Water and Waste Water Treatment
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Lecture -30
Disinfection By-products (DBPs) and Disinfectant Removal

Hello everyone, welcome back to the latest session. In the last session we were looking at the different oxidizing agents that are used as disinfecting agents. And in that context we looked at HOCl and OCl^- and the relevant acid-base chemistry and equilibrium why because HOCl is a much stronger oxidizing agent compared to OCl^- and their ratio, it is like a balance. If the total OCl^- is this depending on the pH it is going to either tip this way more HOCl and less OCl^- or if I increase the pH it is going to tip this way.

So what we wanted to illustrate in the last session was that pH will play a role in deciding this equilibrium between the acid and its conjugate base and pKa the acid dissociation constant will come into picture.

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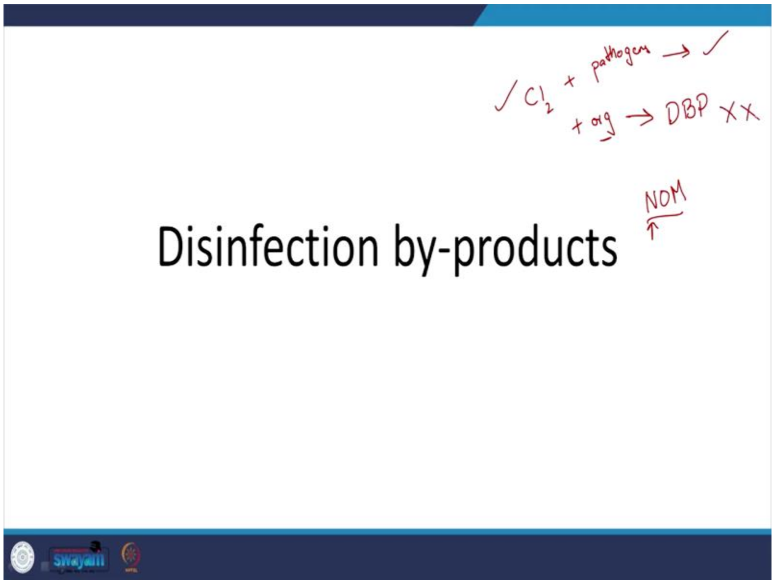

Disinfection by-products

✓ Cl_2 + pathogen → ✓

+ org → DBP XX

NOM

So let us move on and look at what else we were discussing. Then we started looking at disinfection byproducts for example I am adding my oxidizing agent Cl_2. As long as it reacts with my pathogens this is fine I want this to happen but it is not just pathogens that are present in the solution you will still have some organic matter. And this organic matter can be the organic matter left from my treatment activated sludge process after activated sludge process some of the microbes can come out which are not pathogens or some of the substrate can come out because you cannot really achieve 100% deficiency you Are always going to have body of 10, 20 or even 30 depending upon the type of process you are using.

So you always will have some organic content in water natural waters river waters you will have what is referred to as natural organic matter. Why do we say natural because the sources are from natural sources leaves, dead aquatic plants that is a dead aquatic life. So you when they die they are going to leach into the water and you are going to have natural organic matter. So but if chlorine or this oxidizing agent reacts with organic matter I will have what are called as disinfection byproducts this I do not want to form.

So the case is clear, I want to choose that oxidizing agent depending upon the its ability to effectively inactivate the pathogen at hand while not forming a lot of our relatively limited disinfection byproducts. So that is the key. Another aspect to limit formation of disinfection byproducts is to see to it that the organics concentration is less so that even if I add the chlorine then disinfection byproducts are not going to be formed, let us dig further.

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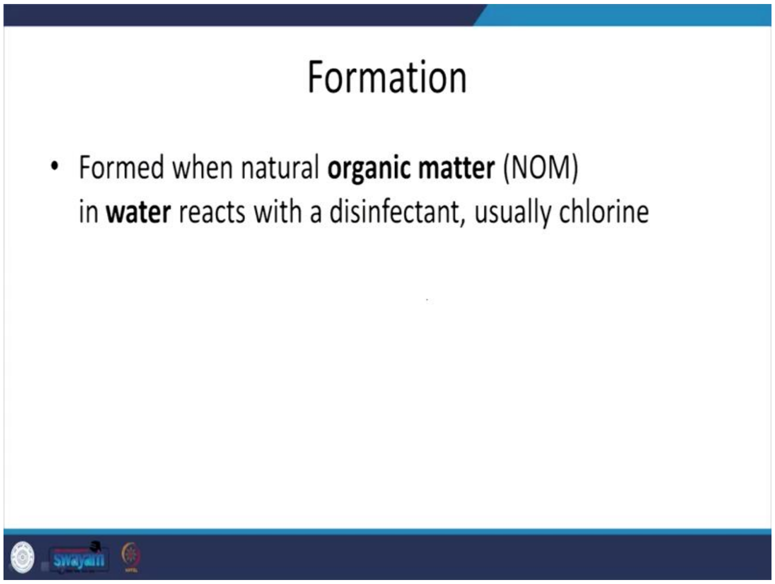

Formation

- Formed when natural **organic matter** (NOM) in **water** reacts with a disinfectant, usually chlorine

So formation we already looked at this the key aspects are we want an oxidizing agent which is usually chlorine and we need an electron donor this is an electron acceptor. And for the redox reaction here the electron donor is the organic matter , let us move on.

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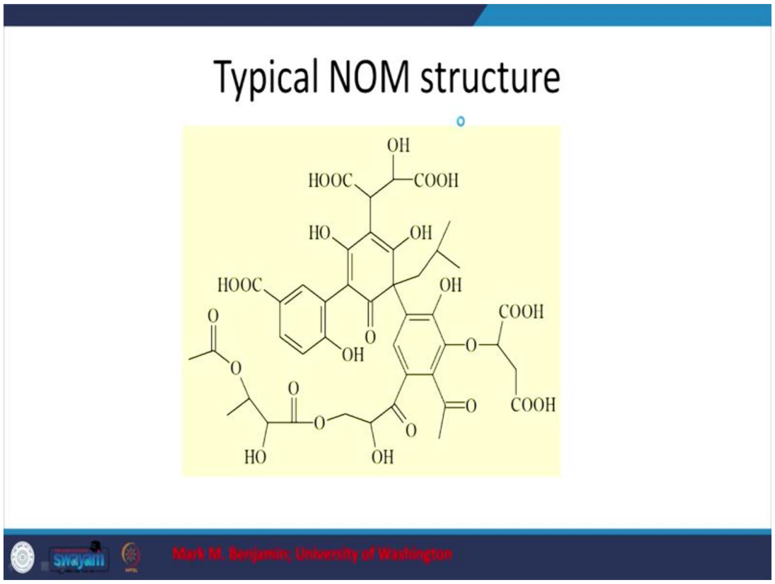

Typical NOM structure

Mark M. Benjamin, University of Washington

So typical natural organic matter structure as you can see it is not a simple compound and there is no one structure. You have it is pretty long chain you have a lot of aromaticity. So it is a complex molecule life. So you have humic acid fulvic acids so they are all part of this natural organic matter. So what we want to illustrate is that it is a pretty complex molecule . this is only a typical representation.

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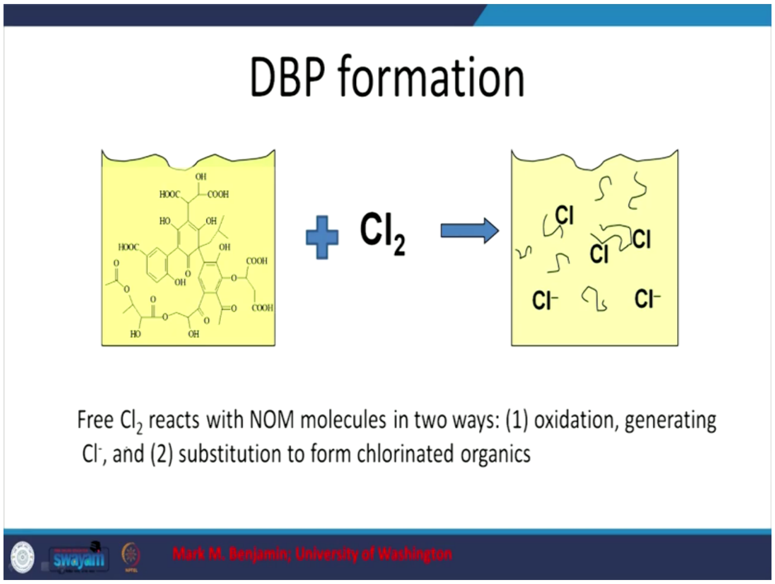

DBP formation

Free Cl_2 reacts with NOM molecules in two ways: (1) oxidation, generating Cl^-, and (2) substitution to form chlorinated organics

Mark M. Benjamin, University of Washington

So what happens when we add Cl_2 so when we add Cl_2 it can lead to oxidation and the byproduct of that case will be OCl^- that is fine or it can lead to substitution to form chlorinated organic which are called the disinfection by products . So this is fine it is not toxic to us at those levels but when we have substitution to form chlorinated organic that is when we are going to have issues.

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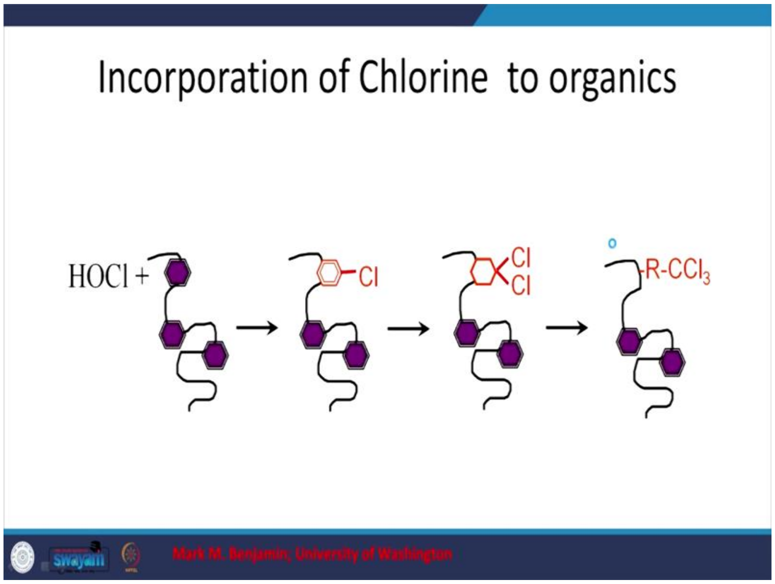

Incorporation of Chlorine to organics

So how will it work so I have HOCl or Cl_2 and I have these aromatic rings I am going to have substitution 1Cl, 2Cl or 3Cl .

