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Lecture-20

Models for UF Transport, Mass Transfer Coefficient, Membrane Rejection and Sieving Coefficient

Good morning students today is lecture 20 under module 7 in today's lecture will cover the various models of ultra filtration transport, such as pore flow model and concentration, polarisation model, resistance model etc. Then we will discuss about mass transfer coefficient which is one of the most important parameter which affects the solute transport. And the membrane rejection and sieving coefficient you know rejection we have learned.

But what is sieving coefficient today we will discuss sieving coefficient is very important parameter when discuss ultra filtration, because you know the transport mechanism is sieving, since ultra filtration is a porous membrane.

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Flux equation for ultrafiltration

• The flux equation for diffusion of solvent through the membrane in ultrafiltration is the same as that for the reverse osmosis:

$$J_w = A_w (\Delta P - \Delta \pi)$$

- In ultrafiltration, solutes are generally macromolecules in nature. So, the membrane does not allow the passage of solutes.
- The concentration (in moles/L) of the large solutes is usually small. Hence, the osmotic
 pressure is usually low and can be assumed to be negligible.
- Therefore, the above equation can be re-written as:

$$J_w = A_w \cdot \Delta P$$



And the flux equation for diffusion of solvent through the membrane in ultra filtration is the same as that for the reverse osmosis. So, your J w = A w delta P - delta p is oplease do not worry about the notations many times what happens many books they will write only J in many books you will see J p. So, it try to understand the inherent meaning of the notations instead of going what is the subscript and superscript.

So, in ultra filtration solutes are usually they are macromolecular in nature. So, the membrane does not allow the passage of such solutes. So, the concentration of the last solute is usually very small. Hence, the osmotic pressure is usually low and can be assumed to be negligible. So, therefore, the above equation we can write that J w = A w into delta P so the; you can see your flux is a direct consequences of the pressure drop.

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Flux equation for ultrafiltration

- Ultrafiltration units operate at about 5 100 psi pressure drop compared to about 400 2000 psi for
- Since, the high molecular weight solutes are retained on the membrane surface, a concentration gradient builds up between the surface of membrane and bulk fluid.
- This gradient results in concentration polarisation, which is much more severer than reverse osmosis.
- The same is shown in figure below demonstrates the solute transfer in ultrafiltration membrane,
 (a) without gel layer, (b) with gel formation:

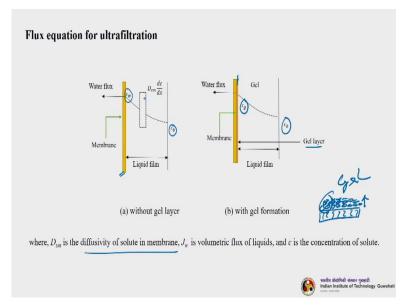


So, ultra filtration units operate at about 5 to 100 psi pressure drop compared to about 400 to 2000 psi the reverse osmosis in the reverse osmosis the pore sizes of the solids that get rejected or transport or whatever in both ways are very small and basically they are in ions and reverse osmosis membrane only allow the solvent to pass through. So, that is why the pressure required is very high, but here it is not. So, it is in the holdup about 5 to 100 psi.

Since high molecular weight solutes are retained on the membrane surface, a concentration gradient builds up between the surface of the membrane and bulk plate. So, since most of the large sized particles will be retained by the ultra filtration membrane, so, the concentration, polarisation and subsequent gel formation or kittler formation as a result, fouling is a major problem or a major challenge in most of the ultra filtration membrane.

Now, this gradient results in the concentration polarisation which is much more severe than the reverse osmosis. The same is shown in the figure next slide in the figure so, you will explain so, without gel layer and with gel formation.

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So, you can see how the flux profile actually looks like here. So, this is first one is the gel layer and second is with gel formation with the first is without the layer. So, this is your membrane and then we have a; this is here liquid film here there is no gel formation is appearing. So, you can see the concentration of the solute on the surface of the membrane is actually a C w then the concentration in the bulk is C b and what is D sm.

So, D sm is the diffusivity of solute in the membrane J w is your water flux and C is the concentration. Now here in this case there is a gel so, this thin layer you are seeing this is your gel layer and the concentration in the gel is C g and the concentration is in the bulk is C b.

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Flux equation for ultrafiltration

- Still further increase in pressure drop does not change cg and the membrane is said to be gel
- Then, the above equation becomes:

$$J_w = k_c \ln \frac{c_g}{c_b}$$

- Gel formation depends on the nature and concentration of the solute, pH, and pressure. Once the
 gel is formed, c_g becomes constant, and the liquid flux decreases logarithmically with increasing
 solute concentration in the bulk liquid.
- The gel layer causes a hydraulic resistance against flow and acts somewhat like a second membrane.



Still further increase in pressure drop does not change C g and membrane is said to be gel polarised. So, what is the meaning of this there is go back and try to understand here. So, what is happening So, initially your membrane is trying to say describe something on the draw a membrane so, initially there will be more or less separation we have discussed this many times earlier then slowly there is another layer on it and then it is consequently it grows up.

So, this is your gel layer. So, you are pressurising the system continuously and with the pressure also the concentration polarisation layer gel formation is the gel is getting actually synced, and further build up is also going on. So, when you increase the pressure beyond certain the gel concentration, concentration of the solute inside the gel does not change and the membrane is said to be gel polarised.

So, you will not get any permeate in this condition, even if you get also it is very small you can neglect it. So, almost no transport what will happen. So, the above equation will becomes $J = K c \ln C g / C b$. Now, K c is the mass transfer coefficient. So, the gel formation depends on the nature and concentration of the solute pH as well as the pressure. So, once the gel is formed, the gel concentration C = C c c0 becomes constant and the liquid flux decreases logarithmically with increasing solute concentration in the bulk fluid or bulk liquid.

So, the gel layer causes a hydraulic resistance against flow and acts somewhat like a second membrane. So, what is happening basically here if you again look at here? So, this is the membrane thickness and this is providing us a resistance call R m especially in case of ultra filtration, ultra filtration is a symmetric layer that means it already has a support and as this skin layer. If so, skin layer 2 layers, so, this is your skin layer and this is your micro porous support.

So, the thickness of this skin layer is actually providing one sort of resistance to the flow of the membrane. So, that is already there. So, that is why we have discussed many times that if the thickness can be minimised. Then the resistance due to this membrane thickness will be very small. Now, now come again to this concentration, polarisation or gel layer. So, there is a gel layer build up here on the surface. Now, what is happening, so, initially it is concentration polarisation layer slowly.

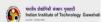
It prompts the cake and it becomes gel. So, at a certain process concentration in this solute C g will not increase it will become constant. So, at the time, this gel is providing a resistance which can be called as R g resistance due to gel. Now your overall resistance you can understand overall resistance become R m + R g. So this is actually not good, so you need to get rid of the gel as well as the concentration polarisation. We will discuss in our subsequent lecture in today's lecture how to do that.

