Chemical Engineering Principle of C V D Processes
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Lecture No 14
C V D in Hot Corrosion

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Good morning and welcome to the next lecture in our course on Chemical Engineering principles of C V D processes. In the last couple of classes we looked at a sort of an unconventional, non-traditional C V D process which is what happens in tungsten filament incandescent bulbs where the tungsten evaporates from the filament and deposits on the bulb walls.

And we saw how by taking a simple P V D process and by providing appropriate chemistry you can convert it into a C V D process and actually in this case prevent the deposition of tungsten from taking place. And I also mentioned that there are what are known as filament C V D reactors where you actually try to provide conditions which promotes the evaporation of material from the filament and deposition on to a substrate and we will discuss this design later on in some detail.

Today I want to take you through another situation where chemical vapor deposition happens in a somewhat unintended fashion and this has to do with combustion of fossil fuels in gas turbines and power plants and so on. Many of the fuels that we use today are getting increasingly of, you know, lower quality because we are running out of reserves.

So for example with coal, you keep on digging deeper and deeper and as you go further down the quality of the coal is not as good as layers that are closer to the earth surface. So when you are burning coal you have a problem with sulphur contamination, ash particles contained in the product gases that deposits, so you have problems like fouling and slagging and corrosion and erosion.

But these are associated with the particulate debris that is present in the combustion gases mostly the inorganic alumina and silicate ash particles. So that is a different problem you know and in order to deal with that problem you have to know something about particle technology. How do particles move around, how do they, how do they deposit on surfaces, how do they stick to surfaces and so on.

But when you talk about systems where a cleaner liquid fuel is employed, typically a liquid hydrocarbon you would expect that the situation is better. That there would be fewer impurities in the fuel that survive the combustion process. And that is true. When you burn, for example jet fuel or distillate fuel or any kind of liquid petroleum or hydrocarbon fuel, it is true that if you look at the products there is hardly any particulate matter.

However what does happen is if the fuel and, or the oxidant that is used in the combustion process contains impurities, the impurities can react and they can form condensable vapors which can then result in the formation of a, of a condensate on, particularly on cooled surfaces that come in contact with the hot combustion gases.

Now these deposits unlike the C V D deposits we have been dealing with earlier which had all been solid deposits are typically molten deposits and one of the implication of that is the deposit once it is formed does not stay where it is formed. It has the tendency to be mobile.

So for example, if the condensation is happening on the rotor blade of the turbine, then as the blade rotates there is a centrifugal force on the molten layer that deposits on the surface. And simultaneously there is also aerodynamic shear, because as the combustion gases flow past the molten deposit, they are exerting a shear force.

So the local thickness at any point at any instant in time is a balance between 3 processes, the deposition process that is causing the film to form, the aerodynamic shear which is trying to move it away from where it is formed and the centrifugal shear which is also imparting essentially a stream wise motion.

So it is really a balance because as at any location, as the film is getting depleted, it is also getting replenished from an upstream location, right? So it is an interesting problem in terms of analysis and modeling and simulation and so on. But certainly the precursor, what initiates this whole thing is the deposition of that film on the surface. The impact that this film has is two-fold.

One is these deposits are sometimes corrosive in nature. For example if you have molten sulfates depositing on the surface, the sulphur has the tendency to participate actively in initiating corrosion on the surface. So the presence of the film can lead to corrosion effects even when the surface on which it is depositing has a protective coating.

For example in the gas turbine industry the turbine blades are typically made of steel for cost reasons and also for structural properties. But steel has a tendency to easily oxidize and corrode. So what they do is they put a protective oxide coating on top which is supposed to shield it from particulate matter as well as, you know corrosive liquids and so on.

But this oxide has a certain finite thickness. And if the film, the molten film that deposits on that oxide starts to dissolve the oxide, eventually you can have excessive thinning of the oxide layer at that location and at that point there is like a threshold thickness. Once the oxide thickness falls below that value, the molten film simply penetrates through the oxide and directly attacks the steel alloy material that is beneath.

The other approach that the industry takes is to use what are known as super alloys. A super alloy is one that has much better rust and corrosion prevention properties compared to a more conventional steel or even stainless steel alloy. And if you use a super alloy and you use an oxide coating on top of it, essentially you are providing double protection. But there is a huge cost impact. Super alloys are typically ten times as expensive for the same amount of material as a more conventional alloy.

So you want to minimize their use. And in fact as we discussed in one of the earlier classes, instead of trying to change the entire substrate material to a different alloy material you can use surface deposition and diffusion processes to provide a super alloy structure only for the first few surface layers, right?

So you can actually use C V D as a process to achieve super alloy type of characteristics but only up to a required depth of the surface. So you have a super alloy on which you have this oxide coating but the continuous deposition of these molten salts eventually will lead to corrosion.

And in fact that particular mechanism is known as hot corrosion because the corrosion mechanism is associated with a, first it is a high temperature process. Turbine blade is at a high temperature. The combustion gases are at a even high temperature.

But the hot corrosion actually also indicates the fact that it is happening because of the high temperature involved in the combustion process itself which leads to C V D mechanisms being set in motion and resulting in the formation of the condensate on the surface.

For example if you take a aircraft application, let us say that you are burning jet fuel which is probably as clean as it gets. So in a jet fuel, your sulphur for example which is a contaminant in virtually all hydrocarbon fuels can be a very low level, may be 1 p p m, may be less than that.

But when you are

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flying in a, for example

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in a marine environment, the air that you inject can have significant quantities of sodium and potassium, alkali salts, sodium chloride being the most common and those can be fairly high levels, up to 10 p p m depending on the environment.

So when the combustion process happens you have the impurity in the fuel which is essentially sulphur reacting with the impurities in the air that is being ingested and forming, for example sodium chloride plus sulphur plus oxygen, you are going to get sodium sulphate plus chlorine being released. You are going to form potassium sulphate, magnesium sulphate, calcium sulphate.

All of these are what are known as molten salts and they all have corrosive characteristics because of the presence of the sulphur. And by the way, sodium chloride itself can deposit as a particle and cause corrosion as well because the chlorine will react with the surface but in terms of C V D we will not deal with that. I mean it is more of a particulate transport and deposition process. But just vapor transport and associated corrosion itself is quite significant.

Now if you have, if you look at naval applications, ships which also use turbines, they tend to use fuel of somewhat lower quality. They are called the navy distillate fuels. These fuels have a higher percentage of impurities. So sulphur itself can be 5 to 10 weight percent in the fuel. And so as you can imagine the potential for corrosion is much greater because of the higher level of impurity in the fuel as well.

And so while the fuel quality as well as the oxidizer quality can vary, there is always a potential that when you burn the fuel and the oxidant together and by the way the temperatures you typically achieve under adiabatic conditions can be of the order of 2000 Kelvin plus so there is an extreme degree of dissociation.

The more the amount of dissociation in the gas phase, the more important the C V D becomes. Because what it implies is that you have taken a finite number of elements and because of this extreme nature of the dissociation they are now incorporated in many, many species containing that element.

For example, the sodium that was in the fuel, sorry in the air as sodium chloride, after combustion is going to be present in the gas phase as sodium vapor, N a O, N a O H, N a 2 O, N a 2 S O 4, N a 2 S O 3, I mean there is going to be literally dozens of species in the gas phase containing sodium as an element.

Similarly the sulphur which was present in the fuel, after combustion is going to be present in the gas phase as S O 2, S O 3, S, H 2 S and so on. And so there are many, many opportunities for these sodium containing species and the sulphur containing species to react and form sodium sulphate. So, that is why this is a classic C V D problem.

The molten material is typically the alkali sulphate, whether it is sodium sulphate or potassium or magnesium or by the way it could be condensate solutions also. So you can have mixtures of various alkali salts forming on surface. But the point is they are not present in the vapor phase as exactly the same species. Sodium sulphate gas is not getting converted to sodium sulphate liquid. So that is why it is, it fits the definition of a C V D process.

So now in the industry what you would like to know is if I have a turbine blade I want to be able to predict the lifetime of the blade or alternatively to achieve a certain lifetime, I want to know how much coating I need to put at different locations on the blade, right? So what I do is something called burner rig testing.

A burner rig essentially duplicates in a smaller scale the combustion process that is actually happening in the field. So it is kind of a miniaturized combustion environment where you mix air and fuel together and you have essentially models of the various surfaces that come in contact with the combustion gases such as stators and rotors and boiler tubes and so on and you expose these materials to the flow of the combustion gases under well-controlled conditions for well-defined periods of time.

And then you take the specimens out and you analyze them to see what has happened to them. So what are the key things they look for is what is known as the corrosion map. They want to look at the surface and map it. It is a 3-D map essentially to describe the thickness of the oxide at various locations on the substrate of, of the specimen.

And they also want to look at any evidences of corrosion which you can do by simple microscopic examination. And if you want, if you want to confirm corrosion you can always do E D S analysis to verify that the composition of whatever you see matches that of a corrosion product. So this corrosion mapping is a very important exercise in determining the, it helps us do two things.

One is, as I said, it helps us predict the lifetime of the actual component in operation; b, based on this, it enables us to suitably design it so that it can achieve the lifetime that we are looking for. And thirdly it also helps us to optimize the operating conditions of the combustor.

For example the flow conditions. You can certainly influence the rate at which the deposition and corrosion are happening by influencing the temperature that is achieved, the pressure that you operate at, the fuel to air ratio is another parameter.

I mean, as a simple measure if your fuel is much dirtier than your air, then you want to run under as low a fuel to air ratio as possible. Where as if your air is more contaminated than the fuel then you want to have a fuel-rich condition, right. So you can do some tweaking of your, the inputs also based on this type of simulation and modeling and so on. And that is really what people do.

