Environmental Chemistry and Microbiology

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Module - 5
Lecture - 23
Chlorine Chemistry and Disinfection (Part-A)

Welcome everyone to our online NPTEL course of Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself, Professor Anjali Pal. We are from the Civil Engineering Department, IIT Kharagpur. We have divided this course into 2 parts. The first part is Environmental Chemistry. It will be covered by myself. The second part is Environmental Microbiology. It will be taught by Professor Sudha Goel. In my first module, I have discussed about the acids, bases and salts. In the second module, I have discussed about the chemical equilibrium. In the third module, I talked about the chemical kinetics and in the fourth module, I covered the catalysts. This is my fifth module. This is my twenty third lecture. Here I will cover the chlorine chemistry and disinfection. This is the part A.

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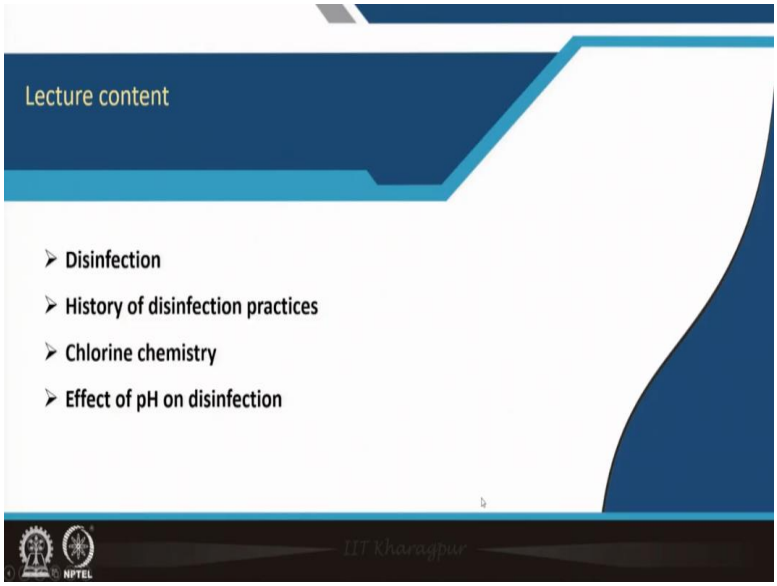

Now, in this lecture, I will cover disinfection, history of disinfection practices, chlorine chemistry and effect of pH on disinfection. We all know what is disinfection.

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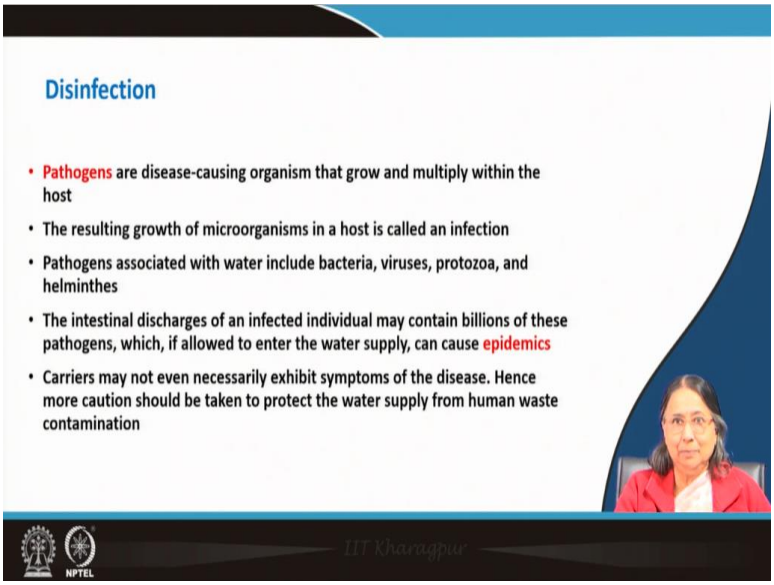

There is some difference between disinfection and sterilization. By disinfection, we kill the pathogenic bacteria (pathogenic microorganisms) and by sterilization we kill all types of microorganisms. Now, what is pathogen? Pathogens are the disease-causing organisms. They grow and multiply within the host. The resulting growth of microorganisms in a host is called the infection. Under this pandemic, that COVID situation, we all know all these things. Now pathogens associated with water include bacteria, virus, protozoa and helminthes. These things you will know much more elaborately in the environmental microbiology part with Professor Sudha Goel.

