Physico-Chemical Processes for Wastewater Treatment
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Lecture 5
Water Quality Monitoring Chemical Parameters - I

Good day everyone, and welcome to this lecture on water quality monitoring in the course on Physico-chemical processes for wastewater treatment. So, in the previous lecture actually we discussed regarding chemical parameters, and in the last we were discussing regarding the various ions which are present in the water. So, we will be broadly continuing with the same topic and interpret various chemical parameters if there are various ions present in the water.

So, we will be continuing with the chemical parameters, and within the ions after determining the various ions which are present in the water, we can interpret various results with respect to various parameters, and one of the important parameters is hardness.

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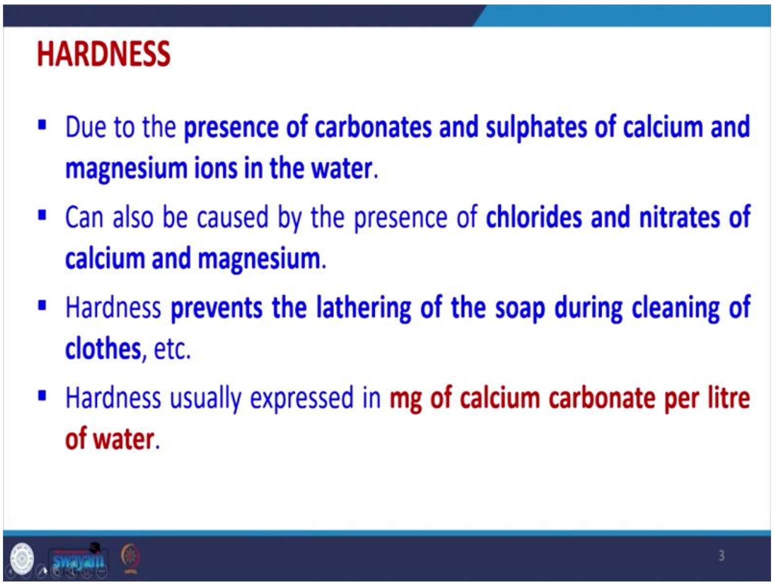

So, presence of hardness in the water causes many problems, and these problems may be the lathering of the soap during the cleaning of the clothes in the households. So, if hardness is there, so, the cleaning of clothes becomes very difficult because the whichever soap we are using, that gets lathered away and that is actually not used in the cleaning itself.

And then also in the industries, industries require water we should have minimum hardness, if that water has to be used for a steam generation and also as a utility, because if the water has to be heated, if any of the hardness and other types of ions are present in the water, then that forms scales which is not desirable.

So, why this hardness is present, how to measure this hardness and what are its classifications that we are going to learn. So, this hardness is due to the presence of calcium and magnesium ions in its various forms. So, that may be the carbonate form or sulphate form of calcium and magnesium ions. And these are due to the presence of also these calcium and magnesium ions may be due to their chloride form or nitrate form, but generally carbonate form and sulphate form are more present.

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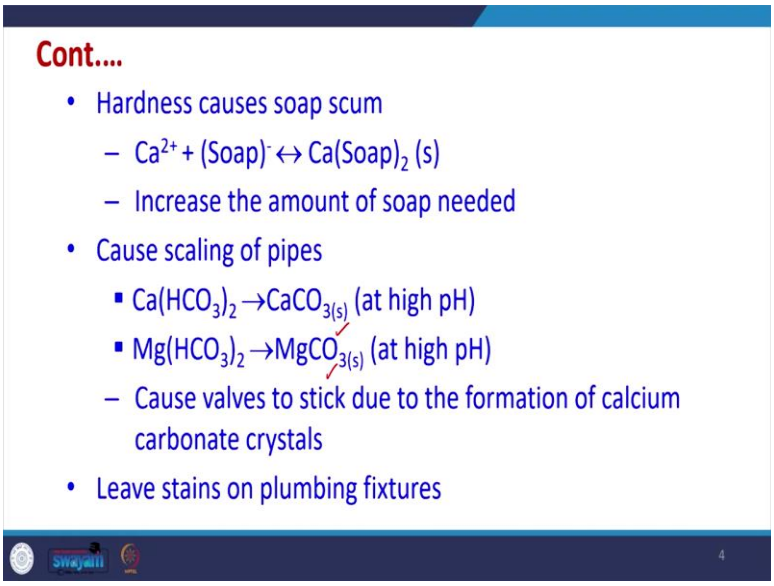

Now, hardness, why hardness causes soap scum that is there because the Ca 2 plus is like which is the major ion in the hardness it interacts with soap anions and forms a neutral specie which is like calcium combining with the soap. So, that actually, whichever soap we are using, its anionic form easily combined with the calcium, in place of combining with the dirt and other things. So, this causes the scum.

Similarly, scaling of the pipes, which occurs because of the presence of calcium and magnesium ions in the water, is due to the conversion of bicarbonate form of these calcium and magnesium ions in to calcium carbonate and magnesium carbonate forms which are basically a solid state species and they get settle on this pipe forming the scales and these calcium carbonate and magnesium carbonate they cause various problems because they will be in crystalline form and slowly and slowly they will accumulate.

So, the corrosion and other issues start happening within the pipes. So, they cause lot of problems. Similarly, if the water is to be used in the steam turbine or other places for generation of steam, and that steam has to be further used. So, which whichever place that water is there, which contains this hardness, it will have lots of issues, also these hardness things they leave lot of stains on the plumbing fixtures whichever may be there in the whole pipeline system. So, they have lot of issues there. So, how we determine the hardness?

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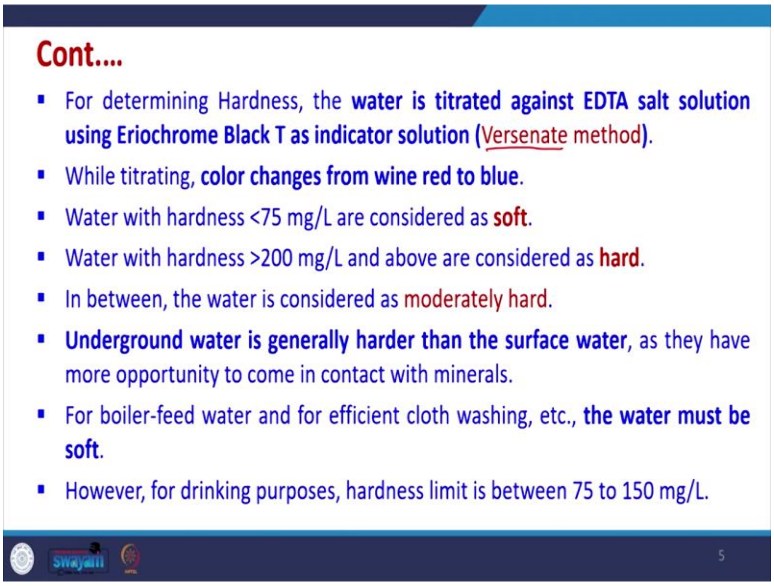

For determining the hardness in water, the general very common method which is there, that water is titrated against EDTA salt solution using Eriochrome Black T as indicator, and this method is called Versenate method and this is very common method, and during the titration actually the colour changes from wine red to blue.

