Physico-Chemical Processes for Wastewater Treatment
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Lecture 38
Ion-exchange - II

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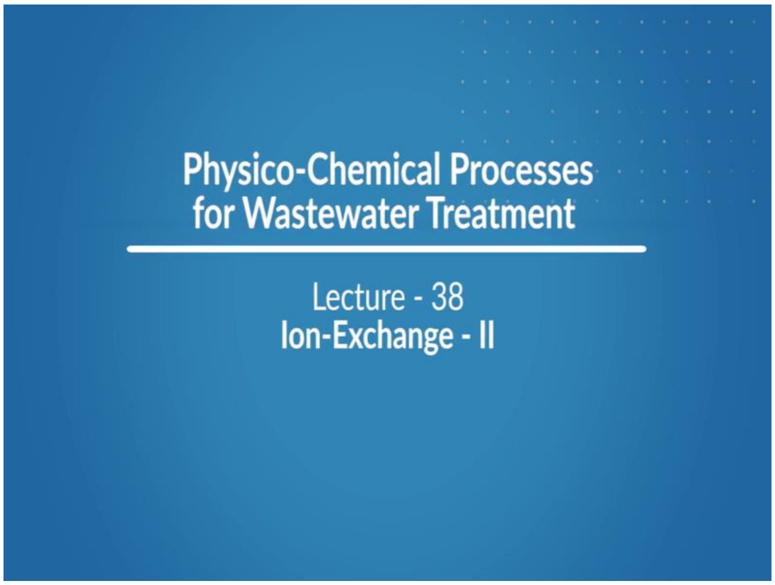

Good day everyone and welcome to these lectures on Physico-Chemical Processes for Wastewater Treatment. In the previous lecture, we started studying the ion-exchange processes, which are used for removing various types of ions from water. So, ion-exchange process is very commonly used for removal of calcium, magnesium, hardness, etc., from the water. And in the ion-exchange process, we used some resins and on those resins, there are some cations and anions.

So, anions are like they form the basic groups which are attached to the resin itself and then from the anion some cation is attached. Now, this cation is exchanged when the water containing different ions pass through the ion-exchange bed. So, this is the ion-exchange process which happens and through this we can remove not only hardness we can remove other types of undesirable toxic ions also from the wastewater or water if you have to use it for drinking purpose or otherwise. So, this way ion-exchange process is used.

Now, in today's lecture, what we are going to study some of the important characteristics of the ion-exchange resins. And so, one of the important properties which helps in determining that whether we have to use that ion-exchange resin or not. So, it is very similar to adsorption capacity in the case of adsorbent. So, whenever we are selecting, so previously we discussed that if we have to select any adsorbent, one of the key parameters that we look is that what is the adsorption capacity of that adsorbent when with respect to pollutant in the water.

Similarly, for ion-exchange resin, we have to see that what is the exchange capacity of the ions vis-à-vis the ion or cation which is already present in the resin itself and the exchange which happens with respect to ions which are present in the water. So, exchange capacity is one of the very, very important properties in selection of any ion-exchange resin.

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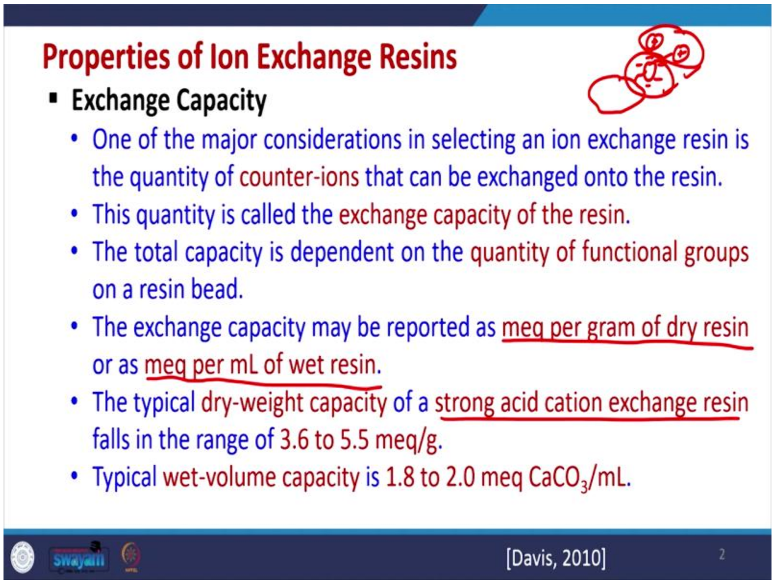

So, one of the major considerations with respect to is that, what is the quantity of counter ions that can be exchanged onto the resin via using the exchange capacity or via the term which is called as exchange capacity. So, we always try to find out this quantity which is called as exchange capacity of the resin. The total capacity of any resin with respect to ion-exchange depends upon the quantity of functional groups which are present on a resin bead.

So, if we have a resin bead which is there, so it will be having some functional groups which will be having, first they will be having negative charge and with these negative charge there will be another functional groups which will be having positive charge. So, these positive charge which get exchanged, but these both an ionic charge and this positive charge, how many charge they are present on ion-exchange bead or resin bead that will determine what is the total capacity of that particular resin.

Now, going further the exchange capacity is generally reported as milli-equivalent per gram of the dry resin, also it can be reported as milli-equivalent per ml of the wet resin. So, this way we can report the exchange capacity of any ion-exchange resin. The typically drive it capacity of a strong acid cation exchange resin is in the range of 3.6 to 5.5 milli-equivalent per gram. And similarly, typical wet-volume capacity is in the range of 1.8 to 2 milli-equivalent with respect to calcium carbonate per mL.

So, through these, so whenever we are going for finding out whether what should be the ion-exchange resin that we have to use. So, we should always try to see that what is their capacity with respect to exchange of ions. So, depending upon that we can project. Certainly other parameters are also important that what is the selectivity of that resin with respect to different ions which may be present in the water. So, another parameter which is very important in selecting any ion-exchange resin for ion exchange bead, it is the selectivity.

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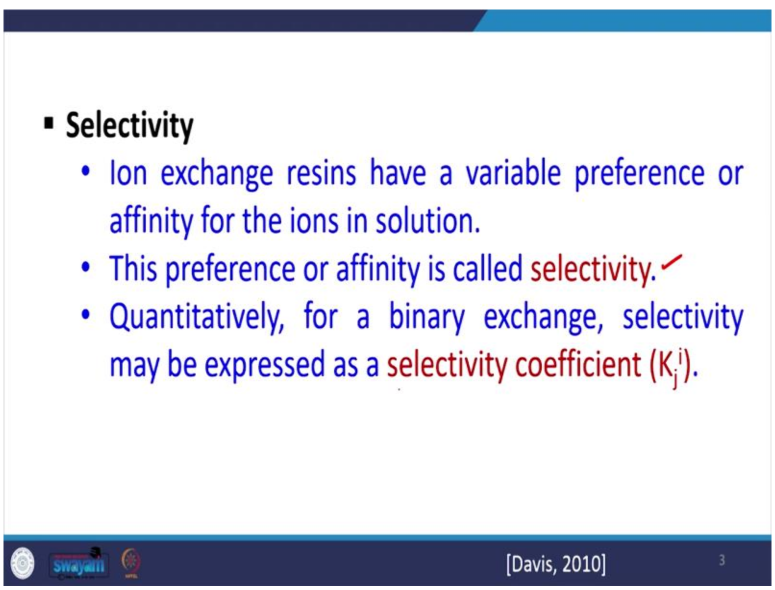

So, ion-exchange resins may have variable preferences or we may call it as an affinity for different ions which are present in a solution. So, this preference or affinity is called as selectivity. And quantitatively we can for a binary exchange selectivity is expressed as Kji. So, we are going to understand these parameters little bit more.

