Course Name: Industrial Wastewater Treatment

Prof. Alok Sinha

Department of Civil Engineering, IIT(ISM), Dhanbad

Week - 02

Lecture 03: Ion Exchange Process

Welcome back. We are in Module 2, Lecture 3 and here we will talk about the ion exchange applications. In the earlier lectures, we have seen that what is the ion exchange chemistry, what are the ion exchange reactions, how we can calculate the fraction of ions present in the solution and present on the resins. We have also seen that how we can calculate the ion exchange capacity, and we have also talked about that how the regeneration can be performed, what is the selectivity coefficients. Now, today after gaining these concepts, we are going to talk about what are the various applications of the ion exchange. When we talk about the ion exchange applications with regards to the water or the wastewater, so there are mainly three things that comes into our mind that is first of all is the nitrogen control that is required that is the removal of the ammonia or removal of nitrate which can be performed by using ion exchange resins.

Similarly, we can talk about the water softening which is a very very common application of the ion exchange and lastly we will talk about the removal of the heavy metals particularly the removal of heavy metals which are present in the electroplatic path and then we will talk about whatever the concepts we have gained till now how we can apply it for solving the numerical of our calculation of different parameters of the ion exchange. So, when we talk of the ion exchange applications, nitrogen control is one of the most important applications that comes to our mind. So, nitrogen control in wastewater treatment it involves the removal of ammonium ions and nitrate ions from the wastewater stream as we are talking of the nitrogen here. So, synthetic ion exchanges are preferred because they are more durable but there are certain natural resins like clinoptilolite which is a Zeolite which can be used for the ammonia removal because the clinoptilolite is effective, cost efficient and has got a very high affinity for ammonium ions and in comparison, to other materials.

So, the regeneration of clinoptilolite use calcium hydroxide. So, calcium hydroxide mainly is used so that we can convert ammonium ions into ammonia due to high pH as the ammonia ions gets converted to ammonia gas at high pH. So, we use lime calcium hydroxide so that we can convert we can increase the pH, and we can convert the ammonium ions into ammonia gas so that it can be removed by air stripping process. But the main challenge here lies that the formation of calcium carbonate crystals takes place in the zeolite exchange bed, and this can be removed by backwashing. So, we have to employ backwashing so that these carbonate deposits which are there in the filter bed they can be removed, and we can ensure an efficient operation.

We can see here that the secondary effluent which comes from wastewater treatment so it goes into the filtration first of all so we filter this secondary effluent so that the suspended solids they can be removed and then this filter can be backwashed later on, so the waste basically is taken for proper treatment further. And then it passes through the carbon adsorption column so this carbon adsorption column is used so that we can remove the organics which are present in the wastewater so that they may not impact the zeolite that we are using for our nitrogen control. So here we can see that the waste is coming out from here and the water which gets treated after the carbon adsorption so we can see here that the filtration and the carbon adsorption, so they are just acting like a pre-treatment for the secondary effluent process. After the carbon adsorption so the water or the wastewater it goes into the zeolite exchanger here. So, there can be certain after filtration also we can bypass some of the water so that it can be taken to the zeolite exchange depending upon the amount of organics which are present in the wastewater.

So, this zeolite exchanger basically what it does that it exchanges the ammonium ions because it is highly selective for ammonium ions, so these ammonium ions are exchanged here and the water which now becomes free from this ammonium ions the treated effluent it goes out for the further disposal. And here we can see that when we are backwashing it and we are also not only backwashing it we are also basically passing the lime here so that whatever the calcium carbonate precipitates that are formed inside this zeolite exchanger so they may be removed so here lime is passed so that whatever the ammonium ions which are present here so they can be converted to ammonia gas and this ammonia laden water then is goes to a stripping tower the air stripping tower where the ammonia can be removed by passing air from the bottom and on the top the ammonia laden water is passed and air is passed from the bottom so that the air and ammonia basically are removed from here and they go to the acid scrubber for the further treatment. And here we can also see that we are backwashing the filter so that whatever the particles of calcium carbonate crystals that are formed so they can be removed from our zeolite exchanger. That's how the treatment of ammonia takes place by using zeolite which is electrolyte and this electrolyte is very effective in removal of ammonia. Then we come to the nitrate removal which is another form of nitrogen that can be present in the water so when ammonia basically gets oxidized, so it gets converted to nitrate and nitrate also basically we cannot put nitrate directly into the wastewater we have to remove the nitrate from the wastewater so that the nitrate does not impact the aquatic life.