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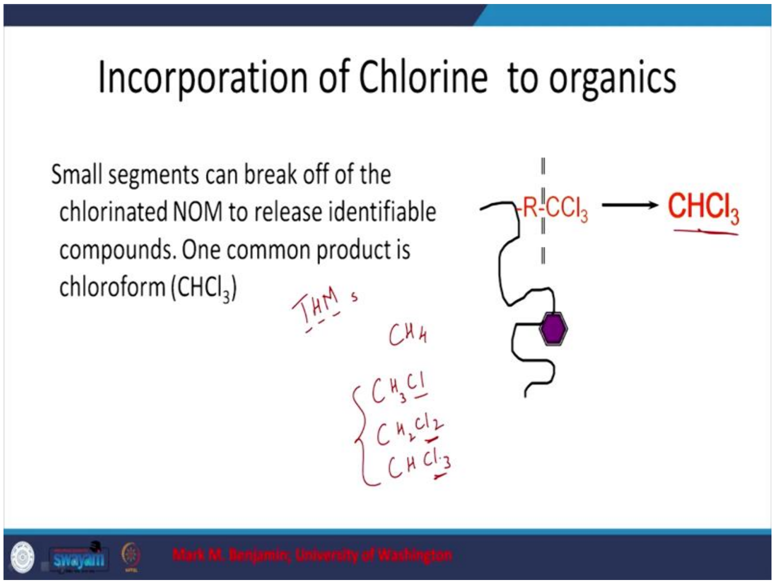

Incorporation of Chlorine to organics

Small segments can break off of the chlorinated NOM to release identifiable compounds. One common product is chloroform ($CHCl_3$)

THM s

CH_4

CH_3Cl

CH_2Cl_2

$CHCl_3$

And small segments can break off and one common product is $CHCl_3$ chloroform . So these kinds of disinfection by products are called trihalomethanes methane is ch4 so the different kinds of THM's are CH_3Cl; CH_2Cl_2; $CHCl_3$ so trihalo Cl is a halogen Cl^- is a halogen and you have trihalo methanes, so trihalomethanes.

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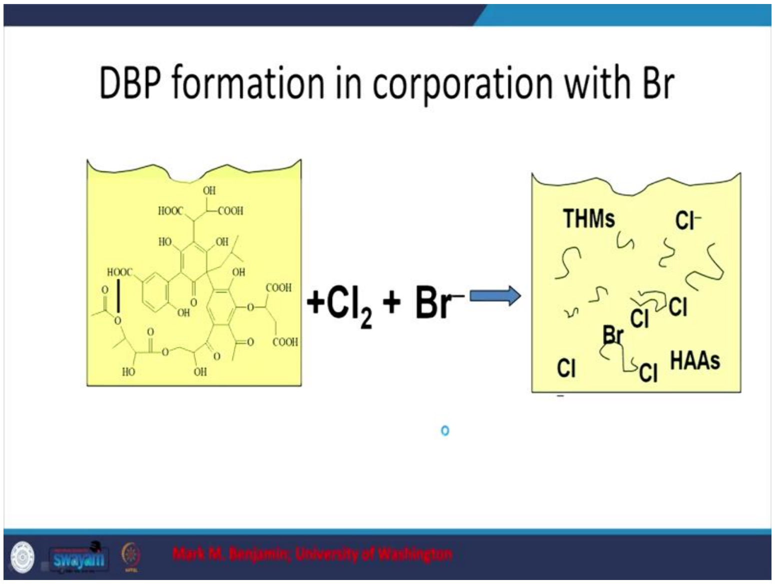

DBP formation in corporation with Br

Mark M. Benjamin, University of Washington

And these are toxic to us and if there is bromide Br^- present. It can also lead to kind of formation of disinfection by parts but in general when we there is bromide we are typically concerned with its reaction with ozone . We saw earlier that ozone can also sometimes form disinfection by products but that is the case when there is Br^- that is something to keep in mind.

So different a kind of disinfection byproducts one class is the trihalomethanes other class is the halo acetic acids.

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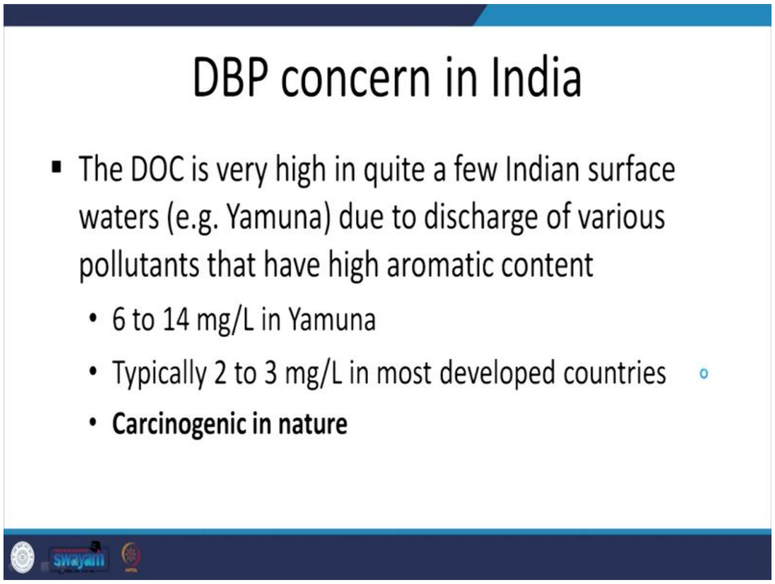

DBP concern in India

- The DOC is very high in quite a few Indian surface waters (e.g. Yamuna) due to discharge of various pollutants that have high aromatic content
  - 6 to 14 mg/L in Yamuna
  - Typically 2 to 3 mg/L in most developed countries
  - **Carcinogenic in nature**

So in India at least based on my limited experience the dissolved organic matter is a concern. When there is high dissolved organic matter and chlorine comes in contact with it you are going to have disinfection byproducts which are carcinogenic to humans depending on the concentration level of exposure and time of exposure. But they are certainly toxic and a sure way to kill the aquatic life that is something to keep in mind.

So that is why whenever in India at least wash water treatment plants people try to use chlorine they do it for two reasons because their activated sludge process or the biological treatment does not work very well due to poor maintenance or due to poor operation sludge retention times being very less or soil retention time being less. So here they use chlorine for two purposes not just for disinfection chlorine is also an oxidizing agent.

So you can oxidize the organics left so it will be as if BOD is less but by adding this amount of chlorine you are forming a hell lot of disinfection byproducts which you are releasing into the water body and killing or affecting aquatic life greatly. So thus the enforcement agencies aren't looking at it but if you are either an informed citizen or end up being in charge of a plant hopefully you will look into that.

Do not add chlorine to what we say wastewater treatment plant effluents at least that is based on science too. So in India though what is it now the DOC is very high I am not calling it dissolved organic matter why in the context of Indian surface water bodies it is not just the organic matter from the natural sources that is of issue or I am not calling it NOM pardon me I am not calling it natural organic matter I am calling it dissolved organic carbon or dissolved organic matter.

Because here we have high influence of the humans or anthropogenic sources of organic content are pretty much prevalent . So that is why I am not calling it as num and that is the reason why it is pretty high DOC or DOM levels are very high in India especially in Yamuna. In general it is two to three or two milligram per liter in most developed countries. When I add chlorine either for water treatment or for wastewater treatment.

So at least for water treatment I add chlorine to disinfect the water I add a lot of chlorine or how to add a lot of chlorine to take care of this high organic matter. The disinfection by products that are going to be formed are going to be at very high concentrations that is something to keep in mind.

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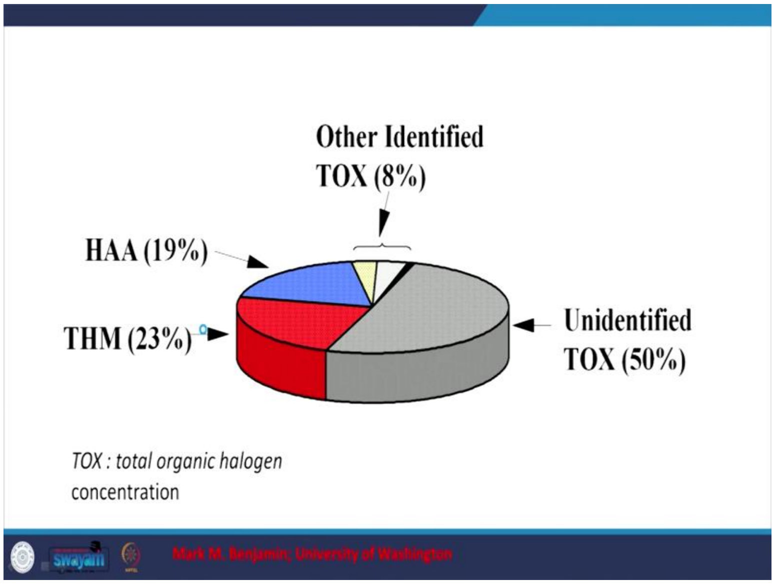

TOX : total organic halogen concentration

Mark M. Benjamin, University of Washington

So types of DBPs so try halomethanes we looked at that and halo acetic acid acetic acid is CH_3COOH halo acetic acid so here instead of H_3 you can have CHClCOOH, I think you can even have CHBrCOOH and so forth that is different combinations H_2 so these are called halo acetic acids. But as we can see for the total organic haloes Cl^- Br^- these trihalomethanes and halo acetic acids only cover around what is it 40% or 42% of the total organic halogen concentration there are other unidentified organic haloes out there.

So these havoc with the aquatic ecosystem you should not try to or you should try to limit this whenever possible.

