Water and Wastewater Engineering
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Lecture – 12
Softening

Last class we were discussing about coagulation and flocculation and we have seen what is the necessity of this coagulation and flocculation and by going for or by add adding coagulants how we can remove the turbidity. Today, we will discuss about the next treatment unit that is softening. Softening is usually used for ground water because most of the time surface water will be having hardness within the permissible limit. And we have discussed about hardness when we were discussing about water characteristics.

For drinking purpose hardness up to 150 milligram per liter of calcium carbonate is acceptable. If the water is having high hardness it is known as hard water and if the hardness is low then it is known as soft water. And we have already discussed what is this hardness. Hardness is nothing but the presence of polyvalin, the presence of polyvalin metal ions in the water. But not all polyvalin metal ions are considered in using hardness. Usually we take the presence of calcium and magnesium in water as hardness and hardness we can divide it into different categories carbonate hardness non-carbonate hardness calcium hardness magnesium hardness or temporary hardness and permanent hardness. We have already seen this one in detail but I will just mention what each one of them represents.

Carbonate hardness is nothing but the hardness which is equivalent to alkalinity so that is known as carbonate hardness and non-carbonate hardness are the ones which are excess in terms of alkalinity or the ions like calcium and magnesium present in the form of sulphate, nitrate, chloride etc then it is known as non-carbonate hardness.

Then, coming to temporary hardness which can be removed by boiling that is known as temporary hardness. That means the temporary hardness is equal to carbonate hardness and permanent hardness is the one which cannot be removed by mere boiling we have got some extra chemical for the removal that is known as permanent hardness and calcium hardness is nothing but the hardness caused by calcium ions that is calcium hardness and magnesium hardness is the one which is magnesium ions.

Why we are not considering the presence of monovalent metal ions for hardness?
The reason is, if we add soap to the solution the soap formed by TGE reaction of this monovalent metal ions and soap they are of soluble form so we will not consider them for the hardness determination or as hardness causing element.

So what are the disadvantages of hard water?
The most important one is if hard water is there the soap consumption is very very high. If the water is hard the lather formation is very difficult with low quantity of soap. Another one is it creates or it forms scale on all heat exchangers and boilers. So in industrial purpose hard water is not recommended because if it is used in the boiler it will be forming thick scale and the heat

exchanging capacity will be reduced drastically. So, for industrial purpose we need almost zero hard zero hardness for most of the purpose and for cooling purpose and all they recommend in the range of 60 to 70 milligrams per liter as calcium carbonate. So today we will discuss what all are the different methods usually employed in water treatment plants for the removal of hardness. There are basically two different methods which is being used they are one is chemical precipitation and another one is ion exchange.

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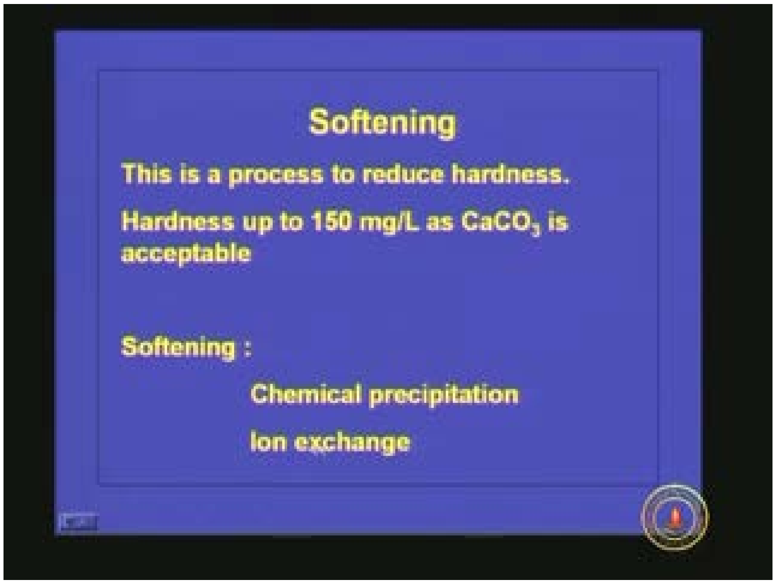

Softening

This is a process to reduce hardness.

Hardness up to 150 mg/L as $CaCO_3$ is acceptable

Softening :

Chemical precipitation

Ion exchange

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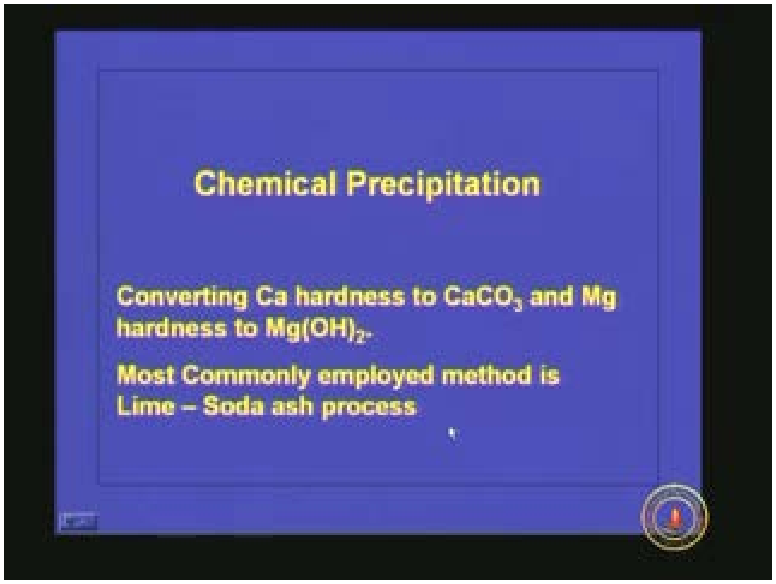

Chemical Precipitation

Converting Ca hardness to $CaCO_3$ and Mg hardness to $Mg(OH)_2$.

Most Commonly employed method is Lime – Soda ash process

The most commonly used one is chemical precipitation but we have to remember that by chemical precipitation we cannot achieve zero hardness because this is working on the precipitation principle. So we know that if some compound have to be precipitated the soluble concentration should exceed the solubility product constant. So, the concentration corresponding to that solubility product constant will be remaining in the water so we cannot remove 100 percent or we cannot remove 100 percentage efficiency by chemical precipitation. In chemical precipitation what is happening. Here we are converting calcium hardness to calcium carbonate and magnesium hardness to magnesium hydroxide because these two compounds calcium carbonate and magnesium hardness is having very low solubility and they will be precipitating out easily and these precipitates are dense enough so we can settle them properly.

The most commonly employed method of chemical precipitation is lime soda ash process. So we will discuss about this process in detail. In hardness removal we have to add lime and soda ash depending upon the type of hardness present. So we will first discuss about the reactions involved with these chemicals and the hardness present in the water.

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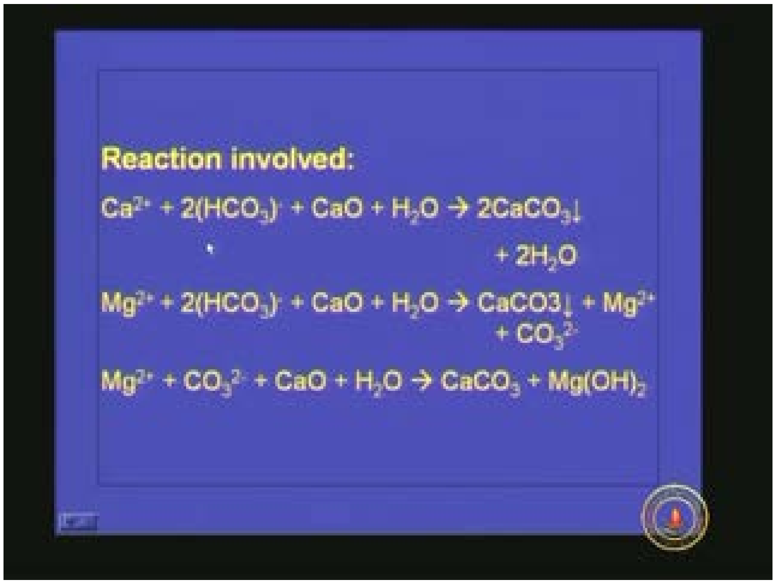

Reaction involved:

$Ca^{2+} + 2(HCO_3)^- + CaO + H_2O \rightarrow 2CaCO_3\downarrow + 2H_2O$

$Mg^{2+} + 2(HCO_3)^- + CaO + H_2O \rightarrow CaCO3\downarrow + Mg^{2+} + CO_3^{2-}$

$Mg^{2+} + CO_3^{2-} + CaO + H_2O \rightarrow CaCO_3 + Mg(OH)_2$

So first what will happen is calcium carbonate hardness is present. That means calcium is associated with anions which causes alkalinity. That means bicarbonate or carbonate so the reaction is like this (Refer Slide Time: 6:31) calcium plus 2 bicarbonate that means calcium bicarbonate reacts with lime calcium oxide and water to give 2 calcium carbonate and 2 water molecules. So here the calcium carbonate is formed this is a precipitate and that is enough to settle down.

Now coming to magnesium carbonate hardness because the anion is bicarbonate magnesium bicarbonate plus calcium oxide will give calcium carbonate plus magnesium carbonate. Here calcium carbonate is easily settleable and the solubility is very very less so we can remove that very easily. But magnesium carbonate is having high solubility so magnesium we cannot remove in the form of magnesium carbonate but we have to convert this magnesium carbonate into magnesium hydroxide that is the second step of equation; magnesium carbonate plus calcium oxide gives you calcium carbonate plus magnesium hydroxide both are precipitates which can be removed easily.

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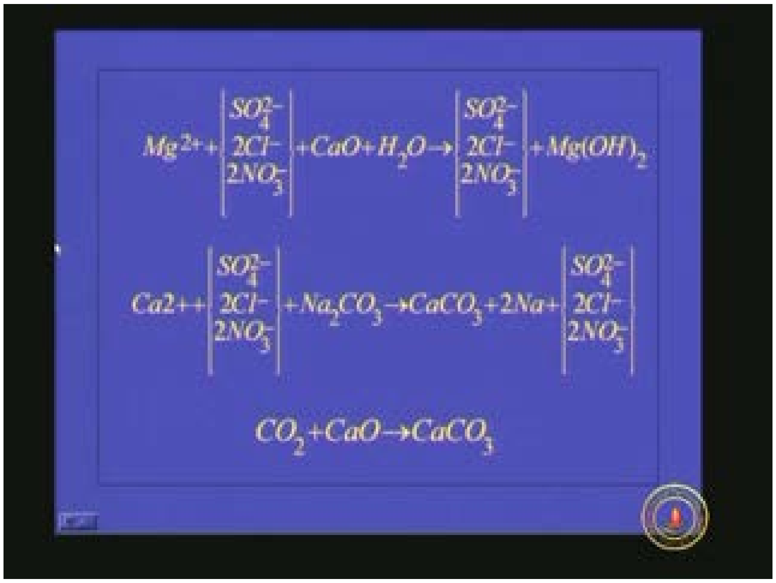

$$Mg^{2+} + \left|\begin{matrix} SO_4^{2-} \\ 2Cl^- \\ 2NO_3^- \end{matrix}\right| + CaO + H_2O \rightarrow \left|\begin{matrix} SO_4^{2-} \\ 2Cl^- \\ 2NO_3^- \end{matrix}\right| + Mg(OH)_2$$

$$Ca2+ + \left|\begin{matrix} SO_4^{2-} \\ 2Cl^- \\ 2NO_3^- \end{matrix}\right| + Na_2CO_3 \rightarrow CaCO_3 + 2Na + \left|\begin{matrix} SO_4^{2-} \\ 2Cl^- \\ 2NO_3^- \end{matrix}\right|$$

$$CO_2 + CaO \rightarrow CaCO_3$$

Now we will see how the non-carbonate hardness are removed. The magnesium whether it is associated with sulphate, chloride or nitrate so magnesium sulphate or magnesium chloride or magnesium nitrate when it reacts with lime we will be getting the corresponding magnesium hydroxide and calcium sulphate or calcium chloride or calcium nitrate all these compounds are soluble in water or the air solubility are very very high and magnesium hydroxide is air precipitate which will settle down easily.

Now, coming to calcium non-carbonate hardness calcium whether it is present in the form of sulphate, chloride or nitrate and when it reacts with sodium carbonate that means this is soda ash (Refer Slide Time: 8:15) it forms calcium carbonate plus sodium sulphate or chloride or nitrate so these compounds are soluble and calcium carbonate is the precipitate so we can remove calcium carbonate hardness as well as calcium non-carbonate hardness. So, for all hardness that means calcium carbonate hardness, magnesium carbonate hardness and magnesium non-carbonate hardness the chemical required is lime. But for calcium non-carbonate hardness we have to add soda ash. This is the important point that is going to be remembered here.

If the water is having dissolved carbon dioxide that also will be consuming quite amount of lime so this is the reaction: carbon dioxide plus calcium oxide gives you calcium carbonate. But if the dissolved carbon dioxide concentration is more than 10 milligram per liter it is always advisable to go for aeration so that the carbon dioxide can be expelled from the system so the lime consumption will be very very less. Instead of lime we can go for caustic soda.

Now how can we find out the lime and soda ash requirement?

