Chemical Process Utilities
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Lecture - 14
Inhibition and Water Treatment

Welcome to the concept of inhibition and water treatment under the aegis of chemical process utilities. We have previously covered the concept of the mineral scale and deposits in the water. We had a brief discussion about the concept of biofouling, colloidal fouling, and corrosion-related fouling, and we discussed the concept of inhibition and different aspects of inhibition.

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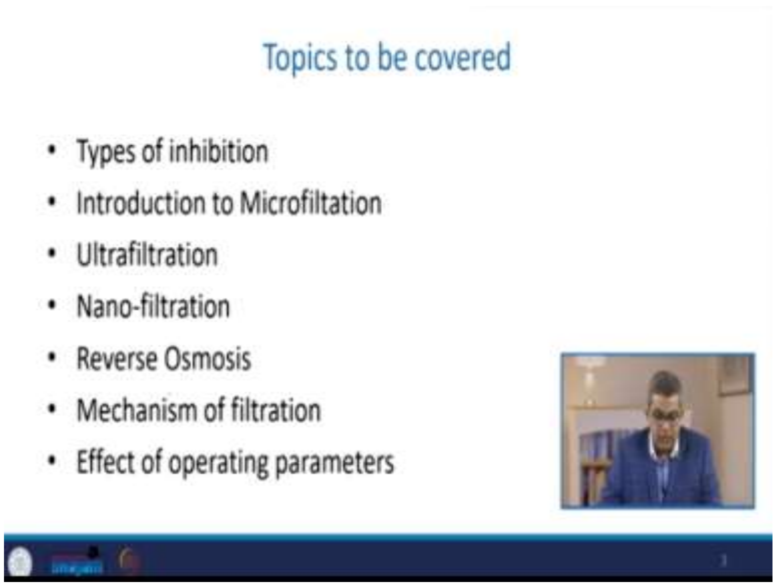

In this particular lecture, we will discuss the remaining part of the types of inhibition, and then we will introduce the concept of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. We talked about reverse osmosis quite frequently in the previous lectures, the mechanism of filtration, and the effects of various operating parameters, which are important for consideration.

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Let us discuss the incorporation of various impurities. Impurities adsorbed on the crystalline interface can reduce the growth rate by reducing or hindering the movement of steps on the crystal surface. Depending on the amount and strength of adsorption, impurities can be completely immobile to completely mobile on the crystal surface. So, that depends on the various scenarios.

The strength of bonds between the lattice molecule and the impurity determines the relative mobility of the impurity in question.

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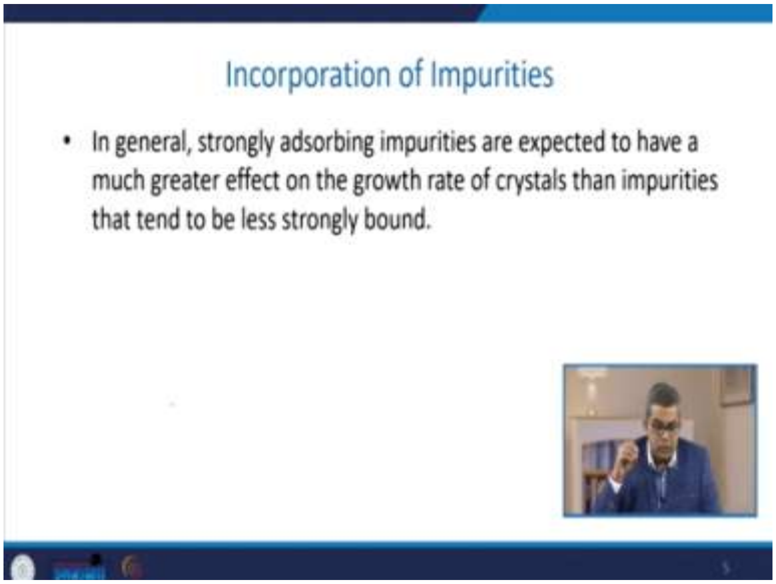

So, in general, strong adsorbing impurities are expected to have a much greater effect on crystal growth rate than impurities that tend to be less strongly bound.

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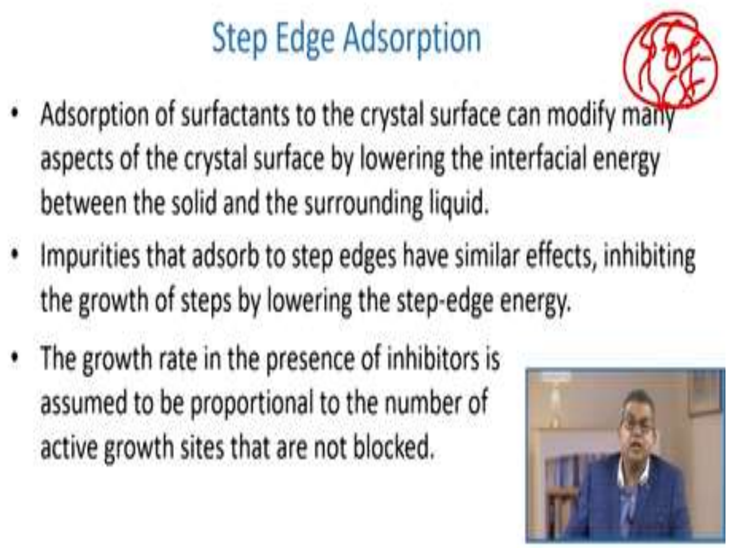

Again, coming back to this step edge adsorption, the step adsorption suggests that surfactant adsorption to the crystal surface can modify many aspects of the crystal surface by lowering the interfacial energy between the solid and surrounding liquid. So, you know that the interfacial energy or surface energy is triggered every time and all these phenomena. Impurities that absorb the step edge have similar effects, inhibiting the growth of steps by lowering the step-edge energy.

The growth rate in the presence of inhibitors is usually assumed to be proportional to the number of active growth sites that are not blocked. So, these active growth sites play a very important role in this step-edge adsorption.

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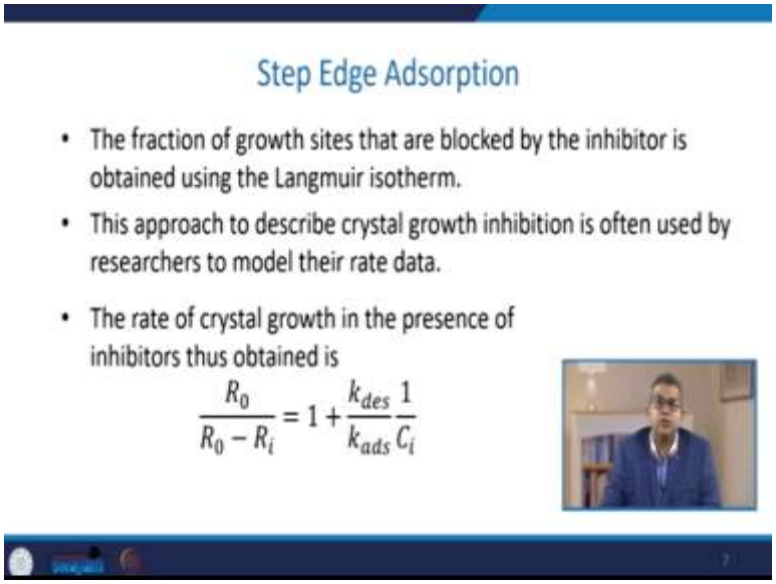

The fraction of usually the growth sites that are blocked by the inhibitor is obtained using the Langmuir isotherm, and it is a very common isotherm. The approach usually describes the researcher using crystal growth inhibition to model their rate data. The crystal growth rate in the presence of an inhibitor is obtained as

$$\frac{R_0}{R_0 - R_i} = 1 + \frac{k_{des}}{k_{ads}} \frac{1}{C_i}$$

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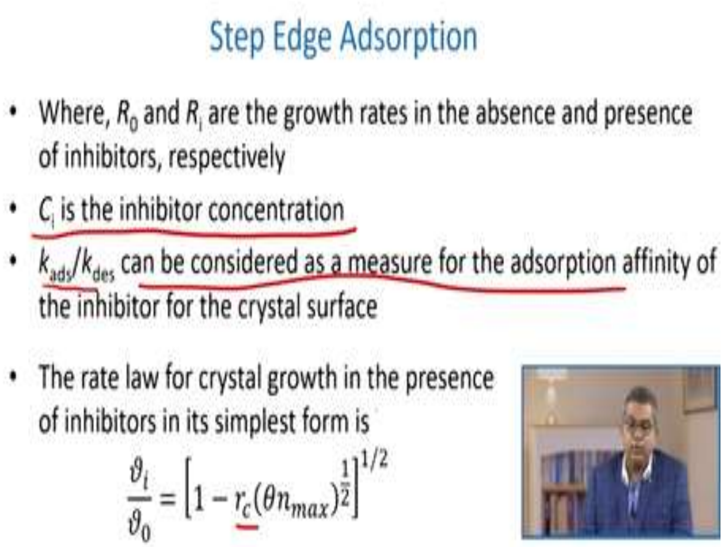

Where, R_0 and R_i are the growth rates in the absence and presence of inhibitors, respectively

C_i is the inhibitor concentration

k_{ads}/k_{des} can be considered as a measure for the adsorption affinity of the inhibitor for the crystal surface.

