Course: Adsorption Science and Technology: Fundamentals and Applications

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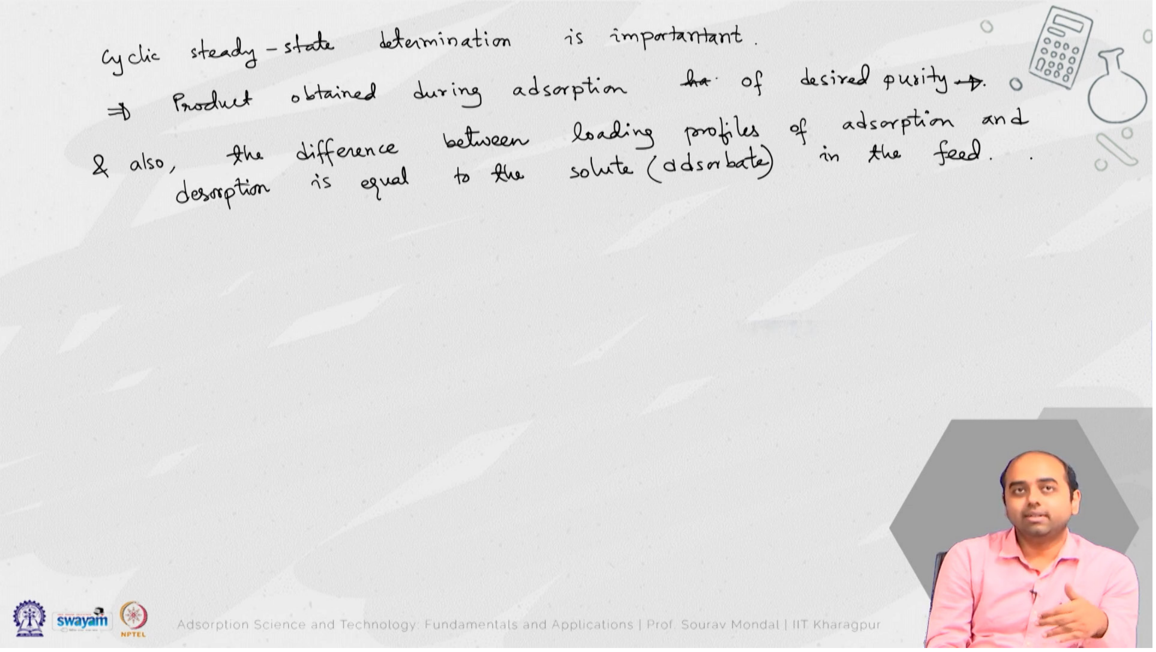
Week 06

Lecture 29 | Modelling PSA Systems

Welcome to this class on this second lecture related to this topic of pressure swing adsorption. In this pressure swing adsorption as you know there are two beds at least a minimum of two beds which operate in cycles you know in synchronization where one beds is actually in adsorption and the other bed is actually in desorption mode and during this desorption the bed is getting regenerated while the other bed is actually getting generated or with actually in production mode and produces the desired component and typically these are you know determined by this Skarstrom cycles. Now these beds or these cycles are generally controlled either by you know equilibrium or by kinetics but the important bit is that in thermal swing adsorption for example, the during the regeneration or during the desorption step or the state it gets produced I mean the regeneration is almost close to a clean situation or to back to the original situation. But whereas, during the pressure swing adsorption this regeneration does not produce a clean or like you know a fresh adsorbent rather there is some residual amount which is present and that affects the subsequent cycle of the adsorption. So, this achieving this sort of cyclic steady state is very important and that is why modeling the transient nature of this bed in cycles over a multiple cycles is also very important. So, determining this cyclic steady state or how many cycles do you need to attend the steady state is also a very important factor in the design or model of this pressure swing adsorption system.


Cyclic steady-state determination is importantant.

⇒ Product obtained during adsorption ~~ha~~ of desired purity →.

