let us now look at that concept how we can determine or write the rate equation in terms of surface concentration and not in terms of in terms of bulk concentration and not in terms of surface concentration.

And just now I have written in the left about the nickel oxide hydrogen reaction; so this is what I have intent to drawn here; this is the nickel oxides sphere actually and whatever is shown here, this distance is the concentration boundary layer.

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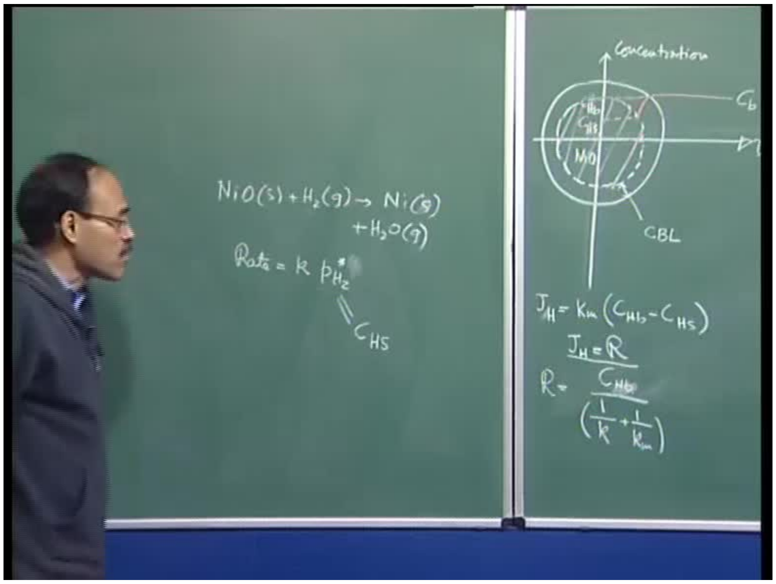

So, the outer solid line represents the boundary layer and the solid nickel oxide is this; now this is the bulk concentration and as per our assumption, that the bulk concentration prevails lighter to the interphase and then it drops gradually; we have surface concentration, which is equal to C sub h s, which I have represented at partial pressure of hydrogenic; I would have written the same equation as nickel oxide solid plus hydrogen gas is equal to giving rise to nickel oxygen nickel as solid and then H 2 O as gas.

So, the rate of the forward reaction is represented in terms of C H s, if activity is equal to 1 and then, what is shown here is that how the concentration from the boundary layer reaches to the gas in the surface concentration.

So, this C H of s is actually partial pressure of hydrogen at the surface, which I would write that the rate is equal to rate constant k into p H 2 and I can say and if I assume that the rate is first order with respect in that case n does not.

So, this is an assumption as I have said. How do you know that the rate is first order? We have to carry out experiments, introduce more and more hydrogen and see how does the rate of the reaction changes with the concentration if there is a linearity between the two that is an essential indication that it comes to that the order of the reaction is equal to 1.

So, for the time being if you assume that the rate the order of the reaction is 1, then this becomes expression and this is the surface concentration and which is equal to C H sub s, which is shown in this particular figure.

Now, we know that we have a through the boundary layer we have a boundary layer transport theory and based which is the driving force; the driving force is this C H sub b minus C H s and multiplied with the mass transport coefficient gives me the total flux or convective flux of hydrogen through across the boundary layer.

Now, this surface has very little capacity to accumulate material and that chemical reaction is the rate limiting and mass transport is not the rate limiting, because we are discussing now chemical kinetics. So, we can assume that whatever the convection current is taking hydrogen to the interface, that itself is responsible that is exhibiting as the rate of the chemical reaction.

So, therefore, I can say that J sub H is approximately the convection flux is approximately is equal to the rate of the chemical reaction and if I do the manipulation, of course I am not going to the details of it these are available in standard books and you can see that, in that case, the overall rate of the reduction reaction- nickel oxide reduction reaction- can be expressed in terms of this interfacial concentrations C A alpha as well as you know the two rate constants which are nothing but the mass transport resistance to mass transport and the distance to chemical reaction, which are also known as the respective mass transport coefficient.