And there are certain classification of water based upon hardness, if the water is having hardness less than 75 milligram per liter then that water is called as soft, whereas, if the water is having hardness more than 200 milligram per liter, there, these water are considered as hard water, and in between they are moderately hard.

So, this is their underground water generally is harder than the surface water, because, they have more chances of accumulating calcium and magnesium from the various rocks and also because the carbonate, bicarbonate and carbonate ions always occur in the water due to the natural dissolution of CO_2 into water.

So, they form these calcium carbonate, calcium bicarbonate and other things and their present is more in the groundwater as compared to in the surface water. For boiler-feed water or for efficient cloth washing the water must be soft. So, this is desirable. So, the hardness should be at least less than 75 milligram per liter. For drinking purpose if hardness is higher also there is no issue it causes no problem as such.

Now, how hardness gets formed or gets into the water. So, during normal condition in the soil, we have topsoil, subsoil and limestone at the bottom. Now, whenever there is rain or precipitation that happens, likely it will percolate through this topsoil.

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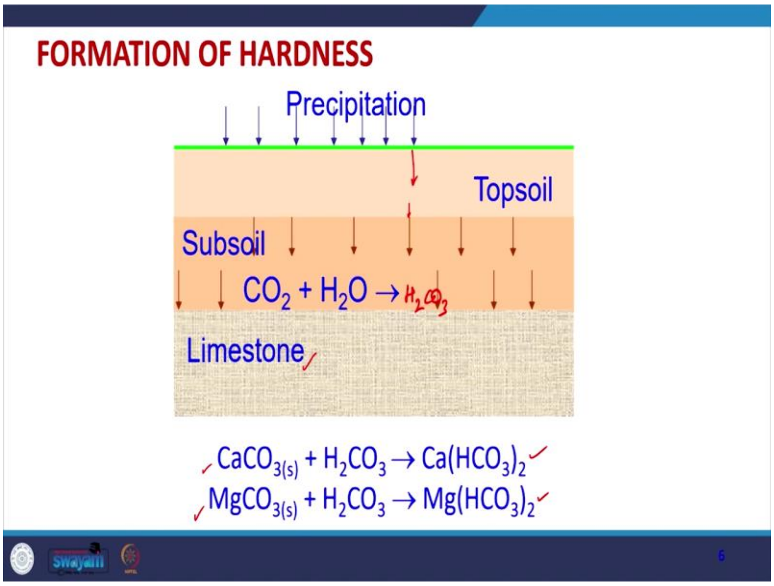

And in the subsoil if CO2 is there, which may have also percolated during the period when the rain was not there. So, this CO2 will combine with H2O. So, we can have lot of bicarbonate which will be there, and these bicarbonates later on combine with calcium carbonate and magnesium carbonate rocks, which may be present like in the limestone and they combine with them to form the calcium bicarbonate and magnesium bicarbonate, and these get dissolved into the water.

So, that is why the groundwater has more hardness as compared to the surface water and this is how the hardness comes into the water. Now, types of hardness there are like we have already defined the total hardness is like addition of calcium and magnesium and present in the water.

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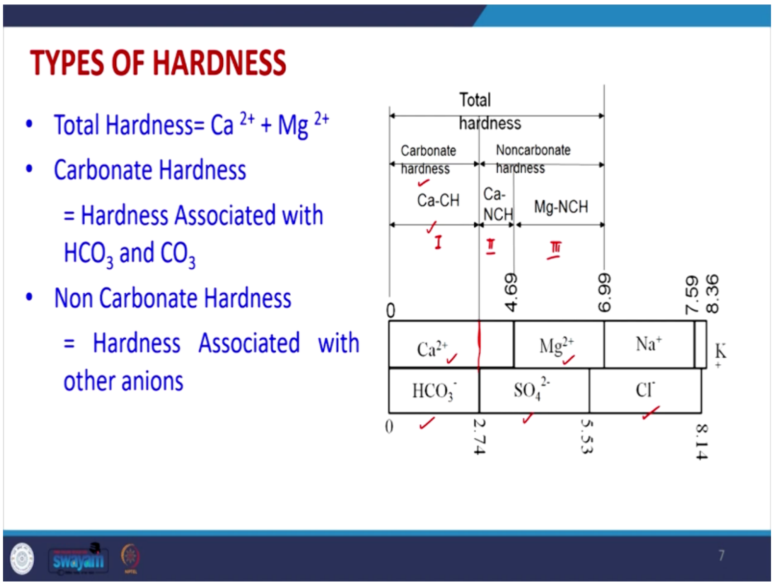

So, the hardness can also be defined in terms of carbonate hardness or non-carbonate hardness. So, if hardness is associated with bicarbonate ion, or carbonate and it is called as carbonate hardness. If it is associated with other anions then it is called as non-carbonate hardness. So, here some values and example is given in this figure. So, we can see the calcium and magnesium is present up to 6.99 milliequivalents per liter.

Now, out of this the carbonate, bicarbonate ion is present, no carbonate ion is present, and after we have sulphate and chloride ion. Now, whatever hardness which is associated with carbonate or bicarbonate ion, it is called as carbonate hardness. So, we have up till 2.74 milliequivalents per liter, it is called as carbonate hardness, and beyond that whatever is the value that is the non-carbonate hardness which can be obtained by subtracting the carbonate hardness from the total hardness value.

So, this is there. Now, out of the other hardness we can define in terms of calcium hardness and magnesium hardness also. So, calcium hardness is generally considered first. So, calcium in the present case whole of the calcium hardness is because of two reasons, one is carbonate hardness and another is non carbonate hardness.

So, one fraction is from here, and then second fraction of calcium hardness which is associated with non-carbonate hardness. And then whole of the magnesium hardness is associated with the non-carbonate hardness, which is given here. So, we can interpret many results out of these type of diagrams. So, we will continue to learn.

