Principles of downstream techniques in Bioprocess – a short course

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Lecture-11

Membranes

In this class, we are going to talk about membranes and I am going to take two classes on membranes because there are different types of membranes, large variety of membranes that are used. They act as filters they act as separating liquids they act as separating proteins and so on actually. So different types of membranes each using different principles of operation.

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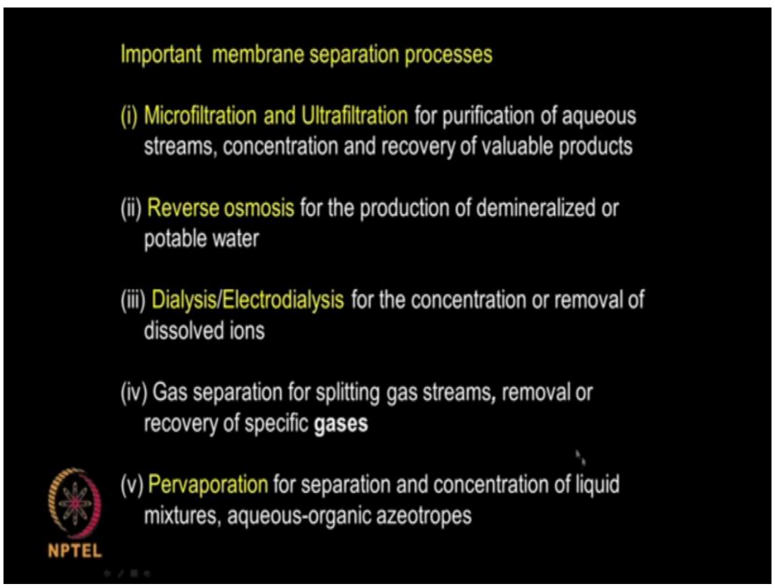

So what are the different types of membranes, especially the important ones that are used for separation? The simplest ones are the microfiltration and the ultrafiltration. So they are almost like your normal filter, so you they separate based on the sizes, they are used on the purification of the aqueous stream concentration and recovery of valuable product. So they can separate based on the size, sometimes they can be separated based on the molecular weight and so on.

Then we come to reverse osmosis, okay this is a useful technique, if you want to remove the minerals present for making the portable water, if you are desalinating sea water, reverse osmosis is the technique that is used. Then we come to dialysis and electrodialysis, they are based on concentration gradient okay and electrodialysis are based on applying electric voltage and the charged ions move based on the voltage that is applied actually.

And dialysis is very very common in medical setting, where patients who suffer from kidney damage, kidney failure are generally treated with this type of technique. So that the salts present in their blood are removed. So we will talk about that. For separating gases, so if I want to separate gases of various sizes, then we can use membranes. Pervaporation is another technique, where we can separate and concentrate liquid mixtures, suppose you have water and an organic

So I want to remove the water present even the minutest amount of water can be removed using this type of technique. Especially this is very useful, if you are concentrating fruit juices. We cannot really heat fruit juices in a distillation column because they may get charred. So we can use this type of technique called pervaporation, so will so many different types of membrane based processes and they all use different principles for their operations okay and we are going to spend some time in each one them.

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So membranes are about 150 microns thick and of course you also have thin microns, which are 1 micron thick, if you look at worldwide consumption of membranes. So it has although this data is 2001, it keeps increasing and increasing because the membrane is used in water treatment in environmental applications in separation processes and many industries. So their usage is going up and up so composite membrane.

That is reverse osmosis membrane take up chunk of membranes application, then comes nanofiltration membrane, then ultrafiltration membrane and so on then the microfiltration membrane okay.

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Characteristcs of membrane separation processes

Process	Driving force	Characteristic features membrane pore size	Separation mechanism
MF	Pressure 0.1-1 bar	0.02-10 μm	Sieving
UF	2-10 bar	0.001 – 0.02 μm	Sieving
RO	10 – 100 bar	Non- porous	Solution diffusion
Dialysis	Concn. differences	1-3 nm	Sieving and diffusion
Electrodialysis	Electrical potential	Mol.wt < 200	ion migration

So these are the driving forces by which membranes operate. If we look at microfiltration generally the pressure is at the order of 0.1 to 1 bar and the pore size is generally 0.02 to 10 micron and what is the principle it is based on sieving that means almost like your filter it captures or retains large particles and allows particles of smaller size. So that is the microfiltration then comes ultrafiltration.

Now you can see the pressure is higher and the particle membrane pore size also has come down. So it is gone down to 0.001 to 0.02 again this is also based on sieving. So I can capture smaller particles I can act also capture molecules of different molecular weights using this but of course the pressure is high. Then comes you have the nanofiltration, that still smaller and then comes the reverse osmosis and we are applying very large pressure almost 100 bar pressure, there are no holes here.

Okay absolutely no pores here and the technique or the mechanism is diffusion based here. Then comes dialysis, as I said they used quite a lot in medical settings. It is based on the concentration difference. So you have a very high salt concentration in the blood which whereas on the you have the dialysite which has very little salt. So which has the concentration difference there is a flow of salt from high concentration to low concentration okay.

The pore size is quite small okay in nanoscale actually, so it is more of a diffusion based although here it is mentioned as sieving it is more of diffusion based. Then you have the electrodialysis, you are applying the electrical potential. So the separation is based on the electrical potential, you can go down to molecular weight less than 200 and the principle is based on ion migration. The ions get moves or migrates based on the electrical charge okay.

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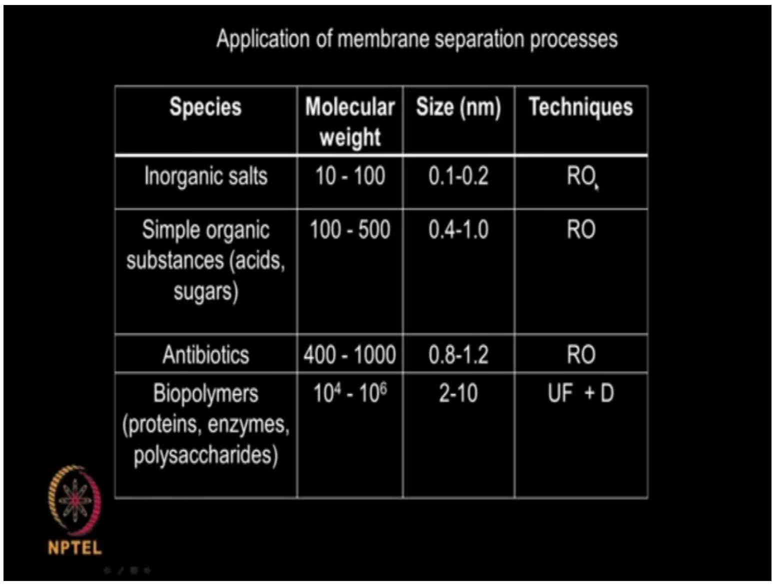

Application of membrane separation processes

Species	Molecular weight	Size (nm)	Techniques
Inorganic salts	10 - 100	0.1-0.2	RO
Simple organic substances (acids, sugars)	100 - 500	0.4-1.0	RO
Antibiotics	400 - 1000	0.8-1.2	RO
Biopolymers (proteins, enzymes, polysaccharides)	10^4 - 10^6	2-10	UF + D

Then comes what are the applications of these membrane separation process? Suppose I have inorganic salts and I want to separate okay, sodium chloride okay, potassium chloride and so on okay and then I use reverse osmosis type of membrane. If I have simple organic substances like acids and sugars okay of slightly higher molecular weight you can go to nanofiltration or we can go to reverse osmosis.