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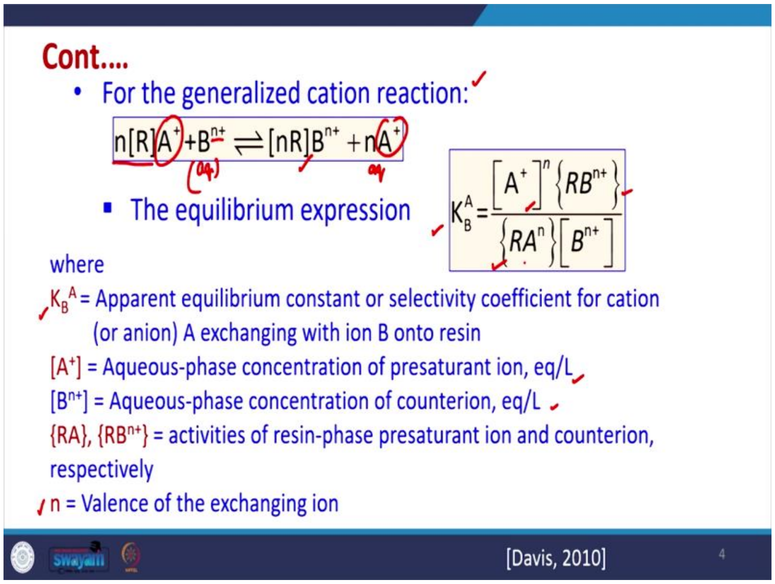

So, selectivity suppose, any generalized cation exchange reaction is given like this. So, we have a resin on which some cation is there already present and in the water aqueous-phase we may write. So, this B is present which is having some n plus its valency. Now, this n plus will go into the resin. And since, it had a ion this valency of n plus, so that is how this Bn plus will go into the resin, but A plus ions which are already there on the resin n number of those ions will come out and be in the aqueous solution.

So, this is how the exchange generalized cation exchange reaction can be written. Now, if general way how we can write the equilibrium expression is given here. So, KA with respect to B we can write like this that this is A plus the concentration of A plus raise to n in the aqueous solution then the resin, what is the amount of resin which is there or activity of the resin in the aqueous-phase.

Similarly, then in the resin initial conditions whatever the resin contains and then the Bn plus is the concentration of ions before exchange in the aqueous phase. So, here the KBA is called apparent equilibrium constant or selectivity coefficient for cation or anion A exchanging ion B with respect to the resin. A plus is the concentration aqueous-phase concentration of presaturate. So, that means, the ion which was earlier present in the bead itself.

So, its concentration is in terms of equivalent per liter it is written here. Similarly, Bn plus is the aqueous-phase concentration of counter ion which had to be removed. So, again equivalent per liter. And these are the activities of the resin phase pre-saturate ion, that was already present on the resin and then the counter ion which was present in the aqueous-phase. And n is the valency of the exchanging ion. So, we can represent the generalized expression like this.

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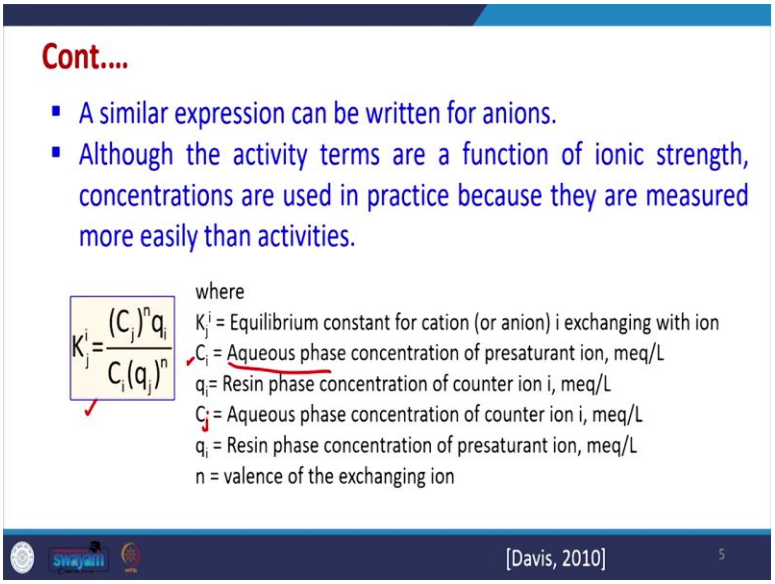

Although the activity terms are a function of ionic strength, concentrations are used in practice because they are measured more easily than activities:

$$K_j^i = \frac{(C_j)^n q_i}{C_i (q_j)^n}$$

where

K_j^i = Equilibrium constant for cation (or anion) i exchanging with ion

C_i = Aqueous phase concentration of presaturant ion, meq/L

q_i= Resin phase concentration of counter ion i, meq/L

C_i = Aqueous phase concentration of counter ion i, meq/L

q_i = Resin phase concentration of presaturant ion, meq/L

n = valence of the exchanging ion

Going further, this expression can, a similar expression can also be written for anions if you wish. Now, although the activity terms are a function of ionic strength, concentrations are generally better to use in practice, because they can be measured very easily than activity itself. So, what we can do is that we can replace that equation with respect to this the changes that have been done is that, that Ci is the aqueous-phase concentration of pre-saturant ion and Cj is the aqueous-phase concentration of the counter ion, so this is there.

Similarly, qi and qj they are the resin phase concentration of counter ion and presaturant, respectively. So, we can write the same expression like this, we can generalize. Now, going further because we have to simplify this equation. So, what we do is that we can simplify it better, but before going to that let us understand that greater the selectivity coefficient, the greater is the preference for the ion by the exchange resin. So, we always want a resin which may be having more selectivity towards the ion that we want to remove. So, this is what we will always desire.

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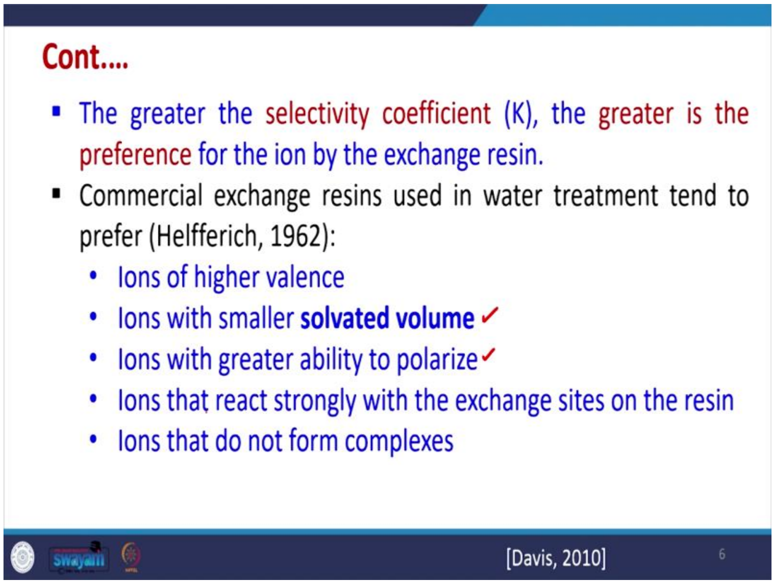

Now, the commercial exchange resins which are used in the water treatment, they tend to prefer certain categories of ions, ions which are having higher valency. So, if suppose, two ions are there, so they will always prefer, generally they will prefer a ion which is having higher valency. Similarly, ions with smaller solvated volume that there, whatever is their size of the ion, ionic size. So, the smaller the size it will be better exchange. So, that is one more thing which is there.

