Mathematical Modelling and Stimulation of Chemical Engineering Process
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Lecture 25
Modelling transport phenomena problems - part 5

Hello everyone. In this lecture. we are going to talk about a pressure swing adsorption process. Now, adsorption is a very sophisticated separation process that can actually have a very high selectivity and this is a very popular technique particularly for gas separation as well as of course liquid separation also adsorbent based methods or treatment as well as separation processes have also evolved recently. For example, chromatography is a very sophisticated technique for separation of highly selective molecules.

But in this lecture today, we are going to talk about the pressure swing adsorption, because recently this use of adsorption technologies for production of oxygen enriched air is very popular. So, you must have heard about this oxygen concentrator that has been in the limelight for the last 1 or 2 years almost ever since the pandemic have started. And the key technology behind this oxygen concentrator is the use of an adsorption process.

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CONCEPTS COVERED

- Mass transport with adsorption
- Pressure swing adsorption → Gas separation

So, what essentially happens here is the adsorption of nitrogen into molecular sieves which results in further enhancement in the oxygen fraction in the produced air. So, typically this is done under pressure because increasing the pressure increases the selectivity of the adsorption of nitrogen over oxygen. So, here typically contains around 80 percent of nitrogen, so if we if you are able to separate out or adsorb most of this nitrogen, then the final stream would be enriched with oxygen and it is possible that you get a very high fraction of oxygen in the output.

Now, basics of adsorption is something which is a part of the undergraduate mass transfer course, so that is something will not dog too deep details into what essentially is adsorption, how does the dynamics of adsorption is related, what about adsorption isotherms, then difference of adsorption with AB absorption is also very important, AD adsorption is an equilibrium governed process, there are various isotherms which relates or which helps you to determine the capacity or the equilibrium capacity of the adsorbent.

So, popular isotherms are Langmuir isotherms, then we have Freundlich isotherms, BET isotherms, Tempkin model, Sips model, there are several of these types and each one of them are relevant in a different context or scenario.

Now, what is pressure swing adsorption? Pressure swing adsorption is generally followed for gas separation techniques, because the adsorption bed becomes fully saturated quickly so you need to have a swing in the pressure or if you try to depressurize it the adsorption bed becomes regenerated once again, so by altering the pressure or changing the pressure cycles or the pressure this is what is known as the pressure swing process you can have a cyclic process of regeneration and adsorption.

So, generally these adsorption beds become very quickly saturated and to regenerated you need to depressurize them. So, with pressure adsorption happens and you get the production and during depressurizing you have the regeneration step. So, this is generally followed in pressure swing adsorption process which is relevant for gas separations.

In the case of liquid separation, you cannot I mean the process does not change by altering any pressure in that case you have to pass a regenerative solution into this bed, so that the bed can once again be reactivated and all the bounded molecules are again released and the bed is regenerated, so that is a slightly more complex process. In the case of gas adsorption, if you just alter the pressure or if you apply vacuum in the same column, you very quickly it gets regenerated.

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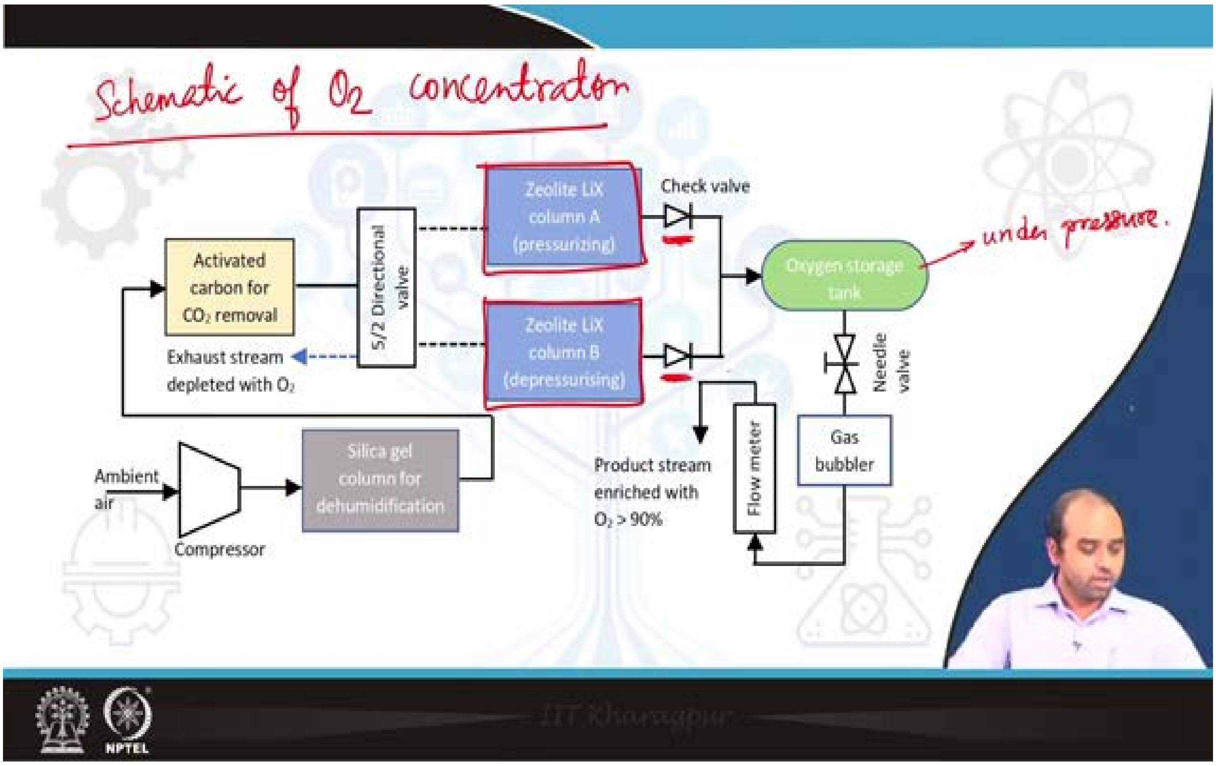

Schematic of O_2 concentrator

under pressure.

