Introduction to Process Modeling in Membrane Separation Process

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Lecture – 06
Concentration Polarization

Welcome to the session once again. So, we have already I quantified the writing the modeling equations for the reverse osmosis systems and the dense membranes, or the osmotic pressure plays very important role. In the last class we have seen what is the flow transport model for quantifying the permeate flux through the membrane. Now permeate now transport flux of the solvent which is basically the volumetric permeates flux through the membrane. Now in this class we will derive, what is the solute flux through a membrane.

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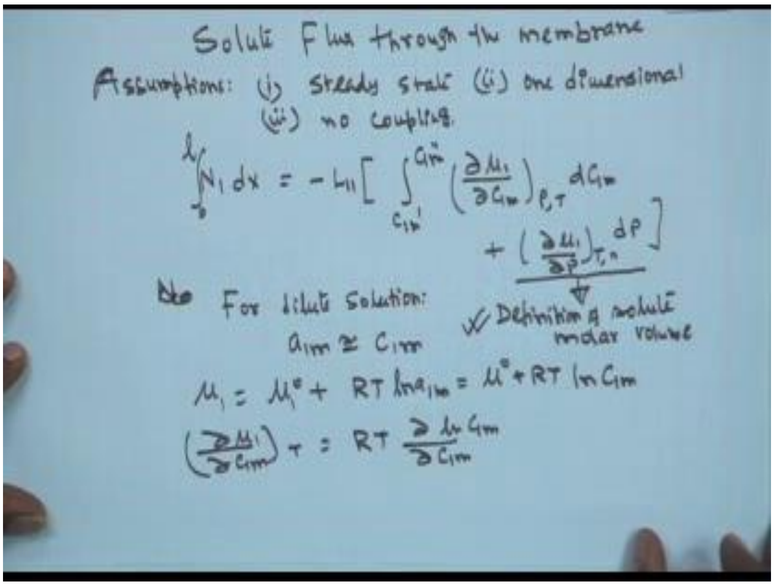

Solute Flux through the membrane

Assumptions: (i) steady state (ii) one dimensional
(iii) no coupling.

$$\int_0^{l} N_1\,dx = -L_{11}\Big[\int_{C_{1m}'}^{C_{1m}''}\left(\frac{\partial \mu_1}{\partial C_{1m}}\right)_{P,T} dC_{1m} + \underbrace{\left(\frac{\partial \mu_1}{\partial P}\right)_{T,n} dP}_{\checkmark\ \text{Definition of solute molar volume}}\Big]$$

For dilute solution:

$$a_{1m} \cong C_{1m}$$

$$\mu_1 = \mu_1^0 + RT\ln a_{1m} = \mu^0 + RT\ln C_{1m}$$

$$\left(\frac{\partial \mu_1}{\partial C_{1m}}\right)_T = RT\frac{\partial \ln C_{1m}}{\partial C_{1m}}$$

So, again we will be doing the solute flux, through the membrane starting from basic equations of irreversible thermodynamics. And the assumptions remain the same; it is a steady state system, 1 dimensional and no coupling. If we now really do that than the previous equation for the solute flux what will be doing we can integrate it, how we already done earlier that in 1 dx is minus L11, c1m prime to c1m double prime; del mu 1 del c 1 m at constant pressure and temperature, d c 1 m plus del mu 1 del p constant temperature n times dp. So, we have already derived the expression for the governing equation of the solute and the governing equation of the solvent. So, I omitted a step. So, we have the gradient of cc 1 m, c d c m 1 m d x and d p d x that we have multiplied processed by d x and now we had integrating it out.

So, if you really do that, if you just integrate it out from 0 to L and assuming the steady state it will be n 1 times L, before doing that we will be doing some simplification for dilute solution, we can write that activity if the membrane of the solute in the membrane phase will be equivalent to concentration of solute in the membrane phase, and chemical potential can be written as mu is equal to mu naught plus r t L n a 1 m, which will be nothing, but mu naught plus r t L n c 1 m.

Now let us look into the derivative of chemical potential with respect to c 1 m. So, what it gives is that, this gives r t del L n c 1 m divided by del c 1 m, after that what we are going to do? We will be replacing this by the definition of the molar volume of the solute, and if you really do that. So, it will be replacing is by definition of solute molar volume. And after substituting this definition solute molar volume here, and del mu del c m del mu 1 del c m c 1 m in this expression and then we can get the final expression of the solute flux as n 1L is equal to L11 r t L n c 1 m prime divided by c 1 m double prime plus v 1 bar L 11 delta p where delta p is the p 2 minus p 1.