Antibiotics although I have put reverse osmosis, you can even go to microfiltration nanofiltration and then of course reverse osmosis, if you have large material like proteins enzymes. We can go up to ultra filtration so you can see very very small size reverse osmosis and as you keep going up we may be able to go up with the nano, micro and even ultrafiltration okay .

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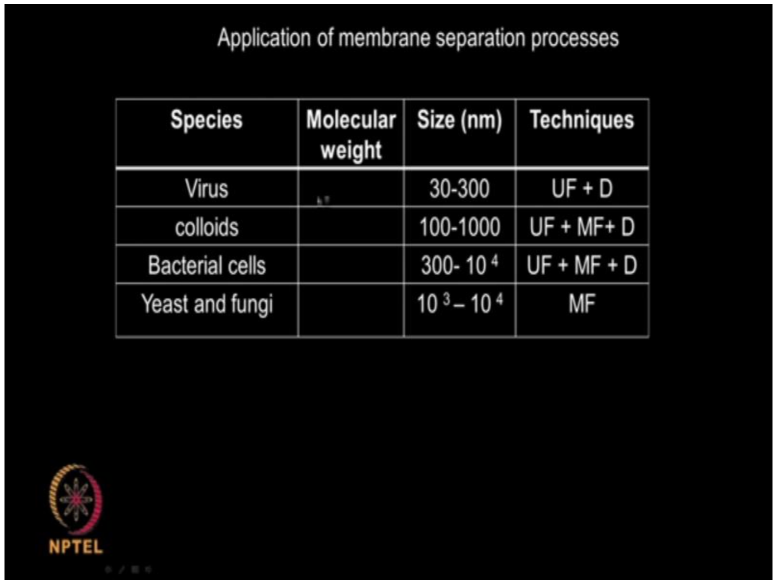

Species	Molecular weight	Size (nm)	Techniques
Virus		30-300	UF + D
colloids		100-1000	UF + MF+ D
Bacterial cells		300- 10^4	UF + MF + D
Yeast and fungi		$10^3 – 10^4$	MF

So if you have viruses which are about 30 to 300 nanometer size, we can go up to ultrafiltration. Colloids, okay they are much bigger in size. They can even go to microfiltration, okay, dialysis, bacterial cells, they are much bigger then you can go to ultrafiltration, microfiltration and dialysis. Yeast and fungi, which are much bigger we can go up to microfiltration.

So depending upon material, metabolite, a polymer, a biopolymer, a bacterial cell, a virus cell, a biomaterial, or a biological molecule, we can use membranes of any type. There are huge number of membranes available and that is the beauty of membrane technology.

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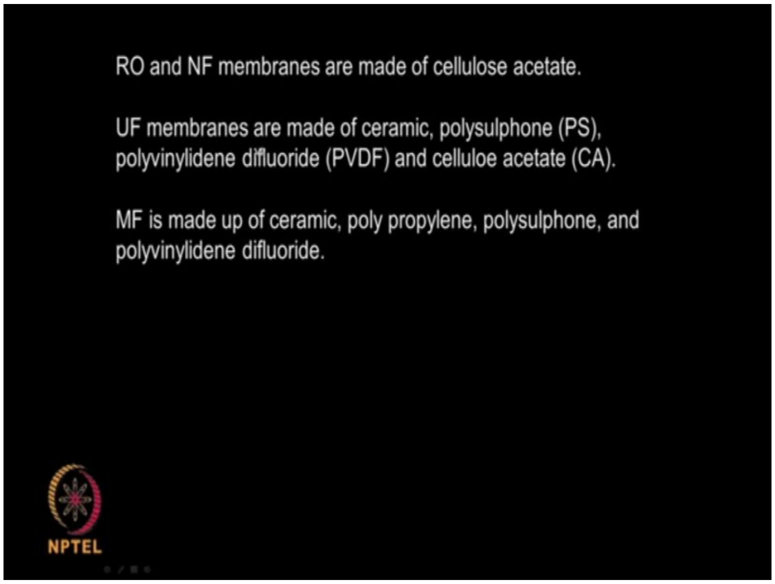

So reverse osmosis and nanofiltration membranes are made up of generally cellulose, acetate, ultrafiltration membranes are made up of ceramics, polysulphone, polyvinylidene difluoride, pvdf, polyvinylidene difluoride and cellulose, acetate so we can see hydrophobic hydrophilic so we can have a wide range of products that could be filtered using ultrafiltration membranes. If you come to microfiltration, it is made up of ceramic propylene, polysulphone, again pvdf type of material okay; again you can have hydrophilic and hydrophobic type of material.

So you have hydrophilic material, we have hydrophobic and hydrophilic material synthetic. These are synthetic polymers and these are inorganic material again, you have some synthetic polymers like pvdf inorganic material, so some of these materials can take up very high temperature some of these materials like cellulose cannot take up very high temperature okay. So we can have wide range of operations depending upon the material of construction of these membranes.

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So operating pressure you have 15 to 150 bar reverse osmosis 5 to 35 bar nanofiltration and 1 to 10 bar ultrafiltration less than 2 bar microfiltration pore size reverse osmosis and nanofiltration is very small 0.002, ultrafiltration 0.02 to 0.02 micron, microfiltration 4 to 0.02 micron again that is the order actually. Because the pore size becoming smaller and smaller and smaller the pressure also inc becomes larger and larger and larger okay.

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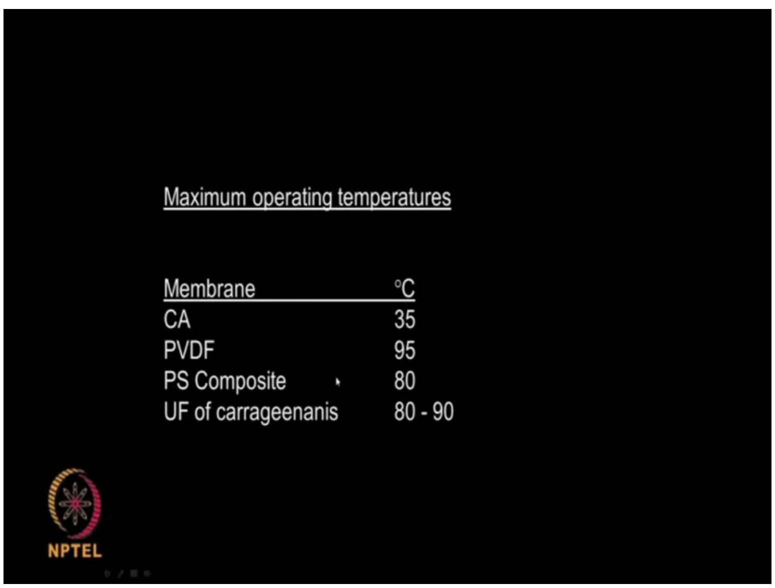

Now maximum operating temperature, as you can see cellulose acetate we have 35 degrees pvdf, 95 degrees polystyrene, composition is 80 and this is about 80 to 90 degrees degree centigrade.

So we can reach almost 100 degree centigrade with synthetic polymers okay as membrane material.

