Introduction to Process Modeling in Membrane Separation Process

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Lecture – 03

Fundamentals of Separation Processes and Introduction of Membrane System (Contd.)

Welcome to the session of our course. Last classes we have looked into, we have started the various properties and definitions of membrane based processes which will be quite frequently will be coming across during our modeling and simulation of the processes. The first term that we have defined is osmotic pressure. And we have seen that how osmotic pressure is defined, and how it will be depending on the various operating conditions; for example, the solutes that we are going to separate and the concentration of the solute.

We have seen that solute it will be proportional to the solute concentration and it is inversely proportional to the molecular weight of the solutes. Therefore, whenever we are talking about the separation of the lower molecular weight solutes its osmotic pressure will be very very high. So therefore, the operating pressure in order to overcome the osmotic pressure in order to get a realizable permit flux or the througput of the process the operating pressure will be very very high in case of reverse osmosis, where we will be talking about the separation of the very low molecular solutes like monovalent sodium chloride that will be having a molecular weight around 58.5.

On the other hand if you really go for the larger sized solutes for example; proteins, paints, clay, etcetera which will be having very high molecular weight the osmotic pressure requirement is negligible and therefore the operating pressure requirement will be less. So, osmotic pressure plays a very very important role whenever you are talking about the separation of lower size solutes. For examples, soils in case of desalination, in case of nano filtration, etcetera.

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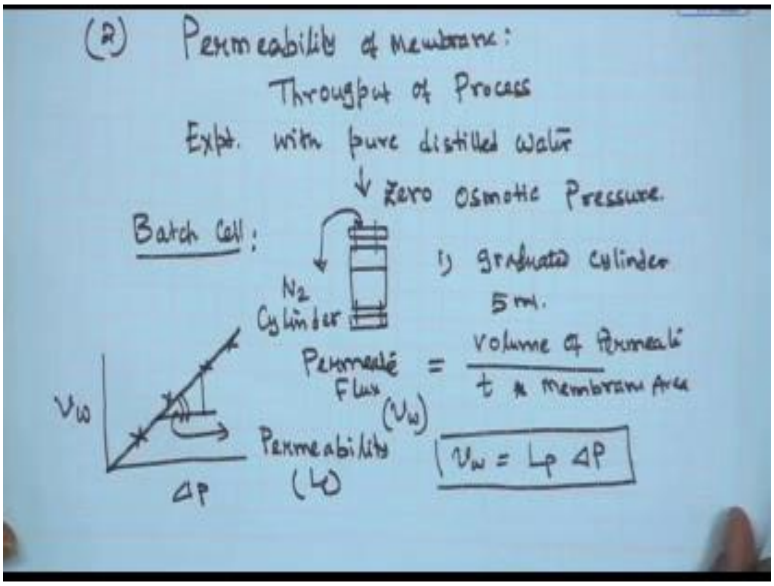

(2) Permeability of Membrane:

Througput of Process

Expt. with pure distilled water

↓ Zero Osmotic Pressure.

Batch Cell:

1) graduated cylinder

5 ml.

$$\text{Permeate Flux } (V_w) = \frac{\text{volume of Permeate}}{t \times \text{Membrane Area}}$$

$$\boxed{V_w = L_p \Delta P}$$

So, next property that will be looking into is the permeability of the membrane. Permeability is very very important, because it is directly related to the througput of the process. It physically means how porous my membrane is? So if my membrane is very porous then I should have a higher permeability of the membrane. It is directly related to the througput of the process and now will be discussing how the permeability of the membrane is measured. Permeability of the membrane is measured in a very straight forward and simple by conducting a simple experiment. We conduct a very small laboratory experiment using the membrane and with pure distilled water.

We do experiment with pure distilled water or deionized water. Why? Because pure water will be having a zero osmotic pressure as we have discussed in the last class. Hence, if you measure the permeate flux at different operating trans membrane pressure drop in a small know batch cell. What is this batch cell? I will be talking about the batch cell and other cells in details later on. Batch cell is basically a small experimental set up having 3 parts; this is a cylindrical body followed by a housing at bottom flange I need to say there is a top flange, we plays the membrane and the bottom flange and then we put that top flange and then there will be tightened by nuts and bolts here, and then we put water let us say filling half of it and then the pressurize using a external nitrogen cylinder.