- The rate law for crystal growth in the presence of inhibitors in its simplest form is

$$\frac{\vartheta_i}{\vartheta_0} = \left[1 - r_c(\theta n_{max})^{\frac{1}{2}}\right]^{1/2}$$

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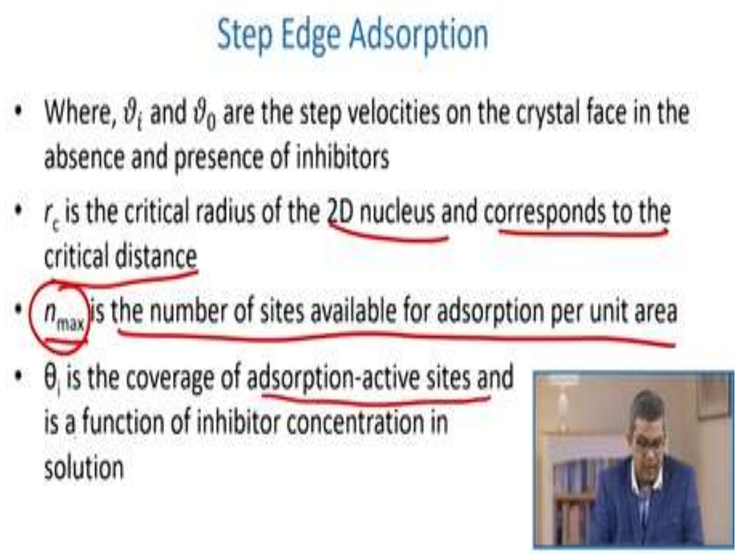

Where, ϑ_i and ϑ_0 are the step velocities on the crystal face in the absence and presence of inhibitors

r_c is the critical radius of the 2D nucleus and corresponds to the critical distance

n_{max} is the number of sites available for adsorption per unit area

θ_i is the coverage of adsorption-active sites and is a function of inhibitor concentration in solution

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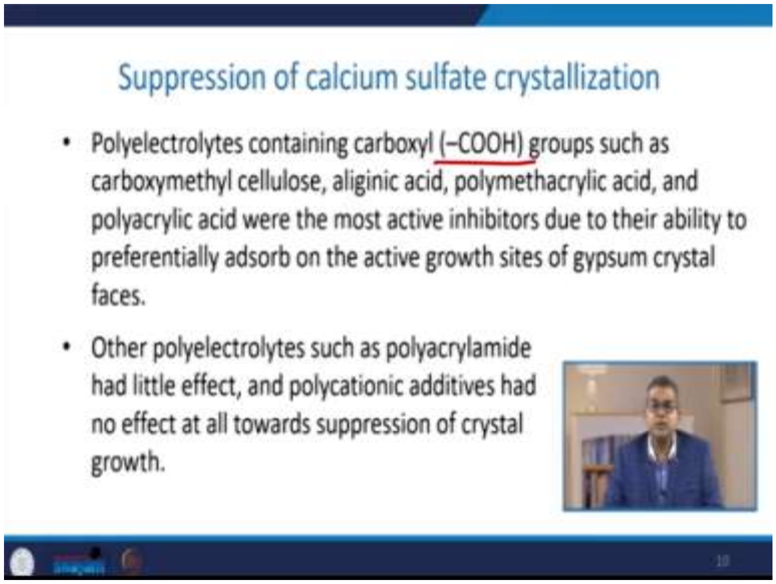

Now, suppression of calcium sulfate crystallization, polyelectrolytes containing the carboxyl COOH groups such as carboxymethyl cellulose CMC, alginic acid, polymethacrylic acid, and polyacrylic acid were the most active inhibitors due to their ability to preferentially adsorb on the active sites of gypsum crystal faces. Other polyelectrolytes, such as polyacrylamide, had little effect and polycationic additives had no effect at all on the suppression of crystal growth.

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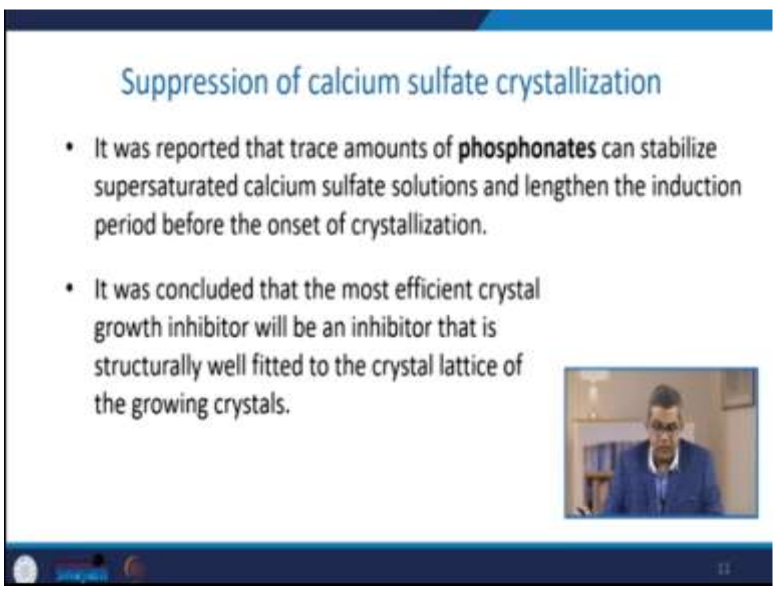

Now, it was reported by various scientists that a trace amount of phosphonates can stabilize the supersaturated calcium sulfate solution and lengthen the induction period before the onset of crystallization. So, researchers have concluded that the most efficient crystal growth inhibitor will be inhibitors that are structurally well fitted to the crystal lattice of the growing crystals.

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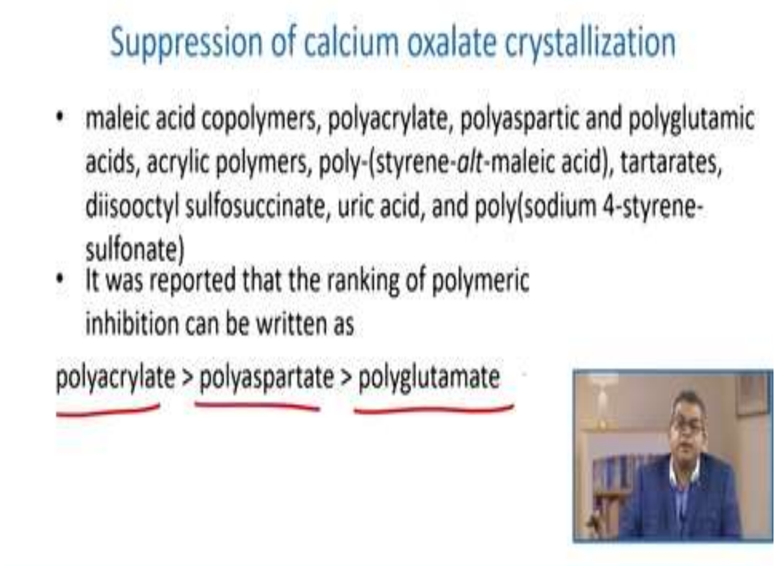

maleic acid copolymers, polyacrylate, polyaspartic and polyglutamic acids, acrylic polymers, poly-(styrene-*alt*-maleic acid), tartarates, diisooctyl sulfosuccinate, uric acid, and poly(sodium 4-styrene-sulfonate). It was reported that the ranking of polymeric inhibition can be written as polyacrylate > polyaspartate > polyglutamate

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Let us introduce the various microfiltration tools.membrane separation technologyare based on the process known as crossflow filtration, which allows the continuous processing of liquid streams.