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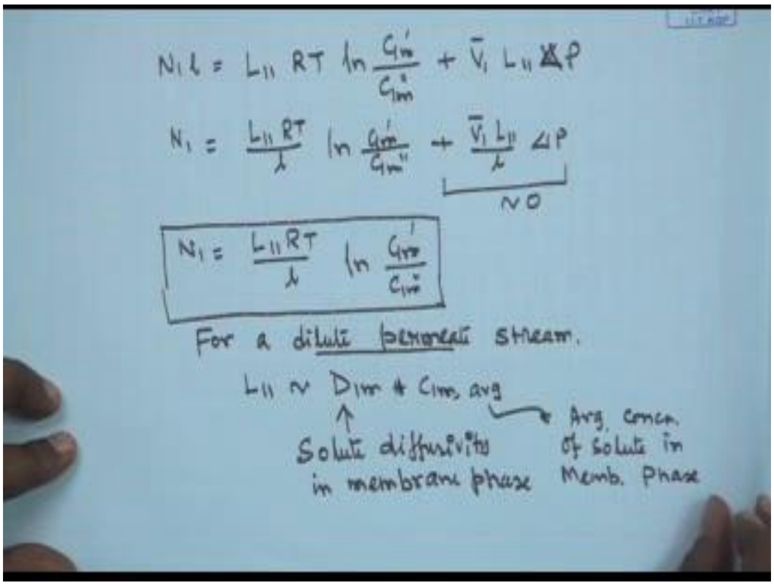

$$N_1 l = L_{11} RT \ln \frac{C_{1m}'}{C_{1m}''} + \bar{V}_1 L_{11} \Delta P$$

$$N_1 = \frac{L_{11} RT}{l} \ln \frac{C_{1m}'}{C_{1m}''} + \underbrace{\frac{\bar{V}_1 L_{11}}{l} \Delta P}_{\sim 0}$$

$$\boxed{N_1 = \frac{L_{11} RT}{l} \ln \frac{C_{1m}'}{C_{1m}''}}$$

For a dilute permeate stream.

$L_{11} \sim D_{1m} * C_{1m,avg}$

Solute diffusivity in membrane phase

Avg. concn. of solute in Memb. Phase

There is the pressure gradient. So, n 1 will be nothing, but L 11 r t where; L l n c 1 m prime divided by c 1 m double prime plus v 1 bar L 110020divided by L delta p in most of the cases the second term will be negligibly 0 and will be getting the expression of solute flux as L 1 one r t over L l n c 1 m prime divided by c 1 m double prime. So, this is the expression of solute flux and again this will be a having a unit moles per meter square per minute time.

Now, this can be further simplified for a dilute case, for a dilute permeation stream. Why it will be a dilute permeation, permeate stream it because that is very, very important in case reverse osmosis because in case of reverse osmosis, we are talking of separation of salts tune of 95 to 98 percent, the permeate that is coming out of the reverse osmosis system will be very, very dilute it is concentration will be very, very less it will be close to the water solution. So, we can always take an assumption of very dilute permeate stream under this condition L 1 one can be replaced as d 1 m multiplied by c 1 m average. So, what is d 1 m? d 1 m is nothing, but the solute diffusivity in the membrane phase of the solute of the solute phase.

What is c 1 m average? It is the average concentration of solute in membrane phase. So, once we have this assumption of dilute permeate stream then, let us look how our solute flux looks like.