Now, ions with greater ability to polarize because we are exchanging ion, so they will always prefer ions which have the greater ability to polarize. So, this is another generalized preferences there with respect to any commercial exchange resin, which is there. Similarly, they prefer ions that react strongly with the exchange sites on the resins.

So, this also we can see that, so through this idea we can always tentatively look that what type of functionalities or what type of sites may be there in the exchange resin and sometimes we can develop those functionalities, while manufacturing or producing those exchange resins also. Similarly, any exchange resin always prefer ions that do not form complexes. So, this is also one of the generic preference which is there with respect to commercial exchange resins, which are used in the ion-exchange system.

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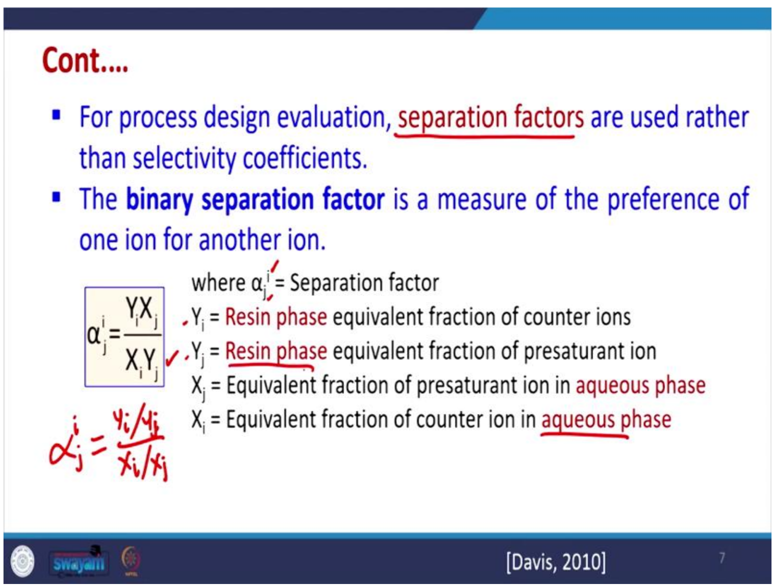

The binary separation factor is a measure of the preference of one ion for another ion.

$$\alpha_j^i = \frac{Y_i X_j}{X_i Y_j}$$

where α_j^i = Separation factor

Y_i = Resin phase equivalent fraction of counter ions

Y_j = Resin phase equivalent fraction of presaturant ion

X_j = Equivalent fraction of presaturant ion in aqueous phase

X_i = Equivalent fraction of counter ion in aqueous phase

Now, going further for process design evaluation along with the selectivity coefficient, there is another parameter which is very important, which is called as separation factors. So, we always in the usual case separation factors have been given in the literature and from that we can find out okay which is better, which is not better. So, in place of selectivity coefficient separation factors are better used for process design calculation or evaluation also.

Now, the binary separation factor is a measure of the preference of one ion with respect to another ion. So, this is there. So, suppose we have i and j, so separation factor can be given like this. So, we can define this one also like this also. So, like the concentration of i upon yj divided by xi upon xj. So, this above equation this equation can be written as this also and opposite way.

So, in this case the yi and yj are resin phase equivalent fractions of counter ions and presaturant respectively. Similarly, xi and xj are equivalent fractions of counter ions and presaturant ions in the aqueous-phase. So, j is with respect to presaturant ion and i is with respect to counter ions. So, these are the separation factors which are there with respect to aqueous-phase and resin phase. So, this is the separation factor which is there.

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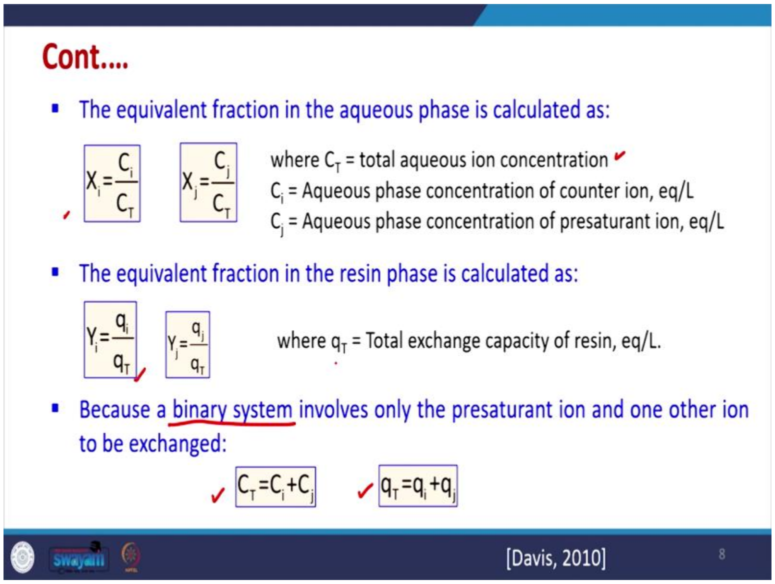

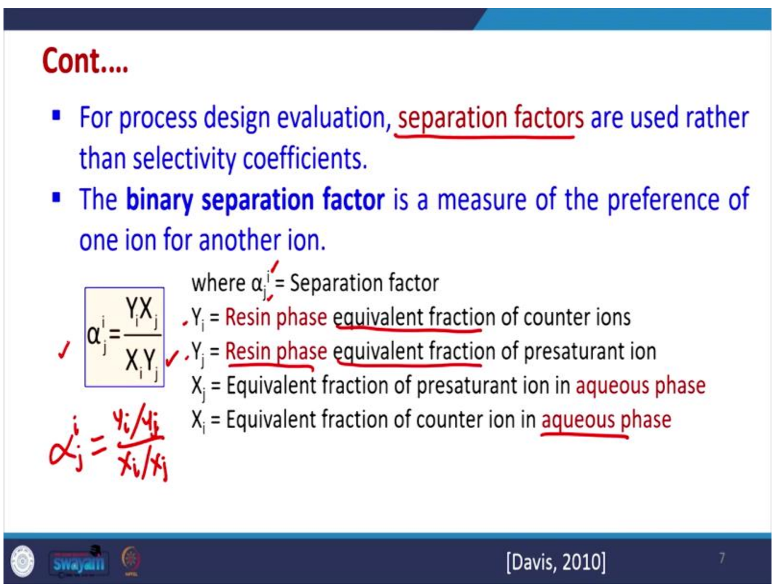

Now, what we can do is that, we can define these xi, so these are equivalent fraction remember. So, what we are going to do is that we will define this xi, xj, etc. Now, xi can be written as Ci upon C total. So, C total is the total aqueous ion concentration. Similarly, Ci is the aqueous-phase concentration of counter ions and Cj is the aqueous-phase concentration of presaturant ion. So, through this we can define xi and xj.

Similarly, we can define the resin phase equivalent fraction yi and yj via this expression where qT is the total exchange capacity of the resin. Because we are only considering a binary system, so the presaturant ion and the other ion that have to be exchanged, so total value will be this. And similarly for qT the total value will be this. Via using these expressions, what we do is that we replace all these expressions in the previous this equation.