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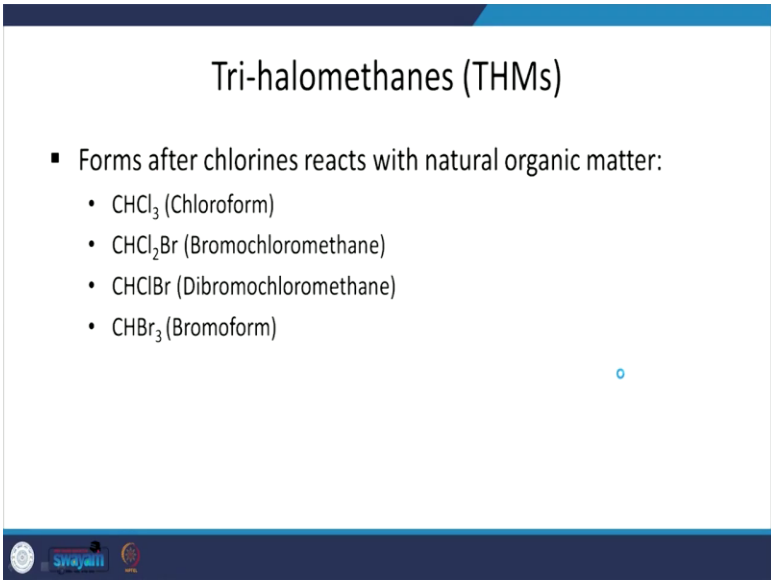

Tri-halomethanes (THMs)

- Forms after chlorines reacts with natural organic matter:
  - $CHCl_3$ (Chloroform)
  - $CHCl_2Br$ (Bromochloromethane)
  - CHClBr (Dibromochloromethane)
  - $CHBr_3$ (Bromoform)

So, we already looked at this $CHCl_3$ chloroform bromo chloromethane dibromochloromethane $CHBr_3$ bromoform I stand slightly corrected earlier I was talking about something like CH_2Cl so or Cl_2 so that is not the case it is trihalo as you see everywhere it is trihalo or three haloes Cl_3, 3Cl or 2Cl, one Br^- here one of it is missing Br_2, it is dibromo so , dibromochloromethane or bromoform . So that is something to keep in mind that is why it was called trihalo I stand corrected.

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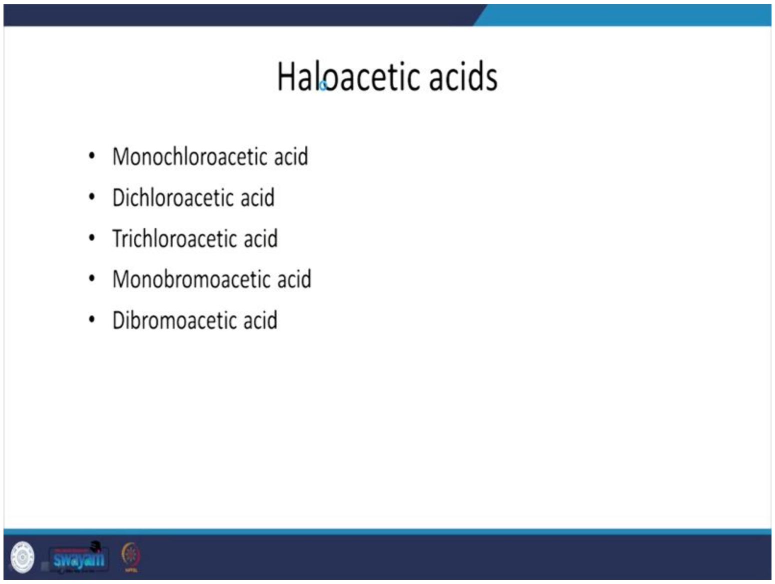

Haloacetic acids

- Monochloroacetic acid
- Dichloroacetic acid
- Trichloroacetic acid
- Monobromoacetic acid
- Dibromoacetic acid

So halo acetic acid , mono chloro one chlorine or OCl^-, dichloro, trichloro, mono, bromo acidic dibromo. So you can substitute accordingly in CH_3COOH all these are halogenated organics.

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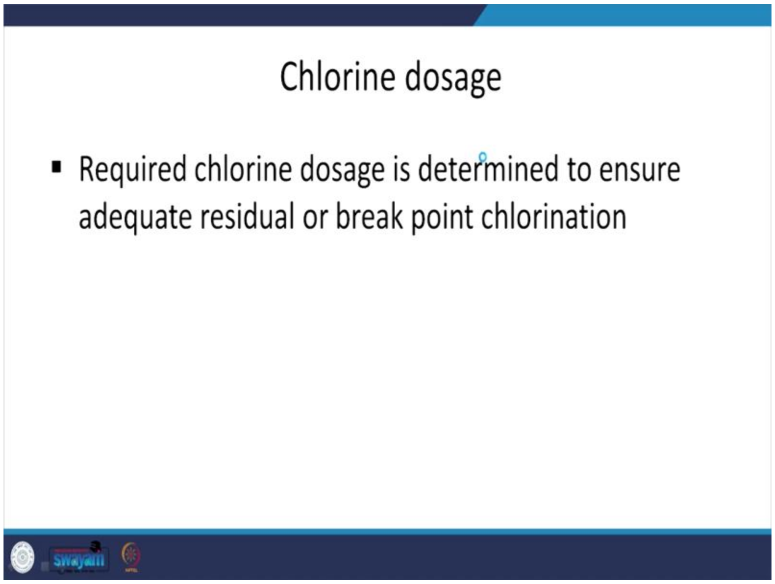

Chlorine dosage

- Required chlorine dosage is determined to ensure adequate residual or break point chlorination

So chlorine dosage now I want to know how much chlorine to add. So we know that I am adding chlorine as an oxidizing agent and when I am adding that I need to take care of both the oxidation of the organics and other reduced forms and also I need to have enough chlorine to kill my pathogens so two aspects. I need to take care of organics and other reduced compounds . manganese, iron or such and then I need to have enough left for my pathogens.

So this is a aspect that I need to add so when I add chlorine or oxidizing agent I need to take care of both. So I need to look at this because I need to ensure adequate residual chlorine or ensure that so for that we have something that is called as break point chlorination.

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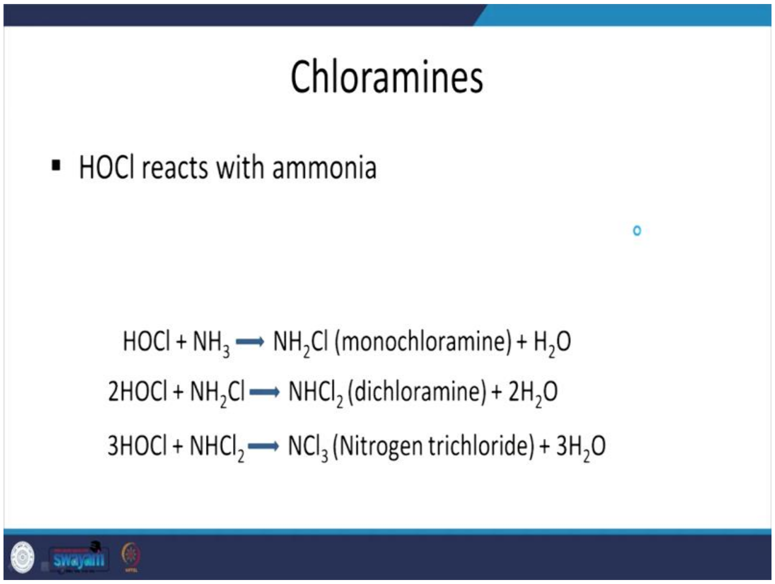

Chloramines

- HOCl reacts with ammonia

$$HOCl + NH_3 \rightarrow NH_2Cl \text{ (monochloramine)} + H_2O$$
$$2HOCl + NH_2Cl \rightarrow NHCl_2 \text{ (dichloramine)} + 2H_2O$$
$$3HOCl + NHCl_2 \rightarrow NCl_3 \text{ (Nitrogen trichloride)} + 3H_2O$$

We will see how that comes about . Before we go further one aspect to note is that we know from our wastewater relevant aspects that we have ammonia or NH_3 in our solution and if we add an oxidizing agent we know that it can go to monochloramine and depending on the concentration of Cl or HOCl it will go to dichloramine and HCl. And if I add it at a higher concentration or finally it can end up into NCl_3 which is pretty unstable and it will end up going to N_2 nitrogen gas finally.

So this is some background we looked at why did we look at that we were looking at formation of NH_2Cl and $NHCl_2$ which are themselves forms of combined chlorine which we add as disinfecting agents. But we also need to be aware of this why because that in our waste waters you can have NH_3. So if I am adding HOCl to kill the pathogens. The HOCl will not just react with the pathogens it will react with whatever it sees out there it is not so specific it is an oxidizing agent it when we react with other organic matter.

It can react with the ammonia that is present. And after all this then not after assuming that all of them are taken out then we will come to what we say providing the residual chlorine or free chlorine so that pathogens can be taken care of so this is the aspect we need to look at. I need to add enough oxidizing agent or chlorine or HOCl to take care of the organic matter to take care of NH_3 before I can take care of the pathogens.

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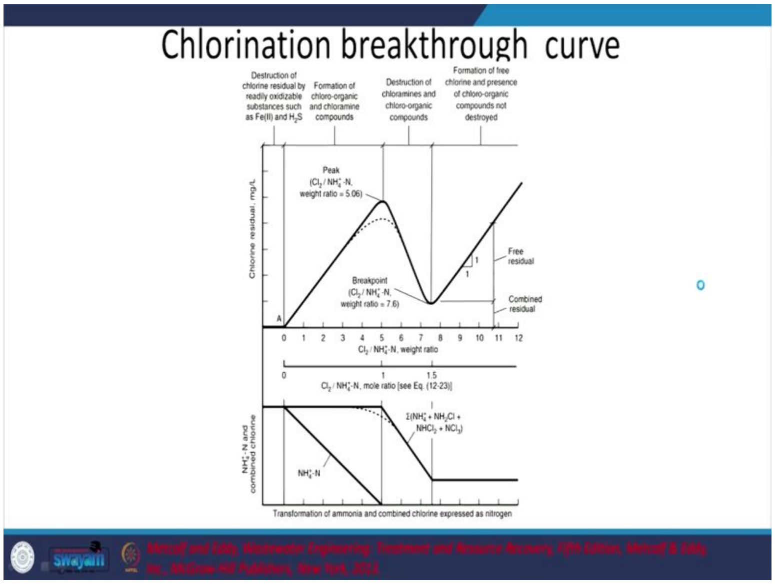

Chlorination breakthrough curve

Metcalf and Eddy, Wastewater Engineering: Treatment and Resource Recovery, Fifth Edition, Metcalf & Eddy Inc., McGraw-Hill Publishers, New York, 2013

So what we have? So here we have a good graph from our two pieces of graphs or two graphs from Metcalf And Eddie. So what do we have we have chlorine residual on the y axis and on the x axis what do we have I think we are increasing it out here transformation of ammonia Cl_2 . So let us look at that so here what is it now as I add it, from here I am starting to add. So here what is happening initially you have destruction of chlorine due to oxidizable substances such as Fe^{2+} can go to Fe^{3+} by giving out its electron so it is an electron donor.