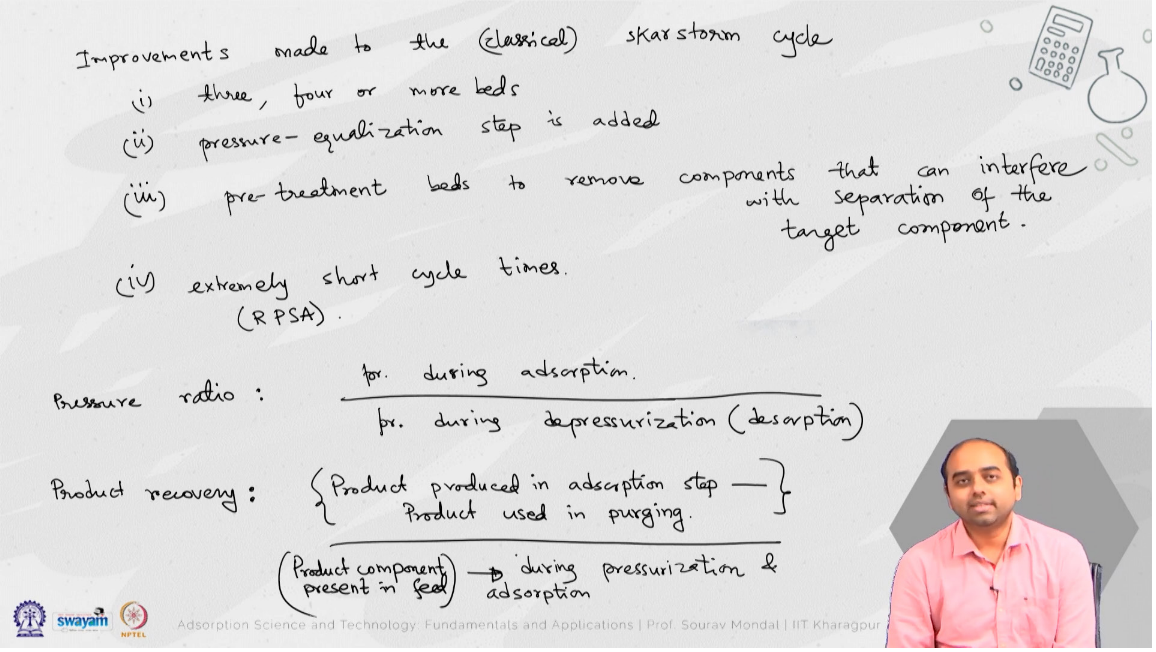
& also, the difference between loading profiles of adsorption and desorption is equal to the solute (adsorbate) in the feed.

So, typically since the regeneration is seldom achieved or attained in this pressure swing adsorption, over one cycle you need a several or to attain a cyclic steady state several cycles are actually needed for the same purpose. This is something I would like to highlight that cyclic steady state determination is important . So, in the cyclic steady state what happens is that that the product obtained during adsorption of desired purity and also the difference between loading profiles of adsorption and desorption is equal to the solute R adsorbate in the feed. So, it is essential that it at every cycle the output purity is constant and this is only possible when the cyclic steady state is attained for this system.

And the other important thing is that the the difference of the loading profiles of adsorption or the difference between the adsorption and the desorption loading profile is equal to the amount of the solute that is present in the feed. So, this is this is particularly very important and to ensure that there is no transient or there is no amount of the mass of the solute which is present or there is this transient effect or whatever this effect is there between the cycles is actually 0 and that is how we call this as a cyclic steady state. So, within the cycle there is always a concentration profile with time during the adsorption, but between the cycles the average concentration should not change and that is how we call this as a cyclic steady state operation and that is why the model is also very important to you know or understand that how does or how long does it take to achieve this cyclic steady state operation or to attain the cyclic steady state. And it requires particularly for different kinds of system it can take anywhere from 10 to almost few hundreds of such cycles before a cyclic steady state is achieved. Now, over the few decades there has been some improvement on the you know this classical Skarstrom cycle that I think is important to highlight at this point, and that will actually form the basis of our different stages for the this cyclic operation besides the classical four steps.

So, one of the important modifications or improvements that is done besides the change in the steps or adding intermediate steps is that instead of having two beds you can have three four or more beds. One improvement is to have three four or more beds. A pressure equalization step is added in which both the beds are equalized with pressure following the purge of one bed and the adsorption of the other. Next is pre-treatment, this is from the application point of view. Pretreatment beds is many a times added to remove components that can interfere with the separation.