Now, with this idea of the pressure swing here is a schematic which tells you that how you can essentially have this this is the schematic for the schematic of O2 concentrator, in fact this can be used for medical grade production of oxygen. So, this O2 concentrator these are the two adsorption columns why two? Because if one of the columns is in a pressurizing cycle the other will be in the depressurizing cycle or will be in a regeneration state, so, there is continuous production of oxygen and there is no there is no what should I say there is no resumption there is no gap or pause in the cyclic process.

So, in this pressure swing case you have to you need a finite time for depressurizing for regeneration of the bed, but in this process if you have two beds these two of these beds can work alternatively and there is a continuous production from one of these beds and that is very important for a medical operation because you cannot produce oxygen intermittently, that is not acceptable, it has to be a continuous production. So, for continuous production often this idea of two cycles or these two columns is used.

Now, just to explain you or give you a brief idea of this process flow diagram here, generally you have a compressor line which then passes through some pre-treatment stages for removal of moist Co2 because they can affect the adsorption capacity of these molecular sieves, the molecular sieves are generally of lithium ion exchanged zeolites of 4A grade. So, this is a very specific particular adsorbent which has a high selectivity towards nitrogen compared to oxygen and in this process nitrogen can be separated out from the air stream.

And there is a directional valve, so which controls alternatively pressurizing and depressurizing cycles or the flow of the air into the system. So, there is also back connection from these columns for the depressurizing section. So, the output outlet part of the column there is a check valve, so there is no back flow from the oxygen storage tank. So, this whatever things are produced it is goes to the oxygen storage tanks which is under pressure. So, the oxygen storage tank is under pressure,

So, this check valves are important, because during the depressurizing cycle of one of the columns there should not be backflow from the oxygen storage tank. After the oxygen storage tank it passes through the gas bubbler and the flow meter because you need to maintain a certain degree of humidity, since it is already dehumidified it is extremely dry and this cannot be used for medical purposes, because that will have a very detrimental effect on the skin as well as on the nasal pathway for that humidity is very necessary.

And then we have a flow meter to control to find out what is the flow rate, so typical flow rates could be anywhere between 2 to 100 lpm liters per minute depending on the criticality of the situation. And this needle valve can be used to control the flow rate, so it can be very high or very low or medium flow rate that is as per the requirement.

So, the important part in this entire design and the process performance is the, is trying to understand or design this column effectively. So, this column performance is very essential which is the heart of the system like what is the production rate? how with time the production rate changes? what is the minimum this volume of the zeolite is needed for a certain amount of the production? these are quite the important settings or the important information needed from this case.

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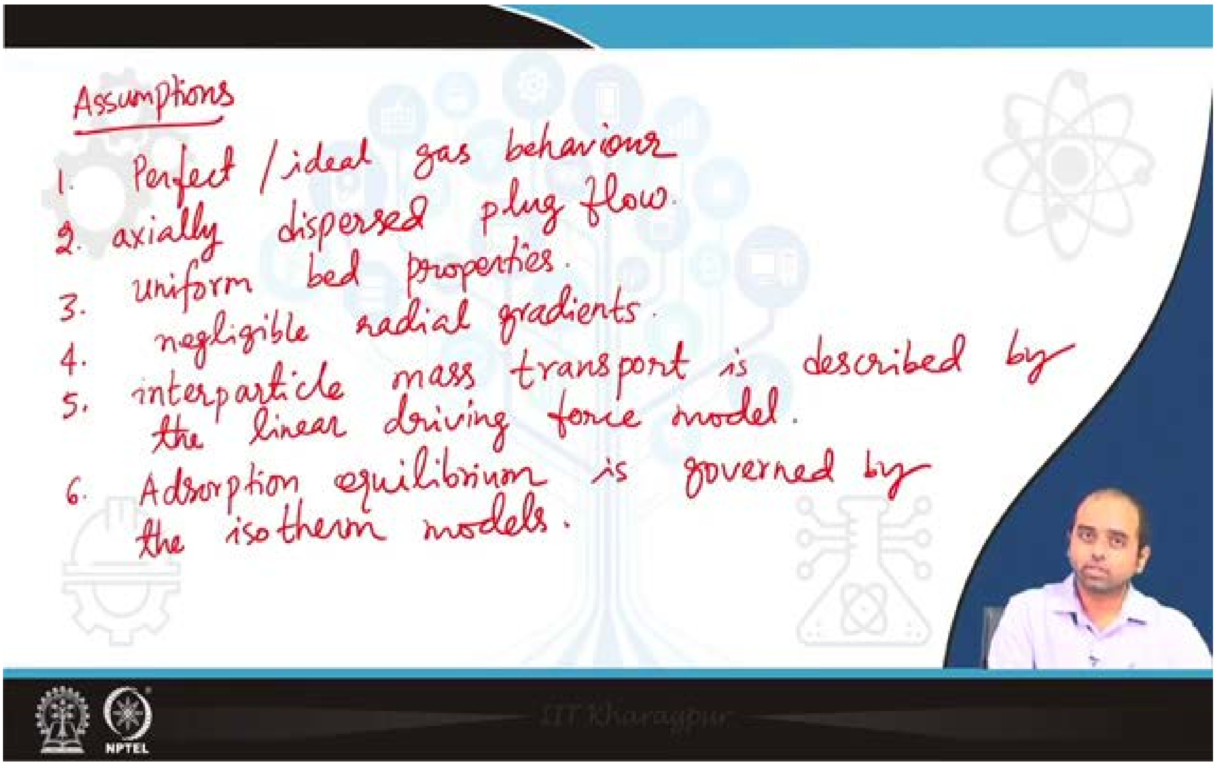

Assumptions

1. Perfect / ideal gas behaviour
2. axially dispersed plug flow.
3. uniform bed properties.
4. negligible radial gradients.
5. interparticle mass transport is described by the linear driving force model.
6. Adsorption equilibrium is governed by the isotherm models.

