Course: Adsorption Science and Technology: Fundamentals and Applications

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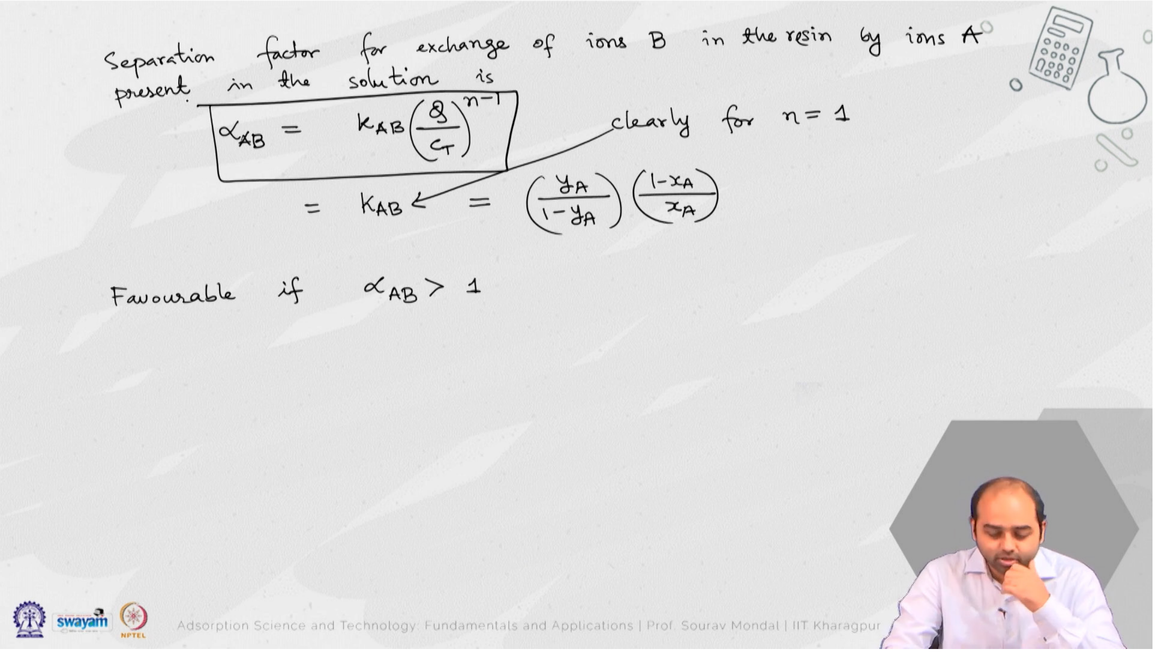
Week 08

Lecture 39 | Ion Exchange Cycle

Hello and welcome everyone to this class on adsorption. So, this is the fourth lecture on ionic equilibrium and today we are going to talk about the ion exchange cycle mechanism. So, in this lecture we are going to cover the ion exchange or the cyclic operation because as you realize this ion exchange mechanism as it works with the process of equilibrium. So, once the ion exchange sites are captured by the you know ions present in the solution which is of course, the objective that you want to remove the undesirable ions or you have to reduce the tedious level of your water is removed from the solution, the ion exchange sites in the resin is actually occupied. And then to reuse this resin you have to first displace this ions and regenerate these ions or these ionic sites for that subsequently it can be used again for the you know this adsorption or this ion exchange mechanism. Now, before we talk about in details about the cyclic operations and you know mass transfer phenomena involved in the process, let us first understand the separation factors and how do you define the separation factor for this ion exchange process.

So, now the separation factor. So the separation factor you know for let us say exchange of ions B in the resin by ions A present in the solution. present in the solution is defined something like alpha AB as KAB Q by CT to the power n minus 1. Now clearly, for monovalent monovalent system that is n is equal to 1, the separation factor is same as KAB right for this is the scenario for n is equal to 1 which can also be written down as y by 1 minus so this is we are writing in terms of yA, and 1 minus xA by xA. So typically the ion exchange process is considered to be favorable whether it is you know this equilibrium or removal of ions or whether it is regeneration whatever it is then this process if alpha AB is greater than 1 right. So clearly for separation of ions of the same type of valence right between the resin and the solution phase. This becomes independent of the value of the total capacities and this is equal to the selectivity coefficient or this you know equilibrium constant. But clearly if this is not a monovalent divalent system then this depends on the value of this total capacity you know Q by CT.