Here I will just briefly tell you about the disinfection and how we make this process with mainly chlorine and another substance. In the intestinal discharges of an infected individual may contain billions of these pathogens which if allowed to enter the water supply can cause epidemics. Now, carriers may not even necessarily exhibit symptoms. They may be asymptomatic (asymptomatic means there is no symptom). Hence more caution should be taken to protect the water. There are many diseases which are waterborne. Waterborne means water is a carrier for those diseases like typhoid, cholera etc. So, we have to protect the water in the water supply systems so that this type of contamination does not happen. Otherwise, it will create the epidemic.

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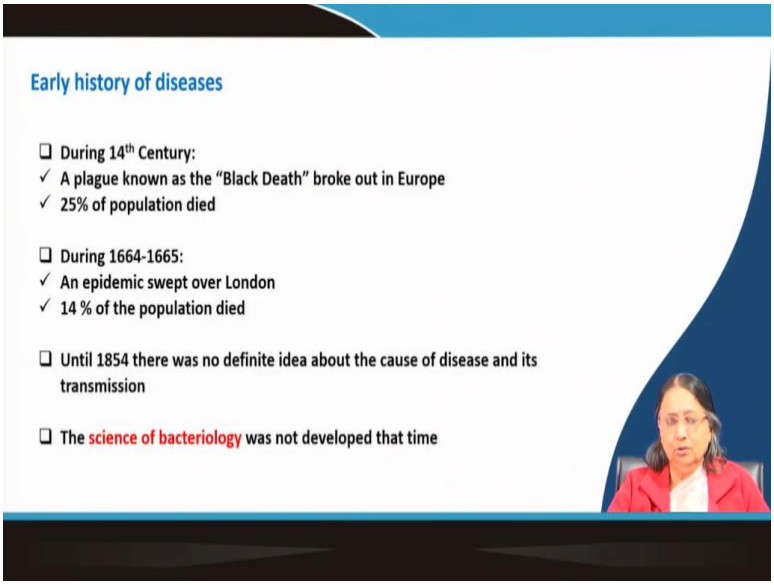

Nowadays you see that this coronavirus. It has come worldwide. But this type of thing also happened earlier. Say for example, during fourteenth century, a plague known as the Black Death broke out in Europe. 25% of the population died due to this disease. It was called plague. Now, during 1664 to 65, an epidemic swept over London. 14% of the population died. I have only talked about some but there are many such occasions. Until 1854 there was no definite idea about the cause of disease. Why this type of epidemic or plague swept over during that time? The cause was not known. How was it transmitting from person to person? That was also not known because the science of bacteriology was not developed that time.

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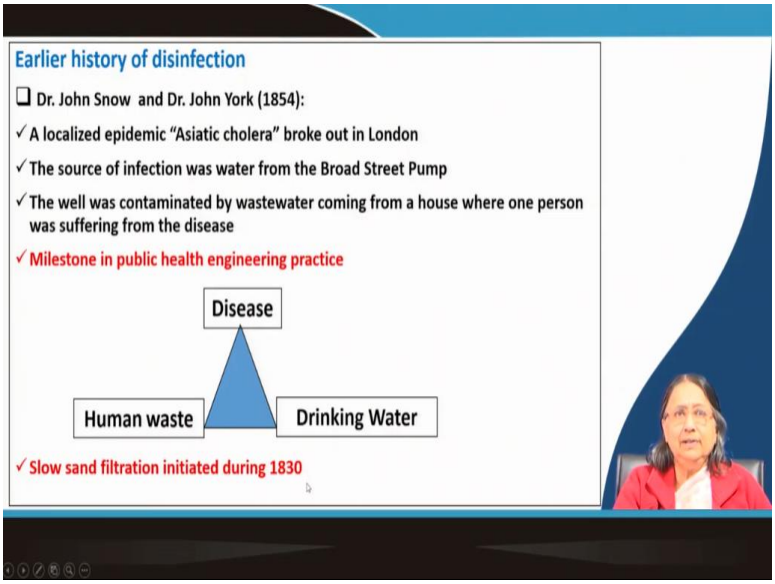