So, the conventional synthetic ion exchange resin they face the challenge when removing nitrate from the water because they are having very low affinity for the nitrate in comparison to sulfate, so which limits their capacity to effectively remove the nitrate. So we know that the wastewater not only contains nitrogen that is nitrate but it may also contain sulfate when we are having water which is coming out from the treatment units like aerobic treatment units like activities such process so when it comes out so the oxidation may convert not only in the nitrate ammonia into nitrate and sulfide into sulfate. So the sulfate if they are present so then there is a problem with the removal of nitrate as sulfate now is having a higher affinity towards the resins and the nitrate is basically displaced and sulfate is basically taken on to the resins so it hampers the removal of nitrate from the wastewater. So, this phenomenon is known as nitrate dumping where resin is having the lower affinity for nitrate over sulfate and sulfate displaces the nitrate onto the resin leads to the release of nitrate and that is why it is called nitrate dumping. Now this generally happens this is more we can say prominent when we are having sulfate present in excess of 25% of the total concentration of sulfate and nitrate if it is the sulfate is more than 25% of the total concentration of sulfate and nitrate so then this problem may arise more.

So, this means that we need to have a certain resin which have higher affinities for nitrate so that the selective removal of nitrate can take place. So, when we deal with the wastewater which is having a very high sulfate concentration so then we require a resin which can selectively remove nitrate over sulfate. Such type of performance of nitrate selective resins may depend upon the composition of the treated wastewater. It will also require that we have a certain pilot scale testing to be done so that we can see that what is the concentration of nitrate over sulfate which can be removed from the base water. So, such type of selective nitrate resins is example tributylamine or triethylamines so they can be used for selective removal of nitrate from the base water.

So, then another application which is which we call it as a very common application for the ion exchange column is to demineralize the water. That is not only it removes the cations in the column, but it also removes anions in the column and this water is known as deionized water or demineralized water. So, it is free from all the ions. So if we are targeting only water softening that is if we only want to remove the cations causing hardness like calcium and magnesium then we can go for only a cation exchanger column. But if we want to demineralize the water that is if we want a water which is pure H_2O only so then we go for two columns here that is first is the cation exchange column and then we take it to an anion exchange column so that we can get a water which is free of any ions.

For example, you can see here that when calcium lead in water it comes in contact with resin which is having H^+ as functional group. So, the calcium is basically it replaces the H^+ ions and H^+ ions go into the water. Similarly, magnesium is also removed by using RH^+ as a resin. So, this means that H^+ ions are basically exchanged by the cations which are present in the water. So, the equivalent amount of H^+ goes into water.

$$2RH^+ + Ca^{2+} \rightarrow R_2Ca^{2+} + 2H^+$$
$$2RH^+ + Mg^{2+} \rightarrow R_2Mg^{2+} + 2H^+$$

Now after this we take the water to anion exchange resin where all the anions which you want to remove so they are basically replaced by an equivalent amount of hydroxide ions which are released into the water. You can see here that chloride basically replaces the OH minus ions similarly the sulfate is there it replaces the OH^- ions. So OH^- ions go into the water. So, we are having H^+ ions and OH^-ions now in the water which have been passed through the cation exchanger and then the anion exchanger so what we get is a pure H_2O. So, this is known as an ion free water or deionized water or demineralized water.

$$ROH^- + Cl^- \rightarrow RCl^- + OH^-$$
$$2ROH^- + SO_4^{2-} \rightarrow R_2SO_4^{2-} + 2OH^-$$
$$H^+ + OH^- \rightarrow H_2O$$

We can see here an example here that we are having calcium, magnesium, sodium and then we are having bicarbonates and chlorides in the water. These are the major cations and anions present in the water. As we take this raw water to a cation exchanger here. So, this cation exchanger all the H^+ ions basically they are exchanged by calcium, magnesium and sodium ions and we get in the water only H^+ ions and the other anions which are present in the water. After this we take it to anion exchanger where now whatever the anions are present that is bicarbonates and chlorides, so they are exchanged by OH^- ions.

So, we what we get here is a product which is called a demineralized water that is pure H_2O. right and then basically we can take it to a degasic fire and a storage tank where we can store this type of treated water, and this can be used for various purposes where we need a highly pure water demineralized water. And then the acid regenerate can be used to regenerate the cation exchanger and alkali regenerate can be used for regenerating the anion exchanger. So here also we can see that this is for the softening process only it can be called as softening process also or we can also call it as a demineralizing process where we are having the hard water, so it is basically getting passed through a cation exchange resins which are there on a bed of gravel right. So, these are the gravel bed these are the resins which are there in the column. This is passed here, and the water goes to anion exchanger where again we are having anion exchanger resins which are there on the gravel bed and later, we get a water which is soft water, or we can say it as a demineralized water also right.