So, let us try to look into this modelling perspective of this pressure swing column of course before we start any model it is necessary to write down the assumptions. So, some of the assumptions that is quite relevant for the model in this case are that we consider that there is the gas behaviour, since the gas process.

So, perfect gas or ideal gas behaviour that is just to simplify the problem, then we consider axially dispersed plug flow, next is uniform bed properties which is generally the case and we do not want there is any characteristic difference in the adsorbent particles at different layers of the bed, so the bed is of uniform sized particles as well as their properties are uniform there is no multi-layer arrangement in the bed.

And there is negligible radial gradient. Since we are dealing with a problem of gas and gas diffusion is generally quite fast, so it is it is reasonable to assume that in the radial direction which is mostly you are having diffusive flux, the diffusive flux is too fast, so the gradient along the, there is negligible gradient along the radial cross section.

And we also consider this is an important concept based on which we will also build, in the subsequent weeks on the packed bed theory that the inter particle mass transport is described by the linear driving force model. So, we will talk about this, in this class today itself. And we say that the adsorption equilibrium is governed by the isotherm models. So, these are generally the, this assumptions in this problem as I have already said this is an adsorption problem, so adsorption isotherms plays a very important role.

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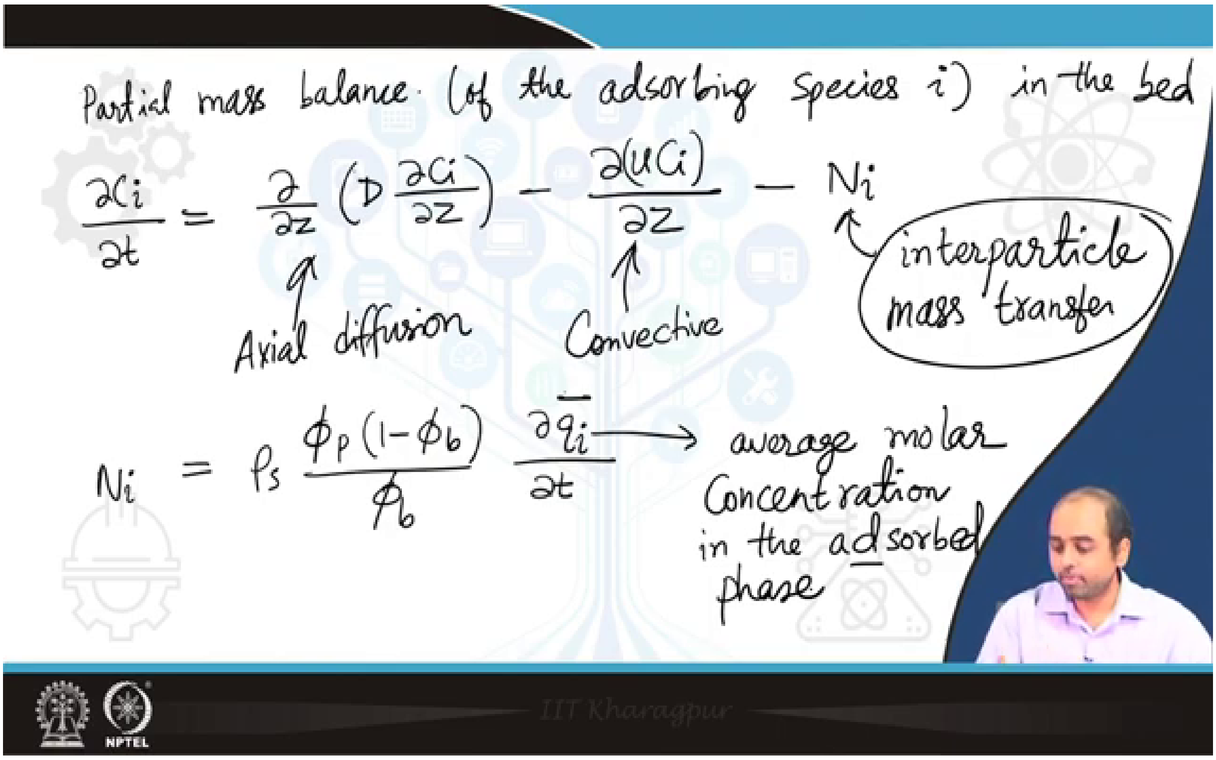

Partial mass balance (of the adsorbing species i) in the bed

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial z}\left(D\frac{\partial C_i}{\partial z}\right) - \frac{\partial (uC_i)}{\partial z} - N_i$$

Axial diffusion

Convective

interparticle mass transfer

$$N_i = \rho_s \frac{\phi_p(1-\phi_b)}{\phi_b}\frac{\partial \bar{q}_i}{\partial t} \longrightarrow$$

average molar Concentration in the adsorbed phase

Now, with this idea if we are trying to write down the this mass balance of course I am not going to do again that shell balance thing you can work that out yourself, but if you make a partial mass balance of any species which is adsorbing in this process of the adsorbing species sorry not absorbing adsorbing species i so I can write this is the accumulation term d ci dt and then we have the axial diffusion, the axial convection and this is the inter-particle mass transfer.

So, this is the balance in the bed or in the column, so this is the axial diffusion, so since this is a gas flow where diffusivity of gases generally very high and Peclet number is low for the problem. So, diffusion cannot be ignored relative to convection as unlike the scenario for liquid cases, where in the last problem we have just seen that if you the diffusion in the axial direction can be ignored because convection is stronger than diffusion, but it is not the case for gaseous problems.

So, here we are considering only the axial conditions because there is hardly any radial gradient in the problem. And next is to write down or to understand that how this inter particle mass transfer can be written down. So, the inter particle mass transfer Ni is generally related this mass exchange what is this intra particle or sorry inter particle mass transfer?

So, this inter particle mass transfer is the mass exchange rate between the particle and its surrounding assuming that there is no intra-particle effects, so intra-particle effects can also play a very important role and that is something we will see when we try to work on the problem related to catalysts and that how intra-particle mass transfer also plays a big role. But essentially it is the mass exchange from related to the particle to its surroundings, this is very important because most of the adsorption actually happens in the particle not in the bulk.