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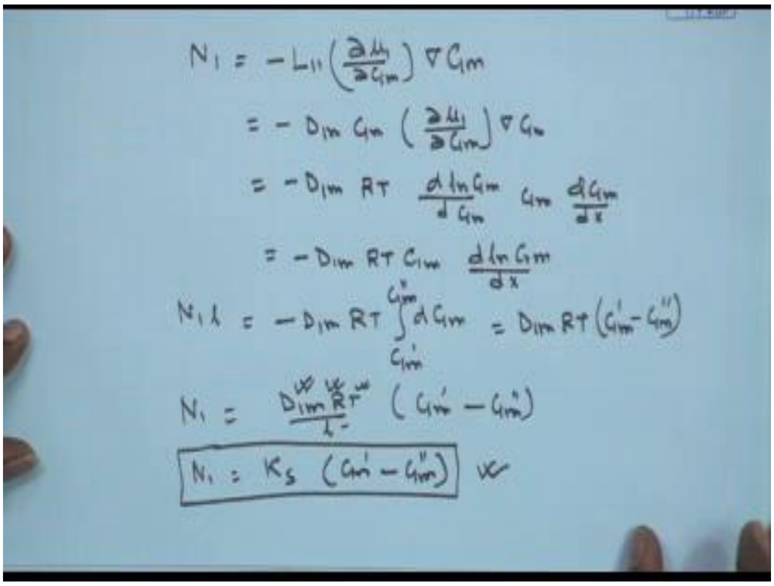

$$N_1 = -L_{11}\left(\frac{\partial \mu_1}{\partial C_{1m}}\right)\nabla C_{1m}$$

$$= -D_{1m} C_{1m}\left(\frac{\partial \mu_1}{\partial C_{1m}}\right)\nabla C_{1m}$$

$$= -D_{1m} RT \frac{d\ln C_{1m}}{d C_{1m}} C_{1m} \frac{dC_{1m}}{dx}$$

$$= -D_{1m} RT C_{1m} \frac{d\ln C_{1m}}{dx}$$

$$N_1 l = -D_{1m} RT \int_{C'_{1m}}^{C''_{1m}} dC_{1m} = D_{1m} RT (C'_{1m} - C''_{1m})$$

$$N_1 = \frac{D_{1m} RT}{l} (C'_{1m} - C''_{1m})$$

$$\boxed{N_1 = K_s (C'_{1m} - C''_{1m})}$$

So, n 1 can be minus L 1 1 del mu 1 del c 1 m, gradient of c 1 m. We neglect the second term on depending on the pressure. So, minus L 1 one I can write d 1 m, c 1 m del mu 1, del c 1 m gradient of c 1 m and this can be written as minus d 1 m, r t d L n c 1 m, d c 1 m, c 1 m, d c 1 m d x and this can be replaced as written as minus d 1 m, r t c 1 m, d L n c 1 m divided by d x and final expression after integration will be nothing but, n 1 L is equal to minus d 1 m r t d c 1 m integration form c 1 m prime to c 1 m double prime. And this will be nothing, but d 1 m r t c 1 m prime minus c 1 m double prime the minus sign will be included in in the parenthesis. So, n 1 trans out to be d 1 m r t were L c 1 m prime minus c 1 m double prime.

So, this will be constant or this inversely gas constant and t is the temperature L is the thickness. So, n 1 can be k times s c 1 m minus c 1 m double prime. So, therefore, the solute flux will be will be proportional to the concentration difference. Now if you look into the solvent flux through the membrane is basically the membrane permeability multiplied by the effective pressure difference. So, delta p minus delta pi. On the other hand in case of the solute flux, solute flux is proportional to the difference in concentration across the membrane solute concentration in the upstream minus solute concentration in the downstream, multiplied by a proportional de constant k s. So, this quantifies the concentration, the transport laws of solute and solvent through the porous membrane. Now let us quantify the permeate flux volume in the in the term of volumetric permeate flux.

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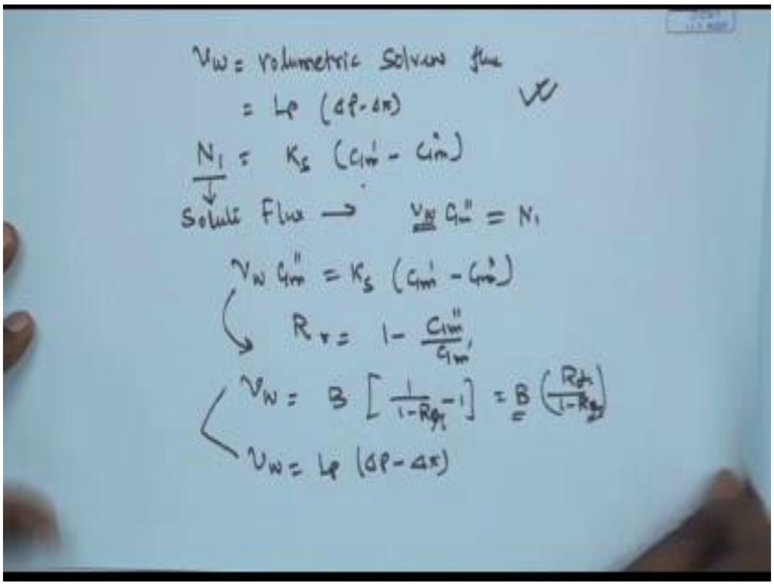

