Physico-Chemical Processes for Wastewater Treatment
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Lecture 04
Water Quality Monitoring Physical and Chemical Parameters

Good day everyone. This is the fourth lecture in this series and on the course on physico-chemical processes for wastewater treatment. And in the previous lecture, we started studying the water quality monitoring. And within that we studied the physical parameters. And we studied that came, temperature, specific conductivity and color.

Now, we will continue from the color further, and we will study the physical parameters and after that, we will continue with chemical parameters.

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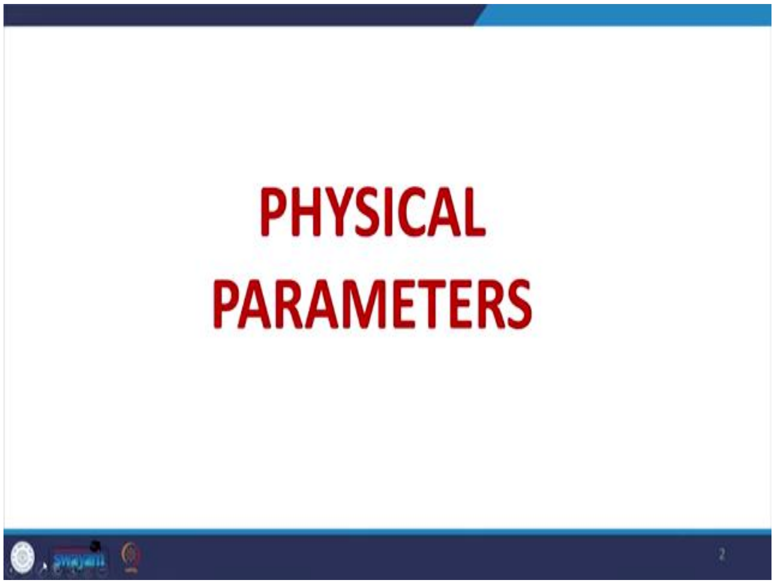

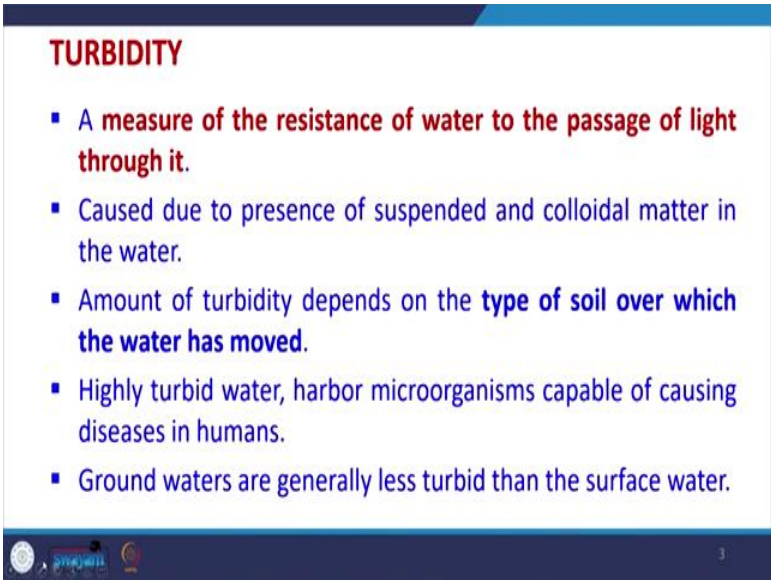

So, with physical parameters, last time we studied color. A similar parameter is turbidity. And actually, it measures the resistance of water to the passage of light through it. And if any water is highly turbid, that means it is more opaque in nature and it will not allow pass, allow light to pass through it, and that may be due to the presence of suspended and colloidal matter present in that water.

So, amount of turbidity that is present in any water depends upon the soil over which the water has moved. So, this is very important parameter. And actually if any water is turbid then generally any people will feel that okay, that water is not good enough for drinking, or any further uses.

So, highly turbid water, they may harbor microorganisms, which may be capable of causing diseases human beings. So, that is why high turbid water is never preferred. Ground waters generally less turbid than the surface water, because they have more chances of dissolution, lesser chances of dissolution of any other colloidal matter, or other.

Surface water whereas there is a lot of chance of dissolution of colloidal metal, because the surface water if it is river, so in the river the water may have got collected after rainfall and that rainfall may have moved over different types of soils. So, it may have collected a lot of colloidal matter.

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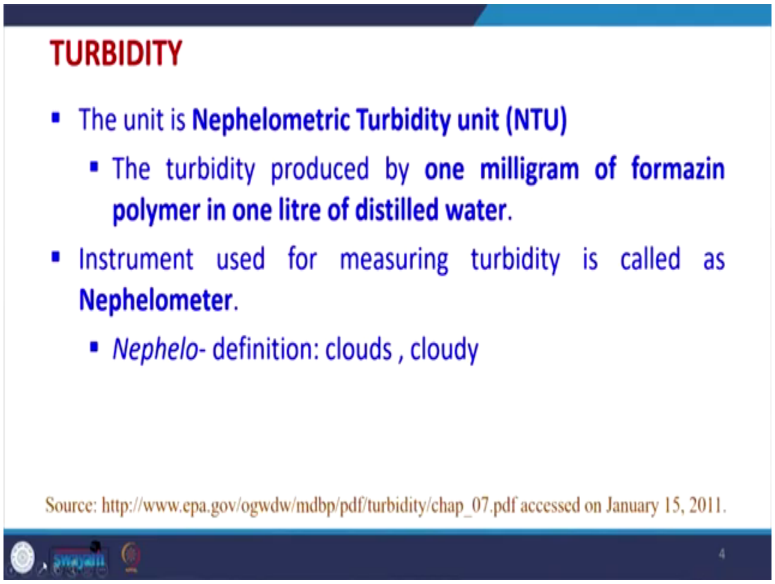

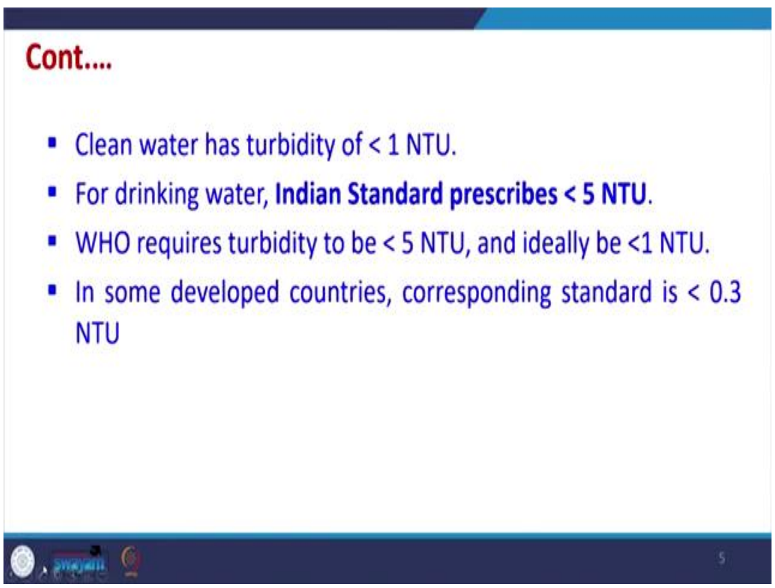

Now, turbidity is measured using an instrument, which is called Nephelometric turbidity unit and this actually that turbidity produced by one milligram of for formazin polymer in one liter of distilled water. It is said to be this is the unit and it is equal to one NTU. So, one NTU is like one milligram of formazin polymer dissolved in one liter of distilled water.

So, actually the calibration that we studied in the previous lecture, the same thing is used here. So, we for any turbidity Nephelometer, what we do is that, we make a calibration graph by dissolving different amount of formazin in distilled water and then we measure the whatever light that has been deflected.

