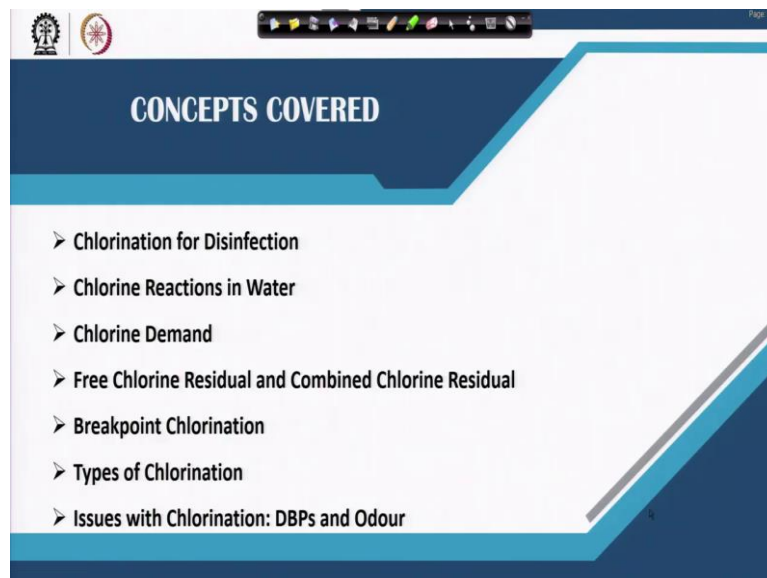


Water Supply Engineering
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Lecture-36
Chlorination

Welcome back friends, so continuing from the previous lecture we will discuss the chlorination process in this particular class. In the previous class we talked about the basics of disinfection why disinfection is needed and what are the different alternatives for disinfection and as we discussed its the chlorination which is by far the most popular disinfection method particularly for the centralized water treatment facilities. So, we will discuss the details about the chlorination in this particular class.

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So, what we are going to cover is the basics of chlorine reaction in water. We will talk about what is chlorine demand and then free chlorine residuals and combined chlorine residuals which are important for chlorination prospective. We will talk about break point chlorination and the different other types of chlorination as well. And we will discuss the issues with chlorination specifically the disinfection by-products or DBP's.

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Chlorination for Disinfection

- The most common disinfection method involves addition of some form of chlorine or its compounds such as chloramine or chlorine dioxide.
- Chlorine is a strong oxidant that rapidly kills many harmful micro-organisms, through:
 - ☛ Oxidation of membrane-bound enzymes for transport and oxidative phosphorylation
 - ☛ Oxidation of cytoplasmic enzymes
 - ☛ Oxidation of cytoplasmic amino acids to nitrites and aldehydes
 - ☛ Oxidation of nucleotide bases
 - ☛ Chlorine substitution onto amino acids
 - ☛ DNA mutations and lesions

Chlorine, when added to water, reacts with reduced state compounds present in the water, and further reacts with the water itself. The chlorine reacts to water or nitrogenous compounds present in water produces chlorine residual, which are able to kill microorganisms in the water.

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So, chlorination by far is the most common disinfection method as just we were discussing. It involves the addition of chlorine or any of its compound not any in fact the select group of compounds so we can use either chlorine or chloramines or chlorine dioxide. The chlorine is used as a disinfectant because it is very strong oxidant and it rapidly kills many harmful microorganisms. It can kill these microorganisms through the oxidation of the membrane-bound enzymes.

So, it can like work on the making the oxidative phosphorylation of the membrane-bound enzymes it can also lead to the oxidation of the cytoplasmic enzymes. It can lead to the oxidation of cytoplasmic amino acids this can actually leads to oxidation of the nucleotide bases as well. It can substitute the amino acid and it can cause the DNA mutation and lesions as well. So, when chlorine is added in the water it reacts with the reduced state of compound which are already present in the water first and then it reacts with the water.

So, it is going to react with like it is being a strong oxidant it can it will oxidize whatever the compounds are in the reduced state or whatever compounds which may get oxidized by reacting with the chlorine. So, whenever we add chlorine some part of chlorine in fact first starts these oxidation reaction and then chlorine will consume in these reactions. If there are more chlorine present in the system then it will react with the water itself and then other kind that kind of nitrogenous compounds present in the water.

And as a result it will produce chlorine residuals which are able to kill microorganisms in the water. So, that is what typically chlorine does in the water.

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Chlorine Reactions in Water: Chlorine Demand

- When chlorine enters water, it starts reacting with organic compounds and other reducing agents such as hydrogen sulfide, ferrous ions, manganese ions, nitrite ions etc.
- The chlorine added usually first react with all such compounds (if present) in the water, before forming any chlorine residuals.
- The amount of chlorine that is required (or consumed) for these reactions is termed the 'Chlorine Demand.' This can also be considered as the amount of chlorine needed before any free chlorine can be produced.
- Sufficient quantity of chlorine must be added for disinfection, so that, after the chlorine demand is met, there is adequate chlorine left to produce chlorine residuals in the water.
- Examples of these reactions:
 - $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$
 - $\text{FeCl}_2 + \text{Cl}_2 \rightarrow 2 \text{FeCl}_3$
 - $\text{H}_2\text{S} + 4\text{Cl}_2 + 4 \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 8 \text{HCl}$
 - $\text{CH}_2 = \text{CH}_2 + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl} - \text{CH}_2\text{Cl}$
 - $\text{Cl}_2 + 2 \text{KBr} \rightarrow 2 \text{KCl} + \text{Br}_2$

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If we see the reactions of chlorine in the water so when chlorine enters in the water the first it starts reacting with the reduced state compounds. So, it particularly reacts with the with the organic compounds it will react with the other reducing agents such as hydrogen sulphide if there are ferrous ion present manganese ions present nitrite and present. So, it will basically react with these and convert these to the higher oxidation state compounds.