And my Cl_2 or HOCl or oxidizing agents they will accept an electron. So whenever I have Fe^{2+} they will readily consume my oxidizing agent . So that is why when I have reducing agents such as Fe^{2+} or H_2S they will be immediately consumed so there is no residual chlorine as I keep adding it. Keep adding my oxidizing agent or the chlorine so it is everything will be oxidized or all the oxidizing agent is consumed.

And then by here I am done with all the readily oxidizable compounds like Fe^{2+} and H_2S. So, now as I keep adding more chlorine what is going to happen now? So here the NH_3 that is in the water will start reacting with the HOCl or Cl_2 that I am adding. And it will first form monochloramine and if I increase the concentration it will form dichloramine so that is what you will see here. So formation of chloro organic and chloramine organ and chloramine compounds .

But keep in mind this is chloramine residual so even if it is a combined form that is why we are saying that it is increasing . So this is increasing but if I keep adding more what is going to happen? if I keep adding more I know that it is going to be further oxidized to nitrogen trichloride which is unstable and it will go to N_2. So it is leaving the system . So the form of this combine chlorine it is not now NH_2Cl and then $NHCl_2$ is increasing here.

But after I keep adding more chlorine now it is going to NCl_3 which will readily go to N_2 gas it is leaving the system there is no oxidizing agent or the combined chlorine is now decreasing. So that is what we see destruction of chloramines and chloro organic compounds they transform to nitrogen gas and go so. That is why even though I keep adding chlorine now the residual chlorine is now coming down.

These combine chlorines also we are considering as residual chlorine that is why in this phase we see that it increasing until a peak. After I add more chlorine due to the relevant stoichiometry you see that it now starts degrading to NCl_3 and N_2 this is NCl_3 and N_2 gas . So at this point there is no more H_2S or Fe^{2+} no more organics and all the ammonia has been consumed by this point and this is called that break point .

So whatever chlorine I add from here will be the free residual chlorine so combined residual and this is the free residual chlorine and this I can be sure will be available to kill the pathogens. What do we have here formation of free chlorine and presence of chloro organic compounds which are not destroyed, so free residual chlorine. This is break point chlorination. Whenever I add chlorine I need to add this enough chlorine to take care of all the compounds that can oxidize my chlorine or the oxidizing agent like HOCl and then I will get that so that is what we have here the breakpoint chlorination.

So here we have the NH_4^+ and combined chlorine initially most of it is present as NH_4^+ but as I add Cl_2 I know that chloramines are being formed so NH_4^+ concentration comes down. But this total which is NH_4^+ chloramines it is still there, why? Because during this point NH_4^+ is being transformed into NH_2Cl but after a certain point I know that nitrogen gas will be given out that is why this total is decreasing and that is this break point that we saw just a different profile.

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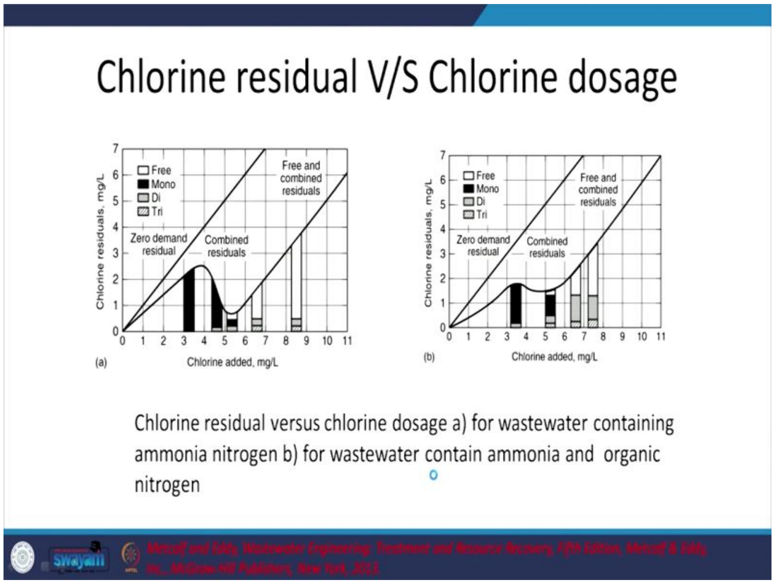

Chlorine residual V/S Chlorine dosage

Chlorine residual versus chlorine dosage a) for wastewater containing ammonia nitrogen b) for wastewater contain ammonia and organic nitrogen

Metcalf and Eddy, Wastewater Engineering: Treatment and Resource Recovery, Fifth Edition, Metcalf & Eddy, Inc., McGraw-Hill Publishers, New York, 2013

So another aspect to note is that if I have wastewater containing ammonia nitrogen or wastewater containing ammonia and organic nitrogen the profile will be slightly different depending on the organic content. So that is what you see here you will not see such a sharp break point but you will see such a tapered one so that is something to keep in mind.

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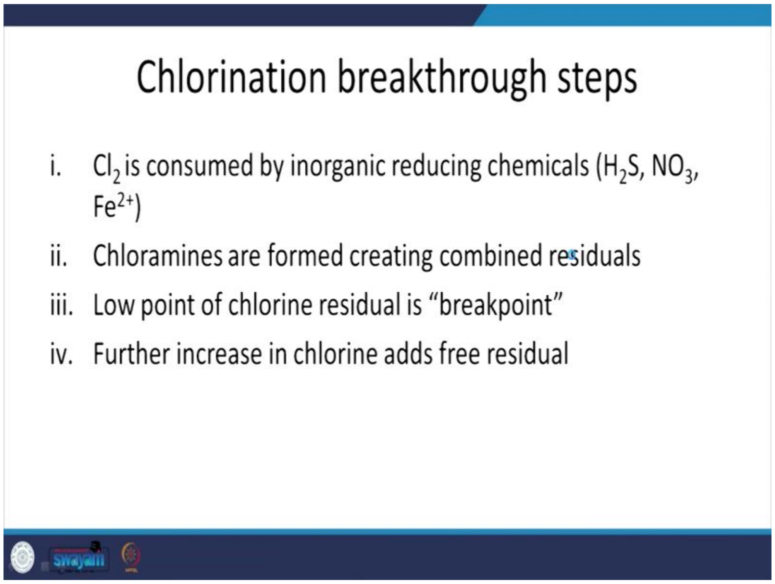

Chlorination breakthrough steps

i. Cl_2 is consumed by inorganic reducing chemicals (H_2S, NO_3, Fe^{2+})
ii. Chloramines are formed creating combined residuals
iii. Low point of chlorine residual is "breakpoint"
iv. Further increase in chlorine adds free residual

So chlorination break point we already looked at that low point of the chlorine residual is called break point. So for example we saw something like this initially everything is consumed then chloramines are formed and then the peak comes N_2 is being given out all the chloramines are going to N_2 and this is the minimum and then whatever I add keeps increasing that is why it is linear here all this is the residual clothing from here this is the break point here that is something to keep in mind.

And in general we want it residual chlorine such that it is 0.2 mg/L at the end of the or at the furthermost point on the distribution system why? I am staying far away and I need to see to it that there is enough chlorine to tackle any microbial growth or any intrusion of sewage or such that can tamper or pollute my distribution network. So I need sufficient residual chlorine and sufficient one is supposed to be 0.2.

But if it is greater than 0.5 mg/L it becomes objectionable and in India typically we exceed this particular limit.

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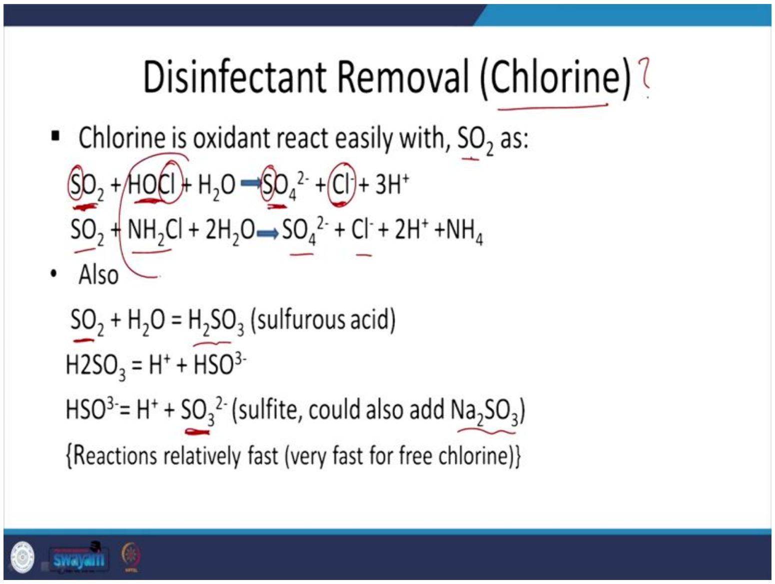

Disinfectant Removal (Chlorine) ?

- Chlorine is oxidant react easily with, SO_2 as:

$SO_2 + HOCl + H_2O \rightarrow SO_4^{2-} + Cl^- + 3H^+$

$SO_2 + NH_2Cl + 2H_2O \rightarrow SO_4^{2-} + Cl^- + 2H^+ + NH_4$

- Also

$SO_2 + H_2O = H_2SO_3$ (sulfurous acid)

$H2SO_3 = H^+ + HSO^{3-}$

$HSO^{3-} = H^+ + SO_3^{2-}$ (sulfite, could also add Na_2SO_3)

{Reactions relatively fast (very fast for free chlorine)}

So disinfectant removal so as we mentioned earlier disinfection byproducts can be formed so you do not want to have too much chlorine or even other than formation of disinfection by products too much chlorine is also toxic to us and objectionable. So you can remove chlorine but how will you remove chlorine? that chlorine is an oxidizing agent it is an electron acceptor.

So you can add any other benign electron donor or reducing agent. Chlorine is an oxidant so it can readily react with SO 2 so if I add SO_2 to HOCl so SO_2 a reducing agent will be oxidized to SO_2^-, HOCl which is an oxidizing agent will be reduced to Cl^- you can check the oxidation states of sulfur and oxidation states of Cl let is and then you will understand which one is increasing .

