Water and Waste Water Treatment
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Lecture -29
Chlorination Disinfection

Hello everyone welcome back to the latest lecture session. In the context of wastewater treatment we were talking about the last aspect that is relevant to us which is killing or inactivating the pathogens the disease causing or those microorganisms which can which are capable of causing disease . So there are different disinfecting methods or agents pardon me and one common aspect among all the chemical agents is that they are oxidizing agents.

But oxidizing agent’s different levels of efficacy and different levels of effectiveness st different pathogens .

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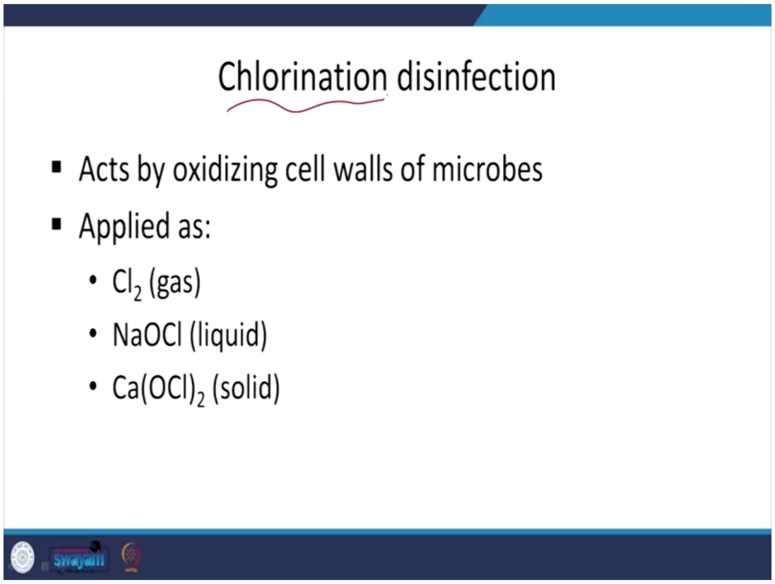

Chlorination disinfection

- Acts by oxidizing cell walls of microbes
- Applied as:
  - Cl_2 (gas)
  - NaOCl (liquid)
  - $Ca(OCl)_2$ (solid)

In that context we saw that we typically apply chlorine. Chlorine can be applied as Cl_2 itself or NaOCl . So typically we are trying to form HOCl, OCl^- it will always be in equilibrium with HOCl whenever you form HOCl. Because HOCl will dissociate to form H^+ and OCl^-; OCl is an acid depending upon the pH it will be in equilibrium with H^+ and OCl^- we will look at this later .

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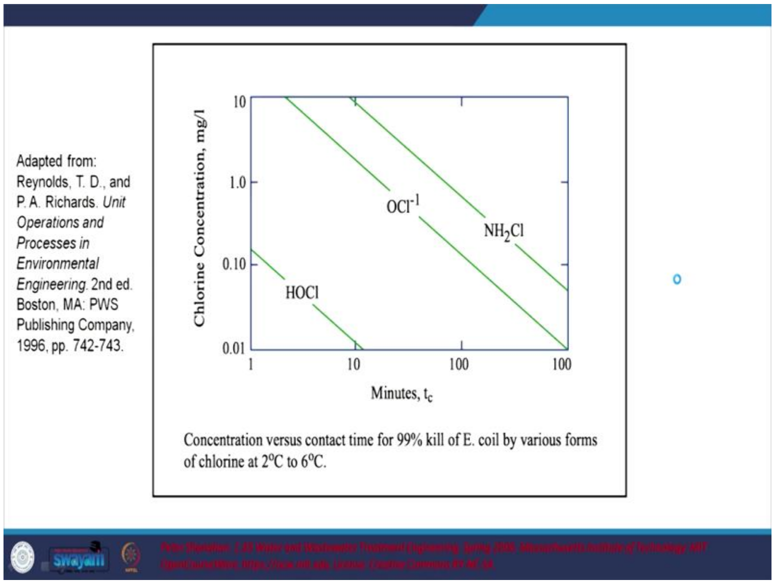

Adapted from: Reynolds, T. D., and P. A. Richards. *Unit Operations and Processes in Environmental Engineering*. 2nd ed. Boston, MA: PWS Publishing Company, 1996, pp. 742-743.

Concentration versus contact time for 99% kill of E. coil by various forms of chlorine at 2°C to 6°C.

So to look at the efficacy we looked at this particular graph or piece of information here we saw that HOCl requires much lesser Ct than OCl^- or NH_2Cl thus it is much more effective to kill the relevant pathogen. Here the pathogen of interest is E. coli . So move on here we see the other aspect we are just looking at HOCl in the context of its effectiveness st different kinds of pathogens.

So virus E coli virus so we see that for different types of virus different contact times are required and you see that the range is considerable, 100 minute contact time is a lot. So you need to look at what it is that you are trying to achieve. So for wastewater treatment disinfection relevant standards are different for water treatment standards are much more stringent .

In the context of wastewater treatment it is relatively different but I wanted to point out that there is no such case as if there is one dose at which almost all the viruses or pathogens are going to be inactivated.

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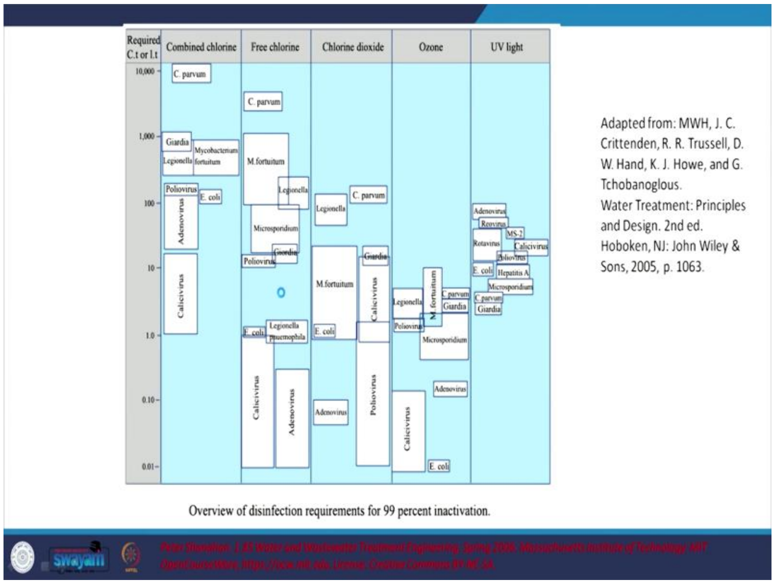

Overview of disinfection requirements for 99 percent inactivation.

Adapted from: MWH, J. C. Crittenden, R. R. Trussell, D. W. Hand, K. J. Howe, and G. Tchobanoglous. Water Treatment: Principles and Design. 2nd ed. Hoboken, NJ: John Wiley & Sons, 2005, p. 1063.

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 that is what we saw here so typically in India we look at chlorination free chlorine but its effectiveness st Giardia and cryptosporidium is relatively limited cryptosporidium we have some think microsporidium listed here. But the effectiveness is pretty limited and why, are they of interest because they can cause diarrhea which is one of the leading cause of diseases not diseases deaths in India.