v_w = volumetric solvent flux

$= L_p(\Delta P - \Delta\pi)$

$N_1 = K_s(C_{1m}' - C_{1m}'')$

$\downarrow$

Solute Flux $\rightarrow$ $v_w C_{1m}'' = N_1$

$v_w C_{1m}'' = K_s(C_{1m}' - C_{1m}'')$

$R_r = 1 - \frac{C_{1m}''}{C_{1m}'}$

$v_w = B\left[\frac{1}{1-R_r} - 1\right] = B\left(\frac{R_r}{1-R_r}\right)$

$v_w = L_p(\Delta P - \Delta\pi)$

So, volumetric solvent flux will be nothing but L p times delta p minus delta pi that we have already talked about earlier and the solute flux n 1 is k s multiplied by c 1 prime minus c 1 m double prime, and what is n 1 it is the solute flux. Now we express the solute flux in terms of solvent flux. So, in terms of solvent flux is basically the amount of solute that will be carried, that will be entrained that will be carried away with the solvent flow. So, what is that this will be nothing but v w times c 1 m double prime.

That will be the amount of solute or that will be carried out with the solvent. So, it is basically the solute flux, this will be equal to n one. So, you can write v w c 1 m, double prime is equal to k s c 1 m prime minus c 1 m double prime, and we can now invoke the definition of retention. So, it will be in this case it will be real retention and the real retention is basically 1 minus c p. c p is the solute concentration in the filtrate site. So, c 1 m prime divided by c 1 m prime double prime divided by prime, if you really do that and express the v power permeate flux in terms of this, will be getting v w is equal to b 1 minus r naught minus 1. So, it will be b r naught divided by 1 minus r naught.

So, b is again some kind of constant what will be obtained from here. So, these and also we know what is the solvent flux? It will be obtained from this equation. Therefore, we can write v w is equal to L p del p minus del pi. Now we can equate this 2 equation and can obtain the expression of the expression of real observed retention this will be the real retention and the expression of real retention can be obtained by this. So, what is the by combining this two, I am omitting a step in between the final expression of retention will be L p del p minus del pi is equal to after simplification.

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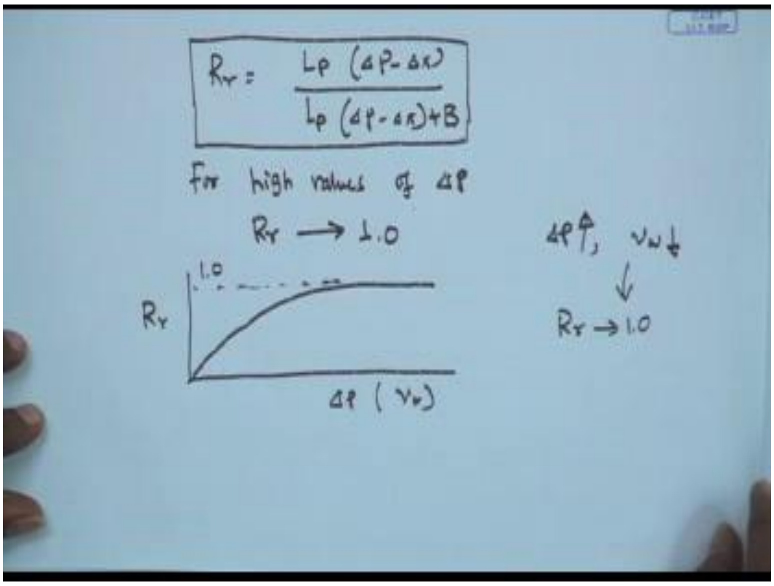

$$\boxed{R_r = \frac{L_p(\Delta p - \Delta \pi)}{L_p(\Delta p - \Delta \pi) + B}}$$

For high values of Δp

$R_r \rightarrow 1.0$

$\Delta p \uparrow, \; v_w \downarrow$

$\downarrow$

$R_r \rightarrow 1.0$

We are getting this expression del p minus del pi plus b. This shows that at very high values of delta p what the, delta pi will be negligible. So, this term will be dominant and b will be less dominant and r r will be approaching to 1.