So this, this, generation of the, the corrosion maps experimentally is an important step but you also need to be able to do modeling and simulation of what happens. And that is where we again get back to the thermodynamics and transport modeling of the C V D process.

Now in terms of the thermodynamic analysis, as with many C V D reactors because the temperature is so high, it is very reasonable to assume equilibrium prevails. So you use your free energy minimization algorithm. For a given fuel composition, for a given pressure and if you assume that adiabatic conditions apply, you can do a free energy minimization simulation to calculate the composition of the product gases.

You can do that at various temperatures. You can do the calculation at the mainstream temperature of the combustion gases and you can also do the calculation close to the substrate where the film condensation is happening. And the calculated mole fractions of the vapor species will then provide you data on the gradient that is going to be driving the diffusion process.

And similarly your temperature distribution simulation will tell you what is going to be the effect of thermal diffusion. You remember I mentioned that a temperature gradient can also drive mass diffusion and that is called thermal or Soret diffusion.

And of course the velocity distribution will tell you what are the convective flows present at different locations particularly along the surface. Because convection is not going to be significant in the boundary layer adjacent to the substrate so it is not going to have a direct influence on the rate of deposition by diffusion.

However it has an indirect effect because it is the convection process that dictates the temperature distribution as well as the species concentration distribution outside the boundary layer. So certainly you have to solve all three conservation equations.

First you have to solve the momentum conservation equation, then the energy conservation equation and finally the mass conservation equation to obtain the temperature distribution, the velocity distribution and species concentration distribution and using that you can estimate the rate at which different species are getting transported to the surface.

So the, the typical equation that you would use is the same one that I had written down for the case of the tungsten filament bulb. For any, now in this particular case what is going on is you have a turbine blade over which the flow is happening and there is a boundary layer that develops on top of the surface.

And so the convective portion, the flow of combustion gases at a particular velocity

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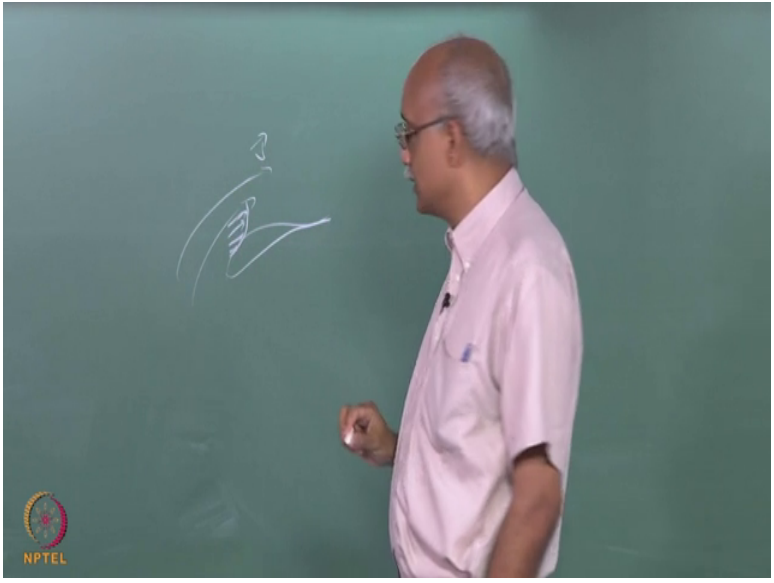

is happening outside the boundary layer. However the deposition process itself is happening due to the diffusive process which is characterized by a Fick diffusivity of the species i and a thermal diffusivity of the species alpha T i using the same formula that we wrote down yesterday that the diffusional flux of any species i is going to be equal to minus rho D i gradient in omega i plus omega i alpha T i times grad T over T.

So this is this Fick diffusion portion and that is the thermal diffusion portion. And by the way you can

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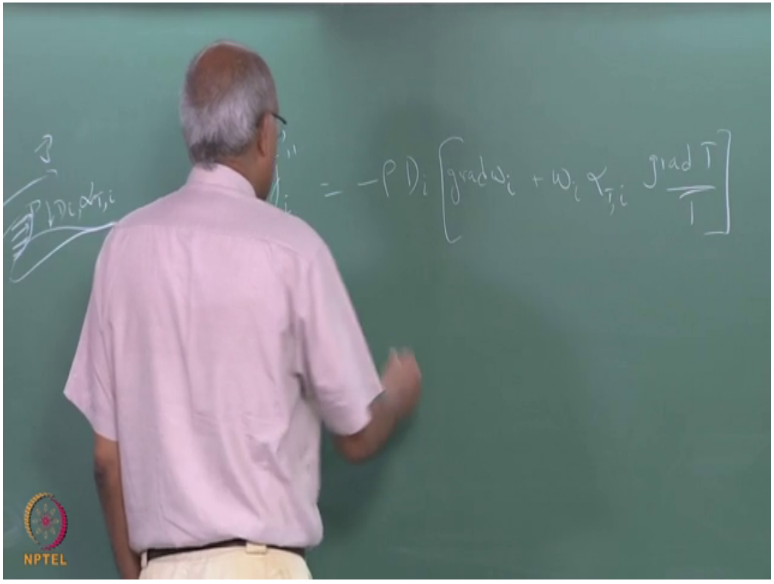

also write this in terms of the Nusselt number, right? You can write this as minus rho D i over some reference length L

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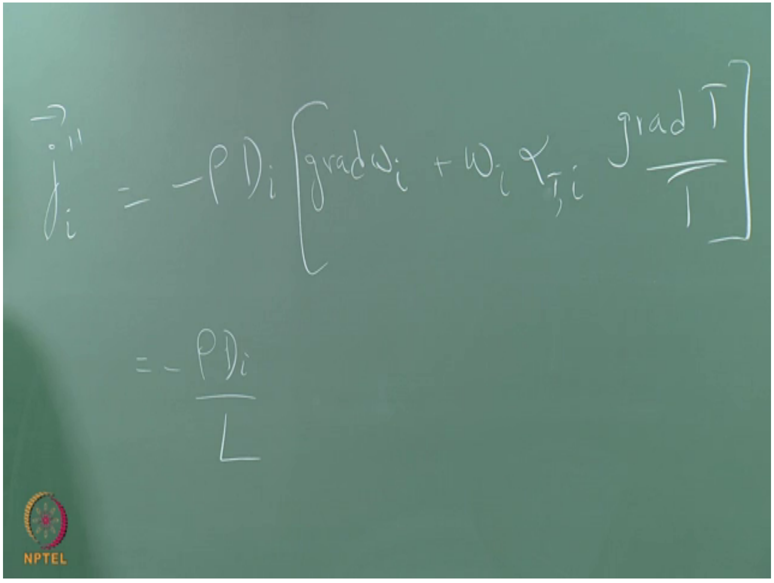

times Nusselt number times, gradient in omega i can now be written as omega i, if you call the substrate W and if you call the mainstream of the combustion gases as e you can now write this as omega i e minus omega i W plus omega i W times alpha T i times grad T d T by d L times T e minus T w over T w.

So essentially you can rewrite the diffusion equation in terms of the

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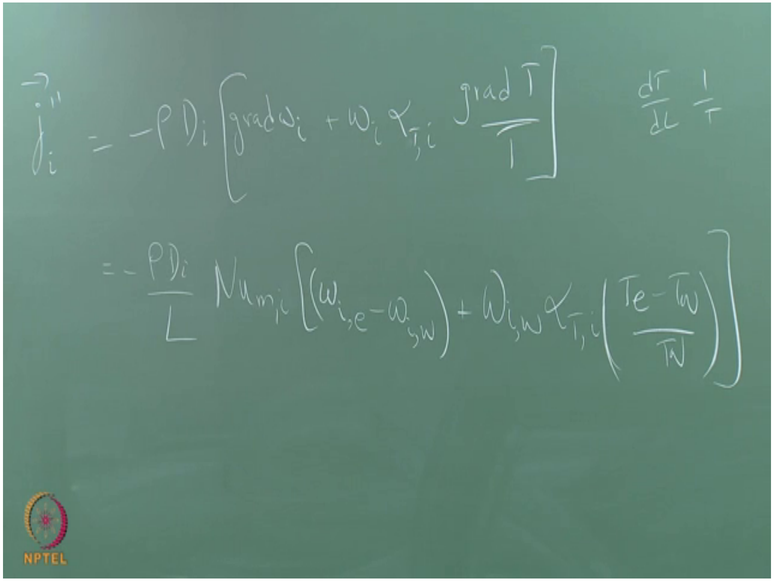

$$\vec{j}_i'' = -\rho D_i \left[\text{grad}\,\omega_i + \omega_i \alpha_{T,i} \frac{\text{grad}\,T}{T} \right] \qquad \frac{dT}{dL}\frac{1}{T}$$

$$= -\frac{\rho D_i}{L} Nu_{m,i} \left[(\omega_{i,e} - \omega_{i,w}) + \omega_{i,w} \alpha_{T,i} \left(\frac{T_e - T_w}{T_w} \right) \right]$$

Nusselt number for mass transfer. So you can calculate the diffusive flux for every species. Now supposing the condensing material is sodium sulphate liquid.