We set up an operating pressure delta P one and then we measure the permeate flux. How will you measure the permeate flux? Is this permeate flux can be measured by two methods using; first one is using a graduated cylinder. A graduated cylinder you just clock how much time is required to occur to fill up a particular fixed amount of volume let us say 5 ml. So, how much time is required to collect 5 ml of water and. Similarly, this once you gives up get the volume of water or volume of permeate the filtrate is known as permeate in membrane process. Volume of permeate divided by time divided by the area of the membrane area. These will be given the permeate flux. So, we measure the permeate flux at different trans membrane pressure drop and then plot permeate flux typically the permeate flux is denoted by symbol vw, then we plot vw verses delta P.

Now, since we are talking about water its osmotic pressure is low. So therefore, the permeate flux as a function of delta P will be a straight line through origin. So will be getting the data something like this for different pressure drop and then we fit a straight line through them through origin. The slope of this curve will be given by the permeability. And permeability is typically denoted by a symbol L P. Therefore, flux the relationship is linear flux is L P delta P, the proportionality constant is permeability. Therefore, let us look into what is the unit of permeability. The unit of permeability will be.

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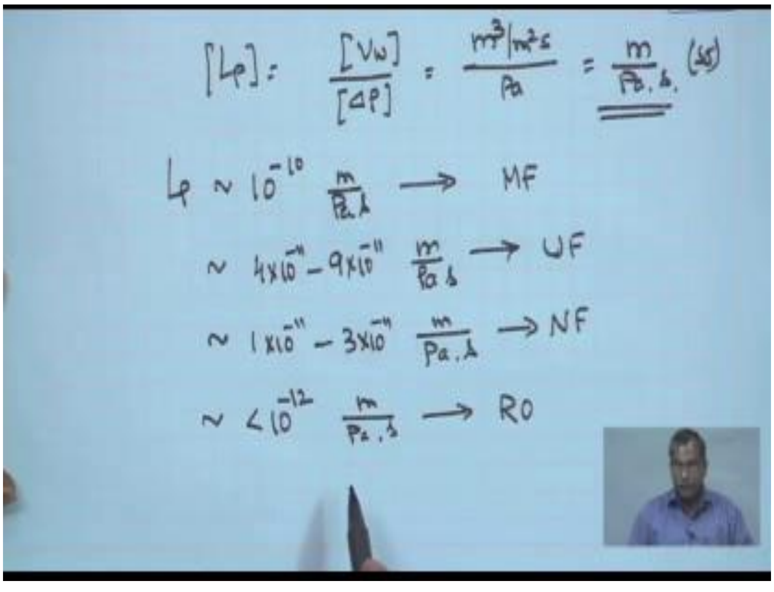

$$[L_p] = \frac{[v_w]}{[\Delta P]} = \frac{m^3/m^2 s}{Pa} = \underline{\underline{\frac{m}{Pa.s.}}} \quad (ss)$$

$$L_p \sim 10^{-10}\ \frac{m}{Pa.s} \longrightarrow MF$$

$$\sim 4\times10^{-11} - 9\times10^{-11}\ \frac{m}{Pa.s} \longrightarrow UF$$

$$\sim 1\times10^{-11} - 3\times10^{-11}\ \frac{m}{Pa.s} \longrightarrow NF$$

$$\sim < 10^{-12}\ \frac{m}{Pa.s} \longrightarrow RO$$

Therefore the unit of permeate flux divided by delta P, what is the permeate flux meter cube per meter square second divided by delta P is in pascal so 1 meter will be cancel out so it will be meter by pascal second. This is the SI unit of membrane permeability. Now by looking into the value of permeability, one can suppose whether you are generated membrane you have cost of membrane and you would like to you know characterize the membrane.

The (Refer Time: 07:08) first characteristic should be the membrane permeability. How porous my membrane is? By looking into the value of membrane permeability in SI unit then one can really get an idea in which membrane you have landed into. For example, if the value of permeability is in the order of 10 to the power minus 10 meter per pascal second that is the SI unit. So, meter by pascal second then you have landed into a micro filtration membrane that is the general conclusion. If you are talking about a membrane which will be having a permeability in the range of let say 4 into 10 to the power minus 11 to 9 into 10 to the power minus 11, so that will be meter by pascal second. That will be the typical range of ultra filtration membrane.