So, in this particular process, the bulk solution flows over and parallel to the membrane surface and because the liquid is pressurized, it adopts a force water is forced through the membrane.

The turbulent flow of the bulk solution over the surface minimizes the accumulation of particulate matter.

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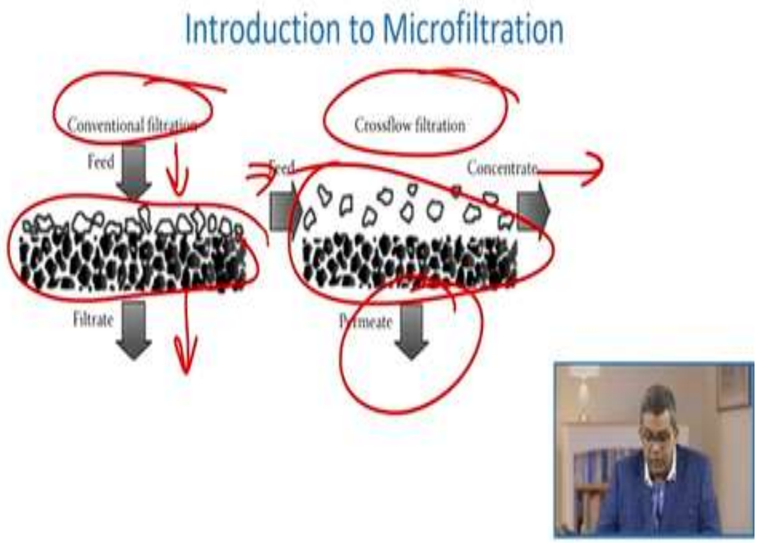

Here you see this conventional filtration, this is the membrane you are supplying the feed over here, and the filtrate is coming out. Where is this is the conventional filtration, where this is the crossflow filtration, where feed is supplied, and the concentrate is coming out and permeating over here, so this is your filtering media or filtration media.

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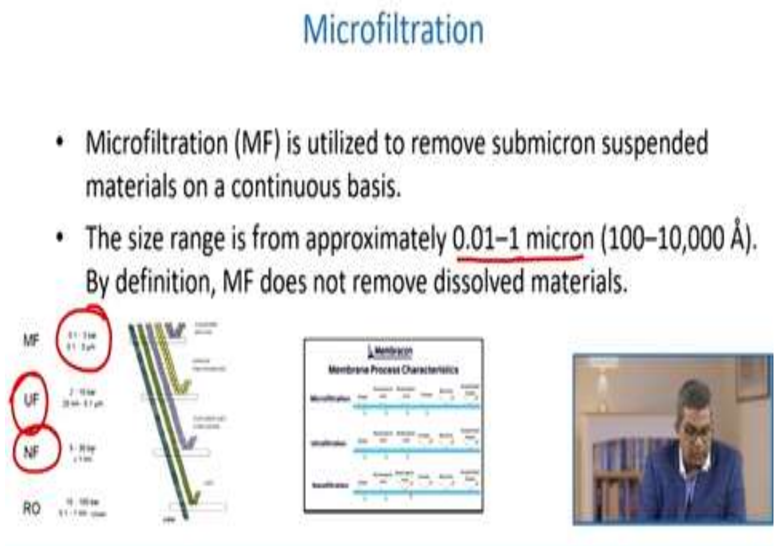

So, microfiltration is utilized to remove the sub-micron suspended material on a continuous basis. The size ranges from approximately 0.01 to 1 micron or 100 to 10000 angstrom. By definition, microfiltration does not remove the dissolved materials. You can see that the different specification of microfiltration lies in 0.1 to 3 bar 0.1 to 5 micrometer, similarly ultra-filtration 2 to 10 with the pressure applicability and 20 nanometres to 0.1 micrometer. Nanofiltration 5 to 30 bar greater than 1 nanometre, and reverse osmosis is 10 to 100 bar 0.1 to 1m; that is very close.

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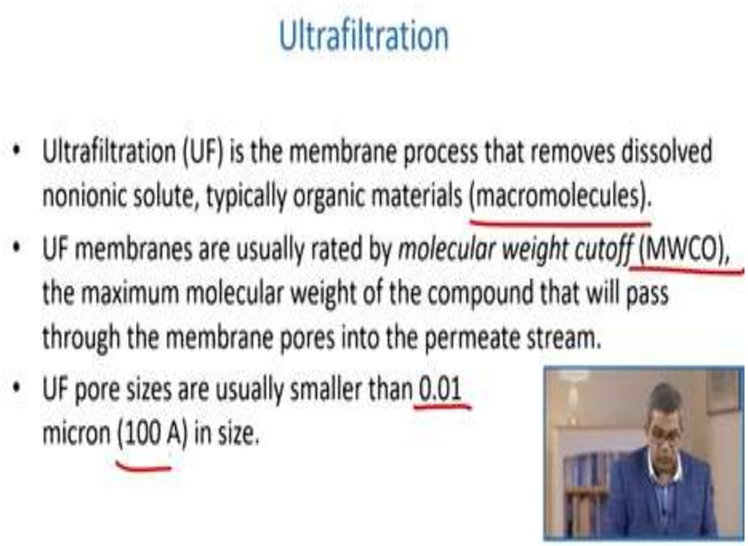

Let us briefly discuss ultrafiltration. Ultrafiltration is the membrane process that removes dissolved non-ionic solutes, typically organic material or sometimes referred to as macromolecules. Ultrafiltration membranes are usually rated by the molecular weight cut off and sometimes referred to as MWCO, the maximum molecular weight of the compound that will pass through the membrane pores into the permeate stream. So, ultrafiltration pore size are usually smaller than 0.01 micron or 100 angstroms in size.

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The microfiltration and ultrafiltration separate contaminants based on the sieving process; and that is, any contaminant too large to pass through the pore is rejected and exists in the concentration stream, which we have shown in an earlier photograph.

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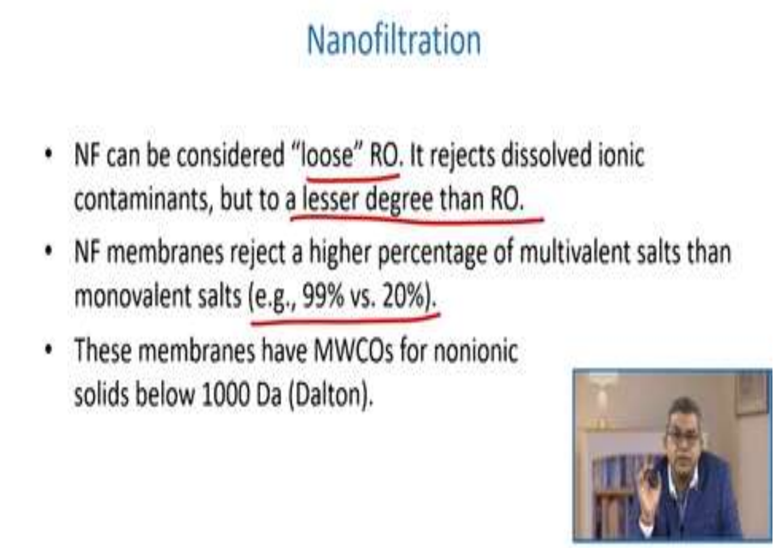

Now, let us have a discussion about nanofiltration. The nanofiltration can be considered loose reverse osmosis. It rejects the dissolved ionic contaminants, but to a lesser degree than reverse osmosis. Nanofiltration membrane rejects a higher percentage of multivalent salts than monovalent salt, which is 99% versus 20%. These membranes have molecular weight cut off for non-ionic solids below 1000 Dalton.