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Models for UF transport

Pore flow model

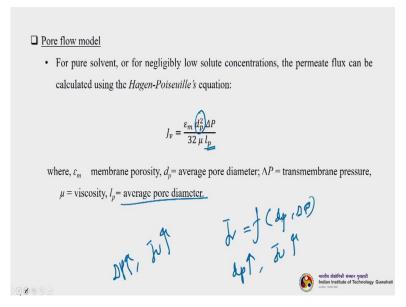
- The flow of solvent through ultrafiltration membrane due to transmembrane pressure can be described in terms of a pore flow model.
- · It assumes ideal cylindrical pores normal to the membrane surface.
- The solvent molecules are much smaller in dimensions than the pore diameter and their transport is not hindered within the pores.
- On the other hand, the solute molecules being comparable in dimension to the pore diameter are hindered and can either be partially or totally rejected by the membrane.
- The permeate flux (J_v) depends on the transmembrane pressure, the hydrodynamic conditions, the solute concentration, the membrane, and the properties of solute and the solvent molecules.



So, now, let us understand the various models, which are recommended for the transport inside the ultra filtration membrane. So, the first one is the pore flow model. In this model, the flow of solvent through ultra filtration membrane due to transmembrane pressure can be described in terms of a pore flow model it assumes ideal cylindrical pores normal to the membrane surface. The solvent molecules are much smaller in dimension than the pore diameter and their transport is not hindered within the pores.

On the other hand solute molecules being comparable in dimension to the pore diameter are hindered and can either be partially or totally rejected by the membrane. Now, the permeate flux J v depends on the transmembrane pressure, the hydrodynamic conditions the solute concentration the membrane and the properties of solute and solvent molecules.

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So, these are the equations in the pore flow model the equation is given by the, our well known Hagen Poiseuille's equation this we have discussed earlier also, but for our better understanding again I am describing it here. So, J p = epsilon m d p square delta p / 32 mu l p. So, epsilon m is the membrane porosity many times as I told you in the beginning of the lecture, you will see it is an epsilon does not matter so, that is also the membrane porosity. And d p is the average pore diameter delta p is the transmembrane pressure mu is viscosity and l p is average pore diameter this one.

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☐ Pore flow model

- The above equation shows that the permeate flux is very sensitive to the pore diameter.
- The permeate flux also increases with increase in trans-membrane pressure and the membrane porosity.
- On the other hand, the permeate flux decreases with increase in viscosity and membrane thickness.
- The pressure drop of membrane module is given by:

$$\Delta P = \frac{P_i + P_o}{2} - P_f$$

where, P_i and P_o are the inlet and outlet pressure on the feed side and P_f is the pressure on the filtrate side.

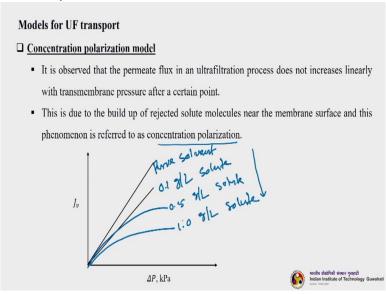


So, the above equation shows that permeate flux is very sensitive to the pore diameter the permeate flux also increases with the increase in transmembrane pressure and the membrane porosity. So, you can see this pore diameter actually ((()) 09:12) big role here because it is

square and J p. So J p is a direct function of your pore diameter and delta p. So is your d p increases your J p increases similarly, as your delta p increases your J p also increases.

On the other hand the permeate flux decreased with increasing viscosity and membrane thickness because they are in the bottom. So, the pressure drop of membrane model is given by delta p = P i + P 0 divided by 2 - P f. So, this is how you can calculate the pressure drop the membrane system so, P i and P 0 are the inlet an outlet pressure on the feed side and P f is the pressure on the filtrate side or your permeate side.

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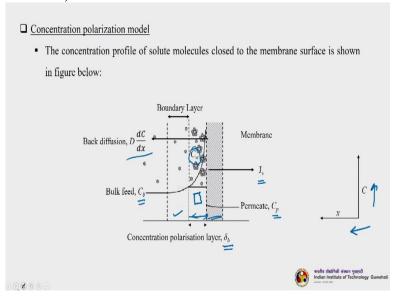


So, the next model is concentration polarization model. So, it is observed that the permeate flux in an ultra filtration process does not increase linearly with transmembrane pressure after a certain point because they become saturation then the flat plateau actually reaches. So, this is due to the build up of rejected solute molecules near the membrane surface and this phenomenon is referred to as concentration polarisation.

Now, if you can see in this particular first will apply this see to which one I will try to draw it again. So, this is the effect of permeate flux transmembrane pressure and permeate flux at different solute concentrations. Now, you can see this particular line as passing through almost in the origin. So this is your pure solvent. Now, I will try to plot it for different concentrations so, this is let us say 0.1 gram per litre solute concentration. Now we can have something else here.

So it is point let us say 5 gram per litre of solute then we will decrease it further. So it will be having 1 gram per litre of solute. So, we can see the effect of solute concentration on the permeate flux you can see this when you are increasing the permeate solute concentration, from 0.1 to 0.5 to then 1.0 you can see here corresponding values of the permeate flux are getting decreased and that is permeate flux will which is highest for you, pure solvent.

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So, the concentration profile of solute molecules closed to the membrane surface is shown in the figure below. So, you can see here this is your membrane and the bulk feed C p and the permeate is C p flux, this is your flux C w is the concentration of the solute on the membrane surface and this is your concentration polarisation layer the thickness is given by delta p this is your concentration polarisation layer and this is your boundary layer this one and this is bulk. And here the diffusion term is given by d = dC / dX, your C direction is here and X direction is here.

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☐ Concentration polarization model

 At steady state, a material balance of solute molecules in a control volume within the concentration polarization layer yields the following differential equation:

$$J_v C - J_v C_p + D \frac{dC}{dx} = 0$$

Integrating the above equation with boundary conditions, $C = C_w$ at x = 0; $C = C_b$ at $x = \delta_b$ we get:

since, mass transfer coefficient,
$$k = D/\delta_h$$
 $J_v = k \ln \left(\frac{C_w - C_p}{C_b - Cp}\right)$
 $E_{Q,n}$
 $F_{Q,n}$
 $F_{Q,n}$

Now, at steady state we can write a metrical balance of solute molecules in a control volume within the concentration polarisation layer. So, you take a control volume here inside the concentration polarisation layer small control volume and try to have a mass balance. So you can write $J \ v \ C - J \ v \ C \ p + D \ / \ dC \ dX = 0$. Now this $D \ / \ dC \ dx$ is the back diffusion term back diffusion apart back diffusion of the solute see this the actually the contribution of this back.

