Chlorination concepts

Inactivation of microbes by chlorine

Chlorine inactivates all types of microorganisms: protozoa, bacteria and viruses. The rate of inactivation varies widely, but is more rapid when more chlorine is present in the water.

For practical purposes, cysts and eggs of protozoa and helminths may be considered resistant to disinfection with chlorine. They are killed at high doses or after prolonged contact times, but these are often impractical. Cysts and eggs of protozoa and helminths should be removed by filtration prior to disinfection or, in the case of groundwaters (springs and wells), excluded by source protection.

An important advantage of chlorine as a disinfectant is that it remains in the water and continues to protect against the effects of re-contamination. Chlorine remaining in water after disinfection is referred to as chlorine residual.

The efficiency of inactivation of microbes by chlorine is affected by a number of factors including pH, contact time and the reactions of chlorine with the water. These are discussed in the following sections. Nevertheless, microbes may be protected from chlorine if they are attached to or within particles in the water.

For this reason, water to be chlorinated must be clear. It should always have a turbidity of less than five turbidity units and ideally less than one turbidity unit. Methods of water treatment for piped supplies are discussed in Fact Sheet 2.8 and in Fact Sheet 2.29.

Chlorine in water

When chlorine is added to water, it is involved in three types of reaction. These affect the availability of chlorine and its efficiency as a disinfectant.

First, substances such as manganese, iron and hydrogen sulphide dissolved in the water will react irreversibly with chlorine. This reaction removes these substances, thereby improving water quality and taste. Chlorine, which reacts in this way is, however, lost and does not contribute to disinfection.

Secondly, chlorine may react reversibly with organic matter and ammonia in water. The compounds formed are weak disinfectants. The products are referred to as combined chlorine or residual combined chlorine.

Thirdly, the chlorine may react with and dissociate in water. The products are efficient disinfectants unless the water is alkaline and are referred to as free chlorine or free residual chlorine.
Chlorine demand

The total amount of chlorine which will react both with compounds like iron and manganese and with organics and ammonia is referred to as the chlorine demand. The chlorine demand of different waters can vary widely.

Chlorine demand is therefore the difference between the amount of chlorine added to the water (the chlorine dose) and the free chlorine detectable in the water.

The chlorine demand for some waters, for instance some river waters, can increase dramatically, particularly after heavy rain. Measurement of chlorine demand is important for control of water treatment processes and is detailed in Fact Sheet 2.31.

Break-point chlorination

The type of chlorine dosing normally applied to piped water supply systems is referred to as break-point chlorination. Sufficient chlorine is added to satisfy all of the chlorine demand and then sufficient extra chlorine is added for the purposes of disinfection.

![Break-point chlorination diagram](image)

**Figure 1. Break-point chlorination**

Figure 1 shows the break-point chlorination curve. It indicates the effect of adding more chlorine to water which contains an initial ammonia nitrogen content of 1 mg/l.

The initial rise in residual is predominantly monochloramine (combined chlorine residual). The subsequent fall with further addition of chlorine is due to the decomposition of monochloramine to form nitrogen (the chlorine detected in this phase is also combined residual).

Finally, the oxidation of ammonia is complete and any additional chlorine will cause an equal increase in the free chlorine residual.
Contact time

Disinfection with chlorine is not instantaneous. Time is required in order for dangerous microbes (pathogens) present in the water to be inactivated.

The time taken for different types of microbes to be killed varies widely. In general, amoebic cysts are very resistant and require most exposure. Bacteria, including free-living Vibrio cholerae are rapidly inactivated by free chlorine under normal conditions. For example, a chlorine residual of 1 mg/l after 30 minutes will kill schistosomiasis cercariae, while 2 mg/l after 30 minutes may be required to kill amoebic cysts. Thus it is important to ensure that adequate contact time is available before water enters a distribution system or is collected for use.

Contact time in piped supplies is normally assured by passing the water, after addition of chlorine, into a tank from which it is then abstracted. In small community supplies, this is often the storage reservoir (storage tank). In larger systems, purpose-built tanks with baffles may be used. These have the advantage that they are less prone to “short-cutting” than simple tanks.

The pH of the water also affects the efficiency of chlorination; contact time is therefore also related to pH.

Chlorine chemistry

Chlorine, whether in the form of pure chlorine gas from a cylinder, sodium hypochlorite or calcium hypochlorite in any of its presentations, dissolves in water to form hypochlorous and hydrochloric acids. Chlorine dioxide, however, does not dissolve in water.

The reaction of chlorine in water follows the reaction shown below:

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} \]

Hydrochloric acid dissociates in turn to form hydrogen and chloride ions

\[ \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \]

Hypochlorous acid however dissociates only partially

\[ \text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^- \]

It is undissociated hypochlorous acid which acts as a disinfectant. The equilibrium between undissociated hypochlorous acid, hydrogen ions and hypochlorite ions depends on pH. At high pH (alkaline conditions, pH greater than 8), the dissociated forms predominate and at low pH (acidic conditions) undissociated hypochlorous acid predominates.