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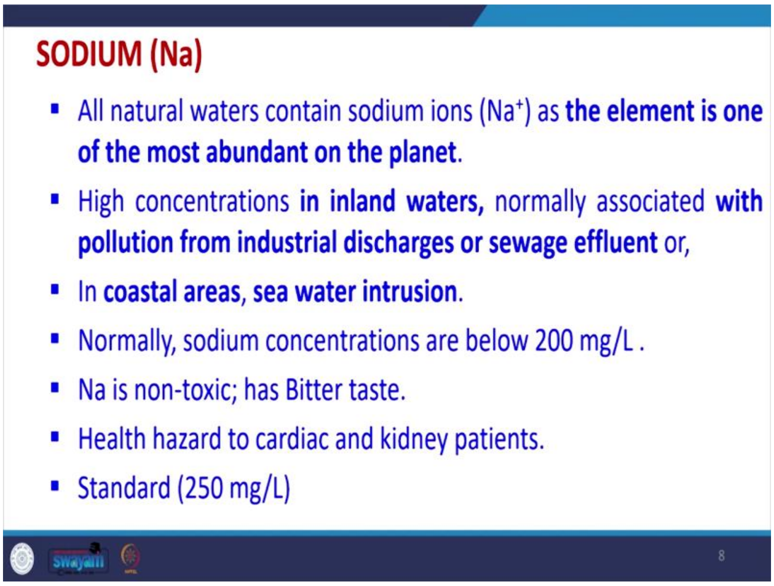

Now, after this calcium and magnesium, which is which are associated with the hardness there is another very important element which is called as sodium. Generally, people neglect this sodium ions, but sodium ions have lot of importance with respect to irrigation of water, also their essential salts which must be there in the water for our uses.

So, we have a dilemma here at how much sodium should be present, and sodium is always present in the water because it is one of the most abundant element on the planet. Now, high concentration of sodium in inland waters, it is associated with discharges from either industry, or sewage effluent, which is coming out of the residential colonies and other places.

So, this is there. So, if any water contains high amount of sodium, it may be because of this. Also in the coastal areas, sea water intrusion may occur. So, the lakes and reservoirs which are close to coastal areas may have higher amount of sodium as compared to inland water, lakes or other reservoirs. So, normally sodium concentrations should be below two hundred milligram per liter.

So, this is the usual case, sodium as such is nontoxic though it has a bitter taste. Now, health hazards which are there because of sodium, we know very well that there is there are issues that blood pressure may be high if we have more sodium in our blood, and also cardiac and kidney issues may happen if the sodium concentration in the water is high, and we are continuously taking water with higher sodium concentration.

Now standard for sodium is that it should be below two hundred fifty milligram per liter. Now, there are many parameters which are directly related to sodium. So, one by one, we will try to understand those parameters, and they are related to irrigation and other things.

So, which water has to be used for irrigation or otherwise, some of the examples are given in today's lecture, but there are many other parameters also, which will not be covered because they will require a very detailed lecture, or a separate course may be itself. So, sodium has a negative effect on the soil structure.

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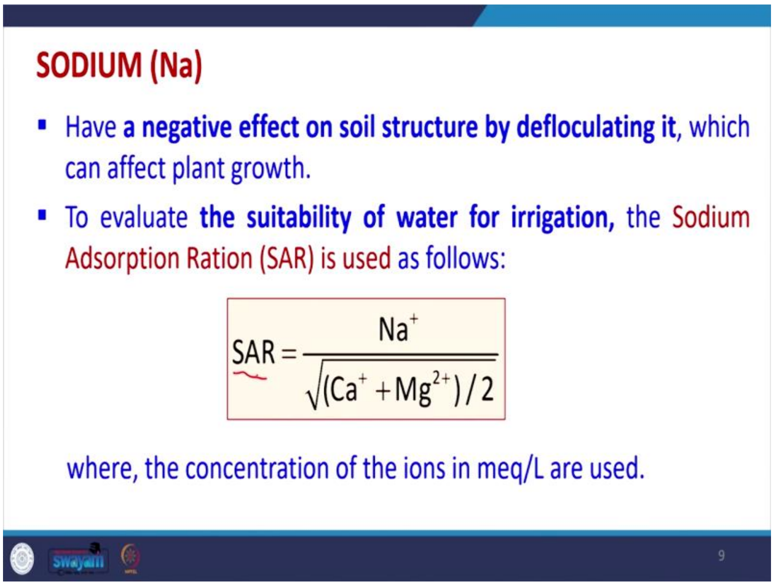

Because it deflocculates the soil, and we have seen that in all those soils which have, which are not fertile, they have some fluffy type of things. So, they contain lot of sodium and because of deflocculating nature, it becomes fluffy or otherwise. So, it actually has a negative effect and the fertility of that soil is very, very less.

To evaluate the suitability of any water for irrigation, there is one term which is called as sodium absorption ratio and that is used. So, there are parameters, how it is defined in the short form we call it SAR. So, SAR is like ratio of Na+ divided by the average under root of average of calcium and magnesium ions. So, this is how it is defined, and all the concentrations in this equations have to be used in milliequivalents per liter.

To evaluate the suitability of water for irrigation, the Sodium Adsorption Ration (SAR) is used as follows:

$$SAR = \frac{Na^+}{\sqrt{(Ca^+ + Mg^{2+})/2}}$$

where, the concentration of the ions in meq/L are used.

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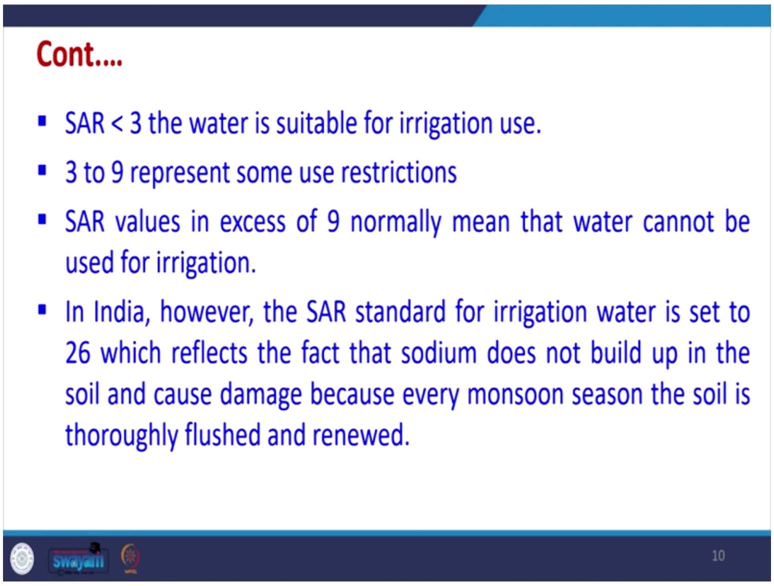

Now, if SAR value is less than three, the water is suitable for irrigation use. So, it is good that if you can have a irrigation water which is having SAR value of less than three. Now, between three and nine, we can still use the water with some restriction, but if SAR value is more than nine, that means that water is not good enough for us as irrigation and in the long run, if we continuously use that water, then there may be issues and the whole of the land may become infertile also.