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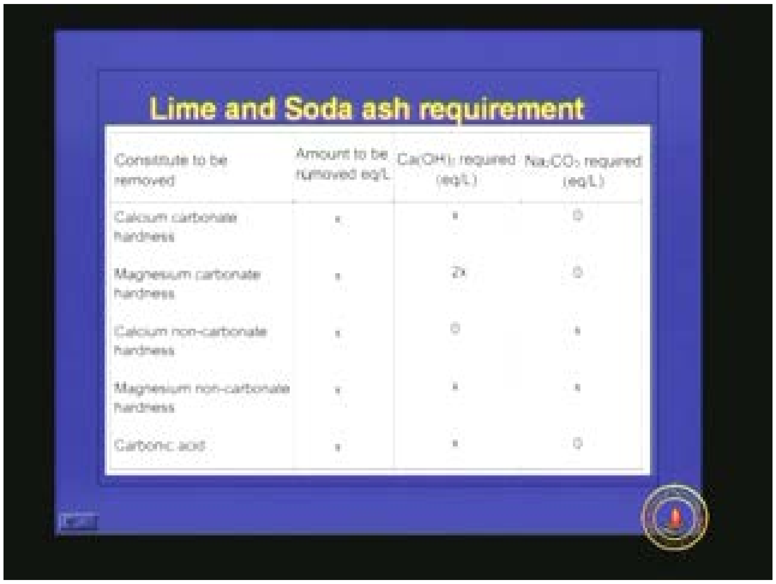

Lime and Soda ash requirement

Constitute to be removed	Amount to be removed eq/L	$Ca(OH)_2$ required (eq/L)	Na_2CO_3 required (eq/L)
Calcium carbonate hardness	x	x	0
Magnesium carbonate hardness	x	2x	0
Calcium non-carbonate hardness	x	0	x
Magnesium non-carbonate hardness	x	x	x
Carbonic acid	x	x	0

This is the table which can be used to calculate the amount of lime required lime and soda is required for the treatment. If calcium carbonate hardness is present and if we express the amount in equivalence per litre or milliequivalence per liter so say x milliequivalence of calcium carbonate hardness is present; we have seen the equation earlier like this:

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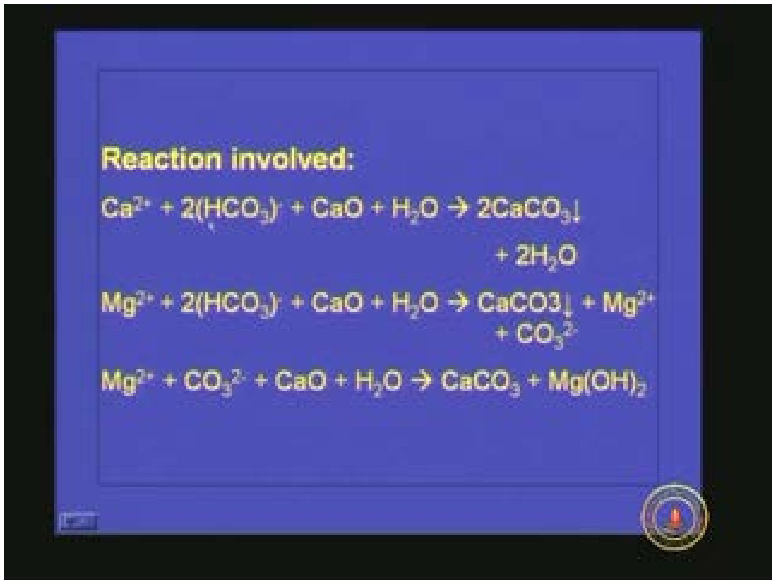

Reaction involved:

$$Ca^{2+} + 2(HCO_3)^- + CaO + H_2O \rightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg^{2+} + 2(HCO_3)^- + CaO + H_2O \rightarrow CaCO3\downarrow + Mg^{2+} + CO_3^{2-}$$

$$Mg^{2+} + CO_3^{2-} + CaO + H_2O \rightarrow CaCO_3 + Mg(OH)_2$$

Calcium carbonate hardness on one mole requires one mole of lime. So that is what here it is represented calcium hydroxide required is X and soda ash required is zero. So coming to magnesium carbonate hardness if we have to remove X equivalence or milliequivalence of magnesium carbonate hardness we have to add calcium hydroxide 2 equivalence. The reason is first magnesium bicarbonate will be converted into magnesium carbonate which is highly soluble compound so we have to convert this magnesium carbonate again to magnesium hydroxide and for that one 1 mole of lime addition is again required that is why here 2x is coming and Na 2 Co 3 required is 0.

Now coming to calcium non-carbonate hardness the amount removed is x so calcium bicarbonate required is 0 and soda ash Na 2 Co 3 required is x equivalence per liter; and magnesium non-carbonate hardness if you want to remove we have to add if we want to remove x then we have to add 1 mole of or 1 equivalence of calcium bicarbonate or lime so it will converting it to corresponding calcium salt and then afterwards that has to be precipitated out as using sodium carbonate or soda ash. So, if magnesium non-carbonate hardness is present we have to add 1 mole of lime or 1 equivalence of lime and 1 equivalence of soda ash.

And coming to carbonic acid or carbon dioxide present in the system if we want to remove x equivalence per liter of carbon dioxide we have to add x equivalence per liter of lime. Similarly instead of lime we can go for caustic soda also or NaOH. The reactions are like this.

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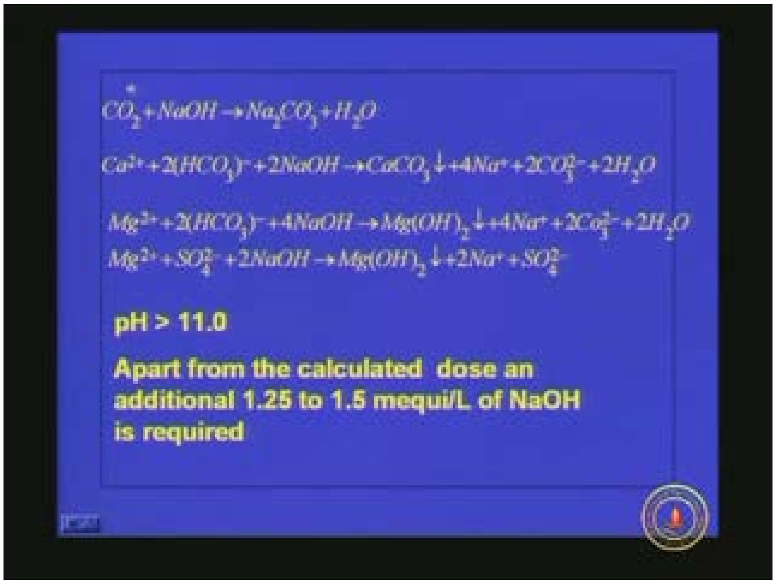

$CO_2 + NaOH \rightarrow Na_2CO_3 + H_2O$

$Ca^{2+} + 2(HCO_3)^- + 2NaOH \rightarrow CaCO_3\downarrow + 4Na^+ + 2CO_3^{2-} + 2H_2O$

$Mg^{2+} + 2(HCO_3)^- + 4NaOH \rightarrow Mg(OH)_2\downarrow + 4Na^+ + 2Co_3^{2-} + 2H_2O$

$Mg^{2+} + SO_4^{2-} + 2NaOH \rightarrow Mg(OH)_2\downarrow + 2Na^+ + SO_4^{2-}$

pH > 11.0

Apart from the calculated dose an additional 1.25 to 1.5 mequi/L of NaOH is required

One advantage of caustic soda is we have seen that for calcium non-carbonate hardness we have to add sodium carbonate or soda ash. But if you add caustic soda or NaOH caustic soda will be generated as a byproduct. Here we can see. So we can reduce the amount of soda ash to be added to the system. So these are the reactions when we add or when we use caustic soda.

Carbon dioxide plus sodium hydroxide gives Na 2 CO 3 plus H 2 O and calcium bicarbonate plus calcium carbonate plus sodium carbonate plus water. And magnesium bicarbonate plus sodium hydroxide gives magnesium hydroxide plus soda ash plus water magnesium non-carbonate hardness plus soda ash gives you magnesium hydroxide plus sodium sulphate. So we can see that sodium carbonate is coming as a byproduct so soda ash dose can be reduced. So if you have more non-carbonate hardness compared to carbonate hardness if soda ash can be generated by the process itself it is advisable to go for soda ash but compared to calcium oxide. Sodium hydroxide is costly so we have to compare the cost involved in each process and we have to select the best out of them.

So again calcium carbonate hardness and non-carbonate hardness are almost equal and if you want to reduce the soda ash dose then it is advisable to go for caustic soda or NaOH because from the calcium carbonate hardness you will be getting enough sodium carbonate that sodium carbonate will be used for the removal of the calcium non-carbonate hardness and magnesium non-carbonate hardness.

And here we can see that the calcium carbonate precipitate the solubility diagram of calcium carbonate. If you see, last class we were discussing about aluminum hydroxide, this calcium carbonate is also somewhat […..14:05] so the solubility will be increasing on both the sides of the optimum pH and the optimum pH of calcium carbonate precipitation is in the range of 9 to 9.5 but coming to magnesium if you want to remove magnesium the pH of the solution should be above 11. So that is very very important. So if you calculate the chemical dose based upon this table (Refer Slide Time: 14:31) that is only we are calculating the chemical required for the chemical reaction but we have to add some chemical which is required for increasing the pH because in most of the cases the natural pH of water is in the range of 6.5 to 7.8 or so.

We have to increase the pH from this range to above eleven so that requires a considerable amount of chemical dose. So whenever we calculate the chemical dose using the chemical equivalents we have to add around 1.25 to 1.5 times the calculated chemical dose to achieve better performance. And one more thing is whenever we calculate the chemical dose we should be careful about the purity of the chemical component.

Here all the calculations are based upon pure compounds. We are assuming that hundred percentage reaction is taking place or whatever we are adding it is available 100 percent but most of the time what is happening the commercially available chemical those will not be hundred percent pure so say sometimes it is seventy percentage pure sometimes it is 75 percentage pure or 80 percentage pure so when we calculate the dose we have to take that purity also into the account.

For example, 0.80 percentage pure compound so if you calculate the dose as 1 kilogram or 1 kilogram say so we have to add anyway 1.25 to 1.5 to increase the pH up to 11 then we have to multiply that quantity by 0.8 divide that quantity by 0.8 to get the actual amount because if you add 1 kilogram you are getting only 0.8 kilogram of actual chemical so that also we have to take into account.

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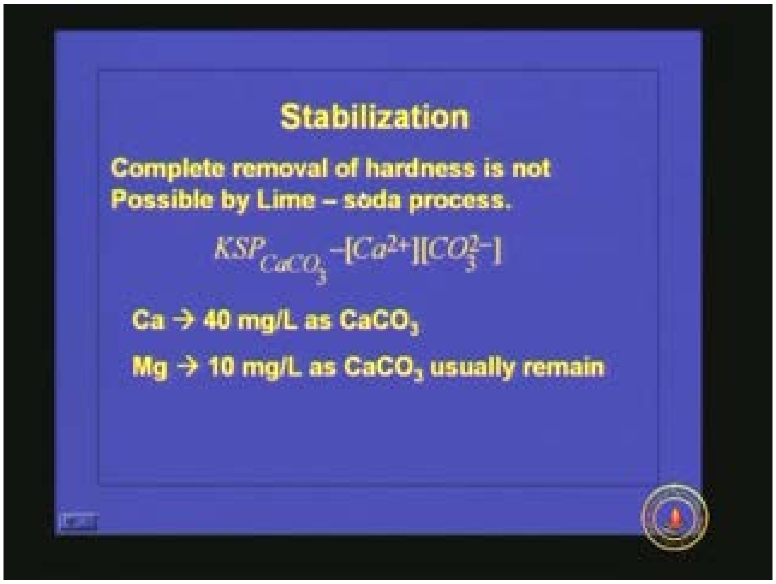

Stabilization

Complete removal of hardness is not Possible by Lime – soda process.

$$KSP_{CaCO_3} = [Ca^{2+}][CO_3^{2-}]$$

Ca → 40 mg/L as $CaCO_3$

Mg → 10 mg/L as $CaCO_3$ usually remain

Now we will talk about stabilization because we have gone for chemical precipitation and at the optimum pH calcium carbonate or magnesium hydroxide is getting precipitated and we are removing that one by settling or by sedimentation and whatever sludge is there we are removing but the time we are giving for the reaction is not very large and you know that precipitation is a time dependent process or in nature super saturated solutions can exist so the calcium carbonate precipitation the solution which is over saturated if you keep for a long time more and more precipitate will be forming so after this lime softening lime soda water ash softening if you allow that water to enter into the distribution system what will happen is this calcium carbonate will be slowly settling down in the water in the distribution systems. So, with respect to time what will happen is this calcium carbonate will be forming a layer over the distribution system and that will keep on growing so your distribution network or the pipe internal diameter will be gradually decreasing. So as a result you will not be getting the design flow and there will be many other problems associated with that one.

Therefore, what can we do to avoid such conditions and one more problem associated with this precipitation is we have seen for the removal of magnesium hydroxide or magnesium hardness we have to increase the pH up to 11 and if you put that water with a pH of 11 into the distribution system for drinking purpose or other domestic purpose. People will not accept because according to the Bureau of Indian Standards drinking water pH should not be more than 7.5 so we have to supply water or maximum up to 8.2 so we have to supply water which is having a pH within this prescribed or specified limit.

So how can we achieve this condition?
That means precipitation of calcium carbonate should be avoided in that distribution network and the pH should be within the prescribed or specified limit. So for that purpose we are going for stabilization. This is what is happening in hardness removal “complete removal of hardness is not possible by lime soda process because I told about the solubility product constant that is nothing but the concentration of calcium ions and carbonate ions whatever is present. So as long

as this product value is lower than this KSP value these ions will be in solution and when it exceeds this KSP value then slowly calcium carbonate will start precipitating. Because of this constraint if you go for lime soda ash precipitation we cannot achieve calcium concentration lower than 40 milligram per liter as calcium carbonate and magnesium concentration of 10 milligram per liter as magnesium ions of 40 milligrams per liter as calcium carbonate. This is what I was explaining till now.