Therefore, if you plot r r verses delta p this will be approaching to 1. So, delta p or you can plot permeate flux, because permeate flux is also proportional to delta p. So, this shows that as a driving force increases as delta p increases more solvent will be permeating through it and but the solute concentration will be remaining same. Therefore, it will be diluted and it keeps on diluted and at a very high pressure it will be the retention will be ending to 1. So, that gives the physical significance of retention as a function of pressure and once that is done the next there will be some.

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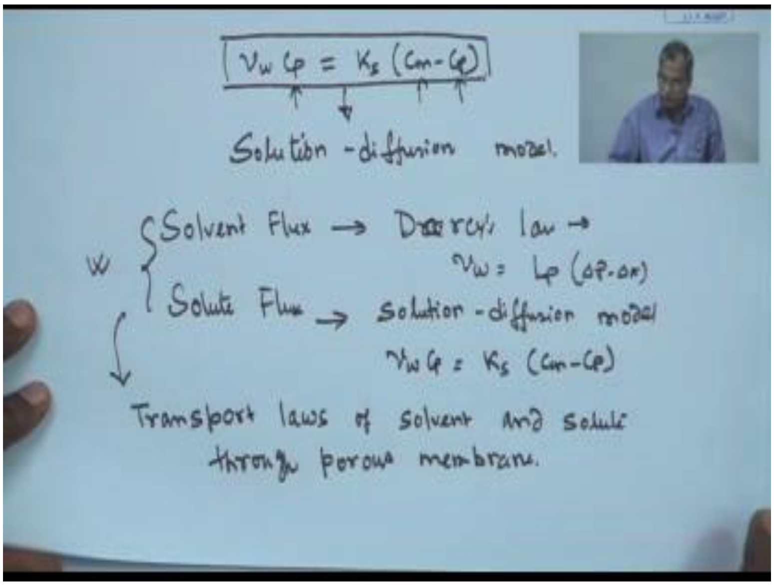

$$\boxed{v_w C_p = K_s (C_m - C_p)}$$

Solution-diffusion model.

W
Solvent Flux → Darcy's law → $v_w = L_p(\Delta P - \Delta\pi)$
Solute Flux → solution-diffusion model $v_w C_p = K_s (C_m - C_p)$

Transport laws of solvent and solute through porous membrane.

The transport of the solute flux through the membrane is that v w c p c m c p is equal to k solvent c m minus c p. So, now, we will just remove the primes etcetera c m double prime is permeate concentration, c m is the solute concentration, c p is the permeate concentration. This is this equation is also known as the solution diffusion model.

So, we have quantified the solvent flux through the membrane, porous media it is Darcy's law, that is v w is equal to L p del p minus del pi. We have quantified the solute flux through the membrane, reverse osmosis membrane it is the solution diffusion model given as v w c p is equal to k s c m minus c p. So, these 2 at the transport law of solute of solvent and solute, through porous membrane.

Now next what we are going to see is that, next will be talking about the solving of the membrane these are transport laws to the porous membrane, but that is not the only story as you have already discussed earlier that, there will be that the flow is really occurring in a channel in the module there is a flow channel. And the top surface and the of bottom surface, the membrane surface; that means, in the flow channel on the 2 boundaries and the membranes are placed and what we have quantified, we have quantified the transport laws of the solute and solvent through the membrane. Through the porous membrane through the porous membrane those are situated at the boundaries or valves of the flow channel. Next, but that is not the only story.