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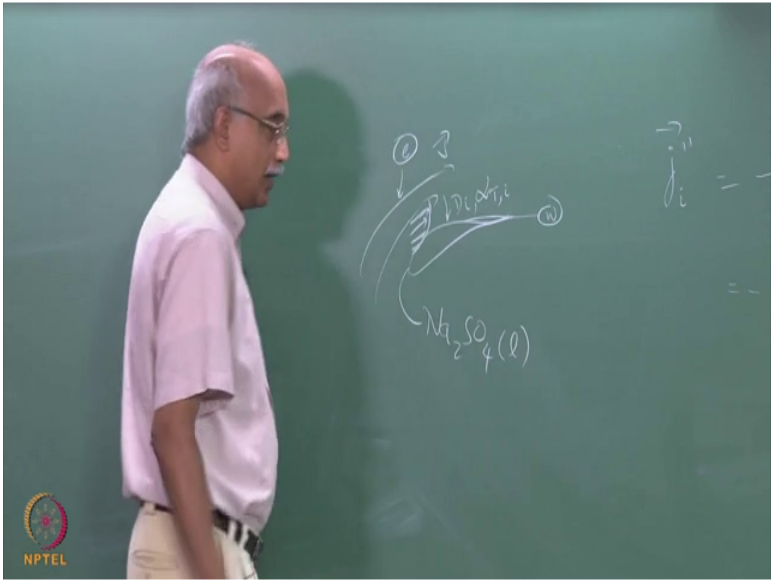

You have to write this equation then for all species containing, for all i containing N a, sulphur because the elemental sodium may be contained, like I said, in many, many species.

The elemental sulphur may be contained in many, many species. So you have to first, estimate the diffusion fluxes for each of these species.

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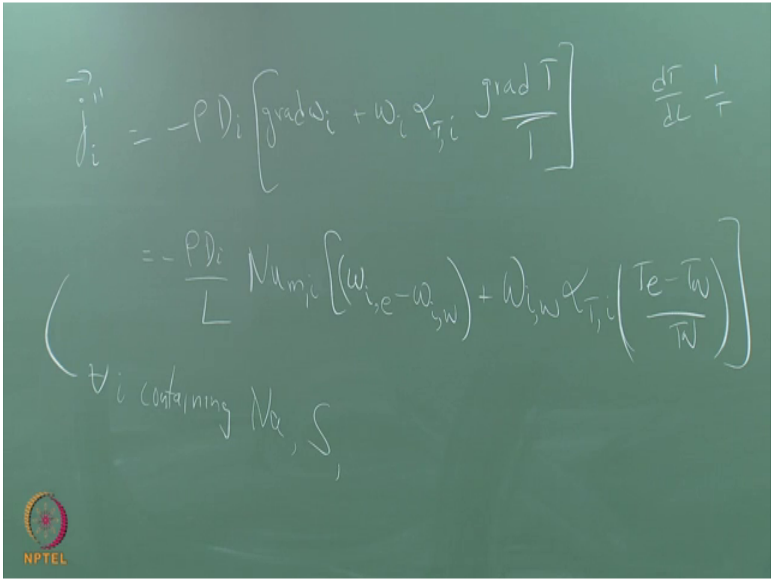

$$\vec{\dot{j}}_i'' = -\rho D_i \left[\text{grad}\,\omega_i + \omega_i \alpha_{T,i} \frac{\text{grad}\,T}{T} \right] \qquad \frac{dT}{dL}\,\frac{1}{T}$$

$$= -\frac{\rho D_i}{L} Nu_{m,i} \left[(\omega_{i,e} - \omega_{i,w}) + \omega_{i,w} \alpha_{T,i} \left(\frac{T_e - T_w}{T_w} \right) \right]$$

$\forall i$ containing Na, S,

How about oxygen? Do you also have to write a diffusion equation for oxygen? We do not need to because oxygen is not a trace species. The diffusion flux is only relevant for the trace species. In the case of oxygen you basically make the assumption that there is sufficient oxygen everywhere in your system to enable the reaction to proceed. So we do not have to write a diffusive flux equation for the oxygen.

Ok so let us say you do this and then therefore from this, what can you calculate? Once you have the diffusive fluxes for each species containing these elements, the next step is to write the diffusive flux for the element sodium which will be summation over all i of omega N a i times j i W dot double prime. In other words the diffusive flux of the element sodium will be a weighted sum of the diffusive fluxes of all species containing sodium with the weighting factor simply being the mass fraction of the sodium element in each species.

And similarly you can write j s dot double prime equals summation over i omega S i...

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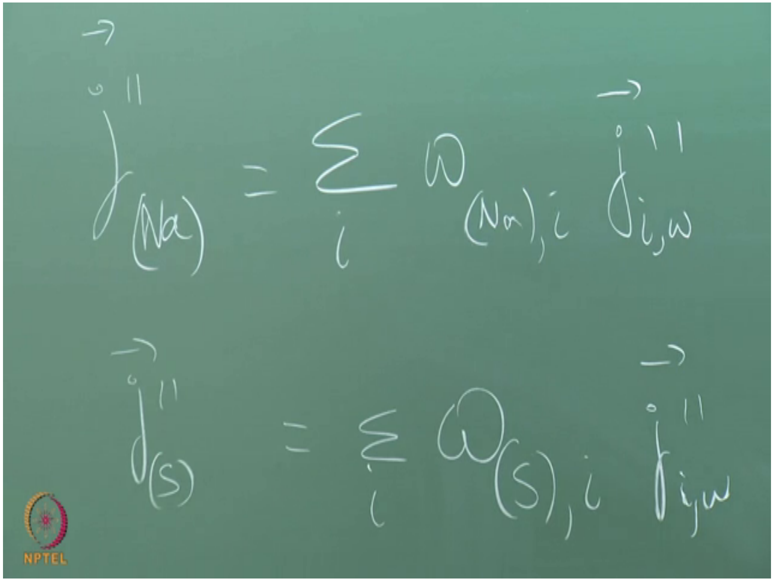

$$\vec{\dot{j}}''_{(Na)} = \sum_i \omega_{(Na),i}\, \vec{\dot{j}}''_{i,w}$$

$$\vec{\dot{j}}''_{(S)} = \sum_i \omega_{(S),i}\, \vec{\dot{j}}''_{i,w}$$

so once you know this then how do you calculate the deposition flux of the sodium sulphate liquid? You simply do a scaling. So if you know this, then deposition flux, let us call that some m dot double prime of N a 2 S O 4 liquid which is the molten deposit on the, on the turbine blade surface will be equal to j N a dot double prime divided by omega of N a in N a 2 S O 4.

So if you know the deposition flux of the element sodium and you know the mass fraction of that sodium

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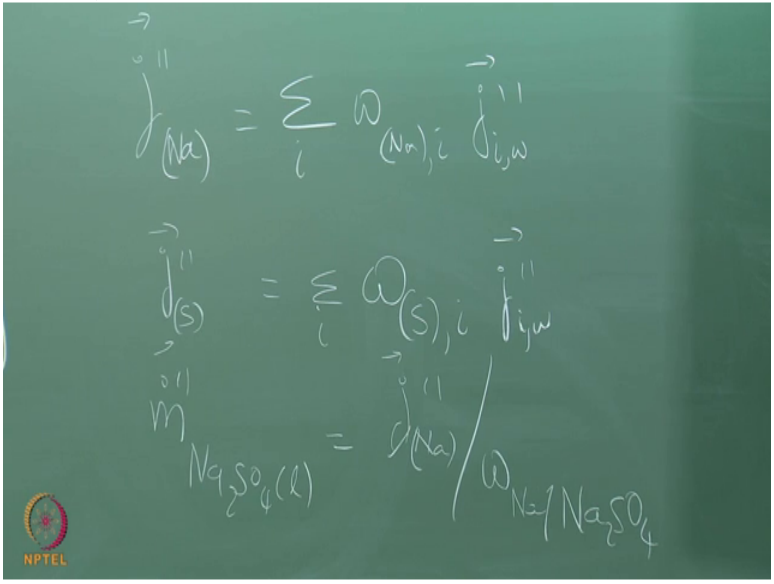

$$\vec{\dot{j}}''_{(Na)} = \sum_i \omega_{(Na),i}\, \vec{\dot{j}}''_{i,w}$$

$$\vec{\dot{j}}''_{(S)} = \sum_i \omega_{(S),i}\, \vec{\dot{j}}''_{i,w}$$

$$\vec{\dot{m}}''_{Na_2SO_4(l)} = \vec{\dot{j}}''_{(Na)} \Big/ \omega_{Na/Na_2SO_4}$$

in your deposit then you simply divide by the mass fraction that will give you the total flux of salt on to the surface. Of course this has to be equal to j S dot double prime divided by omega of S in N a 2 S O 4, I mean they have to be self-consistent basically.

So that is how you calculate the deposition flux of sodium sulphate on the surface. And once you know the flux rate or the rate at which the sodium sulphate is depositing you can, from this calculate the local thickness

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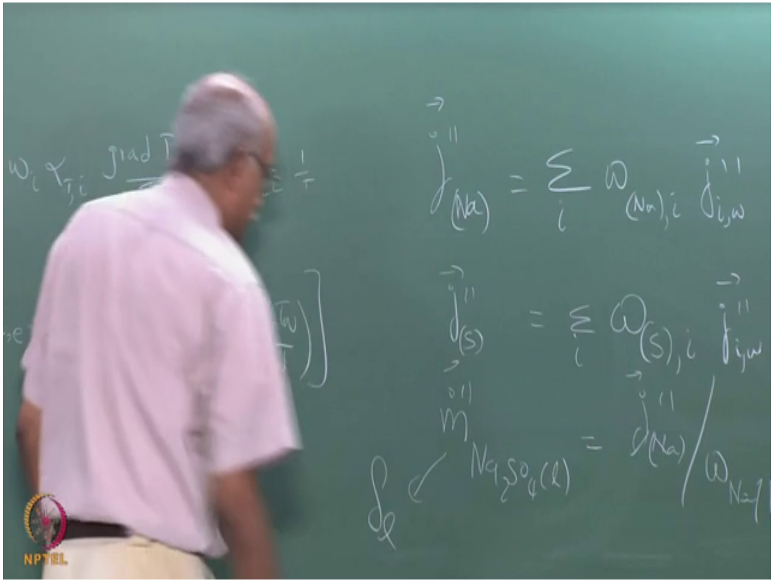

of the molten layer, some delta subscript l which is going to be the function of spatial dimensions as well as time.