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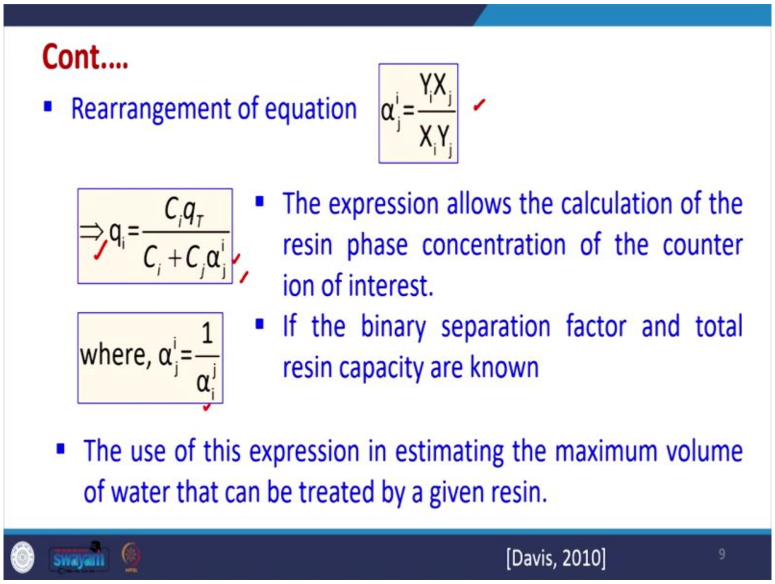

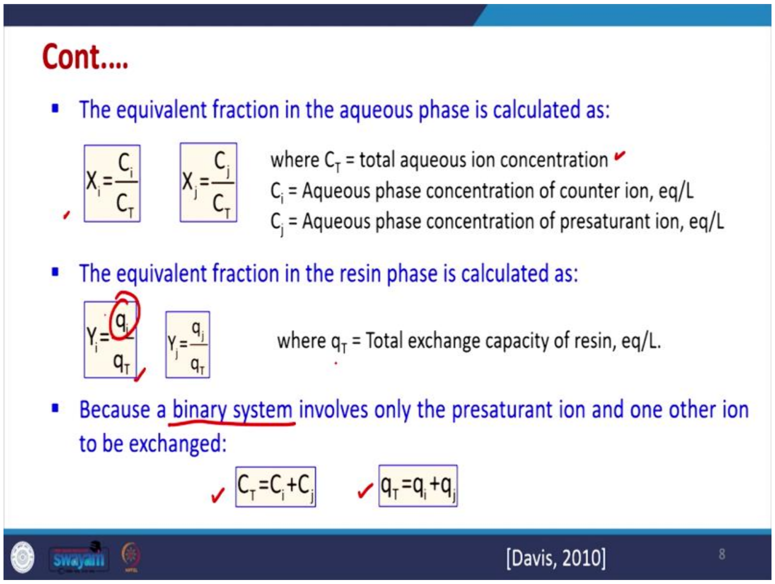

So, if we replace all these expression in this equation we can reduce this particular equation into this, and where we can define all the things like this. So, what we have done is that, we have actually manipulated the equation a little bit and we have written the equation in terms of qi. So, qi is like this, we have tried to write the equation in terms of qi, that what is the capacity of the resin with respect to ith ion, which is there.

And this has been done with little bit manipulation. So, and in this expression the alpha ij expression has come here. And so, we can use this expression for calculation of resin phase concentration of the counter ion whatever is the interest. So, if suppose, we have to remove calcium, so we can always look for the calcium. So, we can similarly find for others. And there is one important thing is that, that we can always the alpha ij is like reciprocal of alpha ji.

So, this is there. And through this we can determine the total resin phase concentration of the counter ion of the interest. Now, the use of this expression is in estimating the maximum volume of water that can be treated by a given resin, if the concentration of counter ions in the resin is already known. So, this we can determine very easily via this expression. Now, let us solve one problem to understand the use of this expression.

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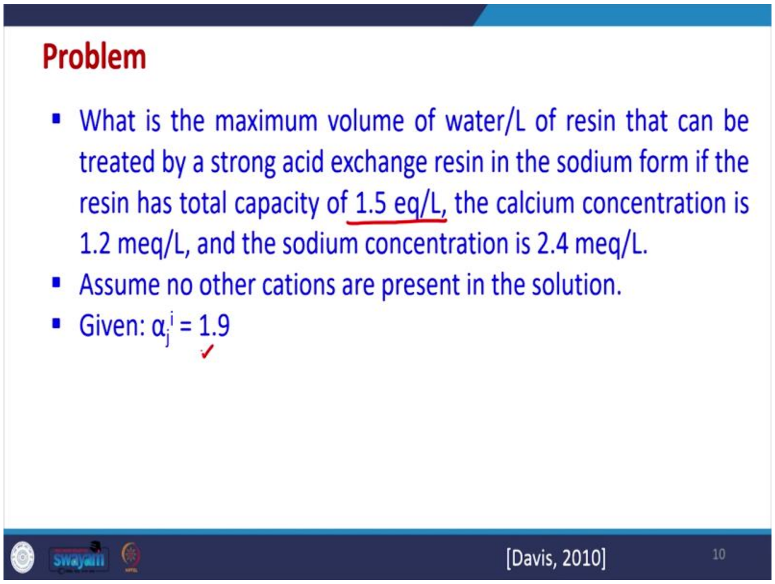

So, what is the, question is given, what is the maximum volume of water per liter of resin that can be treated by a strong acid exchange resin in the sodium form, if the resin has a total capacity of 1.5 equivalent per liter. So, the total capacity of the resin is given. The calcium concentration is 1.2 milli equivalent per liter and the sodium concentration is 2.4 milli equivalent per liter. It has been given.

So, and also it is given that except to calcium and sodium, no other cation is present or we are assuming that they do not have any affinity towards the ion-exchange resins. So, this is there.

Now, the alpha ij value has been given to be 1.9 in this case. So, let us try to solve that what will be the maximum volume of water that will be required per liter of the resin.

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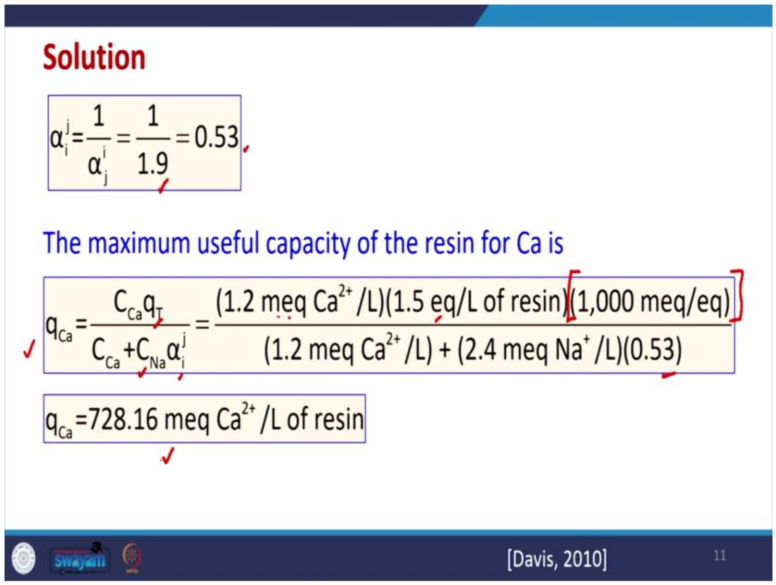