So, there is a mass transfer so when we are trying to model the bulk mass transport phenomena there has to be a contribution from the particle mass transport and the particle mass transport is mainly governed by the adsorption. So, this is the term which relates the inter-particle mass transport.

So, let me write it as phi b and phi p, so phi b phi p is the particle porosity, phi b is the bed porosity, rho s is the particle density and here I write d qi by d qt, so what is this d qi I mean this qi? So, qi is the average or I can write it as bar because we are not talking about the concentration effects at different surface locations on the particle, we are considering a particle as a point mass which is which have some mass and the adsorption happens there. So, it is sort of the consumption of the species.

So, average molar concentration, average molar concentration in the adsorbed phase, so this q or this adsorbed concentration or the adsorbate concentration is something which is related to the isotherm model as well as this adsorb adsorbed phase or the adsorbate concentration rate or the dynamics of the adsorbate concentration in this problem is given by the linear driving force model.

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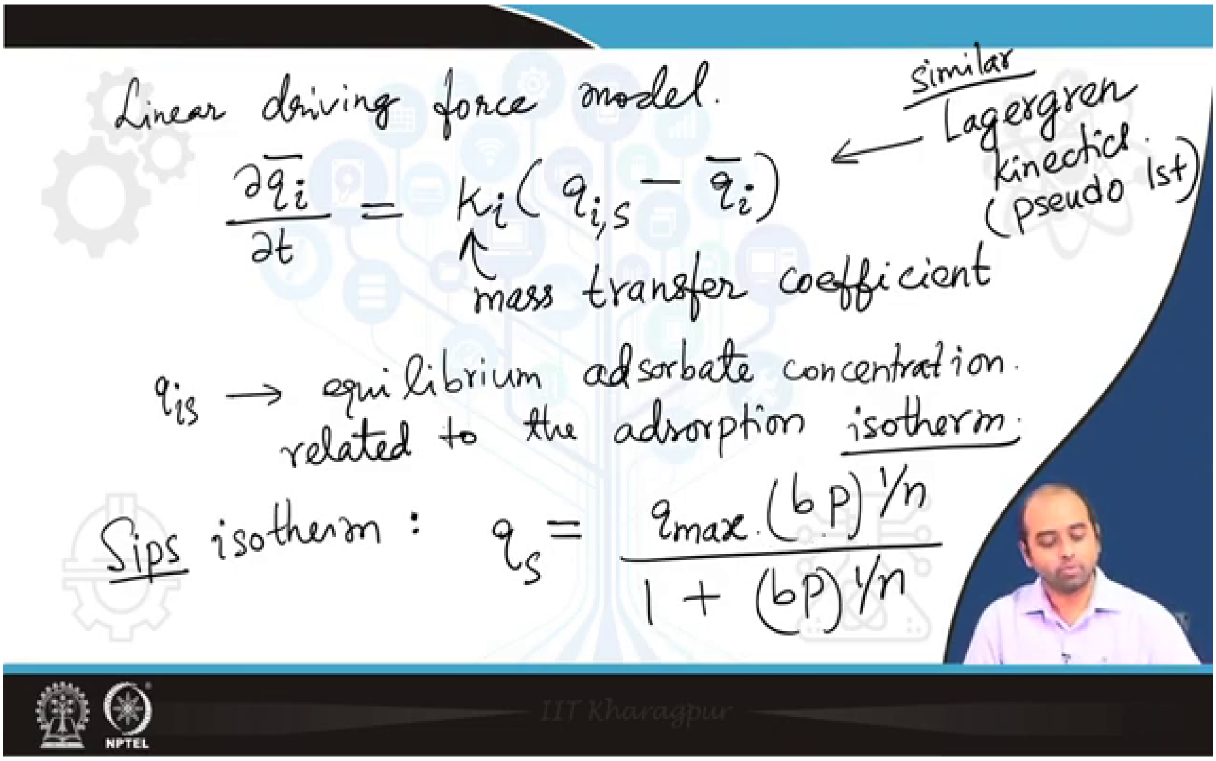

Linear driving force model.

$$\frac{\partial \bar{q}_i}{\partial t} = k_i (q_{i,s} - \bar{q}_i) \leftarrow \text{similar Lagergren kinectic (pseudo 1st)}$$

$\uparrow$ mass transfer coefficient

$q_{is} \rightarrow$ equilibrium adsorbate concentration. related to the adsorption isotherm.

Sips isotherm : $q_s = \dfrac{q_{max} (bP)^{1/n}}{1 + (bP)^{1/n}}$

So, this linear driving force model tells you that the rate dynamics of the adsorbate concentration is given by this mass transport model, where this is this K is the mass transfer coefficient of the adsorbing species in the bed. So, you can have several bed models where based on the different assumptions or the bed properties this mass transfer coefficients has been already reported or it is calculated.

So, this is the idea or the basis of the driving force model this driving force model can also be this model is also equivalent to the first order these are also relevant I should not say this to first order but Lagergren and there are several types of Lagergren kinetic model pseudo first order first order.

So, this is essentially the pseudo first order models and which is based on the this is very similar to the I should not call this to be the same because Lagergren models are essentially developed for kinetic theories, adsorption kinetics and this is for the this linear driving force model is based on the fact that diffusion is more dominant in this problem.

So, if you try to compare diffusion and adsorption you will find if you see that diffusion is more dominant in this intra particle mass transport, then this model is quite likely but the quite likely scenario but this is very similar to the Lagergren kinetics or the pseudo first order kinetics.

So, this qi s so this qi, s is something which is so this qi, s is something which is modelled this is nothing but the equilibrium adsorbate concentration and this is related to the adsorption isotherm. So, if you choose let us say a Freundlich or Sips model, so Sips model is a very generalized form of the Freundlich model and also the Langmuir model, so it is a combination of something like this and this is the most popular model.

So, this q is written down as q max, so this is a three constant model, so q is the q is nothing but this qi, s, so I should not write i because this is a generalized form qs, so these are three constant model q max, b and n. So, if n is equal to 1 this is equivalent to the langmuir model and also if n is equal to not 1 this can also be equated to the Freundlich model if n is if this b is very small to say, if b is very small this model can also be related to the Freundlich model.