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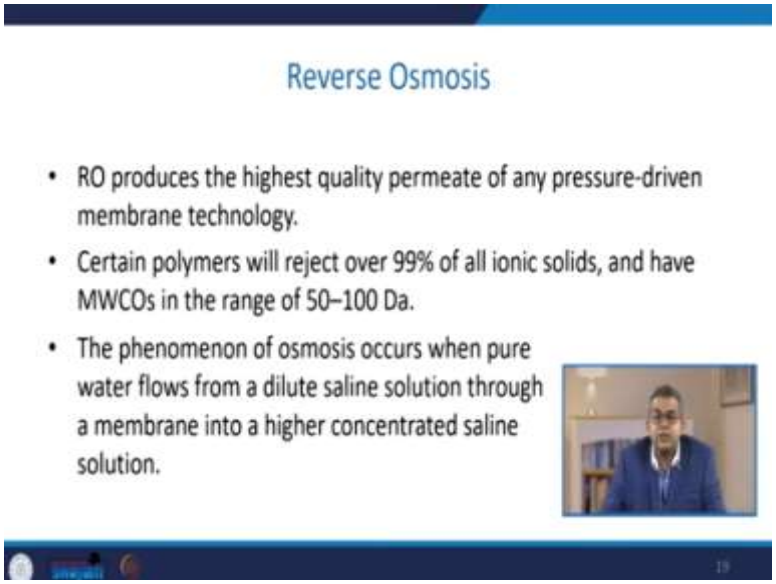

Let us have a discussion about reverse osmosis. The reverse osmosis produces the highest quality permeate of any pressure-driven membrane technology. Certain polymers will reject over 99% of all ionic solids and have molecular weight cut off in the range of 50 to 100 Dalton. The phenomenon of osmosis occurs when pure water flows from dilute saline solution through a membrane into higher concentration saline solution.

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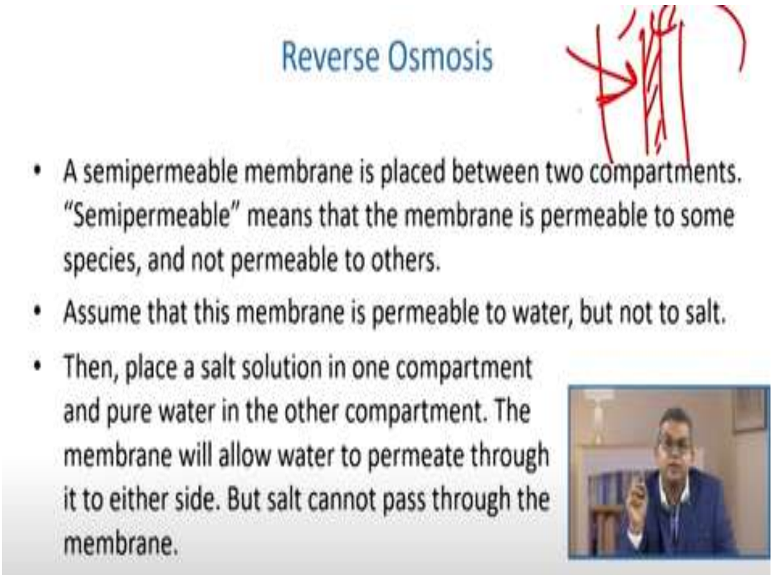

The semipermeable membrane is usually placed between the two compartments like this, and these are the compartments. The semipermeable, sometimes referred to as the membrane, is permeable to some species and not permeable to others, or you can say it is a very selective one. Assume that this membrane is permeable to water but not to salt. So, place the salt solution in one compartment and pure water in the other.

The membrane will allow water to permeate through it to either side, but salt cannot pass through the membrane.

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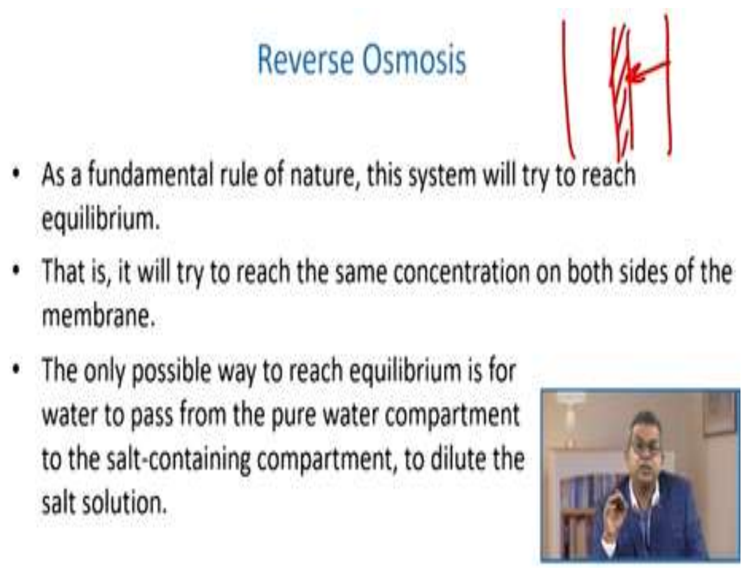

Now, as a fundamental rule of nature, the system will try to reach equilibrium. Obviously, because one compartment has a higher concentration, the other is a lower concentration. So, it will try to match the equilibrium, and that is it will try to reach the same concentration on both sides of the membrane. The only possible way to reach equilibrium is for water to pass from the pure water compartment to the salt-containing compartment to dilute the salt solution.

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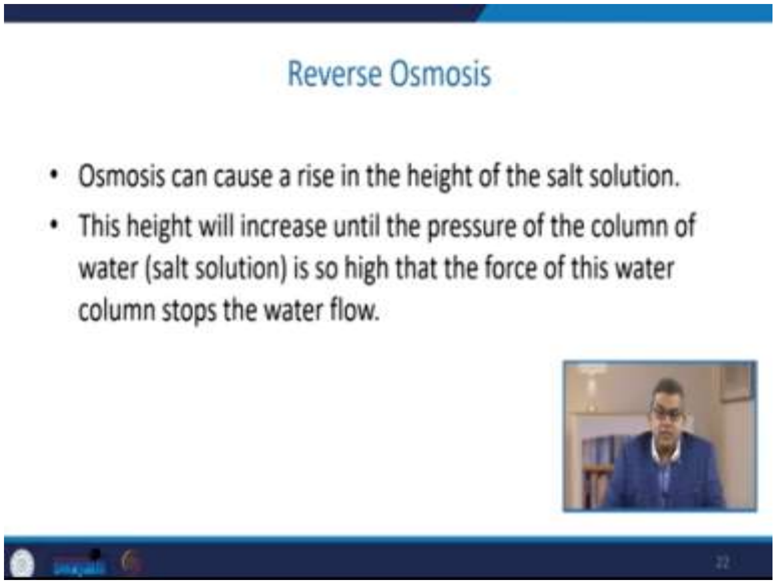

Now, thereby the osmosis can cause a rise in the height of the salt solution. This height will increase until the pressure of the column of the water, that is, the salt solution, is so high that the force to this water column stops the water flow. From the equilibrium point of view, this water column height in terms of water pressure against the membrane is called the osmotic pressure. It is a very common phenomenon.

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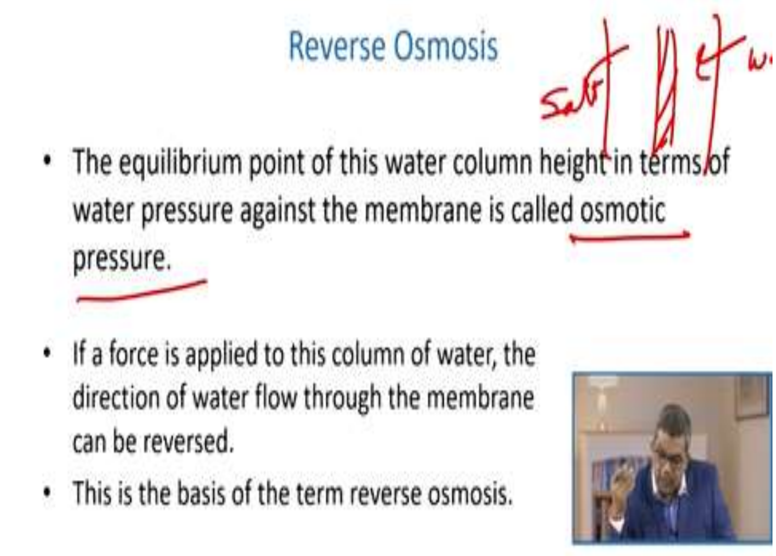

Now, if a force is applied to this column of water, the direction again I am reproducing the rough figure. So, the direction of the water flow through the membrane can be reversed, so if we apply the force to this column, the direction will be reversed, the direction can be reversed. This is the basis of the term reverse osmosis.