Diffusion may be small or last that depends upon what type of solute we are trying to separate or reject and what is the other properties exclude excluding including the membrane properties also. So, if you integrate this above equation with the condition that C = C w when x = 0, then C = C b when x = delta b, delta b is the concentration polarisation layer. So, you can we will get this equation.

So J $v = k \ln C$ w - C p divided by C b - C p, C p is the permeate concentration, but we know the mass transfer coefficient is written as k = D / delta b d capital D is the diffusivity and delta v is the thickness of the concentration polarisation layer.

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☐ Concentration polarization model

• The above equation is known as the concentration polarisation equation for partially rejected solutes. For total solute rejection, i.e. when $C_p = 0$, the equation reduces to:

$$J_{v} = k \ln \left(\frac{C_{w}}{C_{b}} \right)$$

• When the solute concentration at the membrane surface reaches the saturation concentration for the solute (C_s) , or the gelation concentration at the macromolecule (C_g) , there can be no further increase in C_w . Thus,

$$J_v = k \ln \left(\frac{C_s}{C_b} \right) = k \ln \left(\frac{C_g}{C_b} \right)$$
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So, the above question is known as the concentration polarisation layer polarisation equation for partially rejected solutes. So, this equation is telling us that this is actually the equation for concentration, polarisation concentration polarisation equation for partially rejected solutes now, because all the concentration camps out there, C w C p C b C w is the concentration of the solute in the gel layer or on the membrane surface C p is the permeate concentration C b is the bulk concentration.

Now, it is telling that a win for total solute rejection and that means, when C p becomes 0, there is no solute is passing through the membrane. Then in that above equation will reduce us to J $v = k \ln C$ w / C b. Now, when solute concentration at the membrane surface reaches the saturation concentration for the solute that is C becomes C w become C s or the gel concentration of the macromolecules that becomes C w become C g then there can be no further increase in the C w. So, we can write that same equation J $v = k \ln C$ s / C b or k $\ln C$ g / C b.

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☐ Concentration polarization model

• The above equation is referred to as the *gel polarisation equation*.

• This equation indicates that when C_w equals C_s (or C_o), the permeate flux is independent of the

transmembrane pressure.

• In the pressure independent region, the permeate flux for a given feed solution is only

dependent on the mass transfer coefficient.

· For a particular mass transfer coefficient, the pressure independent permeate flux value is

referred to as the limiting flux (J_{lim}) .

· According to the gel polarisation model, the existence of the limiting flux is consequence of

gelation of the solute at the membrane solution interface.

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Now, this particular equation is called gel polarisation equation so, you can see the concentration of the gel layer concentration. gel layer concentration comes into picture so, this is gel polarisation equation. Now, this indicates that when C = Cs or let us say Cg the

permeate flux becomes independent of that transmembrane pressure. Now in the because

there is see why it is because you can see in this particular equation there is no delta p terms.

So, the air flux is a direct consequence of either C s or C g and immediate mass transfer

coefficient. So, in the pressure independent region the permeate flux for a given period

solution is only dependent on the mass transfer coefficient. So, that is what I was telling you

the beginning of the class that mass transfer coefficient plays a very important role, especially

in case of ultra filtration.

So, for a particular mass transfer coefficient, the preset independent permeate flux value is

referred to as the limiting flux J limit according to the gel polarisation model, the existence of

the limiting flux is a consequence of the gelation of the solute and the membrane solution

interface.

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Gel polarisation model

- As a result of concentration polarisation effect, concentration of solute at the membrane surface increases compared to that of bulk concentration.
- lacktriangledown Eventually the solutes form the slimy layer, known as gel, if a limiting concentration c_g is
- Gel formation depends on the nature and concentration of the solute, pH, and pressure. Once the
 gel is formed, c_g becomes constant, and the liquid flux decreases logarithmically with
 increasing solute concentration in the bulk liquid.
- The gel layer causes a hydraulic resistance against flow and acts somewhat like a second membrane.

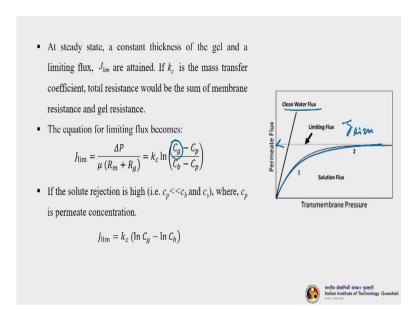
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So, gel polarisation model as a result of the concentration polarisation effect concentration of solute at the membrane surface increases compared to that of bulk concentration. Eventually solutes from the slimy layer known as gel if a limiting concentration C g is reached so when you are C w become C s the saturation constant then your membrane pressure transmembrane pressure is still playing a role then when C s becomes C g.

Then it what happens actually then tell phenomena is out of your transmembrane system. It does not depend on your transmembrane pressure anymore. So the concentration of saturation concentrations has become has reached the gel concentration C g. So, the gel permission depends on the nature and concentration of the solute pH as well as pressure. So, once the gel is formed, the gel concentration becomes constant and the liquid flux decreases logarithmically with increasing solute concentration in the bulk feed.

When you are a solute concentration is increasing. So here are the liquid flux permeate flux decreases logarithmically with increasing solute concentration in the bulk liquid. So you can see here actually how I will just try to draw something. So if you see this is your J v liquid permeate flux versus solute concentration, concentrations so let us say 1 2 3 4 5, so 1 2 3 4 5 gram per litre any unit so the permeate flux decrease will happen something like this. So, this tells us that actually our permeate flux decreases as the solute concentration increases.

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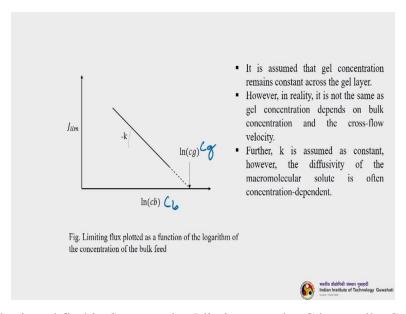


Now at a steady state a constant thickness of the gel and a limiting flux are attained. So, you can see from this particular equation it is flux versus transmembrane pressure so this is your solute flux which is increasing like this and this is your clean water flux. So, that means when there is no solute and when it reaches a saturation on whatever the flux corresponding to that equals to limiting flux J limit.

So, the equation for the limiting flux becomes J limit = 2 delta p divided by mu R m + R g you remember I told you that once the gel layer from and C g is no more increasing. So, transmembrane pressure is playing no role. So, the resistances are governed by 2 first is the R m the actual resistance provided by the membrane itself plus the resistance that is being offered by the gel layer.

So, R m + R g so, you can write that in terms of mass transfer coefficient and concentration K c ln C g - C p divided by C b - C p. so your C w is replaced by C g. So if the solute rejection is very high, that means C p is very, very less than actually C b and C s book. So, C p is the permeate concentration that can be neglected. So, you can write J limits are the limiting flux becomes K c into ln C g - ln C b.