So, this is one of the generalized form, something in between the Freundlich or the iso Langmuir models both the Freundlich and the Langmuir isotherm models are two constant models and this sips model is a three constant model. So, but this can be simplified to any one of these models. So, this relates the equilibrium capacity sorry the equilibrium value or the equilibrium adsorbate concentration and that is something which should be fed to the linear driving force model.

Now, there is one more important thing that I should mention here is that of course I should also say here that these values of q max and b are generally dependent on temperature. So, they have a strong effect on the temperature and at different temperatures the adsorption capacities as well as their adsorption isotherm profiles changes drastically. So, and that change is incorporated through this change in the q max and b.

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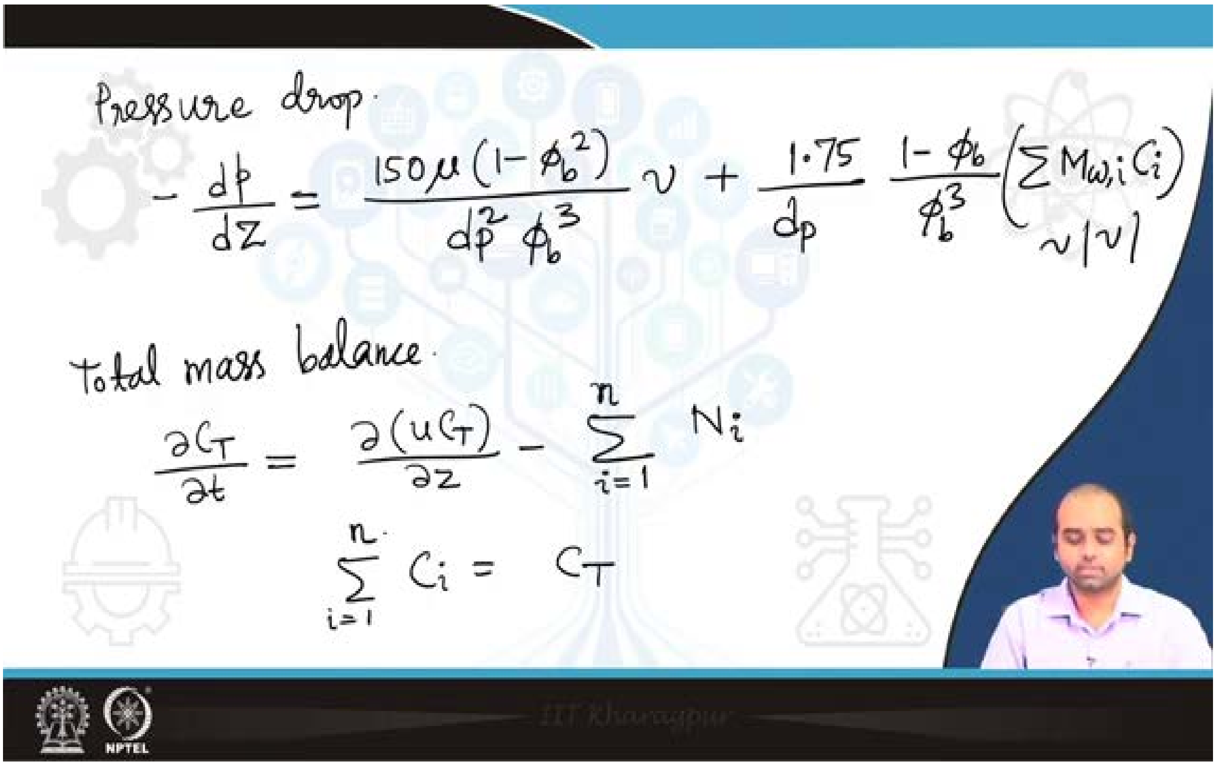

Pressure drop.

$$-\frac{dp}{dZ} = \frac{150\mu(1-\phi_b^2)}{d_p^2\phi_b^3}v + \frac{1.75}{d_p}\frac{1-\phi_b}{\phi_b^3}\left(\sum M_{w,i}C_i\right)v|v|$$

total mass balance.

$$\frac{\partial C_T}{\partial t} = \frac{\partial(uC_T)}{\partial z} - \sum_{i=1}^{n} N_i$$

$$\sum_{i=1}^{n} C_i = C_T$$

Now, one more thing I should also mention here is the, this pressure drop, so this pressure drop or this pressure variation this pressure drop for any flow through a porous media, this pressure drop occurs due to the viscous energy loss and to the drop in the kinetic energy. So, typically this pressure drop is modelled by the Ergun equation which is a very popular famous equation that most of you have already studied in unit operations.

So, this is the famous Ergun equation, dp is the particle diameter which is in this case the adsorbent particles and all this phi is sorry not epsilon phi is actually phi b bed porosities and here you have the summation terms. So, this is the Ergun equation through which the pressure drop in the problem is actually related.

So, now this framework is complete or the equation framework we complete we have one equation for the mass balance, one equation which relates the intra particle sorry inter particle mass transport, one equation which relates the isotherms or the equilibrium capacities and then finally one equation for the pressure drop.

There is also one more equation which needs to be written down here and that is the total mass balance which I forgot actually in fact that should have been written in the beginning from so from the total mass balance what you get is the summation of the let us write down the flux form. Ct is the total concentration, number of components let us say so this is the total mass balance that we have for this problem.

So, you have the unknowns as your u the concentrations and of course the concentration of all the so this has to also satisfy, so this should give C and then we have the pressure drop, so the pressure, so number of equations and the number of unknowns are same they are equivalent now.