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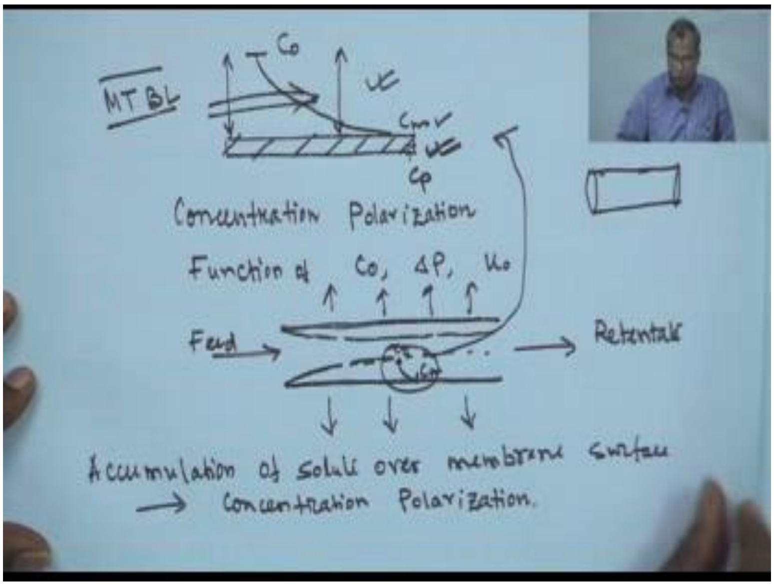

If you remembered in a previous class, we have already discussed about this that in a flow channel what are the flow taking place over the membrane, and there will exist a concentration gradient starting from bulk concentration up to membrane surface concentration forming a mass transfer of boundary layer.

So, in short we write m t b L to denote the mass transfer boundary layer. Therefore, and till now whatever we have done we have formulated the transport laws between the across the membrane from c m and c p in the permeate site, but we have not considered this film of mass transfer boundary layer in concentration to formulate our transport laws of the solute and the solvent. In fact, there are 2 resistances are invoked in this process 1 is the membrane, there are 2 media involved in the process; 1 is the membrane surface; 1 is the mass transfer of boundary layer, these 2 are placed 1 after another in series and these 2 will be considered. So, the polarization of the solute over the mass transfer boundary layer ranging from concentration c naught in the feed and the c m in the on the membrane surface is known as concentration polarization.

In an actual membrane separation system this concentration polarization should be considered and it will be depend it will be function of fit concentration, Trans membrane pressure drop and cross for velocity because p d is flowing like this. This is known as the cross for velocity. So, it is known as the u naught what is cross for velocity? The flow will be basically occurring through a rectangular channel in a spiral module or through a tube in a tubular module. Now membrane is placed in case of rectangular channel on the top surface as well as on the bottom surface and here in the tube along the surface of the tube. Now we are we have we are sending them, we are pumping the fluid or the feed in the membrane channel like this and the filtrate or permeate comes out this from the wall.

And the retentate goes from the outside the module. Now outside the module, there will be a formation of mass transfer boundary layer over the membrane surface. These are mass transfer of boundary layer over the membrane surface and the concentration profile will be from c naught to c m. From c naught to c m the exponent version of this has been shown here. So, we have to solve the governing equation in the channel outside the membrane and then we have to hook it up with the flow through the porous medium that is the situated on the boundary of the channel. So, then it will be giving you a complete description of the modeling of the solute and the solvent through the membrane system and ultimately we are going to get a system performance in terms of solute, solvent flux and the solute concentration in the permeate anyway.

Now, what is concentration polarization? The formation or accumulation of solutes over the membrane surface of solute over membrane surface is known as concentration polarization. Now concentration polarization will lead to membrane fouling. As we you must have understood that this mass transfer of boundary layer will be basically offering a mass transfer for resistance against the solvent flux. Therefore, more be the thickness of mass transfer of boundary layer more be the resistance again the solvent flux and it will be it is value will be going down and as temperature as the time of filtration progresses or duration of filtration progresses the concentration of polarization layer builds up decreasing the throughput with respect to time.

So, one has to really calculate or quantify the decline in permeate flux which will be ultimately causing the membrane fouling. So, once the membrane is fouled it is performance goes down and it is life is decreased, Therefore, 1 has to basically quantify that whether the membrane fouling can be you know really controllable or it will be going uncontrollable, which will be if it is too much then the throughput of the process will be too less and the commercial (Refer Time: 21:49) of the process will be very, very low.

So, in that case, So, in this contest we look into the problem of membrane fouling the fouling is of 2 types.