So, if you get this order of magnitude of permeability then you have landed into an ultra filtration membrane. Similarly, if you get a permeability of lower range of 10 to the power of minus 11 let us say 1 into 10 to the power minus 11 to 3 into 10 to the power minus 11 then meter by in SI unit then you have landed into a nano filtration membrane. If you get permeability which will be less than 10 to the power minus 12 meter by pascal second, then you have landed into the reverse osmosis method.

So, by looking into the value of the permeability one can really identify which membrane you have generated or you have cast. So permeability is very very important, it is a really important parameter for modeling the system and identifying the membrane and these can be measured quite easily by conducting an independent experiment as we have discussed earlier. The next important parameter is selectivity or retention.

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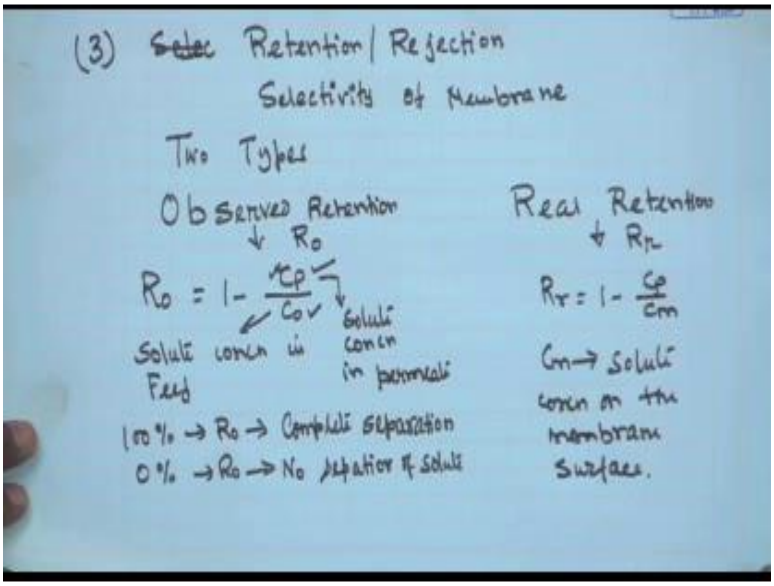

(3) ~~Selec~~ Retention / Rejection

Selectivity of Membrane

Two Types

Observed Retention
↓ R_o

$R_o = 1 - \frac{C_p}{C_o}$

Solute concn in Feed

Solute concn in permeate

100% → R_o → Complete separation

0% → R_o → No separation of solute

Real Retention
↓ R_r

$R_r = 1 - \frac{C_p}{C_m}$

C_m → Solute concn on the membrane surface.

Retention or rejection sometimes it is called Solute Rejection or Solute Retention these gives selectivity of the membrane. So, both permeability and membrane rejection are important properties. Membrane permeability in indicates how porous my membrane is, selectivity size the rejection or retention shows how selective my membrane is. The first one is relate to the througput of the process, thus these one the second one is relate to the extent of separation that can be effected by this membrane.

There are two types of rejection or retention we can talk about. One is the observed retention another is real retention. So, observed retention is denoted by symbol R naught and real retention is denoted by a symbol R r. So, what is R naught? R naught is defined as 1 minus C p divide by C naught. So, what is C naught? C naught is the solute concentration in feed. What is C p? C p is the solute concentration in permeate. So, 100 percent are not indicates complete separation and 0 percent are not indicates no separation of solute.

Therefore, the extent of solute separation can be directly obtained by observed retention and it is a miserable quantity one can really measure the observed retention, because one can get a sample of the filtrate or the permeate stream can measure its concentration through any analytical instruments like refractive index, ultraviolet violet (Refer Time:

11:50) for spectrophotometer, atomic absorption spectrophotometer, there are many equipment or analytical instruments are available for measuring the concentration. So, one can take a sample of the permeate stream and can measure its concentration and C p can be determined. One can take a sample of the feed stream and can measure its solute concentration and can get the value of C naught.

So therefore, R naught is a measurable quantity and it directly indicates that how much separation the membrane is resulting. What is that the real retention? the real retention is the actual potential of the membrane to separate. So, it is defined as 1 minus C p by cm. Now let us define what are the C p and C m are. C p is the having the same definition like here C p is the solute concentration in the filtrate or in the permeate stream. So, what is cm? C m is nothing but the solute concentration on the membrane surface. So, what is the difference between the real retention and observed retention, I will be coming to that in a next minute.