Separation of the desired or the target component. Another thing is not this purge, this extremely short cycle times. Many a times this is referred to as rapid pressure swing adsorption. So, if you reduce the cycle times to less than 10 seconds or maybe less than 20 seconds then this comes under the category of rapid pressure swing adsorption. And in that case you would actually take advantage of the shorter depressurization time or the blow down time to reduce the overall cycle time and the net productivity or the net recovery of the target compounds can be increased.



Improvements made to the (classical) skarstorm cycle

(i) three, four or more beds

(ii) pressure-equalization step is added

(iii) pre-treatment beds to remove components that can interfere with separation of the target component.

(iv) extremely short cycle times. (RPSA).

Pressure ratio : $\dfrac{\text{pr. during adsorption.}}{\text{pr. during depressurization (desorption)}}$

Product recovery : $\dfrac{\left\{ \begin{array}{c} \text{Product produced in adsorption step} - \\ \text{Product used in purging.} \end{array} \right\}}{\left(\begin{array}{c} \text{Product component} \\ \text{present in feed} \end{array} \right) \rightarrow \text{during pressurization \& adsorption}}$

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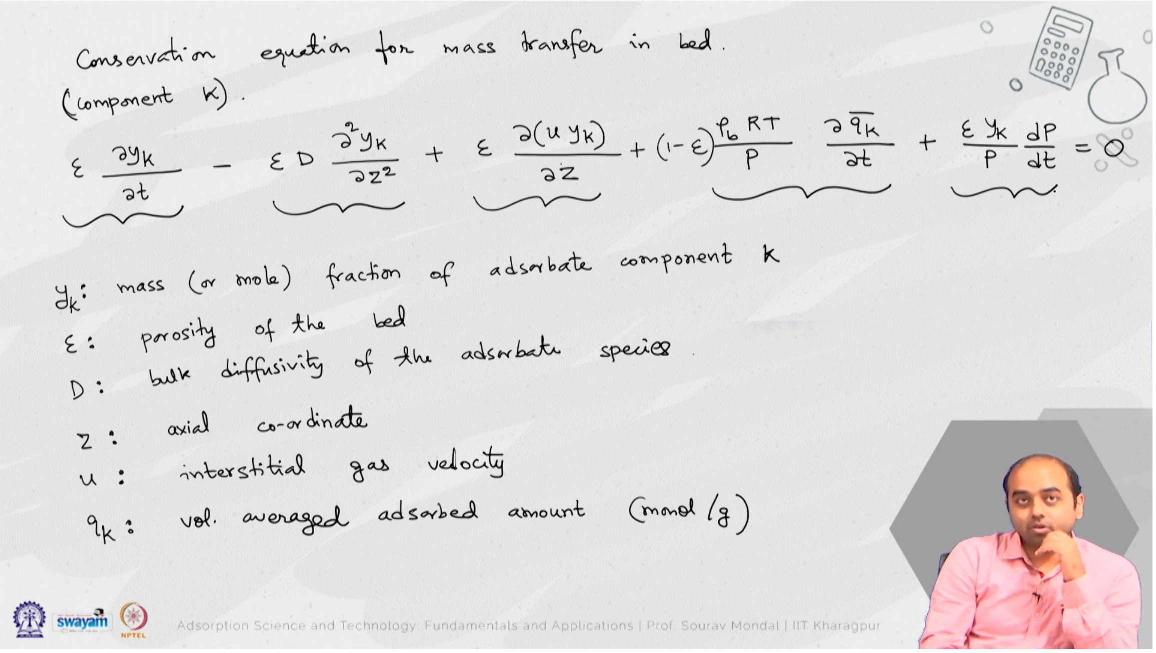
In that case of course, you will not be you know adsorbing or you will not be doing the adsorption till the bed attains complete saturation, but you in that case you take advantage of the shorter you know blow down cycle times. And in that case if the bed is not completely saturated, you also take advantage of you know further reduction in the time of the blow down or depressurization so as to regenerate the bed. so see if the bed is not completely saturated then regeneration would also be faster so that is the idea that you take advantage of in this rapid pressure swing adsorption and many times that helps in increasing the overall recovery of the product now coming to some of the terminologies this these are some important terminologies that often that is used that how do you define recovery how do you refine purge to feed ratio or the bsf bed size factor So, first is of course, the pressure ratio. So, this pressure ratio defines as the ratio of the pressure during adsorption with respect to pressure that is maintained during depressurization or higher is this pressure ratio, higher is the separation, but then again increasing the pressure ratio increases the energy. So, this pressure ratio can be improved by increasing the adsorption pressure or decreasing the desorption pressure also with the help of vacuum.