So, I can write this equation; I can write for J H is equal to R and then for R I can write down this equation, manipulate with the two and then, I can derive at this equation, which is a trivial exercise and we should be able to do.

So, now, you see that although by initial rate expression was this, which contains surface concentration, I have been able to modify by using my knowledge of the subject are write in expression for rate, which is now in terms of C A alpha of which is actually in this case is not A alpha, which is going to be C H sub bulk; so the alpha has no meaning.

C H are bulk. So, earlier it is p H 2 and this p H 2 is basically synonymous my C H sub s that is what is the surface concentration and now, I have been able to convert this into this particular expression and now you see that this has come into that.

And you on the basis of this, you can also plot from this analysis that how does the rate varies as the function of temperature.

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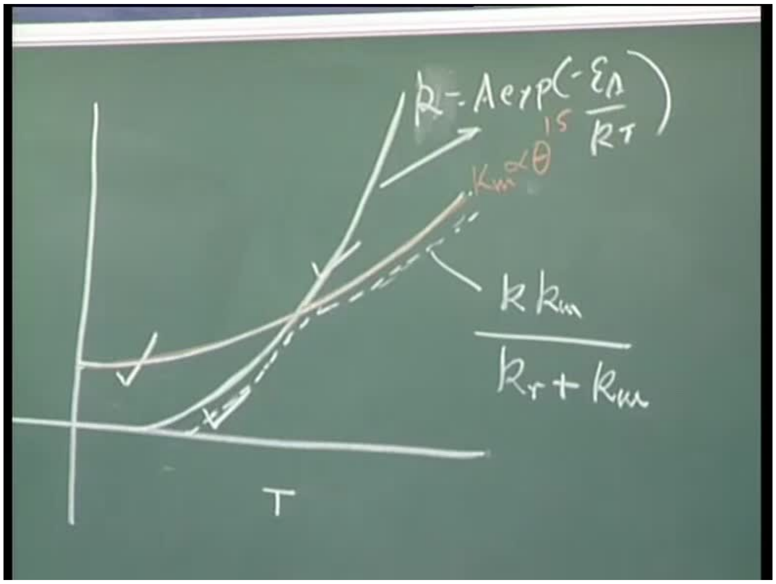

So, this is the cheapest one line which I have drawn; this line essentially to out tells us about the exponential rate of variation; this is that how does the mass transport coefficient varies; so this is rate k is equal to A exponential minus A by R T so that is what it is; this particular line and this tells us about the dependence of mass transport coefficient on temperature, which is theta is the absolute temperature in this particular case and this gives us a situation when we have mixed control and we have how does the rate will vary as a function of.

So, initially towards the lower temperature, the rate is more chemically controlled, because this line as you can see goes parallel to this line and at higher temperature this goes to parallely with this particular line, which is the mass transfer line and therefore, this gives us a scenario when the rate is controlled by both mass transfer as well as chemical reaction.

So, this is the curve of response of chemical reaction rate controlled processes with temperature; this is the curve for response of mass transport controlled reaction with temperature and this is the curve for the response of both mass transport and chemical reaction control with temperature and the last one, as we have shown you know as path characteristics a lower temperature characteristics which is a kin to the top line or the steepest line and towards the lower higher temperature we see that chemical reaction is now very fast therefore, it is mass transport controlled and the equation bounds down this.

Now, we can also on the basis of this, say that look at the… you can find out the value of this; you can find out the value of this and then, you can conclude that which is the rate limiting step.

So, whichever phases whichever steps is going to show the largest resistance, that controls the rate and these are direct measure of the resistances to mass flow. Therefore, due to chemical reaction and due to mass transport so, therefore, will looking at the value of k m and k r, you should be able to conclude that whether mass transport its rate limiting or chemical reaction in the rate limiting.