So in this process actually some chlorine will get consumed and these reactions will take place before formation of any chlorine residual. So, if we add just this much of chlorine which is consumed in these reactions the example of these reactions could be like if it is there say FeCl_2 is there chlorine will react it will form twice FeCl_3 it will react with H_2S it can react with methane it can react with $\text{CH}_2\text{-CH}_2$.

It can react with the KBr so with these all these agents it can react and as a result whatever chlorine is being added may get actually consumed in the process. So, as when the chlorine is getting consumed it is not actually reacting with the water so that any sort of chlorine residuals are not being formed which can lead to the disinfection of the water and as a result unless the chlorine is reacting with all these presents of constituents if they are present in the water.

If there is no such constraint present in the water it is good whatever chlorine we are adding is going to form the chlorine residual but if these reducing agents are present in the water so first thing chlorine will do it will react with these. And once these reactions are complete then

only it starts reacting with the water to form the chlorine residuals. So, the amount of chlorine needed for these reactions if they are present in the water let us say some water is having X amount of iron and Y amount of manganese and say Z amount of H₂S.

So correspondingly there will be a requirement of chlorine to react these agents and whatever chlorine we add if it is within that requirement it will all get consumed in reacting to these agents only and there would not be any formation of the chlorine residual. So, the first thing we should ensure that the amount of chlorine that we are going to add for disinfection purpose is adequate enough to meet all these requirements of the chlorine which is typically known as the chlorine demand.

So, whatever chlorine we are actually we are adding and if it is getting consumed in these reactions so that chlorine is known as chlorine demand. Chlorine demand is a term is basically specified for water, so chlorine demand of water is a term is that this much amount of chlorine is demanded from water for the for its oxidation reactions. So, whatever up till that much amount of chlorine if it is added in water it will all get because water already has a demand of that much chlorine for it.

So this can be considered as the amount of chlorine needed before any free chlorine can be produced and we must ensure that like sufficient quantity is added for disinfection purpose so that after the chlorine demand is met means after all these reactions are over adequate amount of chlorine is left in the water to act as a disinfectant. So, that is what is like that is very important and one must ensure that adequate amount of chlorine is being added.

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Chlorine Reactions in Water: Free Chlorine Residual

- Usually, after satisfying the "Chlorine Demand" of water, chlorine reacts with water to form HOCl (hypochlorous acid) and OCl⁻ (hypochlorite ions) in water. These are known as "Free Chlorine Residuals" and have good disinfection abilities due to their strong oxidizing potential.
- Chlorine may be added in the form of chlorine gas, hypochlorite, or chlorine dioxide.
- Chlorine gas is the most pure form of chlorine, but is difficult to handle in gaseous form as it is toxic, heavy, corrosive, and an irritant. Usually, it is compressed into a liquid and stored in metal cylinders.

$$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} \qquad \text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^- \quad (\text{pH dependent})$$

- The interconversion of hypochlorous acid and hypochlorite ions are pH dependent, as HOCl dominates at lower pH (<7.5), while OCl⁻ dominates at higher pH (>7.4).
- Between the two, hypochlorous acid has much higher disinfection abilities than hypochlorite ions. Therefore, disinfection with chlorine is more efficient at a low pH than at a high pH.

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Now once the chlorine demand is met then water reacts with the **the** chlorine reacts with the water itself and it forms the HOCl which is known as the hypochlorous acid. So, chlorine will react with the water it will form HOCl and this HOCl can further great broken into H ion and OCL ion, OCL ion is basically the hyper chloride ions and this reaction is the pH dependent. So, means this HOCL can get inter-converted now both this hypochlorous acid and hypochlorite ions are substances which are which are basically having the strong oxidative properties and act as a disinfectant.

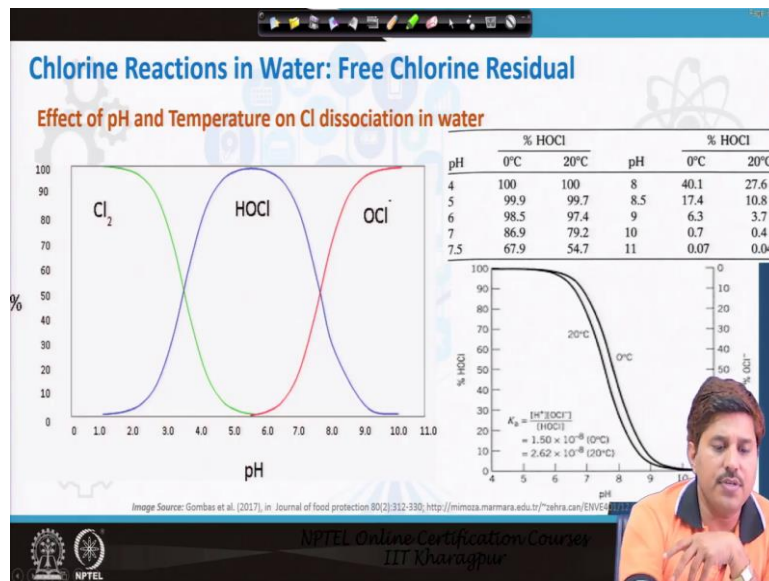
So both of these are known as basically constituents of free chlorine residual because chlorine we call this free chlorine because chlorine is just present in more or less it is free from it is just associated with the hydrogen and oxygen so we call that free chlorine. Its pH dependent system HOCl will dominate at lower pH is specifically less than 7.5 while the hypochlorous hypochlorite ions will dominate at higher pH.