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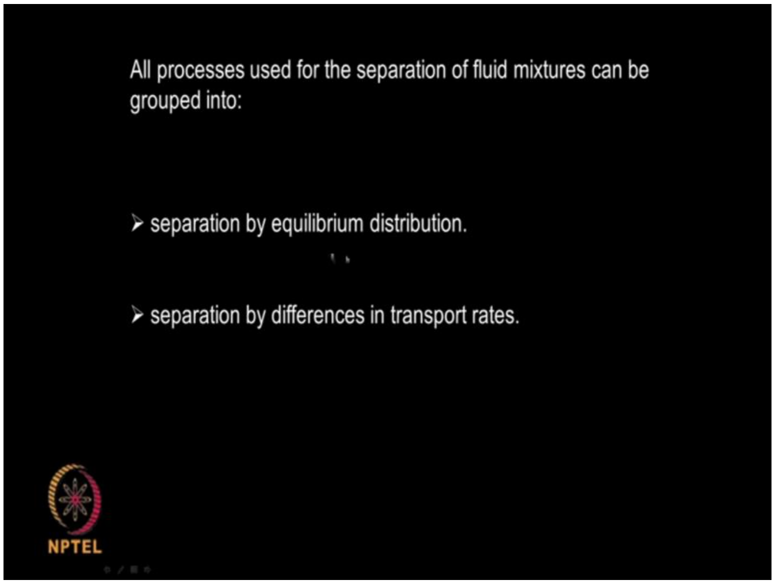

So basically they can the membranes technology can be based on equilibrium distribution separation based on differences in transport rates, okay transport rate happens because of chargers. Transport rate happens because of concentration gradient and so on actually or osmotic pressure okay so these are the proven principles by which the membranes happen.

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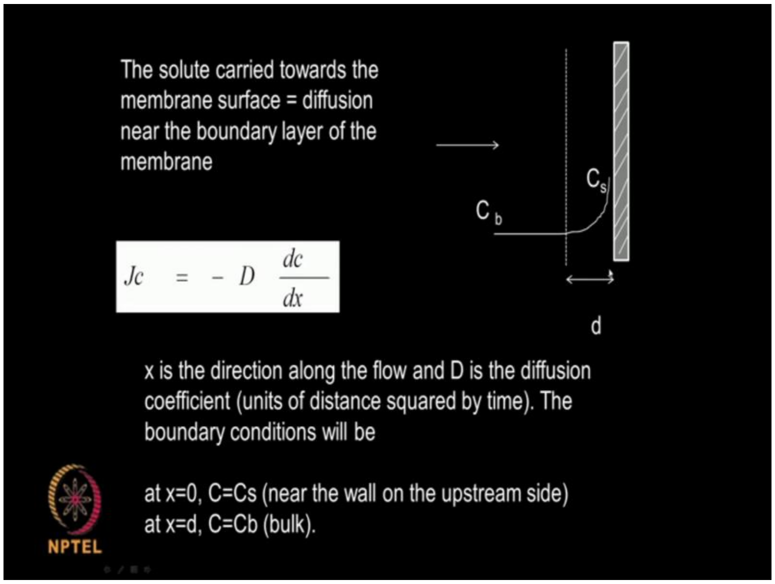

One important point which you need to understand, that is called concentration polarization. So when I am doing a membrane operation, as the fluid moves in this is the membrane material, this is the downstream. Okay so the concentration of the solute keeps building up and generally the concentration of the solute near the upstream wall is very very high okay, much higher than the bulk. So as the concentration keeps building up, that is called the concentration polarization.

The flow keeps going down and after some time, there is no flow at all of the liquid here because of the buildup of this solute here. We can develop a small module for this buildup of this concentration and we can calculate what will be the concentration at the surface of the upstream side of the membrane, okay that is called Cb whereas Cb the concentration in the bulk okay. So we can use Fick's law, we have flow of solute in the bulk and then you have the diffusion here.

So you have J is the flux, then the concentration = - D dc/dx okay, so x is the direction, so x = zero, that means near the wall and upstream side concentration is Cb and at x = d, if you call this as the thickness of a boundary layer a stagnant boundary layer here, at d at x = d concentration is Cb okay. So this is the first order differential equation. Simple equation and we have two boundary condition C = Cb at x = zero and x = d, C =Cb so we can solve them and end up with a simple relation.

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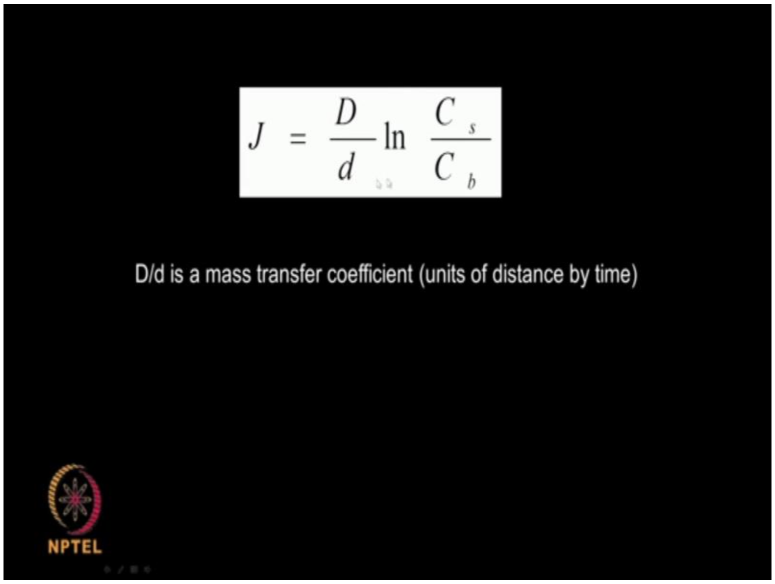

J the flux = D that is the diffusion coefficient small d is the thickness of the bound boundary layer, log Cb / Cb. Cb is the concentration of the solute on the upstream side near the membrane wall, Cb is the concentration at the bulk okay. Now d by d that is D by d is also called mass transfer coefficient. The units will be distance by time, okay whereas D is called the diffusion coefficient.

So I can calculate, if I know the flux and if I know the diffusion coefficient of the solute and if I know the small d that is the thickness of the bilayer, I will be able to calculate what will be Cb that is the concentration that build up on the upstream side of it okay.

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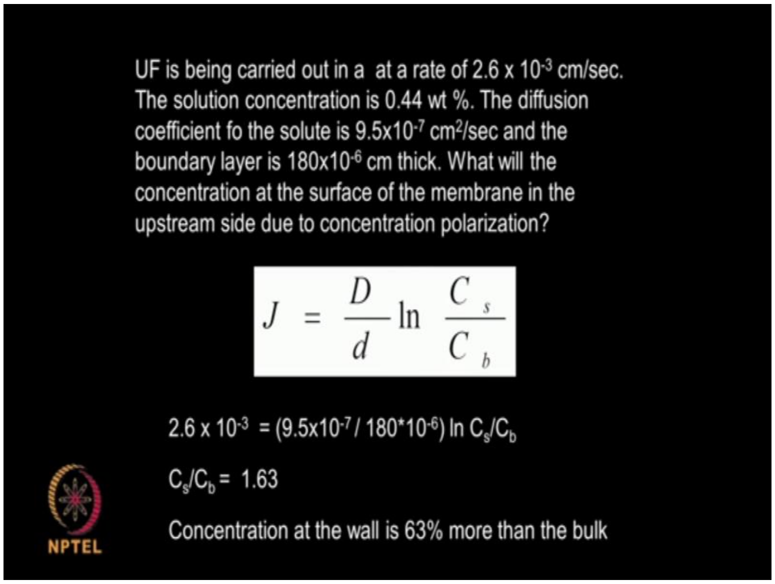

This is a simple problem, am carrying out a ultrafiltration process at a rate of say 2.6 into 10 power - 3 centimeter per second, okay the concentration of the solution in the bulk that is Cb is 0.44 weight square, diffusion coefficient is given like this 9.5 into 10 power - 7 centimeter square/second and the boundary layer is about 180 into 10 to the power - 6 centimeter that means 180 microns okay. What will be the concentration of the surface, that is Cb, I just use the equation okay.