Separation factor for exchange of ions B in the resin by ions A present in the solution is

$$\boxed{\alpha_{AB} = K_{AB}\left(\frac{Q}{C_T}\right)^{n-1}}$$

clearly for n = 1

$$= K_{AB} = \left(\frac{y_A}{1-y_A}\right)\left(\frac{1-x_A}{x_A}\right)$$

Favourable if $\alpha_{AB} > 1$

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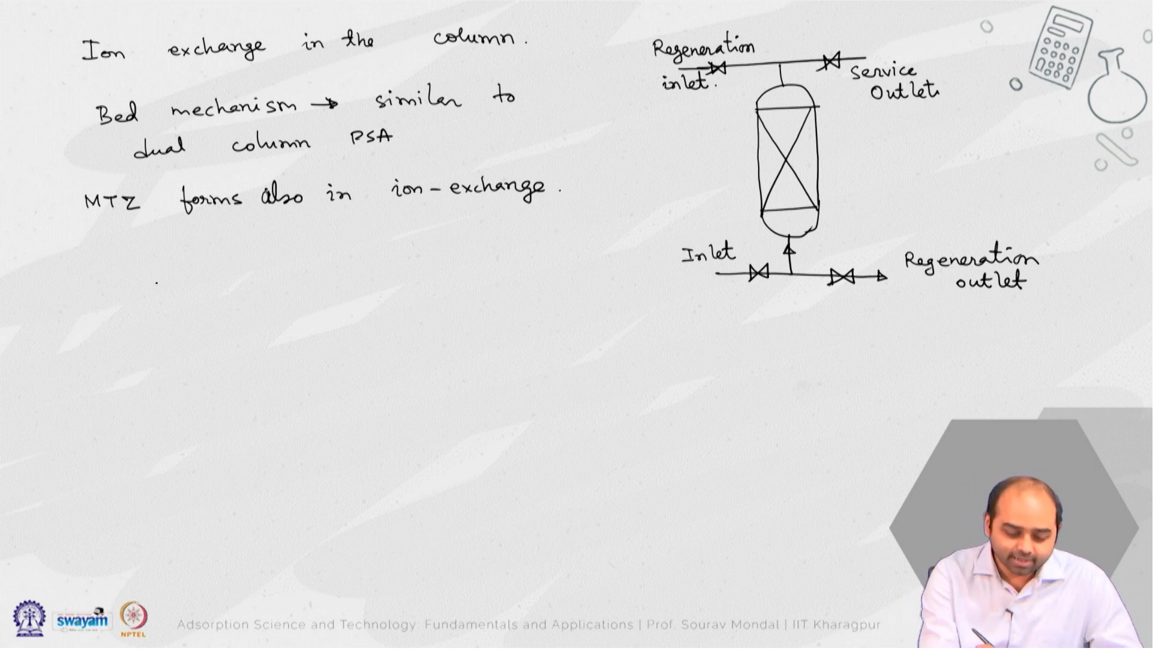
So, this is like the total you know generic expression for n is equal to 1, this is replaced with the individual you know this equivalent fractions, but essentially for non you know between exchange between unlike you know valence or different you know this valence or divalent monovalent systems then this is not true. Now, coming to the process of ion exchange in the column. So, this ion exchange in the column ion exchange in the column looks something like this let us say this is an ion exchange column or very similar to a fixed bed adsorption system so this is inlet this is regeneration line. This is like service outlet. So, all of these are controlled by a lot of this, you know, valves present at various sections.

This regeneration outlet. So, this happens counter currently within the column. Of course, changing the resin also can be done in a you know within this column etcetera. So, this is like a during the process of your operation or the direction of this flow of the actual liquid through this resin bed will be counter current to the regeneration cycle. So, this is like a bed configuration you can also have this resin operation present in a stirred vessel or even in a fluidized bed.



Ion exchange in the column.

Bed mechanism → similar to dual column PSA

MTZ forms also in ion-exchange.