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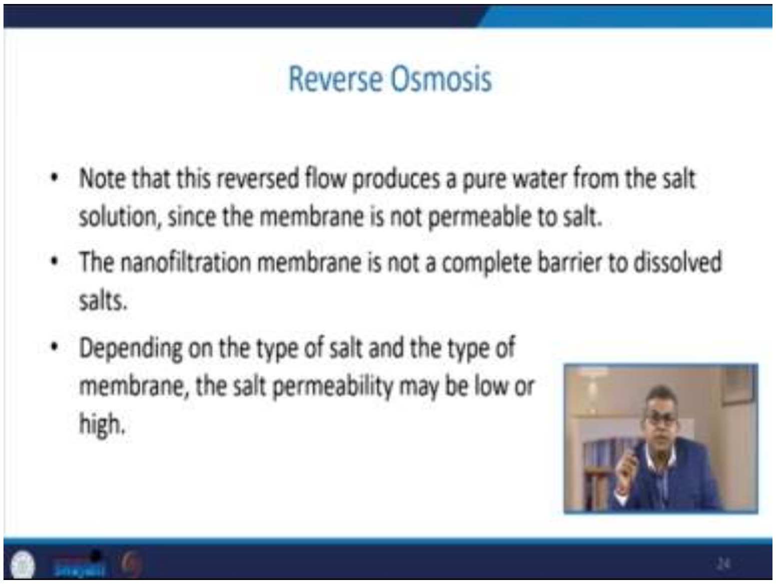

Now, this is the reverse flow that produces pure water from the salt solution since the membrane is not permeable to salt. So it prevents the flow of salt to the other column. The nanofiltration membrane is not a complete barrier to dissolving salts. So, depending on the type of salt and membrane type, the salt permeability may be low or high.

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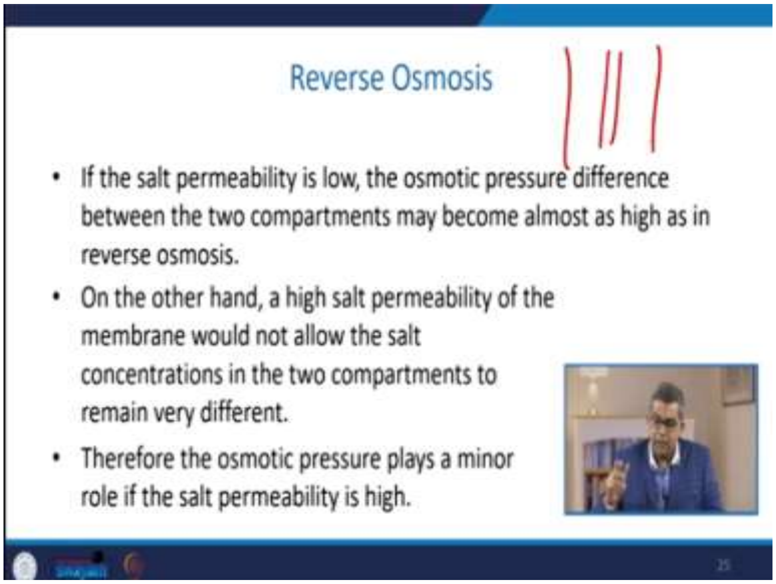

If salt permeability is low, the osmotic pressure difference between the two compartments may become almost as high as in reverse osmosis. On the other hand, a high salt permeability of the membrane would not allow the salt concentration in the two compartments to remain very different. Therefore, the osmotic pressure plays a minor role if the salt permeability is high. This is a piece of very useful information in designing all these reverse osmosis concepts.

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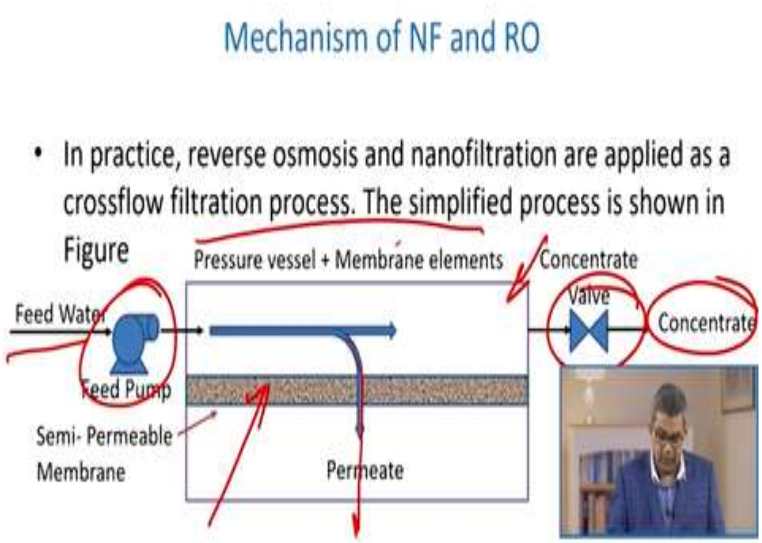

Now, let us have a discussion about the mechanism of nanofiltration and reverse osmosis. So, in practice, reverse osmosis and nanofiltration are applied as a crossflow filtration, which we had already discussed. The simplified process is shown in this one, here you are supplying the feed water, this is the feed pump, and this is our semi-permeable membrane, and this wall and these here we are passing through the concentration.

Now, this is a pressure vessel plus membrane element, so this is my pressure vessel. So, this feed water comes out through this feed pump and permeate comes out over here and the concentrate goes in this particular direction.

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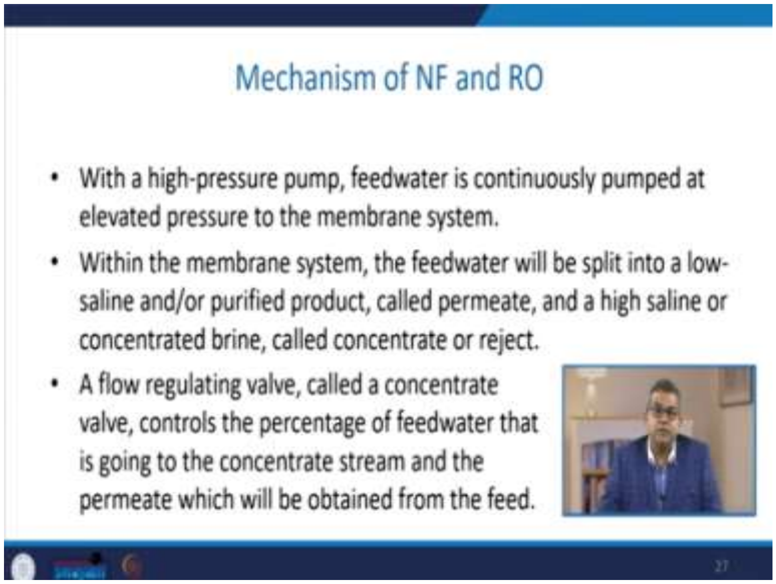

The feed water is continuously pumped at elevated pressure to the membrane system with a high-pressure pump. The feed water will be split within the membrane system into low saline and/or a purified product called permeate and high saline or concentrated brine called the concentrate or reject. A flow regulating valve, usually called the concentrate valve, controls the percentage of feedwater going to the concentrated stream and the permeate obtained from the feed.