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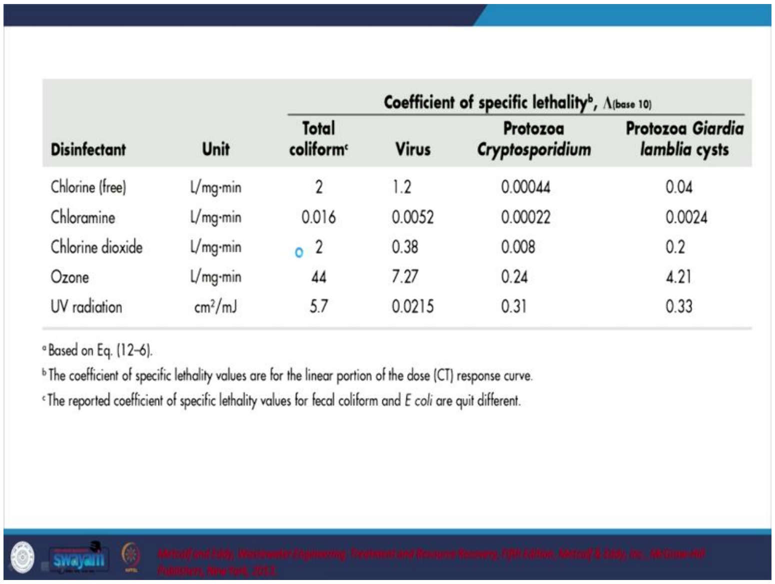

Disinfectant	Unit	Coefficient of specific lethality[b], $\Lambda_{(\text{base }10)}$ Total coliform[c]	Virus	Protozoa *Cryptosporidium*	Protozoa *Giardia lamblia* cysts
Chlorine (free)	L/mg·min	2	1.2	0.00044	0.04
Chloramine	L/mg·min	0.016	0.0052	0.00022	0.0024
Chlorine dioxide	L/mg·min	2	0.38	0.008	0.2
Ozone	L/mg·min	44	7.27	0.24	4.21
UV radiation	cm²/mJ	5.7	0.0215	0.31	0.33

[a] Based on Eq. (12–6).
[b] The coefficient of specific lethality values are for the linear portion of the dose (CT) response curve.
[c] The reported coefficient of specific lethality values for fecal coliform and *E coli* are quit different.

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

So here we have another table from Metcalf and Eddie and here we have the different disinfectants the units. Units here are milligrams per liter so concentration mass per volume and time. So these are Ct values. Only for UV radiation we do we have different values because it is intensity into time so that is what we have to look at. So what else we have here we have different types of microorganisms of interest total coliform why or when did we come across total coliform I think we looked at this in the context of water quality.

Total coliform will give us an idea about the quality of the water but in what sense? In the sense that they are indicator organisms for microorganisms or pathogens that can or live in the intestines of warm blooded animals. So it will give us an idea about contamination due to human feces . But total coliform is what we say having different sets of coliform. If you want to look at feces contaminations basically we look at fecal coliform.

But in general total coliform is also fine for wastewater and here we have coefficient of lethality to the base 10 but we will not look at that in detail, just let us look at the numbers for now. So for total coliform we see that ozone and UV are doing pretty well but chloramines in general I think we also looked at this graph. Combined chlorine you need a lot of time with respect to combined chlorine.

And also they are relatively what we say limited in effectiveness and also that is what you see here much more time and concentration are required . So that is what you see it is consistently poor faring poorly. And these are the protozoa or pathogens that I talked about cryptosporidium and Giardia. So with respect to chlorine which is widely used it does well st viruses.

Coliform we do not discuss that a lot but does not do well st protozoa or like cryptosporidium and Siardia so that is what you see here. So that is of concern to us but it does well st viruses. Chlorine dioxide decent effectiveness but it is not great though that is what you see decent but not great it is not as poor as chloramine. But with respect to ozone you see that in general it is much better than all the other oxidizing agents.

UV , but with respect to virus it has limited looks like it has limited effectiveness but it depends on the kind of virus and the type of RNA that it has. But with respect to fecal coliform and cryptosporidium and Giardia you see that it does pretty well. So the choice will depend upon what you are trying to achieve what is prevalent in that waste water or water and so forth.

But there is no one particular agent that is effective st everything. But in general if you are thinking about viruses and you do not have a lot of money to spend chlorine but this is in water. Why I want to mention this here is you would have seen I mean this is the age of or at least this year is 2020 and people spraying HOCl or chlorine dioxide (ClO_2) are a solution of or a solution of HOCl or OCl^- they put it in a tanker put it like as if it is an insect side spray tank.

Put it inside an insect side spray tank and then they spray it you would have seen that. But I mean think of how dumb it is. Firstly you do not know when he prepared the solution it is going to decay the oxidizing agent the capacity or the effectiveness will decay typically they would have used ClO_2 or HOCl and OCl^- or some form of chlorine it is going to decay it is an oxidizing agent.

And then actually what is it that we are trying to kill this is air the air and I have corona positive and I have breathe in this air and I leave it when they say disinfection what can you really do can you clean this all the air in this 10 by 10 room. It is not feasible even when you spray you are just throwing out mist well that go and come in contact with the particular virus and then oxidize it no it is not going to happen.

But why do people do that well people do not listen to science people do that for a lot of reasons typically to pacify the population to show that people are doing or the people in charge are doing something. For example a more effective way would be to see the areas that I have been touching or coming in contact use a solvent and then wipe those areas the door knob .

But no they come and spray with the spray you do not really catch the entire area or the oxidant is limited to only those droplets. So people act in weird ways I wanted to mention that aspect here.

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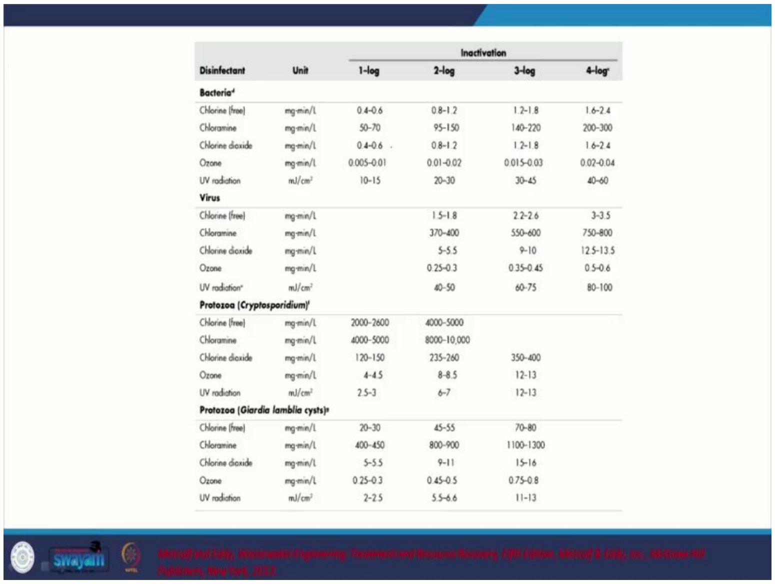