Next is product recovery. So, typically product recovery is defined as oxygen or whatever this product produced in adsorption step minus product used in purging, divided by the product or this amount of the product fed during pressurization. Of course during pressurization as well as adsorption. So, something like product you should write product present in feed product component present in feed during pressurization and desorption. And numerator is like the you know after the separated you know component that is the product that is you are getting from the adsorption stem and the product is already used for purging.

So, recovery is a very important parameter besides the purity. Next is the purge to feed ratio. So, purge to feed ratio is something known as P by F. So, amount of product used in purging step divided by the product or the product component present in pressurization and adsorption step. Another important terminology is this bed size factor.

So, this is referred to as the weight of adsorbent in the bed with respect to the product throughput. So this is like kg of product that is produced per hour in the product stream of course and this would be like kg of adsorbent. So, this actually gives us the idea on the you know adsorbent productivity. So, lower is the bed size factor the better the performance of the bed is. Now, coming to this conservation equations of the balance equation for the target species within the bed.

So, conservation equations for mass transfer, conservation equation for mass transfer in the bed. We write this for component k the generic you know way because there could be multiple compounds which can be you know adsorbed by this bed and the relative adsorption efficiency or the selectivity of a particular compound over the other compound it what makes its selective or to remove or to separate these products. So, that is why it is inevitable that we write the different components you know in terms of the generic value of k. So this is we write this expression epsilon is the bed porosity. This is the convection term.



Conservation equation for mass transfer in bed.
(component k).

$$\underbrace{\varepsilon \frac{\partial y_k}{\partial t}} - \underbrace{\varepsilon D \frac{\partial^2 y_k}{\partial z^2}} + \underbrace{\varepsilon \frac{\partial (u y_k)}{\partial z}} + \underbrace{(1-\varepsilon)\frac{\rho_b RT}{P} \frac{\partial \bar{q}_k}{\partial t}} + \underbrace{\frac{\varepsilon y_k}{P}\frac{dP}{dt}} = 0$$

y_k: mass (or mole) fraction of adsorbate component k
ε : porosity of the bed
D : bulk diffusivity of the adsorbate species
z : axial co-ordinate
u : interstitial gas velocity
q_k : vol. averaged adsorbed amount (mmol/g)

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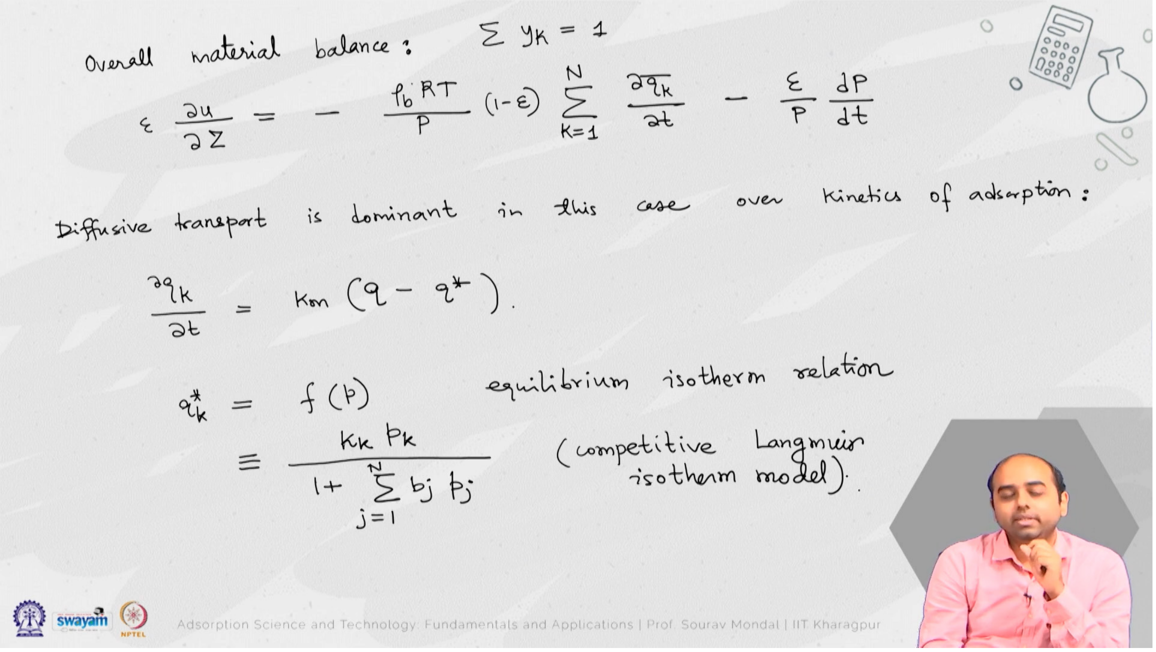
So, here y refers to as the mass fraction or mole fraction of adsorbate components, k. Epsilon represents the porosity of the bed. D represents the bulk diffusivity of the adsorbate species. Then we have this z, z is the axial coordinate. So, we are trying to write down a one-dimensional balance.