Now, let us come to the earlier history of disinfection: A localised epidemic, Asiatic cholera broke out in London. The source of infection was water from the Broad Street Pump. The well was contaminated by wastewater coming from a house where one person was suffering

from the disease. There was actually a broken sewer. From the broken sewer, this contamination entered to that pump water and the broken sewer was carrying the water from another house where one person was suffering from this disease (Asiatic cholera). Exhaustive scientific studies were done by two persons named John Snow and John York in 1854. It is realized that there is some relationship between human waste, drinking water and disease. Before that slow sand filtration was started in 1830 to purify the water.

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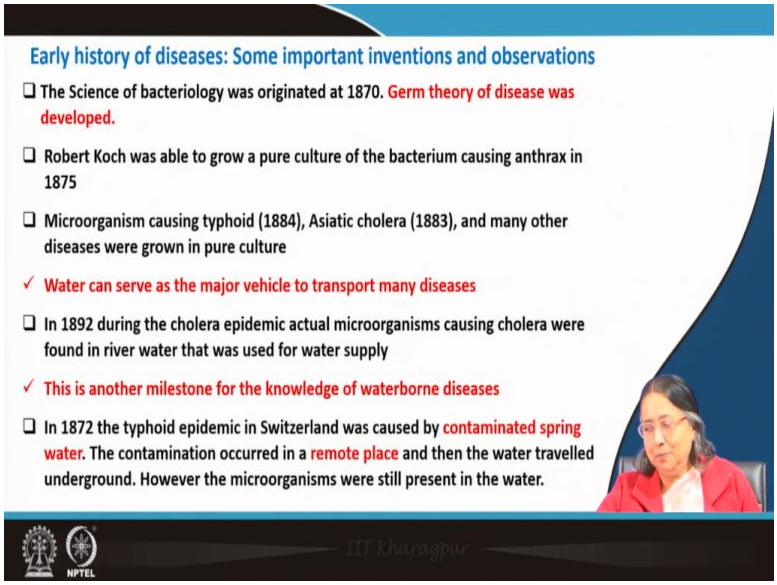

The science of bacteriology was originated at 1870. Famous person Robert Koch was able to grow a pure culture of the bacterium causing anthrax in 1875, microorganism causing typhoid in 1884 and Asiatic cholera in 1883. Microorganisms causing many other diseases were also grown in pure culture. It was also that time known that water can serve as a major vehicle to transport many diseases.

In 1892, during the cholera epidemic, actual microorganism causing cholera were found in the river water that was used for water supply. This is another milestone for the knowledge of waterborne diseases.

In 1872, the typhoid epidemic in Switzerland was caused by contaminated spring water. The contamination occurred in a remote place and then the water traveled underground. Even if the contamination source is far away, but still it is carried and then it is contaminating the water.

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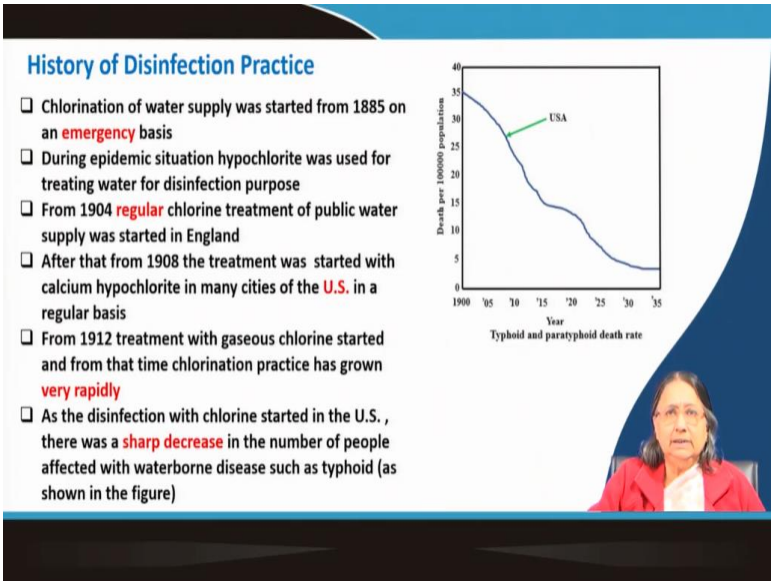