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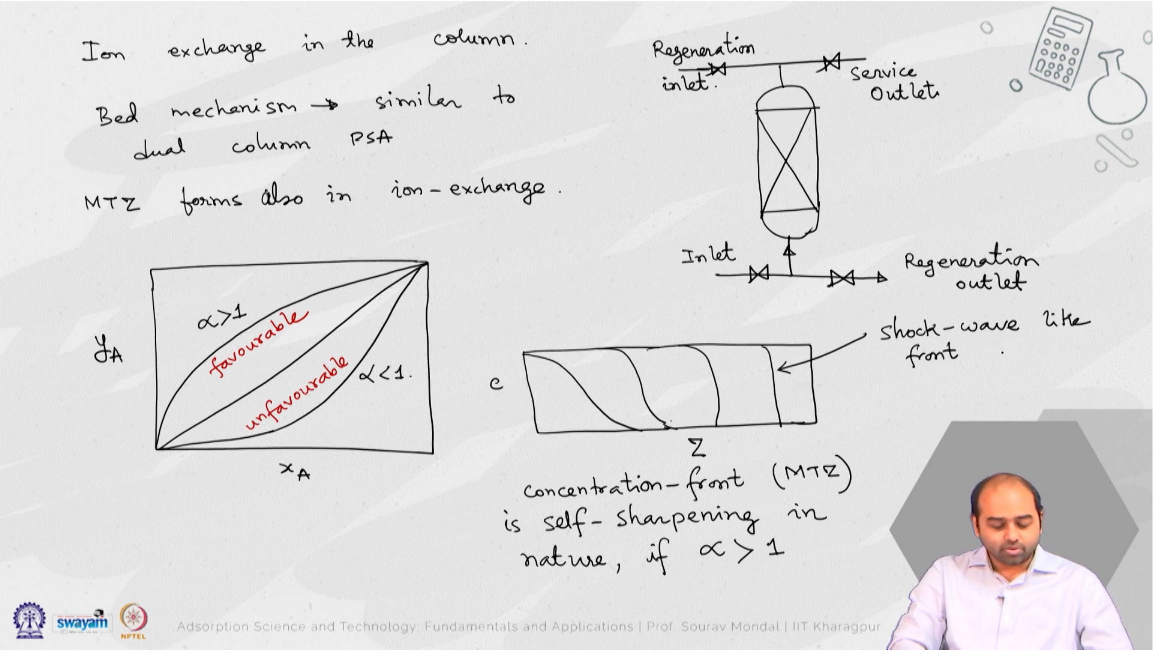
So, this bed mechanism, so, this bed mechanism is very similar to, very similar to dual column pressure swing adsorption system where one bed is in you know active mode or it undergoes adsorption and there is another bed which undergoes regeneration so that there is a continuous output of the operation. So, till breakthrough is achieved one of the beds is continuously in the you know this adsorption or in the ionic exchange process and the other bed is in you know this regeneration, but once the breakthrough is achieved then the beds are simply interchanged and the newly regenerated bed is again used for you know this active you know ion exchange process. Now as in the case of gas adsorption also here also you have a you know mass transfer zone and this is something we are going to talk about today itself. This mass transfer zone forms also in also in ion exchange column. So, of course, this MTZ zone moves from the leading edge or from the entrant till the outlet and this is governed by the I mean the shape of the concentration fund is governed by the separation factor alpha.

So, typically if I try to draw this you know diagram of y versus x or this equilibrium phenomenon. So this is the scenario when alpha is greater than 1. So this is the scenario when alpha is less than 1. So of course alpha greater than 1 signifies situation of favorable equilibrium and less than 1 is unfavorable. So, in the case of favorable you know situation this mass transfer zone within the bed if I try to draw that at different times at as how it moves let us say this is the concentration with respect to z or length fraction of the bed.



Ion exchange in the column.