And that light through that light we draw the calibration graph and later on for unknown samples, we determine the turbidity using this Nephlelometer. And Nephelo, just for the definition sake it is, it means clouds, or cloudy.

Now, clean water has turbidity of less than 1 NTU. So, this is NTU means, Nephelometric turbidity unit. For as per Indian standard for drinking water the NTU should be less than 5 NTU, the turbidity should be less than 5 NTU. WHO also recommends the same value less than 5 NTU of turbidity. And it also tells that ideally it should be less than 1 NTU. In some of the developed countries the standards are as low as 0.3 NTU as well.

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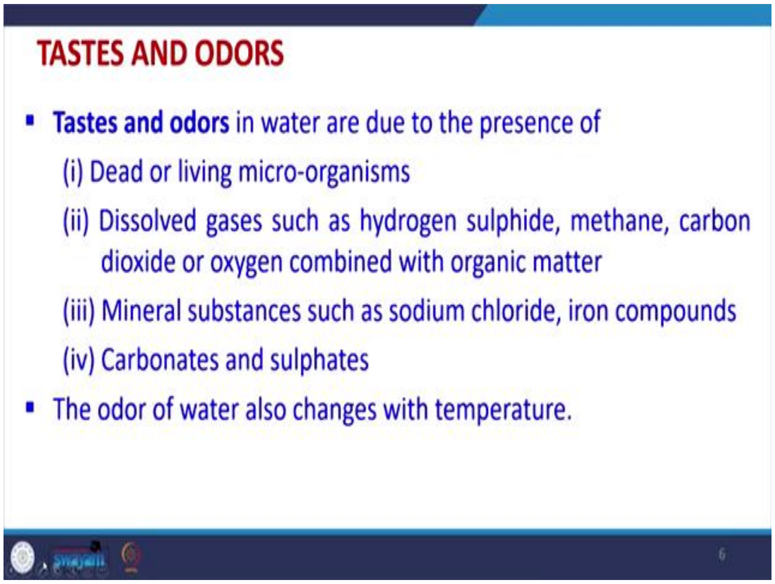

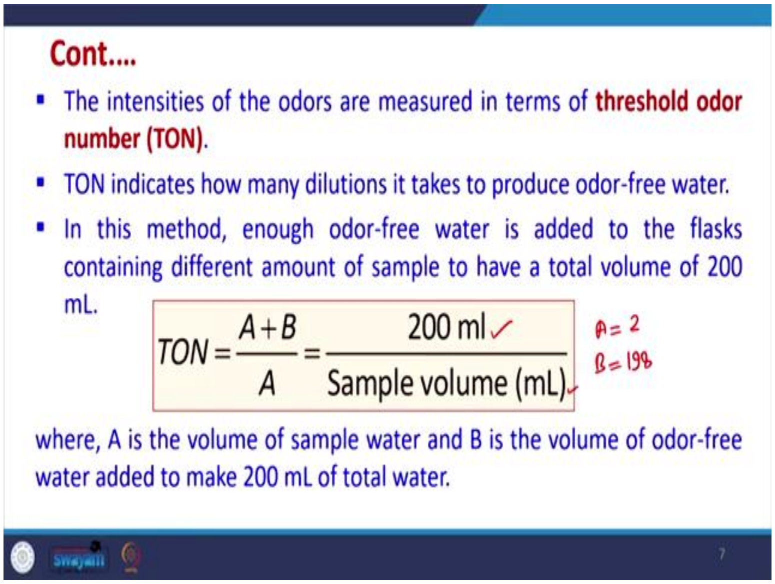

Then the next parameter is taste, or odor, certainly taste is never water taste can be reported but it is not one of the preferred parameters, it is only for applicable for drinking. Odor is one of the parameter, which is essential and many times it is reported.

So, taste or odor in the water may be due to the dead or living microorganisms. Dissolved gases such as hydrogen sulphide, methane, carbon dioxide, oxygen in combination with organic matter. So, they may cause a lot of odor or taste as well.

Mineral substances such as sodium chloride, iron compounds, etc., also cause these two parameters, odor or taste. Then carbonates and sulphates in combination with other compounds, other cations may also cause these parameters to be their present in the water.

Now, the odor of water also changes with temperature. So, as the solubility changes with temperature, odor of water also changes with temperature. So, if you have to report the odor, we have to be highly careful that there should not be no change in temperature, when we are determining the odor of the water.

Now, the intensity of the odor of water samples are measured in terms of threshold odor number. So, it is called as TON, and how to determine that TON? So, it is reporting of TON is a little difficult, it is defined here you can see, and then we will discuss in the next slide that how the TON is actually determined.

$$TON = \frac{A+B}{A} = \frac{\text{200 ml}}{\text{Sample volume (mL)}}$$

where, A is the volume of sample water and B is the volume of odor-free water added to make 200 mL of total water.

So, any water sample is taken and that water sample is diluted with fresh water, which is having no distilled water which is having no odor, and the total volume is kept as 200 ml. So, original sample plus diluted water both should be equal to 200 ML as written here. And out of this the sample volume is only this.

So, if the we have taken the sample volume of 2, that means the A is 2 and then we will add B is equal to 198. So, that the total amount of water is 200 ml and through that we determined that TON.

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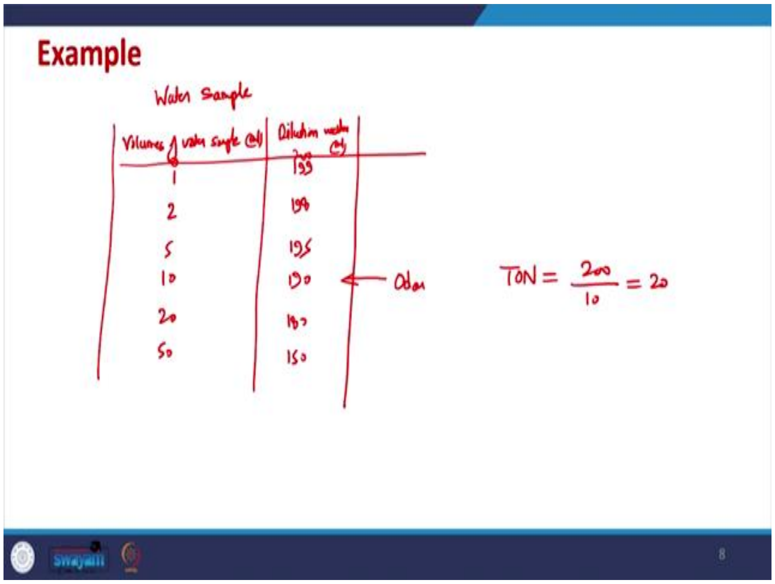

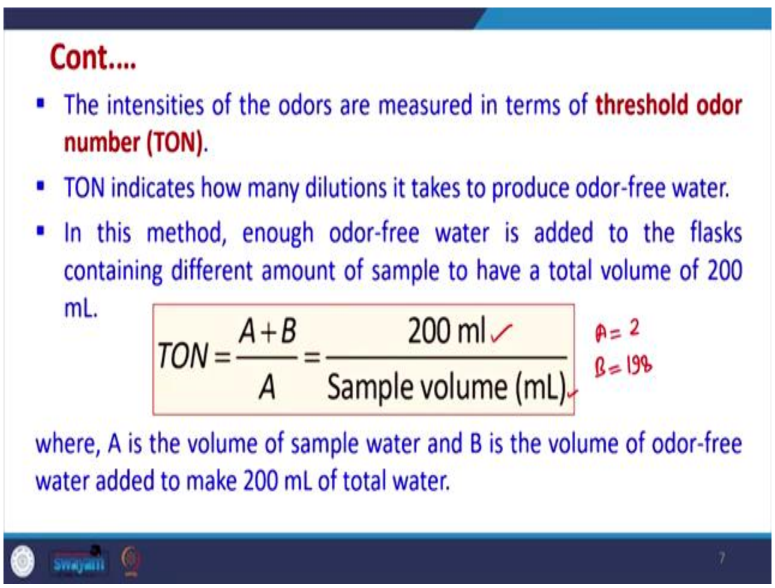

So, how we do this, let us understand. So, suppose any water sample is there. So, what is done is that, in that water sample, some amount of different volumes of that water sample will be taken, volumes of water sample. So, that may be like different volumes, 1 ml, 2 ml, we are writing like this 1 ml, 2 ml, 5 ml, 10 ml, 20 ml, 50 ml, as such we can have different.