So, this is a possibility, in India however at many places that irrigation water with very large SAR values are being used. So, this is a, this will cause lot of problems in long run. So, they, we should understand these things and determine the SAR values after, for all the waters that we are using for irrigation and we should find out the SAR values for all the canal systems which are there, which are being used further for irrigation.

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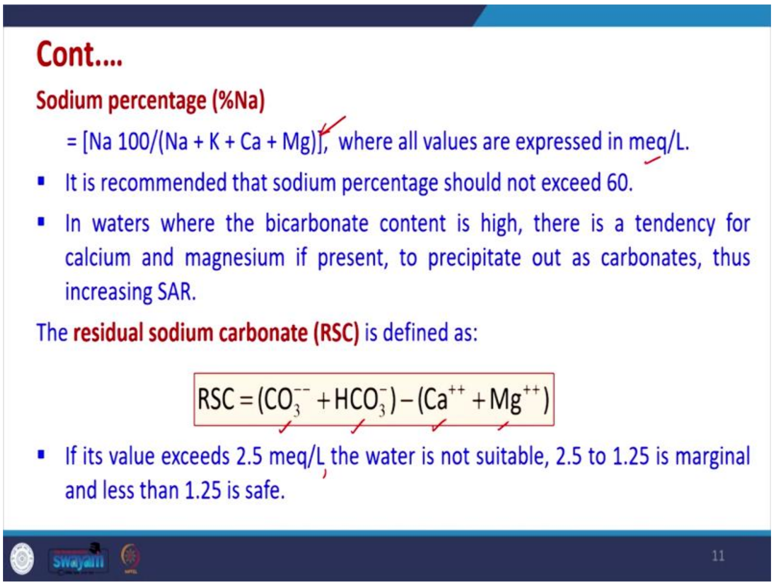

Now, there is another parameter which is related to sodium, it is called sodium percentage. So, this is basically how much percentage of sodium is there vis-a-vis sodium, calcium, potassium and magnesium, and all values are expressed in milliequivalents per liter. So, this is the formula which is given here. So, this is, it is recommended, certainly that sodium percentage should not be, should not exceed sixty percent.

So, the majority of the total cations which are there, the sodium value should be restricted less than sixty. So, this is there, in waters where bicarbonate content is high. So, that means water which are having more amount of bicarbonate, there is a tendency for calcium and magnesium which present to precipitate out. And if they are getting precipitated out, we have higher percentage of SAR as well as the sodium percentage.

So, it has a problem. So, another parameter was defined, which is called as residual sodium carbonate. And it is like difference between the carbonate ion, bicarbonate ion, and the calcium and magnesium ion. So, this RSC was defined in short form we call it RSC and if its value exceeds two point five milliequivalents per liter, the water is not suitable for irrigation, between 2.5 to 1.25. It is a marginal value it can be used and less than 1.25 it is considered to be safe. So, we have three parameters which are related to sodium.

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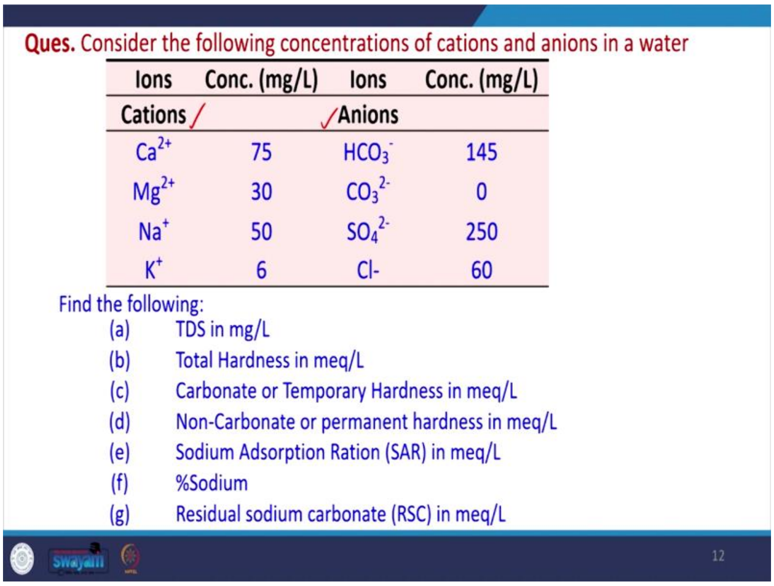

Now, what we do is that we will solve one problem with respect to in a water the concentration of cations and anions are given, and we have to find out different parameters out of this. So, we have all the cations which are reported here, and the anions, and their concentration in water is reported.

Now, what we have to do is that, we have to find out that TDS, total hardness, carbonate or which is called as temporary hardness, that also we have to find out, then we have to find out non-carbonate or permanent hardness, then sodium absorption ratio SAR value, percentage sodium, and the RSC in milliequivalents per liter. So, these parameters we can get from this table itself. So, we will try to solve it.

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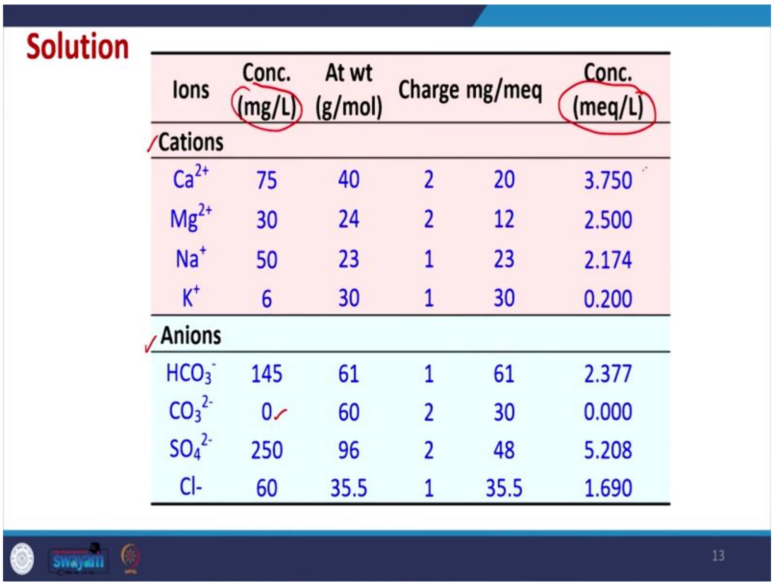

Now, as we have done in the previous lecture. So, once the cations or anions are known, what we have to do in the first step is that, to convert the concentration values in milligram per liter, which is given here, into milliequivalent per liter. So, this is done here using the atomic weight, then charge, how much charge is there on each cation or anion. And then finding out milligram per milliequivalent, and dividing the concentration by milligram per milliequivalent, we can convert into milliequivalent per liters.