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Now, we can plot it and find it. So, you plot J limit versus Im C b actually. So, what you will see is that a straight line the slope will give will - k and we can find that C g. So, this is actually C g. So suffix C g, this is also C suffix b. So, it is assumed that gel concentration remains constant across the gel layer. However, in reality it is not the same as gel concentration depends on the bulk concentration and the cross flow velocity.

We have not discussed the effect of cross flow velocity till now our discussion cross flow velocity plays a very important role in reducing the concentration polarisation as well as the gel layer support the mass transfer coefficient assumed constant however the diffusivity of the macromolecular solute is often concentration dependent.

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☐ Mass transfer coefficient

- The membrane wall-liquid mass transfer coefficient (k) is a measure of the hydrodynamic condition within a membrane module for a given feed solution.
- Most models used in the description of concentration polarisation phenomena during cross flow membrane filtration require the knowledge of the mass transfer coefficient.
- The mass transfer coefficient can be estimated from correlation of Sherwood number (Sh = k d/D) in terms of Reynolds number (Re = d u/v) and the Schmidt number (Sc = v/D) where d is module diameter, D is solute diffusivity, u is cross-flow velocity and v is kinematic viscosity.



So, let us now understand what is mass transfer coefficient and what is its role in ultra filtration systems. The membrane wall liquid mass transfer coefficient k is a measure of the hydrodynamic condition within a membrane model for a given feed solution. So, most models used in the description of the concentration polarisation phenomena during cross flow membrane filtration require the knowledge of mass transfer coefficient.

Now, the mass transfer coefficient can be estimated in various ways, first we can find it out from the Sherwood number. So, Sherwood number is a dimensionless number it is equals to k and d in by divided by D. So, k is the mass transfer coefficient, D is the diameter of the pores and divided by the diffusivity. So, in terms of the Reynolds number d u / v mu and the Schmidt number nu / D, where d is the module diameter d is the, D is the solute diffusivity u is cross flow velocity nu is the kinematic viscosity.

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☐ Mass transfer coefficient

• In case of fully developed laminar flow, the Graetz-Leveque correlation can be used:

$$Sh = 1.62 \text{ Re}^{0.33} Sc^{0.33} \left(\frac{d}{l}\right)^{0.33}$$

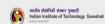
• For turbulent flow (Re > 2000), the Dittus-Boelter correlation can be used:

$$Sh = 0.023 \text{ Re}^{0.8} Sc^{0.33}$$

 An alternative correlation for mass transfer coefficient in case of fully developed laminar flow is given in terms of the shear rate (γ) at the membrane surface.

$$k = 0.816 \gamma^{0.33} D^{0.67} l_t^{0.33}$$

where, $\gamma = 8u/d$ (for tubes), and $\gamma = 6u/b$ (for rectangular channels, here 'b' is channel depth)



So, you can see this I have given certain correlations. So, these correlations can be utilised to calculate the mass transfer coefficient first you know to understand actually what are correlations. So, correlations are one set of equations which were derived or developed from doing certain experiments. That is why you will see that most of the correlation has certain boundary layers or it has a certain range.

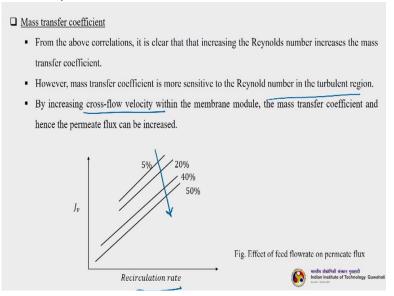
Let us say this Dittus Boelter equation which is given here. So, it is valid for Reynolds number from let us say from 1000 to 5000 Schmidt number from 30 to 100. I am just giving an example. The reason is that whenever you do an experimental when you carry when you do some experiments, so you have experimental parameters you are varying by keeping 1

parameter fixed let us say I fix the diameter of the tube and vary the cross flow velocity where is the temperature well as the solute concentration, where is the feed flow rate.

Now, next one I will go I will change the diameter of the tubes by and by fixing all of the parameters constant like that, in that way the various correlations are developed. So, the first one is the Graetz Leveque of correlation which is very well known. So, he has a Sherwood number is 1.62 are announced to the power of 0.33 it is Schmidt number to the power of 0.33 and d/l t to the power of 0.33.

The next one is one of the most famous correlations, which is called Dittus Boelter correlation is Schmidt number = 0.023 to the Reynolds number to the power of 0.8 Schmidt number to the power of 0.33. So an alternative correlation for mass transfer coefficient in case of fully developed laminar flow is given in terms of shear depth at the membrane surface. So k = 0.816 this gamma to the power of 0.33 D to the power of 0.67 is to the power of 0.33. So, your shear depth is a 8u / d for tubes, 6u / b for rectangular channels, where b is actually the channel depth.

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Now, from the above correlation it is clear that increasing the Reynolds number increases to mass transfer coefficient. However, mass transfer coefficient is more sensitive to the Reynolds number in the turbulent region, by increasing the cross flow velocity within the membrane module, the mass transfer coefficient enhance permeate flux can be increased. So, one of the way to achieve permeate flux increase or to get enhanced permeate flux is to increase the mass transfer cooperation.

So, this particular figure it is actually showing the effect of feed flow rate on permeate flow rate permeate flux. So you can see this 5% 20% 40% 50%. So, these are the concentrations of the solutes as we are increasing our solute concentration, and this is your recirculation receptors flow velocity your permeate flux is decreasing.

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Models for UF transport

☐ Resistance model

- There are two types of resistances that are generally encountered in ultrafiltration, one is membrane resistance (R_m) and another is cake resistance (R_c).
- Both the membrane and thin cake layer offers the resistances to the solvent transport.
- The flux equation can be written as:

$$J_w = \frac{\Delta P}{\mu \left(R_m + R_c \right)}$$

• The resistance to flow through the cake can be estimated from the Kozeny-Karman equation:

$$R_c = \frac{180(1-\varepsilon)^2 l_c}{d_s^2 \varepsilon^3}$$

where, $\underline{\varepsilon}$ is porosity, l_c is cake thickness, $\underline{d_s}$ is diameter of the particles forming the cake, R_c is the resistance to flow offered by unit thickness of cake, also known as *specific cake resistance*.



So, in the next model is the well known resistance model. So, usually 2 types of resistances are encountered in ultra filtration the first one is the membrane resistance R m and the second one is the cake resistance R c or the gel resistance you can see R c also. So, both the membrane and thin cake layer offers the resistance solvent transport. The flux equation can be write or rewritten that J w = to delta p divided by mu R m + R c.