And here we are having the regenerate solutions which are again put after the service cycle is over then we regenerate the resins that is cation exchange resins and anion exchange resins by using acid or alkaline regenerate so that the next cycle can start. So then there is another important application of ion exchange which is known as the metal removal. Now metal removal is very very important in the system where basically we are having lot of metals going into the wastewater. So, for example the municipal wastewater may not contains very high amount of metals in it, but it is there in the industrial wastewater. So, when we talk about the industrial wastewater then it is very very necessary that we remove the metals which are there which are produced from the industries before it goes into the municipal sewer system or before it goes to the treatment plant.

This will prevent the accumulation and toxicity of these metals in the farm. So, it is very necessary that when we are putting our industrial effluent into the municipal sewer systems or any type of sewer systems which are dedicated also so that these metals can be removed from the wastewater before going to the treatment plant. So here we use again ion exchange process is used for removal of metals in various industries like metal processing like electronics manufacturing, metal plating, pharmaceuticals, laboratories, vehicle service shops. So here we find a number of metals which comes from various processes which are used, and it goes into the water, and it becomes wastewater with a very very high metal concentrations. So, it is very necessary that we remove these metals before we discharge the waste, or we take the waste to a treatment plant where it is possible that these metals may not be removed during the conventional treatment processes.

So industries with fluctuating metal concentrations so they may require flow equalization so that the ion exchange becomes feasible in the sense that if we are having a fluctuating flow of the industrial flow which is coming out so if we are putting it the different flows are being put onto the ion exchange column so it is possible that they may not work as basically we have designed it for a particular type of flow. So, it is very very necessary that a flow equalization to be done so that we can put a known amount of flow to the ion exchange column so that our ion exchange process becomes feasible as we have also seen that if the flow becomes lesser or before flow becomes higher then it impacts the operating capacity or the exchange capacity of the resin. It can be said that the ion exchange process can be costly so if we want to make the ion exchange process economically viable then we have to focus on the removal and recovery of the valuable metals from the streams. So ion exchange process is highly dependent on the pH so if we are using strong acid or strong base resins so it can be used for a different range of pH for the entire range of pH but when we are using weak acid or weak base resins so this will also depend upon the pH of the solution that we are treating and similarly the pH also affects the metal species that in which form they are present depending upon the pH and this impacts the interaction between the ions and the resins in the sense that the pH affects the metal species pH also affects the efficiency of the resin so depending upon the pH the interaction of ions and resin will also be impacted and then there can be several factors which impact ion exchange application for removal of heavy metals for example operating conditions the temperature ionic species and the chemical background influence of the selectivity of the resin so these all factors they impact the resin as we have also discussed the previous lectures. Similarly the presence of oxidants the particles the solvents the polymers they also can impact the performance of the ion exchange resins it is very very important that we go for pre-treatment or the wastewater which we are putting onto the ion exchange column so that these species if they are present so they can also degrade the resins which are used for our ion exchange process and the management of the generated regenerates so when we are basically having a regeneration process so regeneration process may again lead to the concentrated solutions of the metals or other forms so we also have to look for the management of the generated regenerates so that we can treat it properly and then we can dispose it off.

We can see here a very important example for the removal of the chromium so it can be applied for electroplating bath solution we are having a electroplating base water coming which contains a number of metal signs as well as the chromate which is used for the electroplating bath solution so it is passed through a cation exchanger here so that whatever the metal signs they are present so they can be exchanged here and we get a water which is now only laden with the chromate and this cation exchanger then is regenerated by using H_2SO_4 as you already discussed so then what happens that metals sulfate basically comes into the effluent as the H^+ ions are not now exchanged by the metal ions and metal ions goes into the solution and then it can be taken for the further treatment. Similarly this chromate then goes into the base water so this chromate is now passed through the anion exchanger where the chromate is now exchanged with the OH^- ions and we get a water which is free from these metals as well as the chromate solution and now it is now regenerated by using sodium hydroxide so this sodium hydroxide the chromate ions basically are replaced by OH^- ions and sodium chromate goes into the solution. Now this regenerant the waste regenerant pollution is now again passed through a cation exchanger so where this sodium is now exchanged by H^+ ions. So now it is removed as H_2CrO_4 and this can be used for the electroplating bath solution that's how we can recover the chromate for our further applications in the electroplating bath. Similarly, now this cation exchanger can again be regenerated by using H_2SO_4 and similarly sodium sulphate results from here and this can be again taken for a further treatment.