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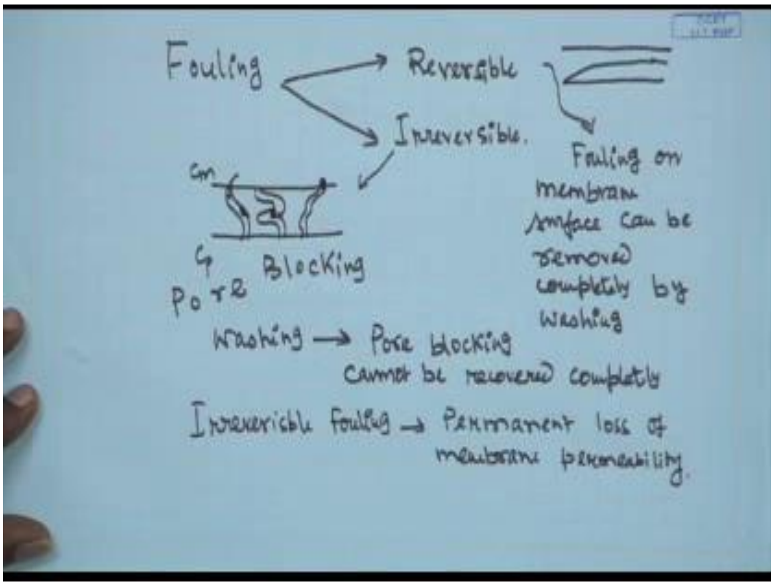

One is the reversible fouling, another is the irreversible fouling. So, in case of reversible fouling, whatever the layers that will be deposited over the membrane surface that can be you know washed away by adopting a proper washing protocol. So, fouling layer deposited over the membrane surface can be removed by proper washing. Fouling on membrane surface can be removed completely by washing there by recovering the membrane permeability completely, on the other hand in case of irreversible fouling there are there are force in the membrane surface, and this force cannot can be interconnected port they are not necessarily the straight cylindrical force.

There are various type of force are available in the membrane surface, in the membrane matrix membrane cross section and since the concentration of solute on the membrane surface is more compared to concentration solute in the permeate site solutes will be probably may be because of the defusing because of the concentration gradient. And since there will be a distribution of the force size there will be some force always available in the membrane surface which will be larger compare to the size of the solute, and they will be traversing on the membrane site blocking the membrane force partially or completely or they may be absorbed on the pore mouth and sitting on the pore mouth of the of the membrane surface blocking that particular pore.

So, all this phenomena will be causing to blocking of membrane force. So, these are known as the pore blocking phenomena. So, even after proper washing you know sites of the blocking may be opened, but not all. Therefore, the pore blocking cannot be recovered completely; therefore, some of the some fraction of membrane permeability is permanently lost and this is known as irreversible fouling. So, in case of irreversible fouling even after proper washing some fraction of permeability is permanently lost. So, it leads to permanent loss of membrane permeability. Now we will look into the various manifestations of concentration polarization.

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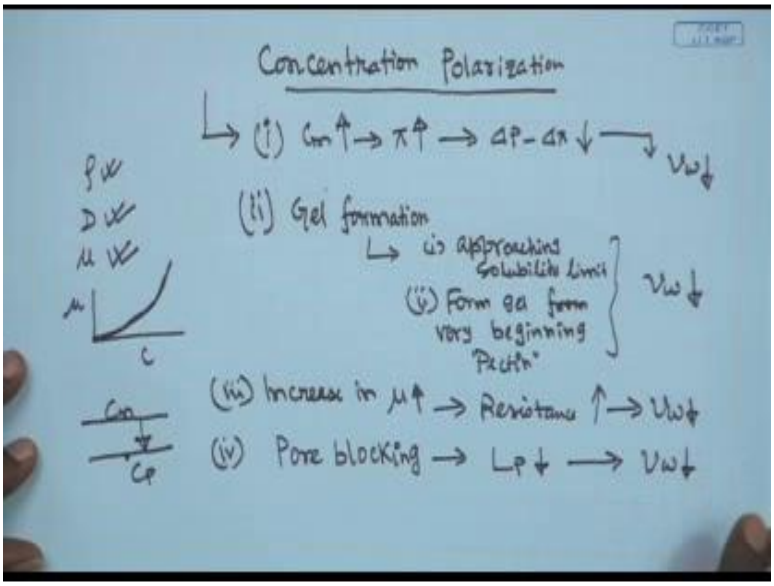

Concentration Polarization

↳ (i) $C_m \uparrow \rightarrow \pi \uparrow \rightarrow \Delta P - \Delta \pi \downarrow \rightarrow v_w \downarrow$

(ii) Gel formation
↳ (i) approaching solubility limit
(ii) Form gel from very beginning "Pectin"
} $v_w \downarrow$