J =D/ d logarithm Cb by Cb, so D is given here 9.5 * 10 power - 7 small d is 180 * 10 power - 6 micron okay. The flux is given on this left hand side, from there I can calculate what I the con Cb by Cb ratio it is coming out to 1.63 that means concentration of the wall on the upstream side will be 63% of the bulk okay. So whatever be the bulk concentration there is a buildup of almost 63%, so as you keep on doing the membrane process the buildup keep on happening and the rate will keep on decreasing actually.

That is the big problem with this type of process actually okay, so you use this equation of course quite a simple equation but quite a simple problem but it will give you a idea about their process.

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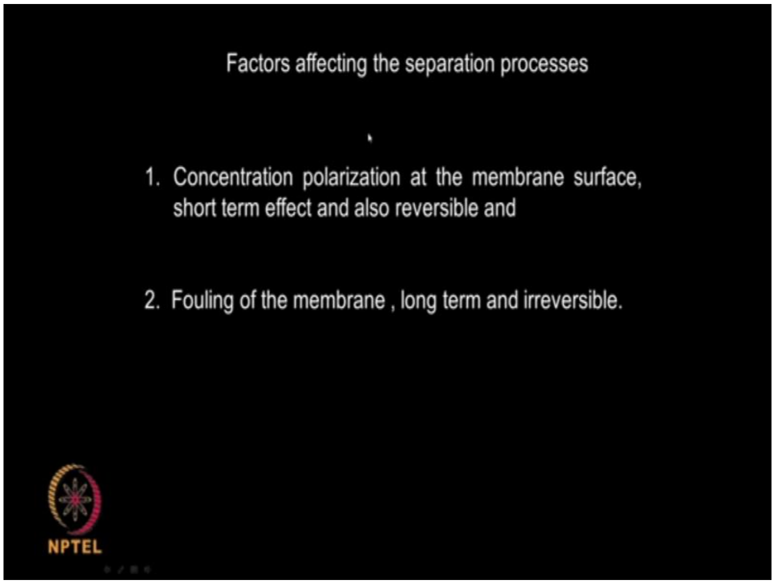

Now what are the factors that affect the separation concentration polarization is a big problem and it is reversible. We can always flush the membrane surface of the upstream, so that whatever has buildup can be removed. Fouling of the membrane, this is a very long term problem and sometimes it is irreversible because the whole membrane surface, there could be a bacterial contamination, biofilm formation and so on actually. So fouling is a big problem.

Whereas concentration polarization can be overcome because it is a reversible process. We can do a back flushing of a cross flow type of approach to remove that okay.

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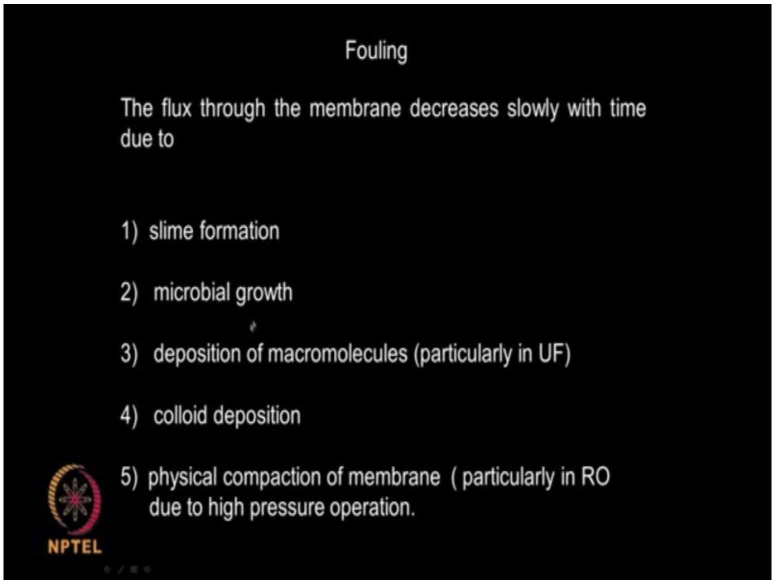

So what are the fouling, the flux through the membrane decrease slowly with time because of slime formation, microbial growth, deposition of macromolecules, especially in ultrafiltration, if you have large molecules they will start depositing. Colloid deposition sometimes physical compaction especially RO membranes, we are talking about 150 bar. So what happens is the whole membrane could get compact. So the flow becomes big problem and finally it may stop.

So all these are problems which are an issue in membrane technology. So there are some ways for overcoming this problems and after sometime, we may have to throw the membrane and buy a new one, so that is operating cost, the cost of the membrane becomes the operating cost.

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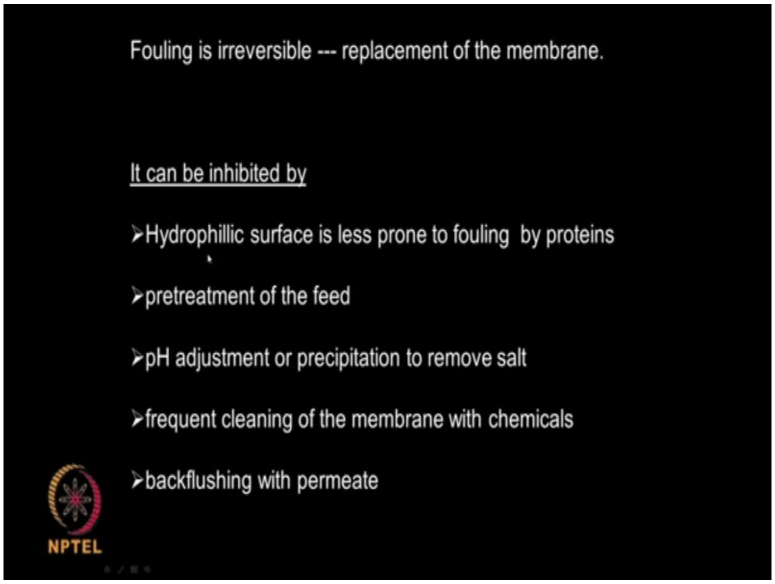

Okay so how fouling is irreversible, so you have to ultimately replace it, can be inhibited, that means it can be slowed down by using hydrophilic surfaces because they are less prone for fouling by protein. Pretreatment of the feed, so we can pretreat the feed, so that fouling does not happen. We can adjust pH initially, so that some salt that are present, it dissolve from precipitate out. So we remove that precipitate and then we can carry out the membrane process.

Frequently we have to clean the membrane with chemicals, back flushing, so you flush backwards, so that whatever if there is concentration polarization or fouling that gets dislodged and removed.