So that's how we can get rid of not only the metal ions but we can also get rid of the chromate or we can not only get rid of chromate but we can also reuse the chromate which is a very very costly chemical and it is also toxic to the environment also so if we are reusing it so then we are also saving our environment from the disposal of chromate into the environment. As you all of you know that the chromium 6 can be highly toxic as well as it can cause cancer also. So then after the application we should also focus on the operational conditions where the use of regenerate and distillates which can not only remove the inorganics, but they can also remove the organic material from the resin. So, we can use a certain regenerants and the restaurants so they remove the inorganic material from the spent resins as well as they will also remove the organic material which is trapped by the ion exchange resin columns. So, we can use sodium hydroxide HCl or methanol or bentonite so that we can remove the organics which are present in our ion exchange resin which are used after the service cycle.

So here we generally find that this ion exchange process may have a limited use because of the extensive pretreatment that we have to do. Similarly, it will also depend upon the life of the ion exchange resins and the complex regeneration system which also limits its use. So, we have to go for a pretreatment process. Similarly, the ion exchange resins are also having a certain age they degrade with time so that is also basically limits their application as well as the complex regeneration system that is employed during the use of the ion exchange process so that may also limit the use of ion exchange process. But when we are using it so then we have to see that the higher total suspended solids may lead to the clogging and loss of the head, and it can also lead to the inefficient operation of the ion exchange treatment process.

So, this needs to be treated so that's why we need a pretreatment whenever we are going for ion exchange process so that our ion exchange process becomes more and more efficient. Similarly, organics which are present in the wastewater they may also bind to the resin so that also should need to be removed. For example we have seen in the previous slides where we are talking about the treatment of the ammonia right so there you have seen that we have gone for the filtration and then you have gone for the carbon adsorption so this is required so that we can remove the total suspended solids and this is also required so that we can remove the organics which are present in the wastewater which otherwise may impact the ion exchange process. So, this means that the pre-filtration is required, and we can also use a certain scavenger exchange resins so that the organics which can pose problem to the ion exchange column so that can be removed from the water or the wastewater. So, these are the things that we need to consider before we go to the ion exchange process.

So now let us take an example here so we are having a column study is being conducted so that we can determine the capacity of the ion exchange resins right so in this study we are using 0.1 kg of the resin which was warmed washed with NaCl until the resin is in the form of R Na, And then the column is washed with the distilled water so that we can remove the excess chloride ions which are there in the resins and then the resin was titrated with a solution of calcium chloride right and the concentration of chloride and calcium are measured so we can see here that the concentration of chloride and calcium are measured and it is written here which are passing into the throughput volumes which are passing through the ion exchange column and then we have to using this data we have to find the exchange capacity of the resin and we have to also find out the volume of the resin that is required so that we can treat a 4000 cubic meter of wastewater which contains 18 mg per liter of ammonium ions and take the density of the resin is also given here. So, how we can do this thing so we first of all we will draw the two curves which are the normalized concentration of the chloride and the calcium ions which are there in the throughput volume because a nominal concentration means that is a concentration which is coming out of the effluent divided by the initial concentration that we have put onto the ion so basically C/C° will ultimately become equal to 1.

So then we see that if we want to find out at C/C° equal to 0.5 so we can find out that what is the throughput volume that has gone here for example here 22.1 liters is totally required for at the normalized concentration of 0.5 similarly the throughput volume required for the chloride ions is around 7.5 liters so we can find out the exchange capacity by the throughput volume that has been passed so we are talking about in terms of calcium ions because we want to find out the exchange capacity for the cations so this is the throughput volume required for the calcium removal and then C° is the initial concentration of the calcium that we have put and R is the resin amount of resin that we have put into the column so we are finding out the the concentration at the capacity at C/C° is equal to 0.5 so we can find out the total volume that is there so 22.1-7.5 because 7.5 represents the chloride ions and 22.1 represents the calcium ions which are applied to the column and this is presenting the equivalent concentration of our calcium ions that we put onto the column that is 40 milliamp per liter we have put to the column so this is equal to around 2 milli equivalents per liter and similarly 0.1 kg of the resin we have put so by calculating we can find out that the capacity the exchange capacity at C/C° is equal to 0.5 is around 292 milli equivalents per kg of resin.

$$\mathrm{EC} = \frac{(22.1\mathrm{L} - 7.5\mathrm{L})\left[\frac{(40\mathrm{mg/L})}{20\mathrm{mg/meq}}\right]}{0.1\ \mathrm{kg\ of\ resin}}$$