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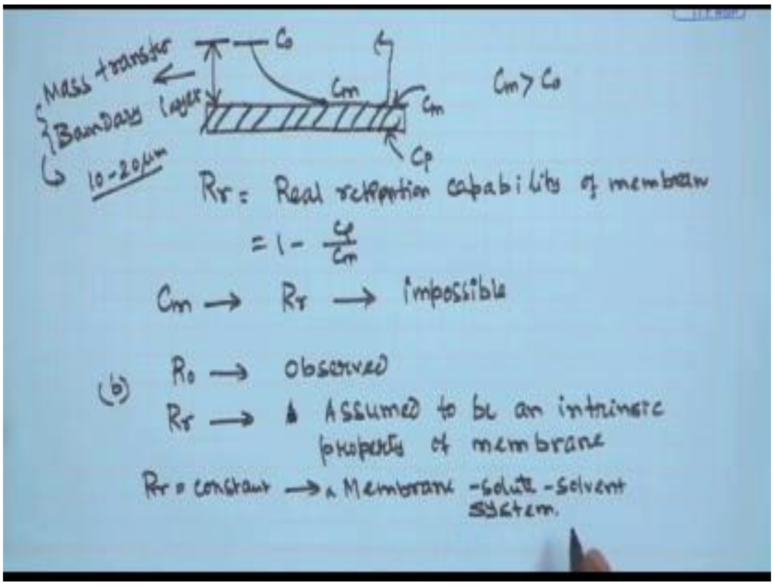

R_r = Real retention capability of membran

$= 1 - \frac{C_p}{C_m}$

$C_m \rightarrow R_r \rightarrow$ impossible

(b) $R_0 \rightarrow$ observed

$R_r \rightarrow$ Assumed to be an intrinsic property of membrane

R_r = constant → a Membrane -solute -solvent system.

In order to explain that just look into an exploded view of what is happening over the membrane surface during a separation process. In a membrane surface it is a pressure driven process, so solutes will be accumulated over the membrane surface. There will be a gradient of solute over the membrane surface starting from concentration in the feed C naught to membrane surface concentration C m. So, concentration since by convection since you are applying pressure into the system by convection or solutes will be convicting towards the membrane surface its concentration will be more at the membrane surface compared to bulk, because they are accumulating on the membrane surface.

So, C m is always greater than C naught. So, what is the actual separation capability of the membrane? The actual separation capability of the membrane is the concentration that is available across two faces of the membrane; these are the upstream side, this is the downstream side of the membrane. In the upstream side what is the concentration of the solute this is C m. What is the concentration of the solute in the downstream or the permeate side? It is C p.

Therefore, real retention capability of the membrane is 1 minus C p divided by C m. So, what is the difficulty in measuring it? The difficulty measuring the real retention is that that C m is very very difficult to measure experimentally, because membrane surface concentration is first of all this is a pressurized system; we are talking about a pressurized system. How do you measure the surface concentration of the membrane? One possibility is that you release the pressure open up the system take a very small sample close to the membrane and measure its concentration, but it will be erroneous because first of all once you are releasing the pressure some of the solutes those are been deposited over the membrane surface again they will be diffuse back to the serve to the bulk. So, that will be reducing the concentration of the on the membrane surface.

Secondly, there will be an existence of gradient of solute from the feed to the membrane surface and this layer is known as the concentration boundary layer or mass transfer boundary layer. And typically the thickness of this mass transfer boundary layer will be in the order of few microns may be 10 micron, 20 micron or even may be 50 micron 120 microns something like that. Now where these masses transfer boundary layer is really a assembly really existing into the system.

Now if you take a sample very close to the membrane first of all whenever you will be collecting a sample close to the membrane some amount of solvent in the bulk that will also be collected. Secondly, even if you are collecting 100 micron of sample from the system close to the next to the membrane skin then you will be really getting an a average concentration you will not be getting an idea of what is the membrane surface concentration over the membrane surface.