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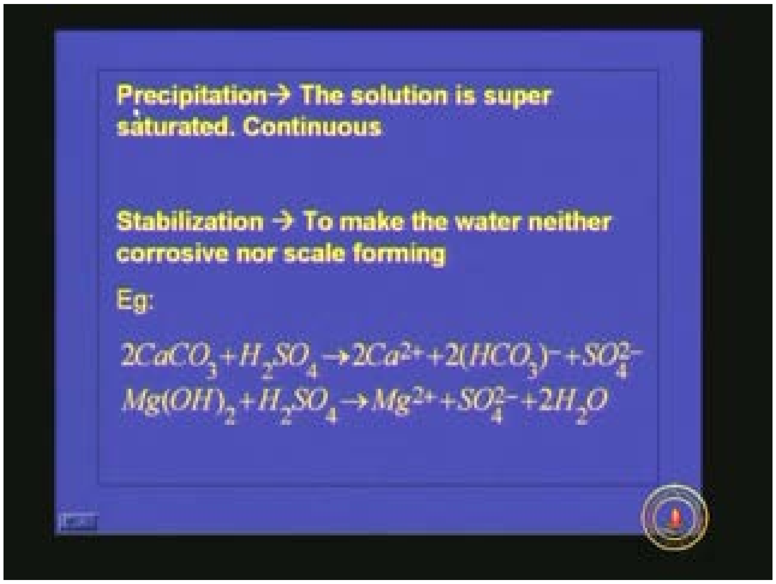

Precipitation→ The solution is super saturated. Continuous

Stabilization → To make the water neither corrosive nor scale forming

Eg:

$$2CaCO_3 + H_2SO_4 \rightarrow 2Ca^{2+} + 2(HCO_3)^- + SO_4^{2-}$$

$$Mg(OH)_2 + H_2SO_4 \rightarrow Mg^{2+} + SO_4^{2-} + 2H_2O$$

The precipitation in the solution is super saturated and the precipitation is a continuous process so there precipitation will be taking place in the distribution network. So what is the purpose of stabilization to make the water neither corrosive nor scale forming. Because what will happen is we can make the water under saturated by adding acid so whatever precipitate of calcium carbonate present in the system with respect to pH as the pH lowers the solubility of calcium carbonate will be increasing so we can make it under saturated but if the acidity of the water is too high then what will happen it will become corrosive it will be corroding the distribution network or wherever it comes in contact with any other metal or material.

So what we usually do is after the lime soda softening we add some acid to make it non-corrosive or non-scale forming but the acid quantity should be adjusted in such a way that it should not be corrosive so this is what usually happens in stabilization for the calcium carbonate present we add some say H 2 SO 4 so we will be getting calcium bicarbonate plus sulphate or for magnesium hydroxide if you add sulphuric acid what will happen magnesium sulphate and water will be formed. But if you have the mineral acid it is very very difficult to control the pH because if one extra drop is there the pH will be reducing drastically. So in water treatment plants mostly we go for stabilization using carbon dioxide so the reactions are as follows.

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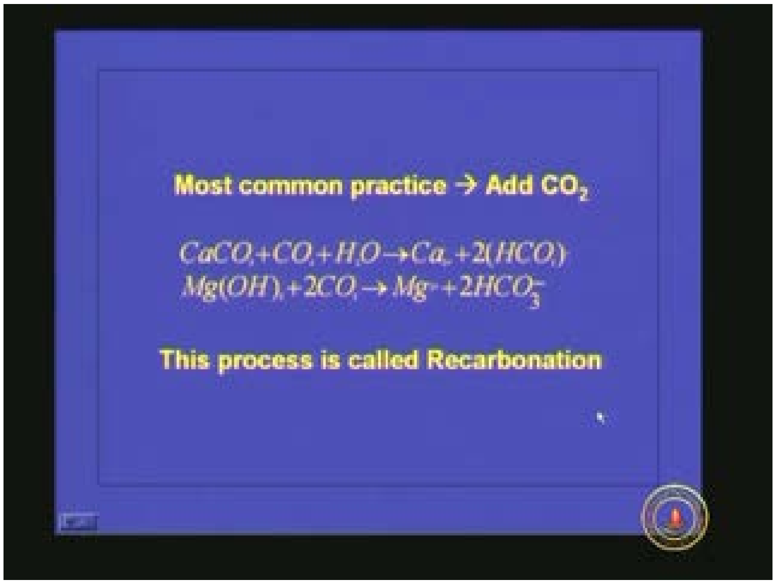

Most common practice → Add CO_2

$CaCO_3+CO_2+H_2O \rightarrow Ca^{++}+2(HCO_3^-)$

$Mg(OH)_2+2CO_2 \rightarrow Mg^{++}+2HCO_3^-$

This process is called Recarbonation

Calcium carbonate plus carbon dioxide plus water gives calcium ion plus bicarbonate. Here what is happening is you know when calcium carbonate is dissolved in water it will be forming carbonic acid and that carbonic acid is acting as the stabilizer here and it will be solubilizing calcium carbonate present in the system. And similarly magnesium hydroxide; when carbon dioxide is added magnesium and bicarbonate ions are formed. So if you use carbon dioxide for the stabilization the process is known as recarbonation.

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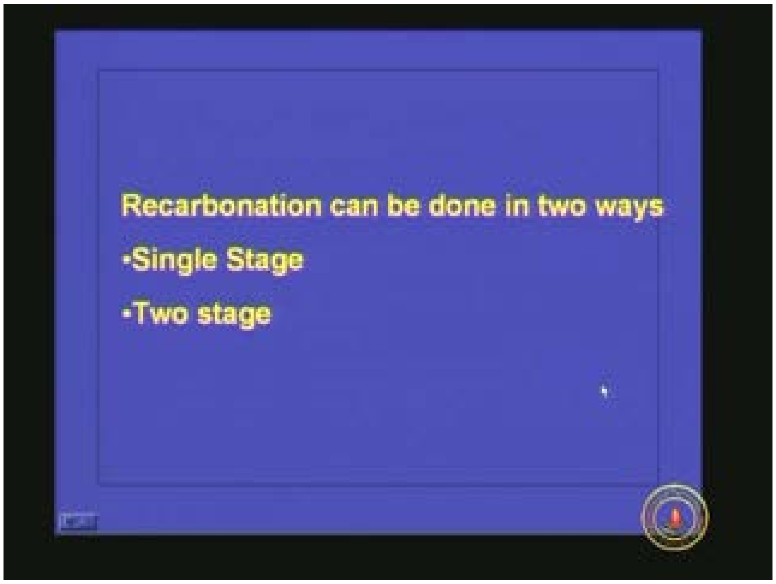

Recarbonation can be done in two ways

- Single Stage
- Two stage

And in practice recarbonation can be done in two different ways one is single stage and another one is two stage. In single stage the carbon dioxide addition will be only once and in two stage what we do is once it is added and the pH is brought down to a particular point and allow the Calcium carbonate to precipitate again that will be removed and again add carbon dioxide to adjust the pH that is two stage. Now I will show you the line sketch of this one stage and two stage recarbanation.

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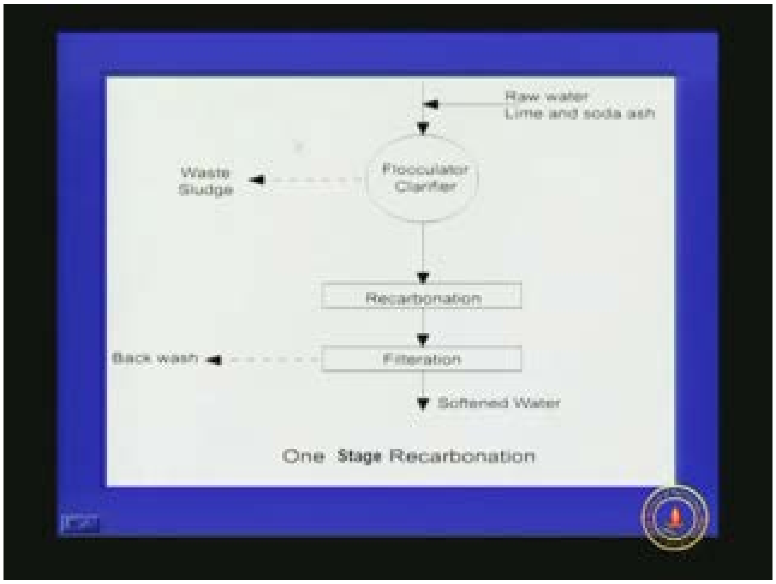

One Stage Recarbonation

This is the one. The raw water is coming and along with the raw water we are adding lime and soda ash and this is a flocculator plus clarifier or carry flocculator whatever we have seen in the coagulation flocculation system. So here lime is present and soda ash is present it is reacting with the calcium and magnesium hardness present in the water and it will be precipitating as Calcium carbonate and magnesium hydroxide and the sludge will be settling down in the carry flocculator and it is removed as waste sludge. Here what we are doing is we are adding carbon dioxide so carbon dioxide will be dissolving the excess carbon dioxide whatever is present in the system which is not removed completely. Then, after this recarbanation we are going for filtration again and softened water will be available and now for this filter we have to do back washing whenever the pressure drop becomes more than the specified limit.

Now we will see what is a two stage recarbanation. Now this shows how the recarbanation is done. Recarbanation or stabilization can be done by adding carbon dioxide. This carbon dioxide addition can be done either making some combustion or ignition inside the water so you know that if any fuel is burnt the byproduct is carbon dioxide and water if complete ignition or complete burning is taking place. So usually what people do is make that happen inside the water and allow the carbon dioxide thus created to pass through the water so that the carbon dioxide will be mixing with that one.

Another way of providing carbon dioxide is nowadays carbon dioxide is available in pure forming cylinders so take the cylinders and adjust the flow rate according to the requirement and supply that one to the water and make sure of proper mixing.

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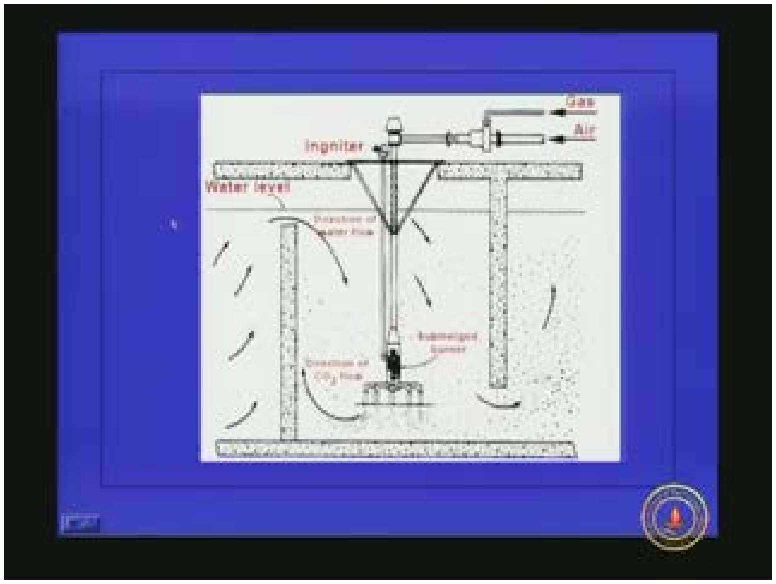

This picture shows the carbonation system with an ignition. So here (Refer Slide Time: 24:48) we can see that air is coming and the fuel gas is coming and this is the igniter so here the ignition is taking place and this is a submerged burner so whatever carbon dioxide is produced because of burning it is coming out. This shows the direction of flow and it is getting mixed up and this is the water inlet so whatever is happening it will happen in this chamber and the treated water will be going out. But nowadays this type of carbonation is not used and most of the time we go for pure carbon dioxide because if the ignition is taking place in water in submerged condition not always a 100 percent ignition will be taking place so what will happen is some amount of unburned fuel will be entering in the water and the water quality will be deteriorated. Thus, it is always advisable to go for pure carbon dioxide cylinders for recarbanation.

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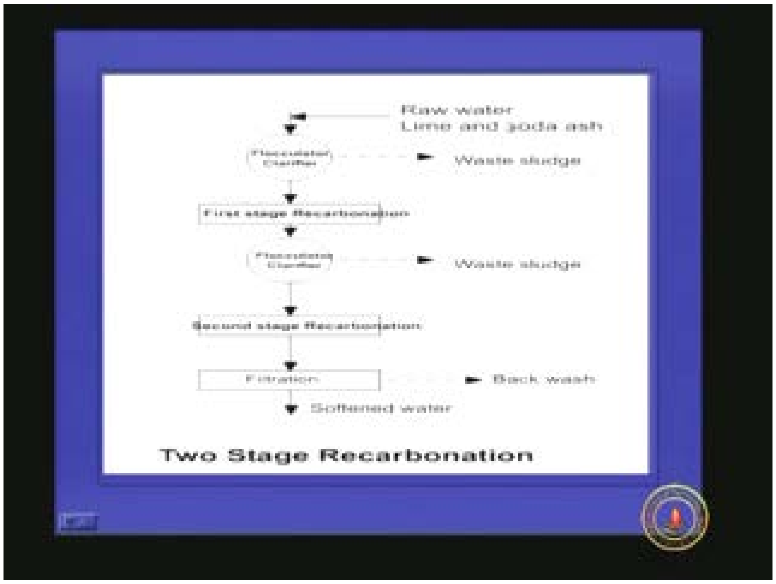

Two Stage Recarbonation

This is the example of a two stage recarbanation unit. So here what is happening raw water is coming and lime and soda ash is added here and this is the carry flocculator (Refer Slide Time: 25:58) waste sludge is going out and here first stage recarbanation is taking place and again here in the carry flocculator the waste sludge is being removed. Here it is the second stage recarbanation, filtration. So, two stage recarbanation is always advisable if you are dealing with a large quantity of water. Here we can reduce the quantity of carbon dioxide to be added and we will have better control over the system.