= 292 meq/kg of resin

So now we want to treat water which is having 18 milliamp per liter of as ammonium ions so we know that the concentration of ammonium ions in the solution that we need to treat is around 1 milli equivalents per liter so the required exchange capacity comes out to be around or the ammonium ions it comes out to be around 4×10^6 milli equivalents because we are passing a water which is around 4000 cubic meter.

$$\mathrm{NH_4}^+,\ \mathrm{meq/L} = \frac{(\frac{18\mathrm{mg}}{\mathrm{L}}\ \mathrm{as\ NH_4}^+)}{(18\frac{\mathrm{mg}}{\mathrm{meq}})} = 1\ \mathrm{meq/L}$$

The required exchange capacity

$$= \left(1\frac{\mathrm{meq}}{\mathrm{L}}\right)(4000\mathrm{m}^3)\left(\frac{10^3\mathrm{L}}{\mathrm{m}^3}\right)$$

$$= 4\times10^6\ \mathrm{meq}$$

So this means that around 4×10^6 milli equivalents of ion needs to be exchanged and we know that our the resin capacity is around 292 milli equivalents per kg so we can divide the total ions that we need to remove divide by the exchange capacity so this gives us the total weight of the resin that we require for treating 4000 cubic meter of water which is laden with around 18 milliamp per liter of ammonium ions.

The required mass of resin ($\mathbf{R_{mass}, kg}$)

$$(\mathrm{R_{mass}, kg}) = \frac{4\times10^{6}\mathrm{meq}}{(292\,\frac{\mathrm{meq}}{\mathrm{kg}}\ \text{of resin})}$$

$$= \mathbf{13700\ kg\ of\ resin}$$

Similarly, we know the density of the resin so we can also calculate that what is the volume of the resin that is required for the treatment of ions.

Required volume of the resin (R_{vol}, m^3)

$$(\mathrm{R_{vol}, m^3}) = \frac{13700\ \text{kg of resin}}{700\ \mathrm{kg/m^3}}$$

$$= \mathbf{19.6\ m^3 of\ resin}$$

So, the required volume of resin will be usually around 1.1 times to this. Actually, the volume of the resin which we have got theoretically but we generally take it 1.1 to 1.4 times based on the exchange capacity we take it higher so that we can have a factor of safety into consideration.

So now we also discuss exchange capacity that is also known as the operating exchange capacity so here we are having a solution which contains calcium ions here in this case and these ions are being put onto the column which we can see that we are having a breakthrough curve that is so we have to compute the operating capacity of the cation exchange resins and the breakthrough curve is given here which is shown in the figure the resin column is required to treat the total hardness of around 5 milli equivalents per liter and the volume of the resin in the column is around 10,000. So, we need to treat it to a point where we are having 0.4 as C/C° concentration so we can see here that the area under this curve right from this point to this point will give us the total capacity till C/C° is equal to 0.4. Right, so we have to now set the intervals for example we can see from here that the first interval that we take is 0.05 that is Yt here is C/C° equal to point at 0.05 here that is 0.05 so the volume is nearly 1200. Right, so this total volume into this the concentration the equivalent concentration or we can say the fraction of the concentration so this will give us the leakage till this point.

We can see that 0.05×1210 liter that is passed till this point, so this gives us a value of around 60.5. Similarly we take we make another strip where we are taking it from 0.05 to 0.1 so the middle point is 0.075 so we take this as 0.075 as the average of C/C° into the volume that is this minus this one so we can see here that the volume is 1280 till this point and minus 1210 so 70 liters here so this gives us a value of Yt×V equal to 5.3. Similarly then we can take the next strip here that is the next strip represents from 0.1 to 0.2 right and the average value is 0.15 right and we multiply it by this volume right so this volume is around 1440 minus 1280 so this gives us 24 and similarly we can take the middle of the next strip as 0.25 right here and 0.35 here and the volumes corresponding to these strips that is delta v1 delta v2 delta v3 delta v4 and delta v5 represents a volume that is there corresponding to these strips that we have considered. So this gives us around 154.8 as Yt summation of yt×Vt so this will be the we can say the amount of calcium that will be eluting from the volume so we can see that the total capacity the operating capacity of the resin corresponding to C/C° equal to 0.4 will be equal to the amount of the resin so the hardness that you are putting here that is 5 milli equivalents per liter of hardness is being put here and 1660 represents the total amount of we can say the volume that is put onto the resin right okay so this is 1660 divided by 10000 and minus the leakage that has happened during this process so this represents the leakage that has happened during the process and we can say that this is equal to around 0.75 milli equivalents per ml of resin.