So once you know the molten salt thickness

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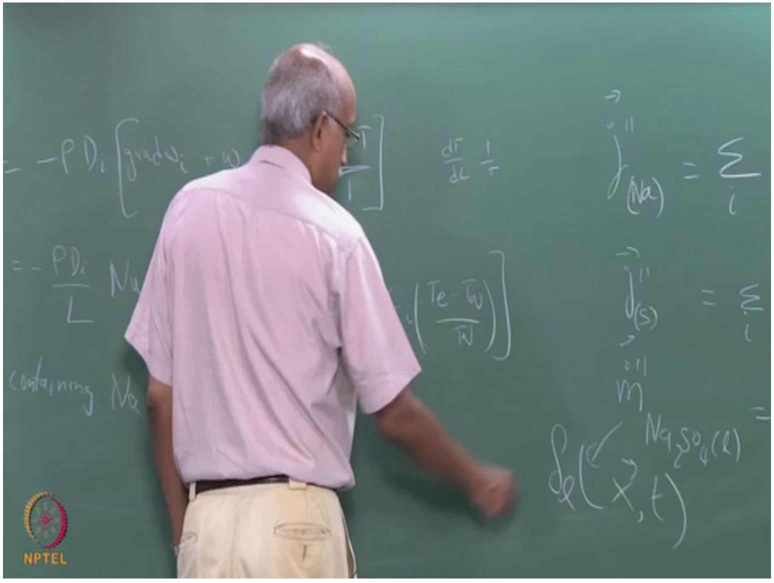

and you know its physical properties such as the liquid diffusivity, its density, viscosity and so on, from this, once you know this you can extract j O W dot double prime where this O refers to the protective oxide coating, right?

So far it is a three-step process.

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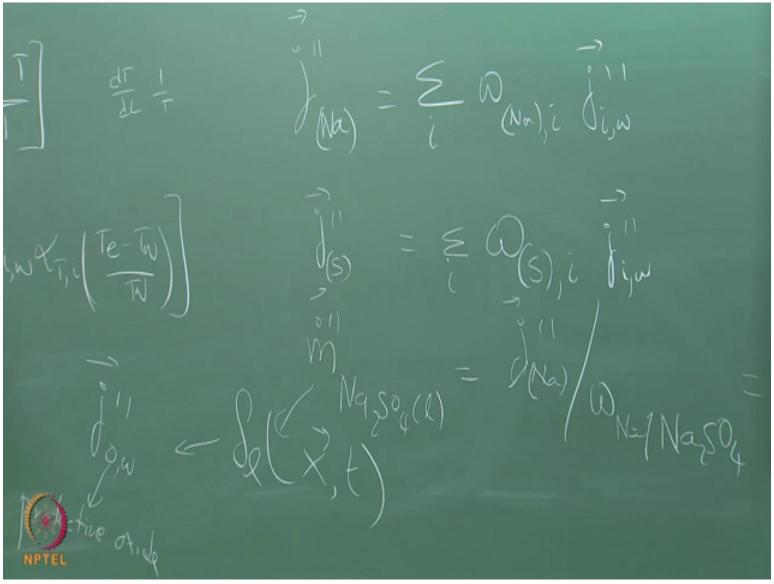

First you estimate the rate at which deposition of the molten salt is happening. Using that as well as the centrifugal and shear and aerodynamic shear forces that are present in the system you calculate the local thickness of the molten layer.

From that you calculate the rate at which the protective oxide is getting dissolved at any location. From that you estimate delta O at x comma T which is the local thickness of the protective oxide layer as a function of again, spatial dimensions and time. And from this then you calculate

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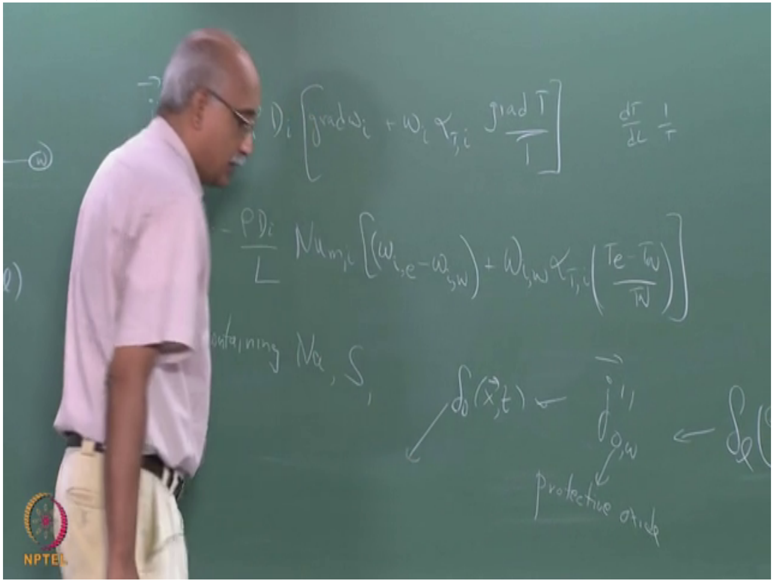

the local rate of corrosion.

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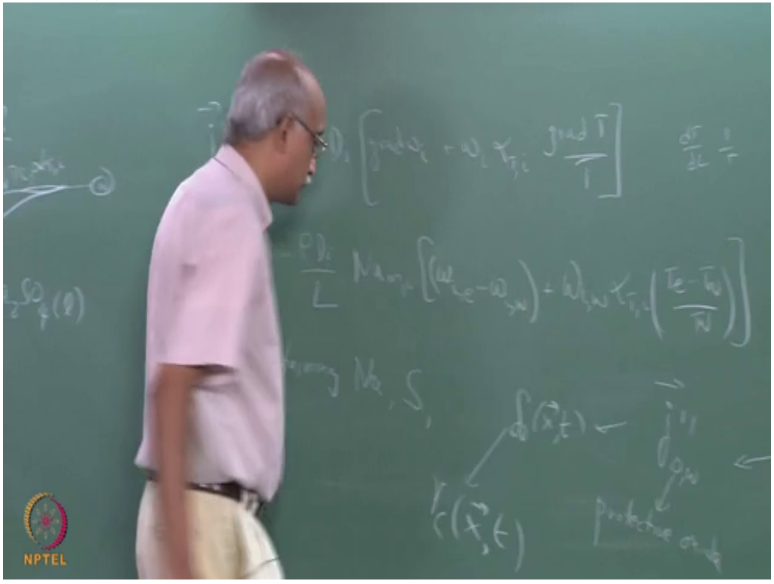

Because there is a direct relationship between how thick the protective layer is and rate at which the corrosion is happening at that location.

So you can see it is a very sequential process that enables us to start by all we know at the beginning is the fuel to air ratio, the fuel composition, air composition including impurities and the operating pressure. That is all you need to know.

From that, by applying equilibrium thermodynamic considerations, by applying appropriate transport laws you can calculate everything up to this point.

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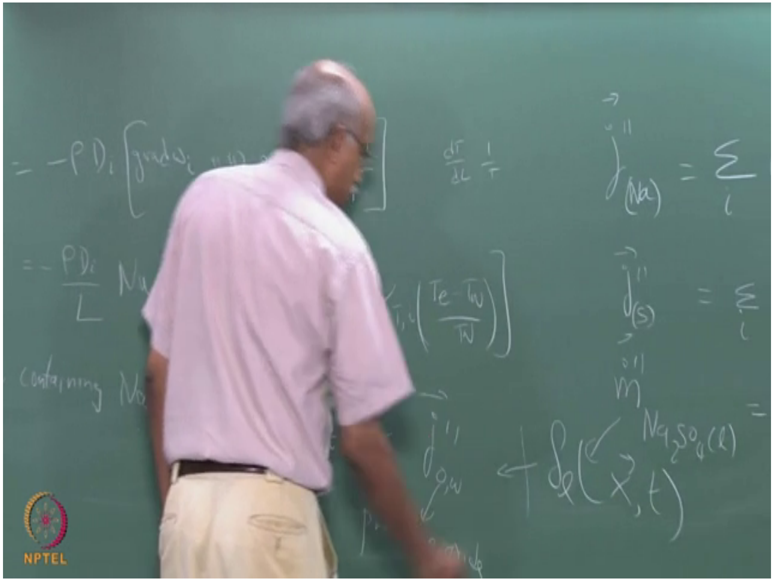

And then by knowing the properties of the protective oxide coating including its molecular weight, its dissolution characteristics, its diffusivity in the liquid and its local thickness distribution you can calculate this part of it.