Disinfectant	Unit	Inactivation 1-log	2-log	3-log	4-log[c]
Bacteria[d]					
Chlorine (free)	mg·min/L	0.4–0.6	0.8–1.2	1.2–1.8	1.6–2.4
Chloramine	mg·min/L	50–70	95–150	140–220	200–300
Chlorine dioxide	mg·min/L	0.4–0.6	0.8–1.2	1.2–1.8	1.6–2.4
Ozone	mg·min/L	0.005–0.01	0.01–0.02	0.015–0.03	0.02–0.04
UV radiation	mJ/cm^2	10–15	20–30	30–45	40–60
Virus					
Chlorine (free)	mg·min/L		1.5–1.8	2.2–2.6	3–3.5
Chloramine	mg·min/L		370–400	550–600	750–800
Chlorine dioxide	mg·min/L		5–5.5	9–10	12.5–13.5
Ozone	mg·min/L		0.25–0.3	0.35–0.45	0.5–0.6
UV radiation[e]	mJ/cm^2		40–50	60–75	80–100
Protozoa (*Cryptosporidium*)[f]					
Chlorine (free)	mg·min/L	2000–2600	4000–5000		
Chloramine	mg·min/L	4000–5000	8000–10,000		
Chlorine dioxide	mg·min/L	120–150	235–260	350–400	
Ozone	mg·min/L	4–4.5	8–8.5	12–13	
UV radiation	mJ/cm^2	2.5–3	6–7	12–13	
Protozoa (*Giardia lamblia* cysts)[g]					
Chlorine (free)	mg·min/L	20–30	45–55	70–80	
Chloramine	mg·min/L	400–450	800–900	1100–1300	
Chlorine dioxide	mg·min/L	5–5.5	9–11	15–16	
Ozone	mg·min/L	0.25–0.3	0.45–0.5	0.75–0.8	
UV radiation	mJ/cm^2	2–2.5	5.5–6.6	11–13	

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

Come back so just to understand the kind of doses that are required here we have the disinfectant. Disinfectant is listed st the kinds of pathogens that we want to kill different types of protozoa that can lead to or will lead to diarrheal diseases or diarrhea and virus and bacteria . And here we have different levels of inactivation. So for; log meaning 99.99% removal .

So it depends on whether it is used for waste water or for water so let us not go into that now. So with respect to virus we know that chlorine is decently effective. So even at relatively low dose it is milligram per liter a minute. So this is Ct value the units are Ct values you see that you can kill the viruses. Chloramine not very effective and that is why you see a lot of very high Ct values required and with respect to ozone very effective or remarkably strong oxidizing agents.

So you see remarkably less Ct values and UV to we see this. And in the context of the cryptosporidium or the protozoa both the protozoa we see that chlorine not really effective you see that it is remarkably high value of Ct that you require. But with respect to ozone and UV, yes you can achieve that. Same case with respect to protozoa so; that is something to give you an idea about. So in general if you are trying to kill only viruses as you can see that is fine but if you are trying to look at diarrheal diseases just acting adding chlorine at the usual amounts to kill virus will be of no use.

So that is something to keep in mind. So in general with bacteria we will not go there but I wanted to compare this so that you can look at the actual or get an idea about the kind of values that are required. So this is one of the reasons why some of our water distribution networks still do not cut down on the relevant transmission of protozoa or such. So that is something to keep in mind.

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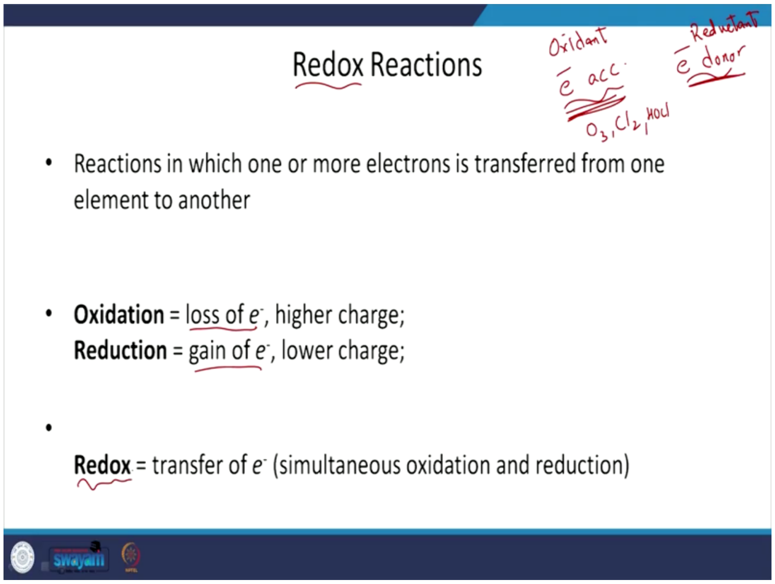

Redox Reactions

Oxidant

$\bar{e}$ acc.

O_3, Cl_2, HOCl

Reductant

$\bar{e}$ donor

- Reactions in which one or more electrons is transferred from one element to another
- **Oxidation** = loss of e^-, higher charge;
  Reduction = gain of e^-, lower charge;
- **Redox** = transfer of e^- (simultaneous oxidation and reduction)

So redox reactions I wanted to discuss this because we have been talking a lot about oxidizing agent and so forth. Oxidizing agent what is it, it is an electron acceptor but electrons do not float around freely not in the solution not in the air. So unlike H^+ they do not float around so it has to be a direct collision between compound A and compound B for the electron to be transferred. So if I am an electron acceptor I also need an electron donor only then will the relevant reaction go through. So we are going to have an electron donor.

So oxidizing agent or oxidant and reducing agent . So let us look at that. So in redox reactions we have one or more electrons being transferred from one element to the other it is a transfer of electrons. Oxidation is the loss of electrons when we say compound is being oxidized it means that there has been a loss of electrons. And when its reduction it is a gain of electrons keep in mind that here we say it is an oxidant.

When it is an electron acceptor so here we have O_3; Cl_2; HOCl. Electron donor is a reducing agent a reductant will reduce the other compound while being oxidized . So that is one aspect to consider so that is what we have to look at. But oxidation and reduction they do not happen what do you say independent of each other. When we are talking about oxidation certainly reduction will happen why because you cannot have what we say electrons only going in one direction.

if I need and I will have an electron donor I need an electron acceptor also. So only when you have both oxidation and reduction occurring will you have redox reactions . So it is not as if oxidation will occur in or being independently of reduction but when we do when do we say oxidation. For example we were talking about organic compounds. So I am talking about oxidation there.

So why am I calling it oxidation because my compound of interest which is the wastewater or the body or the organic content is being oxidized. So that is why I am calling it as oxidation. But for that I need an electron acceptor which is oxygen. Oxygen is taking the electron from the organic matter and it is being reduced . , so let us not go there if you are confused you can just look at it twice.

But in general if I gain an electron, electron has a negative charge so the charge on that particular element will decrease. So reduction in the charge maybe that is where you can try to understand it, let us move forward.