$$X = \frac{5 \times 1660}{10000} - \frac{5 \times 154.8}{10000}$$

$$= \mathbf{0.75\ meq./ml}$$

Calculate the operating capacity corresponding to this C/C° is equal to 0.54. Okay so that's how we can calculate the operating capacity of the resin. Now we come to another example where we see that we are having two types of wastewater here that is wastewater A and wastewater B which are having different concentrations of cations and anions here so we are mainly concerned with the anion concentration because we are removing here the nitrate right so with with with sulfate and without sulfate so you can see the first wastewater where we are having the sulfate present in the base water sulfate not present in the wastewater whereas in the second part we are having sulfate present in the base water right so we have to determine that what is the maximum amount of water that can be processed per liter of the strong base anion exchange resin with a cap exchange capacity of two equivalents per liter.

So here first of all we have to calculate the selectivity coefficient so we will be calculating the selectivity coefficients depending upon what amount of ions are present for example if we see the wastewater A here the wastewater A contains mainly bicarbonates right it contains chlorides it contains nitrate okay so we have to calculate the and we want to remove the nitrate from the system so we will calculate the selectivity coefficient of nitrate over the bicarbonate. Okay so the selectivity coefficient for nitrate is around 4. from the table that we have already given in the previous slides right and similarly the selectivity coefficient for bicarbonate is around 0.4 so we can say that the nitrate over bicarbonate is equal to 10 so the value of k for the nitrate replacing bicarbonates is equal to 10. similarly, the nitrate replacing the chlorides comes out to be 4.

$$K_{HCO_3^- \rightarrow NO_3^-} = \frac{4.0}{0.4} = 10$$

$$K_{Cl^- \rightarrow NO_3^-} = \frac{4.0}{1.0} = 4.0$$

so, this is estimated that the nitrate replacing both bicarbonates and chlorides can be estimated as the average value of around 7.

$$K_{[(HCO_3^-)(Cl^-)]\rightarrow NO_3^-} = 7.0 \text{ (estimated)}$$

So, we can say that when we are having the equilibrium conditions where C/C° is equal to 1 that is our ion exchange is completely exhausted so in that case the X nitrate which is present so basically this is a fraction of nitrate which is present in the solution so this is equal to 0.91 that is we can see here that we are having 0.91 of the nitrate present in the solution divided by the total ions present in the solution that is 8.11 equivalents per liter okay so this is fraction of the nitrate present in the water.

$$X_{NO_3^-} = \frac{0.91}{8.11} = \mathbf{0.112}$$

so as we have discussed already that we can calculate the fraction present in the water and present in on the resin by using this equation for the monovalent ions so we can replace here this value is known to us that is this value we have already calculated as 7 right and divided by the fraction present in the in the wastewater so this is this can be calculated from here so this x bar can be calculated but that is what is the fraction of the nitrate which is there present on the ion exchange resin so around 47 percent of the exchange sites they are basically helpful in the removal of the nitrate right okay so we know that the two equivalents per liter is the total capacity of the resin so into the 47 percent that is there for the nitrate removal.

$$\frac{\overline{X}_{NO_3^-}}{1 - \overline{X}_{NO_3^-}} = 7.0\left[\frac{0.112}{1 - 0.112}\right]$$
$$\overline{X}_{NO_3^-} = \mathbf{0.47}$$

so, we know that the capacity the limiting operating capacity in this case for nitrate when it is when it is present in combination with bicarbonates and chloride it is around 0.94 equivalents per liter.

Limiting operating capacity= (2 eq/L of resin)(0.47)
=0.94 eq/L of resin

And then we can calculate similarly we can calculate that what is the amount of water that can be treated by this type of because we know that the nitrate removal capacity of the resin right and we know that what is the solution of what is the concentration of nitrate in the solution and calculate what the amount of water that can be removed.

$$\text{Vol} = \frac{\left(\text{nitrate removal capacity of resin}, \frac{\text{eq}}{\text{L}} \text{ of resin}\right)}{\left(\text{nitrate in solution}, \frac{\text{eq}}{\text{L}} \text{ of water}\right)}$$

$$= \frac{\left(0.94 \frac{\text{eq}}{\text{L}} \text{ of resin}\right)}{\left(0.91 \times 10^{-3} \frac{\text{eq}}{\text{L}} \text{ of water}\right)}$$