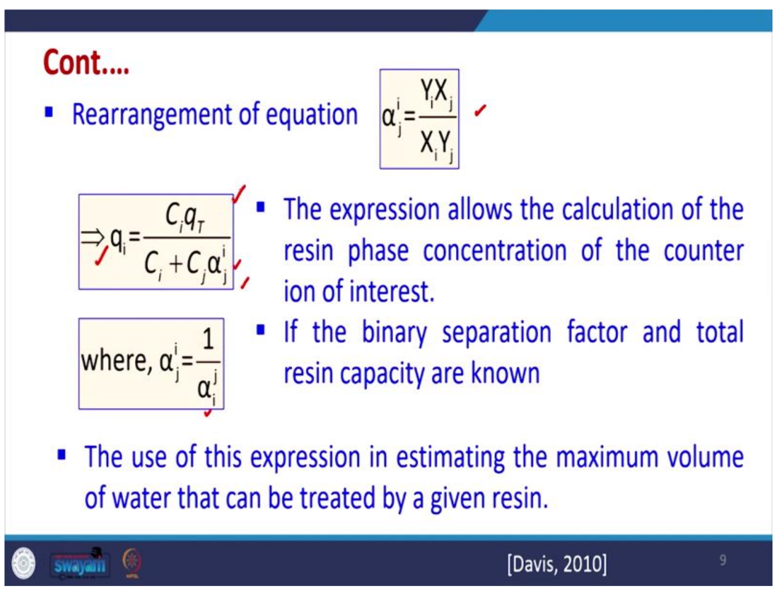

Now, alpha ij is given 1.9. So, that means, alpha ji is equal to 0.53. So, this expression was already given earlier. So, we are using the same expression. Now, the maximum useful capacity of the resin for calcium can be calculated via this expression which was given earlier. So, this expression is given here, so we have written this expression with respect to calcium. Now, if we write with respect to calcium, here the concentration of sodium will come and alpha ji value will be there.

So, what we do is that we write all the parameters and their respective units also. So, like for calcium 1.2 million equivalent calcium per liter. Now, the maximum capacity is 1.5 equivalent per liter of resin. Similarly, the calcium again 1.2 milli equivalent per liter. For sodium, we have 2.4 milli equivalent sodium per liter and alpha ji is 0.53. So, it is already written. So, now, if we try to solve it without using, so units will not be correct.

So, here what we have done is that, we have converted this milli equivalent, which is there with respect to sodium or calcium, so that into equivalent. So, here because for resin it is equivalent, but for calcium it is in milli equivalent. So, we use this expression, 1000 is the number of milli equivalent per equivalent. Now, if you solve we will be finding that the quantity of calcium that can be exchanged is 728.16 milli equivalent calcium per liter of the resin. So, this will come out. Now, we have to find out the volume of water.

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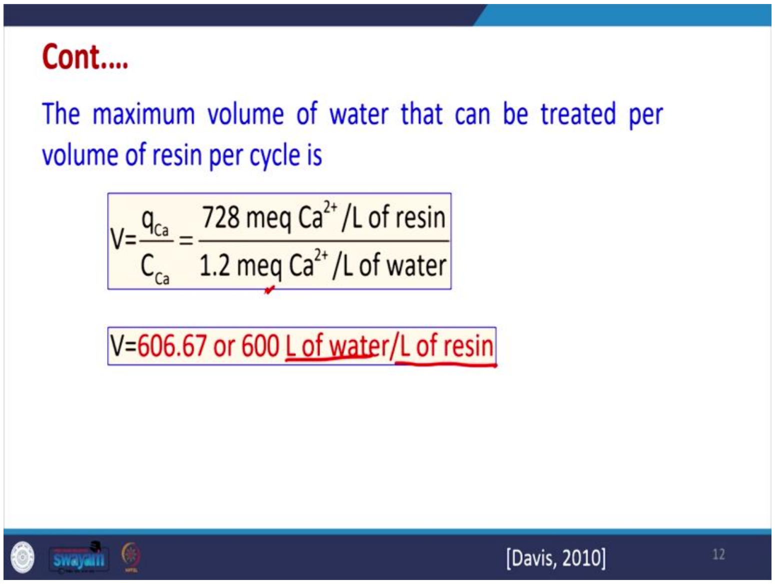

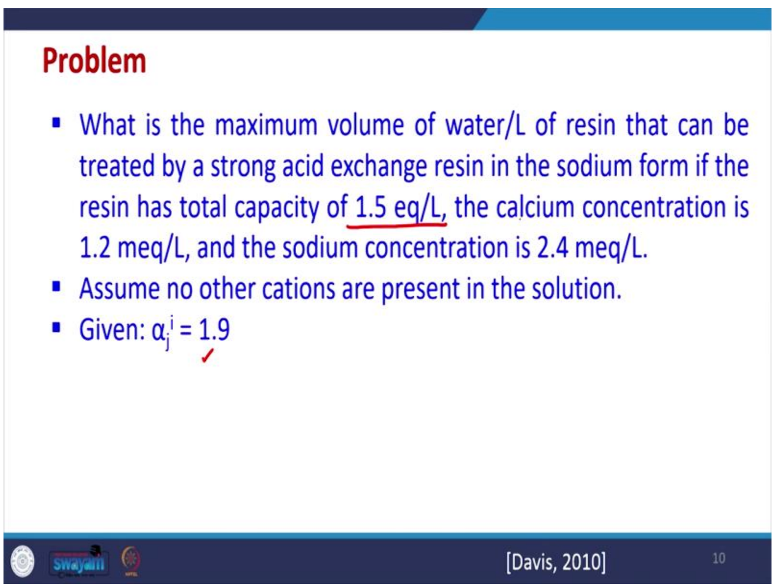

Now, the maximum volume of water that can be treated per volume of the resin per cycle will be obtained if we divide by 1.2 milli equivalent calcium per liter of the water which is the capacity which is already present in the water. So, using this, what we, if we divide we will be finding that liter of water that can be treated per liter of resin. So, it is like 600 liter of water it is there.

So, through this we can understand that for any ion-exchange resin that has to be used in the home or any residences or for any industrial complexes etc., we can always find that, how much water will be treated per bed if the same resin is used in the bed. And if we know the capacity, what is the flow rate of water or amount of water that has to be generated per day through that we can find out, after how much time we will have to remove that resin or we have to regenerate that resin. So, through this we can understand.

So, we can find out the time required after with the degeneration has to be done or otherwise it is totally the chemical bonding type of things are happening. So, we have to see that we have to exchange the resin. So, this is how we can perform this calculation. Now, going further, we will discuss different process operations that can be performed with respect to ion-exchange beds, etc.