Now, the subject is unless you may I can go on and on, but I think it is just to revise and give you or remind you or the basic concepts you know as you go through this subject of steel making. So, all these things starting from thermodynamics, fluid flow, heat transfer, mass transfer, chemical kinetics they are all essential for us and we have good idea of all these subjects in order to handle steel making, you know topics very elegantly or in a smart way or quantitatively whatever you can say.

So, I mean, we will not be able to do perform a many design calculations or process calculations, unless however, fundamental knowledge of this subjects are really adequate.

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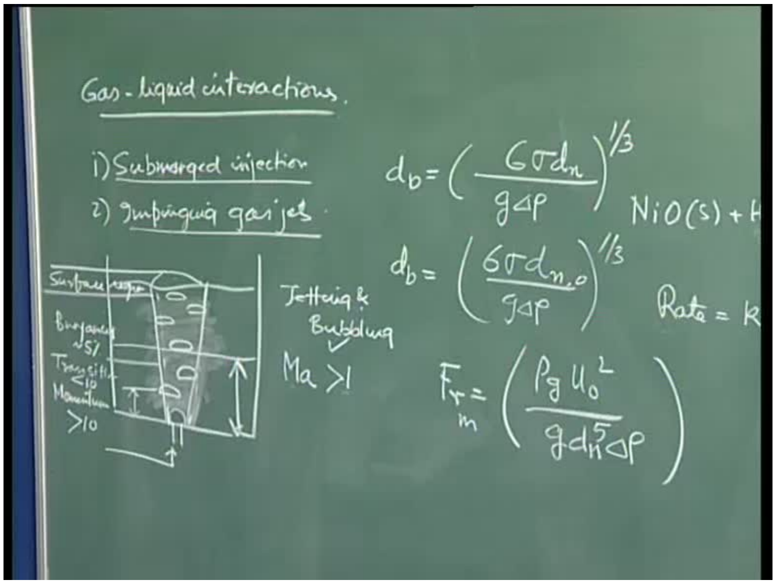

Gas - liquid interactions.

i) Submerged injection

2) Impinging gas jets

$$d_b = \left(\frac{6 \sigma d_n}{g \Delta \rho} \right)^{1/3}$$

NiO(s) + H

$$d_b = \left(\frac{6 \sigma d_{n,o}}{g \Delta \rho} \right)^{1/3}$$

Rate = K

Jetting & Bubbling

Ma > 1

$$F_{r_m} = \left(\frac{\rho_g u_o^2}{g d_n^5 \Delta \rho} \right)$$

Now, very briefly one more additional topic, which is of quite importance to us is gas liquid interactions, which is basically I will discuss this later on in the context of secondary steelmaking and this is a topic which goes beyond all this and is of prime fundamental importance to us when you look at oxygen steelmaking, we have reacting gasses, oxygen is being blown into molten metal.

We talk of argon start ladle, we say argon is going into ladle, tundish also we have gas injection, mold also we have gas injection, everywhere there is gas liquid interaction and gas liquid interaction is a subject very close to the heart of steel makers and we have to have adequate background in order to handle or quantitatively tackle the molten phase measure of steel flows particular gas injection systems.

Now, we have encountered two different modes of gas injection, for example, one is the submerge injection and the other is impingent. So, submerge gas injection basically is encountered in ladles, in oxygen steel making converters, whereas if you go to LD steelmaking or if you go electric arc furnaces, where you have lances injecting oxygen at the surface you find out that gas that is impinging on the surface of the gas.

Submerge gas injection is very common in ladle, tundish, mold, etcetera impinging gas gets are very common in AOD converters in LD converters as well as in electric arc furnaces. And the nature of the gas liquid interaction could be reactive interaction, if your oxygen is injection, then oxygen reacts with metal; on the other hand, if we are injecting inert gasses, in that case there is only hydrodynamic interaction and thermal interaction, but there is no material interaction, because inert gas does not dissolved.