But as you can clearly sulfur is being oxidized and Cl is being reduced so that is what you can do. And SO_2 with NH_2Cl or combined type of chlorine different kinds of reactions or SO_2 in water can form sulfurous acid not sulfuric acid and sometimes we can add this itself directly sulfite a strong reducing agent it can be added as Na_2SO_3 sodium sulfide all these are reducing agents.

Why are we adding them? To take care of the high or possibly high oxidizing agent concentration that is why we looked at electron transfer or briefly looked at the redox reaction weighted aspects.

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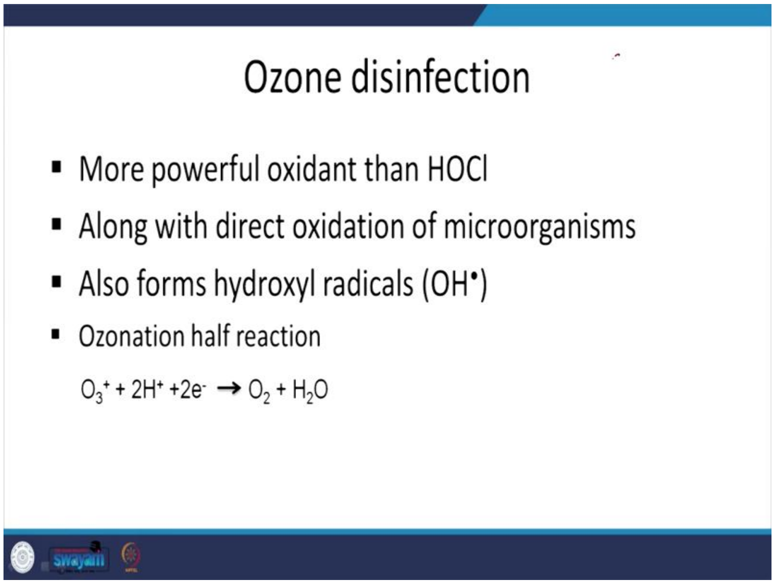

Ozone disinfection

- More powerful oxidant than HOCl
- Along with direct oxidation of microorganisms
- Also forms hydroxyl radicals ($OH^•$)
- Ozonation half reaction

$$O_3^+ + 2H^+ + 2e^- \rightarrow O_2 + H_2O$$

So ozone disinfection until now we were looking at Cl_2 or combined forms of chlorine and so forth. Now let us look at ozone it is the most or one of the most I think second most oxidized strongest oxidizing agent available the strongest one is the hydroxyl radical that is also formed in or during ozonation of water. Ozone is a gas it can be produced in situ with corona discharge you have ozone generators.

As we mentioned it is much more powerful than HOCl it will directly oxidize the cell wall of the microbes similar to the action of your particular chlorine or the chlorine based oxidizing agents depending on the pH it can also form another strong oxidizing agent which is OH^- and the half reaction where we see that it is an electron acceptor is this it can also lead to increase in concentration of water.

So that is one reason why I like addition of ozone addition of ozone why is that when I add ozone the dissolved solids total dissolved solids in the water are not increasing. But if I add Cl_2 or such we see that we are adding Cl^- to the solution. So we are adding the total dissolved solid which is never good in general. So here with ozone though we are adding oxygen to the water and also ozone we know is a very strong oxidizing agent it will also be able to degrade the residual organic content pretty well and disinfection by parts are pretty less or non-existent especially if there is no Br^-.

If there is Br^- it can react with ozone to form some disinfection byproducts but that is typically not not an issue. , as I mentioned it depends on Br^- concentration so this is dissolved so let us move on.

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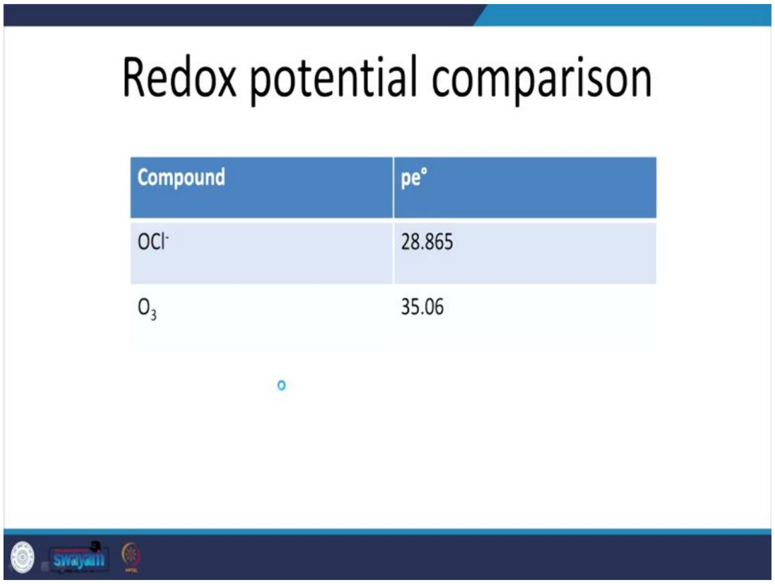

Redox potential comparison

Compound	pe°
OCl^-	28.865
O_3	35.06

So how do I understand that it is a strong oxidation oxidizing agent compared to OCl^- we look at P_0. So P_0 is at the standard conditions minus log activity of this hypothetical electron. So it is logarithmic based so 28 and 35 so 10^7 times so 35-28 = 7. But P is log so you understand how strong the oxidizing agent is or ozone is compared to OCl^-.

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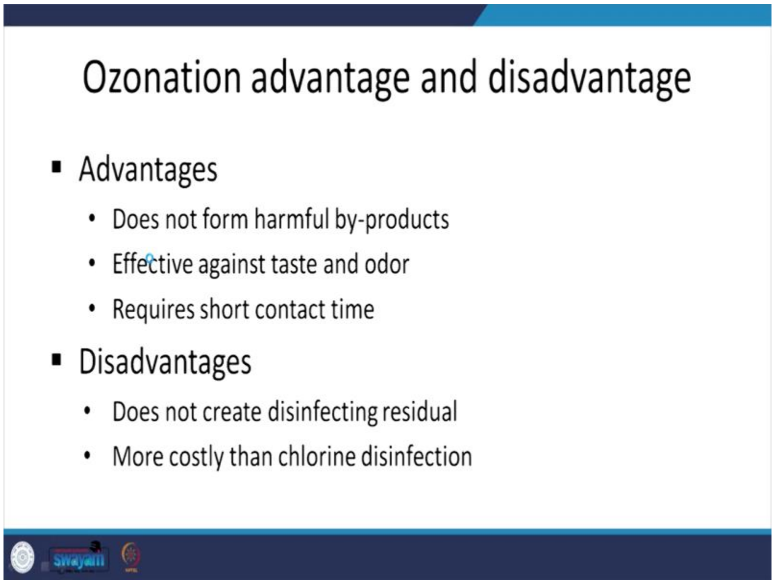

Ozonation advantage and disadvantage

- Advantages
  - Does not form harmful by-products
  - Effective against taste and odor
  - Requires short contact time
- Disadvantages
  - Does not create disinfecting residual
  - More costly than chlorine disinfection

So advantageous in general does not form harmful DBP’s very effective st taste and water causing compounds and because of its fast kinetics and relatively high oxidation potential you are going to have less contact time. But does not create disinfecting residual why because it is so fast acting the kinetics are so fast of this particular accident that it does not stay in water for long.

So if I ozonate it now I think 30 minutes later you are done with most of the ozone will be degraded .

But that is not the case with chlorine so you can have ozonation to take care of your residual organics and pathogens and add some chlorine so that you can have your what is this residual chlorine . And it needs a more capital intensive setup because it is more costly than chlorine disinfection.

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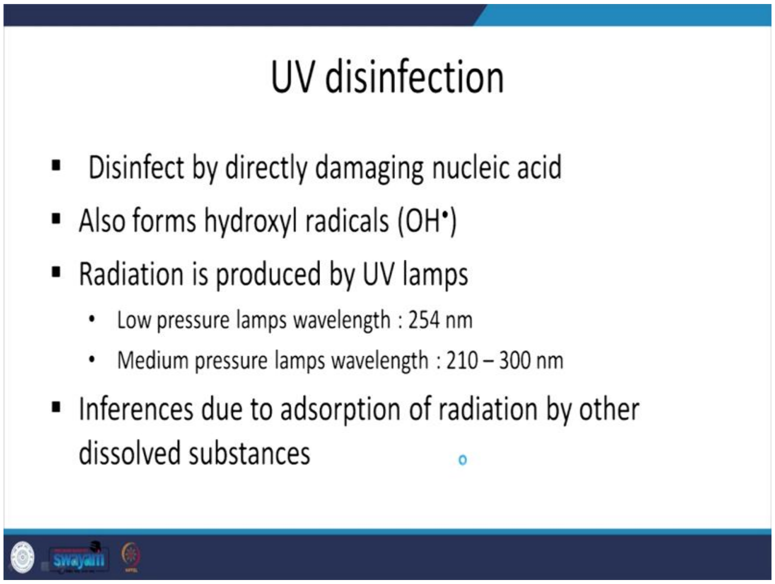

UV disinfection

- Disinfect by directly damaging nucleic acid
- Also forms hydroxyl radicals ($OH^{\bullet}$)
- Radiation is produced by UV lamps
  - Low pressure lamps wavelength : 254 nm
  - Medium pressure lamps wavelength : 210 – 300 nm
- Inferences due to adsorption of radiation by other dissolved substances

So UV the last one which is not a chemical based UV. So we have visible light here light you can see my face because they have the light set up here. UV you cannot see that ultraviolet radiation, yes. So here the disinfection is caused by directly damaging the nucleoids or nucleic acids I think I have picture later. Depending on the mode of operation it can form hydroxyl radicals but we are not concerned about it now.

Especially when you have UV and in water and add H_2O_2 to water you will form this very strong hydroxyl a very strong oxidizing agent which is this hydroxyl radical. The radiation is produced by UV lamps and there are different kinds of lamps low pressure though it is a misnomer to say it is low pressure but the primary aspect of low pressure or UV-L, UV low pressure is that they emit light not light radiation only at one wavelength, this is 254nm.

Are to be specific 253.7 nm it is of great relevance because at this particular UV wavelength or wavelength pardon me most of the DNA and RNA of concern will absorb the UV or the radiation and if they can absorb it at that particular wavelength the energy is going to be transferred and you will have damage of the RNA or DNA and thus inactivation of the relevant pathogens.