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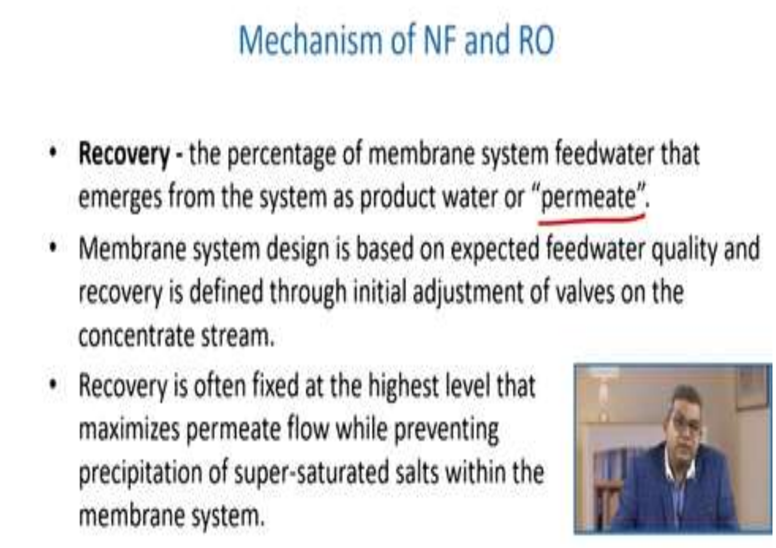

Next is the recovery: the percentage of membrane system feed water usually that emerges from the system as product water or permeate. Membrane system design is usually based on expected feed water quality, and recovery is defined through initial adjustment of valves on the concentrate system. Recovery is often fixed at the highest level, maximizing the permeate flow while preventing precipitation of supersaturated salts within the membrane system.

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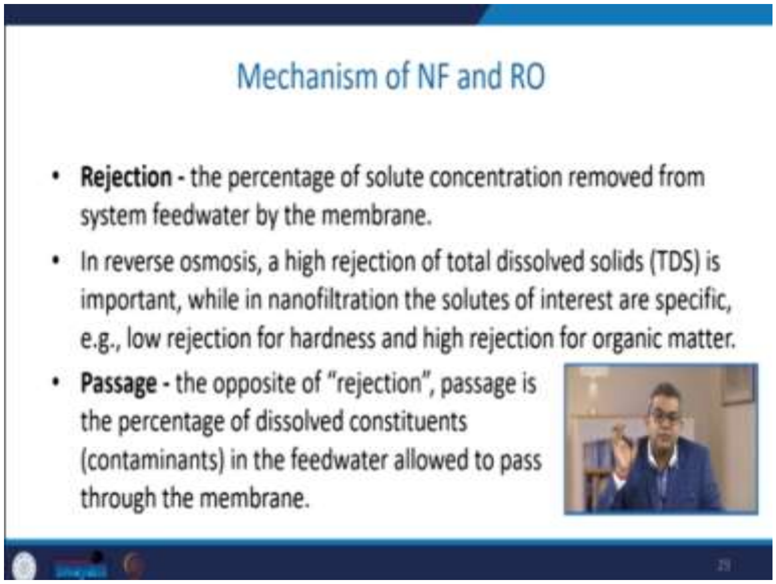

The rejection is called the percentage of solute concentration removed from the system feed water by the membrane. So, in reverse osmosis, the high rejection of total dissolved solids, sometimes referred to as TDS, is important, while in nanofiltration, the solute of interest is specific: the low rejection for hardness and high rejection for organic matter. The passage: this is the opposite to the rejection, the passage is the percentage of dissolved constituents, that is the contaminants in the feed water allowed to pass through the membrane.

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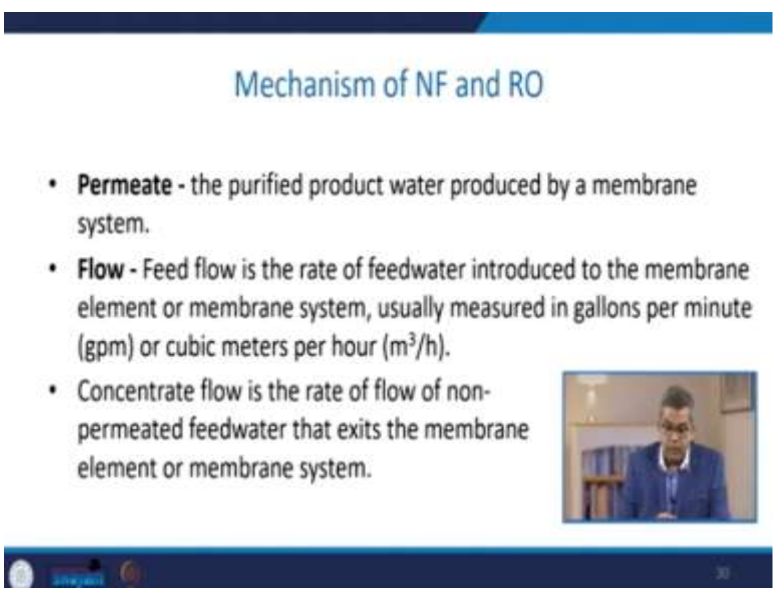

Permeate: the purified product water produced by the membrane system. The flow: the feed flow is the rate of feed water introduced to the membrane element or membrane system, usually measured in gallons per minute or any unit applicable to or sometimes cubic meters per hour. The concentrate flow is the flow rate of non-permeated feed water that exists in the membrane element or membrane system.

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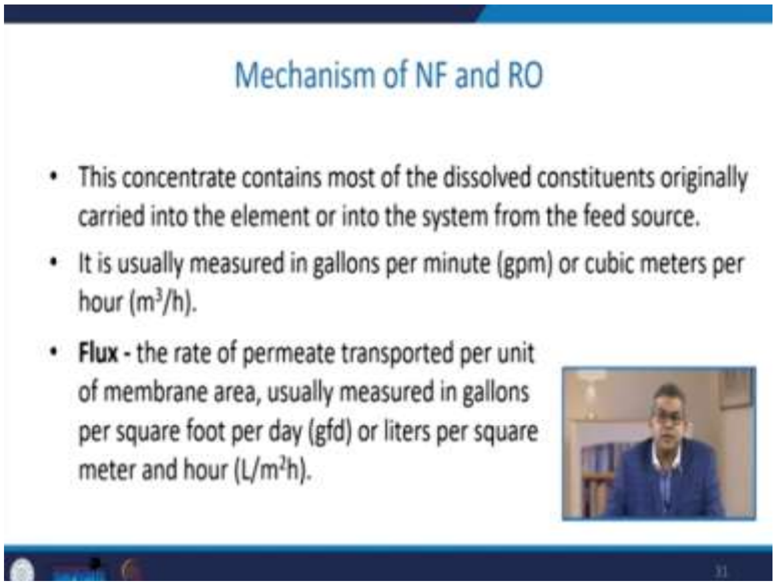

Now, this concentrate contains most of the dissolved constituents originally carried into the element or into the system from the feed source. It is usually measured in gallons per minute or cubic meters per hour. Let us define the flux: the flux the rate of permeate transported per unit of membrane area and is usually measured in the gallon per square foot per day, gfd or liters per square meter an hour.

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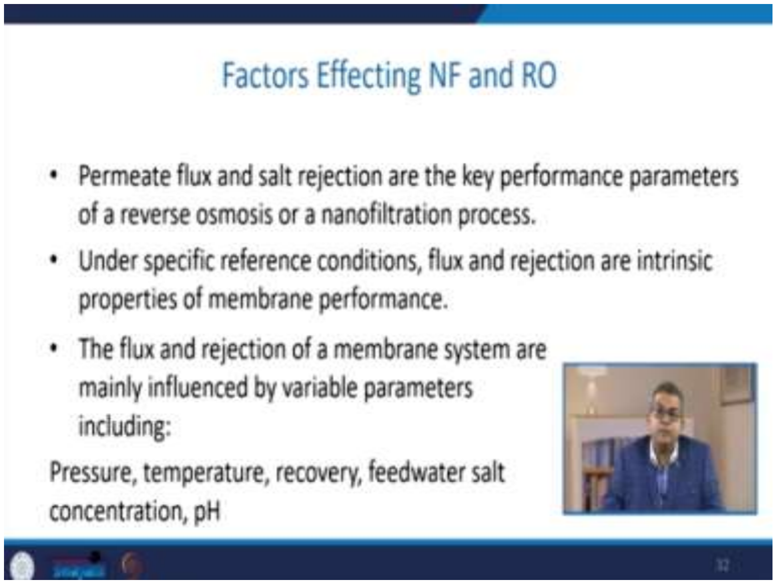

Now, there are certain factors affecting nanofiltration and reverse osmosis. The permeate flux and salt rejection are the key performance parameters of reverse osmosis or nanofiltration process.under specific reference conditions, flux and rejection are intrinsic properties of membrane performance. The flux and rejection of the membrane system are mainly influenced by various parameters like pressure, temperature, recovery, feed water salt, concentration, pH, etc. So, these are the controlling parameters.