So, the resistance to flow through the cake can be estimated from the Kozeny Karman equation R c = 180 into 1 - epsilon square 1 c divided by d s square epsilon cube. So, here epsilon is the porosity 1 c is the cake thickness d s is the diameter of the particles forming the cake that wants a solute diameter and R c is the resistance to flow offered by the unit thickness of cake known as the specific cake resistance.

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☐ Resistance model

Considering the batch filtration of a liquid using a membrane of area A_m and flow resistance R_m.
 If c_b is solute concentration in bulk, R' is rejection coefficient, I_c is the cake thickness at any time 't', then:

$$C_b V R' = \rho_c l_c A_m$$

$$\Rightarrow lc = \frac{C_b V R'}{\rho_c A_m}$$

where, ρ_c is density of the cake layer, V is volume of the filtrate collected after time 't'.

• The solvent flux can be expressed as:

$$J_{w} = \frac{1}{A_{m}} \frac{dV}{dt}$$



considering the best filtration of a liquid using a membrane area A m and flow resistance R m if C b the solute concentration in bulk R is the rejection coefficient l c is the cake thickness at anytime t, then we can write C b V R r prime = rho c l c A m or we can find out l c from this equation l c = C b VR prime / rho c A m. If you know all these things, then we can predict the thickness of the cake layer. So, rho c the density of the cake layer V is the volume of the filter collects at any after any time t. So, the solvent flux can be written as J w = 1 / A m dV / dt.

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☐ Resistance model

Combining the equations, the solvent flux can be expressed as:

$$J_w = \frac{\Delta P}{\mu} \left[R_m + \frac{r_c C_b R'}{\rho_c A_m} V \right]^{-1}$$

• The above equation can be integrated to obtain a relation for flux decline with time in batch ultrafiltration. The initial concentration is: V=0 at t=0

$$R_m V + \frac{r_c C_b R'}{2 A_m \rho_c} V^2 = \frac{A_m \Delta P}{\mu} t$$

· Combining the above two equations, we get:

$$\frac{1}{J_w^2} = \frac{R_m \mu^2}{(\Delta P)^2} + \frac{2\mu C_b r_c R'}{\rho_c \Delta P} t$$



So, combining the equations the solvent flux can be expressed as J w = delta p / mu R m + r c C b r prime divided by rho c A m into V in inverse. So, now the above equation can be integrated to obtain a relation for flux declined with time in the batch ultra filtration the initial concentration is V = 0 at t = 0. So, this is the above equation reduces to this and when we combine this equation we can write one about J w square equals to this particular equation.

So, you are expressing a flux in the terms of resistances, pressure and other parameters most of which are extremely constant.

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Models for UF transport

Resistance model

- Concentration polarization not only offers extra hydraulic resistance (R_{cp}), but also results in development of osmotic pressure, which acts against the transmembrane pressure.
- For high flux values, high rejection levels and low mass transfer coefficient k values, the concentration of macromolecular solutes at the membrane surface can become quite high and hence the osmotic pressure cannot be neglected anymore.
- The flux equation then becomes,

$$J_w = \frac{(\Delta P - \Delta \pi)}{(R_m + R_{cp})}$$



So concentration polarisation not only offers extra hydraulic resistance, but also results in the development of osmotic pressure, which acts against the transmembrane pressure for high flux values, high rejection levels and low mass transfer coefficient k values, the concentration of macromolecular solute at the membrane surface can become quite high and hence the osmotic pressure cannot be neglected anymore. So the flux equations becomes J w = delta p - delta p + divided by R m + R cp.

So, actually there is a small mistake. So, this is your osmotic pressure model. So what I was trying to tell you is basically what happens when the flux value becomes very high and we reach the high solute rejection along with a very low mass transfer coefficient value then the concentration of the macromolecules solutes on the membrane surface they become very high that means the thickness of the concentration polarisation layer becomes very high and that time we cannot neglect osmotic pressure.

Because as I told you in the beginning of the class let us see this membrane so there is a concentration polarisation layer initially the membrane is providing certain resistance apart from that there is no other resistance and since these are macromolecules. So there is no osmotic pressure so we neglected delta pi. Now, once the solute deposition becomes very high the thickness becomes this is very high let us say this thickness of the concentration polarisation layer is very high.

So here then at this particular condition what is happening is that we cannot neglect the effect

of osmotic pressure. Now the osmotic pressure effect is coming from this particular layer not

from the membrane itself. So you can use J w = delta p - delta pi R m + R cp.

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• The limiting flux behaviour can also be described by this model.

· With increase in pressure difference, the flux increases and thus the concentration on the membrane surface, c_m .

• This leads to an increase in the osmotic pressure and hence the pressure increase is partly counterbalanced by the osmotic pressure increase.

• The dependence of osmotic pressure of a macromolecular solution on the concentration can be given by,

 $\pi = a c^n$

where a is a constant and n is an exponential factor with a value grater than 1.

 \bullet a and n both depends on molecular weight and type of solute.

So, the limiting flux behaviour can also be described by this particular model with increasing

the pressure difference the flux increases and thus the concentration on the membrane

surface. Now this leads to an increase in the osmotic pressure and hence the pressure

increases partly counterbalance with osmotic pressure increase now, but please remember the

amount of the osmotic pressure is still very less.

When there is no concentration polarisation no clear deposition nothing is there only new

membrane is there. So that time we can neglect osmotic pressure but when the concentration

polarisation layer becomes very thick that time that layer itself is providing some sort of

osmotic pressure. So that pressure has to be taken into account. So the dependence of osmotic

pressure of macromolecules solution on the concentration can be given by pi = a c to the

power of n.

Where a is a constant and n is an exponential factor with a value greater than 1 both a and n

depends on 2 things one is the molecular weight and then the type of the solute on the nature

of the solid basically.

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☐ Membrane Rejection

- The concept of molecular weight cut-off can be arbitrary.
- The consequences of the non-standard protocols, difference in membrane morphology, generic polymer composition, and the chemical nature of the MWCO tests all contribute to this uncertainty.
- The retention properties of the membrane are strongly dependent on the solute shape, solute flexibility, solute-membrane interaction, operating conditions, and the test apparatus configuration.

Now membrane rejection so, the concept of molecular weight cutoff can be arbitrary this we have understood in our previous classes. So the consequences of the non-standard protocols difference in the membrane morphology generic polymer composition and chemical nature of the molecular weight cut off test all contributes to this uncertainty. So the retention properties of the membrane are strongly dependent on the solute shape, solute flexibility, solute membrane interaction, operating conditions and the test apparatus configuration. So, this is called hydrodynamics.