Now, what is done is that, a different amounts of dilution water is added to that and that will be distilled water and so and remember we have to make them 200. So, that means here 199, 198, 195, 190, 180, 150. So, that the total sum of sum of both these waters is equal to 200.

Now, what is done is that? That and these will these will be kept in different, different water bottles. Now, few people will come and start from the most diluted sample. So, this will be the most diluted sample, it may be possible that is only totally dilution water is also kept. So, this is like 0 and 200 is kept here. So, they will start try to see that the odor is present in which bottle.

So, whichever diluted sample majority of people report that this particular water bottle is having some odor, which is which can be they can sense that odor. So, that means that TON will be reported for this, and this TON for this particular thing will be 200 divided by 10. So, that means that TON is 20. As per the formula which is given here.

So, it is the majority of people who are sensing the most diluted sample odor in the most diluted sample possible. So, that is TON and this is how it is determined.

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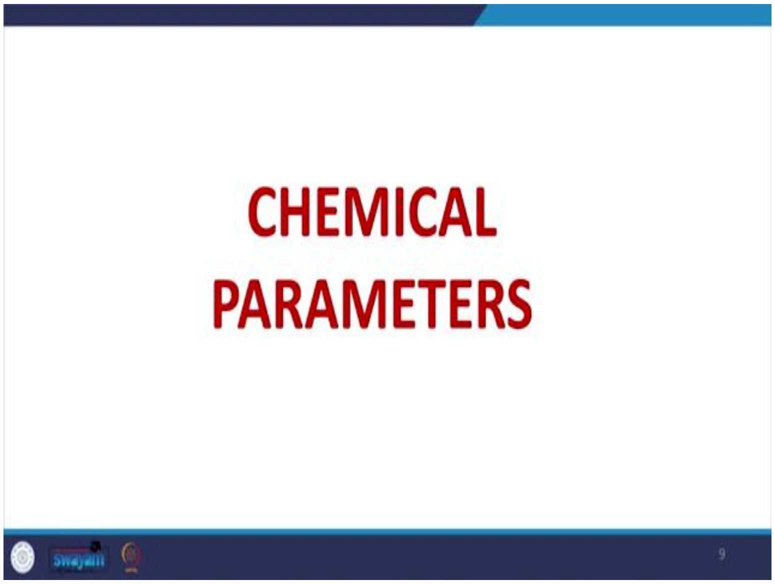

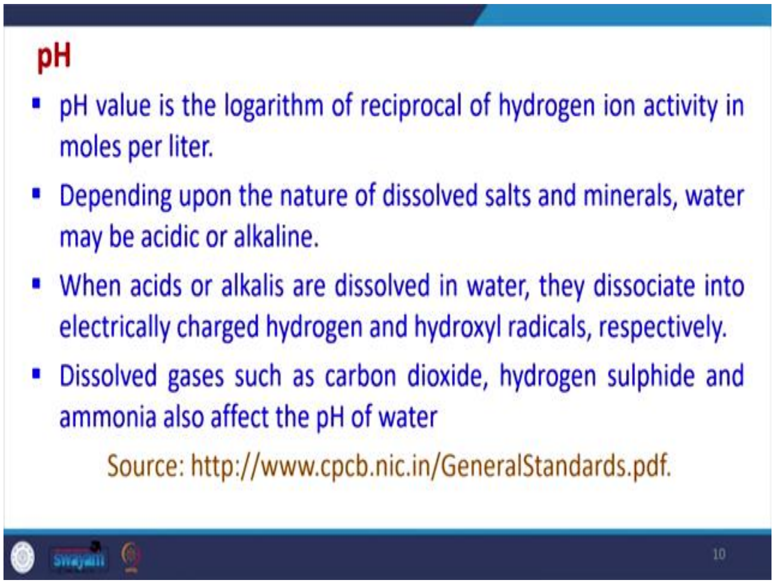

Now, we will go further ahead with the very important chemical parameters today, we will be starting the chemical parameters. So, one of the foremost parameter, which is the most important parameter is pH. Generally, it is neglected and many people do not understands the physical significance, or the significance of this parameter, and this parameter has a lot of effect during treatment.

So, we must understand the basic science behind the pH and how it affects the dissolution of various types of compounds in the water and the that those compounds actually change their orientation at different pH. So, this is very, very important parameter. So, pH by definition is the logarithm of reciprocal of hydrogen ion activity in moles per liter.

So, this we have studied since long, so there is nothing new. Depending upon the nature of dissolved salts and minerals, water may be acidic, or alkaline. So, it will depend upon which type of minerals, or salts are present in the water. When acids or alkalis are dissolved in water, they also dissociate into electrically charged hydrogen and hydroxyl radicals.

So, if any acid is dissolved, the certainly it will give H plus, similarly if alkali is dissolved it will give OH minus. So, and they dissociate these alkali and acid they dissociate and give these hydrogen and hydroxyl radicals. And because of which the pH changes.

Also different types of gases like carbon dioxide, hydrogen sulphide, ammonia, when they are dissolved in the water, they affect the pH. And so how much quantity of these gases are present in the water that depends upon the pH, or you can call it vice versa, if more amount is dissolved, actually it will change the pH. So, this is the pH is very important parameter.

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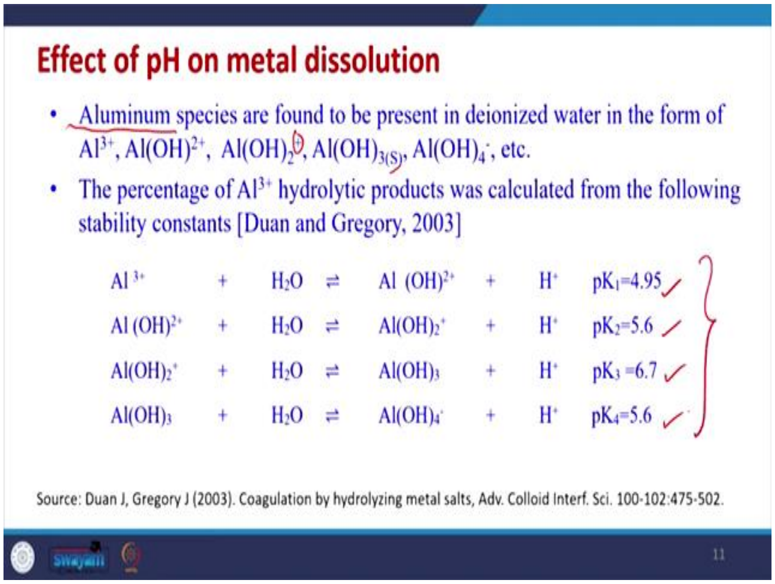

Now, we will try to understand the effect of pH on metal dissolution, that if suppose any water is highly acidic, or if it is alkaline, so whether metal will get dissolved or not. So, it depends upon pH of the water. Now, here I have taken the example of aluminum. So, aluminum is species alkali they can be present in that deionized water if anything thing else is not present except the aluminum is species.

So, they can be present in that deionized water in the form of Al 3 plus Al OH 2 plus Al OH 2 only this is mono, then Al OH 3, which is in like precipitate and then Al OH 4 minus. So, these are the different forms, which are likely to be present for aluminum species.