u represents this interstitial gas velocity and of course, we will be writing down this q etcetera and all. So, this Q the way I have written down here this is the adsorption term here. So, this Q represents the volume averaged adsorbed amount. Something like this could be in terms of millimoles per gram. And that is the reason why I have written down this in terms of RT by P.

So, considering this to be an ideal gas, I convert this into the mass form here because this is entirely a mass balance. And then the final term comes because of the pressure gradient, equal to 0. So, the first one is the you know term due to the accumulation of this transient accumulation of this component. This term refers to the diffusion, this term refers to the convection in the porous bed, this term refers to the adsorption of course, this would be multiplied to with 1 minus epsilon because this adsorption happens only in the solid phase. And this is the term due to the change in the pressure or because of this mass associated with the change in pressure during the flow.

So, if one tries to get you know proper this balance or the continuity of the mass overall mass balance or overall material balance is very important in this case because in the case of the overall I mean the overall material balance relates that as the gases which are present in the system is getting adsorbed the mass flow rate will be changing between the inlet and the outlet. So, this is particularly different from the liquid adsorption scenario where once the target molecule is adsorbed the carrier of liquid which is present does not change its flow rate, but here since the carrier gas itself or the total air that is entering for example, if you are trying to produce nitrogen or oxygen. So, the air that is entering into my bed the mass of this air in the the mass flow rate of this air at the inlet and the outlet will be different because part of its component is getting adsorbed. For example, if one tries to produce nitrogen. So, if I am feeding in 1 mole of this or 1 you know this gram of air at the inlet then at the outlet I will be getting 80 percent 0.8 grams because 20 grams 0.2 grams would be absorbed within this bed. So, there is a you know difference in the mass flow rates between the inlet and outlet and that is why the overall mass, material balance or this continuity of balance is very important and in this case the overall material balance can be obtained based on the fact that one can do this you know balance of y k is equal to 1 then you will land up with this scenario and this gives us an idea about how does you know this velocity actually changes within the bed and that is the reason why I have used this velocity u within the differential term because that is not constant along the length of the bed. So, as more and more of adsorption happens this is unlike the scenario for liquid adsorption I am reemphasizing this. As the gas flows through the adsorption bed part of its by volume is getting captured or getting removed.

So, the flow rate as well as the pressure changes in I mean pressure may not change because you are adjusting the pressure both during the pressurization and adsorption cycle, but essentially the mass flow rate is changing. So, and that is very important to account for and that is the reason why du dz is not you know equal to 0 in this case or the flow is never a fully developed flow in this scenario . So, here I must write. that du/dz is not equal to 0 and this is an important difference between a liquid adsorption and this gas adsorption in this case of pressure swing scenario and this is how the du/dz is given here and it also depends on the pressure. So, this is how du/dz can be evaluated based on the pressure profile and the rate of adsorption.