$$= \mathbf{1033} \frac{\textbf{L of water}}{\textbf{L of resin}}$$

So, now the next case becomes that is when the wastewater is having both sulfates chlorides and nitrate so first of all the sulfates can also remove bicarbonates and chlorides and nitrate so we have to calculate first of all that what is the percentage fraction of sulfate which is present onto the ion exchange resin so we can calculate in a similar way that what is the what are the selectivity coefficient of sulfate replacing bicarbonate sulfate replacing chloride sulfate replacing nitrate so these are the things these are the values of the selectivity coefficient for all these three cases so we can calculate that sulfate replacing the nitrate bicarbonates as well as chloride so this can be estimated to be the average values of these three values so the sulfate present in the solution we can calculate as 0.2 depending upon what is the concentration of sulfate in the solution divided by the total ionic concentration in the solution and we can then use the equation which can be used for the more divalent ions replacing the monovalent ions right in this case and we can calculate the values of x here for example the solution sulfate present in the solution we can put it here and we can calculate the sulfate present onto the ion so you can see here that the sulfate now occupies around 68 percent of the exchange sites right so now only 32 percent of the sites are left where we can have the replacement of nitrate and income in competition with bicarbonates as well as chloride, okay.

$$K_{HCO_3^- \to SO_4^{2-}} = \frac{0.15}{0.4} = 0.4$$

$$K_{Cl^- \to SO_4^{2-}} = \frac{0.15}{1.0} = 0.15$$

$$K_{NO_3^- \to SO_4^{2-}} = \frac{0.15}{4.0} = 0.04$$

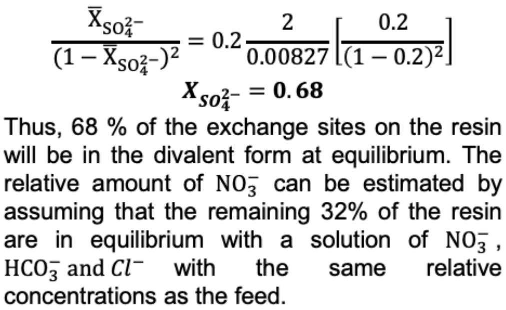
$$K_{[(NO_3^-)(HCO_3^-)(Cl^-)] \to SO_4^{2-}} = 0.2 \text{ (estimated)}$$

2. For the equilibrium condition $^{C_e}/_{C_o} = 1.0$, estimate the sulfate equivalent fraction in solution

$$X_{SO_4^{2-}} = \frac{1.65}{8.27} = \mathbf{0.2}$$

3. Compute the equilibrium resin composition using Eq.

$$\frac{\bar{X}_{B^{2-}}}{(1 - \bar{X}_{B^{2-}})^2} = [K_{A^- \to B^{2-}}] \left[\frac{\bar{C}}{C}\right] \frac{X_{B^{2-}}}{(1 - X_{B^{2-}})^2} \quad \ldots.(2)$$

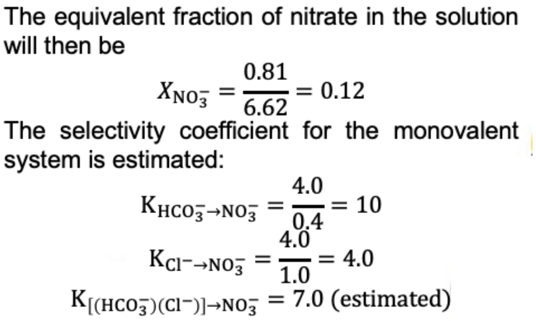


$$\frac{\overline{X}_{SO_4^{2-}}}{(1-\overline{X}_{SO_4^{2-}})^2} = 0.2\,\frac{2}{0.00827}\left[\frac{0.2}{(1-0.2)^2}\right]$$

$$\boldsymbol{X_{SO_4^{2-}} = 0.68}$$

Thus, 68 % of the exchange sites on the resin will be in the divalent form at equilibrium. The relative amount of NO_3^- can be estimated by assuming that the remaining 32% of the resin are in equilibrium with a solution of NO_3^-, HCO_3^- and Cl^- with the same relative concentrations as the feed.

so now we can calculate what is the concentration of the nitrate present in the solution and then we can calculate the selectivity coefficients for nitrate placing bicarbonates nitrate placing chlorides. and then we can calculate the average k values and now we can also calculate based on this that what is the concentration of the nitrate present in the solution what is the selectivity coefficient for the nitrate replacing the bi-carbonates and the chlorides and we can calculate now what is the fraction of our nitrate which will be there on the resin okay occupied by the nitrate okay.