Now between these two it is the hypochlorous acid which has higher disinfection abilities. So, since hypochlorous s it has higher disinfection ability we would like to have more of hypochlorous acid in the water as opposed to hypochlorite ions and that is why disinfection of with chlorine is more effective at low pH than at high pH because at low pH hypochlorous acid will prevail over hypo chloride ions and that will lead to kind of bitter disinfection abilities in the system.

Chlorine may be added in the form of chlorine gas or it can be added as a hypochlorite sodium or calcium hypochlorite or it can be added in the form of chlorine dioxide. Now we

just discussed that when we add in the form of chlorine gas so these reactions will take place and as a result free chlorine residual will form.

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So, if we see the free chlorine residual as just we are saying that it is a pH dependent process. So, at pH around like less than 7.5 or so you see that HOCl is prevailing hypochlorous acid is prevailing whereas when we go towards higher pH it's the hypochlorite ion that prevails and at very low pH like if pH is say less than 3 or say less than 3.5 so we will see that chlorine gas itself will prevail in the water.

If you see the percentage of HOCl which is the considered as more effective disinfectant at varying pH and temperature so at 0 degree Celsius and 20 degree Celsius so at around pH 4 it is like majority is in the form of hypochlorous acid and at pH around 7.5 it is 67% with temperatures at a higher temperature it is around 54.7% and as you see that pH changes to 8 and 8.5 the percentage gets lower and lower and the temperature effect also you can see.

So eventually like at higher temperature the HOCl fraction is lesser as opposed to the OCl fraction.

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Chlorine Reactions in Water: Hypochlorites

- **Hypochlorites (also known as bleach)** are less pure than chlorine gas, thus, are also less dangerous. Further, they decompose in strength over time while in storage. Typically, these are of three types - sodium hypochlorite, calcium hypochlorite, and commercial bleach:
 - **Sodium hypochlorite (NaOCl):** Usually comes in solution form, containing up to 12% chlorine.
 - **Calcium hypochlorite (Ca(OCl)₂):** Comes in both, liquid and solid (powder/granules) forms, and contains around 65-70 % chlorine. This is also known as "HTH" (High Test Hypochlorite).
 - **Commercial Bleach:** Commonly available in grocery stores in both liquid and powder forms with chlorine concentration ranging from under 10 % to over 40 %, depending on the brand.
- Disinfection through hypochlorites occurs similar to that with chlorine. However, the differences lie in quantities to be used (due to different chlorine concentrations), and feeding, storage and handling procedures.

$\text{Ca(OCl)}_2 + 2 \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{Ca(OH)}_2$
 $\text{NaOCl} + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NaOH}$
 $\text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^-$

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Now as just you are discussing that chlorine may be added in the form of hypochlorite so as well. Hypochlorite as the compounds which are typically known as bleach they are less pure than chlorine gas and are also kind of that is why less dangerous as well because chlorine handling chlorine particularly in the powdered form is quite challenge and can be dangerous as well. So, the hypochlorite have advantage in that term because they are like less dangerous to handle.

Because simply because they are less pure than chlorine gas but of course then you need more amount to air in order to ensure that adequate amount of chlorine is coming into the system. Further these decompose in strength over the time in storage but and typically there are 3 types of hypochlorite that are there we have sodium hypochlorite calcium hypochlorite and then the commercial bleaches.

So hypochlorite as just we are saying it is known as simply bleach. So, sodium hypochlorite is usually comes in the solution form and it contains roughly 12% chlorine the calcium hypochlorite comes in both liquid as well as solid powder or granule forms and it contains chlorine somewhere in the range of 65 to 70% roughly around 66% this is also known as the high test hypochlorite which is HTH commonly known and it is like it is one of the one of the compounds which is most popularly used for swimming pools particularly.

Then there are commercial bleach which is available in the market you can just go to any grocery store and buy it comes in both liquid and powder form. The chlorine concentration ranges from in fact less than 10% some bleaches you will get just 2 or 3%t chlorine content to

over 40% in some manufacturers produced bleaches with very high chlorine concentrations. So, it depends on brand which brand we are selecting and then the chlorine concentration in commercial bleaches can vary.

Disinfection process is very similar to that of chlorine the difference lies in the kind of quantities to be used because if you are using hypochlorite so of course because the chlorine concentration is low so more amount of chemical is to be used as opposed to just using the pure chlorine or chlorine gas form. Differences are there in the feeding storage and handling procedures as well.

Chlorine comes in the gaseous form so can be used as a gas or they can be used as a compressed liquid. So, many in fact most of the time it is used as a compressed liquid instead of just direct gas so it can be used as a compressed liquid or gaseous form so handling is that way whereas these hypo chlorides may come in the solid or liquid form. So, like how we are going to store how we are going to handle or what kind of feeding system we are going to have for them can be different.

The mechanism wise they are same so like if you see the calcium hypochlorite so that will also react with the water and produce HOCl sodium hypochlorite will also produce HOCl and then HOCl can convert it to the OCL and again based on the pH of the reaction so it is the same like the free chlorine residual either hypochlorite ions or hypochlorous acid will be used for the disinfection purpose.

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Chlorine Reactions in Water: Chloramines [Chloramination]

- Some plants use chloramines for disinfection of water. Chloramines are chlorine and nitrogen based chemical compounds *formed during a reaction between chlorine (Cl₂) and ammonia (NH₃)*. These are produced when ammonia (either already present or added) reacts with free chlorine (HOCl or OCl⁻, depending on the pH, *ideal pH is 8.4*) to produce *Monochloramine (NH₂Cl)*, which may then react with more hypochlorous acid to form a *Dichloramine (NHCl₂)*, and subsequently *Trichloramine (NCl₃)*.
$$\text{NH}_3(\text{aq}) + \text{HOCl} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \quad \text{NH}_2\text{Cl} + \text{HOCl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O} \quad \text{NHCl}_2 + \text{HOCl} \rightarrow \text{NCl}_3 + \text{H}_2\text{O}$$
- The extent of these reactions depends on the pH of the medium. Organic chloramines can also be formed during these reactions. Monochloramines and dichloramines can both be used as a disinfecting agent (called "*Combined Chlorine Residual*").
- Chloramines are weaker oxidant than free chlorine residuals, so *have lesser disinfection potential*. Among chloramines, monochloramine has the highest disinfection abilities. These are effective at killing majority of pathogenic bacteria and some protozoans, but are not very effective at killing viruses.
- However, chloramines are *relatively more stable*, so many times preferred as the disinfectant in the distribution lines of water treatment systems.