Overall material balance: $\sum y_K = 1$

$$\varepsilon \frac{\partial u}{\partial Z} = -\frac{\rho_b RT}{P}(1-\varepsilon)\sum_{K=1}^{N}\frac{\partial q_K}{\partial t} - \frac{\varepsilon}{P}\frac{dP}{dt}$$

Diffusive transport is dominant in this case over kinetics of adsorption:

$$\frac{\partial q_K}{\partial t} = K_m\left(q - q^*\right).$$

$q_K^* = f(p)$ equilibrium isotherm relation

$$\equiv \frac{K_K p_K}{1+\sum_{j=1}^{N} b_j p_j}$$

(competitive Langmuir isotherm model).

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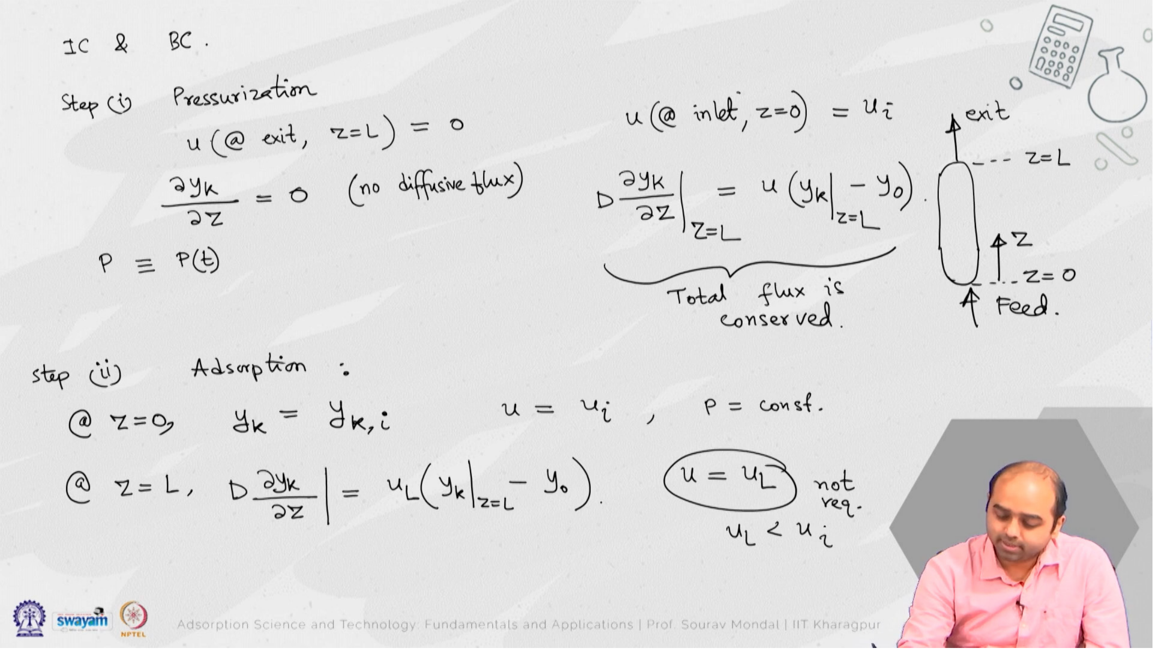
Now, this dq/dt particularly in this kind of scenario is actually governed by the linear driving force model because the mass transport or let us say the diffusive transport is dominant in this case over the kinetics of adsorption. Or in other words, the adsorbent reaches almost instantaneously the equilibrium value. So, the kinetics is very fast and diffusion is generally the slower step even though gas diffusion is much faster compared to liquid diffusion, but again the kinetics of adsorption is much faster here. So, generally it is the diffusive transport is much faster. So, here dq/dt is generally referred to as this mass transfer coefficient c minus c bulk where of course this sorry not c minus c bulk this p minus p bulk of course this p or this pressure p in this case this I have written down as the partial pressure.

So, in this case q, q star not p and q star is related to this through the equilibrium isotherm relation. For example, if you try to consider the Langmuir isotherm then this takes the form of. So, you have to use the competitive model. This is the competitive Langmuir isotherm model. Now, importantly this of course, in writing down this all this balance equation we are assuming that this is an isothermal operation.