And the percentage of these hydrolytic products in the water can be calculated using the stability constants which are given here. So, actually for determining any such type of percentage of various species, which are present in the water, we need to know the pKa values of those species. For aluminum that pKa values are given here, the pKa 1, pKa 2, pKa 3, pKa 4, and during this actually they change the orientation, we can understand they are releasing H plus one by one.

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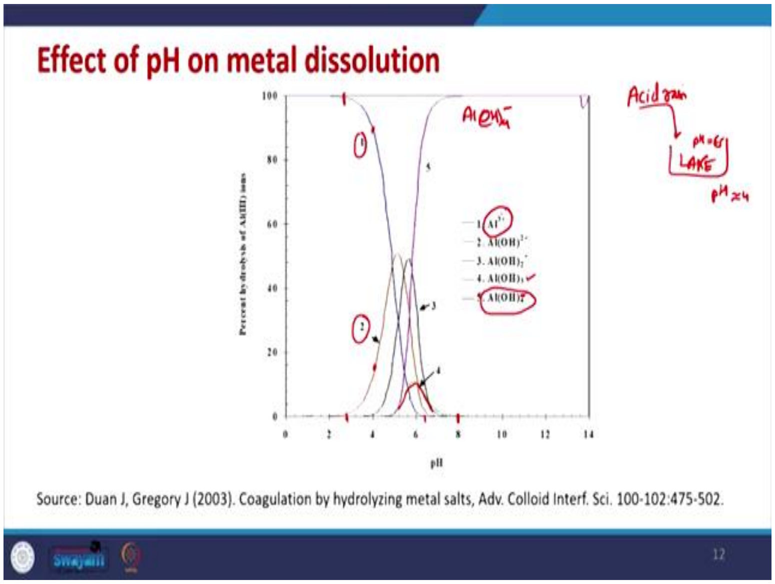

So, and if we have these values exactly and with little bit mathematics and the material balance, we can easily make a diagram like this and these are called speciation diagrams. So, this is a speciation diagram of aluminum at different pH. So, what does it tells? It tells that aluminum, this is 1, 1 is present here and till around 6.5, 6.2, or 3, it is only present till and around this value we can if you consider to be around 2.8.

So, this is 2.8, so till 2.8, aluminum if the pH of water is 2.8, or less and any alumina will be dissolved, it will always be most likely be present in the form of Al 3 plus. Similarly, for pH more than 8, if any alumina will be dissolved, it will always be in the ionic form sorry, this ionic form because this Al OH 4 minus. So, this is fifth. So, this is beyond this 100 percent is Al OH 4 minus. So, this is, this is very important.

So, this is tells us that which specie of alumina will be present at with pH. And how much percentage, why this is very important? Because, this also tells that during coagulation one of the make methods which are physico-chemical method, which is used for removing treatment of water, in that we may use we may use alum.

So, alum if it is added actually it will go dissociation and depending upon the pH the Al 3 plus may be present in different form. So, the same alumina, a same alum, if it is added for water maybe beyond 8 pH, it may not be helpful. Whereas, it may be helpful for pH less than 4.

So, it will depend upon the pH of the water that metal dissolution take place or not. There is second thing also out of this that, if any acid rain happens and the pH decreases, so any lake is there and in that lake actually it is having a pH some pH initially I have been suppose a pH of 6.5, or maybe 7.

So, under this condition 6.5, if alumina is present, it is also likely the alumina will be some amount of alumina will be in the precipitated form, because it is shown by this particular curve. Similarly, it is true for other types of metal dissolution also. And this hydroxide which is in the precipitate form, their values are much higher for like iron and other types. So, if pH is this, they will be in dissolved form.

Now, if suppose the because of acid rain, which is happening and somehow the buffering capacity of the lake goes off and the pH becomes somehow 4 of this lake. So, under that condition, whatever this alumina, which was dissolved, which was actually settled and it was in the precipitate form at the bottom of the lake, it will get dissolved in the water and it will now be in the form of either these 2, or 1, at pH 4.

So, because pH 4, we see only this second form and first form are present. So, around 20 percent will be Al OH 2 Plus and rest 80 percent will be Al 3 plus. So, that means that is why acid with acid rain that toxicity of the lakes increases, because the as the pH decreases most of the metals and other thing get dissolved in the water, in place of settling down as precipitate to the bottom of the lake.

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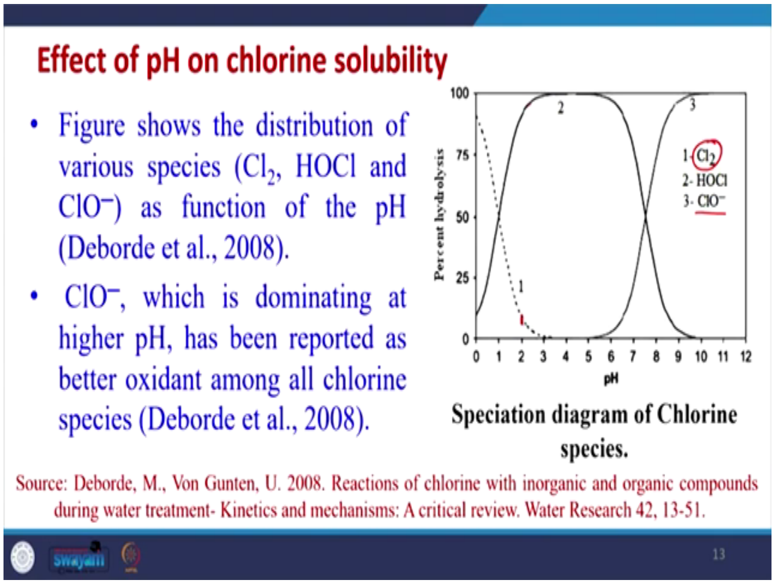

Similarly, with gases also. So, gases they are dissolution changes with pH and here we I have taken example of chlorine and the chlorine solubility actually changes with pH and we can see here, the speciation diagram of chlorine species. So, that this is 1.

So, if you see the chlorine will be more in the form of chlorine if the pH is around 2, whereas it will be in the form of neutral form HOCl, in this range. So, hypochlorite will be there. Then there will be ionic specie, which will be present.

So, fingers shows the distribution of various species like chlorine, HOCl and ClO, as a function of pH. So, it is seen that, the ionic form of chlorine is dominating at higher pH and this has been reported as a better oxidant among all chlorine species. So, if pH is high and if you add chlorine alkali, it acts very well and it helps in the degradation of various pollutants. So, this is then.

So, there is a lot of relationship, which exists between pH, dissolution of metals, dissolution of gases, and also various ionic forms of organic species also, organic species also change their form either from neutral to cationic, or from an ionic to neutral depending upon the pKa values. So, this is true for most of the organic species as well.

So, that is why the pKa value must be determined and from that we can get lot of idea for removal of these compounds by playing with the pH and understanding the basic science behind the same. So, this is there.