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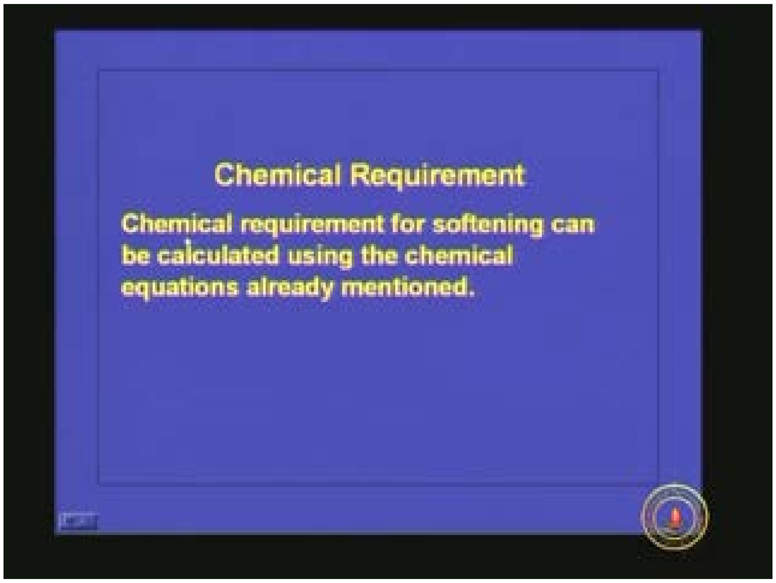

Chemical Requirement

Chemical requirement for softening can be calculated using the chemical equations already mentioned.

And chemical requirement, we have already seen how we can find out the chemical requirement for softening by finding out the equivalent weights and the chemical reactions as how much equivalence of hardness will be reacting with how much equivalence of chemical so from that one we can find out the chemical requirement.

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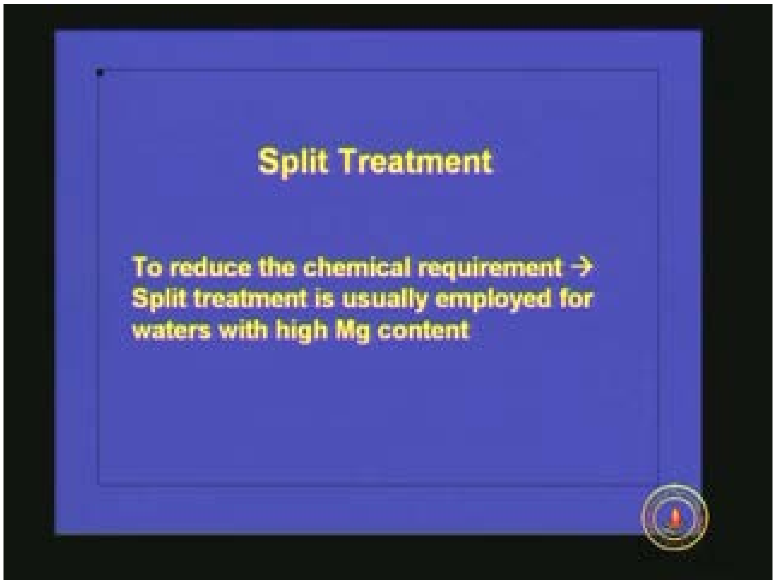

Split Treatment

To reduce the chemical requirement → Split treatment is usually employed for waters with high Mg content

So here till now we were discussing about lime soda precipitation where the entire water is subjected to the treatment and after treatment we have seen that the water will be having a very high pH. That means excess lime will be present in the water because for calcium carbonate removal the pH requirement is 9 to 9.5 but if you want to remove magnesium the pH has to be increased to 11 so so much of excess lime will be present in the system and if you want to put the water into the distribution system we have to reduce the pH considerably[……27:29] drinking water standard so we are wasting so much of chemical unnecessarily.

So, if you want to optimize the chemical use we can go for split treatment split treatment. This means that only a portion of the water is treated and the other portion will be coming without treatment and after the treatment what will happen both the water will be getting mixed up so as a result what will happen is the excess lime present in the treated water that means which is having a pH of 11 or higher that lime will be used for the precipitation of the carbonate hardness present in the bypassed water. So this split treatment the design is based upon the magnesium hardness because after calcium and magnesium hardness removal……… by lime soda softening we have seen that around 10 to 13 milligram per liter of calcium will be present in the form of calcium carbonate and magnesium hydroxide in the system will be 40 milligram per liter expressed in terms of calcium carbonate or it will be around 10 milligram per liter if we express it in terms of magnesium ions. And it is observed that if the magnesium concentration is more than one milligram per liter of magnesium ion or 40 milligram per liter as calcium carbonate then magnesium (….28:56) can take place in the boilers or other utensils which is used in the domestic purpose.

So whenever we go for the hardness removal we have to keep in mind that the magnesium concentration should not exceed that limit but the problem associated with calcium is not so significant. So the split treatment is basically based upon the minimum magnesium concentration value or the maximum magnesium concentration that can be allowed in the distribution system or water supply system.

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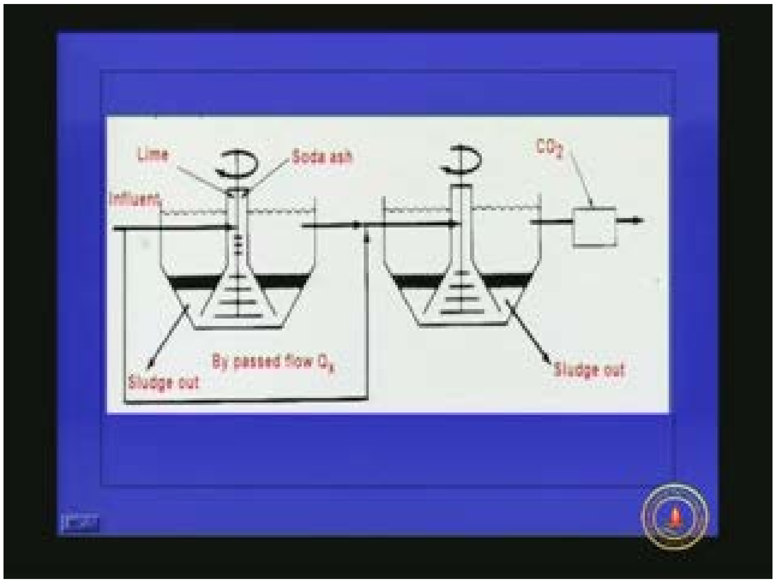

This is the picture which shows a heat treatment. So here what is happening is only a portion of water is coming for the treatment. So this is the bypass flow qs it is coming here (Refer Slide Time: 29:51) and lime and soda ash is added here it is getting mixed and the treated water is going out and carbon dioxide is added and after that one the bypass water is coming and again we are removing some sludge and carbon dioxide addition is taking place. I will explain once again. Here qs is bypassed so 1 minus q minus qs will be coming for the treatment so here we are adding lime and soda ash mixing is there rapid mixing, slow mixing and settling so some sludge is going out. This is the bypass flow (Refer Slide Time: 30:33) so that is coming and joining here along with the treated flow.

This is another unit here. Again we are allowing the precipitation because what is happening here is since magnesium removal is also taking place the pH of the water will be in the range of 11 so that is having excess lime so this bypass water which is having a pH of around 7 to 7.5 will be coming here so this excess lime whatever is present that will be reacting here calcium carbonate hardness whatever is present in this bypass water so it will be precipitating as calcium carbonate so we have to remove the sludge. That is why we are giving a precipitation or settling unit here and whatever water is coming here it is a mixed one with treated flow and untreated flow so we have to go for carbonation to stabilize the water depending upon the pH.

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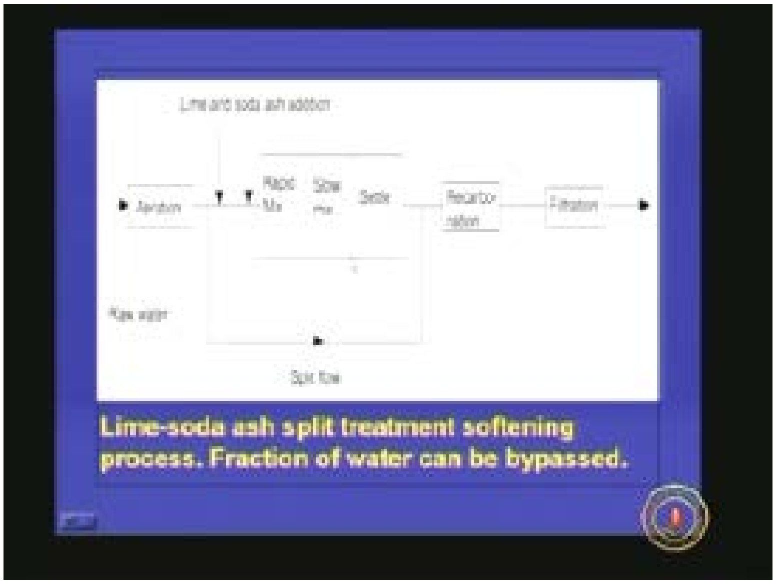

Lime-soda ash split treatment softening process. Fraction of water can be bypassed.

So if you want to show the line diagram this represents very clearly what is happening in split treatment I told you this hardness removal or softening is required most of the time for ground water and for ground water we have to go for aeration because it will be having ion and manganese in the reduced form so we have to oxidize them and remove it from the system. Moreover it may be having dissolved gases which cause bad odors. And moreover if carbon dioxide is present in excess by aeration we can remove that one so that we can reduce the lime dose required for this softening operation. So, after aeration what is happening is the water is coming here (Refer Slide Time: 32:18) and we are adding lime and soda ash here and after the chemical addition it is going for a rapid mix and here the chemical is thoroughly getting mixed with the water coming and then slow mixing is for the flocculation.

After the chemical addition the flocs will be formed and that flocs has to be agglomerated to get bigger flocs then only the settling will be effective. And after the flocculation then we have to go for settling and after settling what is happening (Refer Slide Time: 32:53) this is the split portion of the floc that is coming and entering here so it is advisable to provide another settling unit here or you can directly go for recarbanation then filtration.

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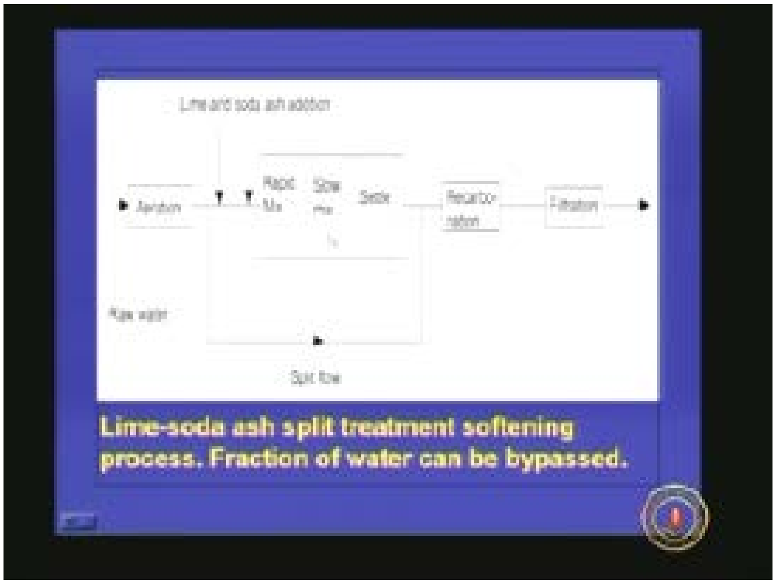

Lime-soda ash split treatment softening process. Fraction of water can be bypassed.

Now we will see how to find out the quantity of water which we have to treat and which we can bypass. It is all depending upon the magnesium concentration that is present in the raw water. We will also see what is the magnesium concentration you need after the treatment and mixing. So we have to take a mass balance based upon magnesium because we are assuming that the calcium hardness whatever is there it is not going to create much problem in the domestic uses.