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Many times like some plants prefer to use chloramines for disinfection of water which is again another form of chlorine. So then the disinfection or instead of chlorination they call it chloramine nation because chloramines are added chloramines are just compounds which contains chlorine and nitrogen. So, they are formed by the reaction between the chlorine and ammonia. Now ammonia may already be present in the water if ammonia is already present in the water.

And we add chlorine so chloramines are going to form if ammonia is not present in the water and we want the disinfection through the chloramines then we may add ammonia also. So, if it is present it will automatically form if it is not present we may add so that it reacts with the free chlorine generally chloramine are forms with a free chlorine reaction with the ammonia so even if like we intend to form chloramine in a water which is not having ammonia.

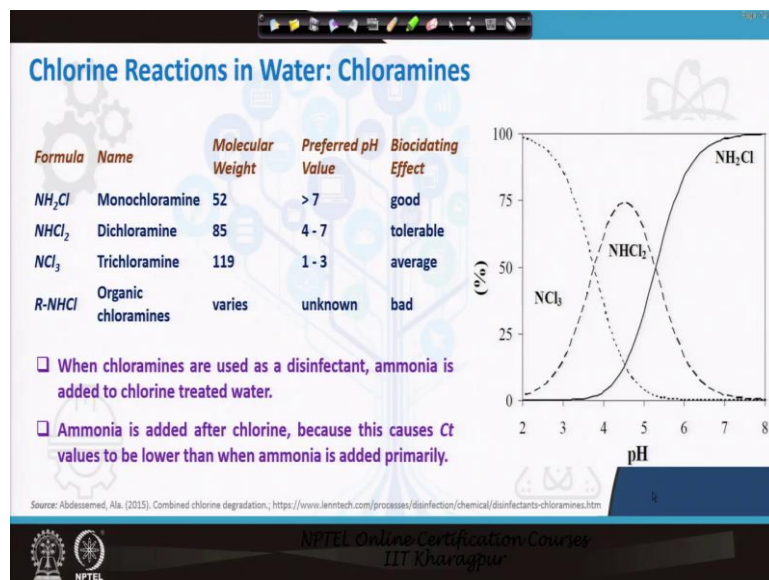
So, we first add chlorine to the water so that free chlorine residuals are present and then we add ammonia so that ammonia can react to these free chlorine residuals and form chloramines. So, it is simple like ammonia will react with the HOCl it will form mono chloramine first NH_2Cl which is known as mono chloramine then this further can react to the again hypochlorous acid to form the dye chloramines.

And similarly dye chloramine can also react to hypochlorous acid to form the tri chloramines. There are organic chloramines can also be formed as a result of these reactions. Now of these tri chloramine almost have no disinfection abilities but the mono chloramine and di chloramine can both be used as a disinfecting agent and these two are called combined chlorine residuals. Now of these two also the monochloramine is having more strength more disinfection potential as opposed to the dry chloramines.

So like mono chloramine will be preferred form between these two although overall the chloramines either mono chloramine or di chloramine are relatively weaker oxidant then free chlorine residual so have lesser disinfection potential. So, overall chloramine have lesser disinfection potential but within the chloramine it is the mono chloramine which has more disinfection potential as opposed to the dry chloramine that is like one of the demerits side.

But on the positive side the chloramines are more stable than the free chlorine residuals. So, many plants prefer the use of like chloramines for putting the disinfectant like putting the residual chlorine in the water in order to ensure the few of our safety. So, that because of their stable nature so because they can last longer times in the water, so they are preferred for using as a disinfectant.

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If you see that like the bio sighting effect or disinfection abilities so monochloramine typically prevails at pH greater than 7 again these are also pH dependent processes. So, at pH greater than 7 most of this will be in the form of monochloramines at pH lesser than this it will be in di chloramine and for lower ph it will prevail in the tri chloramines. The disinfection abilities of tri chloramine is very average and of organic chloramines is bad almost no disinfection is achieved through these.

Whereas of monochloramines is reasonably good and tri chloramines it is still tolerable. So, when chloramines are used as a disinfectant ammonia is added to the chlorine treated water and then we need to ensure like because ammonia is added after chlorine. So, because of these Ct values can be lower then when ammonia is added like primarily. So, these are the like another form of chlorine which can be used for disinfection purpose.

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Chlorine Reactions in Water: Chlorine dioxide

- High solubility in water – 5 times of free chlorine
- High oxidative potentials – 2.63 times of free chlorine (only 20% at neutral pH)
- Effective at a higher pH than other forms of chlorination.

Chlorine dioxide is the most effective form of chlorination since it will kill protozoans, *Cryptosporidium*, *Giardia*, and viruses that other systems may not kill. In addition, chlorine dioxide oxidizes all metals and organic matter, converting the organic matter to carbon dioxide and water. Chlorine dioxide can be used to remove sulfide compounds and phenolic tastes and odors. Contrary to chlorine, chlorine dioxide does not react with ammonia nitrogen (NH_3).

So why isn't chlorine dioxide used in all systems?

- Chlorine dioxide must be generated on site, which is a very costly process requiring a great deal of technical expertise.
- Unlike chlorine gas, chlorine dioxide is highly combustible and care must be taken when handling the chlorine dioxide.