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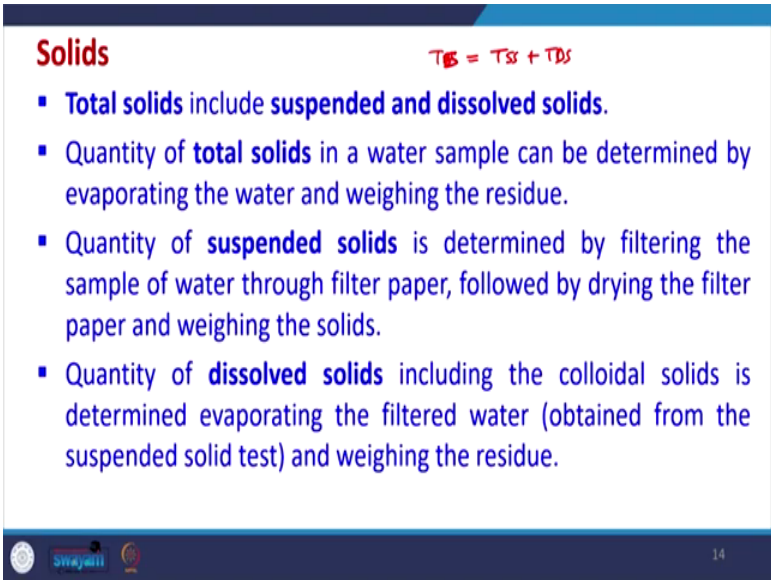

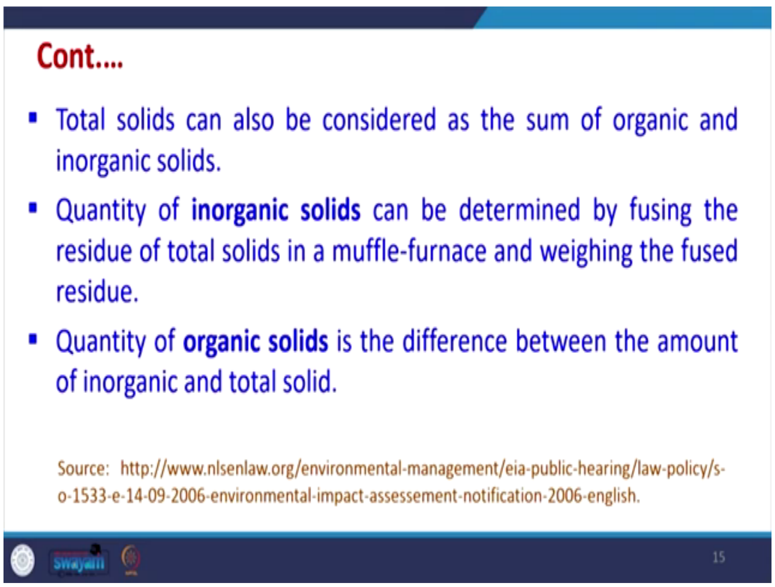

Now, continuing the second parameter with respect to chemical that we are going to study is like solids. So, what are now solids total this is like total amount of solid present in the water. So, this total solid may include suspended solid, dissolved solid. So, like we can write like TSS, this TSS is equal to sorry, TS is equal to TSS plus TDS. So, TSS means total suspended solid, total dissolved solids.

The quantity of total solids in a water sample can be easily determined by evaporating the water at around 105 degrees centigrade and weighing the residue. And some generally these residues are dried for very larger time more than two hours, so that the weight becomes constant, the mass become constant and then we weighed the residue and through that we can determine the total solid in any water.

Now, the quantity of suspended solids in the water, if we have to determine that means, we have to collect the suspended solid and that is collected by filtering the sample of water through filter paper and all these suspended solids get collected under filter paper.

Now, this filter paper is dried and then again it is its weight is taken and before dry, earlier also before filtering we take the weight of the filter paper and through that we can determine the amount of suspended solids.

Similarly, the quantity of dissolved solids can be due to presence of colloidal solids and that can be determined by evaporating the filtered water obtained from the suspended solids test and weighing the residue. It can also be just directly obtained by subtracting, but it is better to determine by this method we can understand the error, which is coming through those approaches.

Now, total solids can also be considered as sum of organic and inorganic solids. So, this also can be determined the quantity of inorganic solids can be determined by fusing the residue of total solid in muffle- furnace and weighing the fused residue.

So, we take the temperature to be very high beyond 900 degrees centigrade, fuse the residue and we assume that under those high temperature conditions all the organics solids have already evaporated and left the residue. So, that is why only inorganic solid will be present and by differentiation we can find out the amount of quantity of organic solids as well.

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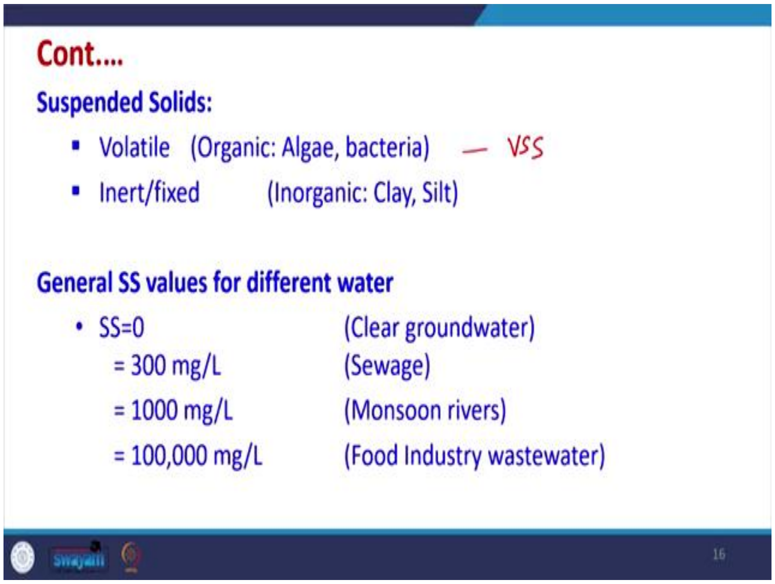

Now, there are certain ideas we can get by getting the values. So, if suspended solids maybe because of maybe volatile, or maybe inert, or fixed. So, these suspended solids, which are volatile, they are called as VSS.

So, in the next slide, we will understand what is VSS and how we can determine it and whatever is left that may be inert, or fixed. So, that may be because of clay, silt, etc. So, this suspended solid and the organic solid which is, which is like volatile, it is because of algae, and bacteria.

Now, generally this suspended solids for water may vary like for clear groundwater it will be 0 for sewage 300 milligram per liter, and for Monsoon river it may be beyond 1000 milligram per liter, up to 3000 milligram per liter or more also. And for food industry wastewater the value is more than 1 lakh also. So, these are typical values, so they may vary a lot as well.

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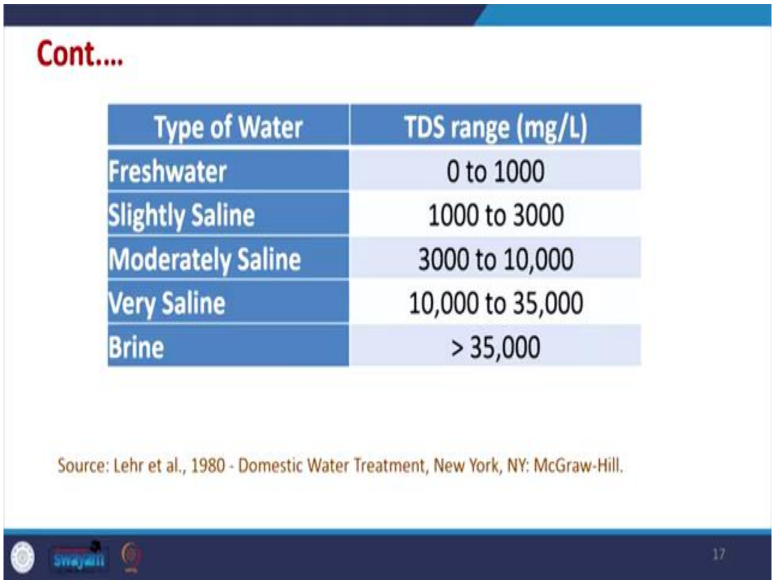