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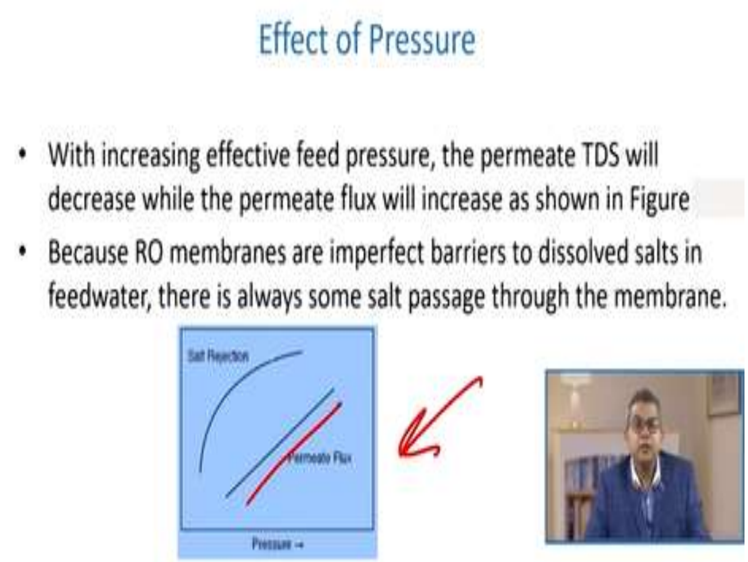

Now, let us have a discussion about the pressure. The permeate TDS will decrease with increasing the effective feed pressure, while the permeate flux will increase, as shown in this figure. This is the pressure, and you see that permeate flux is increasing in salt rejection. Because reverse osmosis membrane are imperfect barriers to dissolve the salt in feed water. There is always some salt passage through the membrane.

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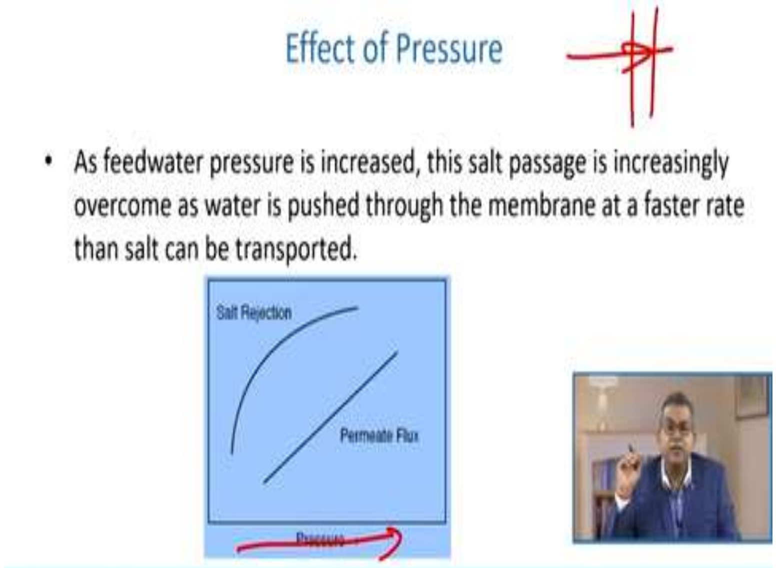

Now, as feed water pressure increases, this salt passage increasingly overcome as water is pushed through the membrane faster than the salt can be transported.

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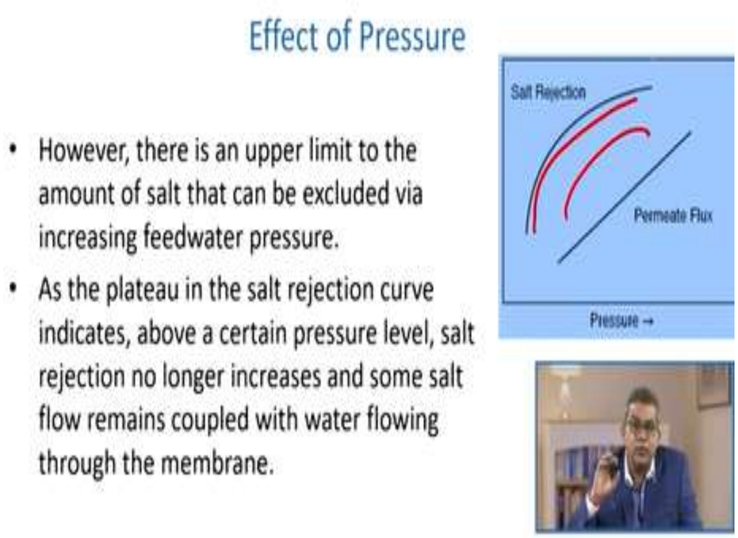

However, there is an upper limit to the amount of salt that can be excluded via increasing feed water pressure. As the plateau of the salt rejection curve indicates, above a certain percentage, above a certain pressure level, the salt rejection no longer increases, you can see over here that some salt flow remains coupled with water flowing through the membrane.

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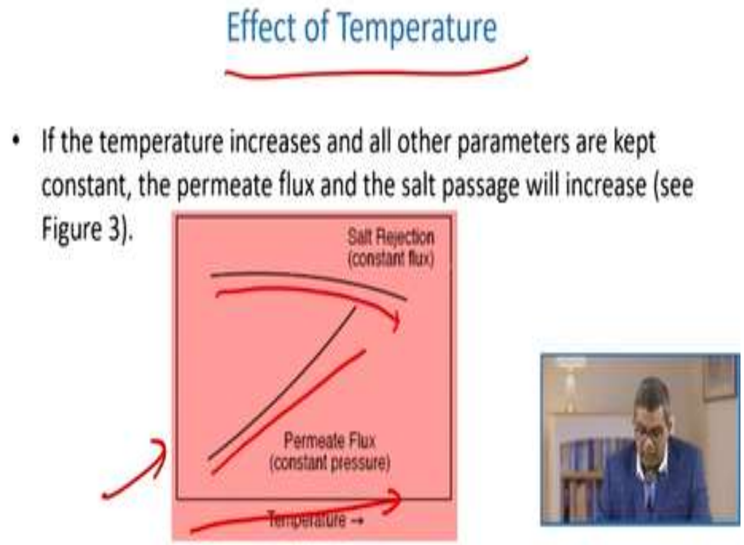

Now, let us discuss the effect of temperature. If temperature increases and all other parameters are kept constant, the permeate flux and salt passage will increase. You can see in this particular figure, that we are keeping the temperature increasing, then the permeate flux you can see that is the incremental trend in the permeate flux and salt rejection slightly on the lower arm. We are maintaining the constant pressure and constant flux.