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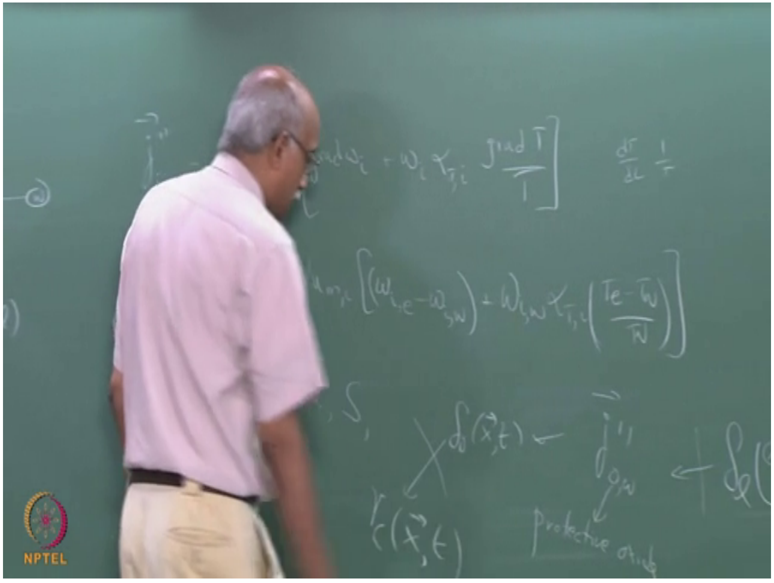

And once you know that you can actually start generating what we had called corrosion maps which is exactly this, rate of corrosion as a function of spatial dimensions and time. Ok, so I think it is a kind of very elegant situation where C V D is happening and once we are able to understand the C V D process and modulate and simulate it and do necessary experiments both large scale as well as pilot scale to validate your model, I mean this is a very real life application.

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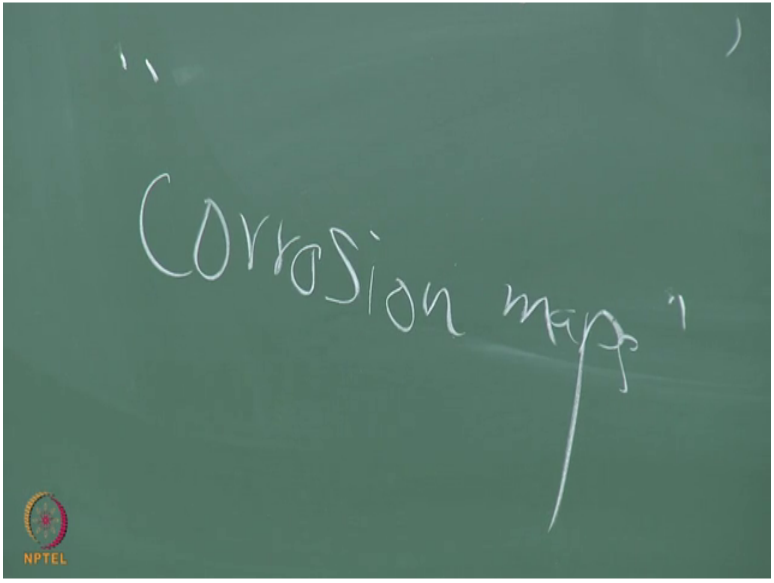

Again corrosion problems in industry account for billions of dollars of loss all over the world. So it is a very practical problem in that we have to design components for long life in extremely aggressive environments. And you cannot do that without the proper understanding of the C V D phenomena that are involved.

Now there is one additional complication which makes this a iterative loop rather than a sequential loop. And that is the fact that in order to form sodium sulphate there is an additional requirement. The moles of sodium and sulphur have to arrive at a certain ratio. In fact the molar flux ratio j of elemental sodium to j of sulphur should be equal to 2. Otherwise the stochiometric film

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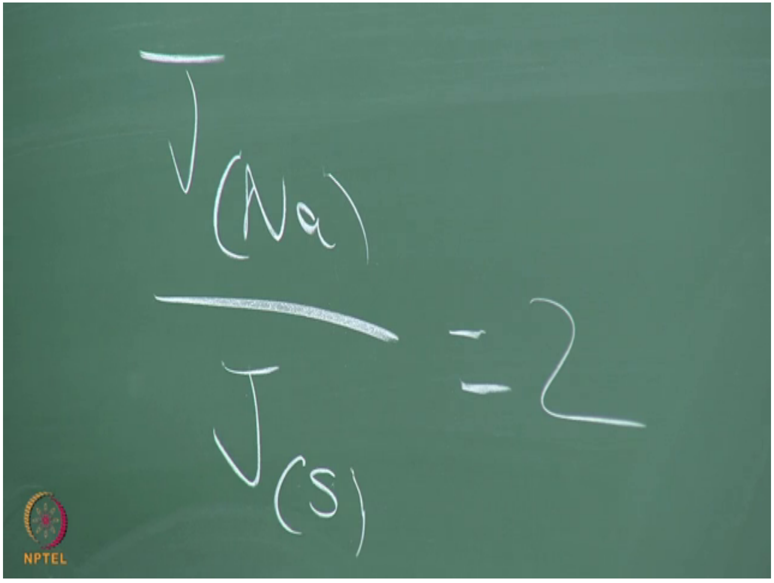

$$\frac{\bar{J}_{(Na)}}{J_{(S)}} = 2$$

will not result.

So what you have to do is once you have calculated these two diffusive fluxes, mass diffusive fluxes you convert them to molar fluxes by applying the molecular weight. And then you check to see if they are in the ratio of 2. If not what you have to do is essentially iterate until you get convergence where the ratio that is being calculated is exactly equal to 2.

So how do you do this iteration? What is the unknown? I mean input conditions are fixed, you cannot iterate those. The mainstream conditions are fixed. I mean whatever the combustion process happens, that is going to set the conditions far away from the substrate. So what is that we are assuming here? What is that we can iterate on?

What we are assuming in this calculation is that the elemental ratios, elemental composition of the gas remains the same wherever you are there in the gas stream; whether you are far away from the substrate or you are close to the substrate. Well that is not really a good assumption because close to the substrate the elements are actually condensing, right. So there is actually a depletion in the elemental concentration near the surface which is not being accounted for in your model.

So what you can essentially iterate on is the, when you do the thermodynamic calculations, the free energy minimization calculation you have to assume that there is a certain quantity of sodium and sulphur that go into the condensate and from that you calculate the vapor phase composition. From that you calculate your transport fluxes and verify that their ratio is consistent with the formation of sodium sulphate.

So you keep doing this process until you get to a condition that satisfies both constraints. It should satisfy the equilibrium thermodynamic constraints of a stochiometric sodium sulphate film being viable at the local conditions and b, you have to satisfy the transport constraints that the molar fluxes must be in the ratio of 2 is to 1. So you just keep iterating till you reach this convergence condition. So the iterative loop is really here.

Once you have reached the converging

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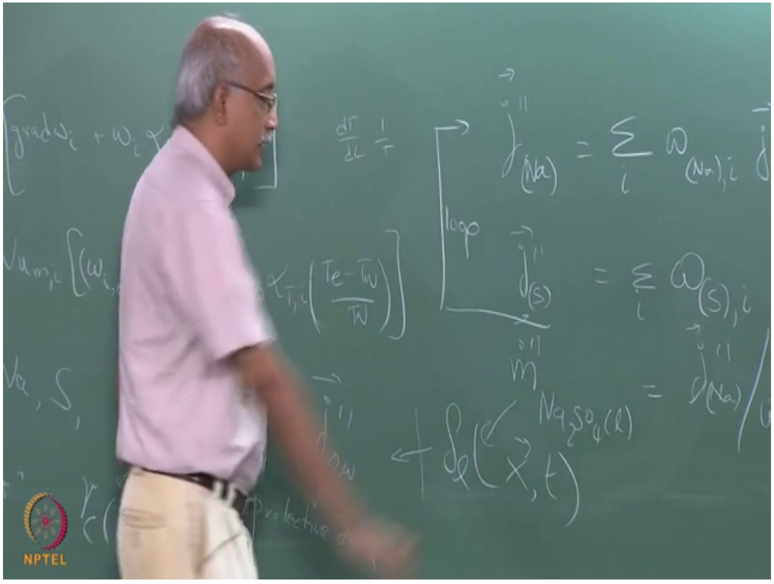

condition here, then you go the next step. And in fact you know this equality, what happens unless you have done this iteration and reached a self-consistent condition where the flux of sodium species, sodium element and the flux of the sulphur element are in the same ratio as their stochiometric ratio in the film. So that is kind of how we do this.

Now supposing you have a case where you are forming not just sodium sulphate but it has also got a mixture of potassium sulphate in it. Ok, then what do you do? I mean can you still go through the same process of calculation and so on?

This is when you have solution forming on the surface,

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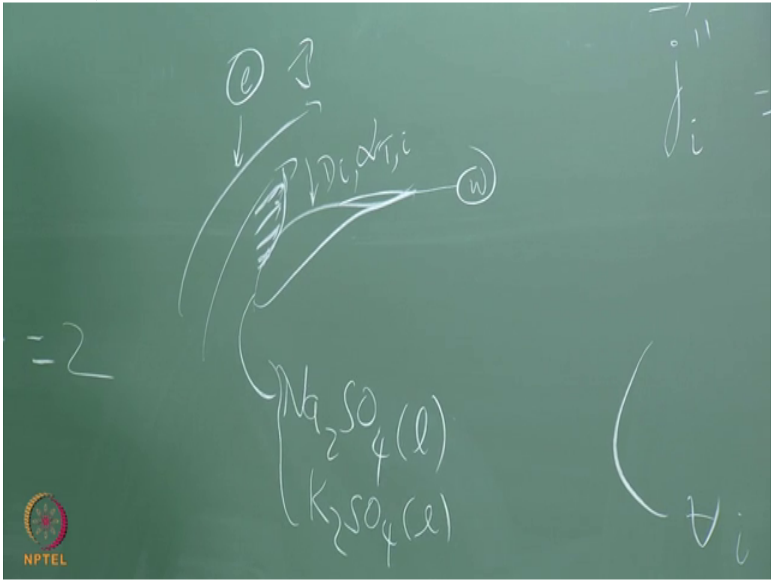

it introduces two complications, one is on the thermodynamic side. You have to know the phase equilibria between the two condensed phases in order to characterize the behavior of the film on the surface.