So, there is no temperature change during this adsorption process or during this you know this cyclic process. Now, the important part comes in the initial and the boundary conditions and exactly that depends on the different stages or the different you know steps. So, let us consider if we have this 4 steps that we have. So, for the step 1, so initial and boundary condition is very important that is how we are writing this step by step. So, in this step 1 where we shape pressurization may be, of the column because until pressurization happens this column can no longer produce any adsorption.

So, during this pressurization step this U at exit or let us call this as Z is equal to L. So, I draw a simple schematic of the column. And I mark this as my Z. So this is like feed.

This is like exit. So this is Z is equal to 0. This is Z is equal to L. So at L this is equal to 0. at L the you know that at the exit concentration this in this case of this pressure during the pressurization this d y k by d z is also equals to 0 because we consider no flux at u at inlet that is z is equal to 0 is equal to u naught that can be found out from the pressure considering what is the kind of pressure that we are maintaining at the inlet and knowing the volumetric fluid one can work out what would be the interstitial gas velocity. And the diffusive flux dyk/dz at z is equal to 0 can be given by this relation.


IC & BC.

Step (i) Pressurization

u(@ exit, z=L) = 0

$\frac{\partial y_k}{\partial z} = 0$ (no diffusive flux)

$P \equiv P(t)$

u(@ inlet, z=0) = u_i

$$\underbrace{D\frac{\partial y_k}{\partial z}\Big|_{z=L} = u\left(y_k\big|_{z=L} - y_0\right)}_{\text{Total flux is conserved.}}$$

Step (ii) Adsorption :

@ $z=0$, $y_k = y_{k,i}$ $u = u_i$, $P = \text{const.}$

@ $z=L$, $D\frac{\partial y_k}{\partial z}\Big| = u_L\left(y_k\big|_{z=L} - y_0\right)$. $\boxed{u = u_L}$ not req.

$u_L < u_i$

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So, we say that the total flux in this case is actually 0. So, this suggest the total flux is conserved and here we say that no diffusive flux Since u is 0, so anyway convective flux is 0 at the exit. So, separately we are writing that no diffusive flux, but whereas the total flux is conserved at the inlet. Similarly, we can also write this pressure during the pressurization cycle to maintain certain profile. So, P would be equal to like a function of time and that one can relate that what would be the P value at pressurization or the highest value and what is the inlet value.

So, that can be a function that you can either define to be like a ramp function or a linear gradient based on what is the cycle or what is the time that you are allocating for this pressure to jump from 0 to that the desired value of the pressurization ratio. So, that can be you know set with respect to the pressure. Now, coming to this step 2 which is the adsorption step. So, during this step at z is equal to z 0, this y can be said to be the Dirichlet condition y ki or the inlet value, u is of course, u naught. In this case p is constant at z is equal to L at the exit, we can once again define that the total flux is conserved.

So, this is at z is equal to L. U will be of course different than the feed. And of course, we do not need two boundary conditions in EAD. So, this condition is not required. But even though just to make you aware that U L is less than U naught or the I should write this as U inlet.