Now, it is known that, there are some microorganisms that causes the disease and we have to protect our water because otherwise waterborne disease may occur. So, what we will do? We will take up disinfection practice. What is the disinfection practice? Chlorination of water supply was started in 1885 on emergency basis. Say for example, sometimes epidemic started. So, the water was treated with chlorine on emergency basis. During epidemic situation, hypochlorite was used for treating water for disinfection purpose. From 1904, regular chlorine treatment to public water supply was started in England. So, it is no more on emergency basis. Regular practice was started. After that, from 1908, the treatment was started with calcium hypochlorite in many cities of the U.S. in a regular basis. From 1912, treatment with gaseous chlorine started. From that time, chlorination practice has grown very rapidly.

You can see here, typhoid and paratyphoid death rate from the graph in the last slide. So, you can see from 1900 to 1935 the death rate gradually decreased with respect to time. As the disinfection with chlorine started in the U.S., there was a sharp decrease in the number of people affected with waterborne disease such as typhoid (as also shown in figure of the last slide). As typhoid is a waterborne disease so, some microorganisms causing this disease is carried in the water. So, if you disinfect the water, then that microorganism will be killed. Then the water will be safe.

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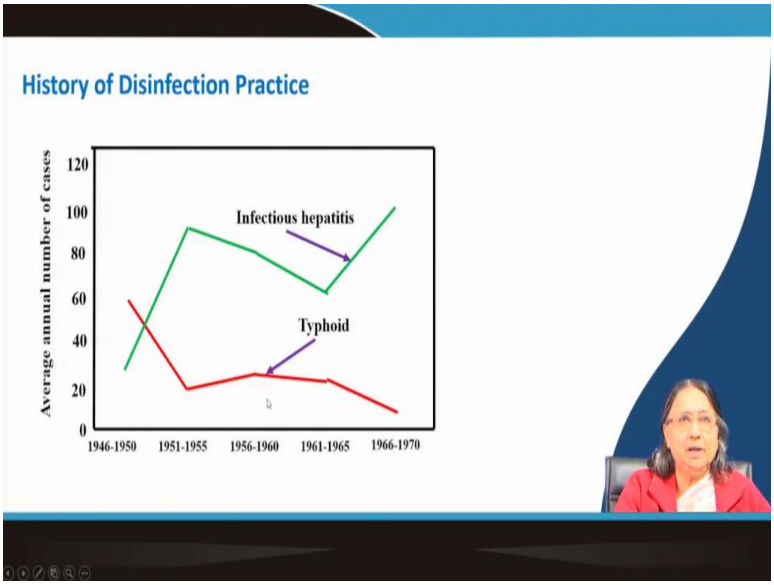

You can see that there are two types of curves in the last slide. In the graph of the typhoid, you can see it is coming down from 1946 to 1970. But hepatitis is not coming down. Why it is so? It is so because hepatitis is caused by virus. But disinfection practice is not effective to kill the virus. Typhoid is caused by bacteria. Disinfection can kill bacteria. So, it can be removed.