The second is in terms of transport constraints, now in addition to j N a by j S being equal to 2, you also have to have j of K by j of S equal to 2 so that you can have sodium sulphate and

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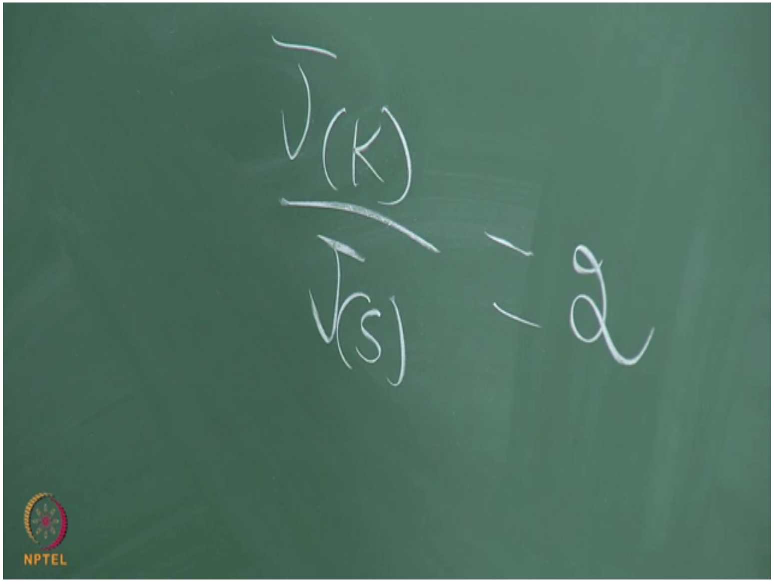

potassium sulphate condensing as two separate molten layers. Of course you can start forming ternary solutions where you have more than one alkali in solution let us say with sulphur.

So you can have situations where you can form something like an M g N a S O 4 kind of a condensate.

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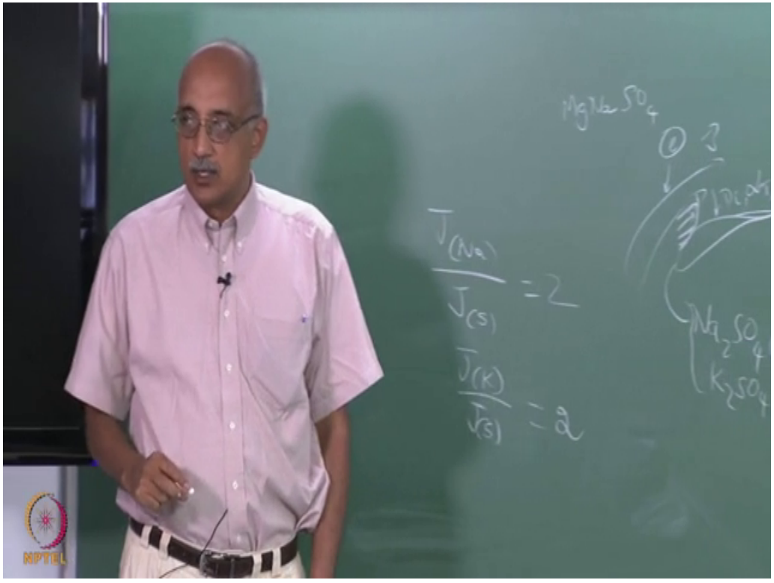

In that case j M g must be equal to j N a must be equal to j S for this film to happen. So just remember that whatever equilibrium

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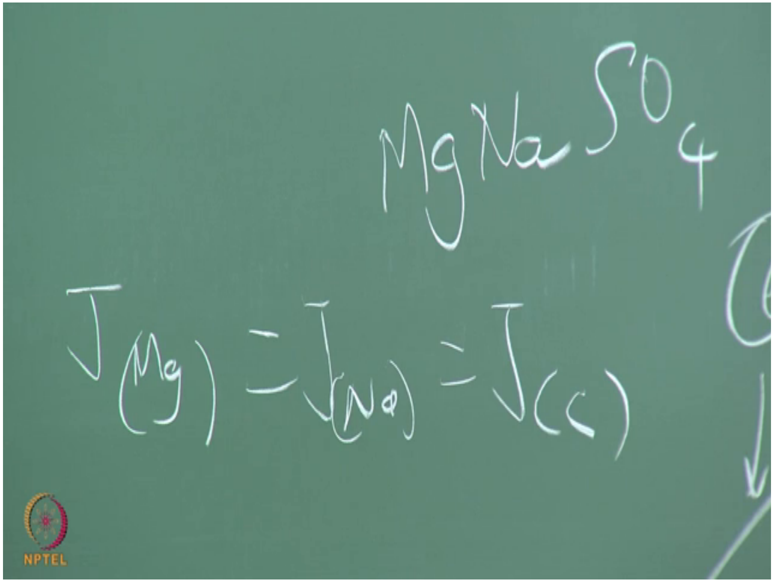

composition you are predicting for the substrate, for the film on the substrate must be consistent with the rates at which they are being transported.

Now supposing that there is a situation where all of a sudden the temperature fluctuates and instead of forming sodium sulphate liquid, let us say that you get a transition from this to N a 2 C O 3 and that is typically a liquid to solid

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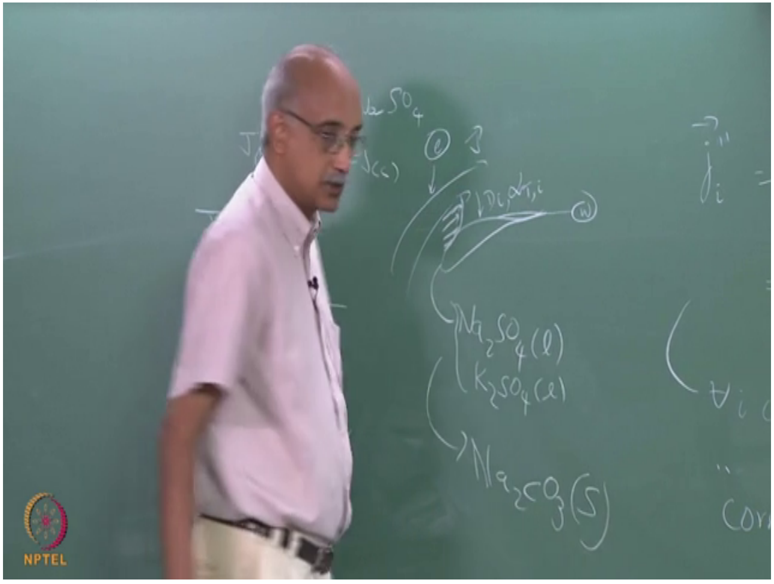

transition as well because sodium carbonate is a solid at much higher temperature than sodium sulphate.

So under conditions where you might expect to get molten sodium sulphate, you may sometimes get sodium carbonate which by the way is a very positive thing. Because sodium carbonate is non-corrosive plus the fact that it is a solid essentially implies that it is not going to be chemically reactive with the surface.

So in this particular case, I mean, essentially as a designer you would try to achieve combustion conditions that favor the formation of

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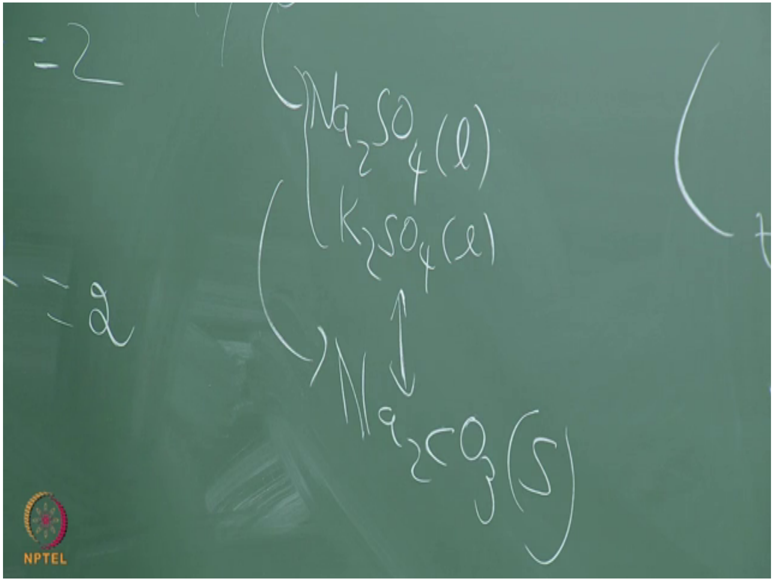

either no deposit or a non-corrosive deposit rather than a corrosive deposit on the surface. So how do you, how do you get sodium carbonate to happen? What would be the transport constraint in this case? Is there a transport constraint or there isn't?

0:36:00.0 Clearly there is 3 elements here, sodium, carbon and oxygen. But carbon and oxygen are again present in excess. So they do not req/require, they are not required to diffuse in a particular ratio compared to the trace element. So in this particular case the only transport constraint will be that the molar flux of sodium must be greater than zero.