For this reason, disinfection with chlorine is more efficient at lower pH values; a pH of less than 8 is recommended for disinfection. Pure chlorine gas from a cylinder tends to decrease the pH of the water slightly; hypochlorite tends to...
increase water pH a little. Formation of combined chlorine is due to a sequence of reactions. Hydrogen in ammonia is progressively replaced by chlorine as shown below:

\[
\begin{align*}
\text{NH}_3 & \rightarrow \text{NHCl} \rightarrow \text{NHCl}_2 \rightarrow \text{NCl}_3 \\
\text{ammonia} & \quad \text{monochloramine} \quad \text{dichloramine} \quad \text{nitrogen trichloride (trichloramine)}
\end{align*}
\]

Where it is desired to produce monochloramine as a more stable, but less efficient disinfectant, the two chemicals may be dosed in appropriate proportions.

\[\text{NH}_3 + \text{Cl}_2 = \text{NH}_2\text{Cl} + \text{HCl}\]

*If a large chlorine dose is applied (relative to ammonia), as is practised in break-point chlorination, then nitrogen is formed:*

\[2\text{NH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{N}_2 + 4\text{HCl}\]

**Chlorine residual**

Chlorine persists in water as residual chlorine after dosing and this helps to minimize the effects of re-contamination by killing or inactivating microbes which may enter the water supply after chlorination. It is important to take this into account when estimating requirements for chlorination in order to ensure that residual chlorine is always present.

The level of chlorine residual required varies with the type of water supply and local conditions. In water supplies which are chlorinated there should always be a minimum of 0.5 mg/l residual chlorine after 30 minutes contact time in water.

Where there is a risk of cholera or an outbreak has occurred, the following chlorine residuals should be maintained:

- At all points in a piped supply 0.5 mg/l
- At standposts and wells 1.0 mg/l
- In tanker trucks, at filling 2.0 mg/l

In areas where there is little risk of a cholera outbreak, there should be a chlorine residual of 0.2 to 0.5 mg/l at all points in the supply. This means that a chlorine residual of about 1 mg/l when water leaves the treatment plant is needed.
Problems of taste and odour

The taste of chlorine in drinking water may lead a population to reject a source of water which is actually safe to drink in favour of a better-tasting source of water which may in fact present a greater health risk. Chlorinous tastes in water are most often due to over-dosing or the presence of chlor-phenols.

Over-dosing may be due to error (which should be prevented by proper monitoring and control); may be deliberate (for instance, in response to contamination of the supply, which should be corrected as soon as possible and chlorine levels returned to normal); or may be due to high-level dosing to ensure adequate concentrations in remote parts of the distribution network (in this case consideration should be given to re-chlorination during distribution).

Chlor-phenols are formed where chlorine reacts with phenolic substances in water. These may be derived from algae, so chlor-phenols are more common in surface waters than in groundwater. Chlor-phenols have a very strong chlorinous taste and very small amounts of chlorine can therefore give rise to very strong tastes. Problems with chlor-phenols are often transient and are best overcome by improving the intake and source.

Although chlorine itself can give rise to problems of taste and odour, chlorination can also help to improve taste and odour by the reduction of organic materials and iron.

Trihalomethanes

It is now recognized that chlorine can react with organic substances in some waters to form trihalomethanes (THMs). There is some evidence that trihalomethanes may be uncommon causes of cancer.

Standards for THMs in drinking water vary between 50 and 300 ppb worldwide - the WHO guideline value for chloroform (the most common THM) is 300 ppb. These concentrations are not commonly found in drinking water.

The benefits of reduced infectious disease through the appropriate chlorination of drinking water is generally considered to far outweigh the risk of cancer caused by trihalomethanes. WHO supports the use of chlorine as a disinfectant for drinking water supplies.

Uses of chlorine

Chlorine has three major uses in water supply:

- Continuous dosing of piped water supplies at source or as a part of treatment.
- Disinfection of pipes and installations after construction, repair or cleaning.
- Disinfection of water stored in the home.
The latter is especially important where water is collected or delivered to the home and where epidemic waterborne diseases such as cholera occur.

**Continuous chlorine dosing**

Although residual chlorine in water will help to minimize the effects of re-contamination in distribution pipes, every effort should be made to minimize re-contamination and not to rely on the residual effect.

Continuous chlorine dosing equipment most commonly uses chlorine gas in cylinders, calcium hypochlorite powder, or calcium or sodium hypochlorite solutions as sources of chlorine.

The advantages and disadvantages of various disinfectants are discussed in Fact Sheet 2.16 and their specific technical characteristics in Fact Sheets 2.18 to 2.20.

Continuous chlorine dosing is covered in Fact Sheets 2.21 to 2.24.

Disinfection of pipes and installations is covered in Fact Sheets 2.25 to 2.28.

**Chlorination in the home**

Chlorine residual is readily and rapidly lost, particularly in open or regularly opened storage containers. Good household storage and handling practice are therefore vital to ensure good quality water in the home, and reliance should not be placed on residual disinfectant effect.

Chlorination of water as a means of household water treatment is covered in Fact Sheet 2.34.