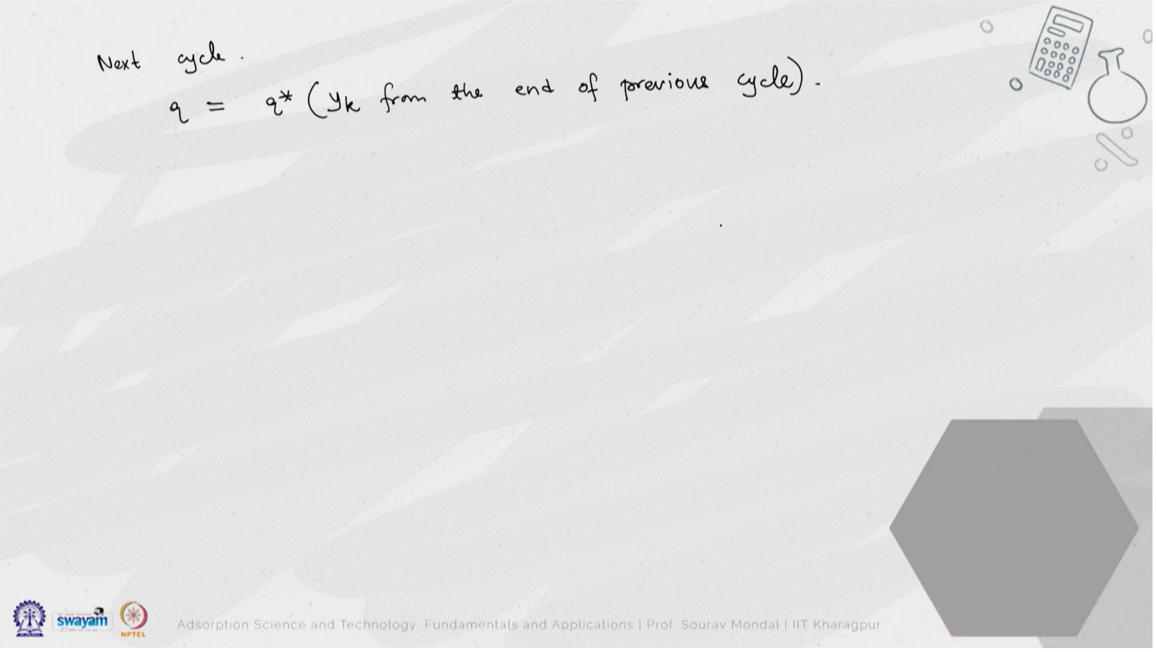
So, U I O is slightly confusing. So, this at z is equal to 0 is actually the inlet, this is outlet or the exit. So, this is about step 2. Coming to step 3, where we have this depressurization Now, depressurization again can be here split into three parts like equalization, co-current, counter current and all this step. So, we can have this you know co-current depressurization, you can have counter current depressurization. So, again or you can club them together and to have one depressurization.

So, in this depressurization stop if you are doing this co-current mode, we are assuming that we are doing this co-current mode. So, at inlet side at z is equal to 0, there will be no inlet of air. So, we are only opening the exit valve. So, at the inlet side dyk/dz at z is equal to 0 will also be equal to 0, no diffusive flux.

And at the outlet condition at z is equal to L. Of course, we do not need any another velocity condition, but dyk/dz at z is equal to L will also be 0 because this is here the concentration change does not happen. So, whatever the feed that is absorbed or whatever the concentration that you have at the exit will be the same beyond the exit. So, this is the far filled boundary condition. And this is like no diffusive flux. If you do counter current, then these conditions would just get reversed.

And the final step is purging. Again, purging can be of two types, co-current and counter current. So, in the case of purging, mostly you do purging as counter current. So, at the so called inlet, so in this case I will not write it as inlet and outlet not to confuse you. At z is equal to L which is like the inlet for the purging scenario, we will have this u is equal to ul and this minus sorry dyk/dz at z is equal to L will be u kill and this is y k at z is equal to L minus y this purge whatever we are using for purging. at z is equal to 0 of course this dyk/dz will be equal to 0 as like the far field condition.

Initially, so the initial condition is also very important. So, the initial condition one can say that yk is equal to yki, q is equal to 0 at pressure p is equal to p ambient pressure 0 or some small value. So, in the next step or in the next cycle when we go it is essentially the value of this p sorry the value of this y that is obtained at the end of the previous cycle or whatever this q that we have for the. So, this is like the clean bed.



Next cycle.

$q = q^*$ (y_k from the end of previous cycle).

So, when one goes to the next cycle. So, for next cycle. The value of q is actually based on q star of the yk value from the end of previous cycle. So this is how the cyclic operation happens that in the next cycle the bed may be also partially you know having this adsorbent concentrations at equilibrium and it is not fully a clean bed as in the beginning and that is how the profiles in the second step or subsequent steps will be different in those cycles. So, it is very important that a cyclic steady state is achieved over multiple such cycles and the difference between this solute loading from the you know this adsorbate of that of the adsorbate profiles between the adsorption and the desorption is actually equal to the amount of the solute that is fed. during this operation or during this adsorption and the desorption.

So, that cyclic steady state is very important and that is the motivation behind the development of this model or behind the framing this model to optimize the cycle time as well as to understand the role of it in the cyclic steady state operation. So, thank you I hope all of you like this lecture and found it useful. In the last class of this week that is the next lecture I will talk about a basic design of a you know a practical this oxygen concentrator which is nothing but a this pressure swing adsorption system essentially. Thank you.