So, we have converted all the milliequivalent per liter, for both all the cations as well as all the anions. It may be noted here that in this example, it is given that the carbonate is zero in the water, but these are arbitrary values we which we have taken here just for demonstrating that how we can perform the calculations in the actual case the carbonate value may be present may not be present.

Now, what we do is that, if we have to find out the first we should always cross check that what is the error in the sum of cations and sum of anions, so and what is the error so, that through that we can check whether the results which have been reported in this analysis report are correct or not. So, all this anions are added together, and all the cations and anions both are added together.

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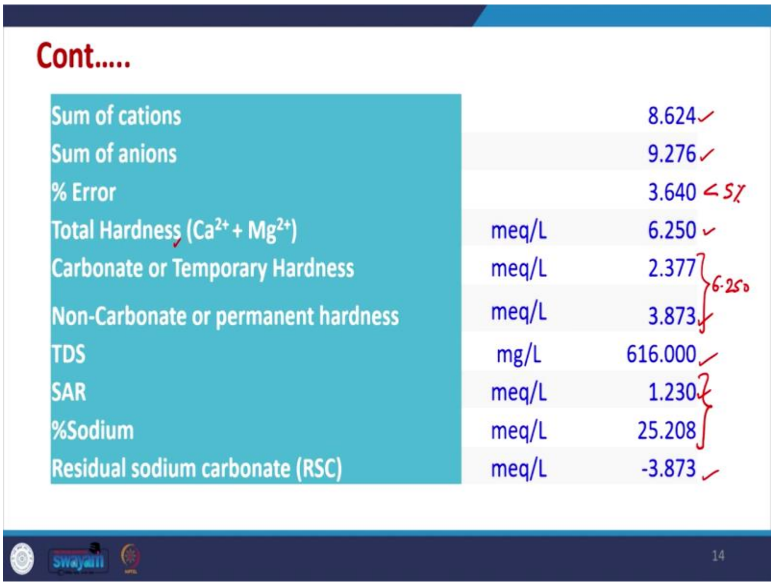

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Sum of cations		8.624	
Sum of anions		9.276	
% Error		3.640	< 5%
Total Hardness ($Ca^{2+} + Mg^{2+}$)	meq/L	6.250	
Carbonate or Temporary Hardness	meq/L	2.377	6.250
Non-Carbonate or permanent hardness	meq/L	3.873	
TDS	mg/L	616.000	
SAR	meq/L	1.230	
%Sodium	meq/L	25.208	
Residual sodium carbonate (RSC)	meq/L	-3.873	

Solution

Ions	Conc. (mg/L)	At wt (g/mol)	Charge	mg/meq	Conc. (meq/L)
Cations					
Ca^{2+}	75	40	2	20	3.750
Mg^{2+}	30	24	2	12	2.500
Na^{+}	50	23	1	23	2.174
K^{+}	6	30	1	30	0.200
Anions					
HCO_3^-	145	61	1	61	2.377
CO_3^{2-}	0	60	2	30	0.000
SO_4^{2-}	250	96	2	48	5.208
Cl-	60	35.5	1	35.5	1.690

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Sodium percentage (%Na)

= [Na 100/(Na + K + Ca + Mg)], where all values are expressed in meq/L.

- It is recommended that sodium percentage should not exceed 60.
- In waters where the bicarbonate content is high, there is a tendency for calcium and magnesium if present, to precipitate out as carbonates, thus increasing SAR.

The **residual sodium carbonate (RSC)** is defined as:

$$\boxed{RSC = (CO_3^{--} + HCO_3^{-}) - (Ca^{++} + Mg^{++})}$$

- If its value exceeds 2.5 meq/L the water is not suitable, 2.5 to 1.25 is marginal and less than 1.25 is safe.

So, here they are shown, the values are given here and if we find out the percentage error, it will be only 3.64 percent. So, which is less than 5 percent. So, that means we can assume the this analysis report to be correct. Now, if you have to find out the total hardness, total hardness is sum of calcium and magnesium ions in milliequivalent per liter. So, what we do is that, we just add these two parameters and that will give the total hardness which is reported here, the total hardness is 6.250 milliequivalent per liter.

Now, out of that we can calculate the carbonate hardness or temporary hardness, which is associated with carbonate. So, for doing this we can easily see because the value of calcium and magnesium is much higher than the carbonate. So, value which is 2.377. So, that means the carbonate hardness is 2.377, and now rest of the hardness we can find out by subtracting. So, this is 3.873, and both if we add them together the value should be 6.250.

So, this is there. TDS is like adding the all the concentrations of cations and anions they have been just added here and this is the value. So, this is straight forward. SAR value as per the formula, because the milliequivalent is given. So, we can calculate so, it was found to be 1.230 so, this 1.230 is less than three, so, that means, this water is suitable for irrigation.

So, this is this is the inference that we can obtain similarly, percentage sodium is also less than 60 percent. So, that is that also tells that we have good water which can be used for irrigation, by chance for this this particular analysis the RSC value is negative and it is not always possible to have the all the results in our positive value.

So, it will depend on various things. So, this is okay, we can either neglect it or otherwise, but these two parameters tell us that water is good enough for irrigation. So, by finding out only all the major anions and cations we are able to find out so many parameters out of this, and it helps in determining whether our water is good enough for drinking of for irrigation or not.

Now continuing, there are other parameters which are very important and one of the parameters is like potassium. So, it is always present in low quantity in natural freshwater.