(iii) Increase in $\mu \uparrow \rightarrow$ Resistance $\uparrow \rightarrow v_w \downarrow$

(iv) Pore blocking $\rightarrow L_p \downarrow \rightarrow v_w \downarrow$

So, if you look into the various manifestation concentration polarizations and what it really do thus look into this concentration polarization, so basically the effect of concentration polarization is accumulation of the solute particles of the membrane surface, there by increasing it is surface concentration. Now let us see what this surface concentration increase in surface concentration will do. So, c m membranes of solute concentration on the membrane surface increases, this increases the osmotic pressure of the solution. If the osmotic pressure of the solution increases then the effective driving force will decrease. If effective driving force will decrease, the permeate flux will decrease, the throughput of the process will decrease.

Now, with increase in membrane surface concentration, in case of some solutes the solute will in the surface concentration keep on increasing and after particular point, the solubility limit may be reached or the solutes can be deposit over the membrane surface forming a gel. Now gel formation can be done, gel formation can occur by 2 ways; 1 pore some solutes the solubility limit will be approached. So, this can be attend by approaching solubility limit and. Secondly, the pore some solutes which are naturally gel forming material they form gel from the very beginning, form gel from very beginning for example, pectin is an example. So, pectin is a well known gel forming agent and this particular solute forms a gel, at the very beginning of the operation. Therefore, it forms a very viscous layer over the membrane surface therefore, the permeate flux. So, resistance increases. So, permeate flux goes down, third phenomena is increase in viscosity.

When the concentration polarization increases, the solute concentration on the membrane surface increases tremendously therefore, the thermo physical properties of the solute in the system may be effected by the increase in solute concentration, what are the typical transport coefficients that appear the three transport coefficients appear 1 is density and another is diffusivity another is the viscosity.

Now density is the weakest function of concentration diffusivity is a moderate function of concentration in some solutes and it is a weak function of concentration most of the solute. And among this viscosity is the strongest function of concentration. In fact, viscosity is an ever increasing is an exponential function of concentration. And typically when the c m is in case of concentration polarization the membrane surface concentration is 3 to 4 time in case of osmotic pressure control filtration for the geller filtration this can go as I as 50 to 100 times even in some case of osmotic pressure control filtration for example using dextran the membrane surface concentration can be as I as 25 to 30 times a feed concentration.

So, in that case the viscosity suffers a lot, because viscosity increases tremendously over the mass transfer boundary layer. Within the mass transfer boundary layer, increase the viscosity what it results it results into very thick highly viscous solvent near the membrane surface it offers additional resistance. So, resistance against the solvent flux increases by increase in mass transfer resistance and it is result is decline in permit flux. The fourth manifestation of concentration polarization is that, as the concentration as I described earlier that across the membrane the Cm is concentration you know solute concentration the membrane surface is high and the solute concentration the permeate is low. So, there exist a concentration gradient across the membrane cross section and some solutes because of these gradient sub solutes will be transported through the membrane pores.

And during it is transport they can block some of the pores permanently or partially or completely. So, it will lead to pore blocking what is the manifestation of the pore blocking, pore blocking is manifested by reduction in membrane permeability. So, permeability; membrane permeability goes down because of the pore blocking. So, therefore, is the effect since the permeate flux is proportional to permeability the permeate flux goes down. So, we can see that the manifestation of concentration polarization in all the cases will lead to a common outcome of common result that will be the decline permeates flux. So, we have because of the concentration polarization we have decline of permeate flux which will be basically reduction in the throughput of the process, which is absolutely undesirable. But one cannot avoid concentration polarization completely, but one can minimize it.

There are various ways of minimization and in order to get a complete system performance prediction, one has to take care of transport in the flow channel and then hook it up which are a which are been yet to this transfer of a flow channel means, we have to solve the solute concentration in this in the mass transfer boundary layer and to quantify the concentration polarization perfectly. And then we have to hook it up with the transport laws through the porous membrane that we have already derived as in the form of solute flux and the solvent flux by Darcy’s law and solute flux through solution diffusion model through the porous medium. These two laws transport laws have to be hooked up with the transport laws that will be occurring in the outside the membrane surface, inside the flow channel within the mass transfer boundary layer.

In the next class, will be looking these connections and then will be completing the first dimensional modeling of one dimensional modeling of the flow through the membrane channel to have a system protection.

Thank you very much.