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If the solute is not totally retained or rejected, the amount of solute going through the
membrane can be quantified in terms of the membrane intrinsic rejection coefficient (R) or
intrinsic sieving coefficient (S),

$$R = 1 - \frac{C_p}{C_w} = 1 - S_i$$

- The solute concentration on membrane surface (C_w) is difficult to determine using experimental methods.
- Therefore, apparent rejection coefficient (R_a) or apparent sieving coefficient (S_a) is preferred:

 $R_a = 1 - \frac{C_p}{C_b} = 1 - S_a$

So, if the solute is not totally retained or rejected, the amount of solute going through the membrane can be quantified in terms of the membrane intrinsic rejection coefficient or intrinsic sieving coefficient. So, you can see the equation what we have seen this equation

earlier also rejection equation R = 1 - C p / C w So, C p is the permeate concentration C w the concentration of the surface of the membrane. So, that we can write 1 - S i.

So, S i is the sieving coefficient which is C p / C w. So the solute concentration on the membrane surface is difficult to determine using experimental methods. How do you determine a solute concentration as a membrane it is a closed system in the membrane itself is on the inside the membrane module which even if you can open you cannot you can only carry out one sort of experiment batch type then you can see it otherwise in a concentration system you cannot do that.

So, for that what is the modification system so a proposed there is something called apparent rejection coefficient or apparent sieving coefficient you know what is the meaning of apparent, apparent is basically readily measurable. So, which we can readily measurable so what are the concentrations we can readily measurable one is the concentration of the bulk that is the width whatever it is there second is the concentration on the permeate.

Which is continuously coming back side of the membrane so these 2 we can measure so, we write R a which is the apparent rejection coefficient is C p / C b which is nothing but 1 - S a which is the sieving apparent sieving coefficient.

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☐ Membrane rejection

 Early attempts to correlate the ratio of molecular diameter of the species and the pore diameter with the apparent rejection coefficient yielded equations of the form:

$$R_a = [\lambda(2-\lambda)]^2$$
 for $\lambda < 1$,
 $R_a = 1$ for $\lambda \ge 1$
where, λ is the ratio of species diameter d_i to the pore diameter d_n .

 It is now recognised that the rejection coefficient depends not only on the solute or membrane properties but also on the operating and environmental parameters such as feed concentration, pH, ionic strength, system hydrodynamics, and permeate flux.

So, early attempts to correlate the ratio of molecular diameter of the species and the pore diameter with the apparent rejection coefficient yielded the equation just like this of the below type. So R a = lambda into 2 - lambda whole square for lambda less than 1. And when

lambda becomes greater than 1 R a becomes 1. Now what is lambda? So, lambda is the ratio of species diameter d i to the pore diameter d p.

So, this is what is lambda, lambda equals d i species diameter to the d p species diameter means the solid diameter divided by the pore diameter. Now, it is now recognized that the rejection coefficient depends not only on the solute or membrane properties, but also on the operating and environmental parameters such as feed concentration, pH, ionic strength system hydrodynamics and permeate flux.

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☐ Membrane rejection

- The transmission of macromolecules carrying electrostatic charge is particularly sensitive to pH and salt concentration.
- The intrinsic rejection coefficient increases with increasing permeate flux, transmembrane pressure, and molecular weight but it is independent of the system hydrodynamics.
- The apparent rejection coefficient increases with increasing molecular weight, cross-flow velocity and concentration.
- The apparent rejection coefficient first increases and then decreases again when the transmembrane pressure is increased.

The transmission of macromolecules carrying electrostatic charges particularly sensitive to pH and salt concentration till now, we have not discuss the effect of charge on the membrane and rejection or sieving coefficient or any such things on the models these are not been taken into account but please remember that charge plays a very important role. So, the charge of solutes as well as charge of the membrane they play a very important role.

Because then there will be some sort of charge based separation or rejection that will happen based upon what is the charge of the solute as well as the charge of the membrane. Now another important parameter is pH you know with changing the pH the charges of the solute as well as the solvent and the membrane all will change. Now so that is why the role of pH is very important when you are talking about some system.

In which you are using membranes which are a little charged either positive or negative or your solutes are carrying as a positive charge or a negative charge. Now, the intrinsic

rejection coefficient increases with increasing permeate flux transmembrane pressure or molecular weight but it is independent of the system hydrodynamics. So, you have rejection coefficient is not has nothing to do with the hydrodynamics.

The apparent rejection coefficient increases with increasing molecular weight cross flow velocity and concentration, the apparent ejection coefficient first increases and then decreases again when the transmembrane pressure is increased.

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- ☐ Membrane rejection
 - A correlation between the intrinsic sieving coefficient and the apparent sieving coefficient can
 - The concentration polarisation equation can be written as:

$$J_v = k \ln \left(\frac{C_w/C_p - 1}{C_b/C_p - 1} \right)$$

• On substituting and rearranging, we get:

$$\ln\left(\frac{S_a}{1 - S_a}\right) = \ln\left(\frac{S_i}{1 - S_i}\right) + \left(\frac{J_v}{k}\right)$$

A correlation between the intrinsic sieving coefficient and the apparent sieving coefficient can be obtained. The concentration polarisation equation can be written as $J v = k \ln C w / C p - 1$ divided by C b / C p - 1 or we can just re substitute and write that in terms of sieving coefficient $\ln S a / 1 - S a$ that is apparent sieving coefficient equals to $\ln S i / 1 - S i$ the intrinsic sieving coefficient + J v / k we can plot this.

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☐ Membrane rejection

- If the intrinsic sieving coefficient is considered to be constant, the equation suggests that the value of S_a increases with increase in value of J_v and decrease in value of k.
- For any given operation, the mass transfer coefficient and intrinsic sieving coefficient can be
 determined from the plot of InfS_a/(1-S_a)] vs J_v.

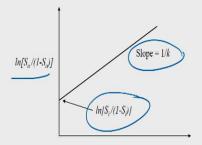


Fig. Determination of S_i and k.

47.15

So, if you plot it $\ln S$ a / 1 - S a versus a permeate flux you will get a straight line of slope 1 / k and the intercept $\ln S$ i / 1 - S i. So, this is how you can determine the intrinsic sieving coefficient as well as the mass transfer coefficient.

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Recent research has suggested that S_i is a function of J_v .

$$S_i = \frac{S_{\infty} \exp\left(\frac{S_{\infty}J_{\nu} \delta_m}{D_{eff}}\right)}{S_{\infty} \exp\left(\frac{S_{\infty}J_{\nu} \delta_m}{D_{eff}}\right) - 1}$$

where, S_{∞} is an asymptotic sieving coefficient,

 δ_m is membrane thickness,

 $\overline{\mathcal{D}}_{\text{eff}}^{n}$ is effective diffusivity of solute in the pore.

So, the recent research has suggested that your intrinsic sieving coefficient is a direct function of the permeate flux. So, you can write S i = S infinity exponential S infinity J v delta m divided by S infinity exponential then S infinity J v delta m divided by D eff - 1. So, what are these parameters? S infinity is an asymptotic sieving coefficient, delta m is the thickness of the membrane and D effective is the effective diffusivity of the solute in the pore.