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One more form of chlorine is chlorine dioxide which can also be used for disinfection purpose in fact chlorine dioxide is the most effective form of chlorination if we are using chlorine as a disinfecting agent so this is the most effective form but is still very rarely used. Why it is most effective because it has very high solubility in water almost 5 times of the free chlorine. The oxidative potential is high so almost around 2.63 times of the free chlorine and it is effective at higher pH than the other forms of chlorination.

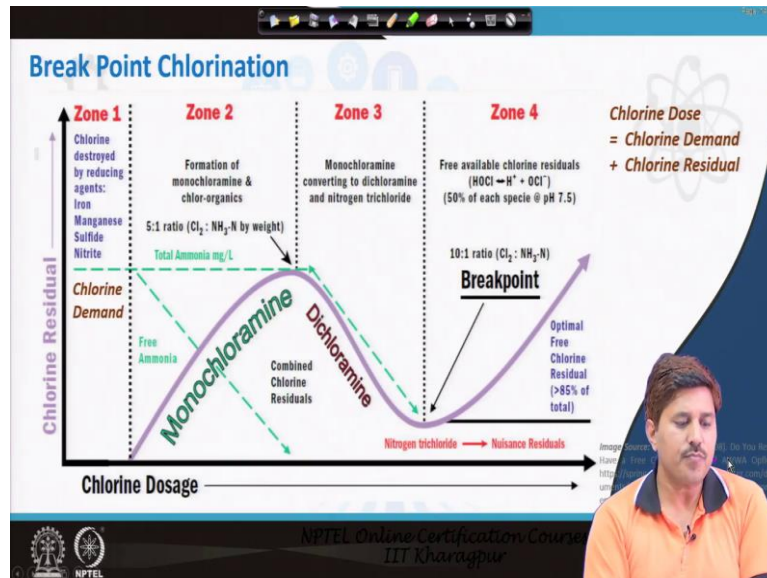
As we discussed that the hypochlorous acid which is most effective in the free chlorine residual forms is more like is preferred at lower pH but the chlorine dioxide can be used as high pH as well. It is because it is high oxidation potential it can basically kill the protozoa *Cryptosporidium* *Giardia* and viruses that other system may not kill other form of chlorination may not kill in addition it can oxidize the metal and organic matters it can convert the organic matter to carbon dioxide and water kind of mineralized that.

It can use to remove the sulphide compounds and phenolic taste and order as well. And contrary to the chlorine, chlorine dioxide does not react with ammonia nitrogen so that the it will actually be mostly through the like major form of the chlorine and it is not going to react with the ammonia to form the monochloramine, di chloramine kind of substances. But it still as we said that it is not very popular it is not used like that popularly is because it must be generated on site which is a very costly process and requires a great deal of technical expertise.

It is a unstable substance chlorine dioxide because it is because of its very high oxidative potential because it can oxidize many things so it is highly reactive and that way it is unstable

as well. So, it has to be basically prepared on site which is basically a costly process. So, lot of technical expertise will also be needed and unlike chlorine gas this is highly combustible. So, are risky also so this comes with basically a risk factor as well.

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That way these are the different forms of chlorine, now what happens that when chlorine is added to the water so there are 4 distinct zones in which the reactions takes place. In the first zone chlorine will destroy the reducing agent iron magnesium pounds and whatever chlorine consumed in that process will not lead any residual chlorine. So, here x-axis is the chlorine doses and y-axis is the chlorine residual.

So, if you see you keep on adding chlorine till this much but there is no residual appearing residue and only starts appearing beyond this point that is because up till this point whatever chlorine is added gets consumed in reacting with these and fulfilling the chlorine demand. So, this is essentially the chlorine demand component of the water. So, until the chlorine demand is met we will not see chlorine residual appearing in the water.

Now after that the chlorine residual starts building and chlorine there will be basically formation of mono chloramines and like chloro organics. So, you will see that formation of mono chloramine take place and as a result the chlorine residual build-up starts and there will be a time coming when all the like all monocular amines are formed and then after that point mono chloramine will start converting to di chloramine and tri chloramine.

And because di chloramine and tri chloramine di chloramine still has disinfection abilities but tri chloramine almost negligible. So, you will see that the residual starts decreasing this infection abilities start decreasing and as well we will see that the residual chlorine takes a like negative slope from in zone 3. Now water will come to a point where all the reactions either with nitrogen or with other reducing agent is complete.

So, whatever chlorine we have added with whatever either it is to be reacting with other agents to fulfilling the chlorine demand or to react with the ammonia compounds for formation of mono chloramines, further react with these monoclonal mines or di chloramines to form the di chloramines or tri chloramines. So, whatever reaction has to happen is over in zone 3 and in zone 4 we do not like chlorine will not react with any other thing except water generally.

So whatever chlorine we add beyond this point is just going to appear as free chlorine residual because it will react with the water and form HOCl and OCL ions. So, it will be either depending on the pH it will be either in the form of hypochlorous acid or hypo chloride ions but there is no any other reaction of chlorine beyond this point and that is why this point is known as break point because by this point all the compounds which chlorine can react with it has already reacted.

So it has achieved to this break point beyond which the break point is are basically point beyond which whatever chlorine is added will appear as a free chlorine residual. So, that is what is known as the break point. And this curve is known as the break point chlorination curve and this kind of guides that what happens when chlorine is added in the water. If we add chlorine say in a pure water which is not having any of these compounds so then we will see that chlorine residual start appearing right away.

There is no demand so it will start from here only if this is dose and this is residual chlorine so the build up will start from right here and it will be almost a straight line. So, because whatever chlorine is added will start appears as residual chlorine. And for a system we considered that chlorine dose whatever chlorine dose we are adding is equal to the chlorine demand and chlorine residual. So, either it will meet chlorine demand means it will undergo reactions where chlorine is consumed or it will appear as a residual form of chlorine.