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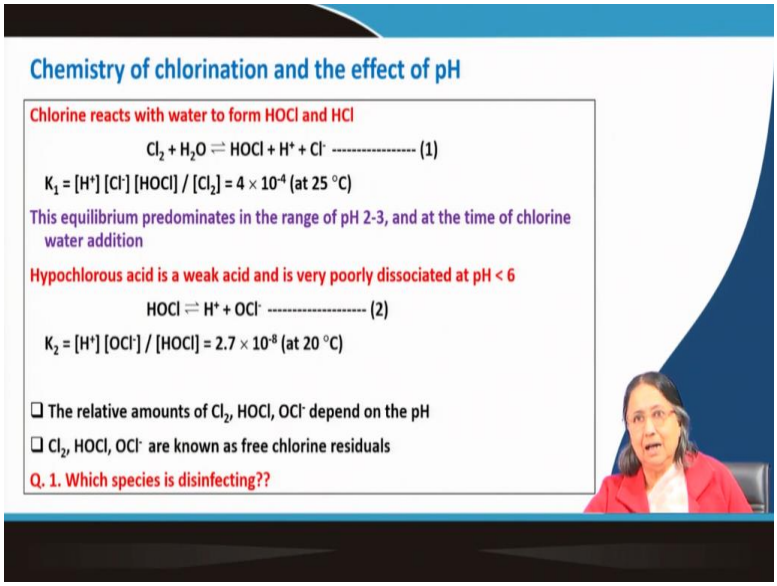

Now, let us see the chemistry of chlorination. Should we use chlorine or some other hypochlorite? What is the relation between them? Chlorine chemistry is very important, because chlorine can exist in different forms and according to pH, their concentration varies. We have learnt in our school days, that if you allow chlorine to dissolve or to allow to react with water, then it will form HCl (hydrochloric acid) and HOCl (hypochlorous acid). It is expressed as:

$Cl_2+H_2O \leftrightharpoons HOCl+H^++Cl^-$……(1)

The equilibrium constant is expressed as :

$K_1=[H^+][Cl^-][HOCl]/[Cl_2]$

The value of K_1 is 4×10^{-4} at 25°C. From this, you can easily understand that equilibrium predominates in the range of pH 2 to 3 and at the time of chlorine water addition. When you add chlorine in the water, immediate this reaction occurs and then the pH goes down. So, H^+ is produced. If you can remove the H^+, then slowly the reaction will shift towards the forward direction, is not it. If you increase the pH more and more, HOCl will be formed and chlorine concentration will reduce. Now, if you increase pH more, then another reaction will start. What is that? Hypochlorous acid (HOCl) is a weak acid. So, it is always in equilibrium with H^+ and OCl^- as shown in (2):

$HOCl \leftrightharpoons H^++OCl^-$…….(2)

The equilibrim constant is expressed as:

$K_2=[H^+][OCl^-]/[HOCl]$ and its value is 2.7×10^{-8} at 20°C.

Now again, if you can remove H^+, then more and more OCl^- will be formed from HOCl. Now, from these 2 reactions ((1) and (2)), you can easily understand that the relative amounts of chlorine HOCl and OCl^- depend on the pH. So, at low pH, chlorine will be predominating and at higher pH the HOCl will be decomposed to form the OCl^-. Cl_2, HOCl and OCl^- are all called free chlorine residuals. Now, the question is that, which species is disinfecting actually? All three are disinfecting agents, but HOCl is very efficient. We will learn more in that environmental microbiology part that how it is killing the bacteria and all.

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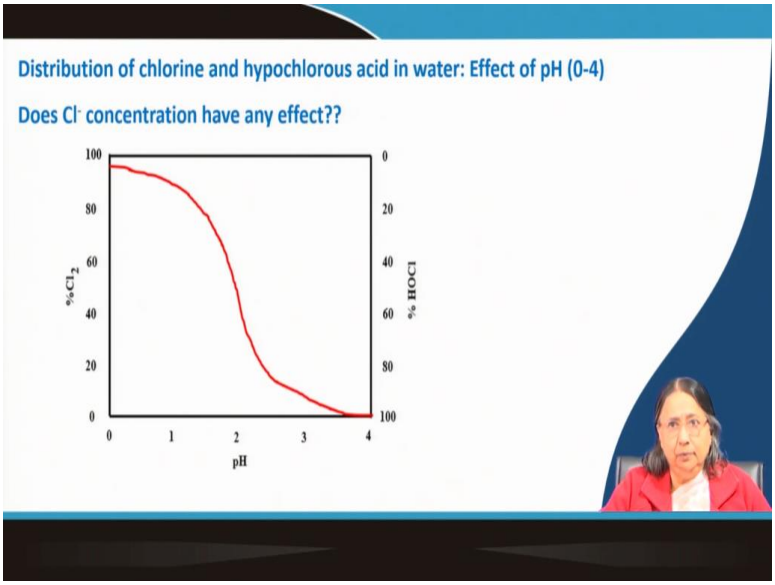