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• From the previous equation:

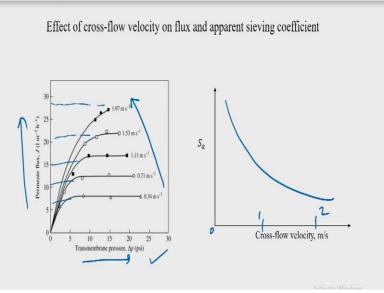
$$S_{a} = \frac{S_{\infty} \exp\left(\frac{S_{\infty}J_{v}\delta_{m}}{D_{eff}} + \frac{1}{k}\right)}{\left(S_{\infty} - 1\right)\left[1 - \exp\left(\frac{S_{\infty}J_{v}\delta_{m}}{D_{eff}}\right)\right] + S_{\infty} \exp\left(\frac{S_{\infty}J_{v}\delta_{m}}{D_{eff}} + \frac{1}{k}\right)}$$

- This clearly shows that the value of S_a depends on the J_v and k. The dependence of sieving coefficient on permeate flux can also be explained using critical flux concept.
- The critical flux is that flux for which the shear induced by the flow through pore is high
 enough to overcome the natural tendency of a solute molecule to maintain its spherical shape in
 solution.
- For a given membrane pore, the critical flux is that flux value for which the flow shear will
 clongate and/or deform the solute molecule such that it will pass through the pore.

So, from this previous equation, just rearranging we can will obtain equation something like this. So, this particular equation is telling you that the value of S a which is apparent sieving coefficient is completely dependent of the 2 factors one is J v and other is k this term J v / k. It is there both numerator and denominator. The dependence of sieving coefficient on the permeate flux can also be explained using something called a critical flux concept.

Now, the critical flux is that flux for which the shear induced by the flow through pore is high enough to overcome the natural tendency of a solid molecule to maintain its spherical shape in the solution. So, for a given membrane pore the critical flux is that flux for which the flow shear will elongate and or deform the solute molecule such that it will pass through the pore.

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Let us understand the effect of cross flow velocity on permeate flux as well as apparent sieving coefficient. So, you see this these are this is a effect of your cross flow velocity on the permeate flux you can see how the cross flow velocity increasing like in this direction, when the cross flow velocity is increasing you can just see that your corresponding flux values also increases. So, flux values is also increases, so at and that transmembrane pressure is also increasing.

So, similarly we can plot the sieving coefficient also. So, along with cross flow velocity, let us say this is 0 this is 1 this is 2. So 1 and 2 cross flow velocity in meter per second so, you will get something like this. So, with increasing the cross flow velocity here apparent sieving coefficient is decreasing.

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Solute fractionation using UF

- For fractionation of a binary mixture of solutes, it is desirable to achieve maximum transmission
 of the solute desirable in the permeate and minimum transmission of the solute desirable in the
 retentate.
- Efficiency of solute fractionation for a binary mixture is expressed in terms of the selectivity (ψ),

$$\psi = \left(\frac{S_{a1}}{Sa_2}\right) = \left(\frac{1 - Ra_1}{1 - Ra_2}\right)$$

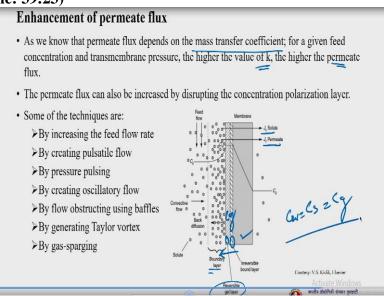
- · Fractionation of macromolecules by UF can be enhanced by the following approaches,
 - > pH optimization
 - ➤ Feed concentration optimization
 - ➤ Salt concentration optimization
 - ➤ Membrane surface pre-treatment
 - > Optimization of permeate flux and system hydrodynamics

Now, we can carry out solute fractionation either binary or multiple using ultra filtration very efficiently. So, this is one of the most important applications of ultra filtration is a solute fractionation. So, fractionation of a binary mixture of solutes it is desirable to achieve maximum transmission of the solute that is desirable in the permeate and minimum transmission of the solute desirable in the retentate. So, efficiency of solute fractionation for a binary mixture is expressed in terms of selectivity. So, selectivity is S a1 / S a2.

Which is nothing but the apparent sieving coefficient divided by of the solute 1 divided by apparent sieving coefficient by of solute 2 equals to 1 - R all divided by R a2. Now fractionation of these macromolecules can be enhanced by following approaches. So, you can usually go by the go for a pH optimization you can go by feed concentration optimization

these are all optimizations, you can go by salt concentration, optimization membrane surface pre-treatment to make it either particular charges and then optimization of the permeate flux and system hydrodynamics.

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So, let us now understand what are the different methods to enhance permeate flux. So, this is very important to understand because most of the times why most of the times actually we want a good permeate flux all of the time all most of the time. So, to achieve that, since the permeate flux is decreasing due to concentration polarisation and as well as subsequent gel layer. So, that is why there are certain ways proposed by various researchers and some of them are commercialized also.

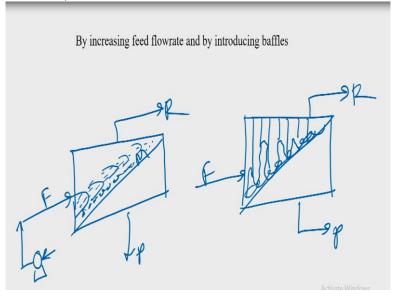
That will help us in enhancing the permeate flux so the enhancing permeate flux reducing concentration polarisation and enhancing mass transfer coefficient are more or less they are the same the techniques are same as we know that permeate flux depends on the mass transfer coefficient for a given feed concentration transmembrane pressure higher the value of k higher with the permeate flux. So the permeate flux also can be increased by disrupting concentration polarisation layer.

So, you can see how nicely this actually figure is giving the description this is your membrane your solute flux is this side your permeate flux is also this one we also expect that the solute flux will be less. So, this is the irreversible bound layer, we can call it as actually the constant gel layer, this is the reversible gel layer because see, as we increase now from this to this. The bonding between the solid particles also decreases.

That is why if you see whatever it is immediately on the surface of the membrane they are more pressurized under more pressure as they become very thick and robust. So, this is almost irreversible bound layer of gel layer then above that there is a layer which is reversible gel layer then of course, there is boundary layer and then back diffusion of the solutes are happening due to the C g here actually we have C s becomes C g C w become C s become C g that time the back diffusion becomes more prominent.

So, we want to disrupt the concentration this concentration polarisation layer. So, these are the techniques by increasing the feed flow rate by creating pulsatile flow by pressure pulsing by creating oscillatory flow by flow obstructing using baffles by generating Taylor vortex and by gas-sparging.