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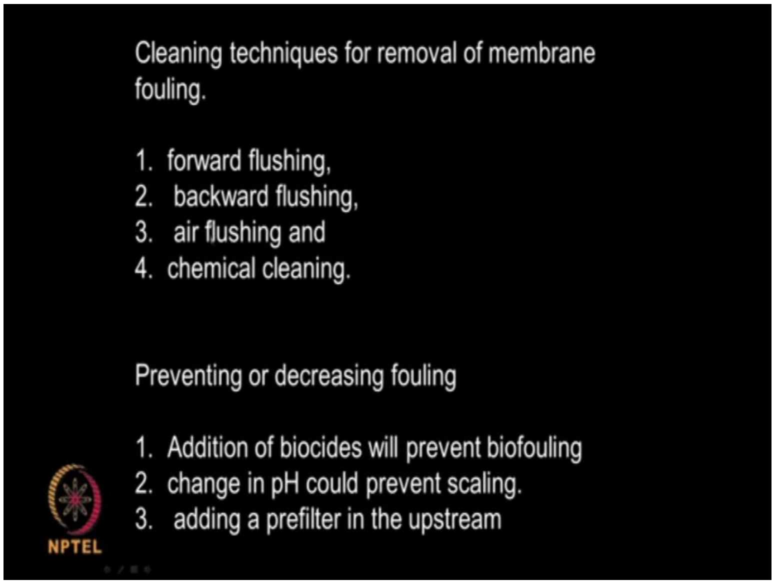

So cleaning techniques forward flushing, backward flushing, air flushing and chemical cleaning all these are different ways methods that are followed to clean your membrane. So how do we decrease or prevent fouling. We can add biocides, so there are chemicals which will prevent biofilm formation and biofouling. We can change the pH so that salts do not precipitate out okay so that will prevent the scaling. We can also have a pre-filter that means you can have a small microfiltration system, which can remove suspended solids.

And then we can adjust the pH once there is a settling of dissolved solids again, we can have another pre-filter. So all these are ways of prevent fouling on a membrane system. And especially for RO membranes they are very very costly so we do not want scaling and we do not want fouling so we may end up having a pre-fill couple for pre-filter in the early stages actually. So we may add a bios pH adjustment filter then you may add biocides and then go to a RO membrane setup.

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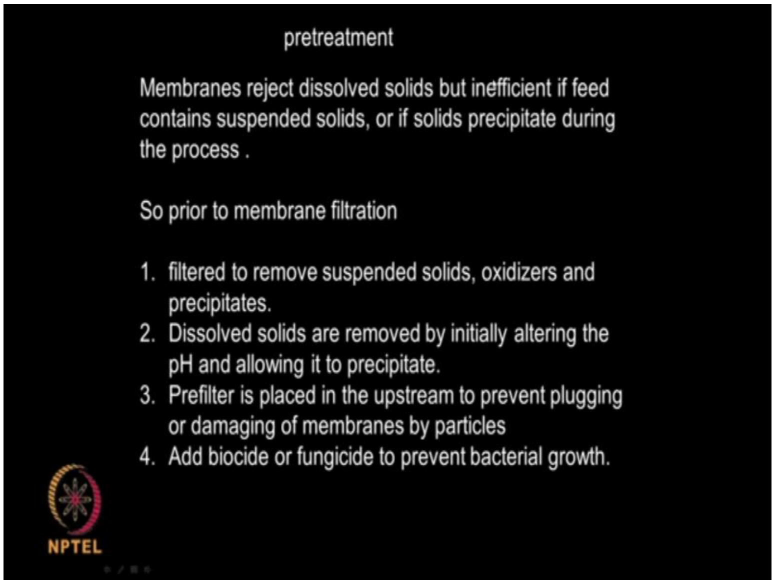

So these are called pretreatments, so if you have dissolved solids, there is no problem but suspended solids are if solids precipitate during the process there is a problem. So prior to membrane filtration, you can have another filter to remove suspended solids oxidizes and precipitates. So we can initially adjust the pH and then dissolved solids may precipitate out and again we can have a settling tank for a filtration, then we can have a pre-filter to prevent plugging, then we can add biocides or fungicides to prevent bacterial growth.

So like I said we can do so many things before they actually go into the membrane, which is very expensive. So we can have different types of membranes early which are cheaper and then go to membrane which are more expensive.

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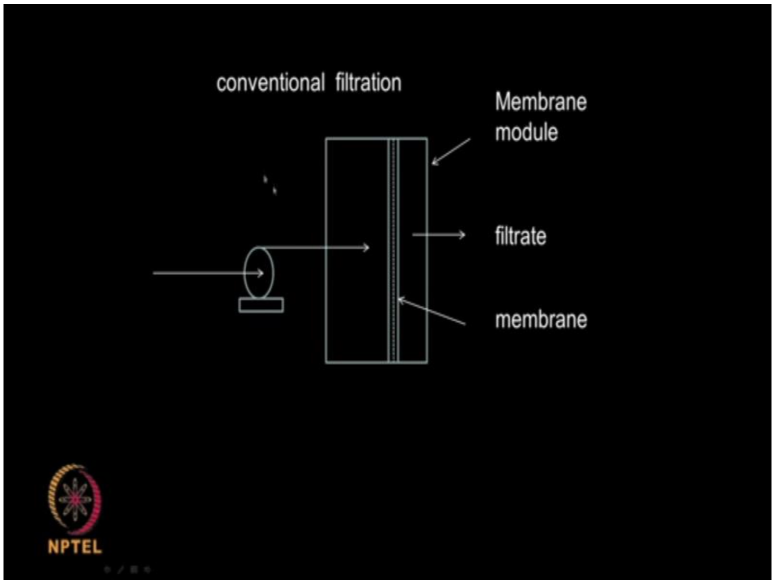

So typically this is how it looks you have a pump and it goes you have the membrane module, then you get the filtrate okay and then this is where the membrane is placed. So this is a direct flow directly hit it is ad then the filtrate comes out. So analogously, we can also have cross flow, I will show you that picture also okay our like we have dead-end filtration and cross flow filtration same way we can have in membranes also.

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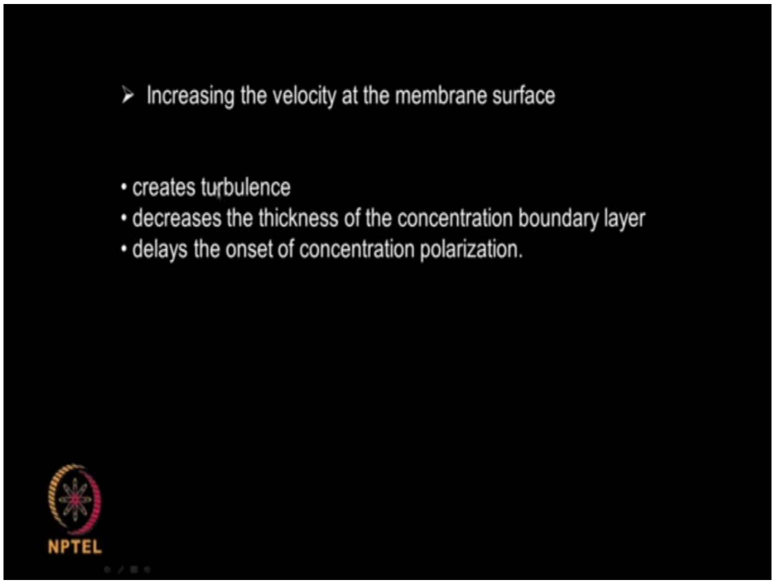

So how do you increase the velocity at the membrane surface? We can create turbulence, we can decrease the thickness of the concentration boundary layer, we can also delay the onset of concentration polarization. All these can increase the velocity of the membrane surface and thereby it can also enhance the entire process that means the separation process.