So, that really is challenging measurements of membrane surface solute concentration of the membrane is a really very very challenging and it creates a difficulty from measuring it directly. So, direct measurement of real retention is very very difficult and it is not possible. In fact, there are research going on how to do an incentive measurement of membrane surface solute concentration on the membrane surface, but all these experiments all these measurements techniques the latest development, that has been obtained, that is been carried out currently those are in a laboratory small scale with a special attachment like now view ports or you know by doing a special arrangement for collecting surface very close to the membrane surface, but these does not give an accurate result.

So, direct measurement of real retention is not possible. So, there are ways to measure the real retention or membrane surface concentration indirectly, we will be doing it later on so that will be the difference one of the difference between the observe retention and real retention. Observe retention is directly measurable property. On the other hand real retention is not directly measurable property, it can be estimated by an indirect calculations. Second difference is that observed retention is basically what is observed. On the other hand real retention it indicate that it is that the actual selectivity of the solute and the membrane. So therefore, it is assumed to be an intrinsic property of the membrane.

So, real retention is supposed to be constant for a particular membrane solute solvent system. Therefore, if I am talking about the separation of salt using polysulfone membrane and its real retention is a 0.95 let us say. Now if I use the same solute let us say sodium chloride in aqueous solution you if I would like to separate that using a different membrane of different polymer for example, cellulose acetate its real retention will be different. It is a constant intrinsic parameter for a particular membrane solute solvent system.

So, what is the way of measurement of real retention?

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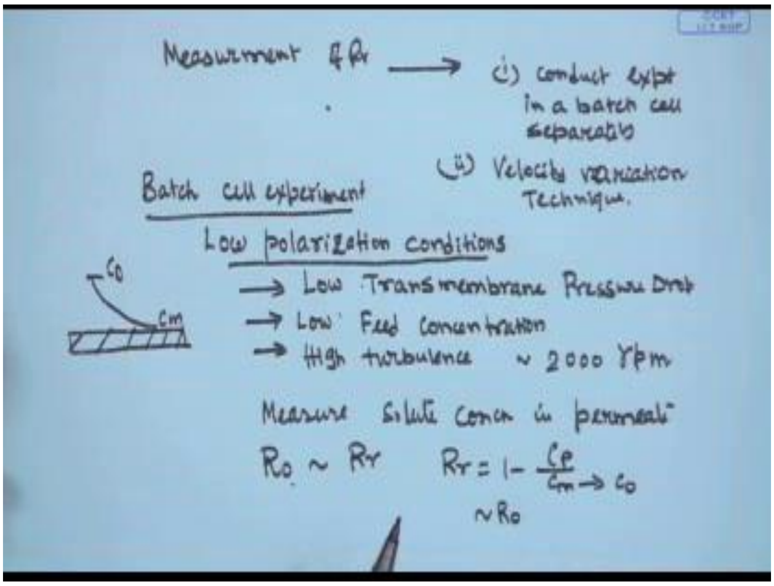

Measurement of R_r → (i) conduct expt in a batch cell separately

(ii) Velocity variation Technique.

Batch cell experiment

Low polarization conditions

→ Low Transmembrane Pressure Drop

→ Low Feed concentration

→ High turbulence ~ 2000 rpm

Measure solute concn in permeate

$R_o \sim R_r \quad R_r = 1 - \frac{C_p}{C_m \rightarrow C_o}$

$\sim R_o$

There are there are two ways; first method of measurement of real retention is you conduct experiment in a batch cell, same batch cell separately. Second by velocity variation technique I will be coming to that later on. Now let us look into the batch cell experiment under a high turbulent. What is this experiment? Now there are certain conditions to control this experiment; to conduct the experiment this conditions are called Low Polarization conditions.

What are the low polarization conditions? One is the low trans membrane pressure drop, low feed concentration, and high turbulence. These 3 conditions are known as the low polarization conditions. What do we mean by low polarization condition? That I am talking about if you remember the figure that I have drawn in the only few minutes back that during the separation process there will be a development of mass transfer boundary layer and there is a polarization of solutes from the feed concentration to the membrane surface concentration.