Now, submerged gas injection you can encounter various… so we have a submerged here or porous plug through which we inject the gas. Now, we can have phenomena call jetting and bubbling and jetting ensures basically when mac number based on the free strip velocity is greater than 1 and on the other hand, but mac number is not less than one or smaller than and the velocity is very small, in that case there is no jetting; in that case we get bubbling.

Basically in the bubbling regime, we have a gas envelope which forms and these gas envelopes basically as we increase the gas velocities it extends and ultimately what happens you get a completely jet core, which looks like you know something like this.

On the other hand, when you have bubbling regimes, you have discrete bubbles which form and this discrete bubbles you can say rise. At the limit of gas flow rate becoming very small, the size of the bubble is governed by only interfacial property and this is I think 6 sigma divided by g delta rho and this is raise to the power 1 by 3.

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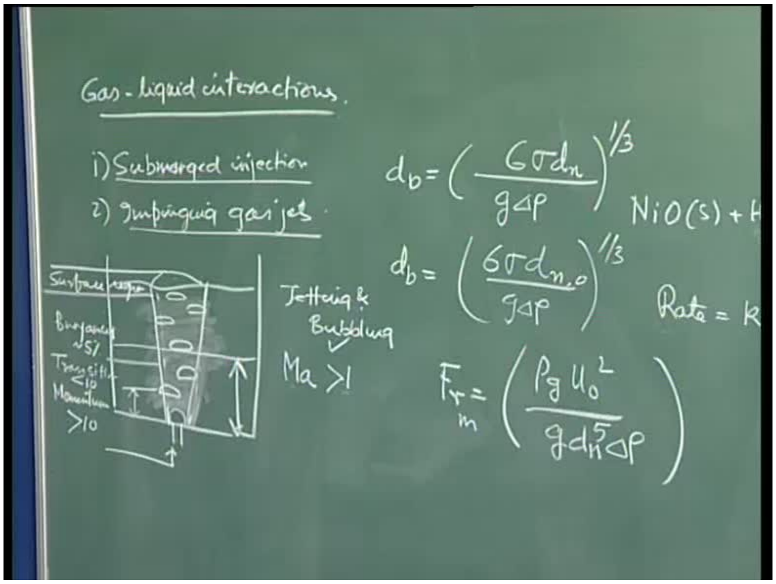

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NiO(s) + H

Rate = K

So that represents the expression of the size of the bubble and we have this is d nozzle here and this d nozzle in the case of metal it takes it. So, d nozzles essentially in water models I would take this d nozzles to be the inside diameter of the nozzle; on the other hand, I will take this is the outer diameter of the nozzle, because the weighting behavior or the gas in high temperature liquid metal system.

So, the small bubbles forming at the orifices are going to be calculated, but these are single bubbles forming at the orifices very rarely such conditions are encountered in the system.

Now, where do we have bubbles? We basically have four different regimes; we have a plume here and we can say the first regime is going to be you know it is the momentum region, where the momentum of the jet gas is going to be felt, then we have something like transition region and then, finally we have buoyancy region and lastly we have surface region.

So, these are the four regions in which the flow rates or the flow regimes are going to be characterized and we have momentum region, gas voidage is very high more than 10 percentage or so; we have transition region where the gas voidage is less than 10 percentage and buoyancy region approximately 2 to 5 percentage and again, the surface region we have a very small gas voidages.

To know the characteristics, so basically large part of this system is buoyancy therefore, when the mac number is much less than 1, the free stream velocity is much less than 1, I will also discuss later on. But the gas is injected as I have mentioned either through a nozzle or a tuyere or through a plug and when you have buoyancy region, you know occupying the major part of it at low flow rate when the mach number is equal to less than much less than one, we can say that these systems are basically buoyancy driven systems.