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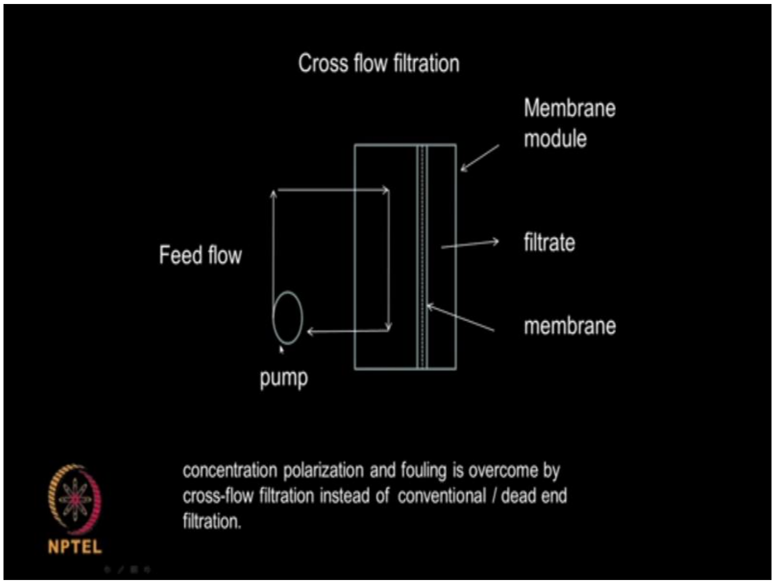

This is the cross flow filtration, if you remember analogous to dead-end, it is cross flow filtration. So here your solution flows parallel, so obviously there is not going be a concentration polarization and there is not going to be a scaling also going to be formed here actually. That is the advantage of this type of design. Just like your filter if you remember few classes back, we talked about cross flow filtration, so here also we can do that.

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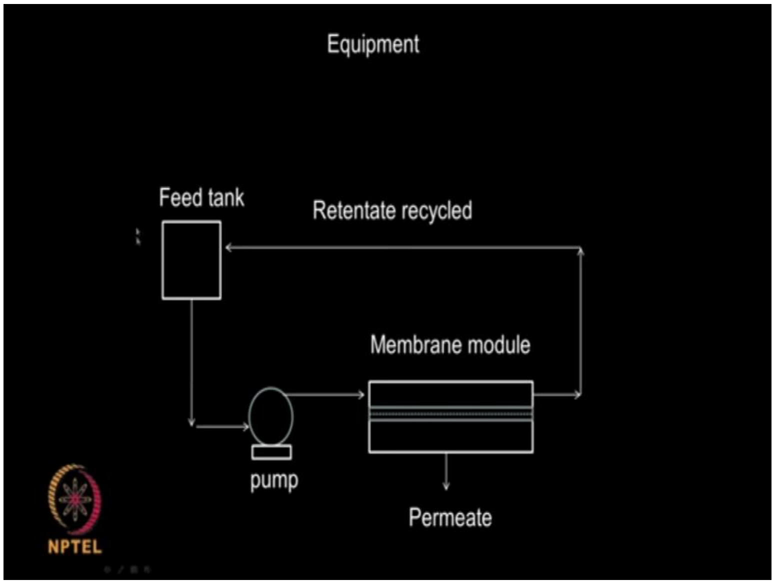

So a typical equipment will look like that, we have a feed tank then you take through a pump have a cross flow, a permeate this is called a permeate okay and then the other one is called the retentate. Whatever that does not pass through the membrane is called retentate and whatever passes through the membrane is called permeate. So we can keep doing this many times until the solution here in the feed tank becomes very very concentrated okay.

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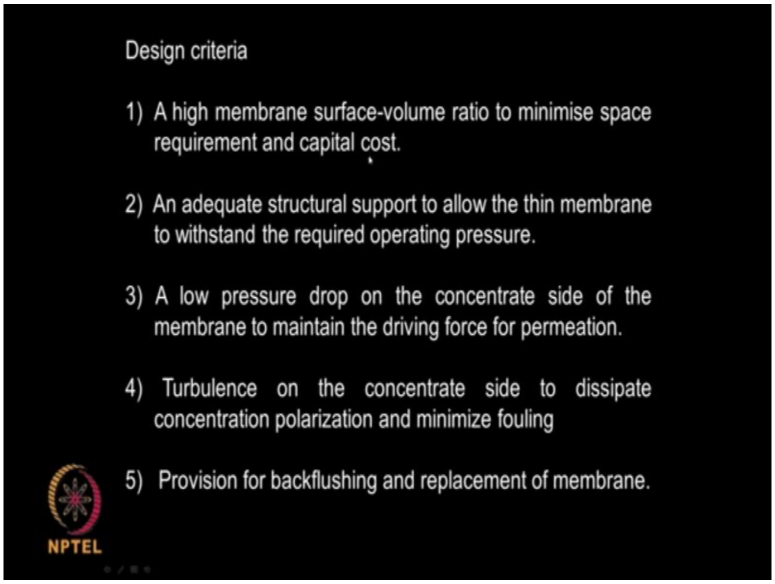

So what are the design criteria? A high membrane surface-volume ratio, this will minimize the space requirement and capital cost, so we can have a very high membrane surface but of course when we I use lot of membranes am going to spend some money on the membrane cost. So you have to remember that. Equipment may be smaller but the membrane cost will go up. So you need to balance that adequate structured support. So that the membrane even thin membranes can withstand very high pressures low pressure drop on the concentrate side.

So we have enough driving force for permeation. Turbulence in the upstream side, so that there is no concentration polarization and minimize fouling provision for back flushing okay, so that whatever scales that are formed can be removed and also we should have option to replace the membrane whatever you do the membrane life is fixed and after sometime, we need to replace the membrane. It could be weeks, it could be months, it could be years. So whenever you replace the membrane, you are adding to the operating cost okay so you need to remember that okay.

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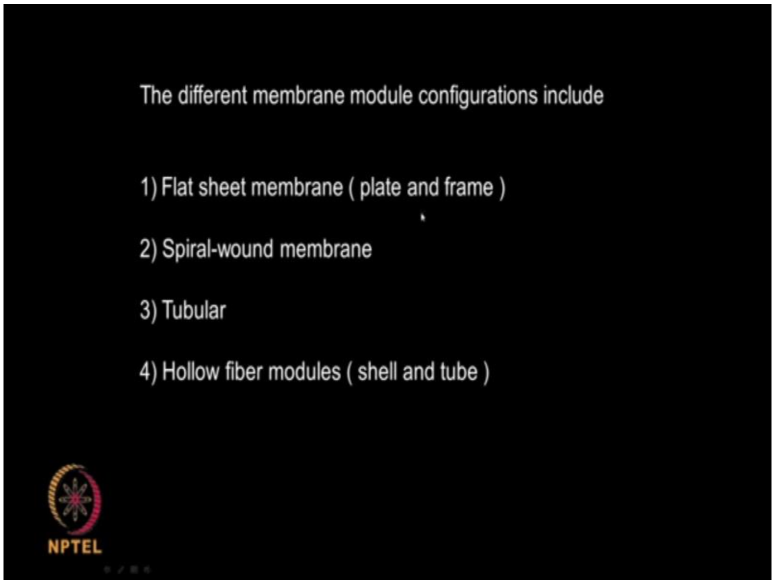

Different types of membranes, that are available, the flat sheet membrane or plate and frame spiral-wound membrane, it is in the form of spiral tubular membrane in the form of tube hollow fiber module that is shell and tube type okay.