In the last slide, distribution of chlorine and hypochlorous acid with respect to the change of pH range. Let us consider (1) (pH range 0 to 4). You can see in the last slide that, percentages of chlorine and hypochlorous acid are written in opposite direction. If you go on increasing pH from 0-4 you will find chlorine percentages are getting reduced and hypochlorous acid percentages are getting increased. That means with the increase of pH, more and more HOCl are obtained. For disinfection what pH we will choose (Lower pH or higher pH or medium p H)? Also, if water has certain pH, then at that pH how effective will be the disinfection process. That is also important. There is another effect, i.e., the effect of chloride. Say, for example, if you increase the chloride concentration then what will happen? Once chloride ion is present equilibrium (1) will be shifted in this fashion. So, chlorine concentration will be more. I have not shown it, but we can draw the curve here.

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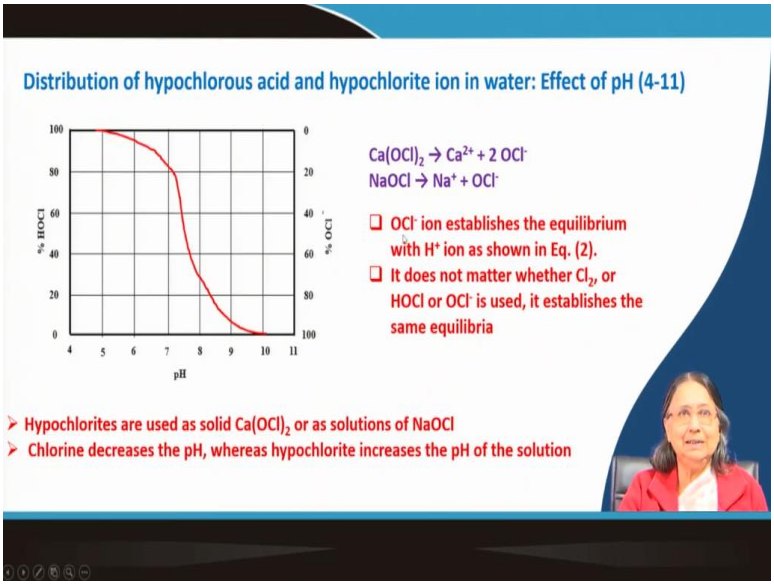

Now, let us come to the distribution of hypochlorous acid and hypochlorite ion as represented by the equation (2). It is predominating at higher pH (say for example pH 4 to 11). Here also effect of pH is there. In the last slide, distribution of HOCl and OCl^- has been shown from pH 4 to 11. On one side, percentage of HOCl and on the other side, percentage of OCl^- is written. Two directions are opposite. Now, say for example, I choose pH 7, you see 80% is HOCl and 20% is OCl^-. But if you bring it to pH 9, you see 10% is HOCl and 90% is OCl^-. Again at pH 10, it is almost 100% OCl^-. So, as you increase the pH, more and more OCl^- is produced. Moreover, OCl^- ion establishes the equilibrium with H^+ ion as shown in (2).