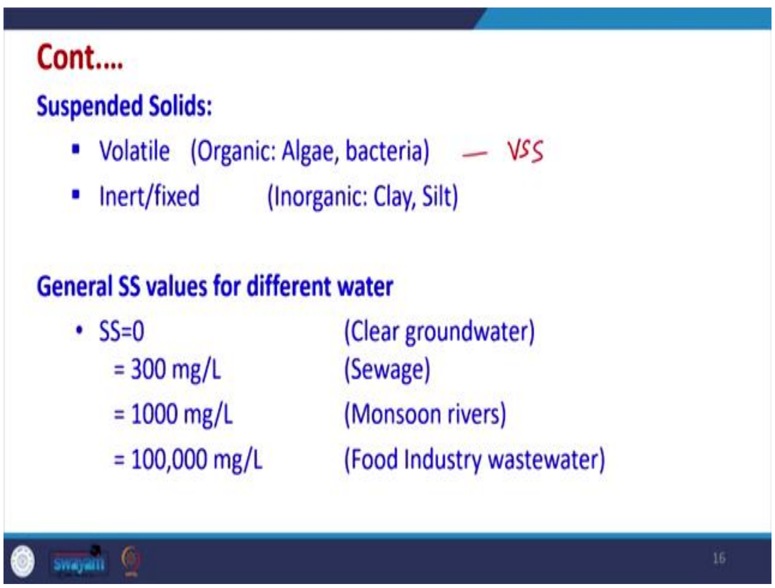

Now, depending upon TDS, so in the previous slide, we were talking about suspended solids, now we are talking about dissolved solids. So, depending upon the TDS range, the water is also classified. So, 1000 milligram per liter TDS, it is freshwater, then slightly saline up to 3000 milligram per liter, then from 3000 to 10,000 milligram per liter it is moderately saline.

Then, highly saline from 10,000 to 35,000 milligram per liter, or 35 gram per liter and it is like a brine solution for more than 35 gram per liter and it is similar to that of ocean water.

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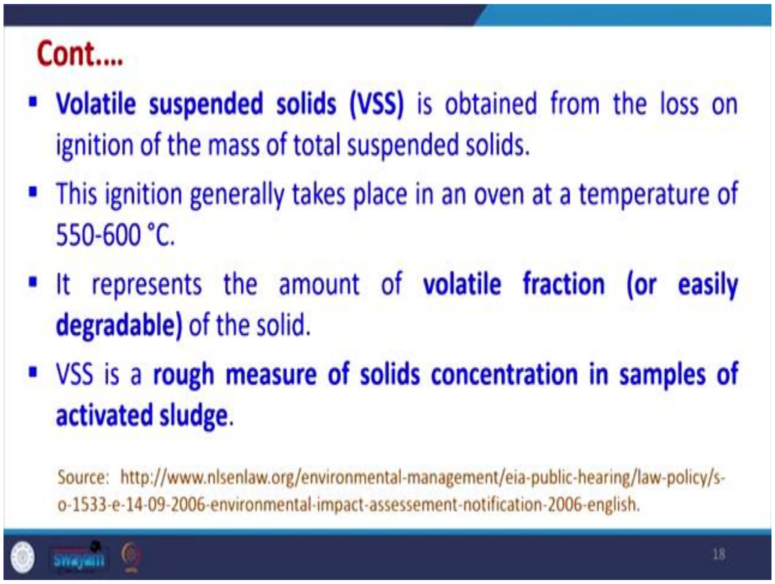

Now, VSS, which was a term that we assess, so this we are trying to understand. The VSS is we can determined the VSS value. What we do in that? Is that the mass of total suspended solids which is obtained by evaporating, actually the water from the filter paper at 105 degrees centigrade in place of 105 degrees centigrade we heat up to 550 or 600 degrees centigrade.

So, under those conditions all those things which are volatile will also go off. So, whatever fraction which has gone off is the degradable fraction. And through that we can measure the VSS. And actually it gives a lot of idea also with respect to treatment whether we should perform biological treatment, or physico-chemical treatment of the water. Because, if there VSS is very high, though that means there is a lot of biodegradable fraction in that solid.

So, it will be easily we can remove that organic fraction by maybe biological treatment, but if VSS is low, that means it has more inert content and or it is not easily biodegradable. So, that means we will have to adopt other techniques physico-chemical for the removal of such solid from the water. So, VSS does give some idea regarding the treatment methodology that we should adopt for treatment of that water.

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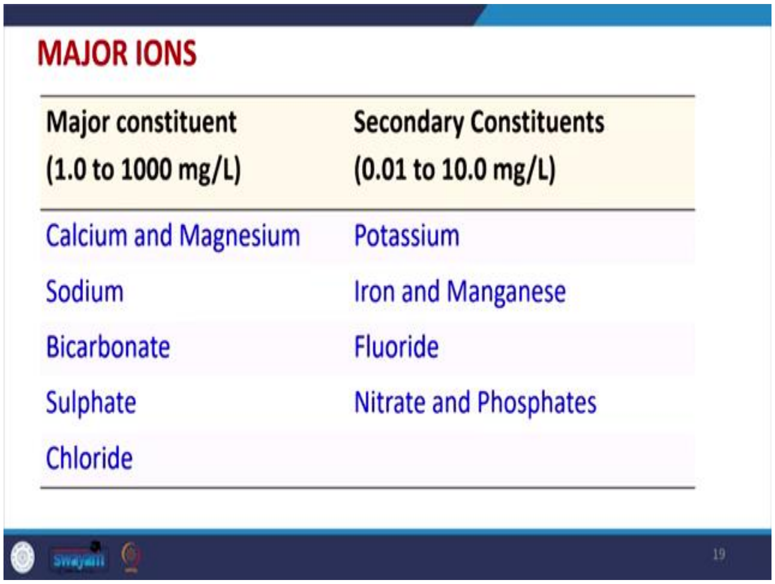

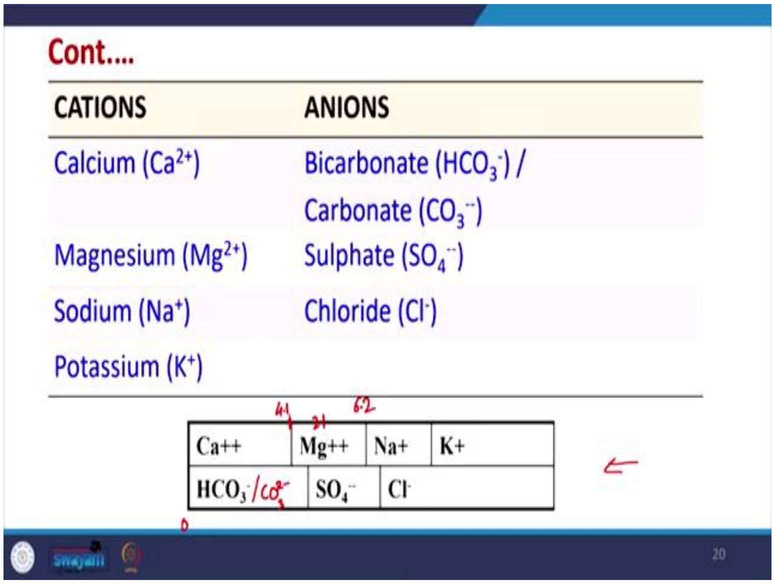

Now, beyond that after total solids, there is a scope that we should go for determining the major constituents and minor constituents, which are present in the water and these may be ions. So, major constituents, which are generally present in the water in the higher range from 1 to 1000 milligram per liter or beyond are given here.

So, these are like calcium and magnesium, sodium, bicarbonate ions, sulfate ions, chloride ions. So, these are the generally the major constituents which are always present in the water. Then there are secondary constituents, which may be present like potassium, iron maganese, fluoride, nitrate and phosphate and other things as well. So, we may have to determine the secondary constituents also.

Now, once we determine these constituents, they give a lot of ideas. So, out of these constituents major constituents and if we determine the secondary constituents also, they are called as cations, or anions. So, we can subdivide into cations, or a anions. So, major cations are like calcium, magnesium, sodium, potassium, and major anions are like bicarbonate, carbonate ions, sulphate ions and chloride ions.