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Residual Chlorine

- Although, the evidences of microbes regrowth in treated water is inconclusive, residual chlorine in water aims at protection against any regrowth or recontamination, by preventing microbes growth in the treated water, specifically when the water is biologically unstable.
- Water temperatures and nutrient concentrations are not generally elevated enough within the distribution system to support the growth of *E. coli* (or enteric pathogenic bacteria) in biofilms. Thus, the presence of *E. coli* should be considered as evidence of recent faecal contamination.
- Viruses and the resting stages of parasites (cysts, oocysts, ova) are also unable to multiply in treated water.
- However, biofilms and coatings of organic and inorganic materials in pipes that harbour, and allow the proliferation of few bacterial pathogens, including *Legionella* and *Mycobacterium avium complex* (MAC).
- Residual chlorine in water can also control non-pathogenic slime-forming organisms.

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So, residual chlorine is for ensuring that like the hypochlorite acid, hypochlorous acid or hypo chloride ions or combined chlorine residual is left in the water so that it can oxidize the microbes and it can ensure safety against them. And in chlorination process one of the distinct advantage of chlorination process is that because we are adding these chemicals which can retain in the system.

So, although like the different forms of chlorine has different stability but as just we were discussing like the combined chlorine residuals have better stability. So, if you are adding if you are leaving chlorine residuals in the water. So, any future growth or any future contamination, so, possibility of any regrowth or any re-contamination is also taken care of because there is all there is chlorine present still in the water when it is in the distribution system so even if in the distribution system say some contaminant exposure comes in or some growth possibly takes place.

So, chlorine residuals are there to take care of that and to disinfect that so those pathogens can be controlled and that is why it is in short to leave certain residual chlorine in the treated water. So, the disinfection generally is that way known as two types there is a primary disinfection where the purpose is that we disinfect the water and the secondary it is in fact secondary disinfection where we leave the residual chlorine for any for countering any regrowth or recontamination of the water.

Regrowth actually is again not very well established there are contradicting literature available on that the water temperatures and nutrient conditions are generally like at a

condition within the distribution system. So, that they are not that high they are not that elevated that they will support the growth of E.coli or any sort of biofilms. So, if these compounds are appearing in the water after treatment it should be considered as a event of recent faecal contamination rather than the regrowth.

Because they cannot grow in the water in absence of the elevated levels of the nutrients and temperatures, virus and like the resting stages of the parasites cysts etcetera are also unable to multiply in the treated water however there has been evidence that the biofilm and coating of organic and inorganic materials in the pipe can harbour allow the proliferation of few microbial pathogens which includes kind of Laguna and MAC.

So residual chlorine in water can also can control these this kind of growth opportunities and can also control the non-pathogenic compounds which may form a slime in the distribution line.

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Ct for Chlorination

As per US Safe Drinking Water Act (SDWA)

- 99.9% inactivation (3-log removal) for *Giardia* and 99.99% inactivation (4-log removal) of viruses is required.
- Giardia* is more difficult to kill with chlorine than viruses, and thus *Giardia* inactivation determines the Ct.

Ct equation for *Giardia*:

$$C_{Cl} \cdot t_{contact} = 0.2828 (pH^{2.69}) (C_{Cl}^{0.15}) (0.933^{(T-5)}) pC^*$$

$$pC^* = \frac{t_{contact} \cdot C_{Cl}^{0.85}}{0.2828 (pH^{2.69}) (0.933^{(T-5)})}$$

log removal = \log_{10} (Influent Conc./Effluent Conc.)
 So, log removal of 1 is equivalent to 90% removal
 log removal of 2 is equivalent to 99% removal
 log removal of 3 is equivalent to 99.9% removal
 log removal of 4 is equivalent to 99.99% removal

- C_{Cl} = Free Cl_2 Residual [mg/L]
- $t_{contact}$ = Time required [min]
- pH = pH of water
- T = Temperature, degrees C
- pC^* = $-\log$ [fraction remaining]

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As we discussed earlier class that it is basically the concentration and time of exposure which governs the disinfection abilities of certain chemical disinfectant particularly. So, for chlorination purpose and 99.9% activation; which is basically 3 logs, removal because generally the activation of the like inactivation of the microorganism is given in the Log form. So, we consider the log removal and log removal is locked in fluent concentration divided by the affluent concentration.

So that means like if 90% removal is there so in fluent concentration is say 100 and affluent concentration will be 10 that means 1 so log 10 scale it will like it will become 10 and then log 10 scale 10 is equal to 1 so we consider this as a log 1 removal which is 90% removal if it is 99% removal then the say fluent concentration is 100 in in fluent concentration is 100 affluent concentration is 1 which is equal to 100 and again log 10 base 100 is equal to 2. So, that is log 2 removal.

Similarly log 3 removal log removal of 3 means 99.9% removal log removal of 4 means 99.99% of removal. So, as per us drinking water act the 99.9% means 3 log removal for Gardea and 99.99% inactivation for log removal for viruses is needed in drinking water supplies and Ct is estimated for these then there are the Ct equation for Gardea which is used at given temperature and pressures.