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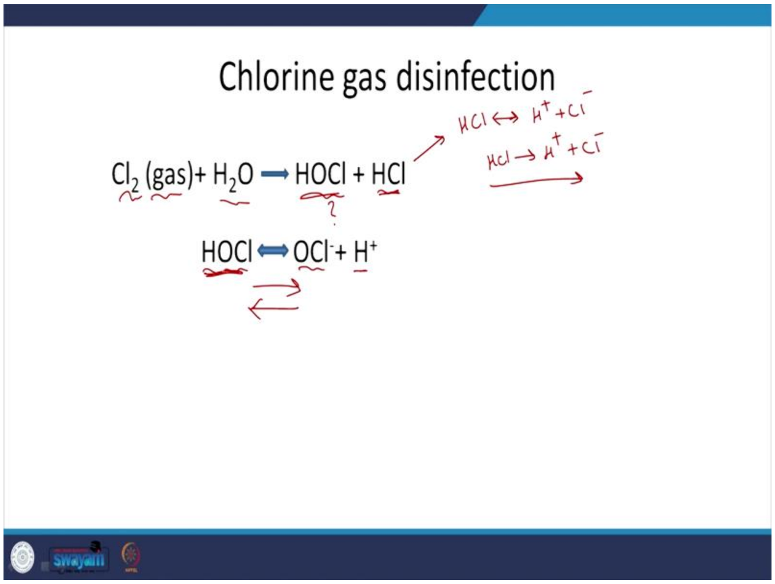

Chlorine gas disinfection

$Cl_2\ (gas) + H_2O \rightarrow \underset{?}{HOCl} + HCl$

$HCl \leftrightarrow H^+ + Cl^-$

$HCl \rightarrow H^+ + Cl^-$

$HOCl \Leftrightarrow OCl^- + H^+$

So chlorine gas once I bubble this chlorine gas or dissolve that in water it will go ahead and form HOCl and HCl, HCl will typically never stay as HCl it will go to though it can be like this H^+, Cl^-. HCl being a very strong acid will go to H^+ and Cl^- and stay like that always. Why we will look at that later but what will happen to this HOCl. Unlike HCl it is not a strong acid we will see what it means when we say it is a strong acid or a weak acid.

So HOCl will be in equilibrium with OCl minus and H^+ so this will can go this way or this way , yes but in general HCl will always dissociate but with HOCl we know that it will be in equilibrium with OCl^-. So it is not a very strong acid but it is a strong oxidizing agent HOCl is a strong oxidizing agent. We will look at these aspects.

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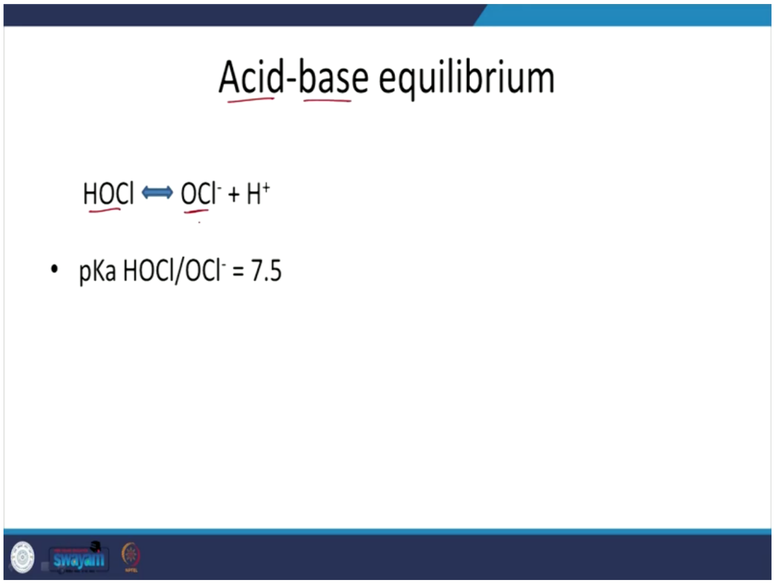

Acid-base equilibrium

$HOCl \Longleftrightarrow OCl^- + H^+$

- pKa $HOCl/OCl^-$ = 7.5

So here we have an acid HOCl and a base OCl^- what is an acid? Acid is one which can give out a proton what is an OCl base what is a base? A base is one which can accept H^+. So that is one aspect so pKa which will give me an idea about how strong the acid is or not is called the acid dissociation constant. It is called the acid dissociation constant so that is what we have.

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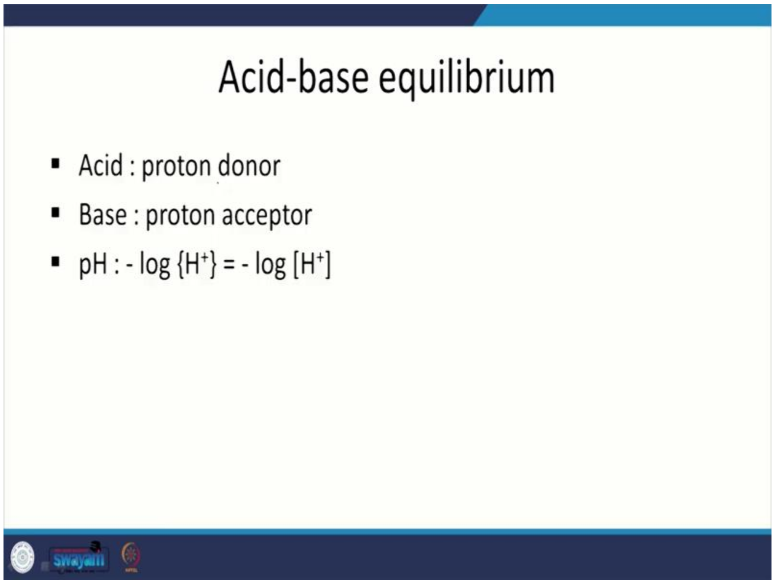

Acid-base equilibrium

- Acid : proton donor
- Base : proton acceptor
- pH : $- \log \{H^+\} = - \log [H^+]$

How or where will I get that from let me see that I have other aspects to mention some terms here. So we have acid HOCl is an acid. So what is the property of an acid it is a proton donor it can give out a proton H^+ and what is OCl^-? It is a base and what is its property? It is it can take up a proton, so it is a proton acceptor , so that is something to keep in mind. Acid donors are something that can donate the acid and thus by releasing H plus you are going to bring down the pH of the solution add an acid if it can dissociate and release the H^+ it will bring down the pH of the solution.

OCl minus on the other hand by taking up the H^+ or removing H^+ from my solution will increase the pH what is pH? I already have it here pH is the negative log activity of H^+ but discussion about activity is a bit too advanced for this course. So we will assume that activity can be approximated by concentration of the relevant compound or element here or ion here pardon me.

So what do we have here we see that pH equal to negative log H plus. So if I increase H^+ which is the case when I add an acid you will see that my pH will decrease. But by adding a base if I remove H^+ or I decrease H^+ what will happen the pH will increase. So when the pH decreases it is called the solution is called acidic and when the pH increases the solution is called basic but the reference is 7.

So pH 7 we say that the water is neutral why is that range of H^+ 0 to 14 H^+ is equal to 10^{-7}. So then we say that the water is neutral so pH is equal to 7 so in this range it is basic in this range it is acidic . So, general or some aspects.