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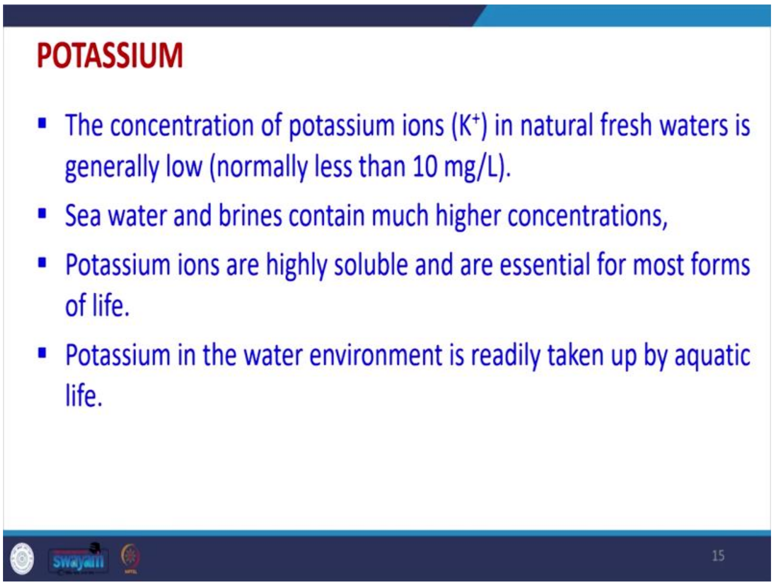

So, generally it should be less than, it will be less than 10 milligram per liter. Seawater and brines they contain much higher concentration, a potassium ions are highly soluble, and they are essential forms of life. So, as such, they are not that much toxic or anything they no issue with respect to potassium, but there is an issue that if they are present in water and that water from after the it is being discharged to some of the lakes and reservoirs.

So, under those conditions, if we have to stop the aquatic life to grow maybe plants, so we have to see that the potassium value should be under certain limit. So, as such it is not a very important parameter, sometimes it is taken care of, so that we can get enough potassium from the water itself to our body. So, this is there. Then another parameter which is called as sulphate.

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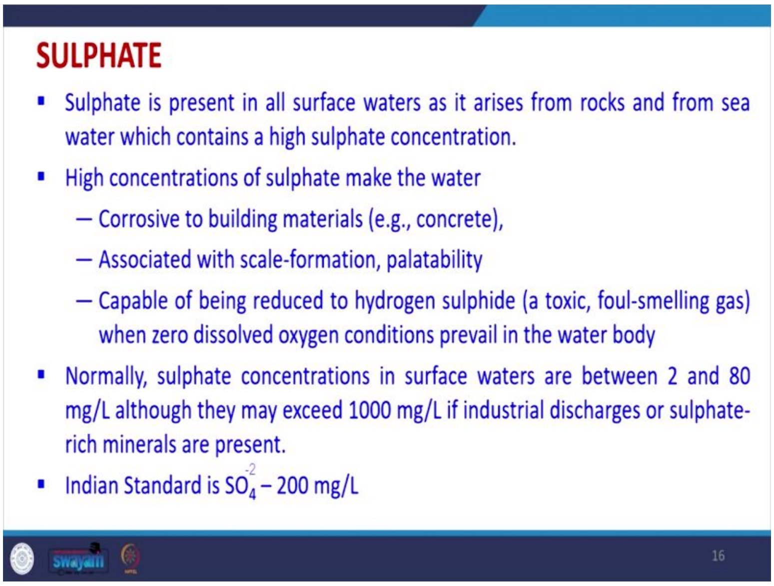

The sulphate is present in all surface waters. And it is because it is it comes sulphate comes from various rocks and from seawater also. So, seawater generally contain very high sulphate concentration, and rocks also give a lot of sulphate into the water. So, the groundwater may contain sulphate also. High concentration of sulphate in any water makes the water highly corrosive to the building material, in particular the concrete.

So, this is the very deterrent thing with respect to sulphate, then it may also be causing the scale formation. So, that is another bad thing with respect to sulphate. And it is capable of being reduced to hydrogen sulphide. So, if sulphate gets reduced to hydrogen sulphide, so it will emit a foul smell. So, we can easily see that okay, H2S formation is taking place, and this may happen in underground water also, where the zero dissolved oxygen conditions are prevailing. So, we do not want this condition to be raise. Generally, H2S is very undesirable.

So, there is a particular limit with respect to sulphate concentration in surface water, it should be between 2 and 80 milligram per liter, but many places up to thousand milligram per liter also have been reported, if the water is from industrial discharges also. Indian standard with respect to sulphate is 200 milligram per liter.

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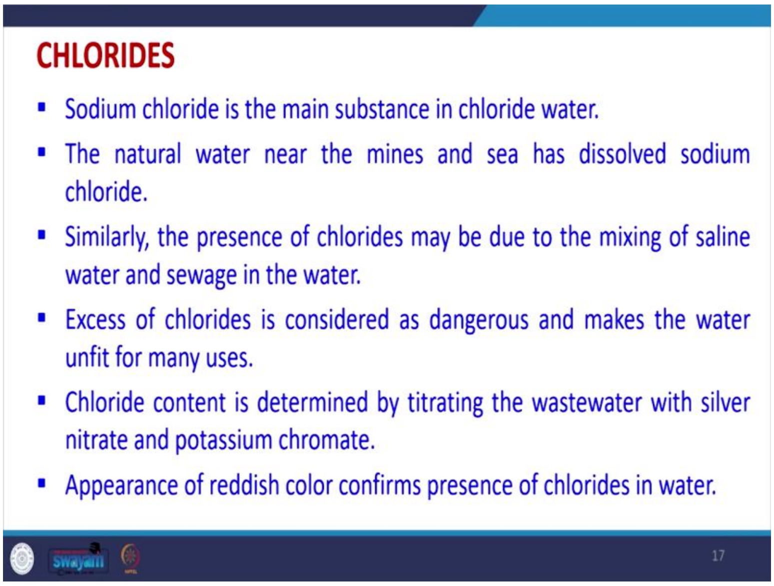

Then similarly, we have chloride ions which are there, the sodium chloride is the main substance in chloride. So, if sodium is present more likelihood that chloride will also be present. So, natural water which is near the mines, or sea has lot of dissolved sodium chloride. So, that means chloride will be present in the water, and excess of chloride is considered to be dangerous, and it makes the water unfit for many uses.

And chloride concentration can be determined by titration method using silver nitrate and potassium chromate, and this is very commonly used method for determining the chloride, and in this method actually, the appearance of reddish colour confirms the presence of chloride in the water. And there is a standard calibration method through which we can determine the chloride concentration via this titration method. Chloride in the freshwater also comes from the rocks.