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Bacteria	Cl ₂ Concentration (mg/l)	Time (min)	Ct Factor (mg-min/l)	Reduction(%)	Reference
<i>Campylobacter jejuni</i>	0.1	5	0.5	99.99	Blaser et al, 1986
<i>Escherichia coli</i>	0.2	3	5	99.99	Ram and Malley, 1984
<i>Legionella pneumophila</i>	0.25	60-90	18.75	99	Kuchta et al, 1985
<i>Mycobacterium chelonae</i>	0.7	60	42	99.95	Carson et al, 1978
<i>Mycobacterium fortuitum</i>	1.0	30	30	99.4	Pelletier and DuMoulin, 1987
<i>Mycobacterium intracellulare</i>	0.15	60	9	70	Pelletier and DuMoulin, 1987
<i>Pasteurella tularensis</i>	0.5-1.0	5	3.75	99.6-100	Baumann and Ludwig, 1962
<i>Salmonella typhi</i>	0.5	6	3	99	Korol et al, 1995
<i>Shigella dysenteriae</i>	0.05	10	0.5	99.6-100	Baumann and Ludwig, 1962
<i>Staphylococcus aureus</i>	0.8	0.5	0.4	100	Bolton et al, 1988
<i>Vibrio cholerae</i> (smooth strain)	1.0	<1	<1	100	Rice et al, 1993
<i>Vibrio cholerae</i> (rugose strain)	2.0	30	60	99.999	Rice et al, 1993
<i>Yersinia enterocolitica</i>	1.0	30	30	92	Paz et al, 1993

This is the effect of chlorination on the bacteria so we can see that like the Ct factor ranges from very low around 0.5 to high at around 60 also so that much of Ct would be required. So, for higher Ct we need to ensure higher contact time or higher concentration. So, this is about the bacteria which is still for virus and protozoa with chlorine we the Ct factors that are available in the literature.

So like for viruses Ct factor is in this particular range whereas protozoa particularly if you see for Cryptosporidium it is very high CT value 72000 for Giardia also it is very high CT value for a good range of inactivation. So, that is how the like Ct values are estimated.

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Chlorination Risks: Disinfection By-products (DBPs)

- Chlorine in water also reacts with natural organic compounds to form potentially harmful chemical by-products typically referred as Disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs).

The diagram illustrates the chemical reaction where Organic Matter (represented by a blue circle) reacts with Chlorine Based Disinfectants (represented by an orange circle) to produce Disinfection Byproducts (represented by a green circle). The reaction is shown as: Organic Matter + Chlorine Based Disinfectants = Disinfection Byproducts.

- DBPs are usually carcinogenic in large quantities and regulated by several regulatory agencies. Regulations regarding disinfection byproducts is complicated, as, thorough, water disinfection is critical to preventing waterborne illness, but disinfection practices also lead to the formation of disinfection byproducts.
- The formation of DBPs may be minimized by effective removal of as many organics from the water as possible prior to chlorine addition.
- Chlorine dioxide and Chloramines usually produce lesser DBPs than Chlorine.

Image Source: <https://www.hydrox.com/blog/water-safety/disinfection-byproducts>

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One of the risk with chlorination is the disinfection by-products which is DBPs. So what happens when because chlorine is a strong oxidant and if some organic matter or natural organic matter present in the system. So, chlorine will react with that and it will form the disinfection by products as the trihalomethanes or ths which is known as THM's or halo acetic acid. So, these are the carcinogenic they are they are basically they have severe health risk.

So DBP's are usually considered carcinogenic and may pose a health risk and that is why they are regulated by several regulatory agencies. However the regulation of the DBP's is complicated because we cannot avoid disinfection which is critical for preventing the waterborne illnesses. So, we should in order to ensure the protection from waterborne illnesses we have to provide disinfection but providing disinfection is also leading to risk of the formation of the disinfection by-products.

So we have to basically counterbalance one is producing DBP's which is going to have a long term impact kind of chronic impacts whereas waterborne controlling waterborne illnesses which are likely to have acute impact. So, that is why it is not that all the countries are regulating DBPS a few places it is being regulated but still like there are a lot of flexibility in those regulations as well.

The formation of DBP is may be minimized with the effective removal of the many organics from the water because it is formed by reacting with the organic compounds. So, if those organic compounds are removed prior hand. So, we can get rid of the DBP's also like few

forms of chlorine are like the HOCl OCl ions produced lot of DBP's whereas chlorine dioxide and chloramine relatively produce lesser DBP's than the form of chlorine.

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Chlorination Risks: Disinfection By-products (DBPs)

Common trihalomethanes (THMs)

Chemical structures shown:

- Chloroform: ClC(Cl)(Cl)Cl
- Bromodichloromethane: ClC(Cl)Br
- Dibromochloromethane: ClC(Br)Br
- Bromoform: BrC(Br)Br

Common haloacetic acids (HAAs)

Chemical structures shown:

- Chloroacetic Acid: ClCC(=O)O
- Dichloroacetic Acid: ClC(Cl)C(=O)O
- Trichloroacetic Acid: ClC(Cl)(Cl)C(=O)O
- Bromoacetic Acid: BrCC(=O)O
- Dibromoacetic Acid: BrC(Br)C(=O)O

Image Source: <https://www.hydrivity.com/blog/water-smarts/disinfection-byproducts>

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So, these are the common trihalomethane's like chloroform and these are some of the compounds of bromoform chloroform these things. And these are some of the common haloacetic acids which are the known DBP is present in the disinfection.

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Chlorination Risks: Taste Issues

➤ Chlorine compounds present in water may induce some specific taste in the water.

Compounds	Order of the taste threshold (mg/L)
HOCl and OCl ⁻	~ 0.5
NH ₂ Cl	~ 0.8
NHCl ₂ and Chloroform	~ 0.1
Carbon tetrachloride	~ 0.3
Dichlorophenol and Dichlorobenzene	~ 0.0005

➤ Residual chlorine species add to some taste in water, which may prevent some consumers from using treated water. Specially, introduction of chlorine into a community that has always drunk water without the addition of chemicals can be difficult.

➤ Need to convince consumers that the chemical taste is healthy. With less chlorine, the less breakthrough of chlorinated compounds into the finished water, and therefore less chemical taste. Reducing the amount of chlorine added might increase the social acceptance of chlorination.