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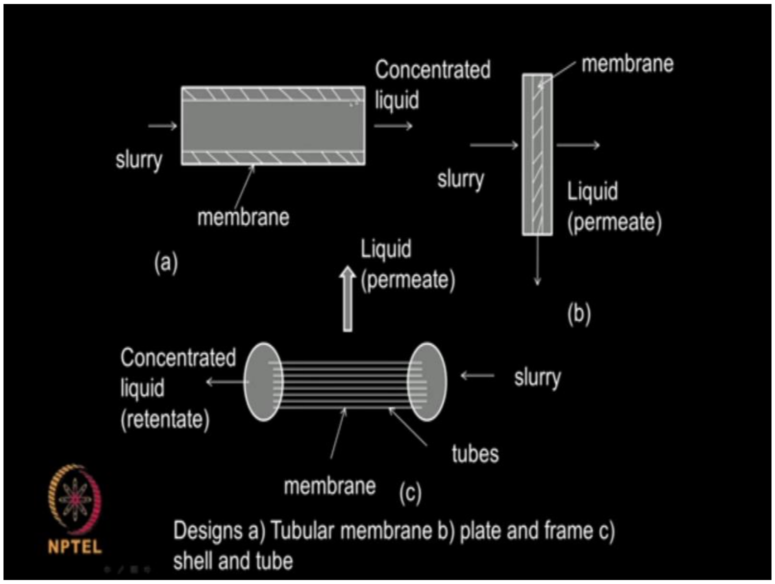

These are some pictures of it right. So this is a tubular membrane, so this is tube and this is a porous membrane and your slurry is flowing like this and the you get the retentate here and then on the along the circumference you get the permeate. The plate and frame type, it is like a plate and frame you have the membrane material in the middle so the slurry flows and then you get the permeate here. Third type is shell and tube almost like heat exchanger; you have lots of cubes, which are made up of membrane materials.

So sort of porous, so the permeate comes on the shell side the retentate comes through the tube side. So you introduce the slurry here, many tubes are there almost like heat exchanger and then the retentate comes out here and then the permeate comes out though the shell side. Okay so these are the various designs, then you have the spiral-wound type also it is like a spiral. So I showed different designs and I showed different materials of construction also that are available for making these membranes.

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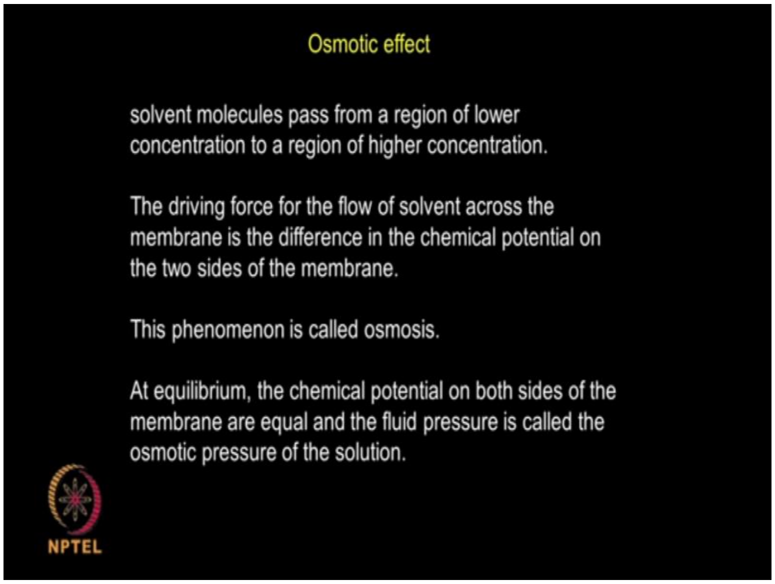

Osmotic reverse osmosis is very important type of membrane process which is used quite a lot for desalinating seawater for making portable water and so on actually. So we need to little bit understand what is osmotic effect and what is osmotic pressure hence we can understand what is reverse osmosis.

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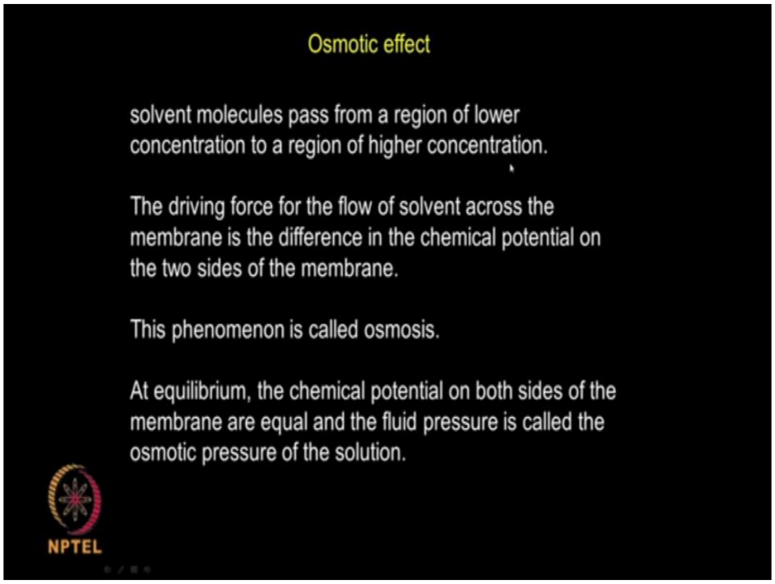

So if you take solvent molecules, they pass through a region of lower concentration okay, to a region of higher concentration, okay lower concentration of solute to a region of higher concentration of a solute. So the driving force for the flow of solvent is chemical potential, so they are trying to balance the chemical potential, so when the concentration of a solution is low, the chemical potential is high.

When the concentration of the solute is high, chemical potential is low and so from a low concentration, a solvent flows to a higher concentration and then there is a balance this is called osmosis. So at equilibrium, the chemical potential on both sides of the membranes are equal and the fluid pressure is called the osmotic pressure of this solution okay.

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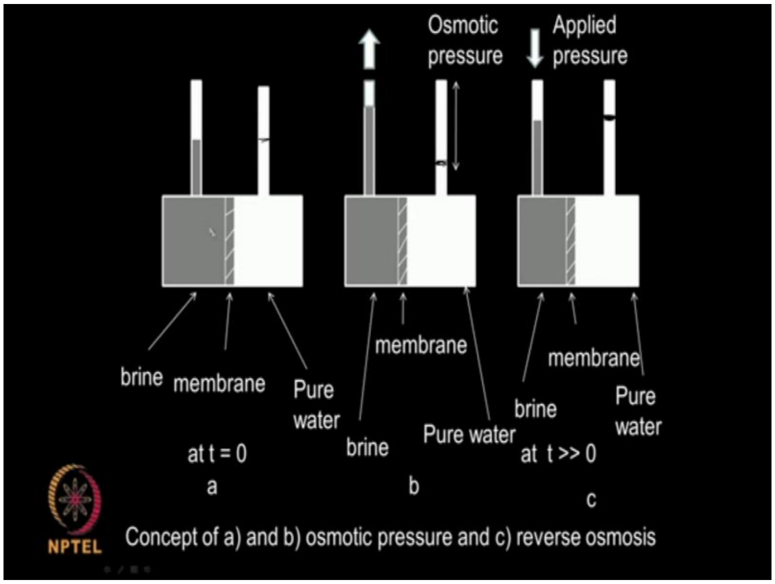

So let us look at this pictorially, so I suppose I have brine salt. Brine is nothing but salt solution. I have pure water okay, so what is happening brine you have salt, so obviously there will be a certain pressure chemical potential and you have pure water. So there will be certain pressure okay and the chemical potential for the water side chemical potential for the brine side. So this chemical potential that this chemical potential, so pure water will start flowing inside across this membrane into this okay until these two chemical potentials match.

So if in order to overcome that if you up this is called osmotic pressure okay. Now in order to overcome that, I need to apply certain pressure, so that they do both balance that is called reverse osmosis okay that is reverse osmosis okay. So we have a pure water on this side and salt solution on this side so because there is salt solution, the chemical potential is low because it is pure water, chemical potential is high. So the chemical potential has to be balanced, the pure water will flow into this and until it balances and that is called the osmotic pressure okay.