So, they are represented generally their values are represented like this in milli equivalent per liter. And they give a lot of idea and we are going to use such type of figures, which are which is shown here later on for understanding various things with respect to water quality. So, like calcium, magnesium, so all the cations are reported by addition. So, that means if it is 0 line so whatever milli equivalent of calcium ions are present will represent up to here.

So, suppose this value is 4.1 Now, what is done is that later on we add magnesium also here. So, suppose this total magnesium is 2.1 here, so it will go up to 6.2. So, this way we go on adding and similarly we go on adding for carbonate ions also. So, carbonate ions maybe not only bicarbonate, then carbonate ions may also be present to both are reported and they are also reported in addition and through that we get to know lot of things. So, this will.

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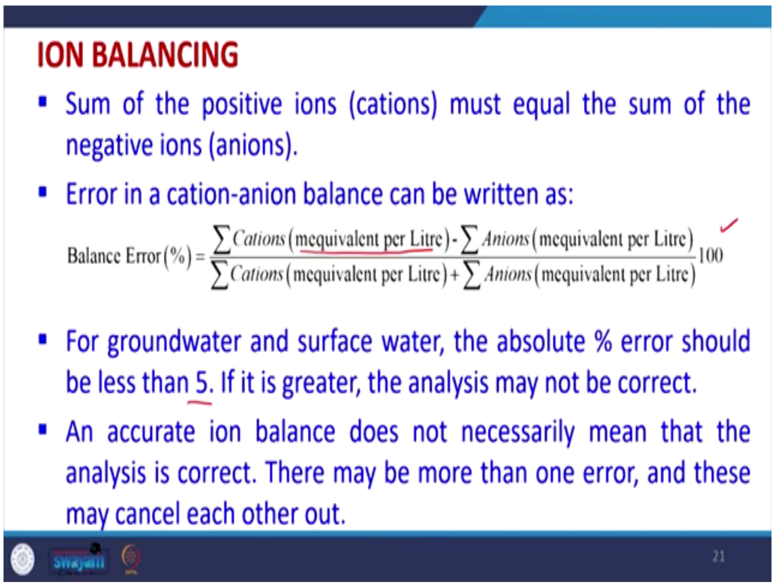

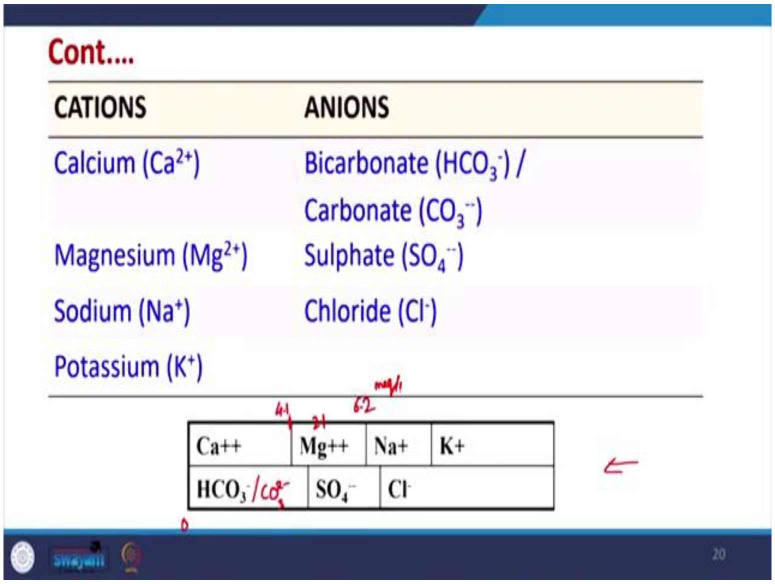

Now, what is done is that? Once we determine all the major cations and major anions, we always check that whatever report we are going to give, whether it is correct or not. So, in actual correct scenario the sum of major anions that major positive ions captains must be equal to sum of negative ions, which are anions. And the error is calculated by this formula which is given here. This is difference between the cations and anions in terms of milli equivalent per liter.

So, we always report in the previous figure also everything is reported in milli equivalent per liter. So, this is there, and here also we report in the milli equivalent per liter and these difference is divided by the total ions present in the. So, that will be cations and anions both added together.

So, for groundwater and surface water, the absolute error the purse, this error which is reported here it should be less than 5 percent. So, generally the error should be less than 5 percent, if it is greater than 5 percent so that means there is some error in the analysis and we should cross check our analysis. And it may be possible that we are missing some major cation, or anion, that is why this error is coming.

Also, there is a second possibility that if suppose the error is less than 5 also is still this analysis report may not be correct. So, we must have a lot of experience in judging, whether our report is correct or not, because sometimes the more than one error may be there, and these error may cancel out and we may feel that. So, that is why any analysis should be performed at least three times and the average of those things that should be reported, this is there.

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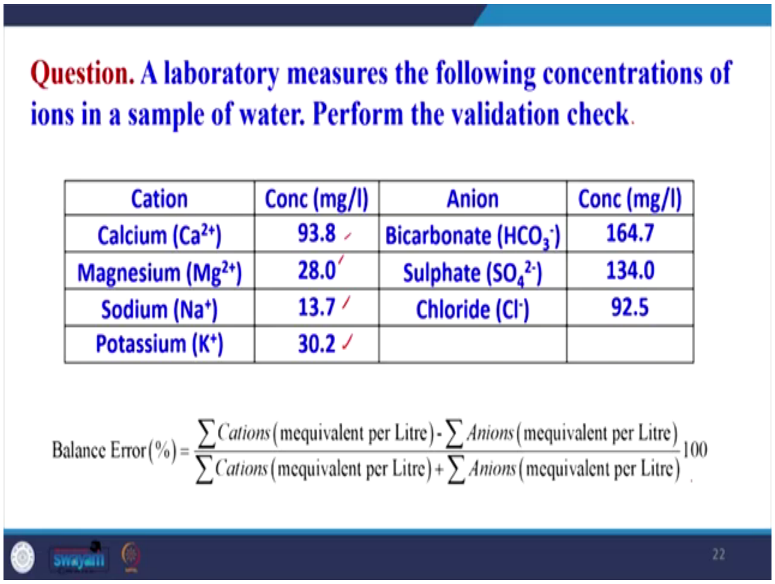

Cation	Conc (mg/l)	Anion	Conc (mg/l)
Calcium (Ca^{2+})	93.8	Bicarbonate (HCO_3^-)	164.7
Magnesium (Mg^{2+})	28.0	Sulphate (SO_4^{2-})	134.0
Sodium (Na^+)	13.7	Chloride (Cl^-)	92.5
Potassium (K^+)	30.2		

$$\text{Balance Error}(\%) = \frac{\sum Cations(\text{mequivalent per Litre}) - \sum Anions(\text{mequivalent per Litre})}{\sum Cations(\text{mequivalent per Litre}) + \sum Anions(\text{mequivalent per Litre})} 100$$

Now, a question is here and a laboratory measures the following concentration of ions in a sample of water and we need to perform the validation check of whether it is this report which has been given to us is correct or not.

So, the concentrations are reported here of calcium, magnesium, sodium and potassium. So, these values you can see her. These values are written. Similarly, for bicarbonate, sulphate, and chloride. So, the laboratory has not reported any carbonate ion and we have to use this formula for finding out whether this report is likely to be correct or not.