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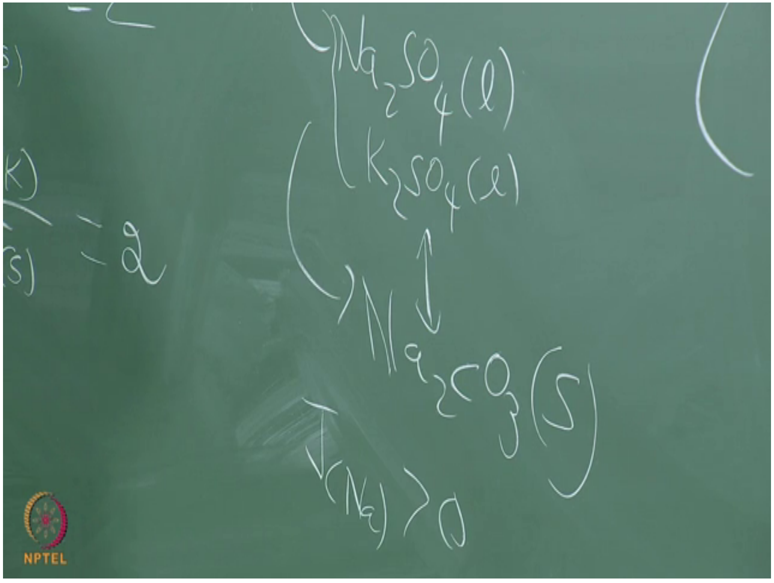

As long as that condition is met, the transport conditions will permit the formation of a sodium carbonate film. In addition if the equilibrium thermodynamics also favors the formation of sodium carbonate film, you are Ok. You will form a sodium carbonate film and corrosion will essentially stop.

Now the condition where j N a equal to zero as I mentioned at you know, the earlier classes is what is called the dew point, right? It is the condition which just separates the onset of condensation from a previously bare surface. And, so this condition must prevail if you want to have virtually no condensate on the film.

And by the way if you are, if this ratio is equal to 2, sodium to sulphur, is it still possible that j of N a equal to zero and j of S equal to zero? Is that even possible? Because it basically gives you a zero by zero condition right?

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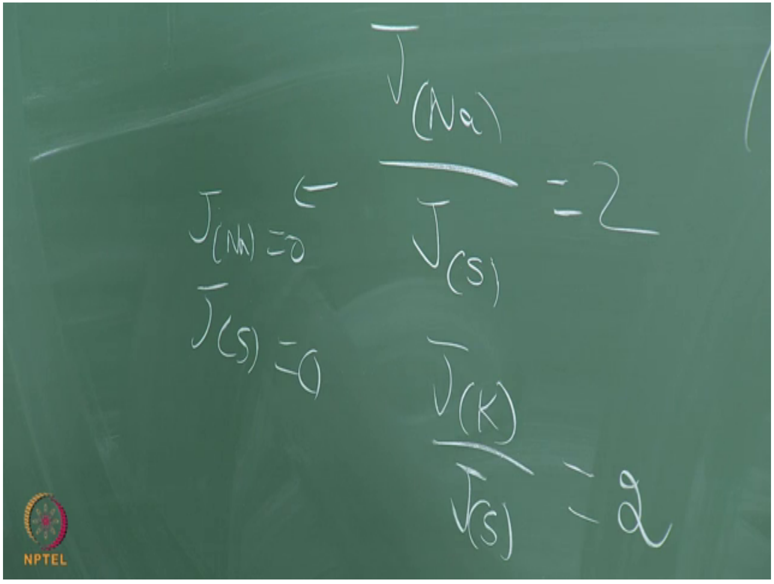

It is possible in the limiting case.

And in fact the definition of the dew point is that in this particular case the deposition rate which we have written as m dot double prime sodium sulphate must be equal to zero but in the limiting case, this is in the limiting case of j N a tending to zero and j of S tending to zero, Ok. So the molar flux of sodium and sulphur must

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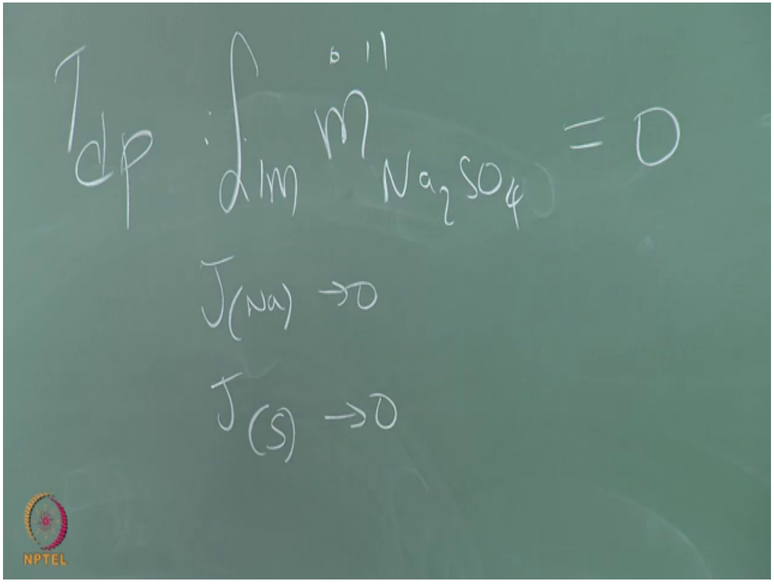

tend to zero but in such a way that ratio is always maintained at 2. So this subject to j N a over j S being equal to 2.

So in other words, graphically the way you would estimate this is, you will draw a curve of T w versus m dot double prime

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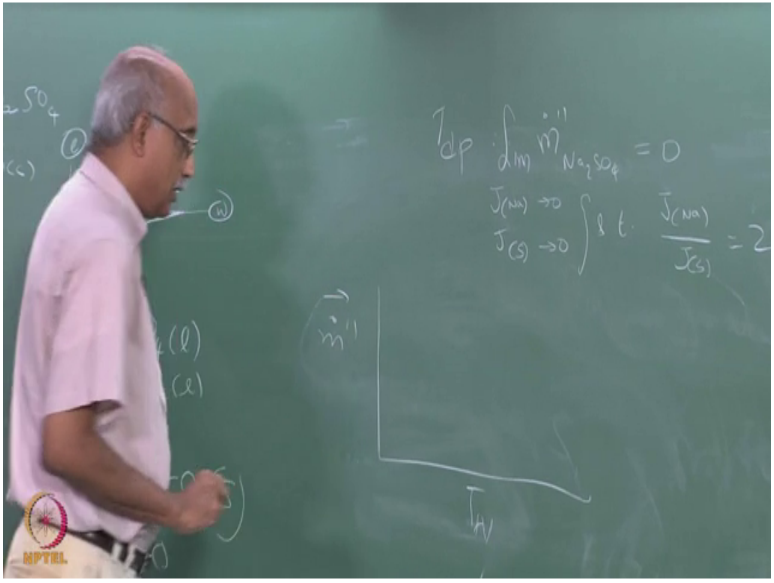

and you will look at

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how this is changing. So you can draw a curve, you know, again the classic dew point curve. At each point on this curve j N a over j S must be equal to 2 if this is giving you sodium sulphate

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as your deposit. So this curve is essentially a graphical formulation of this.

You are taking the limit of the, limit of, essentially you draw this curve and extrapolate it till it hits zero, right? Now this dew point, again which has been achieved by slowly increasing the temperature and by the way this is the reverse of the conventional C V D situation where as temperature is increased the rate of deposition increases. In this case of molten salt deposition, it is actually other way round. As temperature increases the rate of deposition decreases.

So in this particular case the, when you have the film that is present and you slowly raise the

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temperature the first temperature at which you are still satisfying the flux ratio condition but the rate of deposition itself tends to zero is called T d p, the dew point temperature.

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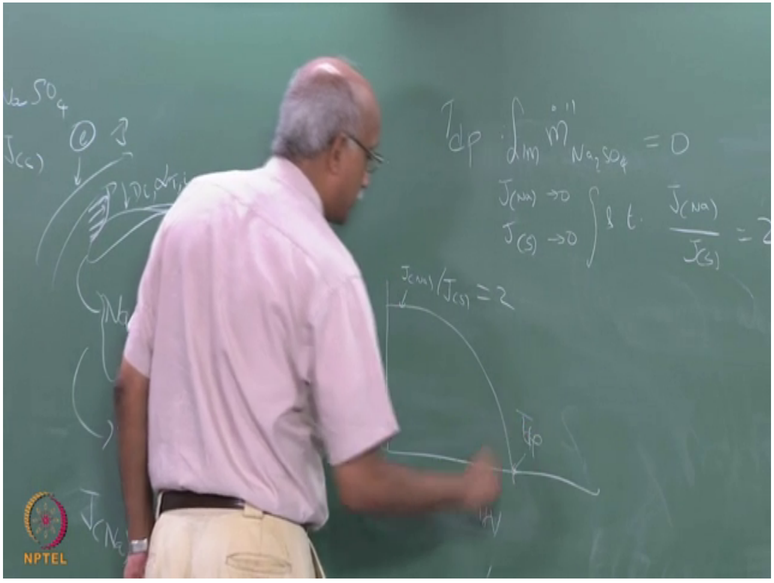

However for this system the dew point is not unique. Because you can also define two other dew points.

One of them is a purely thermodynamic dew point. You can just run your chemical equilibrium simulations and find the first temperature at which the condensate will stop happening and you can call that a thermodynamic dew point. But it will be different from this dew point and it will not be the true dew point because that calculation does not take into account the transport constraints on the system.