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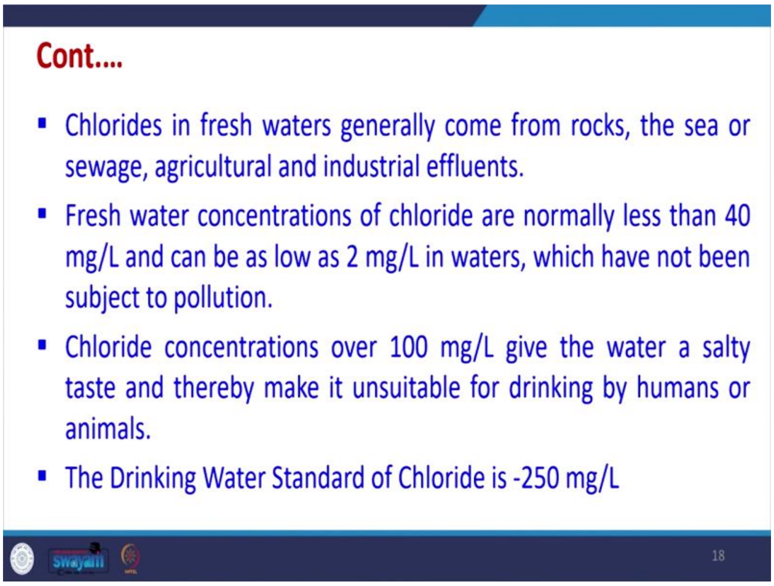

So, there is a possibility of if other rocks in particular chloride rocks are there. So, they may lease some of the chloride and that may go into the water. Fresh water concentrations of chloride are normally less than 40 milligram per liter, and generally they can be as low as two milligram per liters also.

So, drinking water is standard with respect to chloride is 250 milligrams per liter, and if any water is having any salty taste, so, that means, it may be having chloride concentration more than 100 milligram per liter, but up to 250 milligram per liter, it is okay to use the water for drinking purpose.

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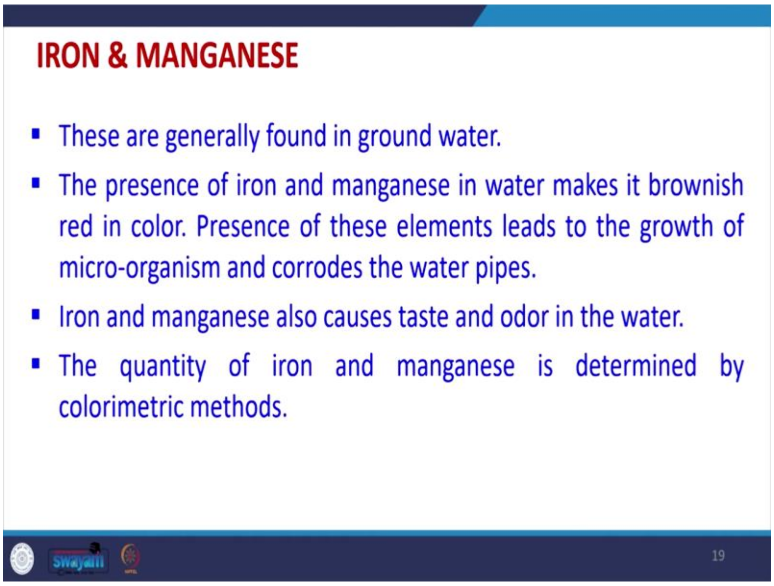

Similarly, other important elements which may be present in the water may be iron and manganese, they are generally found in groundwater and the presence of these iron and manganese makes the water brownish in nature, brownish, reddish in nature. And these elements lead to the growth of various microorganisms and they may also corrode it the same water is used for industrial uses.

So, corrosion is, corrosion of the various equipments and other things where water has to be used. And in particular in pipe, that may be because of the presence of iron and manganese. And they also cause a lot of taste and odor in the water. So, again colorimetric methods are used for determining the quantity of iron and manganese in the water. So, there are various methods which are present, and iron and manganese actually gets dissolved from the rock.

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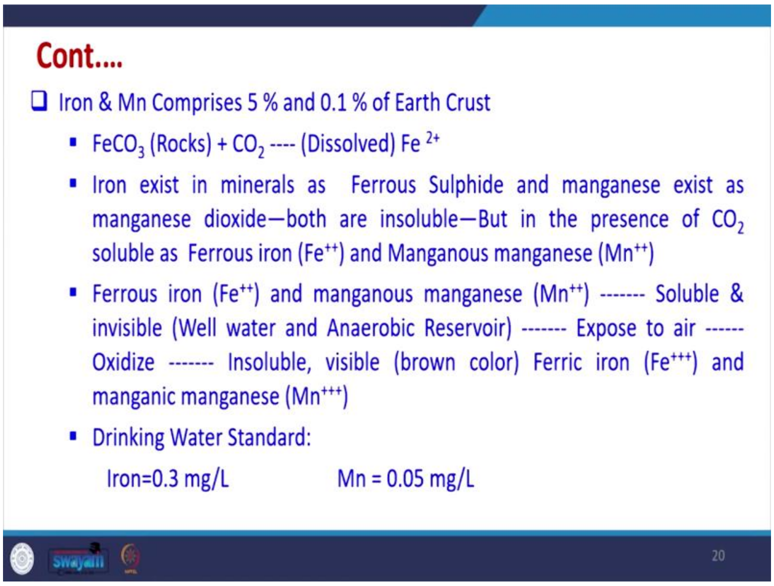

So, this is shown in this particular slide, and that happens because of the weathering effect which is due to the CO2 which is going into the underground, and that causes the weathering of these rocks and from which the iron goes into the water. Iran exist in various minerals as such as ferrous sulphide, manganese also exists in manganese dioxide.

Generally, they are insoluble but in presence of CO2, they will leach out and go into the water. And there are various soluble, various wells and anaerobic reservoirs where oxygen is very less they will be soluble and they will be invisible that means, they will not impart colour. So, we may feel that they are not containing iron and other things, but they may contain. The Indian standards have been set with respect to iron as point three milligram per liter and minus point zero five milligram per liter.

The pH of water which is there, earlier in the previous lecture, we discussed the pH. So, pH has very important role, how much amount of iron or manganese will dissolve into the water. So, generally natural water has a pH in the range of six and eight, but it may vary for industrial wastewater. So, they may contain more amount of these iron and manganese. So, they may have issues also with this.