With respect to medium pressure lamps it is not as if they do not emit UV monochromatically this is monochromatic UV monochromatic radiation here they give it out at a range of wavelengths. But what are the issues here interferences due to absorption of radiation absorption of radiation by other dissolved substances. For example here is my UV lamp submerged and the water is flowing around it the and this is my cell.

And the cell has to absorb or the UV has to penetrate that particular cell or the UV radiation or photon has to reach that cell. But if I have suspended solids or other compounds which absorb the UV meaning other interferences then the effectiveness is going to be limited so I might then need to have higher intensity that is what we are saying.

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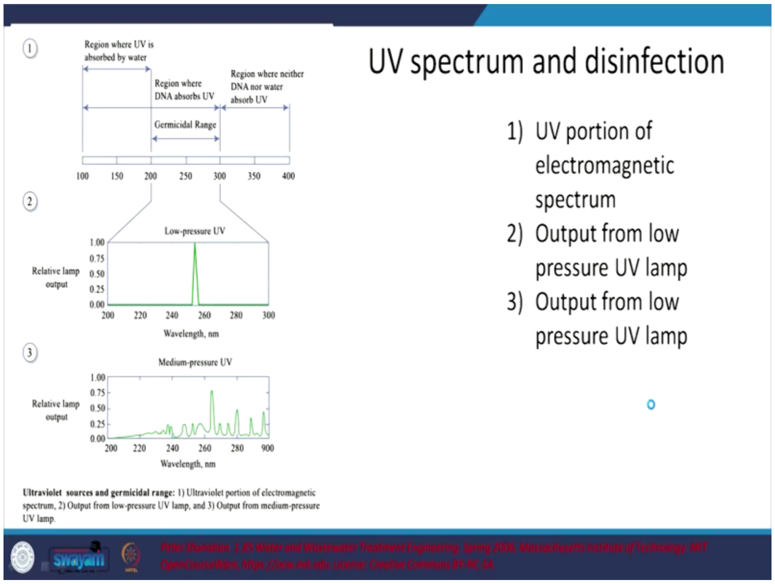

Ultraviolet sources and germicidal range: 1) Ultraviolet portion of electromagnetic spectrum, 2) Output from low-pressure UV lamp, and 3) Output from medium-pressure UV lamp.

UV spectrum and disinfection

1) UV portion of electromagnetic spectrum
2) Output from low pressure UV lamp
3) Output from low pressure UV lamp

Peter Shanahan. 1.85 Water and Wastewater Treatment Engineering. Spring 2006. Massachusetts Institute of Technology: MIT OpenCourseWare, https://ocw.mit.edu. License: Creative Commons BY-NC-SA.

So just let us look at this so what do we have here 100 to 400 nm around this or 502 or beyond 600 nm it is visible . But what is this range let us look at that between 100 to 200 UV is absorbed by water itself and between 300 to 400 region where neither DNA nor water absorb UV. But there is a sweet spot between 200 to 300 where which we call as the germicidal range where the DNA and RNA absorb UV.

and that leads to damage of the what we say RNA or DNA and that will affect the replication of the relevant pathogen. So UV as I mentioned monochromatic low pressure lamp UV L it will emit light or not light radiation only at 254 nanometers that is what we see here. At UV medium pressure it will emit radiation over a range it will be effective if we have pathogens that what we see absorb late at our radiation I should not say light radiation at different wavelengths.

And ineffective if they do not absorb radiation at the different wavelengths so that is something to keep in mind .

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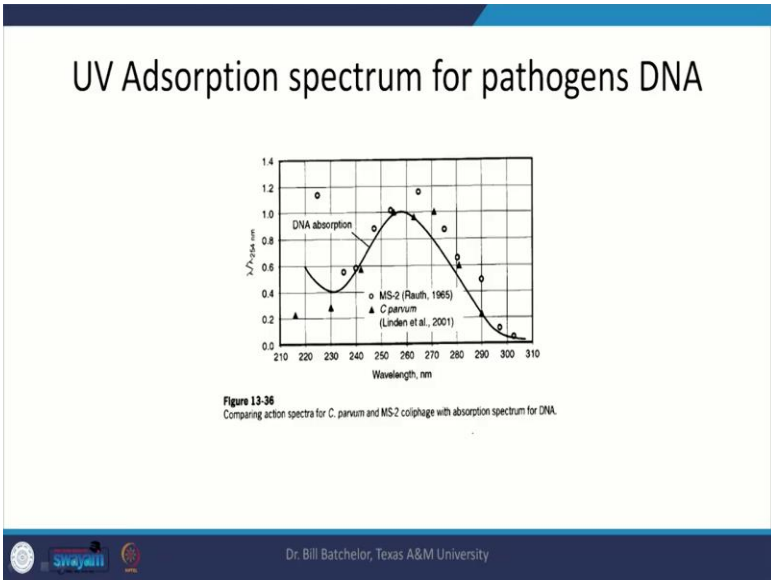

UV Adsorption spectrum for pathogens DNA

Figure 13-36
Comparing action spectra for C. parvum and MS-2 coliphage with absorption spectrum for DNA.

Dr. Bill Batchelor, Texas A&M University

So here is one graph that was presented by my advisor during my time so here we see that at 254 nanometers DNA absorption is pretty good . So ratio of λ / 2λ at 254 nanometers and here we see the wavelength . Comparing the spectra for C. parvum and qualified with absorption spectrum for DNA . So you can see that it is pretty good at 254 nm you see the peak and that is why 254 nm is remarkably effective at killing or not killing inactivating pathogens.

So that is why you would see many people trying to sell UV boxes or UV radiation chambers for as corona killer. But if I have a paper and I put it in a UV chamber the top surface bottom surface not really and contact time is an issue. So these UV base the radiation chambers for killing corona especially corona virus on surfaces I would say all these are mostly trash or short-term stars .

So it is with respect to how effectively the UV can penetrate or be accessible or be absorbed by the corona virus. If it cannot kill the virus .

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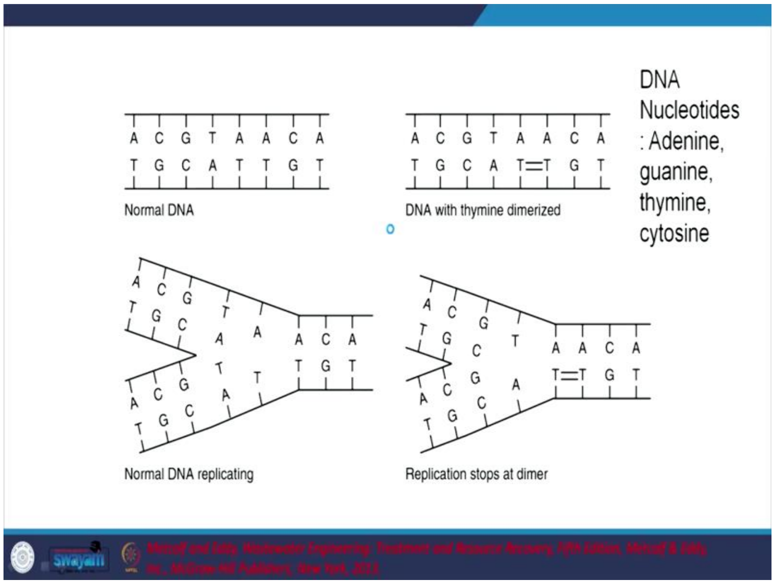

DNA Nucleotides : Adenine, guanine, thymine, cytosine

Normal DNA

DNA with thymine dimerized

Normal DNA replicating

Replication stops at dimer

Metcalf and Eddy, Wastewater Engineering: Treatment and Resource Recovery, Fifth Edition, Metcalf & Eddy, Inc., McGraw-Hill Publishers, New York, 2013

And how is it that it works UV so UV as we know can be absorbed by DNA or RNA. So viruses let us talk about viruses can have DNA or RNA . DNA looks like will help or will tell you how the structure will develop and RNA will dictate how the metabolic process go through or take place. So in DNA as we mentioned earlier we have different nucleic acids so there are four nucleotides of concern adenine, guanine, thymine and cytosine hopefully my pronunciation is not too far off from the correct pronunciation.

So A G T and C and this UV will be absorbed by this thymine yes and after UV radiation dimerization will occur thymine dimerization. So why is this relevant because with normal DNA this is how replication will take place DNA replicating as on this cell is replicating the microorganism or pathogen is replicating it is growing. If it does not grow it will die soon the last lifetimes are pretty short .

So here though with respect to this change in the DNA the replication stops at that dimerization. So that is how you are going to have UV inactivating microbes and sometimes people talk about it does not kill, kill it does not disrupt the cell wall well as you see pathogen does not survive out there for a long time at least in water . So in general replication is what we want to stop if we do that effectively especially if we do that effectively.

As you see the UV radiation is pretty good way to go about it but even with respect to other disinfecting agents different viruses they can repair themselves and that will also be the case with respect to some repairing whenever they are affected by UV radiation but let us not go there .

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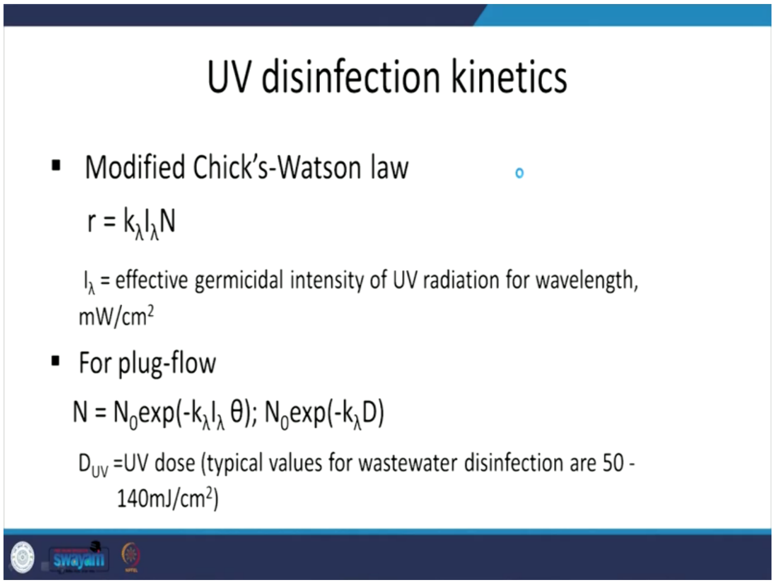

UV disinfection kinetics

- Modified Chick's-Watson law

  $r = k_\lambda I_\lambda N$

  I_λ = effective germicidal intensity of UV radiation for wavelength, mW/cm^2

- For plug-flow

  $N = N_0 exp(-k_\lambda I_\lambda \theta); N_0 exp(-k_\lambda D)$

  D_{UV} =UV dose (typical values for wastewater disinfection are 50 - 140mJ/cm^2)

So disinfection kinetics it is modified Chick Watson's law we have a rate we have another rate constant instead of concentration we have instant intensity. Effective genocidal intensity how intense is it for example if I take a intensity meter and go out there in the sun in the afternoon the intensity is very high the reading is high. In the night intensity is less how much what do we, see energy per unit area per time that is what it is going to give me an idea about.