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The other issue might be the test issue with the chlorination. So, chlorine compound may present in water if they are present in the water main do some specific tests in the water at times. I am sure many of you if have felt if you are getting the chlorinated supplies in your homes. So, some time you will see that some specific taste of chlorine appears particularly if

bleaching powder is being loaded in the form of chlorine and it is not well mixed or the levels becomes a little higher. So, then this kind of taste issues might appear.

Residual chlorine species is add some tests and this may prevent the consumers from using this thing using treated water. So, many times we need to convince the consumer that this test is not bad it is for in during the pathogen-free water supplied to your households and chlorine in this particular range or of the concentrations are not that toxic. We can start with the less chlorine as well then break through and then progressively increase it so that the consumers get acquainted with this. So these are some of the issues with the test.

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Types of Chlorination

Plain chlorination

- Only chlorination for raw water contains turbidity <10 NTU
- The dosage of chlorine for plain chlorination is about 0.5 mg/L.

Pre-chlorination

- May be applied to the water before coagulation for heavily contaminated waters.
- The chlorine dose for pre-chlorination should be 0.1 to 0.5 mg/L.
- Always followed by post chlorination to ensure final safety of water.
- It has become much less common in the western countries due to risks of DBPs.

Post chlorination

- Normal process of applying chlorine in the end.
- Intended to leave a residual-chlorine of about 0.1-0.2 mg/L after 20-30 min contact

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There are different types of chlorination, plain chlorination is when only chlorination of raw water is being provided that contains stability less than 10 into you know other treatment is given. So, we can use chlorine doses at around 0.5 milligram per liter. Then there are pre chlorination when water is heavily contaminated then chlorine may be add as an oxidant so the idea there is not disinfectant in fact.

But chlorine may be added as an oxidant in the range of 0.1 to 0.5 milligram per liter however after that chlorine will be treated in safe filter and other places where the microbial or pathogenic exposure might be there. So, pre chlorination must always be followed off with the post chlorination to ensure the final safety for disinfection purpose. It is still pre coordination is becoming less common in western countries due to risk of DBP is because initially there are more organic contaminants.

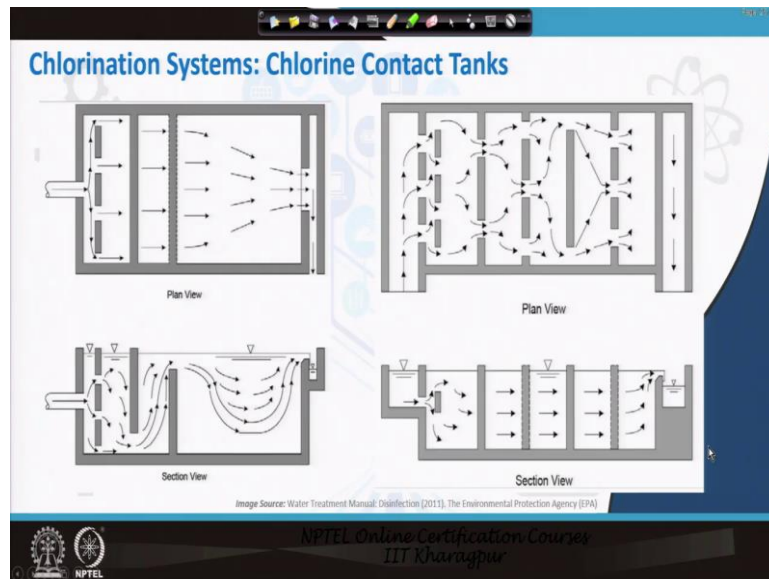
And if we are adding chlorine right there, so there is a high chances of formation of BDP's which might not get removed through filtration and other processes and they may still exist in the system. Whereas if we add chlorine after the filtration another thing so many of the like we presume that in fact substantial amount of such impurities are already taken care of are already removed from the water so the risk of the production of DBP's is also lesser with the post chlorination.

Post chlorination is normal process of applying chlorine in the end for disinfection purpose we generally apply a dose that after meeting the chlorine demand 0.1 to 0.2 milligram per liter residual chlorine still retains after 20 to 30 minute contact time in the water. Then there is a break point chlorination what we discussed that gives an idea of amount of chlorine to be added for like meeting all the chlorine reaction and producing the free chlorine residual.

So especially when one wants to leave the free chlorine residual in the water he has to ensure that breakpoint is achieved and adequate amount of chlorine is added after that in order to ensure the desired level of free chlorine residual. Then there is a super chlorination which is addition of the excessive chlorine 5 to 15 milligram to about 1 to 2 milligram per liter. This may be required in some specific cases when water is very highly polluted or if there is a epidemic of waterborne diseases happening.

Then we in order to like become extra sure super chlorination is done but when the chlorine levels are elevated in the super chlorination we must remove them through dechlorination after that which is like using the sulphur dioxide gas or activated carbon or other like sodium metal sulphate or ammonia kind of substances which one consume some of the free chlorine. So, that is known the process is known as dechlorination and it is usually employed after super chlorination to reduce the chlorine level back in the range of 0.2 milligram per liter.

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Lastly like the simple process could be the chlorine contact tank as well. So, if chlorine is added and then we I need to ensure some residence times if I 15 minutes 20 minutes or at time even lesser 5-10 minutes. So, in order to ensure the chlorine contact time simple buffered tanks can be used they can be designed in a several way like the couple of examples that are here. So, the idea is that it is distributed and well mixed in the system and if it is a plug flow kind of system it is even better.

So with this we conclude the lecture here we discussed about the chlorination which is one of the most popular ways of chlorination one of the most popular ways of disinfection. We will talk about few other disinfection approaches like applying ozone or applying UV light for disinfection purpose in the next class. So, thank you for joining and see you in the next class.