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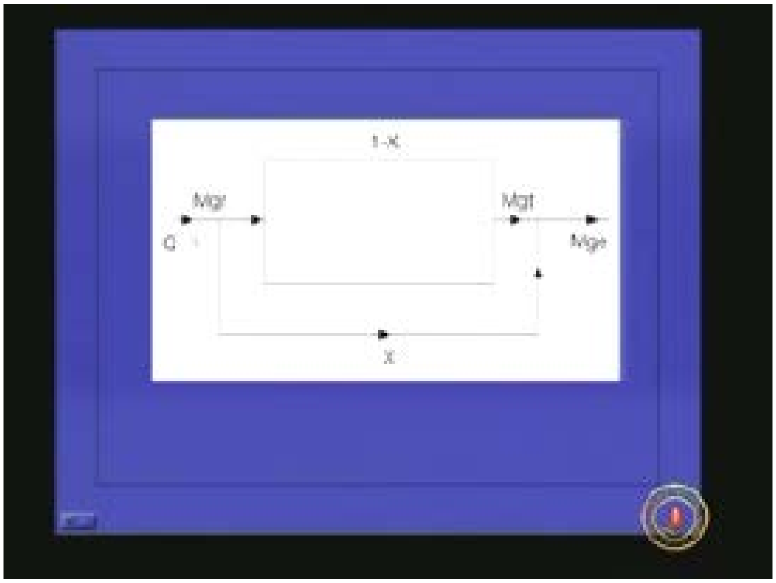

So here what is happening is q is coming q is the flow rate 1 minus x is 1 minus x into q is going for the treatment and x portion is coming without treatment or it is a bypass portion and this Mgr this R here this is the magnesium concentration in the raw water and Mgt is the magnesium concentration in the treated water and Mge is the magnesium concentration in the treated water plus the untreated water together. So remember again; Mgr is the raw water magnesium concentration, mgt is the treated water magnesium concentration and Mge is the mixed water magnesium concentration and exceeds the bypass quantity and 1 by x into q which is the treated quantity so how can we take the mass balance of magnesium in the entire system.

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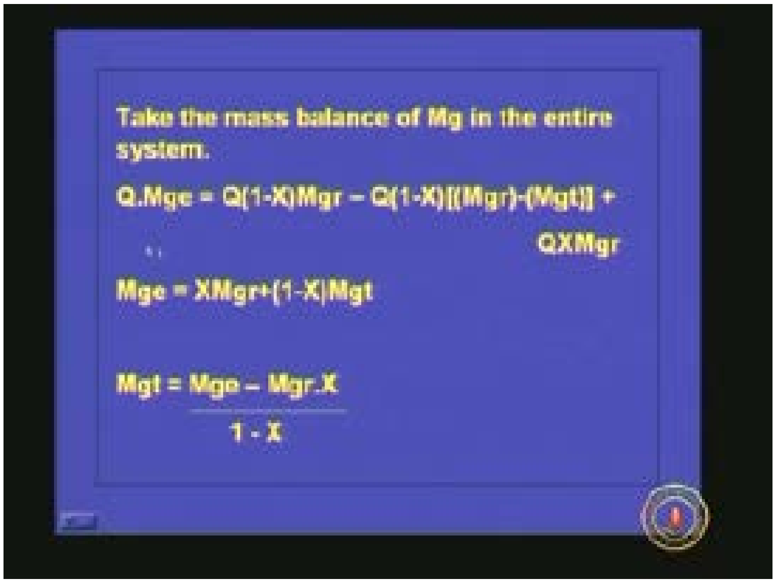

Take the mass balance of Mg in the entire system.

$$Q.Mge = Q(1-X)Mgr - Q(1-X)[(Mgr)-(Mgt)] + QXMgr$$

$$Mge = XMgr+(1-X)Mgt$$

$$Mgt = \frac{Mge - Mgr.X}{1 - X}$$

Q into Mge is the total magnesium concentration coming out see q into Mge so that s equal to q into 1 minus x into Mgr so this is the magnesium concentration whatever is entering in the system of treatment and we will see what is getting removed here. q into 1 minus x into Mgr minus Mgt so that much is getting removed from the system. So the sum of this one will be the thing coming out after the treatment and q into x into Mgr this is the magnesium concentration in the bypass stream see here (Refer Slide Time: 35:16) Mgr is coming q into x is coming so that is the total magnesium concentration coming. So if you cancel the common terms then we will be getting this one Mge is equal to x into Mgr plus 1 minus x into Mgt because 1 minus x is the treated thing and the concentration of treated water magnesium is Mgt. So 1 minus x into Mgt plus x into Mgr gives you Mge.

So if you want to find out Mgt Mgt is nothing but Mge minus Mgr into x by 1 minus x Mgt is treated water magnesium concentration.

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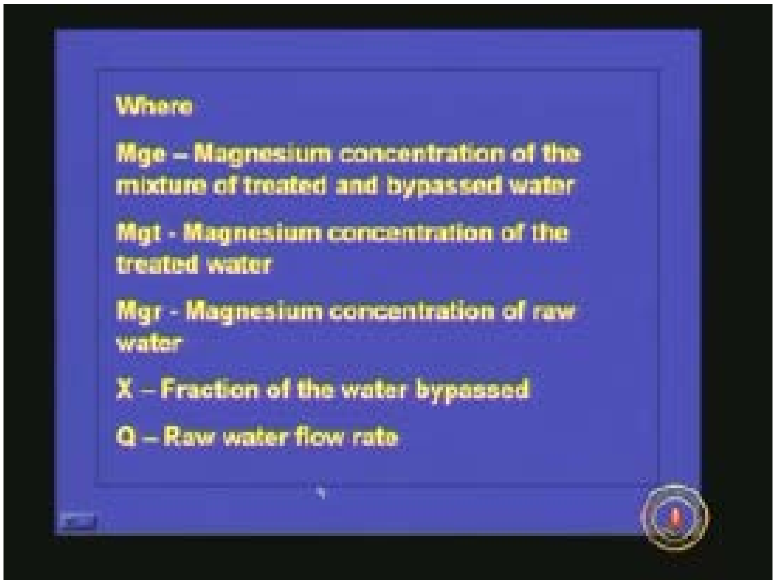

Where

Mge – Magnesium concentration of the mixture of treated and bypassed water

Mgt - Magnesium concentration of the treated water

Mgr - Magnesium concentration of raw water

X – Fraction of the water bypassed

Q – Raw water flow rate

So if you want to find out the x value what we have to do?
We are assuming that Mgt is equal to 0 that is the condition where we can get for what is the maximum quantity we can bypass. We know that magnesium concentration cannot be made zero by precipitation but for easiness we are assuming that magnesium concentration in the treated water is zero. So we will get x max is equal to Mge by Mgr. That means whatever is the required magnesium concentration in the blended water by what is the raw water magnesium concentration that will tell you what is the amount of water that can be bypassed. So again the bypass quantity is a function of what is the allowable magnesium concentration in the blended or final water by the raw water quantity.

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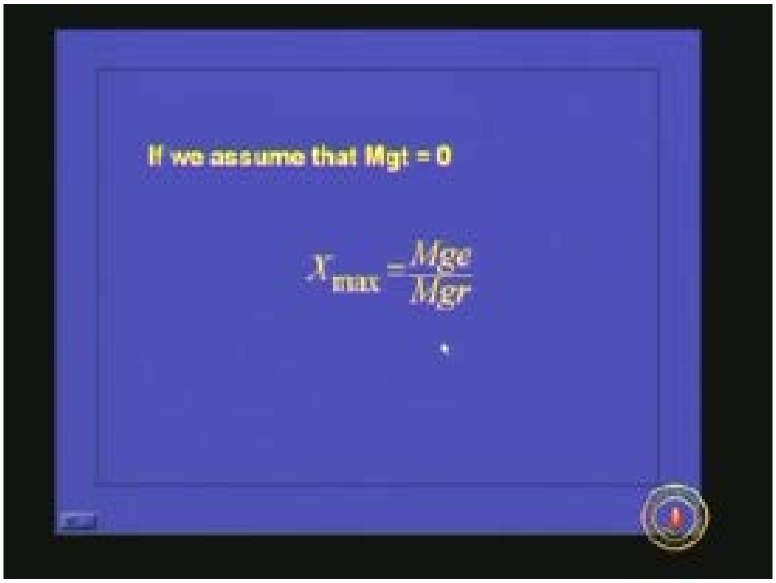

If we assume that Mgt = 0

$$X_{\max} = \frac{Mge}{Mgr}$$

So if the raw water magnesium concentration is very very high then this x max the fraction bypassed will be low and vice versa.

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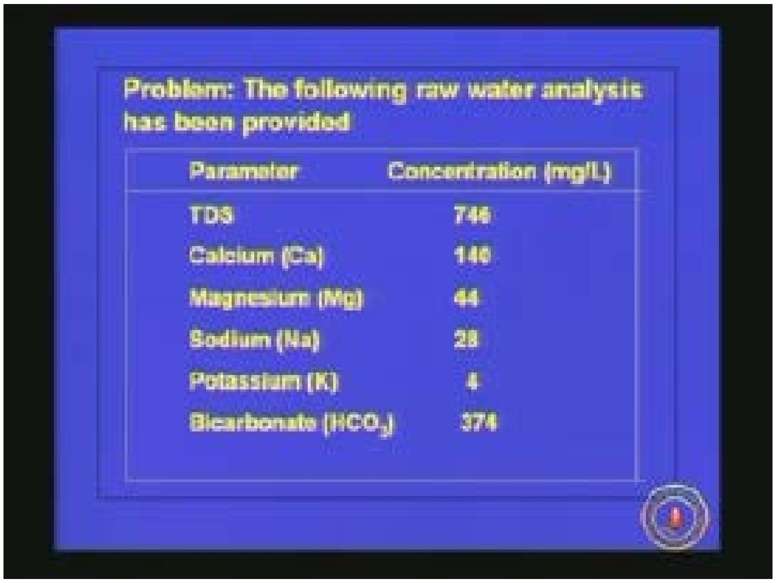

Problem: The following raw water analysis has been provided

Parameter	Concentration (mg/L)
TDS	746
Calcium (Ca)	140
Magnesium (Mg)	44
Sodium (Na)	28
Potassium (K)	4
Bicarbonate (HCO_3)	374

Now we will see how to solve a problem in this softening. This is the problem. The following raw water analysis has been provided and TDS is 746 milligrams per liter, calcium 140 milligram per liter, magnesium 44 milligrams per liter, sodium 28, potassium 4, bicarbonate 374 milligrams per liter and sulphate 236 milligrams per liter, chloride 34 and pH 7.5 so we know that when we talk about water it is electrically neutral so the total amount of anions should be equal to the total amount of cations. So what we have to do here is we have to determine the lime and soda ash dose required for softening this water so we know the constituents we have to do the softening or we have to find out what is the amount of chemical required for the softening process.

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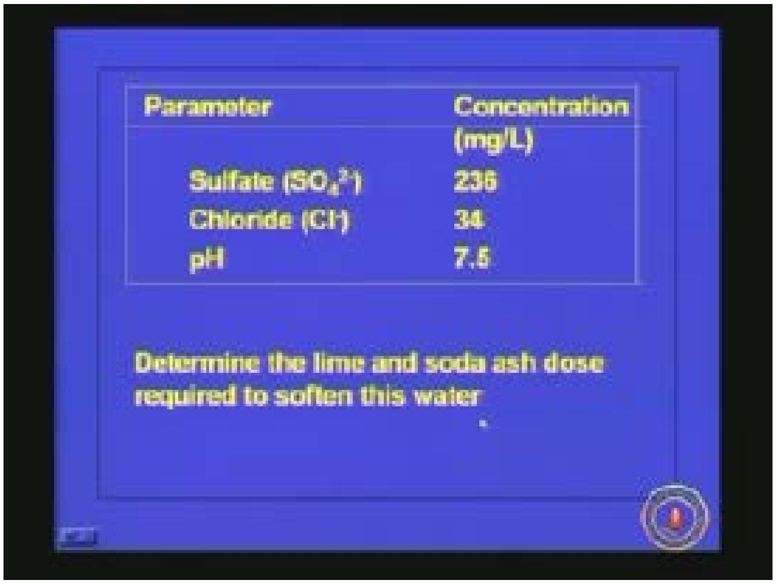

Parameter	Concentration (mg/L)
Sulfate (SO_4^{2-})	236
Chloride (Cl^-)	34
pH	7.5

Determine the lime and soda ash dose required to soften this water

So now we will see how to solve this problem.

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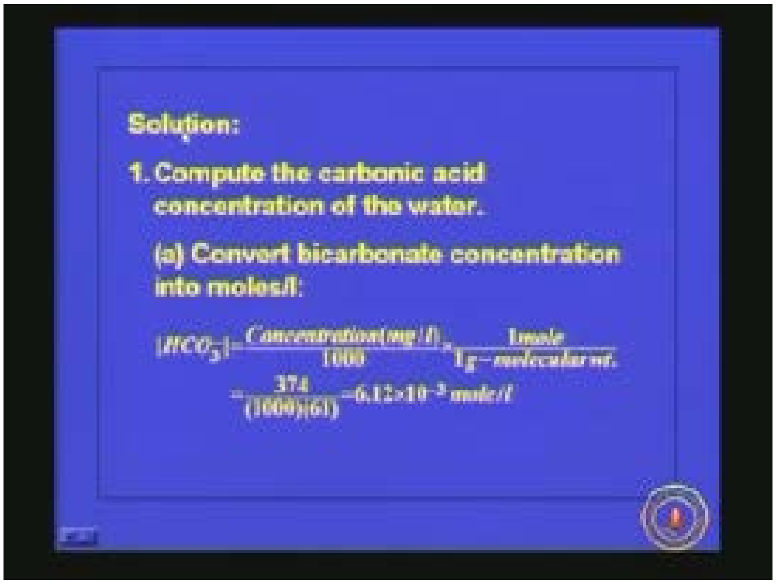

Solution:

1. Compute the carbonic acid concentration of the water.

   (a) Convert bicarbonate concentration into moles/l:

$$[HCO_3^-] = \frac{Concentration(mg/l)}{1000} \times \frac{1 mole}{1 g-molecular\ wt.}$$

$$= \frac{374}{(1000)(61)} = 6.12 \times 10^{-3}\ mole/l$$

The first step is compute the carbonic acid concentration of the water because carbonic acid also will be consuming a portion of lime whatever we are adding to the water so how can we find out this one. So, for computing the carbonic acid concentration what we have to do we have to first convert bicarbonate concentration into moles per liter then to equivalence per liter. So, if you want to convert the concentration into moles per liter what we have to do we have to divide the weight in grams with the molecular weight so that is what I have done here: concentration in milligrams per liter divided by 1000 and you will be getting the concentration in grams per liter and that divided by the molecular weight you will be getting moles per liter so 374 milligrams per liter of bicarbonate is equivalent to 6.12 into 10 raised to minus 3 moles per liter and this 61 is the molecular weight of the bicarbonate.