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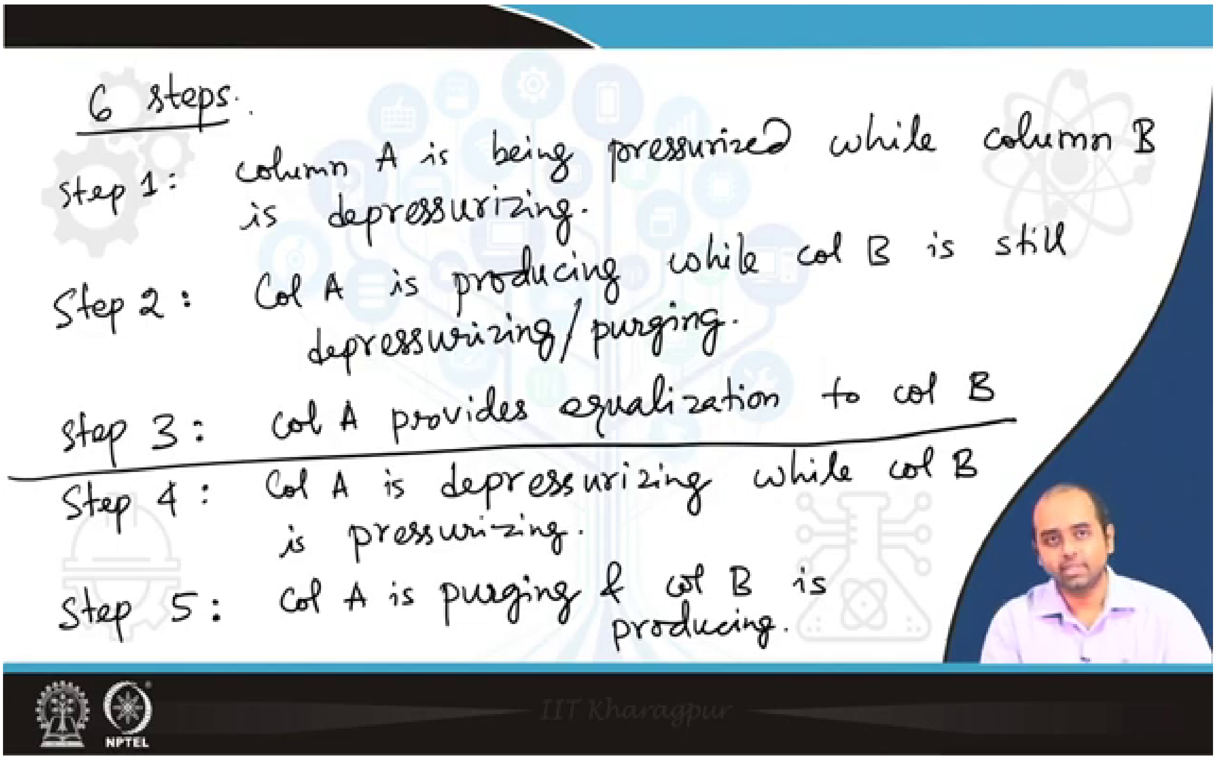


6 steps.

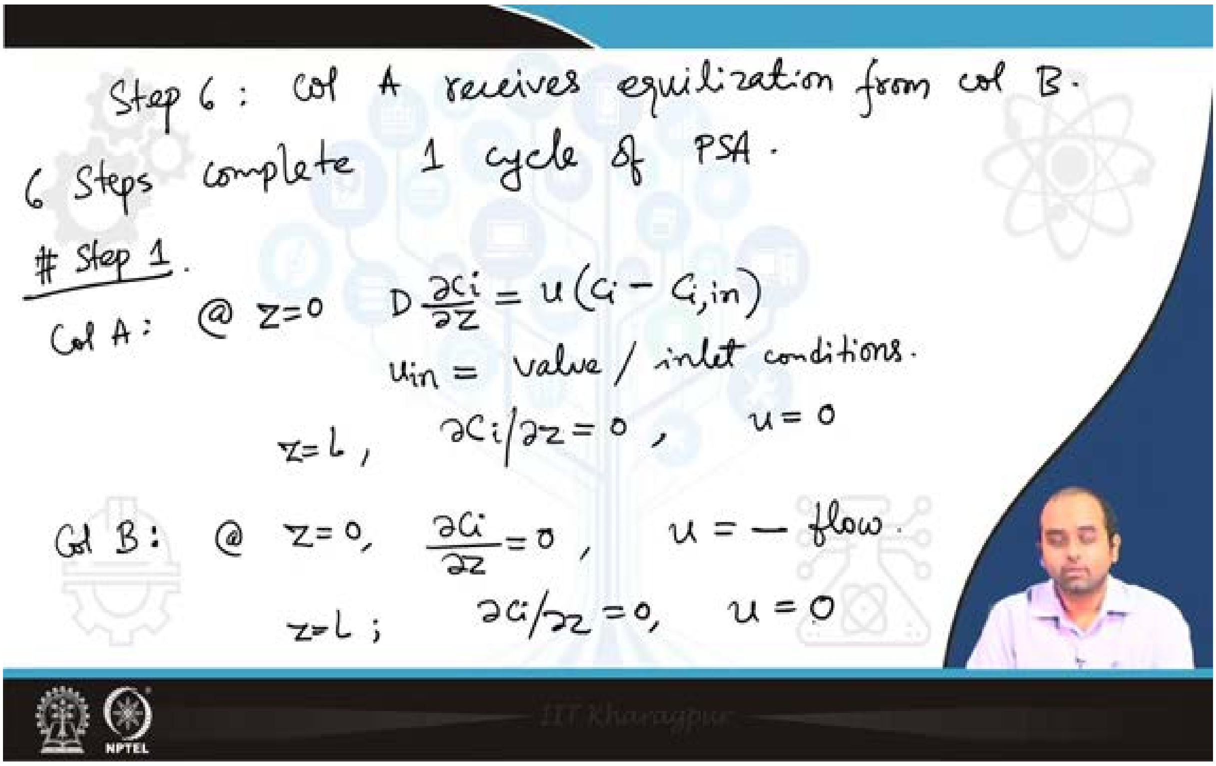
Step 1: column A is being pressurized while column B is depressurizing.

Step 2: Col A is producing while col B is still depressurizing / purging.