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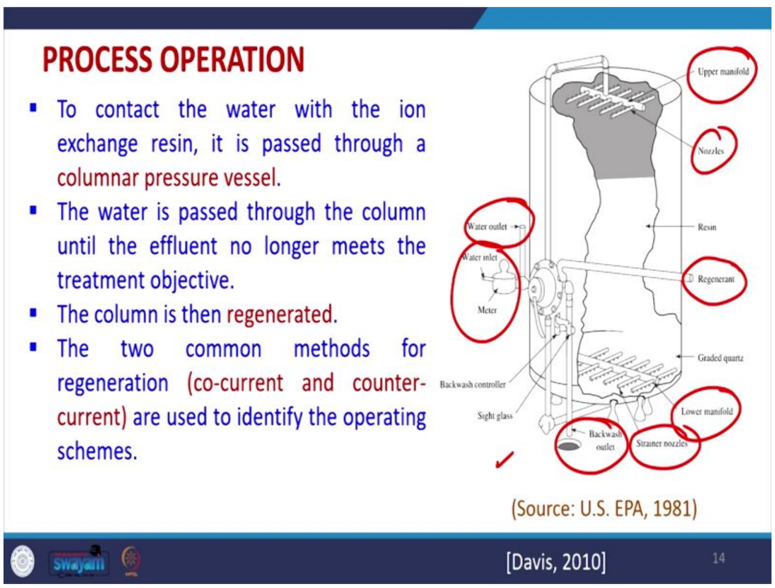

To contact the water with the ion exchange resin it is passed through a column type of pressure vessel which may be there, so which is shown here. So, there may be different sections within the vessel, so that is possible. So, whatever is passed through the column until the effluent no longer meets the treatment objective. So, we will be having a breakthrough type of thing when it happened. So, we will stop the use of the ion exchange resin.

Now, the different sections will be there. Now, after once the breakthrough has been achieved, we have to regenerate the column. So, two common methods of regeneration are there like co-current, counter current. So, they can be used for regeneration. So, there are different methods of operations of the exchange beds also. Now, in the column there will be different sections. So, these sections may be differently place.

So, one example, will be there that there will be a system for water inlet, there will be a system for water outlet, there will be a system for regenerate coming out and similarly there will be a backwash outlet will be there. So, for backwashing or for continuous operation, all the systems are there. Now, whether it is, the flow is counter current or co-current, depending upon that there will be manifolds and nozzle at the top and similarly, there will be manifolds and nozzles at the bottom also in the exchange bed. So, all these things will be present in any exchange bed, depending upon the orientation and type of operation their placement maybe a little different.

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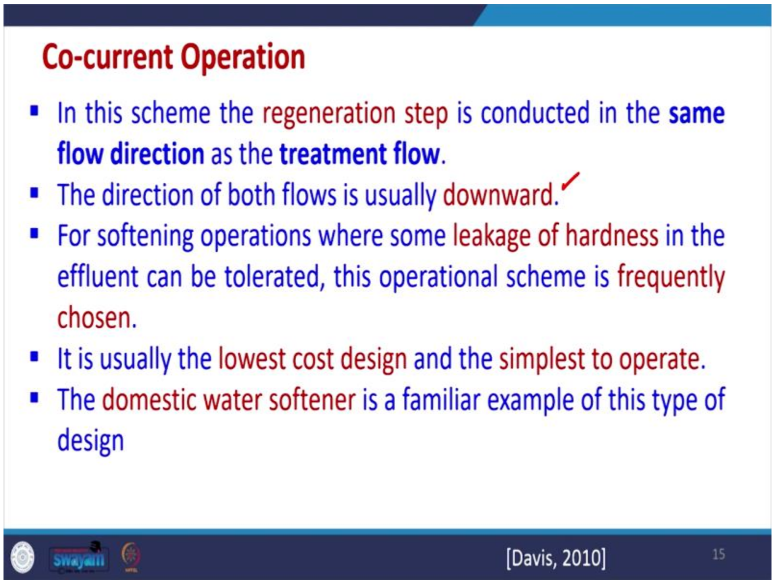

Now, in this scheme, where, there now we have two three types of operation which are possible, one is called co-current operation, another is called counter current operation. And so, in the current operation, the regeneration step is conducted in the same flow direction as the treatment flow itself. So, if the regeneration step, during the regeneration step the flow is in the same direction, it is like a co-current operation as the treatment flow during the treatment happens.

The direction of both flows are usually downwards. Now, for softening operations, where some leakage of hardness in the effluent can be tolerated, the operation scheme is frequently, this operation scheme is frequently chosen. So, if some toleration is there, we can always choose this. And this type of co-current operation is usually the lowest cost design and very simple to operate, because naturally the water will always flow from top to bottom. Now, the domestic water softeners which are used in our residences are similar to this. So, this is there.

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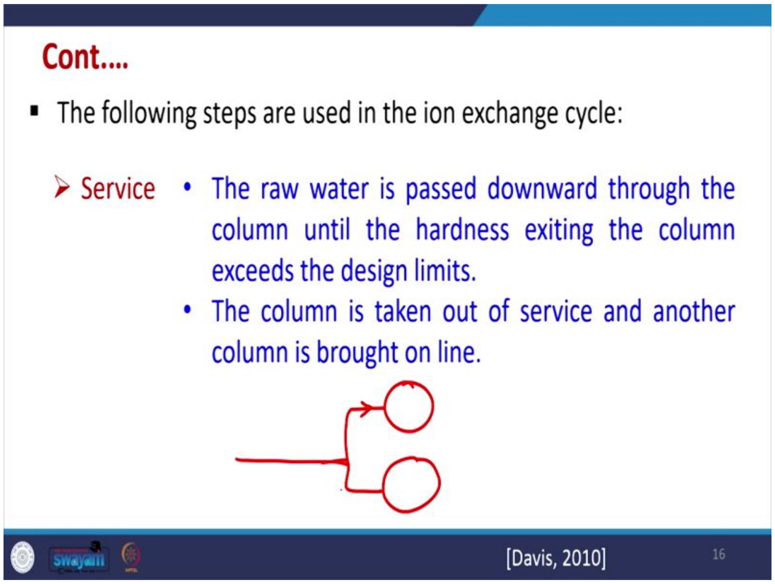

Now, continuing further, there are a number of steps which are used in the ion-exchange cycle in this case. So, during service, what will happen, the raw water is passed downwards through the column until the hardness which is in the exit exceeds that design limit. Always the raw water will be passing downward, then after that the column is taken out of the service and another column is brought in line.

So, that will be there. So, that means, it is possible that flow line is there, and if it topped also packed-bed is here, one ion exchange bed is here. So, first the flow will be only through this, but suppose this is out of operation. So, this flow line will be there and this system will be regenerated. So, this is there. So, this way the system work.

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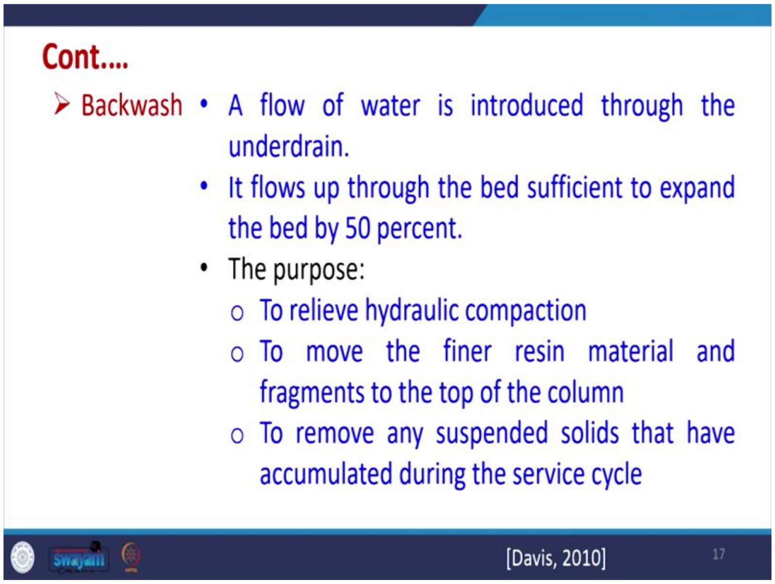

Now, going further in the backwashing condition, when regeneration has to be done, a flow of water is introduced through the underdrain and it flows up through the bed sufficient to expand the bed by 50 percent. The purpose is to relieve the hydraulic compaction which may happen when the flow is from top to bottom. To move the finer resin materials and fragments to the top of the column. So, this is another purpose. Then to remove the any suspended solids that may have accumulated during the service cycle. So, through that also this purpose serves.