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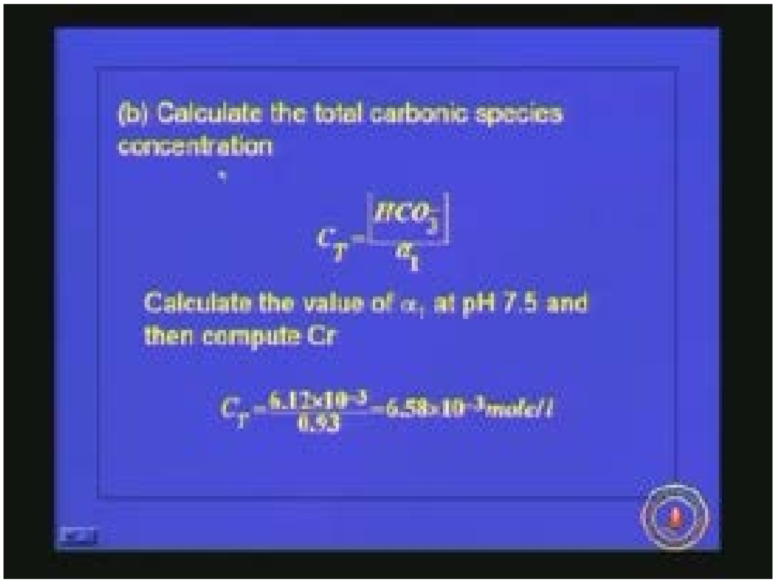

(b) Calculate the total carbonic species concentration

$$C_T = \frac{[HCO_3^-]}{\alpha_1}$$

Calculate the value of α_1 at pH 7.5 and then compute Cr

$$C_T = \frac{6.12 \times 10^{-3}}{0.93} = 6.58 \times 10^{-3} mole/l$$

Now we can calculate what is the total carbonic acid species concentration using this equation C T is equal to bicarbonate concentration by alpha 1 and we can calculate alpha 1 at a particular pH. I have not discussed this one in particular in this lecture so you just remember that there is a formula to find out the total carbonic acid species and by using that one we can get that C T is equal to 6.58 into 10 raised to minus 3 moles per liter.

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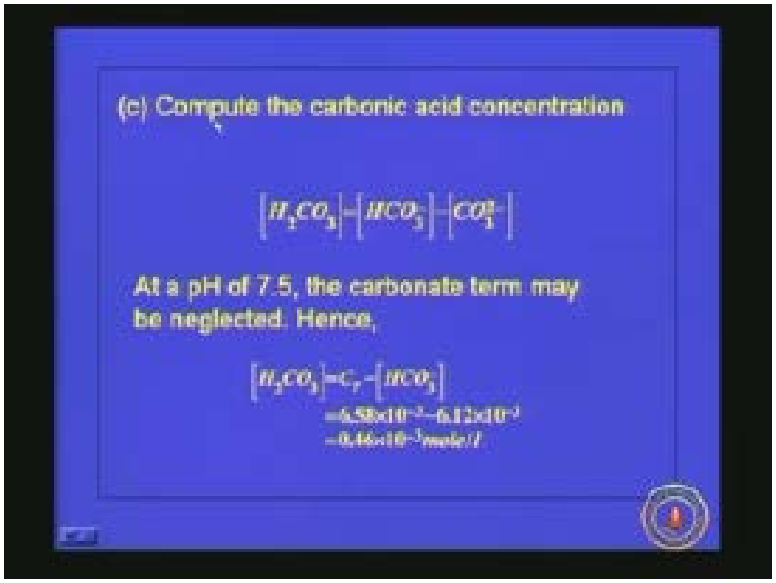

(c) Compute the carbonic acid concentration

$$[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

At a pH of 7.5, the carbonate term may be neglected. Hence,

$$[H_2CO_3] = C_T - [HCO_3^-]$$
$$= 6.58 \times 10^{-3} - 6.12 \times 10^{-3}$$
$$= 0.46 \times 10^{-3} mole/l$$

If you know the total carbonic acid species concentration we can calculate what is the total carbonic acid concentration that is equal to bicarbonate minus carbonate. So at a pH of 7.8 the carbonate term may be neglected this term (Refer Slide Time: 39:59) because you know that the concentration of carbonate bicarbonate etc are pH dependent so at a pH of 7.5 there will not be any carbonate but everything will be in the form of bicarbonate so the carbonic acid concentration is equal to C T minus bicarbonate concentration so you will be getting a value of 0.46 into 10 raised to minus 6 because this is the total c and this is the bicarbonate concentration.

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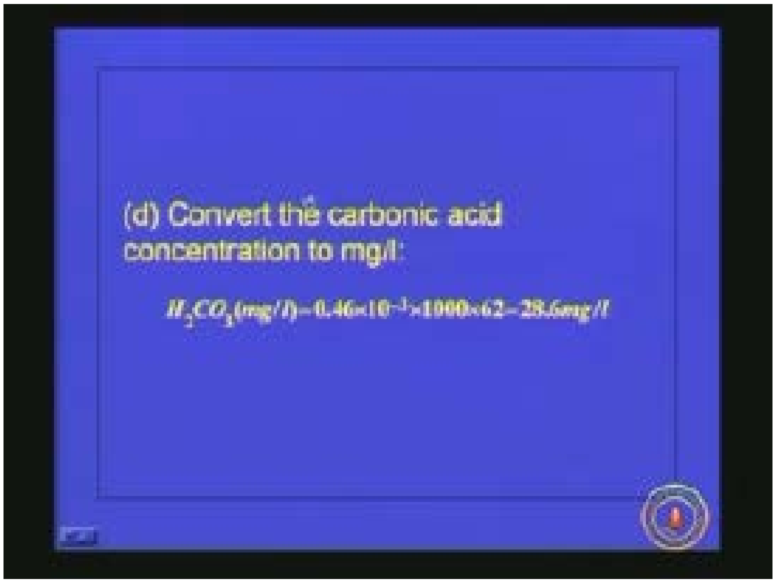

(d) Convert the carbonic acid concentration to mg/l:

$$H_2CO_3(mg/l) = 0.46 \times 10^{-3} \times 1000 \times 62 = 28.6 mg/l$$

Now we convert this carbonic acid concentration into milligrams per liter. What we have to do is multiply it with the molecular weight then we will be getting the quantity in terms of milligrams per liter so H 2 CO 3 present in the system at a pH of 7.5 is only 28.6 milligrams per liter.

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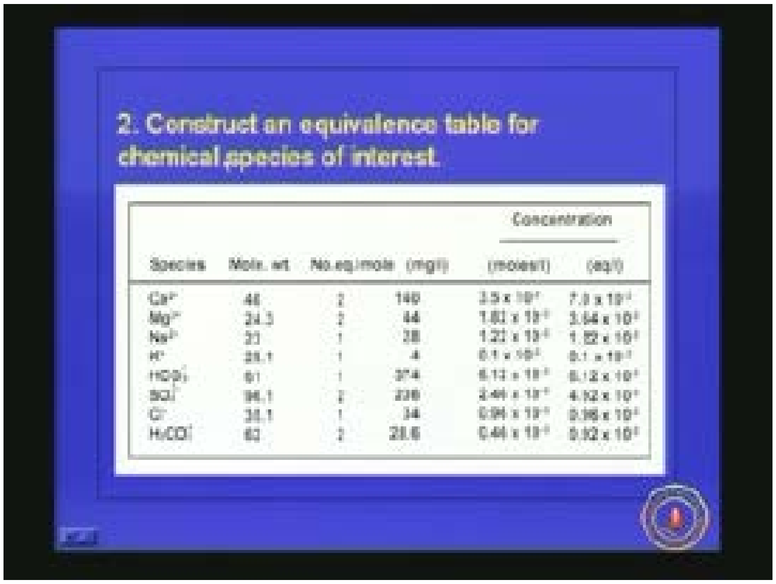

2. Construct an equivalence table for chemical species of interest.

				Concentration	
Species	Mols. wt	No.eq./mole	(mg/l)	(moles/l)	(eq/l)
Ca^{2+}	40	2	140	3.5×10^{-3}	7.0×10^{-3}
Mg^{2+}	24.3	2	44	1.81×10^{-3}	3.62×10^{-3}
Na^{+}	23	1	28	1.22×10^{-3}	1.22×10^{-3}
K^{+}	39.1	1	4	0.1×10^{-3}	0.1×10^{-3}
HCO_3^-	61	1	374	6.13×10^{-3}	6.13×10^{-3}
SO_4^{2-}	96.1	2	236	2.46×10^{-3}	4.92×10^{-3}
Cl^-	35.5	1	34	0.96×10^{-3}	0.96×10^{-3}
H_2CO_3	62	2	28.6	0.46×10^{-3}	0.92×10^{-3}

Now the next step is what we have to do is we have to construct an equivalence table for chemical species of interest because we have seen that for all the compounds we got the concentration in terms of milligrams per liter. But if you want to find out the chemical dose we have to convert them into equivalence per liter that is what I have done here.

We know the molecular weight of each and every species and we know the weight and if we want to find out moles per liter what we have to do the concentration in grams per liter divided by the molecular weight you will be getting moles per liter and multiply the moles per liter by the number of equivalents in a mole then you will be getting equivalence per liter so that is what I have done here. So calcium is 140 milligrams per liter is equivalent to 3.5 into 10 raised to minus 3 moles per liter or that is equal to 7 into 10 raised to minus 3. Similarly I have calculated for each and every species and reported here.

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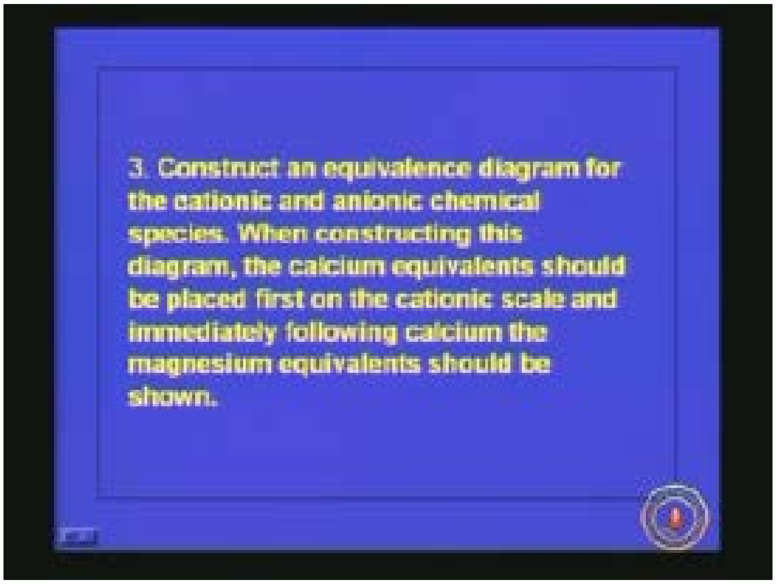

3. Construct an equivalence diagram for the cationic and anionic chemical species. When constructing this diagram, the calcium equivalents should be placed first on the cationic scale and immediately following calcium the magnesium equivalents should be shown.

The third step is construct an equivalence diagram for the cationic and anionic chemical species. When constructing this diagram, the calcium equivalents should be placed first on the cationic scale and immediately following calcium the magnesium equivalents should be shown. Once again I will explain: construct an equivalence diagram for the cationic and anionic chemical species. When constructing this diagram, the calcium equivalents should be placed first on the cationic scale and immediately following calcium the magnesium equivalents should be shown.

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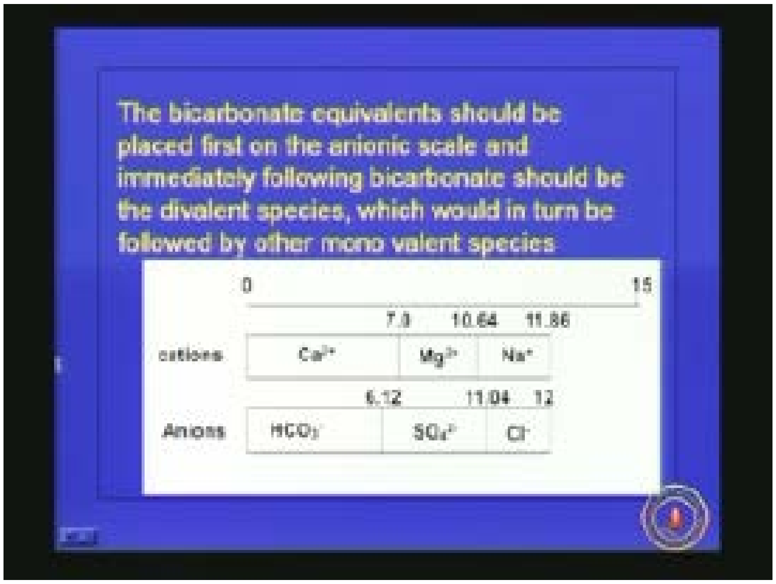

The bicarbonate equivalents should be placed first on the anionic scale and immediately following bicarbonate should be the divalent species, which would in turn be followed by other mono valent species

So that is what I have given here and what about the anion. The bicarbonate equivalents should be placed first on the anionic scale and the immediately following bicarbonate should be the divalent species which would be in turn be followed by the other monovalent species. So this is the equivalence diagram for cations.