Bed mechanism → similar to dual column PSA

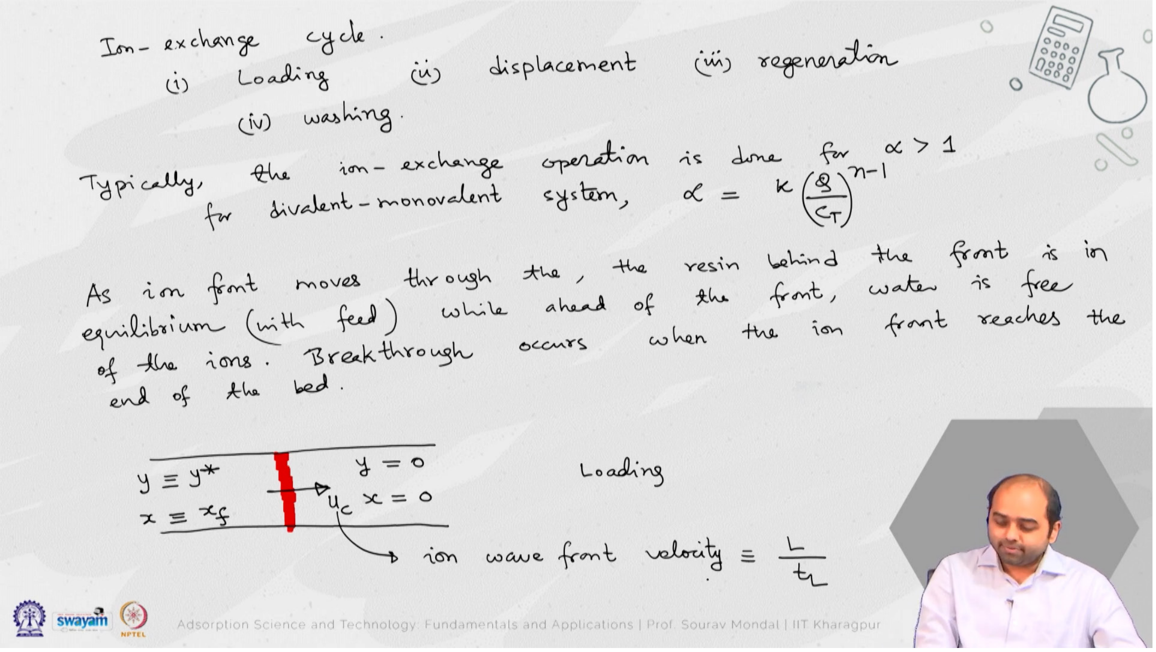
MTZ forms also in ion-exchange.

concentration-front (MTZ) is self-sharpening in nature, if $\alpha > 1$

So, initially if the curves are quite diffuse in nature slowly its self sharpens out. So the concentration front or this mass transfer zone is self sharpening in nature, if the equilibrium is favorable in nature. If it is so this as and as it becomes a self sharpening this becomes more like a shock wave like front. right, and then the you know this role of the diffusion or the dispersion is insignificant and it behaves like an ideal you know constant wave front sorry not constant this ideal you know stoichiometric wave front that it moves into. But if the separation factor is less than 1 which is like the unfavorable case then it becomes diffuse or the wave front becomes diffuse.

So, the movement of the solute wave fronts or the ionic wave front is something that we will talk later in this lecture itself today, but before that I want to talk about that what are the different steps of this ionic cycles here. So, this ion exchange or this ion exchange cycle process involves 4 step. So, first is loading. The next is displacement. So, it is the loading phase when the ions that you want to exchange with or the ion exchange reaction of the active mode is the loading phase that happens.

Displacement and the third is regeneration happens together and the fourth one is washing. So, coming to this scenario of when you know the adsorption is favourable or what and it becomes like a self-sharpening front or whatever this typically you would always want typically the ion exchange operation is done for favorable conditions alpha greater than 1. Now this can be achieved I mean this can be achieved by you know at least for divalent monovalent system. So for divalent monovalent system, this alpha becomes K times Q by CT to the power n minus 1. So, if you increase your Q right, K cannot be increased, since K is an equilibrium constant. If you increase your Q in this process, then it is possible to make this alpha greater than 1 or make this system sharpening in nature right.



Ion-exchange cycle.

(i) Loading (ii) displacement (iii) regeneration

(iv) washing.

Typically, the ion-exchange operation is done for $\alpha > 1$

for divalent-monovalent system, $\alpha = K\left(\frac{Q}{C_T}\right)^{n-1}$

As ion front moves through the, the resin behind the front is in equilibrium (with feed) while ahead of the front, water is free of the ions. Breakthrough occurs when the ion front reaches the end of the bed.