What is energy per time? Job per second per area . And microbial concentration I plug it into the reaction or equation for plug flow this is what I get and I which is nothing but what is it energy per time per area. Energy meaning we know that hc/λ for a photon with λ wavelength so that is how we can get it. So if I multiply that by theta or the time. So I will get energy I into theta will be energy per area which is called the dose that is what we have UV dose 140 milli joules per centimeter square.

So all those people who sell random UV lamps so you need to be concerned about what is the intensity how much is the contact time it will achieve and is there uniform distribution of that UV intensity without that the relevant chamber is just junk.

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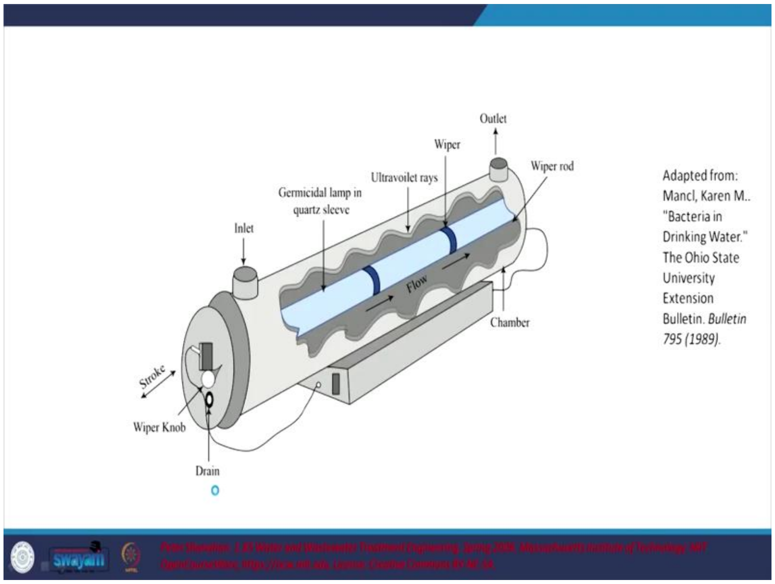

Adapted from: Mancl, Karen M.. "Bacteria in Drinking Water." The Ohio State University Extension Bulletin. *Bulletin 795 (1989).*

So how does it work typically we have the submerged UV lamps and I think we saw this even in the case of the IIT, Roorkee, SBR plant where we had a submerged system. So this is what it looks like there is an quad sleeve white ones because glass will absorb UV. So UV will not pass through and if you do not have the sleeve water will come in contact with the lamp and you are going to have short circuiting.

So you will have a quad sleeve within that you will have the UV and UV will come out and will penetrate the quads or pass through the quad sleeve and then you are going to have irradiation of the water. because the kinetics is so fast especially intensity you can maintain it pretty well you are going to have what we say just small chambers being good enough to cause your relevant disinfection especially with UV. scaling you have to look at it but that is a different aspect.

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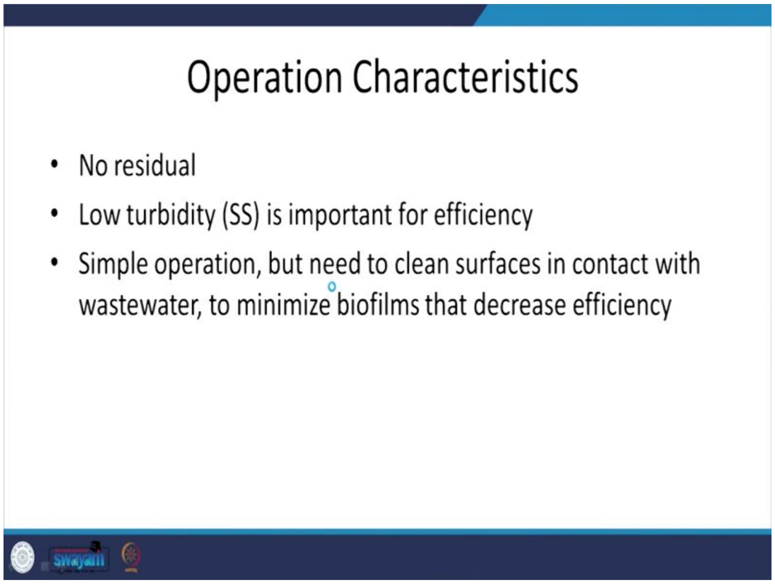

Operation Characteristics

- No residual
- Low turbidity (SS) is important for efficiency
- Simple operation, but need to clean surfaces in contact with wastewater, to minimize biofilms that decrease efficiency

Operation characteristics UV if there is a light, there is disinfection no UV no disinfection so there is no chance of residual so that is one aspect. Turbidity has to be low otherwise due to interferences the other compound suspended solids will absorb the UV simple operation but I need to clean the surfaces that come in contact with wastewater to minimize biofilms that can absorb UV .

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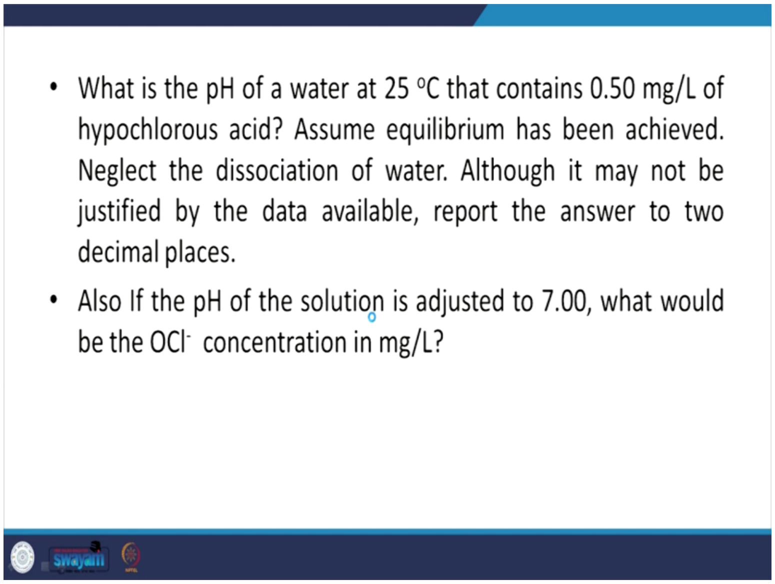

- What is the pH of a water at 25 °C that contains 0.50 mg/L of hypochlorous acid? Assume equilibrium has been achieved. Neglect the dissociation of water. Although it may not be justified by the data available, report the answer to two decimal places.
- Also If the pH of the solution is adjusted to 7.00, what would be the OCl^- concentration in mg/L?

So we have one question and I will end today's session and disinfection and wastewater with this session. What is the pH of water at 25 degree centigrade that contains 0.5 mg/L of hypochlorous acid. So the question is not very well framed but we will frame it better later on. So there is what is the pH of a water that contains 0.5 mg/L of HOCl at equilibrium. Assume equilibrium has been reached. So this is the key it is not as if it is being added initially . So neglect dissociation of water not a great aspect but fine and report the answer to two decimal places. First thing is I have, this which is HOCl concentration and I am going to have to look at it. This is not a well framed question but we will try to make do with what we have. Also if the pH of solution wcreased or decreased to 2 to 7 what would be the OCl$^-$ concentration in milligram per liter.

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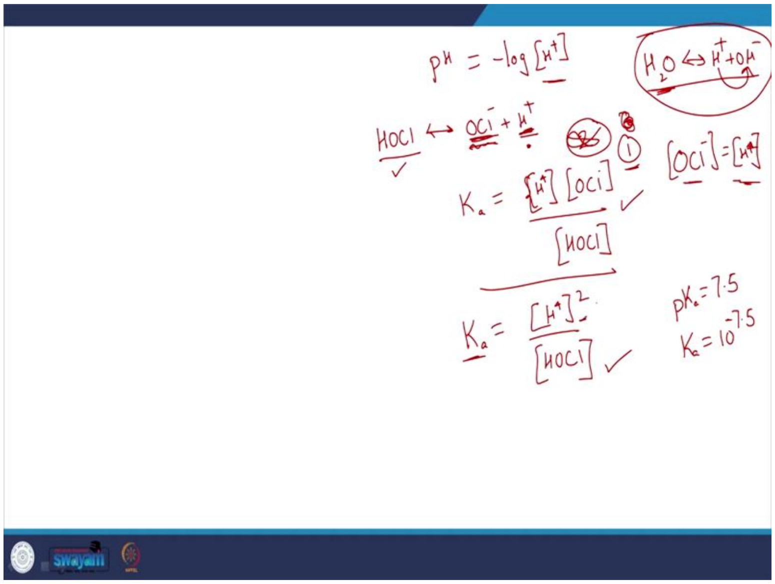

$pH = -\log[H^+]$

$H_2O \leftrightarrow H^+ + OH^-$

$HOCl \leftrightarrow OCl^- + H^+$ ①

$[OCl^-] = [H^+]$

$K_a = \frac{[H^+][OCl]}{[HOCl]}$ ✓

$K_a = \frac{[H^+]^2}{[HOCl]}$ ✓

$pK_a = 7.5$

$K_a = 10^{-7.5}$

First what are the equations that we want are such before that we want pH, pH equal to minus log concentration of H plus; pH = -log[H$^+$] . So one unknown is H$^+$ and HOCl will be in equilibrium with OCl$^-$ and H$^+$. So this is a potential unknown one unknown, one unknown three unknowns. But pH is what we are trying to find and HOCl is what we already have so we need a way to be able to get our, calculate OCl$^-$.

So in effect we have two unknowns in effect we have two unknowns because OCl is known. So how to I need to have two equations to be able to solve for this certainly one equation is that Ka is equal to what? Now I know that Ka equation is equal to activity or concentration of H$^+$ in the concentration of OCl$^-$ by concentration of HOCl. So this is one equation so here you see the issue with why I say the question was not very well framed.