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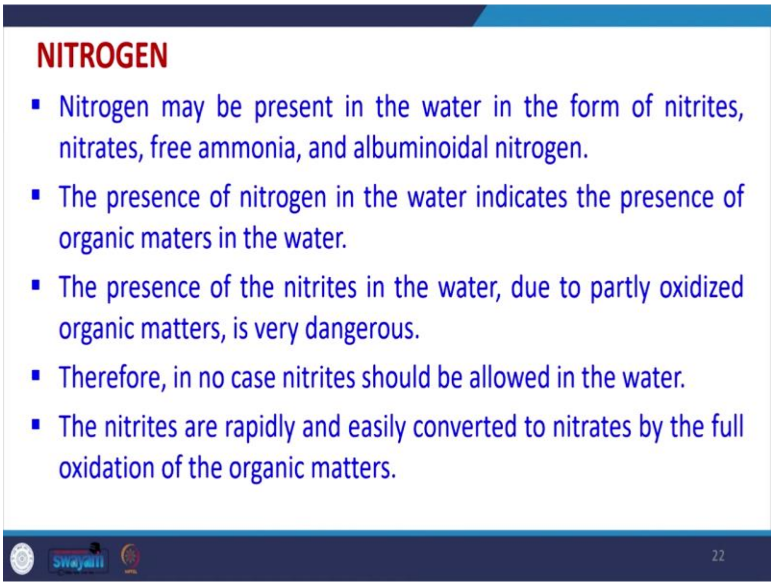

Similarly, nitrogen is a element which can exist in the water in different forms. So, nitrogen has a large number of valences, and managing nitrogen in the water cycle is one of the key aspects in the present era in terms of research also and otherwise as well. So, in the form of nitrogen may be in the form of nitrites, nitrates, free ammonia, and albuminoidal nitrogen etc. And this this presence of nitrogen in the water indicates that there is lot of organic matter present in the water.

Now, nitrogen is present in the water and that water is going into any aquatic body. So, we have challenges that eutrophication may happen. So, this is possible. So, we always limit the nitrogen. So, removing the nutrients in particular the nitrogen out of the water is very important, if nitrogen is present in the nitrite form due to the partially oxidized organic matter, then it is very dangerous.

Nitrite has more toxicity and in no case nitrite should be allowed in the water. Nitrites are easily converted into nitrates, if we can fully oxidised the all the organic matter. So, it is possible.

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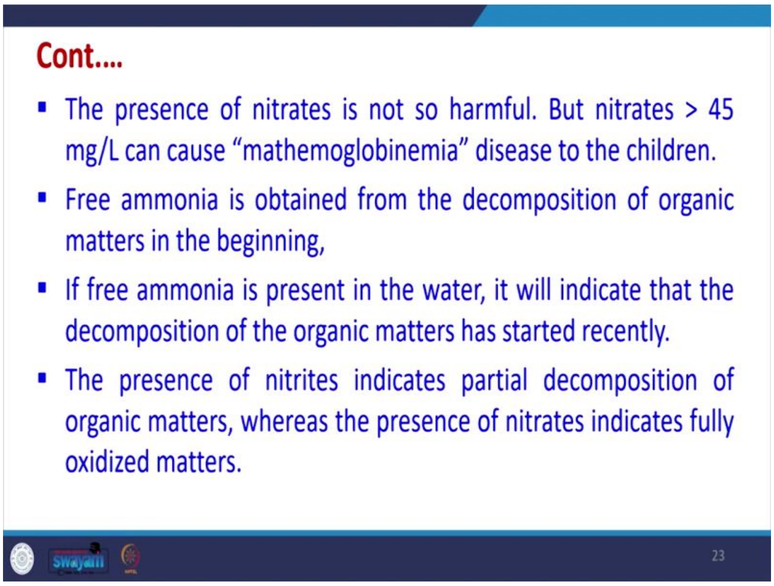

Now, nitrates are not that much harmful as nitrites but still there are certain reports which told that nitrate is present in more than forty-five milligram per litre, they can cause disease like methemoglobinemia disease to the children. So, this one of the disease which is reported in the various places. Free ammonia is obtained from the decomposition of the organic matter in the beginning. So, this is another form of nitrogen, free ammonia.

And if free ammonia is present in the water it will indicate that organic matters are decomposition, their decomposition has started and generally the formation of free ammonia will take lot of time. But still, it indicates the decomposition of all the nitrogenous organic matter in the presence of, in the present in the water.

The presence of nitrites indicates partial decomposition of organic matters, whereas the presence of nitrates indicates full oxidised matters. In summary, nitrogen is one of the undesirable element, we do not want nitrites to be present at all. This is one important aspect, second thing if nitrite is present can we convert in to nitrate, this is possible.

And, we should also after converting into nitrate also we should limit the nitrate within forty-five milligram per litre, which is the standard, which causes diseases to the children, so this is the important consideration. While treatment, when the treatment of wastewater or water has to be done which contains nitrogen.

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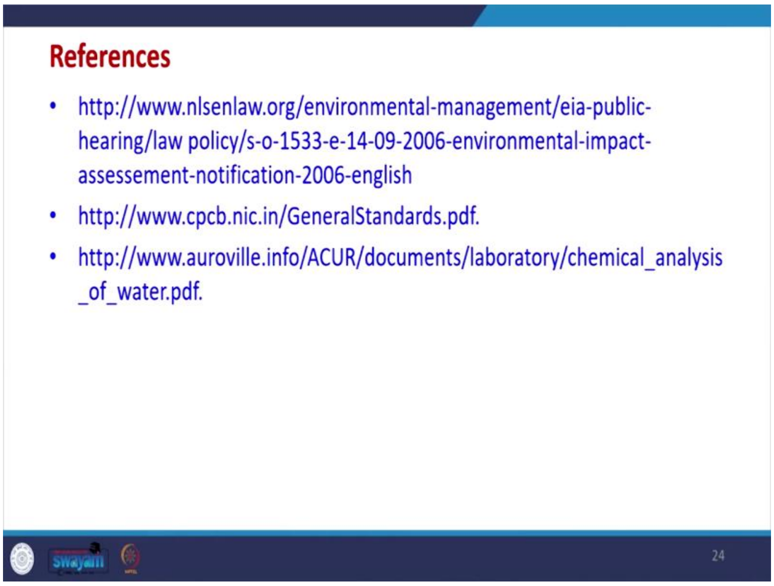

So, these are the some of the references for today's lecture, and will continue the chemical parameter in the next lecture. So, and there are many other chemical parameter of importance, so that we will study in the next lecture.