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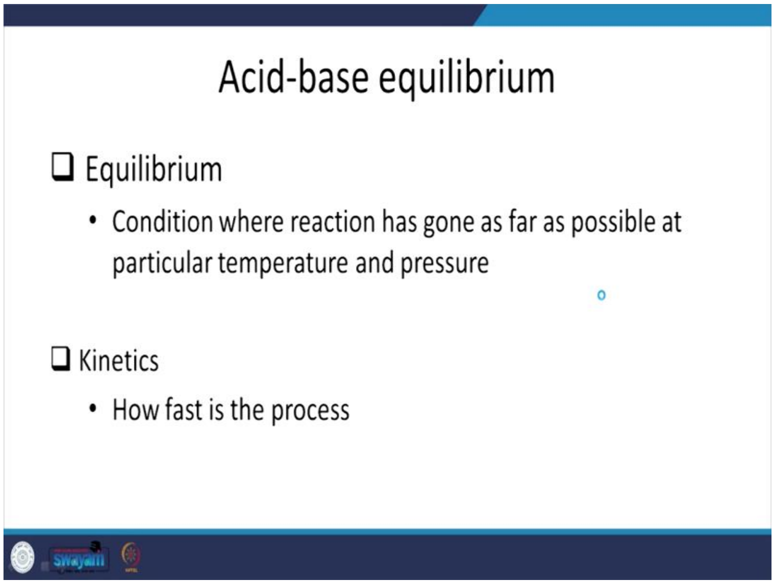

Acid-base equilibrium

❑ Equilibrium
  - Condition where reaction has gone as far as possible at particular temperature and pressure

❑ Kinetics
  - How fast is the process

So two aspects here we need to understand equilibrium acid base equilibrium. When we say equilibrium we are talking about the state of the system. Let me not get too technical but state of the system it to use layman's terms it will tell me how far the system can go . And in that context kinetics will tell me how fast is the system going? , yes so kinetics will tell me how fast the system is going or the process is going.

And equilibrium will tell me given enough time for the relevant temperature and pressure how far the state can the system go. So in general acid base reactions the kinetics are very fast that is why almost always acid base equilibrium is achieved. This is not the case for redox reactions for example you saw in the wastewater what we see relevant aspects with respect to activated sludge process we are giving it considerable time it meaning the redox reaction of organic matter being oxidized by oxygen that is a redox process.

Their kinetics is relatively slow that is why time comes into the picture. But here in acid base equilibrium is always reached why kinetics is pretty fast . So that is something to keep in mind.

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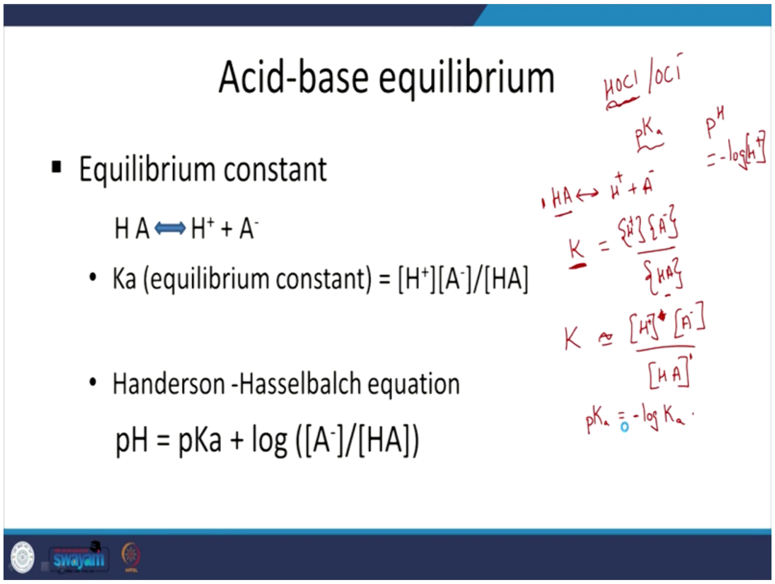

Acid-base equilibrium

- Equilibrium constant

  $HA \Longleftrightarrow H^{+} + A^{-}$

  - Ka (equilibrium constant) = $[H^{+}][A^{-}]/[HA]$
  - Handerson -Hasselbalch equation

  pH = pKa + log ($[A^{-}]/[HA]$)

$HOCl / OCl^{-}$

pK_a

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

$HA \leftrightarrow H^{+} + A^{-}$

$$K = \frac{\{H^{+}\}\{A^{-}\}}{\{HA\}}$$

$$K \approx \frac{[H^{+}][A^{-}]}{[HA]}$$

$pK_a = -\log K_a$

So acid-base equilibrium we will just look at that because we want to understand this concept of HOCl, OCl^{-} because we know that HOCl is much more, stronger oxidizing agent compared to OCl virus here HOCl is an acid and also a strong oxidizing agent. So equilibrium constant for example we spoke about pKa acid dissociation constant and that it gives us an idea about the strength of the acid. what it is or how it comes about.

For any reaction or let me say for this reaction of acid dissociation into H^+ and its deprotonated form which is the base. We will have a equilibrium constant capital K that will give me an idea about or is we depend upon this is equilibrium constant. So it is only applicable when the system is at equilibrium B is equal to activity of H^+ activity of A minus by activity of the reactants rise to their stoichiometric coefficients because the reactant is only HA, I am going to have only HA.

$HA \Longleftrightarrow H^+ + A^-$

$$k = \frac{[H^+][A^-]}{[HA]}$$

Here in this class we are not going to use activities. So we are going to approximate it by concentration of H plus concentration of A minus by concentration of HA. So if it was 2HA then it would have been HA square $[HA]^2$, but that is not what we are looking at. The stoichiometric quotient is only one so that is why it is raised to one. Same case with H^+ and A^-. So this is called the equilibrium constant. It will tell me once the system is at equilibrium what is the situation or scenario going to look like .

Given enough time for the system to reach equilibrium what will it look like. So this is the equilibrium constant. So pKa similar to pH, pH is minus log concentration of H plus;
pH = $-\log[H^+]$, so pKa is also equal to minus log ka; pka = $-\log[ka]$. So how we can get that do I have a back side here, yes I do. So what do I have here? I have HA.

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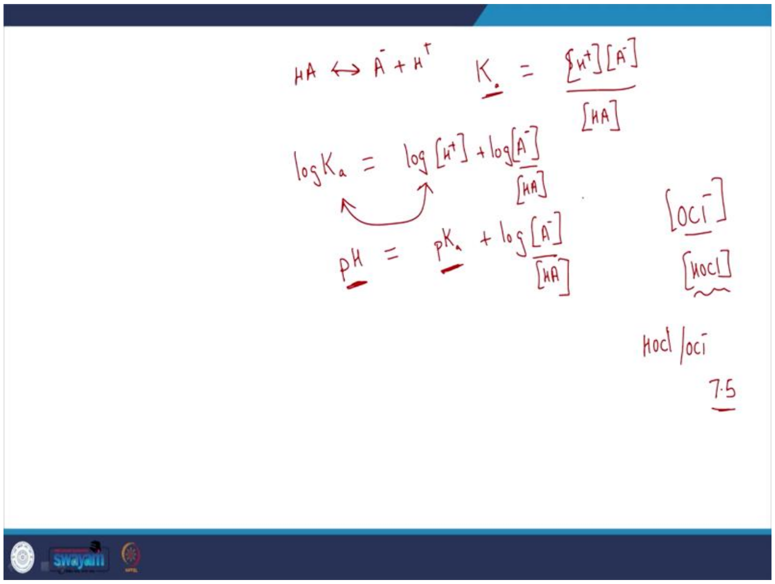