So first we are placing calcium; we have seen that calcium is 7 milliequivalents and then comes magnesium. So 10.64 is the total of calcium and magnesium and then comes sodium. So we are following the order whatever is specified so calcium is seven and magnesium is 3.64 so the sum of calcium and magnesium is coming as 10.64 then sodium. Similarly, anions, first we have to put bicarbonate then sulphate then monovalents anions so bicarbonate is coming as 6.12 milliequivalents then the sum of bicarbonate plus sulphate will give you 11.04 milliequivalents per liter then it is coming as 12.

We know that the total cationic species concentration should be equal to total anionic species concentration. What is the requirement of this equivalence diagram is because with the help of this equivalence diagram we can find out what is the calcium carbonate hardness, what is the calcium non-carbonate hardness, magnesium carbonate hardness and magnesium non-carbonate hardness. So, for that purpose we use this equivalence diagram.

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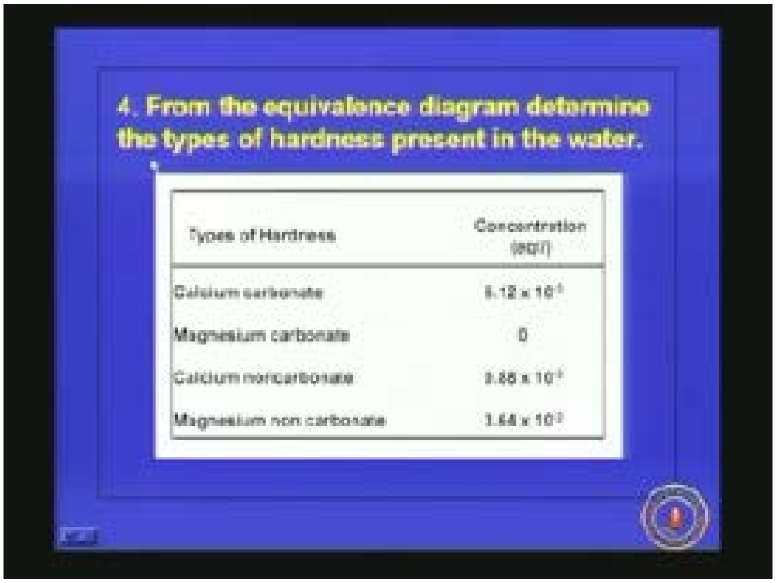

4. From the equivalence diagram determine the types of hardness present in the water.

Types of Hardness	Concentration (eq/l)
Calcium carbonate	6.12×10^{-3}
Magnesium carbonate	0
Calcium noncarbonate	0.88×10^{-3}
Magnesium non carbonate	3.64×10^{-3}

So, from the equivalence diagram this is what I have done here: the calcium carbonate hardness is equal to 6.12 into 10 raised to minus 3 because it is corresponding to this bicarbonate concentration. Then magnesium carbonate hardness is equal to zero, calcium non-carbonate is 0.88 and this is coming from 7 minus 6.12 and magnesium non-carbonate is equal to 3.64.

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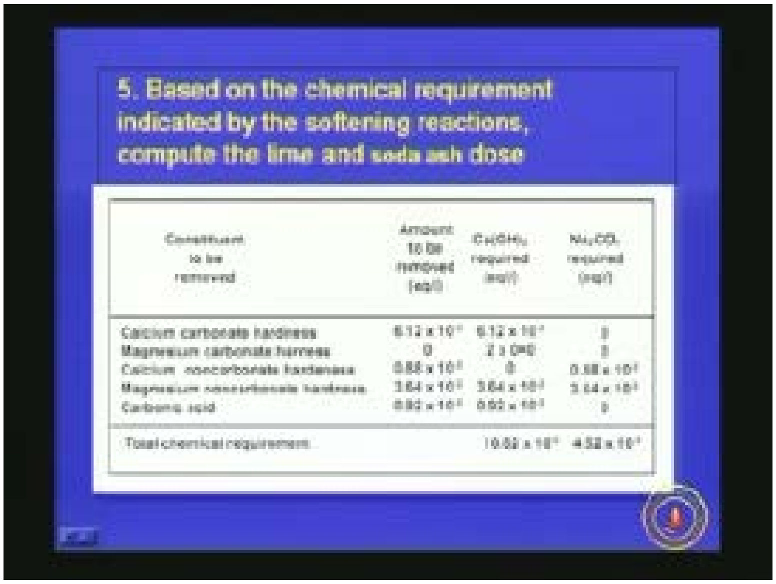

5. Based on the chemical requirement indicated by the softening reactions, compute the lime and soda ash dose

Constituent to be removed	Amount to be removed (eq/l)	$Ca(OH)_2$ required (eq/l)	Na_2CO_3 required (eq/l)
Calcium carbonate hardness	6.12×10^{-3}	6.12×10^{-3}	0
Magnesium carbonate harness	0	$2 \times 0 = 0$	0
Calcium noncarbonate hardness	0.88×10^{-3}	0	0.88×10^{-3}
Magnesium noncarbonate hardness	3.64×10^{-3}	3.64×10^{-3}	3.64×10^{-3}
Carbonic acid	0.86×10^{-3}	0.86×10^{-3}	0
Total chemical requirement		10.62×10^{-3}	4.52×10^{-3}

Now based on the chemical requirement indicated by the softening reactions we have to compute the lime and soda ash dose. We know that if one equivalence per liter of calcium carbonate hardness is present we have to add one equivalence of lime calcium hydroxide so that is what is written here and for magnesium carbonate hardness it is already zero and if it was there we have to add two equivalence and calcium non-carbonate hardness we have to add Na 2 CO 3 the same equivalence and for magnesium non-carbonate hardness we have to add lime and soda ash and for carbonic acid we have to add only lime so the total chemical requirement is coming to 10.62 into 10 raised to minus 3 as calcium hydroxide and 4.52 into 10 raised to minus 3 as Na 2 CO 3.

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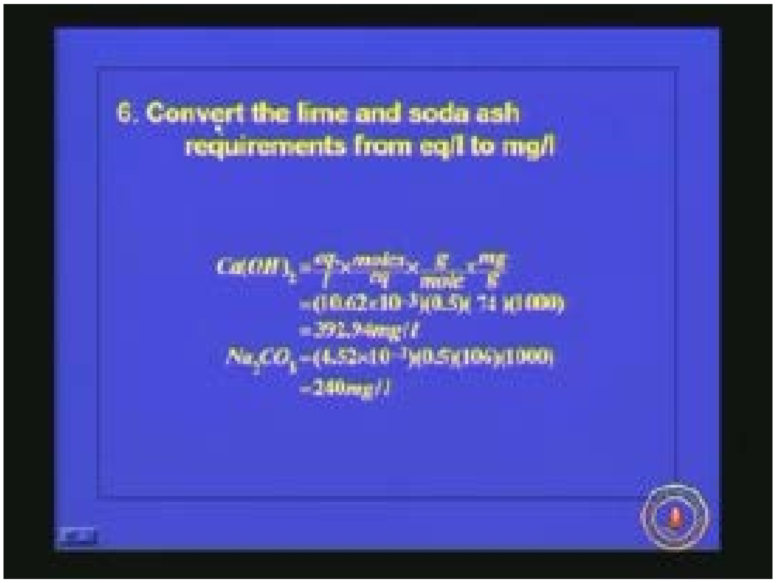

6. Convert the lime and soda ash requirements from eq/l to mg/l

$$Ca(OH)_2 = \frac{eq}{l} \times \frac{mole}{eq} \times \frac{g}{mole} \times \frac{mg}{g}$$

$$= (10.62 \times 10^{-3})(0.5)(74)(1000)$$

$$= 392.94 mg/l$$

$$Na_2CO_3 = (4.52 \times 10^{-3})(0.5)(106)(1000)$$

$$= 240 mg/l$$

So the last step is to convert the lime and soda ash requirements from equivalents per liter to milligrams per liter. So how can we do this one so what we have to do we have the equivalence per liter then you have to convert into moles per equivalence into grams per mole into milligrams per gram so we will be getting in terms of milligrams per liter. So 10.6 into 10 raised to minus 3 into 0.5 because one mole is having two equivalents that is why this point five is coming and this is the molecular weight and this is for converting grams to milligrams (Refer Slide Time: 45:50) so you will be getting the calcium hydroxide requirement as 392.94 milligrams per liter as calcium hydroxide and soda ash requirement is 240 milligrams per liter.

Till now we were discussing about the hardness removal using lime and soda ash process but we have also seen that we can go for hardness removal using ion exchange and this process is commonly used in industry. So here what we use is ion exchange resins are used so in the resins what is happening they will be having some matrix on that; one specific functional groups are attached; mostly it is h plus ions or Na plus ions and for hardness removal resins we usually use sodium exchange resins and sometimes we can even go for naturally available ion exchanges also. So for example natural zeolite that is sodium aluminium silicate, sodium aluminium silicate is a naturally available material it is known as zeolite or green sand that is also having very high hardness removal capacity.

So, in ion exchange process what is happening so one ion will be going which is having more affinity to the functional group it will be going and sitting there and it will be replacing the other ions present there so an equal amount of ion will be going and coming. So in ion exchange process if you take the total solution what will happen the total dissolved constants concentration if you expose in equivalence per liter it will be not changing only specific ions will be getting transferred and other ions will be coming into picture. So I will show you how this is happening.

So we have some matrix (Refer Slide Time: 47:43) so this is a functional group different functional groups are there so these functional groups are having […….47:49] so cation exchange resins…….. so this functional group will be having high affinity to cations. Initially we will be having the resins in the form of Rna or Rh4 that means both are cations Na plus or h plus. So what will happen is this R will be having high affinity to calcium and magnesium compared to this sodium. So when we put this resin, this is the resin matrix, this is the resin matrix so when we put the resin to a hard water, this is the water, hard water which is having lot of calcium ions and magnesium ions so what is happening we have many resins.

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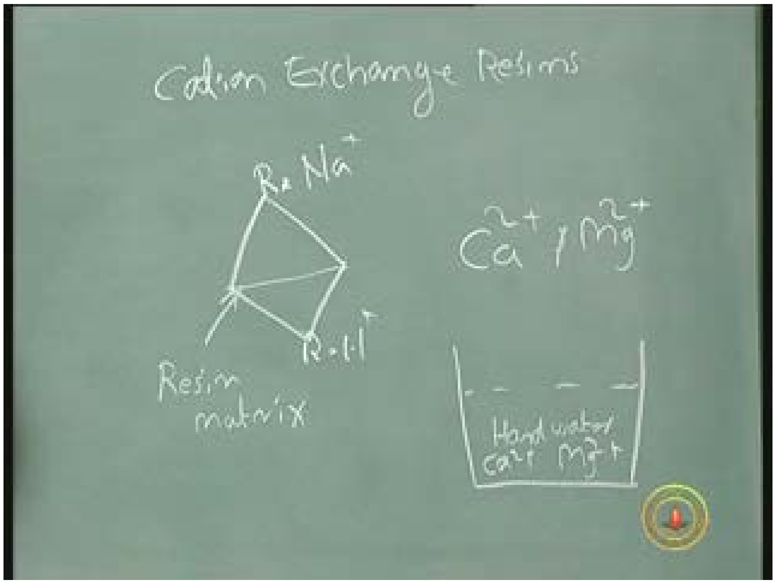

This resin Na plus ions Na plus will be coming to the solution and calcium ion or magnesium ion whatever is present in the water it will be going to the resin so we can see the resin should be electrically neutral so as the water should be electrically neutral so this sodium ion is having plus one charge and calcium ion is having plus two charge so what will happen for each calcium two plus ion which is going to the resin 2 Na plus ions will be coming out this is the basic principle of ion exchange.

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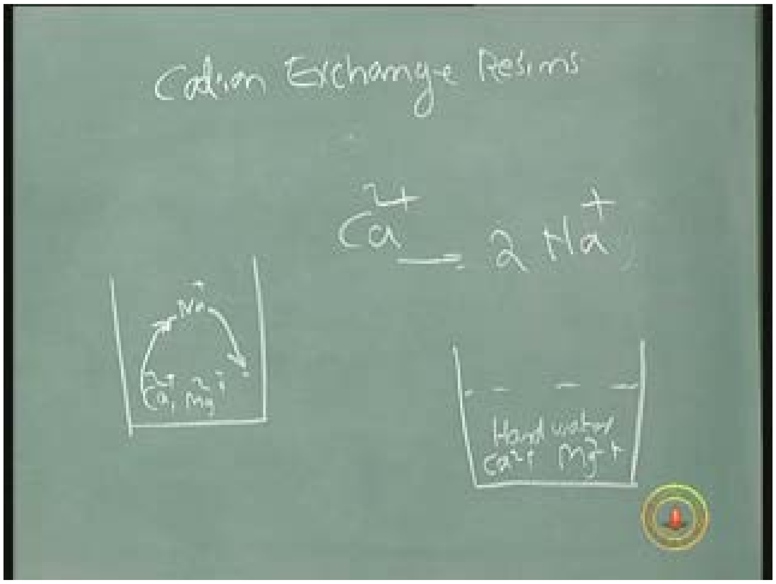

And why this calcium and magnesium is getting absorbed more is because calcium and magnesium are having very high affinity compared to sodium. If you want to write the chemical equation for this one we can write like this: calcium or magnesium plus anion; anion is the functional group present in the resin plus this means calcium and magnesium and this is anion the one that is present in the water because calcium may be in the form of calcium sulphate or calcium nitrate or calcium chloride or calcium bicarbonate so this anion, whatever is the one, it forms the other part of this metal absorbed and that will be compared with Na R where R is the functional group of the resin. Hence, you will be getting calcium and magnesium combined with R plus 2 Na plus anion because calcium and magnesium are divalent ion so naturally 2 Na ions will be coming out.