Step 3: col A provides equalization to col B

Step 4: Col A is depressurizing while col B is pressurizing.

Step 5: Col A is purging & col B is producing.



Step 6 : col A receives equilization from col B.

6 Steps complete 1 cycle of PSA.

Step 1.

Col A: @ $z=0$ $D\frac{\partial c_i}{\partial z} = u(c_i - c_{i,in})$

u_{in} = value / inlet conditions.

$z=L$, $\partial c_i/\partial z = 0$, $u=0$

Col B: @ $z=0$, $\frac{\partial c_i}{\partial z} = 0$, $u = -$ flow.

$z=L$; $\partial c_i/\partial z = 0$, $u=0$

Now, let us talk about the boundary conditions and the boundary conditions are quite explicit there are different steps in this problem, so essentially there are total 6 steps in this cycle. So, the first step is step 1 is column A is being pressurized while column B is depressurizing, so that is step 1.

Then we have step 2, where column A is producing and while column B is still depressurizing. Step 3 of this process is column A provides equalization of pressure to column B. In step 4, the process gets reversed for column B, so column A is depressurizing while column B is pressurizing. And step 5 is column A is still depressurizing sorry this is yeah so there is step 5, so in step 5 we say that column A is what you call purging and column B is producing. So, here pressurizing or purging, so it is a so after step 3 the process is repeated for column B.

And finally, in step 6 you get column A receives equalization to column sorry from column B, so as you can see the first three steps are just repeated for column B and overall these 6 steps this 6 steps complete one cycle of the pressure swing adsorption. So, what about the boundary condition? So, the boundary conditions are different in these steps and essentially once we try to write down the first three steps, it will be same for the remaining three steps for column B.

So, in the first step, so step 1 for column A, we have at z is equal to 0, which is the inlet is 1 by D del c by del z is equal to u. So, this is we are trying to balance the fluxes sorry it is not 1 by D it is D. So, this is we are trying to balance the flux and this u which is nothing but u in, so this u in is actually given from the valve or the inlet conditions. So, how much the valve opening is there and what is the flow rate and all its from that portion, the dependence on how much it is opening in that five-way valve programmable valve and all.

And at z is equal to L, so first step one is column A is pressurizing. So, at that point it is the far field condition or our outlet condition, we say that del z is equal to 0 and there is no output from that part it is just pressurizing. So, for column B, it is depressurizing, so at z is equal to 0, we have d ci this is the condition and u is minus of some flow in the depressurizing section again this depends on the opening of the depressurizing valve. So, this is z is equal to 0 and at z is equal to L, you also have d ci dz is equal to 0 and u is equal to 0, this is for step 1.

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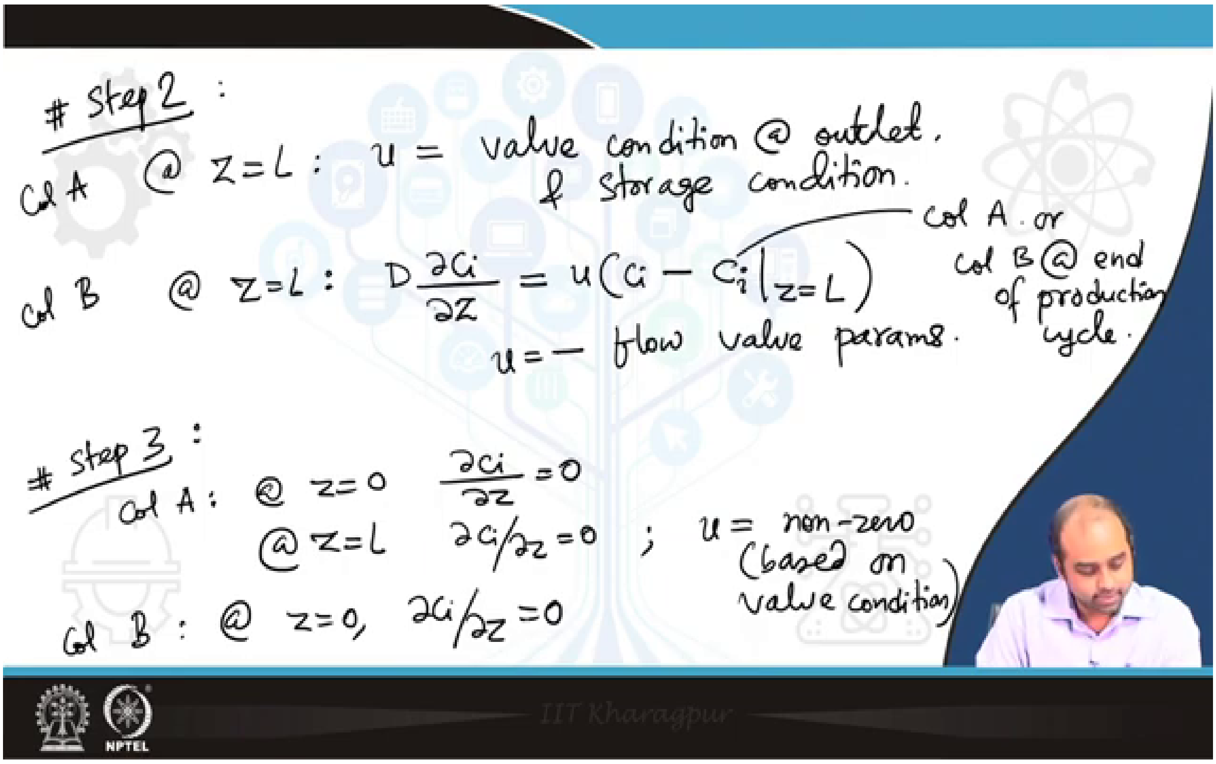

Step 2 :

Col A @ $z=L$: $u =$ valve condition @ outlet. & storage condition.

Col B @ $z=L$: $D\frac{\partial c_i}{\partial z} = u(c_i - c_i|_{z=L})$

$u = -$ flow valve params.