But assuming that water is not dissociating which is not a great way water not dissociating meaning water will always dissociate into H$^+$ and OH$^-$ but here they are asking us to assume that this does not happen, so that is not a great aspect. But why is it that they are asking us to assume that because then you can say that whatever HOCl has dissociated will either be as OCl^- as H^+.

Meaning OCl^- concentration will then be equal to H^+ but that is not the usual case why H^+ can react with OH^- to go to H_2O but that is what they said do not look at that. So in effect our two unknowns become one unknown and with just this one equation we can solve for this unknown. So that is something to keep in mind. So what do we have we have that know that Ka is equal to but we just saw that if it is at equilibrium and if water dissociation is not considered OCl^- and H^+concentration will be the same .

So assuming that this will transform into H plus square by HOCl and I know HOCl concentration I know Ka or pKa is 7.5 so Ka is $10^{-7.5}$. So from that I can calculate my H^+ what we have.

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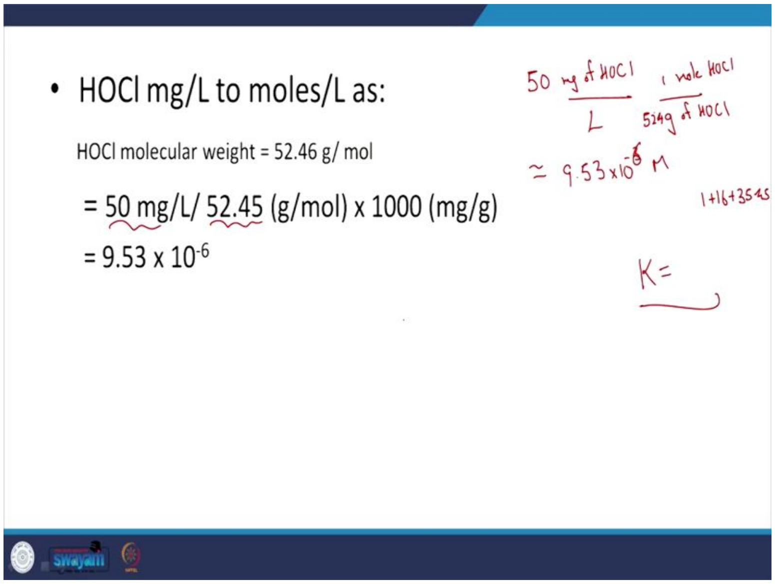

- HOCl mg/L to moles/L as:

HOCl molecular weight = 52.46 g/ mol

= 50 mg/L/ 52.45 (g/mol) x 1000 (mg/g)

= 9.53 x 10^{-6}

$$\frac{50 \text{ mg of HOCl}}{\text{L}} \quad \frac{1 \text{ mole HOCl}}{52.4\text{g of HOCl}}$$

$$\simeq 9.53 \times 10^{-6} \text{ M}$$

1+16+35.45

K =

So HOCl milligrams to moles per liter so what do we have I think how much are we adding HOCl is 0.50 mg/L, so I am not sure why my student took it as 50 mg/L. So we can consider that to be a typo error in the question or here. So let us just say it is 50 mg of HOCl per litre of water. I want to convert this into moles because all these equations in the equilibrium constant.

This equation all the units are in moles per liter let us or molar units . In general it is supposed to be molar but for now we will consider molar units. So how do I do this I need to get the molecular weight . So if I have that I will have grams of HOCl per one mole of HOCl so grams of HOCl grams of H will cancel out and I will get it. What is the molecular weight? So looks like it is 52.45 H is 1+16 and Cl^- is 35.45.

So 17 plus 35.45 52.45 of HOCl per mole, so they cancel out and the units you can look at it if there was an error made here it looks like I see that I get it in terms of 9.53 into 10 power minus 6 moles because of the way it was calculated I am not sure if mg per gram so it should probably be moles we are looking at the approach not the actual answer.

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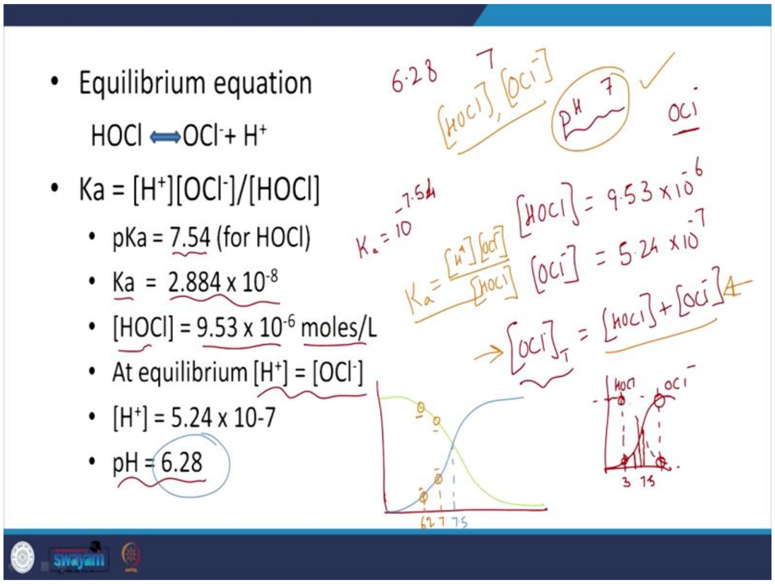

- Equilibrium equation

  $HOCl \Longleftrightarrow OCl^- + H^+$
- $Ka = [H^+][OCl^-]/[HOCl]$
  - pKa = 7.54 (for HOCl)
  - Ka = 2.884×10^{-8}
  - $[HOCl] = 9.53 \times 10^{-6}$ moles/L
  - At equilibrium $[H^+] = [OCl^-]$
  - $[H^+] = 5.24 \times 10\text{-}7$
  - pH = 6.28

Then we move on we know that this is the equation and Ka is equal to this pKa equal to 7.54 it seems so from that ka is equal to $10^{-7.54}$ meaning Ka equal to this you can plug this into the calculator and HOCl we just calculated that to be 9.53×10^{-6} molar or moles per liter. So at equilibrium assuming water dissociation does not take place this is the case but in the questions that I ask I am not going to do this.

So from that I can plug it into that equation that I wrote down earlier and I see to get a pH of 6.28. this is the approach but if there are any calculation errors you can look at that. And then people ask if the pH is increased to 7 what will be the OCl^- concentration? So the approach here should be I know the equilibrium concentration of HOCl to be

9.53 $x10^{-6}$ I know that OCl^- concentration will be equal to the H plus concentration from here that is equal to 5.24 x 10^{-7}.

So the total OCl or OCl total which is equal to HOCl + OCl^- will always be constant because we have this graph if you remember this is HOCl this is OCl^-. So you see the maximum here this is it. So if I at any point the total will be the same this plus this so if the pH is 3 or if the pH is 11 or 10 the total will always be the same OCl total will be the same.

So, using that I can calculate it why I need two equations now because if I change the pH which was at 6.28 and take it to pH of 7. What is happening we have this graph let us have this I know that the pKa is 7.5. So, earlier it was at 6.2. So if I increase it to 7 I am going out here let me try to draw that in a better manner here. So this is my HOCl which is decreasing with increase in pH and the other one is my OCl^- and this point is 7.5.

And earlier I got my pH to be 6.28 so at 6.28 that this is the case at 6.2 this is 6.2 this is the case but if I increase that to pH of 7 this will be the case but one aspect to note is that the total. Total of HOCl and OCl^- will be the same so that is the key to get the second equation. OCl total is HOCl + OCl^- and we already have another equation for Ka. So I have two unknowns which are HOCl and OCl^- these are my two unknowns because pH is 7, H^+ is already known.

So I have two unknowns two equations what are the two equations one is this equation and the other one is the Ka equation. So I have two unknowns and I have two equations I can solve it that is the way to go about it but people typically make blunders if my TA was able to get it or wrong.

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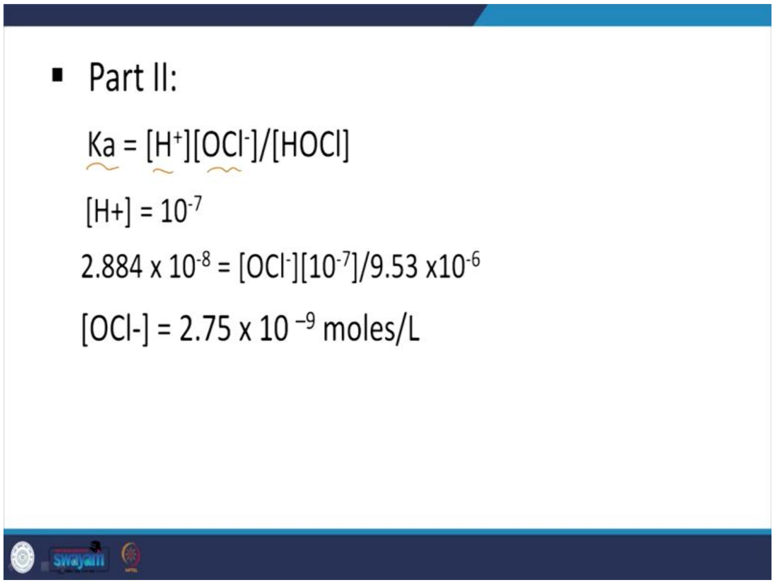

- Part II:

  $Ka = [H^+][OCl^-]/[HOCl]$

  $[H+] = 10^{-7}$

  $2.884 \times 10^{-8} = [OCl^-][10^{-7}]/9.53 \times 10^{-6}$

  $[OCl-] = 2.75 \times 10^{-9}$ moles/L

So he says Ka is equal to H^+, OCl^- by HOCl, H^+ is 10^{-7} fine that is a known value Ka is already known so that is also fine we have that. So now we see that OCl^- and he is substituting this H plus into this which is also fine but as is the case and how this is how people make errors. So he took the HOCl concentration from part A to be the same as here but you should know better as you saw here the HOCl concentration at 6.2 was this but after increasing the pH it will decrease.

So the HOCl concentration is not the same so the approach should have been this so this is a common mistake that people make. So I wanted to use the issue at hand to be able to illustrate this. So with that we are done with disinfection. So we are done with wastewater so from the next session we will start looking at water treatment and how to go about it. what is the principle well I think we looked at this pretty well. So thanking you for your patience I will end today's session.