ion wave front velocity $\equiv \frac{L}{t_L}$

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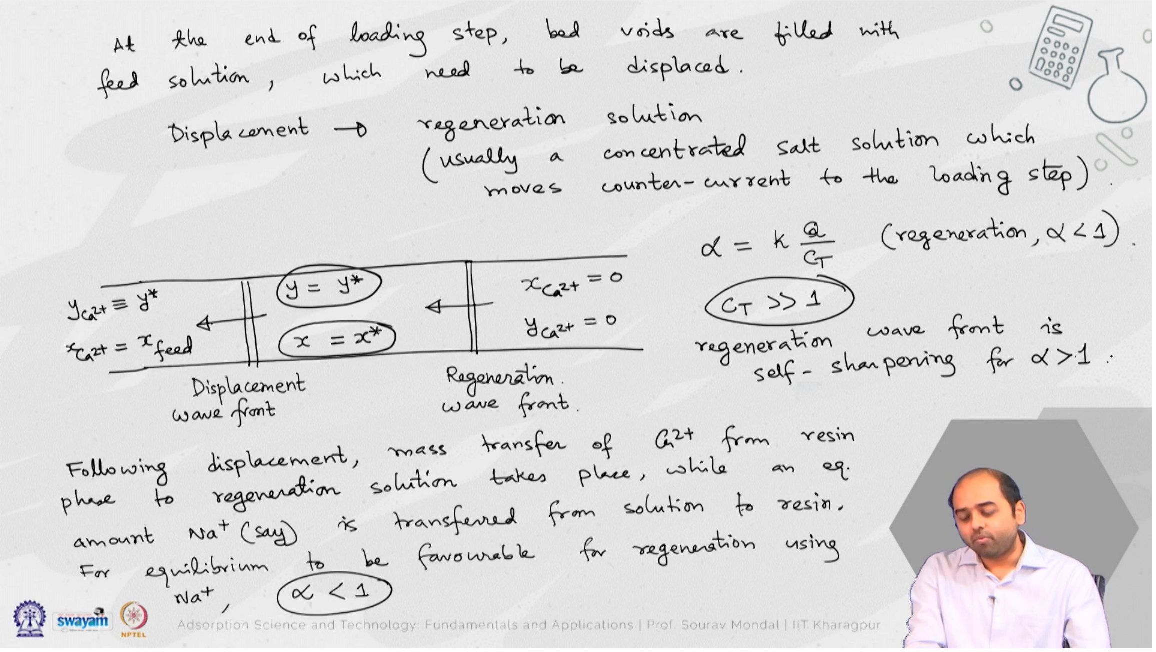
And that is very essential because you do not want to have a diffuse you know this wave front of the solute or the ionic movement within this bed right. So, as the ion front as this ion front moves down through the bed or whatever moves up or down, moves through the bed, the resin behind the front right I think by now all of you got this picture behind the front is in equilibrium, or at already exhausted all its ion exchange sites is in equilibrium with the feed composition while ahead of the front this water is free of the whatever the divalent or monovalent ions free of the ions. So, the breakthrough occurs when this front reaches the end of the column and we can also write this. So, breakthrough occurs when the iron front reaches the end of the bed. So, if I try to draw a picture of this ionic front movement, let us say that this is the front or this ion front, this is the movement or the is moving from left to right, the solute movement U L or you can write this is also U C.

Now before this one this is in equilibrium. So, y is y star right and x is the x in feed of the ions. Let us say if you are trying to exchange between calcium and sodium where sodium is present in the resin bed and calcium is present in the solution. right and in this case this y ahead of the front is equal to 0 and x ahead of the front will be equal to 0 because there is no presence of the calcium because the solution has not moved beyond that point. So, this is the loading phase.

So, in the loading phase it is like the solution as it is moving slowly into the system all the you know ionic exchange sites within the resin is getting occupied or it is bound to the ions present in the solution. So, ahead of this front or this is I am talking about a solute front, not of the water or the aqueous solution front. So, ahead of this solute front there will be this concentration of calcium or this divalent ions that you are trying to remove in the resin phase and in the aqueous phase both will be equal to 0. So, this is the scenario what you see during the loading phase. During the loading phase also this values of Q or the total capacity of the resin total solutions that the total ion equivalents present in the solution both are constant.

So, this is very important that does not change in the system. And this whatever this ion solute wave front velocity, so this is nothing, but the ion, ion wave front velocity. So, in this case it can be you know found out from the relation of the length of the bed divided by the residence time of this you know solute front or the solute within the bed. Anyway we will talk about that later on in this lecture itself. So, at the end of the at the end of the loading step this bed voids are filled with the feed solution which needs to be displaced and this displacement displaced and this displacement is generally done or it is best done using a regeneration solution.