Col A or Col B @ end of production cycle.

step 3 :

Col A : @ $z=0$ $\frac{\partial c_i}{\partial z} = 0$

@ $z=L$ $\partial c_i/\partial z = 0$; $u =$ non-zero (based on valve condition)

Col B : @ $z=0$, $\partial c_i/\partial z = 0$

So, for step 2 in the step 2, when column A goes into production and column B is in purging state, so the these two boundary conditions are different from step one and I write only those two boundary condition, so at z is equal to L the flow rate u is again dependent on the valve condition, it is not 0, so this is dependent on the valve condition at the outlet and it also depends on the outlet as well as the storage condition, because the storage wall parameters and the storage pressure.

If the column pressure is same as the storage pressure or the column outlet pressure is same as the storage pressure then there will be not any flow. So, the storage condition also needs to be taken into account determine this flow and for column so this is for column A. For column B which is in purging state at z is equal to L in step 2 it is slightly different we write this as d ci dz is equal to u ci minus ci at z is equal to L and u is minus of the flow conditions flow pulse parameters.

So, this is ci minus ci at z is equal to L for column A unless there is a since we have a if you have a check valve, then this since there is a check valve, so this depends on what is the last state of the production of this value of ci at z is equal to L for the for column B before during the production cycle. So, this column A or column B at the end of productions sorry this is or column B production cycle. The conditions for z is equal to 0 will be same as in step 1.

Now, in step 3, where you have equalization of the pressures for column A we have at z is equal to 0 d ci dz is equal to 0 and at z is equal to L you have d ci dz is equal to 0, but there is a flow, so flow is let just let me write non zero and based on valve conditions. So, for column B at z is equal to 0 you have d ci dz to be 0.

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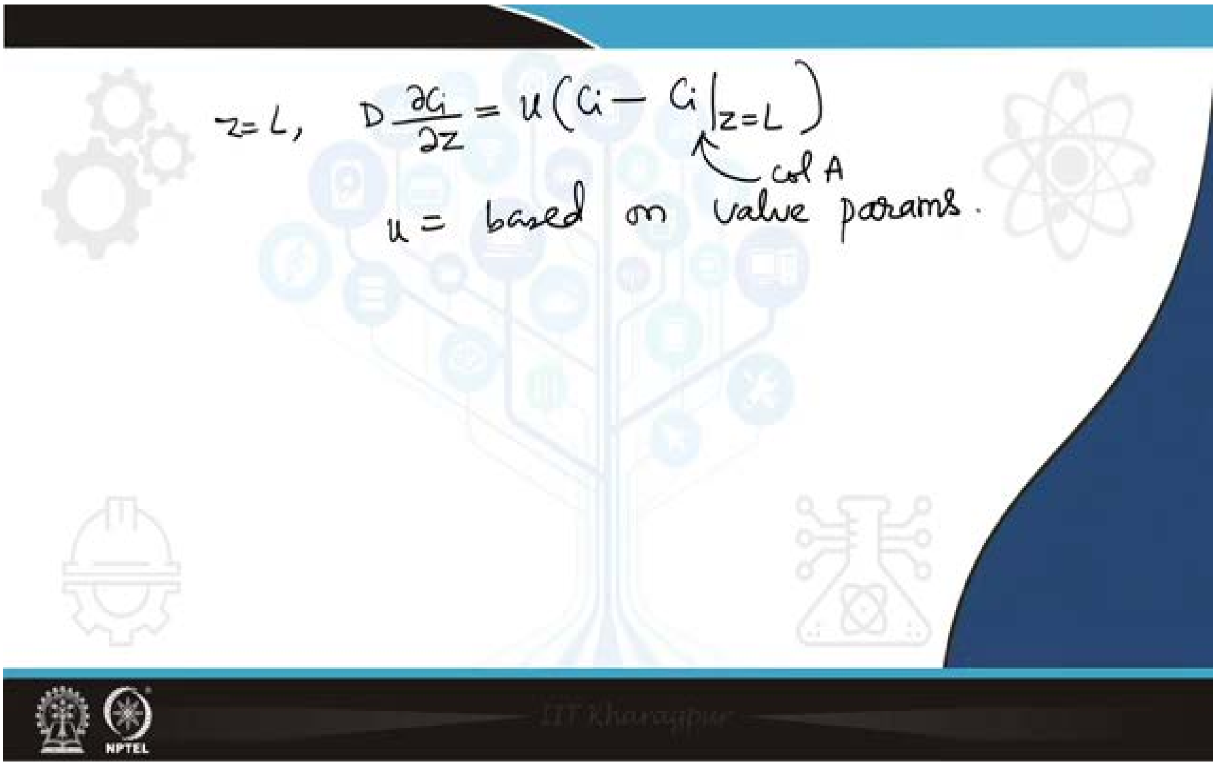

$z = L, \quad D\frac{\partial c_i}{\partial z} = u\left(c_i - c_i\big|_{z=L}\right)$

col A

u = based on valve params.

And so here the column B is actually the column A is actually providing equalization to column B. So, for the case of the column B at z is equal to L you have the following boundary this boundary condition the diffusive flux is equated to the convection. And here it is for column A because this is providing column A is providing equalization to column B and here also the u is non-zero and based on valve parameters.

So, same goes for step 4, step 5 and step 6, where the conditions will be just reversed for the column B instead of column A. So, this valve parameters this wall parameter is essentially very crucial to determine what is the flow rate and this is something which is based on the type of valve they are using whether it is a gate valve, globe valve or a needle valve or what sort of valves that you are trying to use and what is the pressure of the system at that will also be needed to quantify to estimate the flow rate of the gas through the valve apertures.

So, I think this is a very nice discussion on the modelling of pressure swing adsorption and this model framework can be quite useful to find out the optimum cycle times, for example try to understand how the concentration changes during the start-up phase or how the concentration varies with time. So, what should be the optimum cycle time and what should be the optimum pressure given the equilibrium condition or the isotherm conditions.

So, all and this will finally lead to effective design optimization of these setups. So, both from the operational as well as the design perspectives the model results can be very useful. I hope all of you have found this lecture to be useful as it is related to a very practically relevant problem. Thank you.