Now, whenever you will be talking about low trans membrane pressure drop then the (Refer Time: 23:00) operating pressure is less, the amount of convection of solutes to the membrane surface will be less. So therefore, less solute will be deposited above the membrane surface and the thickness of this mass transfer boundary layer will be less. Second is low feed concentration. If the feed concentration itself is less, less amount of solutes will be deposited over the membrane surface by lowering the thickness of mass transfer boundary layer. And similarly under these conditions if you walk in low TMP and low feed concentration. Now if you have high studying or high turbulence typically this turbulence will be around let us say we can effect a turbulence around a with a sterling speed of two thousand rpm in a small laboratory batch cell experiment then the existence of mass transfer boundary layer or formation of mass transfer boundary layer can be nullified.

So, what will happen under the situation? Now if I conduct under this low polarization conditions and experiment in a small batch cell using a solute then a solute of whatever of our interest and conduct the experiment them we measure solute concentration in permeate and we already measured the solute concentration in a in the feed. Therefore, observed retention in this particular case will be tending to the real retention. So, real retention will be 1 minus C p by C m and under these low polarization conditions everything will be mixed up existence of mass transfer boundary layer is minimized, so C m will be approaching to C naught and I will be getting the observed retention. So, whatever the retention I will be observing in this particular case on under this small batch cell experiment in laboratory set ups which is highly under our control the observed retention will be tending to the real retention.

Now this particular low polarization condition may not be realizably in an actual industry scale operation, where the high turbulence you cannot go beyond a particular turbulence in your system because of the limitation of the flow conditions. And low feed concentration may not be realizable because in an actual system whatever concentration you have is up to what we did. And similarly low transformation pressure drop may not be realizable; it is not at all realizable in an industrial system where you are really looking for high througput or higher trans membrane pressure drop.

So therefore, low polarization conditions can be realizable only in a small laboratory scale under controlled experiment, controlled environment and if you really conduct an experiments under that controlled environment then observed retention will be tending to the real retention.

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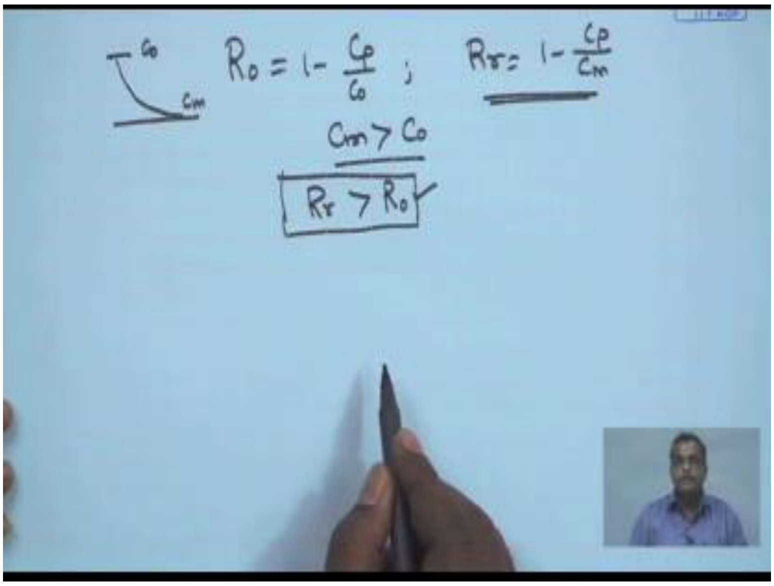

So, if you really look into the compare the value of observed retention and real retention, so that is how the real retention is measured. And if you look into the value of the observed retention and real retention as we discussed earlier all the time that the concentration on the membrane surface will be more compared to the concentration in the bulk. So therefore, C m is greater than C naught, and if you really know do a mathematical manipulation with this relationship between R naught and R r you can find out that real retention will be always greater than observed retention.

So, real retention is basically the actual capacity of the membrane for separating a particular solute or the it really represents the actual selectivity of the membrane, but this is not measurable directly so directly we can measure system performance through observed retention and actual though whatever the retention that we are realizing actually the actual retention capability of the membrane is always higher than that. And real retention is basically an intrinsic property of the membrane solute solvent system and it is an integral part of any model equations in order to quantify how much the actual separation of separation potential of a membrane has in order to separation of the particular solutes.

So, therefore, real retention is a very important parameter as far as the modeling of the membrane base separation is concerned and we have seen at least one method experimental method to estimate the real retention of the membrane towards a particular solute and solvent.

I stop here in this class, in the next class we will be looking into some more properties of the membrane based systems in order to do a proper justice to the process modeling.

Thank you very much.