So this constraint approach to zero will yield a dew point which we call conventionally

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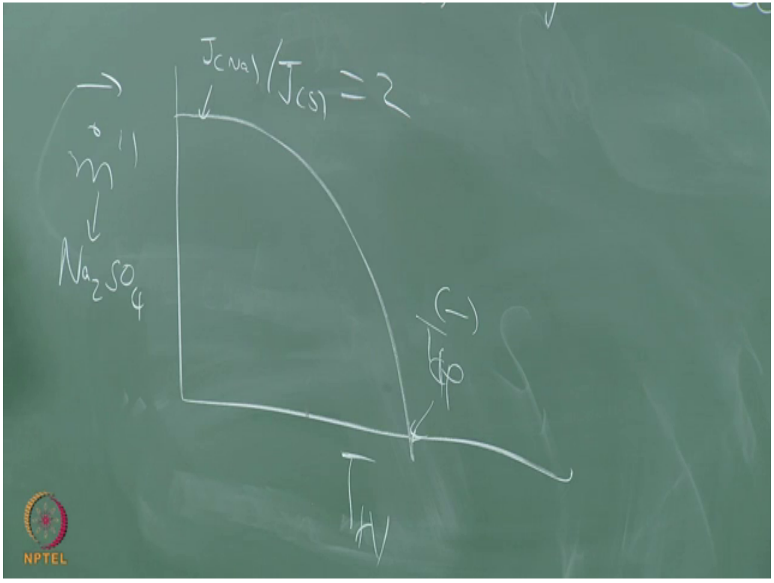

T d p minus. T d p zero which may be over here somewhere is what we call

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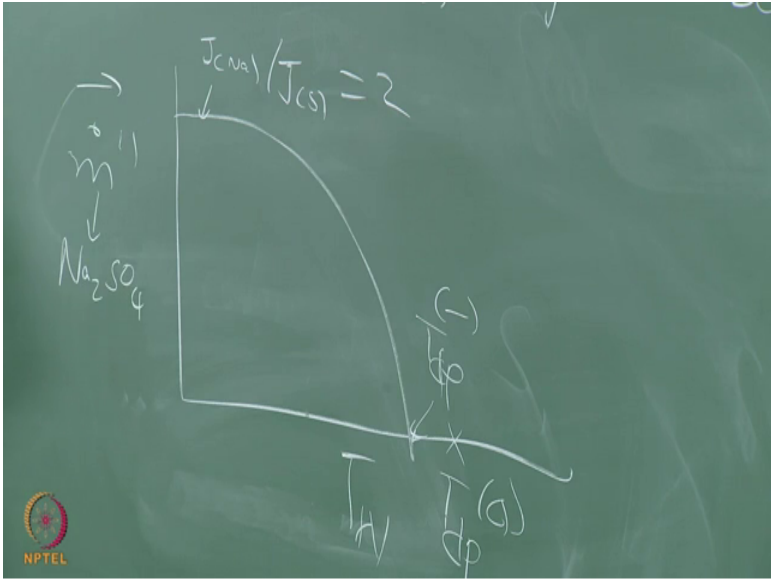

a purely thermodynamic dew point and interestingly there is one more.

Supposing you were to initiate deposition by approaching it from the other side. Suppose you start with a very high temperature and keep lowering the temperature until the first condensate starts appearing. Now from a purely thermodynamic viewpoint there is no difference, right but when you take transport constraints into account the constraint now is very different.

You do not have to satisfy this constraint approach to zero. So when you approach the dew point from the other side, essentially you will be initiating deposition at a temperature T d p plus where deposition will begin. But in this particular case, I mean the first point at which the deposition happens is the first temperature at which j of N a is greater than zero and j of S is greater than zero.

So it is a very different constraint, right. You are approaching the zero point with two separate constraints, one on sodium, one on the sulphur and the ratio constraint does not have to be met until this particular point. So it is different approach or limiting case under different constraint. So naturally this will yield a very different value.

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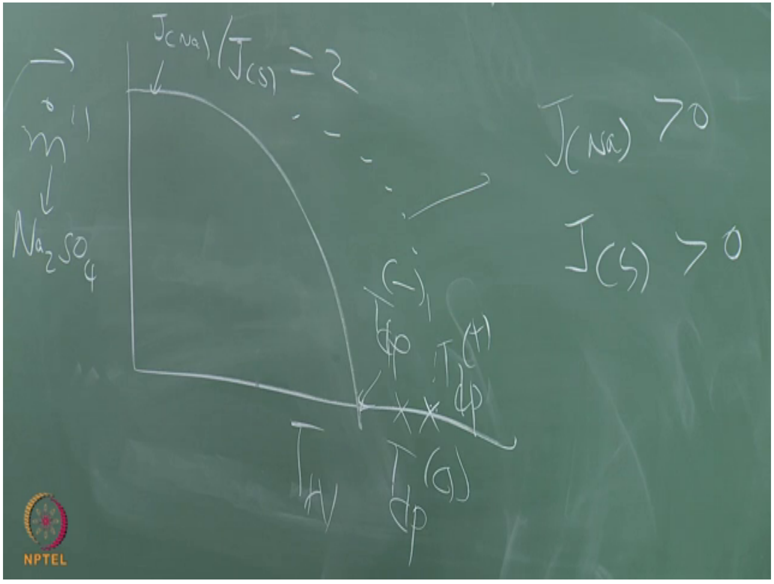

So there are three deep dew points that characterize the C V D system depending on if you calculate strictly based on thermodynamics, or you calculate for the case of a pre-existing condensate that begins to vanish and the third is if you calculate on the basis of no film to begin with and then slowly approaching the condition where condensation begins to happen.

Each of this will yield a completely different dew point and the spread between these dew points will depend on how disparate the molecular weights of the species are in the C V D system. So the more dissociated the system, the more the number of species present the system, the larger will be the range between these dew points.

And actually this, the range between T d p minus and T d p plus is a very interesting area because some very non-intuitive things happen. You can have, for example, the formation of a patchy condensate. Where instead of continuous condensate film you have a film that is present in patches. So essentially what is happening is you are so close to that, you know dew point condition that the system almost cannot decide if the film will form or not form. So what it does is it statistically averages it.

So over a certain area, half the area will have a film and half the area will not have a film, right. So in this particular region if you blow this up

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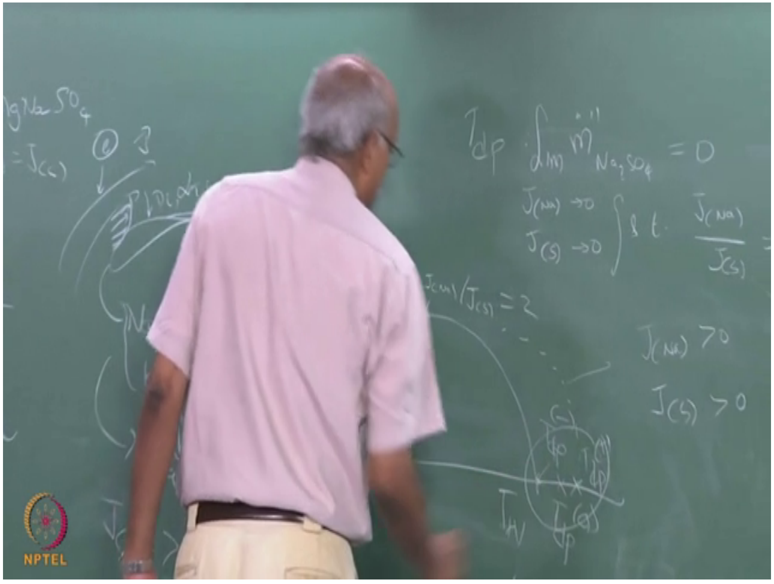

and look at what is happening on the surface you will essentially have a situation that kind of looks like this. There will be stripes in which the fill will appear with

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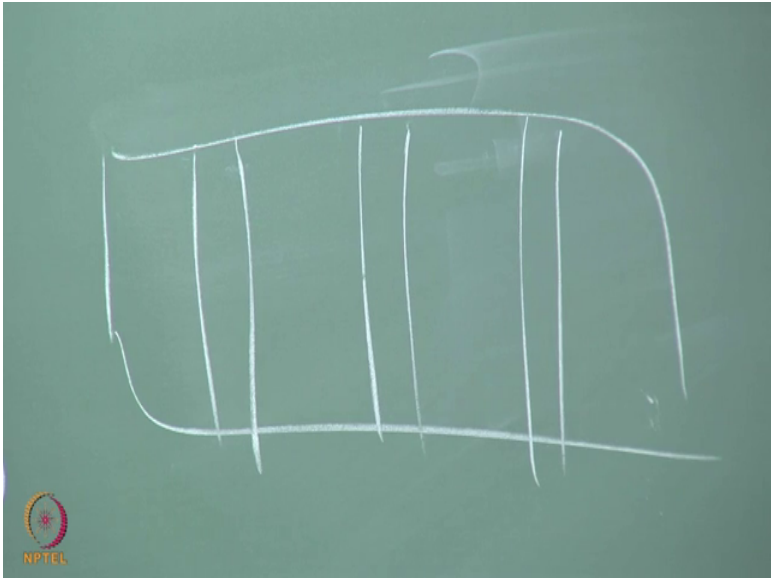

spacing in between. So you can almost get patterns of film by operating in this range.

This temperature range can be small. I mean for example if it is a purely physical vapor deposition problem, then this range is zero, right? There is no difference between the thermodynamic dew point and the transport constraint dew points. However in a situation where you have, let us say very high temperatures, highly reactive, highly dissociative environment, the spread 0:44:57.2 can be of the order of, the largest values that I have observed are 20 to 30 percent of the nominal value.

So if your thermodynamic dew point is 2000 Kelvin the range between T d p minus to T d p plus can be all the way from 1600 to 2400, right. So it can have a tremendous influence and if you are not doing your C V D calculation you can completely mis-estimate the range in which the molten deposit will form and cause corrosion. So you can provide much less protection than you should have or in another case you might over-design and provide protection that is not necessary.

So this is again a classic illustration where the C V D principles, both the thermodynamic aspects as well as the transport aspects have to be fully understood for the design engineer to be able to design the system appropriately. Ok. Ok so let us stop at this point. Any questions? Ok so I will see you at the next class.