$HA \leftrightarrow \bar{A} + H^+$

$$\underline{K_{\cdot}} = \frac{[H^+][\bar{A}]}{[HA]}$$

$$\log K_a = \log[H^+] + \log\frac{[\bar{A}]}{[HA]}$$

$$\underline{pH} = \underline{pK_a} + \log\frac{[\bar{A}]}{[HA]}$$

$$\frac{[\underline{OCl^-}]}{[HOCl]}$$

$HOCl/O\bar{C}l$

$\underline{7.5}$

And this will be in equilibrium with its deprotoned form the base and the proton. Why am I saying deprotonated because it is releasing its proton so for this the equilibrium constant k is or k a is concentration of H plus products by the reactants. So if I take the logarithm on both the sides log k a will be equal to log $[H^+]$log$[A]^-$ by log HA. I am not taking this out because I want to leave it as a ratio.

$$logk_a = \log[H^+] + log\frac{[A^-]}{[HA]}$$

So if I swap both these terms this will become minus log H plus this will become minus log k but minus log H plus is pH. So I know that pH will be depend upon -log [ka] is pka which is the acid dissociation constant plus log of $[A^-]$/ log[HA]. So the ratio of this OCl^- and HOCl which I am concerned about. Why am I concerned about? I want more HOCl because that is a stronger oxidizing agent, so that is something to keep in mind.

Will be depend upon the constant which is the depend upon k or the acid dissociation constant and the pH of the solution. So this is a constant I know that for the this particular system of HOCl and OCl^- the pk a is 7.5. So I know this so depending on the pH, I can calculate the ratio of A^- and HA. And also if I plot this on a graph I can see how the system is going to behave do I have a graph here.

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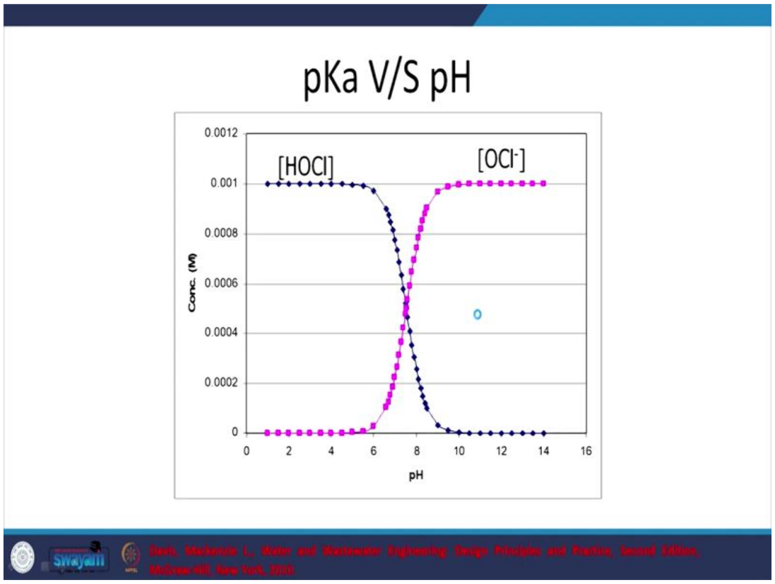

pKa V/S pH

Davis, Mackenzie L., Water and Wastewater Engineering: Design Principles and Practice, Second Edition, McGraw-Hill, New York, 2010.

Yes, I have this graph here. So what do we have on this x axis I have the pH as we mentioned the pKa will be 7.5 we'll come back to that and on the y axis I have the concentration . And initially added in this example I assume that initially I added $HOCl_0$ at the case when the pH is pretty low I sought with that $HOCl_0$ is this is molar concentration. So 0.001 molar equal to 1 milli molar.

And this pH was at 2 we see that most of it is as HOCl itself and little OCl^-. And if I start increasing the pH by adding any base OH^-. So what is going to happen until it reaches a particular pH which is around 6.5 as you can see there is not going to be not 6.5, 5.5 there is not going to be much change in HOCl everything is going to stay as HOCl.

But as I keep increasing the pH we see that the concentration of HOCl is decreasing but simultaneously the concentration of OCl^- is increasing. Note that the total OCl, OCl total which I am representing as $HOCl^+$; OCl^- is still the same which is 1 milli molar it is only that whatever was only present as HOCl now is present in both forms of HOCl and OCl^-. As HOCl is decreasing OCl^- is increasing.

At a particular point both HOCl and OCl^- concentration are the same and let us mark that here did not come out well so somewhere out here. And as I keep increasing it further OCl^- it meaning as I keep increasing the pH further we see that this particular OCl^- concentration keeps increasing and HOCl keeps decreasing until after a certain pH most of it is only present as OCl^-. So how is this happening?

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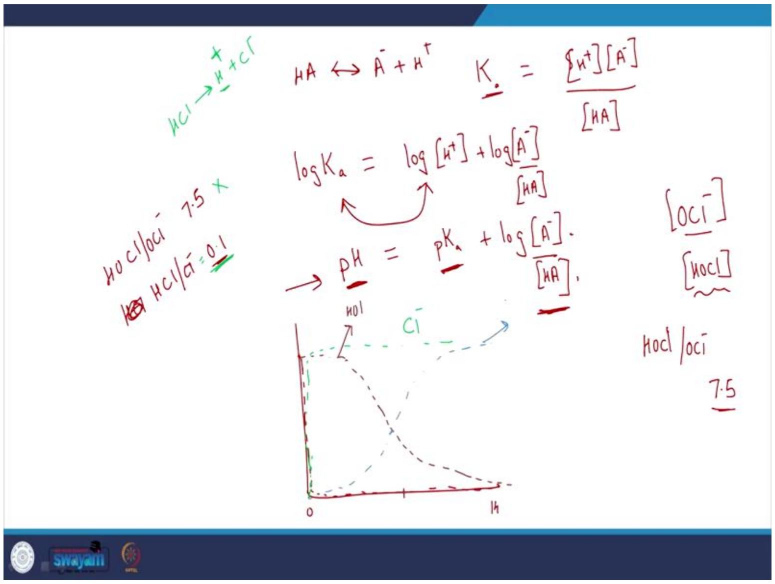

$HCl \rightarrow H^+ + Cl^-$

$HA \leftrightarrow A^- + H^+$

$K_a = \frac{[H^+][A^-]}{[HA]}$

$\log K_a = \log [H^+] + \log \frac{[A^-]}{[HA]}$

$\rightarrow pH = pK_a + \log \frac{[A^-]}{[HA]}$

$HOCl/OCl^-$ 7.5

$HCl/Cl^- = 0.1$

$\frac{[OCl^-]}{[HOCl]}$

$HOCl/OCl^-$

7.5

Let us look at what we have or how we came up with this so this equation that we derived earlier this is called the Henderson-Hasselbach equation. So, a first thing first when is the concentration of A minus and HA is going to be equal. what is this point at which the concentration of HOCl was equal to the concentration of OCl^- what is this point. As you can see here the only time when a minus will be equal to HA is when pH is equal to pKa so that is what you see.