So, which is usually the regeneration solution is usually a concentrated why concentrated I will talk about it is a concentrated you know salt solution which moves counter current to the loading which moves counter current to the loading step. So, once the loading is finished then you do this regeneration and displacement operation. So, during this displacement. So, the display there will be a displacement front and there will be a regeneration front. So, the displacement front will be ahead of the regeneration front.



At the end of loading step, bed voids are filled with feed solution, which need to be displaced.

Displacement → regeneration solution (usually a concentrated salt solution which moves counter-current to the loading step).

$\alpha = k \frac{Q}{C_T}$ (regeneration, $\alpha < 1$).

$\boxed{C_T >> 1}$

regeneration wave front is self-sharpening for $\alpha > 1$.

$y_{Ca^{2+}} \equiv y^*$

$x_{Ca^{2+}} = x_{feed}$

$\boxed{y = y^*}$

$\boxed{x = x^*}$

$x_{Ca^{2+}} = 0$

$y_{Ca^{2+}} = 0$

Displacement wave front

Regeneration. wave front.

Following displacement, mass transfer of Ca^{2+} from resin phase to regeneration solution takes place, while an eq. amount Na^+ (say) is transferred from solution to resin. For equilibrium to be favourable for regeneration using Na^+, $\boxed{\alpha < 1}$

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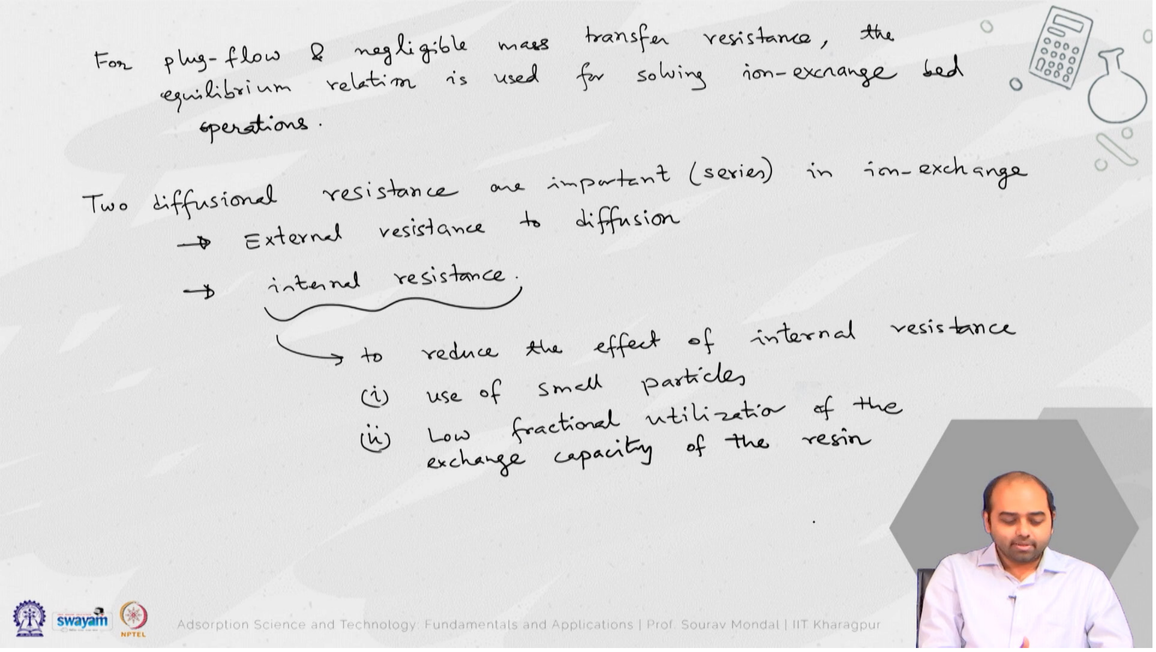
So, how it looks like let us try to draw this scenario. So, like two fronts. So, we are doing this mechanism from right to left. So, this is the displacement front, this is the regeneration front and displacement wave front and this is the regeneration wave front. So, once the bed is regenerated in that part there will be no (this) calcium ions which we are targeting in this kind of you know exercise or in this example this both x of calcium right it is essential now to write x Ca plus y Ca plus is equal to 0.