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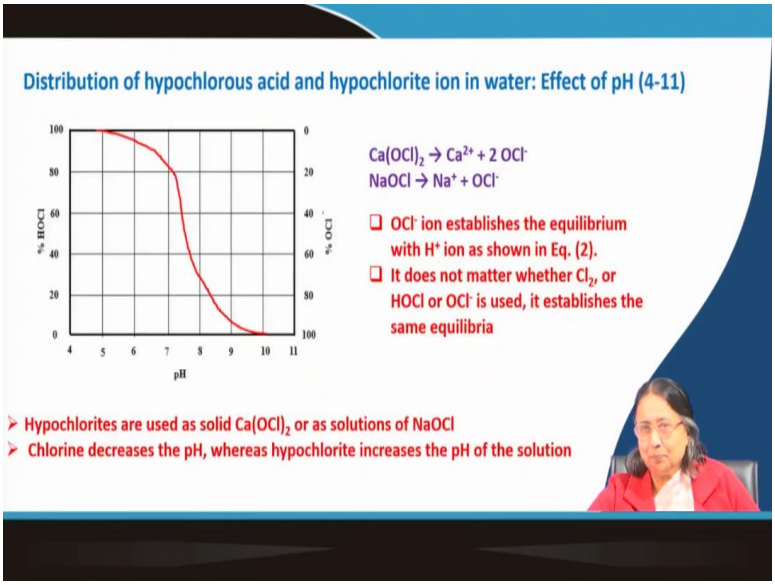

Now, what are the different things we can use for chlorination? We can use calcium hypochlorite or sodium hypochlorite. Nowadays you can see that Aquaguard (Kent) everywhere. But long time back it was not there. So, at that time, especially in monsoon season, when we used to go to some restaurants, we carried zeoline. And then, after going to the restaurant, when I asked for a glass of water, we used to put a few drops of zeoline there and we waited for some time. Then we used to drink the water. Why it is so? It is so because in it sodium hypochlorite is present in certain percentage. When we add it, it will disinfect the water. Then, it will be safe for drinking. Hypochlorites are used as solid or as solutions of NaOCl. We have seen that when chlorine reacts with water it gives HCl and HOCl. So, some acids are produced. So, it is decreasing the pH. When we add NaOCl, then it will form Na^+ and OCl^-. So, what will be the pH effect? That is again dependent on the equilibrium. NaOCl is a salt of weak acid means HOCl and strong base, NaOH. Chlorine decreases the pH, whereas hypochlorite increases the pH of the solution. So, according to the pH of the solution, your disinfection also may vary.

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Please see the reference given in the last slide. I am recommending Sawyer McCarty book again.

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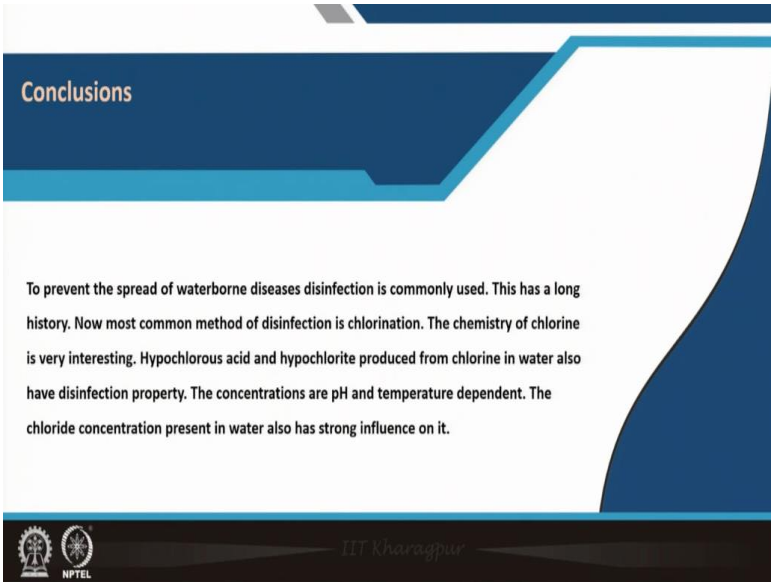

Now, as conclusion for this lecture I can tell, that to prevent the spread of waterborne diseases, disinfection is commonly used. This has a long history. Now, most common method of disinfection is chlorination. The chemistry of chlorine is very interesting. Hypochlorous acid and hypochlorite are produced from chlorine and it has disinfection property. The concentrations are pH and temperature dependent. The chloride concentration present in water has also strong influence on it. I also discussed that. Thank you.