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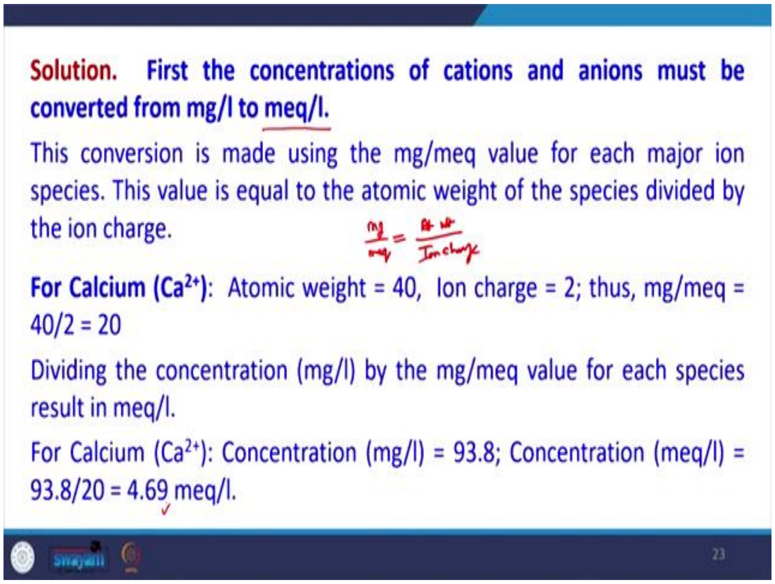

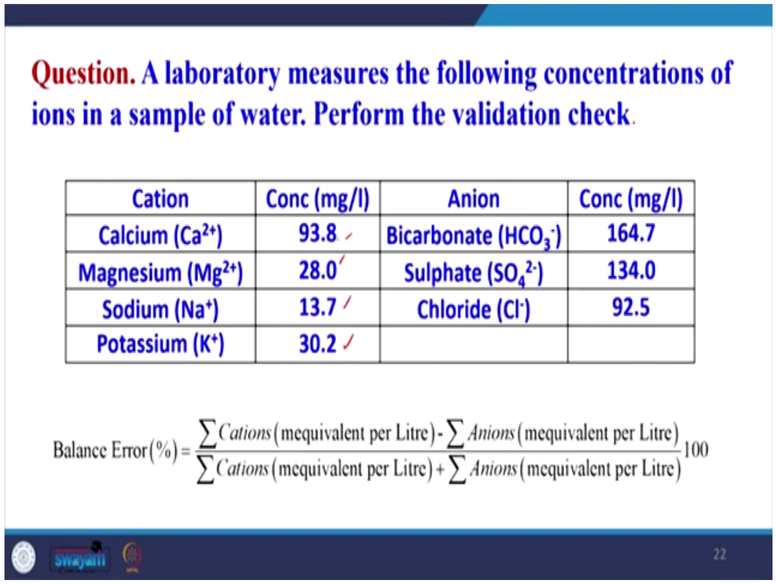

So, what we do? So, first we will have to change the concentration of cations and anions from milligram per liter to milli equivalent per liter. So, this is the first step. So, this conversion is made by using the milligram per milli equivalent value for each of the major ionic species and this value is equal to atomic weight of the species divided by the ion charge.

So, that means what is that? That means milligram per milli equivalent is equal to atomic weight divided by the ionic ion charge of that particular compound. So, for calcium like here the atomic weight is 40, ion charges is 2, thus this milligram per milli equivalent is 20. And if you want to change the concentration from milligram per liter to milligram per milli equivalent value of this, then we should divide by 20.

So, the value which was given for calcium is 93.8. So, we divide by 20 and this is the value 4.69 milli equivalent per liter for calcium.

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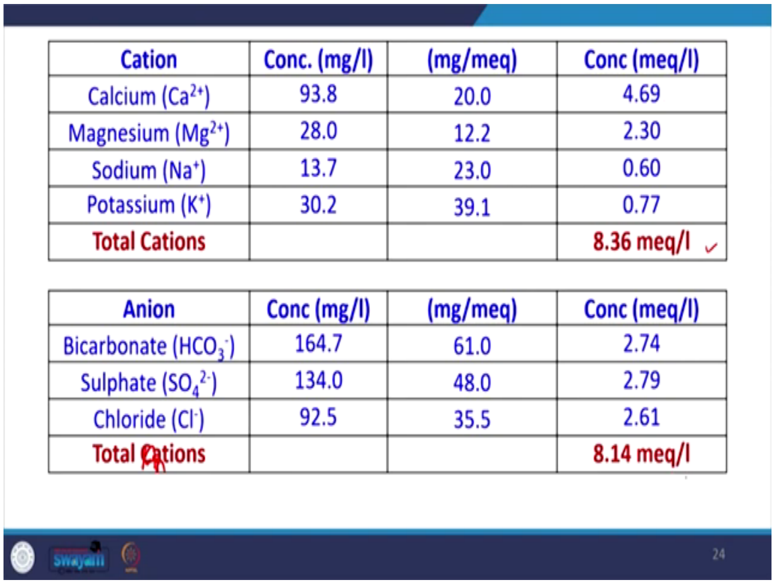

Cation	Conc. (mg/l)	(mg/meq)	Conc (meq/l)
Calcium (Ca^{2+})	93.8	20.0	4.69
Magnesium (Mg^{2+})	28.0	12.2	2.30
Sodium (Na^{+})	13.7	23.0	0.60
Potassium (K^{+})	30.2	39.1	0.77
Total Cations			8.36 meq/l

Anion	Conc (mg/l)	(mg/meq)	Conc (meq/l)
Bicarbonate (HCO_3^-)	164.7	61.0	2.74
Sulphate (SO_4^{2-})	134.0	48.0	2.79
Chloride (Cl^-)	92.5	35.5	2.61
Total Cations			8.14 meq/l

So, here we can see for calcium 93.8. And it is a milli equivalent value is 20. So, its concentration in milli equivalent per liter is 4.69. Similarly, we can determine for magnesium, sodium, potassium and then the total value for a total cation concentration in terms of milli equivalent per liter is 8.36 milli equivalent per liter. Similarly, we can determine the value for total sorry, this is total anions. So, for total anions also we can find out 8.14.

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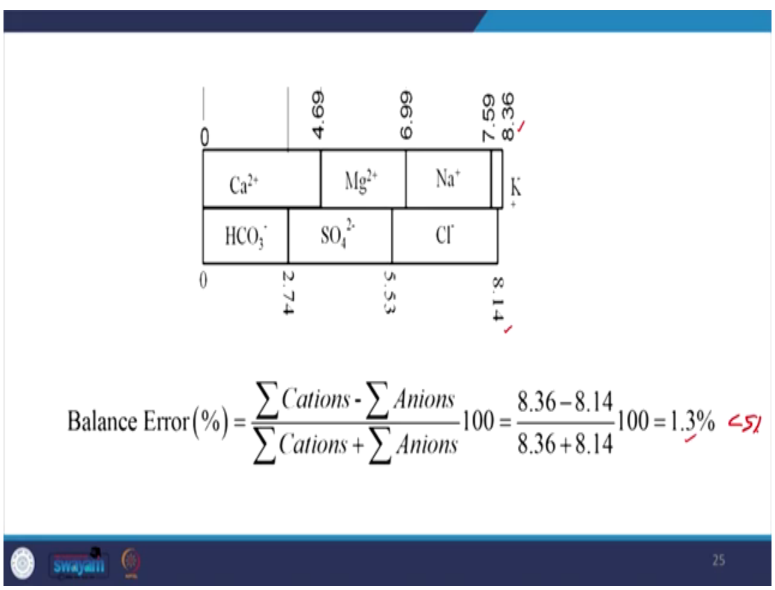

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Total Cations			**8.14 meq/l**

Now, what we do is that? We can draw a figure like this. So, you can see in the previous 4.69 2.30, to 4.69, this is calcium, then for 2.30 has been added to 6.99. So, this way we can find out, so 8.36 is total cations, 8.14 is total anions and we find out the value.

So, it is 1.3 percent less than 5 percent. So, that means the this analysis is correct. And we can believe this analysis. So, through this we can find out whether the reports are correct or not. And this is the way we report these values. And now today we will end this class and we will continue with the chemical parameters in the next class. So thank you very much.