One important characteristic comes when you have, where injecting a reacting flow and then you have small shallow bathtub; ladles now will have bigger bathtub, but when you have shallow bathtub, you have you know swirling motion.

So, even though this configuration looks like a 2- dimensional configuration or an axisymmetric configuration, when you have shallow bathtub and injection at high rate you can introduce, lot of swirling flows or rotational flowing system, which can aid in mixing in the process itself and in OBM converters, this is very commonly encountered.

So, coming back to the buoyancy driven plume, there is a number called the modified froude number, which is very important and this modified froude number basically g d to the power 5 d n to the power 5 this square and delta rho and this froude number is inertial to the buoyancy force and this is a very important number in order to find out the characteristics of the particular system itself.

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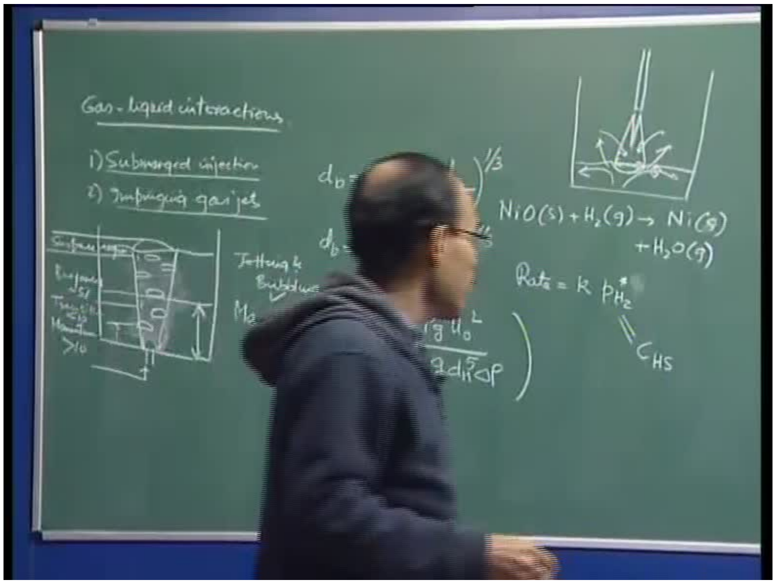

So, the modified froude number is used in order to determine or know the state of the system when submerge gas injection is used. Finally, very briefly about the impinging gas jets, when you have impinging gas jets on a system, for example, you have a nozzle, particularly when you have a LD converter, you have different kinds of a nozzle here and that different kinds of a nozzle means you have a tube and then, you have a 6 holes lams or something like that which distributes some molten metal.

So, there is a core of the jet and then following the core, you have large scale entrainment and so the considerably widening of the jet takes place and this widening of the jet ultimately impinges here. So, by controlling the height of the nozzle you can control the depth of this penetration as well as you can control the impingent area itself.

So, core is very important to us and this core basically is about 3 to 8 percentages and what is this core? This is the supersonic core of the jet and this core is 3 to 8 percent of the jet nozzle diameter and there are technologies to be available like the cojet technology, which can enhance the length of the potential core of the supersonic core of the jet is significant extent.

But beyond the supersonic core, you have large scale entrainment as a result of which the jet diameter increases and once the jet diameter increases, its moment gets distributed and by the time, it extracts the molten metal surfaces; its kinetic energy has lied down significantly.

The two important parameters which determine the extent of stirring and the dynamics of the systems are the cavity depth and the cavity diameter and these are characteristics of the gas injection; there are empirical correlations, etcetera available. You may have a very hard blow and in that hard blow, you can should be able to arrival out lot of molten metals in the form of droplets and so on.

So, one has to have quite a bit of knowledge of submerged gas injection as well as impinging gas jets in order to tackle or handle the multiphase nature of the steel making system, particularly when one talks about the gas liquid interaction, the level of agitation, the droplet formation and all these kinds of issues.