So when pH of the solution is equal to the pKa of the acid and the pKa of this particular acid as I told you was 7.5 or around 7.5, pKa is equal to 7.5 you will see that when the pH is equal to 7.5 meaning it is equal to pKa. We will see that as predicted by our equation both the base and the acid or the deprotonated and protonated forms are going to be at the same concentration. So, why was I calling HOCl not a strong acid but why was it calling HCl a strong acid. Let us look at this. For example for HCl the pKa is native or for example for purposes of illustration take it to be 0.1 and for HOCl the pKa was 7.5 HOCl, OCl^- , the pKa was 7.5 for HCl and Cl^- the pKa was 0.1.

Let me try to draw this graph with HCl, Cl^- so 0, 14. So, what does this mean if it is 0.1 it means that for almost all the range of pH as soon as I add HCl it is going to deprotonate and stay as and stay as Cl^- meaning it will almost always give out the H^+. So at any pH it will give out its H^+

meaning it is a very strong acid. Please note that pKa is not 0.1 it is negative or less than zero. So at all practical pH of water whenever you add acid HCl will always dissociate to give H plus and Cl minus.

So thereby decreasing the pH of the water but that is not the case with HOCl we will see that particular information to here . Let me try to find under for HOCl I know that the pKa is around somewhere here. So for most of the range the HOCl will be something like this and this is HOCl and let me try another color so only at this point will it be equal OCl^-. So this point is 7.5. So as we see at pH of 3 all the HOCl is staying as HOCl.

So that is what we also see here at pH 3; pH 4 maybe even pH 5 what is it staying as HOCl is staying as HOCl it is not giving out its H^+. So it will not affect the pH so that is something to keep in mind. So by looking at the pKa we can tell whether it is a strong acid or a weak acid do I digress I think it is relevant in this context. Why is that because 7.5 is the pKa of this HOCl and OCl^-.

And why am I concerned about that because HOCl is a much stronger oxidizing agent than OCl^-. So if I can say the pKa, pH such that I have more of the HOCl so I will have a greater disinfection capacity in my particular disinfecting tank. So that is one aspect to consider.

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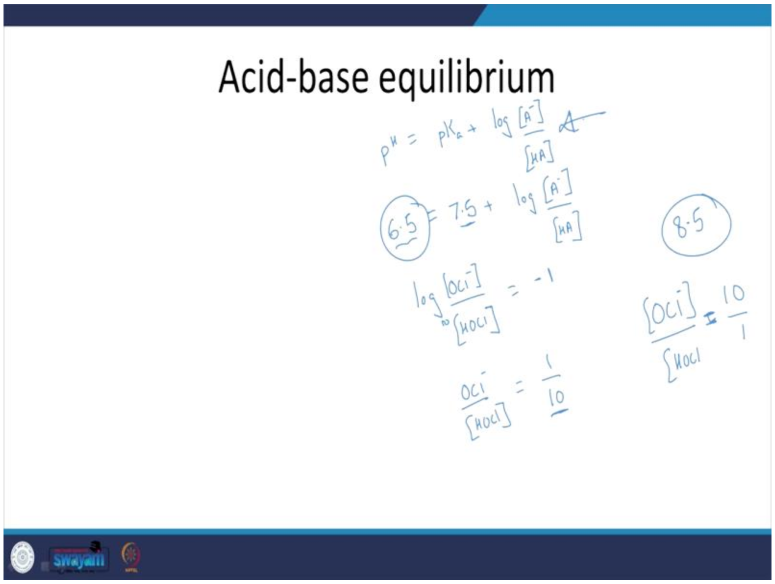

Acid-base equilibrium

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$\boxed{6.5} = 7.5 + \log\frac{[A^-]}{[HA]}$$

$$\log\frac{[OCl^-]}{[HOCl]} = -1$$

$$\frac{OCl^-}{[HOCl]} = \frac{1}{10}$$

$$\boxed{8.5}$$

$$\frac{[OCl^-]}{[HOCl} = \frac{10}{1}$$

So let us move on acid-base equilibrium we just covered most of that aspect. So another aspect to consider is that pH is equal to pKa + log of the deprotonated form by the protonated form.

$$pH = pk_a + log\frac{[A^-]}{[HA]}$$

So I know that the pKa for my system is 7.5 and it is $[A^-]$ by [HA] and if the pH is 6.5 what will this turn out to be? Log of OCl^- by HOCl will be equal to 6.5 - 7.5 = -1 so OCl^- by HOCl will be equal to 10^{-1} or 1 by 10 logarithm, I take the 10 log them to the base 10 so I take it up 10^{-1} or 1 by 10.

So at pH of 6.5 you see that most of the solution will stay as HOCl but at the pH of 8.5 which is one unit greater than 7.5 this situation will be reversed. At that place or at that pH most of it will be present as OCl^-. So you see the key role that pH plays and that is why we had to look at that Henderson Hassleback equation. So let me move on.

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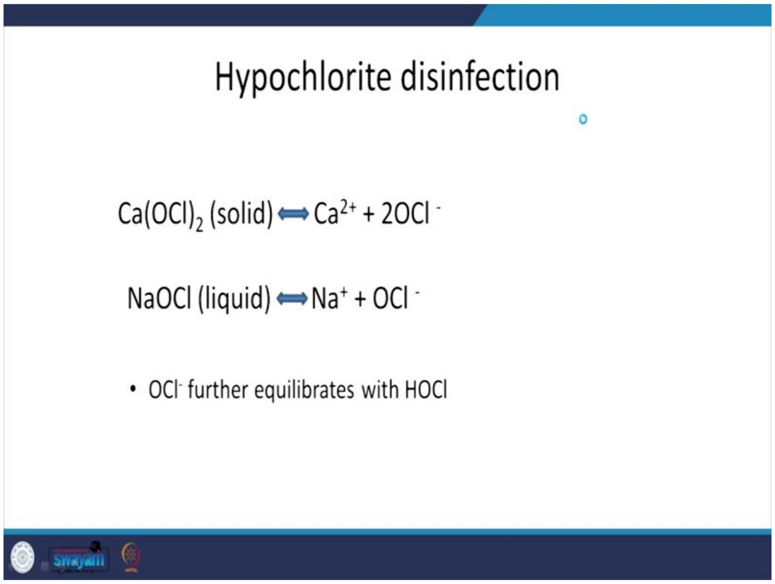

Hypochlorite disinfection

$Ca(OCl)_2$ (solid) $\Longleftrightarrow Ca^{2+} + 2OCl^-$

NaOCl (liquid) $\Longleftrightarrow Na^+ + OCl^-$

- OCl^- further equilibrates with HOCl

So we looked at addition of Cl_2 we can also get this OCl^- in different forms it can be added as Ca OCl 2 solid or a liquid and then you can change the pH so that you have enough HOCl here and as we discussed so different forms of oxidizing agent addition.