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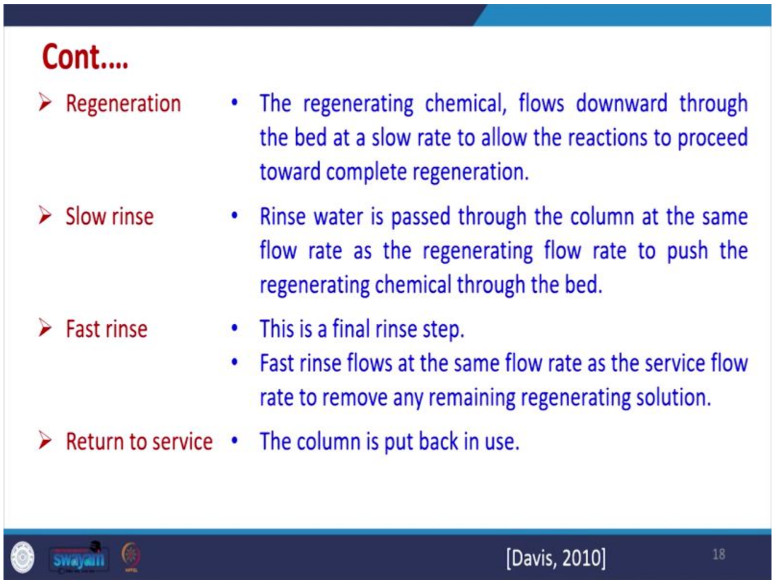

Now, going further there will be other steps also. So, these steps are regeneration, slow rinsing than fast rinsing and then the return to service. So, during regeneration any regenerating chemical. So suppose, we have sodium exchange resin, so we may have a NaCl slurry which may be used. So, this regenerating chemical in the co-current operation flows downwards through the bed at a slower rate to allow the reaction to proceed towards complete regeneration.

So, sodium will get exchange in place of calcium which may have been exchanged earlier during the treatment. After that, what we do is that we performed first slow rinsing. So, in this case the rinsed water is passed through the column at the same flow rate as the regenerating flow rate to push the regenerating chemical through the bed. So, this is there.

And then fast rinsing is done during fast resin the flow is at the same flow rate as the service flow rate to remove any other remaining regenerating solution, it may be there. So, otherwise the treatment efficiencies will not be there, if we do not perform the fast rinsing. And after that, this particular column can be put back into the use again. So, this is there. So, this is one mode of operation.

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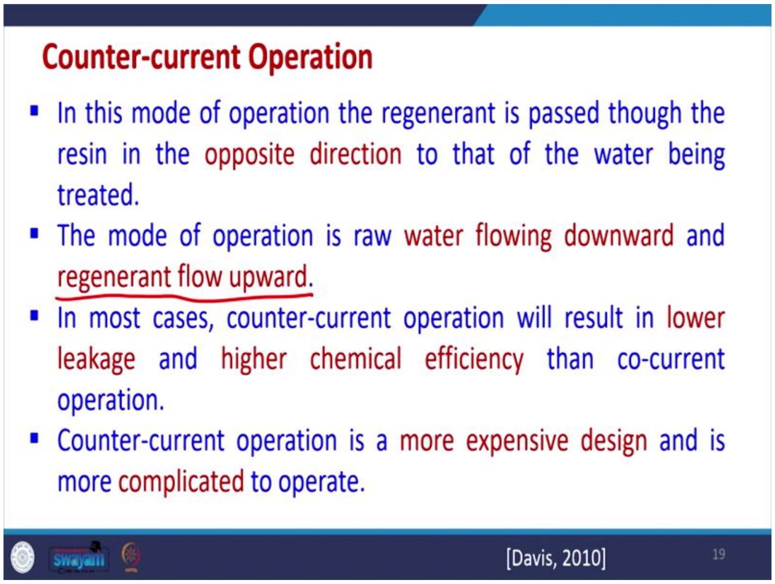

Similarly, we may have counter current mode of operation also. So, in this mode of operation that regenerant is passed through the resin in the opposite direction. So, that means, during backwashing the regenerant will pass in the opposite direction to that of the water being treated. The mode of operation is raw water flowing generally downwards and regenerant flow is generally upward. In most cases, the counter current operation will result in lower leakage and high chemical efficiency than the co-current operation.

And, but counter current operation is generally more expensive design because we have to take care of the flow lines and other things. So, it will be more complicated in nature as compared to. So, we will have to see that okay how the backwashing thing will come out. So, we will be having very different lines as compared to the flow lines and we will be having more walls because the automatic flow walls have to be closed, then the backwashing walls have to be open, so all those things will be there in the counter current operation.

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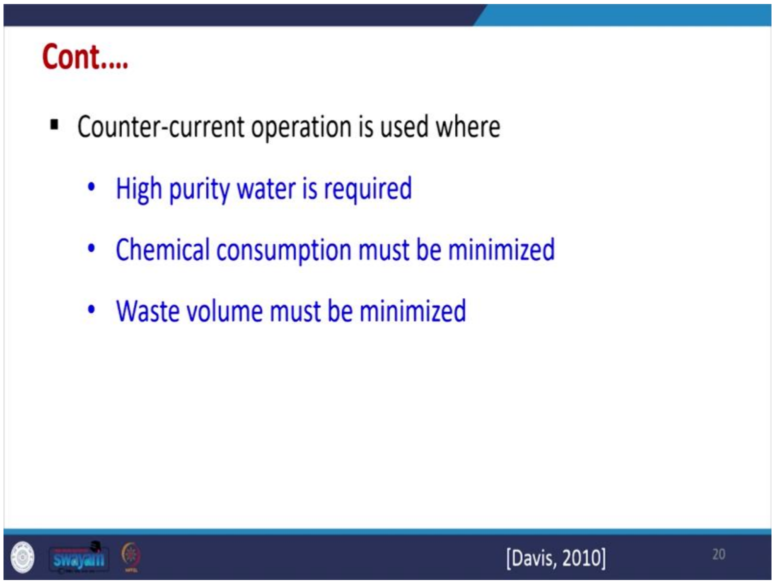

Now, the counter current operation is used, where high purity water is required, where chemical consumption must be minimized. So, this is another condition under which we use the counter current operation because we can always minimize the chemical composition. And the waste volume, the backwash volume will also be minimized. So, all the three aspects are there, but certainly it will be a costlier process as compared to co-current operation.