Ahead of the displacement front already the equilibrium exists because that part is not removed that is already from the loading cycle that part is in equilibrium. So, y of you know calcium is in equilibrium and x of calcium is equal to the x from the feed or from the loading step it is already there. Now, in between these two for the case of the you know this this resin phase concentration y is in equilibrium right and the x is also in equilibrium in this part. So, both the y and the x in between this regeneration and the displacement wave front is in equilibrium. So, this following displacement this mass transfer of let us say calcium ions from resin phase to regeneration phase.

So, this regenerating solution takes place while an equivalent amount of let us say we are replacing this with the monovalent ion sodium ions is transferred from solution to resin. So now for the equilibrium to be favorable so for equilibrium to be for equilibrium to be favorable, for sodium ion and for regeneration using sodium ion for regeneration using sodium ion this factor alpha should be less than 1. Now for between calcium and this sodium this alpha will be your K this Q by CT right this is alpha and for during regeneration this should be less than 1. Now, to make this less than 1 what is generally done? The CT is made to be very very high and that is the reason why a concentrated salt solution is used. So, that the you know this equilibrium becomes favourable for sodium and the regeneration wave front becomes a shelf sharpening.



For plug-flow & negligible mass transfer resistance, the equilibrium relation is used for solving ion-exchange bed operations.

Two diffusional resistance are important (series) in ion-exchange

→ External resistance to diffusion

→ internal resistance.

→ to reduce the effect of internal resistance

(i) use of small particles

(ii) Low fractional utilization of the exchange capacity of the resin

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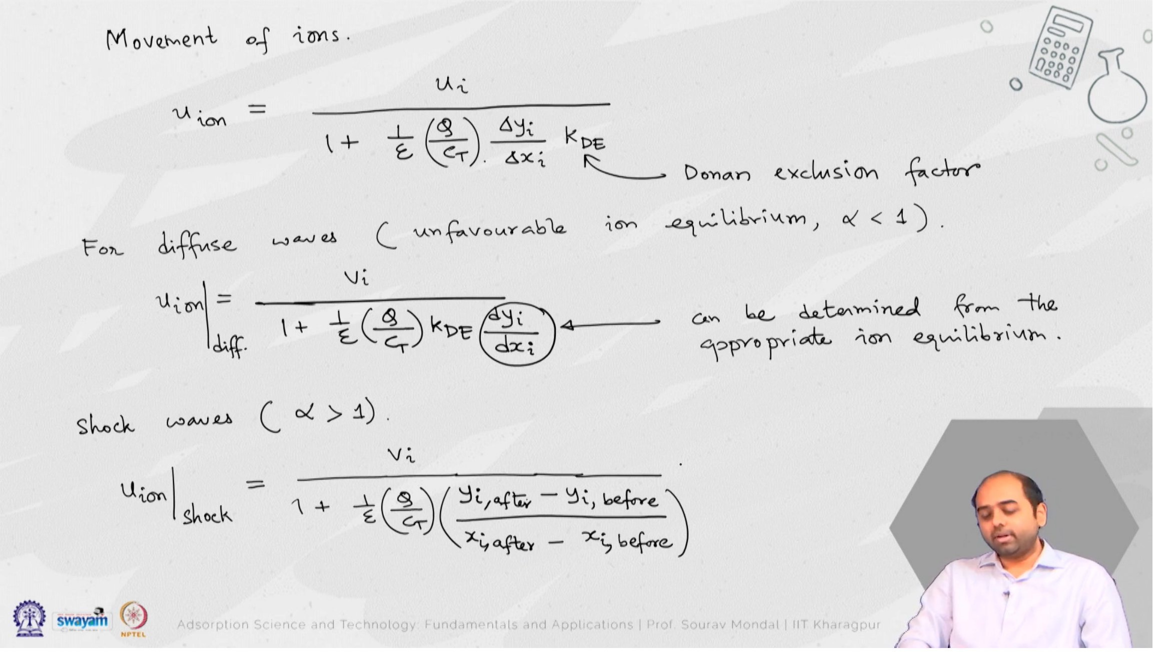
So, this regeneration wave front is self-sharpening in nature and that is criteria why a concentrated solution is generally used. Now, typically the regeneration time is obtained from the material balance and working out the regeneration wave front velocity and that is something probably we will talk about in our next lecture when we work out a small you know illustrative problem in this direction. So, for plug flow and negligible mass transfer resistance, the equilibrium relation is used for solving ion exchange bed operations, both for displacement as well as for regeneration. But however, mass transfer many a times becomes very critical and that is the reason you know diffusional resistances does play a role. So, two diffusional resistance resistance are important and they are in series in ion exchange.