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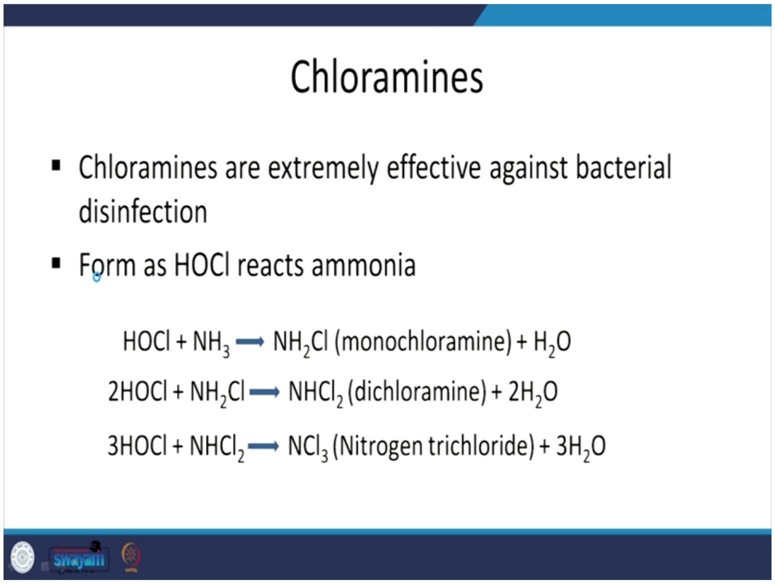

Chloramines

- Chloramines are extremely effective against bacterial disinfection
- Form as HOCl reacts ammonia

$HOCl + NH_3 \rightarrow NH_2Cl$ (monochloramine) $+ H_2O$

$2HOCl + NH_2Cl \rightarrow NHCl_2$ (dichloramine) $+ 2H_2O$

$3HOCl + NHCl_2 \rightarrow NCl_3$ (Nitrogen trichloride) $+ 3H_2O$

So chloramines these are what we call as combined chlorines these are in general effective st bacterial are effective for bacterial disinfection . They form HOCl they form as HOCl reacts with ammonia. These are the combined not these are the combined chlorines that we were talking about chloramines. So these are also sometimes added but not a lot.

So , HOCl reacting with NH_3 gets you these monochloramines or dichloramines but we will look at that later. But we saw that their effectiveness st viruses and the protozoa was remarkably low.

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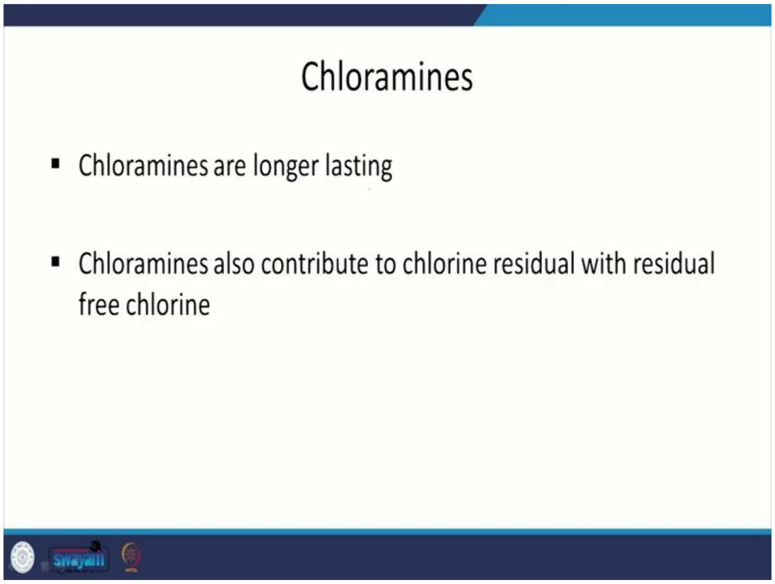

Chloramines

- Chloramines are longer lasting
- Chloramines also contribute to chlorine residual with residual free chlorine

So chloramines are longer lasting so they can be used as a residual disinfecting agent. So if you do not want to have a lot of them added initially chloramines but you can use that as a residual disinfecting agent . That is why we say they contribute to chlorine residual let us move back to that or come back to that later.

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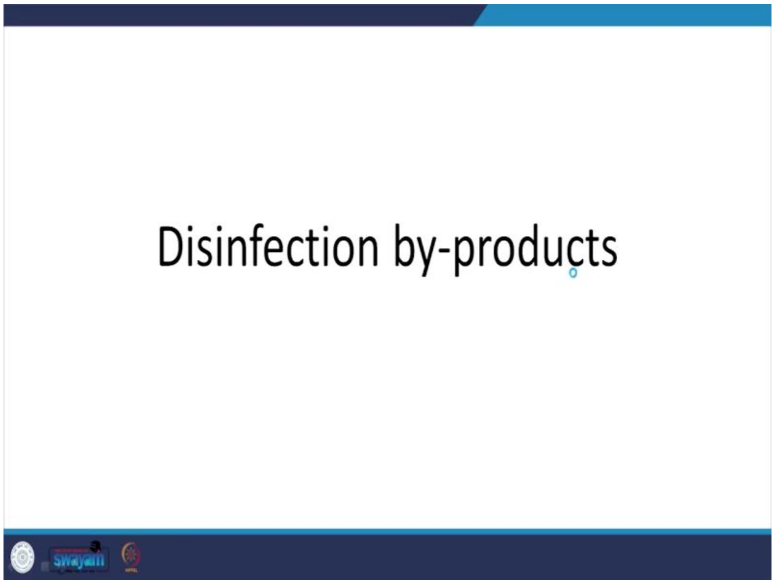

Disinfection by-products

So we discussed this briefly disinfection byproducts when we add Cl_2 or chloramines two in a way or HOCl and OCl^- you can form these toxic by-products which are called disinfection byproducts. Let us look at that briefly before we end today's session how are they formed? For example you have this Yamuna it is pretty polluted downstream of Delhi. Even in other places when it is not polluted due to human reasons or causes you are going to have water coming in contact with dead leaves dead aquatic life for dead plants .

So these leaves they are organic matter everything life cells are organic matter. So they change phase or they leach into the water. So now you have organic matter dissolved in the water.

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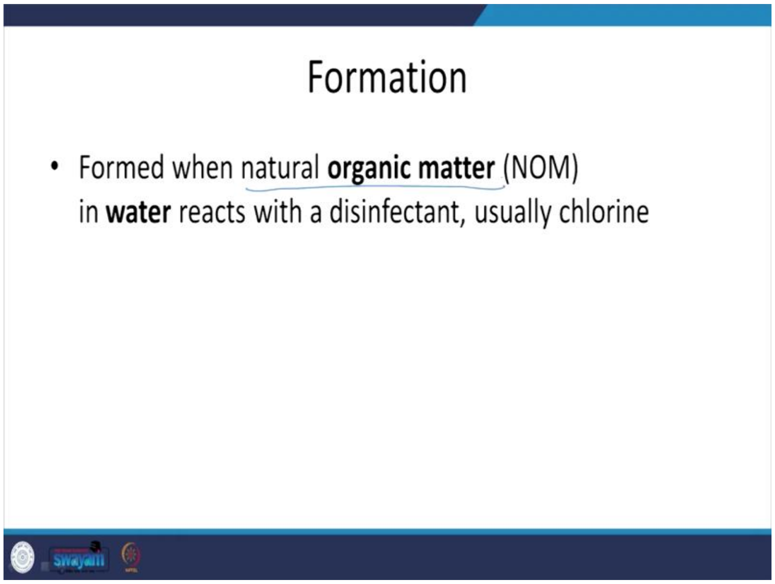

Formation

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

So this is called natural organic matter and depending on the size it is also referred to as dissolved organic matter . And this natural organic matter in water reacts with disinfectant especially chlorine and forms disinfection byproducts. But I am out of time so I will continue this in the next session and as usual I thank you for your patience.