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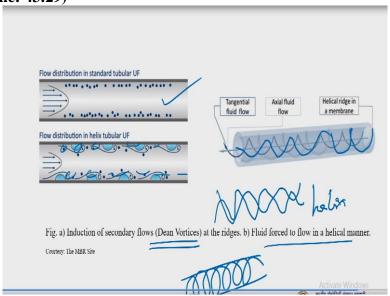
Let us just discuss 2 or 3 of these things what is the meaning of creating actually the feed flow rate let us see. So, let us see this is our cross flow membrane system. So, this is feed is their feed is coming in from a system there is a pump here and you will get here retentate here you will get it permeate here this is a membrane as you know at a certain when the membrane processes is getting carried out your concentration polarisation layer starts to build up on the surface of the membrane.

So, when you increase the flow rate what is happening the feed itself is flowing in a higher rate. So, they will try to wash away whatever is that is getting deposited on the surface of the membrane then you get a retentate here and you get a permeate here. So, another way is to

introduce baffles. You those who have read this one chemical engineering, there must be knowing or mechanical engineering they also must be knowing actually what is your baffles.

So baffles are different obstructions to flow small big, small big, small big, small big small like this. So what is happen the flow will become like this. So, this is some obstruction to here flow. So, in that shear concentration polarisation build up what is that is getting build up here. So, fast in case of non presence of baffles or flow of station will become less.

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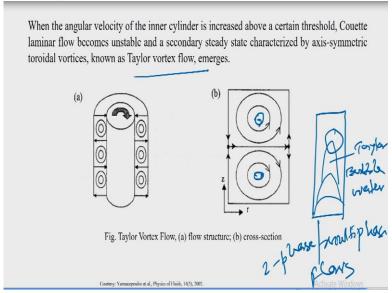
So, the next one is introduction of the secondary flows called dean vortices. This is actually proposed by the MBR site the company; you can see when the it is a tubular ultra filtration membrane here, when there are no secondary flows. So, here flow pattern something looks like something like this. So, the flow distribution in the standard ultra filtration, so, you introduce here secondary flows.

For example, the dean vortices your flow patterns becomes like this. So, this is a better flow pattern and this will not help you to build up your concentration polarisation on the surface of the membrane inside the surface of the membrane here, this is another one which is proposed by this particular company, this is introducing some sort of helix. So, you can see this is the actually the helix which is being introduced this these are.

So, that the helical ridge or something like this you can see something like this that is being introduced inside that template as a result what is happen, so, the fluid that is getting formed is taking a step something like this, then the tangential fluid flow. So, the tangential fluid

flow is one when it is happening like this or it is happening like this in, this in it any time, what will happen is basically that will help in reducing the concentration polarisation or build up of the molecules on the surface of the membrane.

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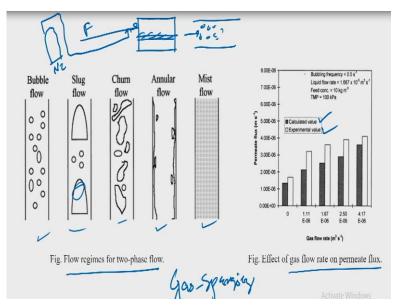


So there is another one. So this is by Taylor vortex or Taylor vortices the Taylor bubbles are very important in fluid flow whether it is a 2 plus layer or multiphase flow. So, when angular velocity of the inner cylinder is increased but the tubular membranes above a certain threshold, the Couette laminar flow becomes unstable and a secondary steady state characterized by axis-symmetric toroidal vortices known as the Taylor vortex emerges.

So, it is just it happens just like this. You have seen how it is getting this direction so; these are called Taylor vortices it this is a cross section how it looks like you know Taylor bubble is very interesting you can easily see. So, in the feed is feed phase happening to phase flow. So, let us say this is a tube in which water is flowing. And then what I do I just squeeze it squeeze the tube and then I slowly released what will water will flow a gas bubble will slowly immerse this will immerse something like this and this becomes center like this.

Now, this is something called a Taylor bubble that this is wide range applications in a 2 phase or multiphase systems flows. So, if we are flowing cross flows, a Taylor bubble is flowing like this. So, it is nose the nose itself will it is not a single one there are many it will help reducing the concentration polarisation thereby washing it on the surface of the membrane.

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So the next one is actually called gas-sparging. So gas-sparging actually is a very effective technique in most of the ultra filtration system whether it is a tff system, whether it is a tubular systems, cross flow or tff or cross flow tangential system or MBRs membrane reactors or bio reactors so this is the flow regimes of the 2 phase flow. So when the velocity is less, we will have a bubble flow, then it increases we will have a slug flow we are seeing this terrible type of things here.

Then we have chum flow the bubbles get bust actually bubbly flow the bubbles continuous generation of bubbles, small bubbles, there coalescence to make a large bubble again, burst due to the pressure to make small bubbles,. So, this is a technique called bubble technology in which we use it to generate more mass transfer area. In case of when we are talking about some separation or some reaction it is a basically 2 phase system, then we have annular flow and then we have a mist flow here.

You can see how it actually helps happens, so, just trying to draw something, so you can let us say your membrane is here your feed is coming. So In the feed what you will do you take a nitrogen gas then spurge it and mix it with the feed line itself. So, what is happening so, your feed is flowing along with the gas bubbles in various steps. So, the sets of bubbles this bubble process will depend upon what is your passing velocity here.

So, this will help you to watch over the concentration polarisation build up on the surface of the membrane you can see this is a effect of gas flow rate on permeate flux you can see when the gas polarisation 2 things one is the calculated value and other is the experimental value calculated value from some theoretical approximation, you can see the experimental filters

that are higher than the calculated values.

So, the bubbling frequency is 0.5 second inverse liquid flow rate is 1.67 into 10 per of minus

per meter cube per second 5 meter cube per second. Feed concentration is 10 kg per meter

cube and transmembrane pressure is hundred kilo Pascal. So, these are constant and then we

are increasing the gas flow rate in this direction. So, you are seeing that increasing the gas

flow rate. Here permeate flow is increasing, but after a certain time it becomes almost

saturation.

So, this is all about various techniques, when you talk about how to how do you enhance the

permeate flux how do you enhance the mass transfer coefficient or how you reduce your

concentration polarisation layer because it is very important to reduce the concentration

polarisation. So, that permeate flux increases and the subsequent fouling which is a result of

your concentration polarisation will also be less. So, with this I wind up today. So, you can

read these books for your reference purposes, or text for questions.

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Thank you

For queries, feel free to contact at: kmohanty@iitg.ac.in

So in the next lecture, we will discuss the various factors that affect ultra filtration performance and the fouling in the ultra filtration as well as we will discuss about various ultra filtration applications 2 to 3 ultra industrial ultra filtration applications with schematic diagram will try to understand. So thank you very much if you have any query, please feel free to write to me at kmohanty@iitg.ac.in Thank you.