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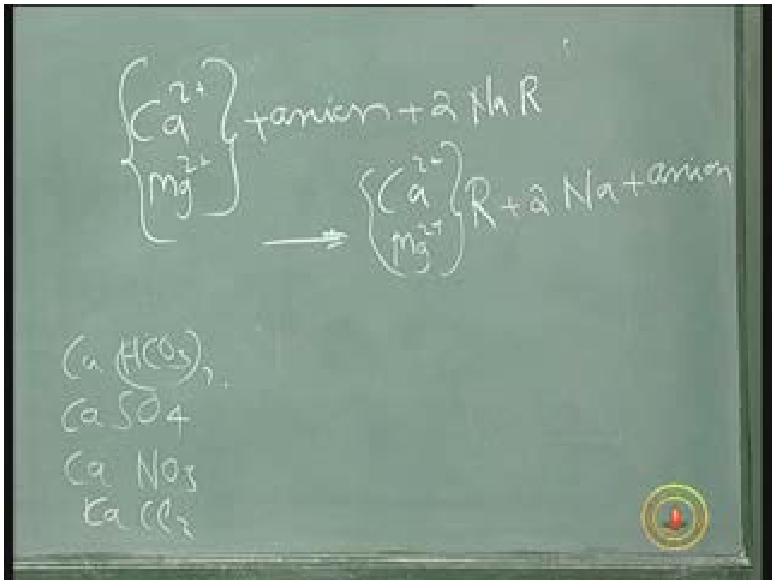

$$\left\{\begin{matrix} Ca^{2+} \\ Mg^{2+} \end{matrix}\right\} + \text{anion} + 2\,NaR \longrightarrow \left\{\begin{matrix} Ca^{2+} \\ Mg^{2+} \end{matrix}\right\} R + 2\,Na + \text{anion}$$

$Ca(HCO_3)_2$

$CaSO_4$

$Ca\,NO_3$

$Ca\,Cl_2$

So after sometime what will happen is your exchange resin the capacity will be exceeding or capacity will be exhausting so it will not be able to take any more calcium and magnesium ions so we have to regenerate the ion exchange resin. So, in the regeneration what will happen; so we have already seen that this calcium and magnesium is having high affinity to the resin so if we want to reverse the reaction how can we do it by adding high concentration of sodium ions if we add very high concentration of sodium ions this reaction can be reversed so we can see the regeneration the regeneration is like this (Refer Slide Time: 52:01) we have already calcium and magnesium in the resin so we are adding very high concentration of Nacl the concentration should be very very high otherwise this reaction will not be possible; then you will be getting calcium and magnesium along with 2 cl and that cl is coming from this sodium chloride and you will be getting 2 Na R as whatever was there; initially this one so the regeneration will be taking place and the resin will be regenerated so we can use that one.

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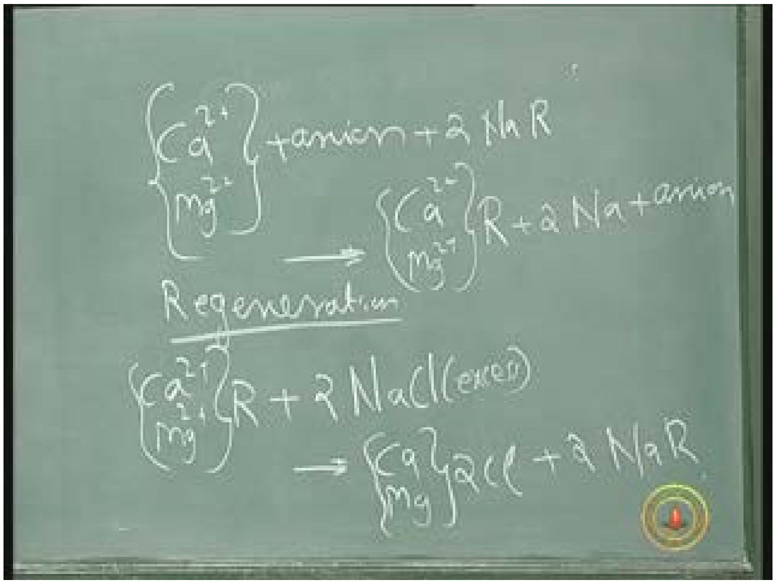

But here the amount of sodium chloride used for the regeneration is very very high so we have to go for a very high concentration of sodium chloride solution and the factors affecting the exchange the factors affecting the exchange are first one is the solid medium solid medium on which the functional group is attached second one is exchange material third one is quality of regeneration material and fourth one is overall quality of water overall quality of water. So this is very very important.

So, if you are going to use ion exchange methods for the hardness removal what we have to do we have to go for sedimentation, coagulation flocculation then filtration and afterwards only we can go for design exchange. Otherwise what will happen whatever…… the calcium carbonate or magnesium hydroxide precipitation taking place or whatever is the flocs remaining after coagulation flocculation that will be coming and depositing on the ion exchange resin and it will be clogging the resin and reducing the efficiency. And if you are using this ion exchange for ground waters; if ion and manganese are present then because the water is coming in contact with air ion and manganese will be getting oxidized and their precipitate also will be formed. In that case also what we have to do we have to go for aeration and then filtration then go for ion exchange.

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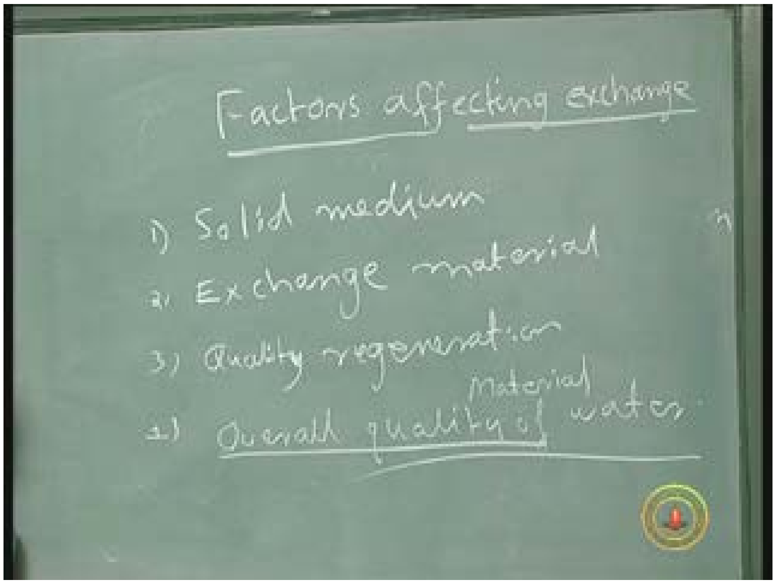

Factors affecting exchange

1) Solid medium
2) Exchange material
3) Quality regeneration material
4) Overall quality of water

Most of the ion exchange resins which is used for this hardness removal is having a capacity of 15 to 100 kilograms per meter cube 15 to 100 kilograms per meter cube that means it can remove around 15 to 100 kilograms of calcium or magnesium ion and the sodium chloride requirement is around 80 to 160 kilogram Nacl per meter cube and we have to provide that one in the form of 5 to 20 percent solution. The solution should behaving high concentration that means 5 to 20 percent that means 5 grams per 100 ml or 20 grams per 100 ml the concentration should be in this range and the velocity or the flow rate with which it has to pass through the ion exchange resin is also specified that is 40 liters per meter squared per minute.

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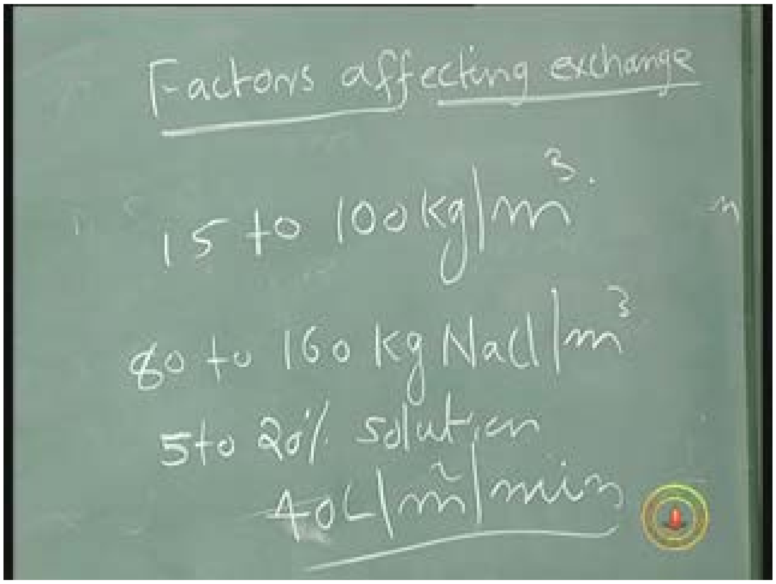

Factors affecting exchange

15 to 100 kg/m^3.

80 to 160 kg NaCl/m^3

5 to 20% solution

40 L/m^2/min

If you pass it at a high velocity the exchange will not be taking place properly so we have to provide a flow rate in this range. So if the flow rate is high the efficiency will not be high. So usually the ion exchangers are provided in close chambers something like this (Refer Slide Time: 56:26) it can be either up flow mode or down flow mode here the ion exchangers are here so water can be distributed equally from here and it will pass through the ion exchange resin and we can collect here the treated water or this way also it is possible so this will be having more efficiency because it will have more contact with the ion exchange resin because short circuiting can be avoided if the if you go for up flow mode. Then the regeneration, we can either go for go in the up flow mode or in the down flow mode but you imagine around 60 to 150 kilogram of sodium chloride per meter cube of the ion exchange resin so that much of sodium chloride is coming along with calcium and magnesium ions. So the regenerate whatever is coming from the ion exchange resin it is having very very high TDS so we cannot just discharge that one we have to have proper provision for collecting them and keep them or treating them and disposing them so that is an important point to be remembered when we go for ion exchange the regenerate whatever is happening that is another form of pollution so we have to control that one because if you discharge it into surface water the salinity will be too much.

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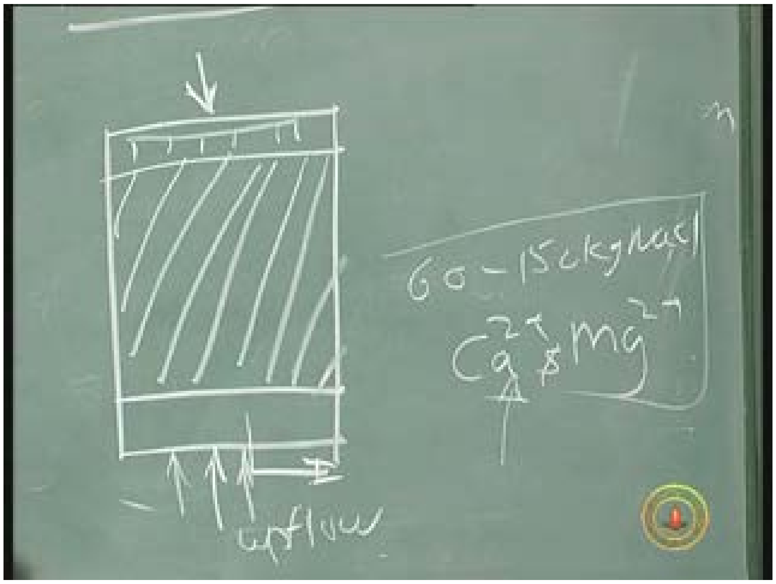

Another advantage of this ion exchange process is we can remove hardness 100 percent 100percent removal of hardness is possible so most of the time what we do or most of the time what industries do is no need of removing the hardness 100 percent so here also we can go for split treatment that means a portion of the water is allowed to pass through the ion exchange resin and the remaining portion bypass the ion exchange resin and finally what will happen blend the water which is treated with the untreated water so you can maintain calcium and magnesium concentration within 50 to 60 milligram per liter which is permissible for drinking purpose and industrial purpose so this is very very important . So, depending upon the quality requirement we can decide which type of treatment you have to go and how much water we need to treat.

So we will summarize today’s class. So we have seen what is hard water what is soft water and what is the treatment we can go for to remove the hardness. So we have seen that the most commonly used methods are ion exchange and chemical precipitation and most of the time we go for chemical precipitation because that is less costly and in chemical precipitation we use lime and soda ash as a chemical but instead of lime we can even go for sodium hydroxide or caustic soda depending upon the type of the hardness and quantity of hardness present. Then in lime soda process itself we can go for split treatment that means we need not treat the entire water so we can go for recarbanation so in split treatment whatever the excess lime we are adding for pH adjustments we can take care by adding the raw water. So whatever water is treated after lime and soda ash process we have to stabilize it before putting it into the treatment system because that will be having high precipitation potential and the pH will be high so we have to reduce both the things so that we have to add either a mineral acid or carbon dioxide.

In water treatment usually we go for carbon dioxide addition so that is known as recarbanation or stabilization. So this recarbanation itself we can do in two different ways single stage or double stage so the major purpose of this stabilization is to make the water non-corrosive or non-scale forming if the scale if the water is scale forming in nature what will happen the distribution system diameter will be getting reduced with respect to time. If it is corrosive the water will be eating away the distribution system.