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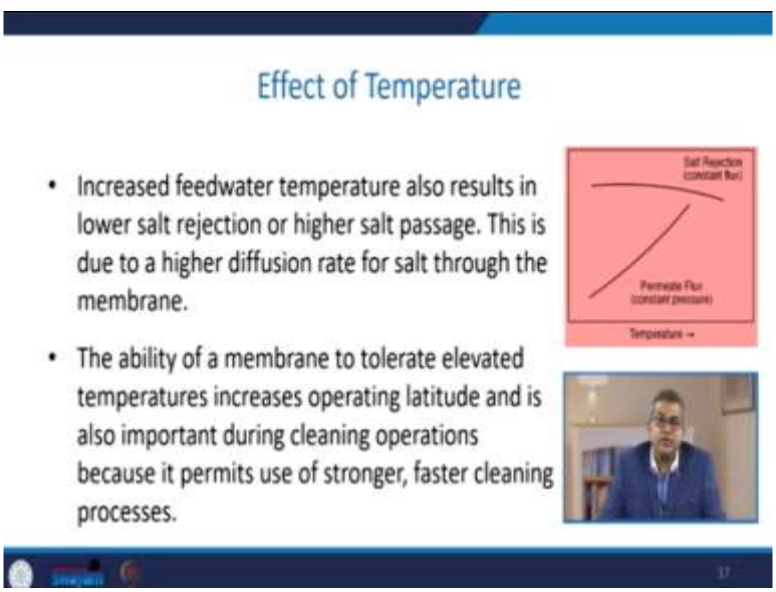

So, increased feedwater temperature also results in lower salt rejection or high salt passage. This is due to a higher diffusion rate for salt through the membrane. The ability of a membrane to tolerate elevated temperatures increases operating latitude and is also important during the cleaning operation because it permits the use of a stronger, faster-cleaning process.

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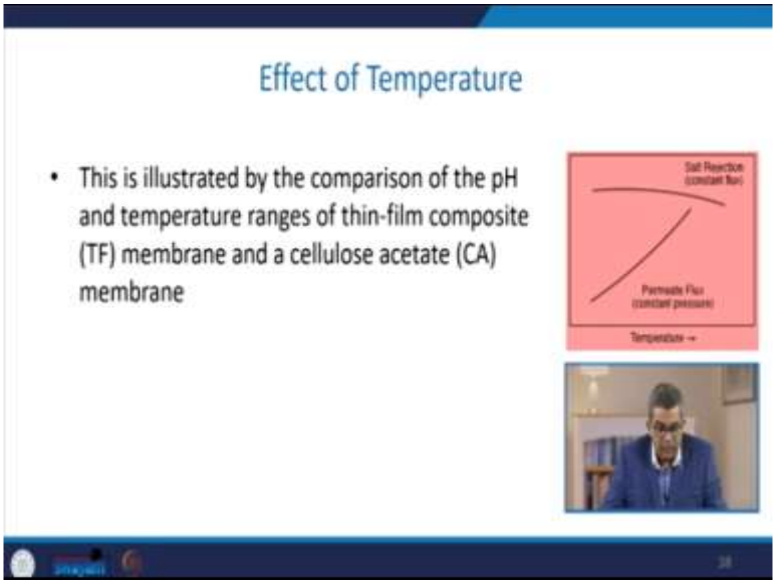

Now, this you can illustrate by the comparison of the pH and temperature ranges of thin-film composites and cellulose acetate membranes. Let us have a discussion about the effect of recovery.

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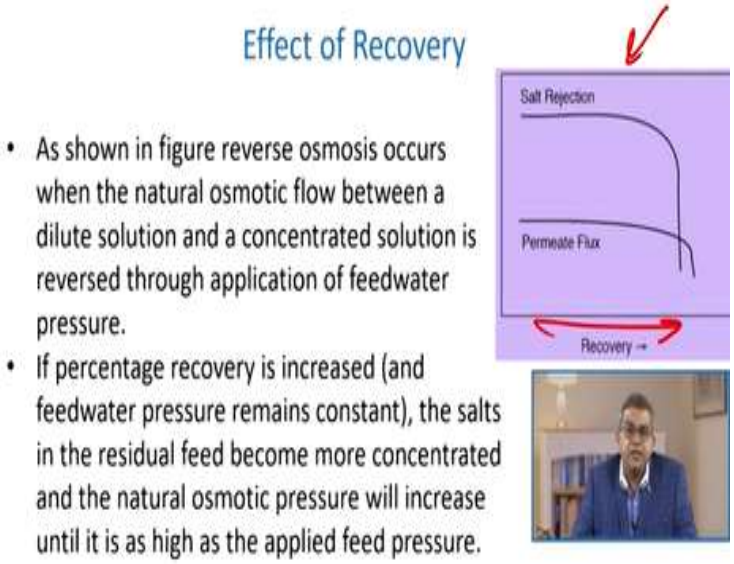

Now, in the figure, reverse osmosis occurs when the natural osmotic pressure between the dilute solution and a concentrated solution is reversed through the application of feed water pressure. So, if percentage recovery is increased, that means the feed water pressure remains constant, the salt in the residual feed becomes more concentrated, and the natural osmotic pressure will increase until it is as high as the applied feed pressure.

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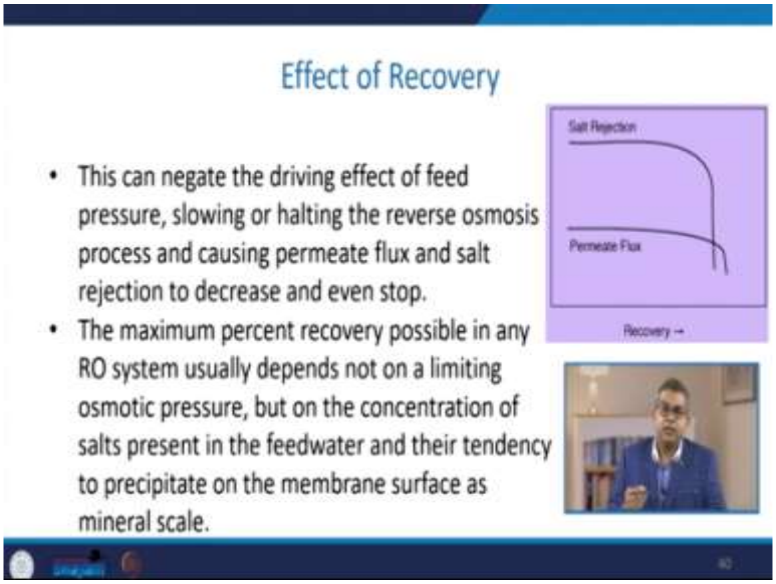

So, this can negate the driving effect of feed pressure, slowing or halting the reverse osmosis process and causing the permeate flux and salt rejection to decrease and even stop. So, the maximum percent recovery possible in any reverse osmosis system depends not on the limiting osmotic pressure, but on the concentration of salts present in the feed water and their tendency to precipitate on the membrane surface as a mineral scale.

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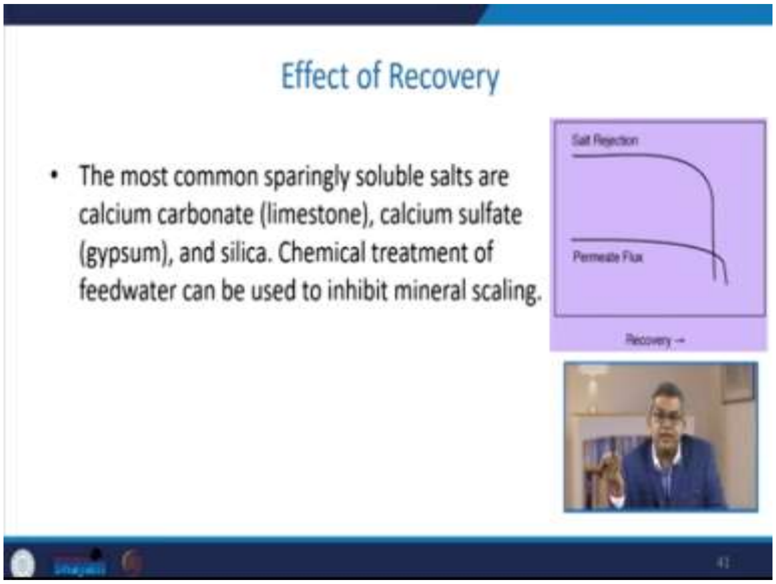

So, the most common sparingly soluble salts are calcium carbonate, sometimes called limestone, and calcium sulfate, called gypsum and silica. The chemical treatment of feed water can be used to inhibit the mineral scaling. In this particular chapter, we discussed the various aspects of inhibition, we had discussed the different aspects of microfiltration, ultrafiltration, reverse osmosis, etcetera.

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And, if you wish to have a further reading, then we have enlisted couple of references for your convenience. Thank you very much.