And if you want to balance this, you apply some pressure, so they get balanced and that applied pressure it is called the reverse osmotic pressure and that is what is happens in reverse osmosis process. okay In the reverse osmosis, when I apply certain pressure, the solvent here alone will flow the salt or inorganics present will not be able to flow. So I can concentrate this side more and more salt.

And I can collect more and more of the pure solvent. That is what happens in the reverse osmosis, so if I have the seawater and I apply that pressure the osmotic pressure in the form of reverse, that is reverse osmotic pressure, water alone will flow through the membrane and this side will become more concentrated brine okay.

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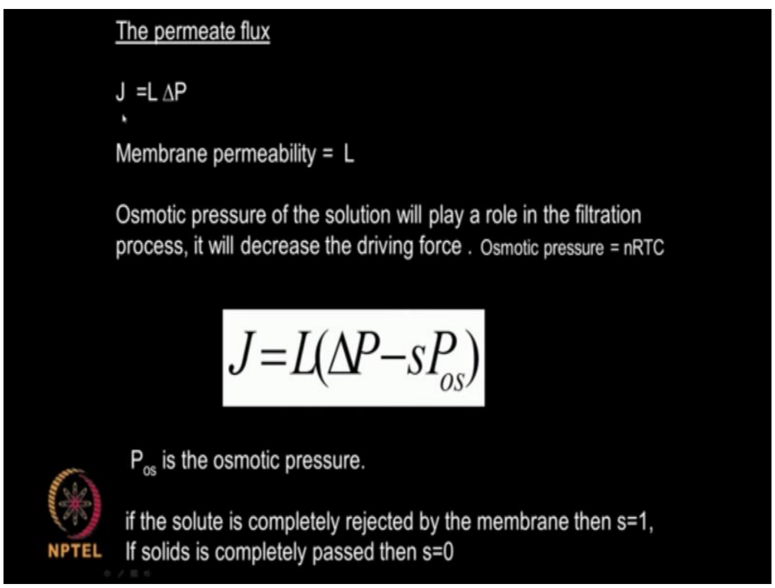

So let us look at some equations the permeate flux J = l into delta p l is called the membrane permeability and delta p is the pressure the delta p is the driving force okay. So but osmotic pressure will also play a very important role, so that will be sort of having a negative effect or it will decrease the driving force okay. J = l delta p - s POS, POS is the osmotic pressure given by if you remember Vant Hoff's relation in rtc, rt gas constant temperature and concentration of the salt.

S, if s = zero okay that means the solids are completely passes s = 1 the solids are completely retained or the solids do not pass through the membrane material. So if the solids do not pass through the membrane material you have on the upstream the concentrated solution with the sol with the solids and you have on the downstream only pure solvent so osmotic pressure will be fully acting.

Whereas if the solid is completely passed, you have on both the sides, solution containing solids. So there won’t be any osmotic pressure acting. So s will become zero so this is the equation which we can use and l is the permeability and generally the manufacturer whose supplier or a supplier of their membrane will give you this l value to you. So if I know the l value from the manufacturer, I can calculate what will be the flux through the membrane.

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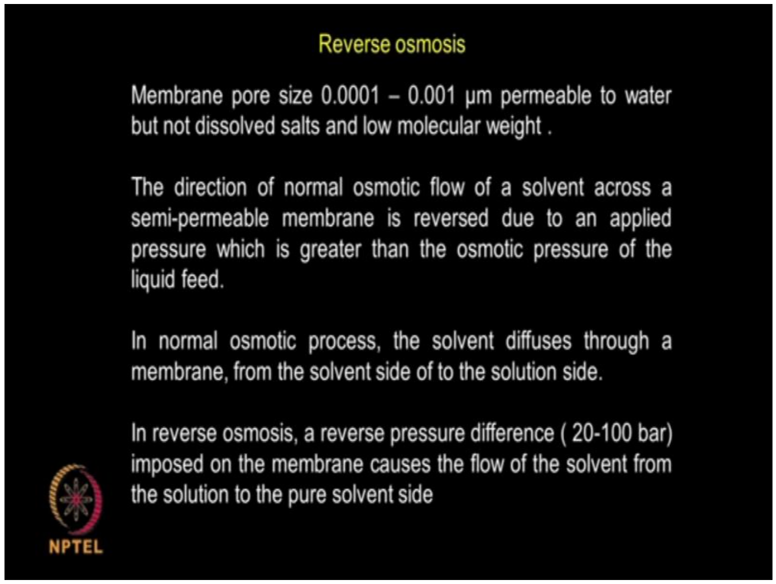

So let us look at each one of the types of membrane when we go along okay in the next class as well as I said we have the starting from microfiltration, we go to ultrafiltration, we go to nanofiltration, we go to reverse osmosis and so on actually. So in reverse osmosis membrane pore size is very very small, okay practically zero and the flow happens okay the flow happens that means the solvent flows through the membrane material and salts and low molecular weight materials are retained.

Okay so in the normal osmotic pressure, as I mentioned before the solvent diffuses before the membrane from the solvent side to the solution side. In the reverse osmosis what we are doing is we are applying very large pressure so that the solvent flows from the solution side to the solution side that is what happens if you remember this. It flows from the solution side to the pure solvent side that is what it does in reverse osmosis.

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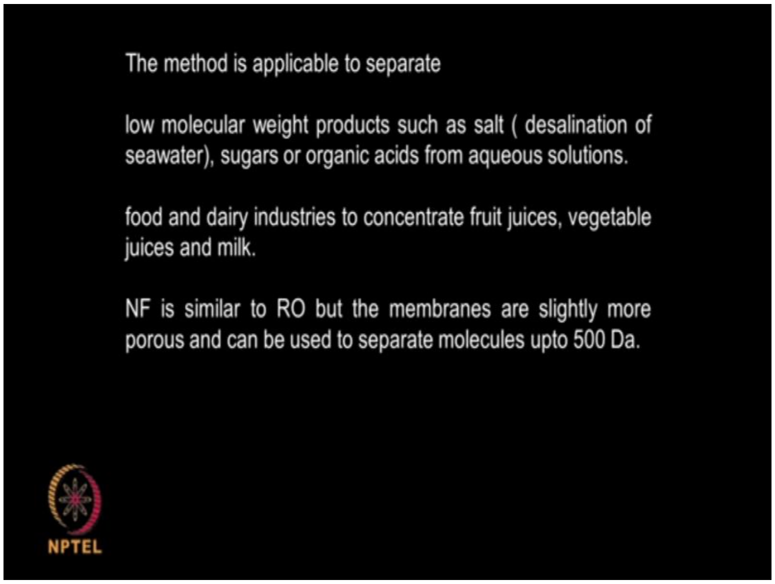

So we can use it for separating low molecular weight products such as salts desalination of seawater, sugars, organic acids from aqueous solution, it is used quite a lot in food and diary industries to concentrate fruit juice that means I can just remove whatever water is present little amount of water present in my fruit juice. We can use it for vegetable juices so I can operate it at room temperature, I do not have to heat up the fruit juices to remove the water okay.

So that is the advantage of reverse osmosis but the running cost is high, the reverse osmosis membrane cost is very high, then comes the nanofiltration. This is almost like a reverse osmosis but the membranes are slightly more porous. So we can use it for separating molecules up to find at Dalton. You can see here it is very very small and here we can reach for up to 500 dalton actually. So we will continue this membranes in next class also.

Thank You Very Much