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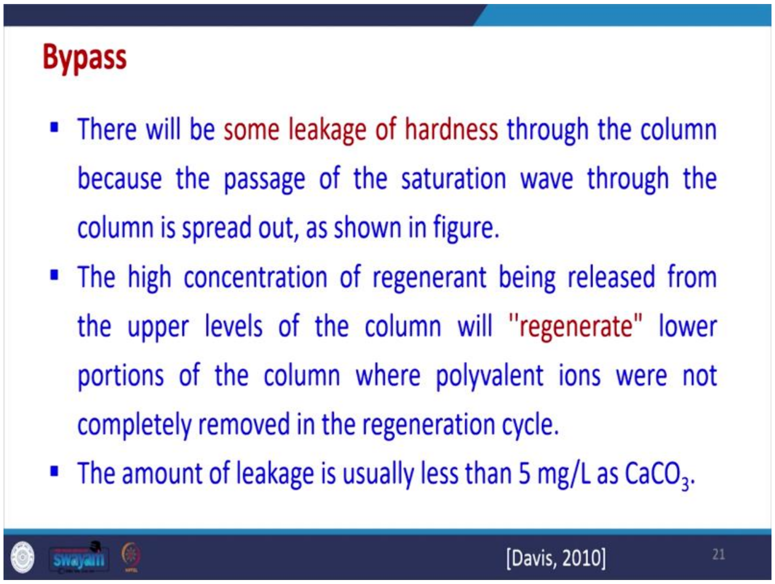

Then also there is a bypass scheme also. So, there will be in the bypass scheme there will be some leakage of hardness through the column because of the passage of the saturation wave through the column when it is spread out. So, high concentration of regenerant being released from the upper levels of the column will regenerate the lower portion of the column where polyvalent ions were not completely removed. So, amount of leakage may be less than 5 milligram per liter of calcium carbonated etc.

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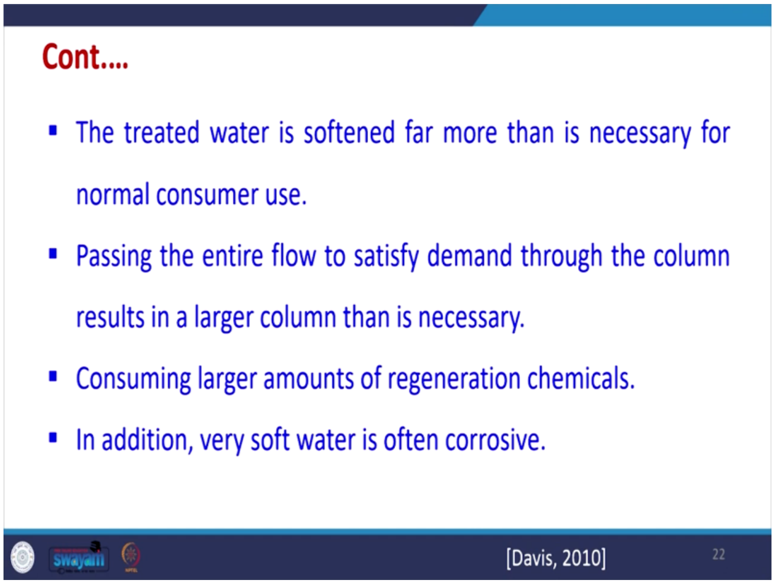

After that the treated water is softened far more then it is necessary for normal consumer use. And entire flow is passed, so as to satisfy the demand through the column results in larger column then the necessary. So, in the bypass scheme the column may be a little larger and it may consume more amount of regenerating chemicals. And sometimes in addition, the very soft water that we get is often corrosive as well. So, through these, these are the different methods of operations of the ion-exchange bed.

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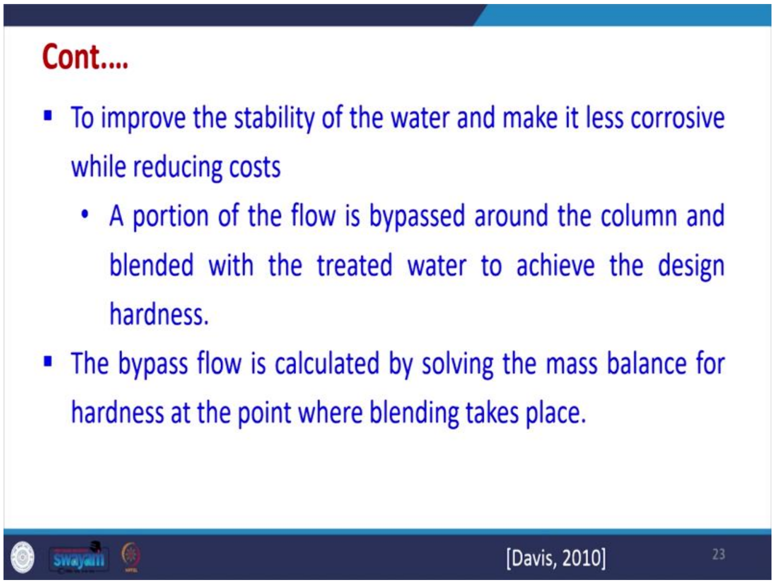

And in the bypass, we are able to improve the stability of the water and make it less corrosive while reducing the cost. A portion of flow is bypassed along the column and blended with the treated water. So, this type of design is also being used in some of the commercial water treatment units which were available for use in the household, because, we always, we can, in this way we can manipulate the amount of minerals or ions which may be present.

So, if suppose we do not desire all the ions to be removed, so we can use the ion-exchange bypasses scheme, such scheme and we mix the without treatment water with the treated water so that we can achieve certain amount of hardness whichever may be required, or TDS which may be required. So, bypass flow is calculated by solving the mass balance for hardness at the point where blending takes place. So, this is how we can do and this is the mass balance that we can perform.

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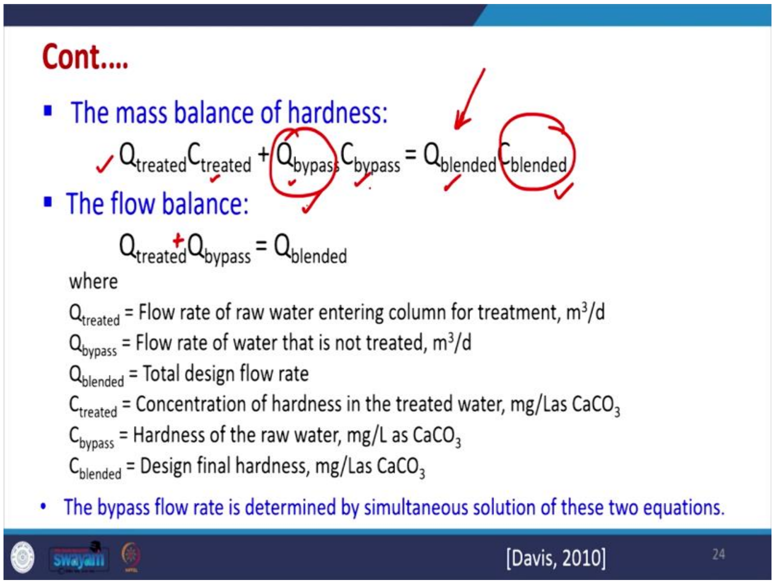

So, the Q, the flow rate which has been treated, the concentration in the treated, the flow rate which is being bypassed and the concentration in the bypass without treatment, so that should be equal to the concentration which is blended. So, this way we can find out. So, the flow balance will be like this Q treated plus Q bypass will be equal to Q blended.

And through these we can find out the bypass flow rate which will be, which has to be determined, because this C blended we already know and the concentration after treatment that will come out this is also known and without treatment also this is known, so all the parameters are known. So, we can easily find out the flow rate that should be bypassed this will be known very easily because Q the flow rate after the blending is also known to us.

So, this is the parameter that we have to find out. So, through this now we end today's lecture, and we will continue that discussing the various ion-exchange things in the next lecture as well. Thank you very much.