One is of course, the external diffusion or the external resistance to diffusion. So, which of course, external resistance to diffusion which of course, occur or happen across a fluid film on the you know resin particle and the other is the internal resistance for diffusion inside the pores of the you know particle. So, to remove or reduce this internal resistance what is generally done is that either you use you know low or small size of this to handle this what is done to you know reduce the effect of internal resistance. What is generally done is a the strategy that is followed is use of small particles or low fractional utilization, low fractional utilization of the exchange capacity of the resin. So, using either or both of these techniques the diffusion path length or the depth of the penetration of these ions within the particle can be minimized.

Now, finally, coming to this aspect of the ion solute movement we will talk about that before we finish today's lecture. So, typically this for the case of you know in general whether it is a diffuse type behavior or a sharp wave front this this ion velocity or this ion wave front velocity can be written down as u interstitial velocity u i very similar way except the fact that here the ion inclusion porosity is a set to 0 or the permeation pores are set to 0 that is why we do not see this relation 1 minus epsilon by epsilon. This is Q by CT then there is delta y i by delta x i. Now, this K_DE is essentially the Donan Exclusion Factor, in this case not the equilibrium constant. And many a times if the ions of the same charge within the solution and the in the resin are used in that case the co ions are excluded and for the co ions K_DE becomes 0.

Whereas, for the if this exchanging ions are when the exchanging ions are not excluded in that case K_DE becomes equal to 1. So, note that the solid density does not appear in this equation because generally this K_DE value is used for in volumetric terms. Now, coming for the diffuse waves or diffuse waves which is the scenario for unfavourable ion equilibrium or alpha <1, in that case this ion velocity is represented as same, but instead of delta y / del delta x i this is d y by d x i where of course, d x i / d y i and d x i is something that one can you know find out from the relation of y versus x. So, this relation can be used or can be determined from the appropriate ionic equilibrium relation. So the shock wave so this is the case for diffuse waves for the case of shock waves it is just the reverse we have favorable ionic equilibrium and alpha is greater than 1.



Movement of ions.

$$u_{ion} = \frac{u_i}{1 + \frac{1}{\varepsilon}\left(\frac{Q}{C_T}\right) \frac{\Delta y_i}{\Delta x_i} K_{DE}}$$

$\leftarrow$ Donan exclusion factor

For diffuse waves (unfavourable ion equilibrium, $\alpha < 1$).

$$u_{ion}\Big|_{diff.} = \frac{v_i}{1 + \frac{1}{\varepsilon}\left(\frac{Q}{C_T}\right) K_{DE} \boxed{\frac{dy_i}{dx_i}}} \longleftarrow$$

can be determined from the appropriate ion equilibrium.

Shock waves ($\alpha > 1$).

$$u_{ion}\Big|_{shock} = \frac{v_i}{1 + \frac{1}{\varepsilon}\left(\frac{Q}{C_T}\right)\left(\frac{y_{i,after} - y_{i,before}}{x_{i,after} - x_{i,before}}\right)}$$

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In this case the, so this is ionic movement when you have diffuse waves and this is ionic movement when you have shock waves. So, in this case in the case of shock waves since there is a sharp wave front instead of writing dy by dxi what is written is this yi before and after the shock. So, this is related as just you know instead of this derivative this ion fractions are reduced to difference equations or difference form across this shock or this you know sharp wave front the relations are reduced to like that. So, in this case of course, we know that across the sharp wave front after the solution if you are talking about the movement of the counter ions then y i after and x i after becomes 0. For the case of the regenerating solutions it is you know before the regenerating solution that becomes 0.

So, accordingly this can be worked out. So, it is simply the ratio of y by x because one of them if you are talking about the counter ions goes to 0. So, this is all you know regarding the ion exchange cycle and this solute movement scenarios for two different situations when you have shock waves and when you have diffuse waves particularly for favourable and unfavourable situations. So, I think with this I will close the lecture for now. See you everyone in the next class.