The equivalent fraction of nitrate in the solution will then be

$$X_{NO_3^-} = \frac{0.81}{6.62} = 0.12$$

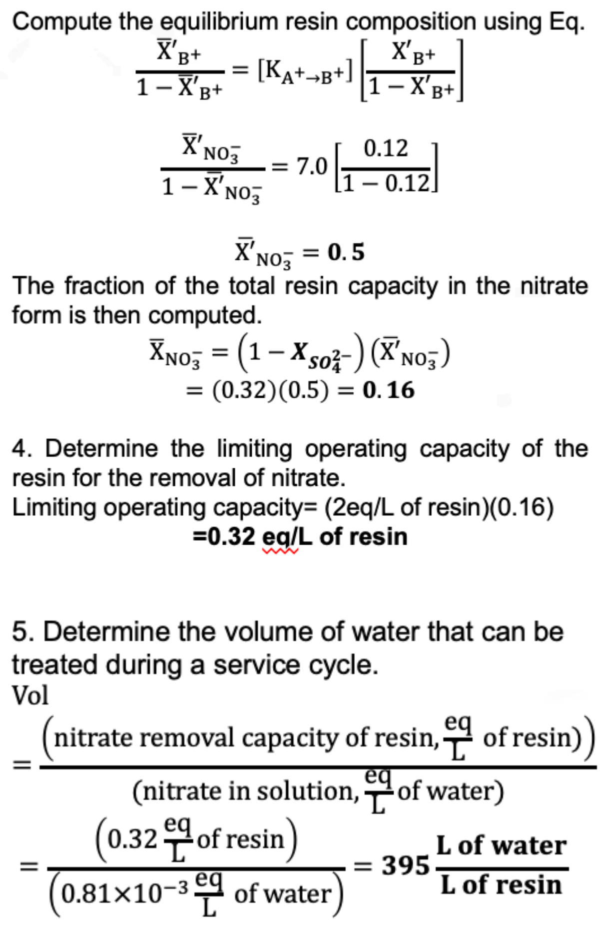
The selectivity coefficient for the monovalent system is estimated:

$$K_{HCO_3^- \rightarrow NO_3^-} = \frac{4.0}{0.4} = 10$$

$$K_{Cl^- \rightarrow NO_3^-} = \frac{4.0}{1.0} = 4.0$$

$$K_{[(HCO_3^-)(Cl^-)] \rightarrow NO_3^-} = 7.0 \text{ (estimated)}$$

Now we know that only 32 percent sites were left after the sulfate have occupied the sites so only 32 percent sites are left for the for our nitrate so we multiply it because in competition with the chloride and sulfate only 0.5 that is 50 percent will be occupied by nitrate so 50 percent of the 32 percent will give us around 16 percent of the sites are now being occupied by the nitrate in presence of our sulfate right. So, you can see that the capacity has reduced a lot so around 0.32 equivalents per liter of resin is the limiting operating capacity and we can now also calculate that we can only treat around 395 liters of water per liter of resin in comparison to the earlier case where we can treat around more than 1000 liters of water per liter.



Compute the equilibrium resin composition using Eq.

$$\frac{\bar{X}'_{B^+}}{1-\bar{X}'_{B^+}} = [K_{A^+\to B^+}]\left[\frac{X'_{B^+}}{1-X'_{B^+}}\right]$$

$$\frac{\bar{X}'_{NO_3^-}}{1-\bar{X}'_{NO_3^-}} = 7.0\left[\frac{0.12}{1-0.12}\right]$$

$$\bar{X}'_{NO_3^-} = \mathbf{0.5}$$

The fraction of the total resin capacity in the nitrate form is then computed.

$$\bar{X}_{NO_3^-} = \left(1-\boldsymbol{X}_{SO_4^{2-}}\right)\left(\bar{X}'_{NO_3^-}\right)$$
$$= (0.32)(0.5) = \mathbf{0.16}$$

4. Determine the limiting operating capacity of the resin for the removal of nitrate.

Limiting operating capacity= (2eq/L of resin)(0.16)

=0.32 eq/L of resin

5. Determine the volume of water that can be treated during a service cycle.

$$\text{Vol} = \frac{\left(\text{nitrate removal capacity of resin}, \frac{\text{eq}}{\text{L}} \text{ of resin}\right)}{\left(\text{nitrate in solution}, \frac{\text{eq}}{\text{L}} \text{ of water}\right)}$$

$$= \frac{\left(0.32\,\frac{\text{eq}}{\text{L}} \text{ of resin}\right)}{\left(0.81\times10^{-3}\,\frac{\text{eq}}{\text{L}} \text{ of water}\right)} = \mathbf{395}\,\frac{\textbf{L of water}}{\textbf{L of resin}}$$

So, we stop here, and we'll continue our lecture in our next module.

Thank you very much.