CIWEM Chartered Institution of Water and Environmental Management

Policy Position Statement

Chlorination and Chloramination of Drinking Water

Purpose

The paper examines the advantages and disadvantages of the type of chlorine based disinfectant used to treat drinking water at the treatment works and maintain a residual throughout distribution.

Free chlorine and chloramine residuals both provide varying degrees of microbial inactivation and protection to drinking water. There are also a number of advantages and disadvantages to the chemical composition of the drinking water afforded by free chlorine and chloramine residuals. Water companies must balance these to determine the most appropriate methods for their individual supply systems and distribution challenges.

This Policy Position Statement (PPS) should be read in conjunction with CIWEM's PPSs on 'Disinfection of water supplies' and 'Chlorine disinfection of water supplies in the UK'.

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Context

Historic Water Disinfection

In the UK, free[1] (available) chlorine has predominantly been used to disinfect water and to protect public health from harmful bacteria such as cholera, typhoid and other waterborne diseases since 1905.

The first ever continuous use of chlorine resulted after a serious typhoid outbreak in Lincoln in 1905. It was believed that one or all of three wells supplying the area had become contaminated. Dr Alexander Houston introduced 'chlorine of lime' to the drinking water and the cases diminished. Since that event over 100 years of chlorine disinfection has protected the public drinking water.

Chloramination has also been used as part of drinking water treatment since the early 1900's. In recent years a number of utilities in the USA and other parts of the world have switched from a free chlorine residual to chloramine residual in the distribution system, in efforts to reduce by-products associated with chlorination and/ or to maintain a disinfectant residual in long distribution networks, since chloramines decay less rapidly than chlorine.

1 Free chlorine refers to all chlorine present in the water as Cl_2(g), HOCl(aq) and OCl^-(aq).

Preparing water for disinfection

Most waters require treatment prior to disinfection. It is important to provide, as far as is practicable, water that is relatively free from anything that may inhibit the disinfection process (for example turbidity) or react with the disinfectant to form undesirable by-products (for example organic matter). Preparation is important for all forms of disinfection with chlorine and also by all other means, including ozone and UV.

Mechanism of disinfection using free chlorine as a disinfectant

When chlorine is added to water it rapidly hydrolyses and forms hypochlorous acid (HOCl) which is a very strong disinfectant. There are various chemicals which may be used to generate HOCl including chlorine gas, sodium hypochlorite and calcium hypochlorite.

Hypochlorous Acid Production: $Cl_2 + H_2O \rightarrow HOCl + HCl$

Hypochlorous acid then dissociates readily in water to produce hydrogen and hypochlorite ions: $HOCl \leftrightarrow H^+ + OCl^-$

The sum of the chlorine containing compounds (HOCl and OCl-) is often referred to as the free chlorine content. The concentration HOCl formed is dependent on pH and temperature.

Chloramination as a secondary disinfection method

Chloramine residuals are a significantly less powerful disinfectant but are also less reactive with organic substances and will persist further in a distribution system. Common practice in the UK is to complete primary disinfection at the treatment works using the more powerful free chlorine disinfectant. Chloramination is then completed to maintain a chloramine residual in the distribution system.

Monochloramine is typically formed by adding ammonia to drinking water which has been disinfected with free chlorine, or by the addition of pre-formed chloramines. It is very important that sufficient ammonia is added to maximise the formation of monochloramine and that the correct ratio of chlorine to ammonia is maintained at the treatment works.

When chlorine and ammonia react the end products formed depend on the ratio of reactants, pH and temperature and result from a series of equilibrium reactions which are given as:

$NH_3 + HOCl \longleftrightarrow H_20 + NH_2Cl$ (monochloramine) (1)

$NH_2Cl + HOCl \longleftrightarrow H_20 + NHCl_2$ (dichloramine) (2)

$NHCl_2 + HOCl \longleftrightarrow H_20 + NCl_3$ (trichloramine or nitrogen trichloride) (3)

Monochloramine has the greatest biocidal capability of the chloramines. Achieving the correct ratio of chlorine and ammonia is critical to ensure that it forms the predominant component of the chlorine residual. Excess chlorine promotes the formation of dichloramine, which is a weaker biocide, and nitrogen trichloride, which imparts an undesirable taste and odour to the water. Excess ammonia ensures that monochloramine is the predominant chlorine residual.

World Health Organisation guidelines of residual concentrations

The World Health Organisation (WHO) publishes and regularly updates Guidelines for Drinking Water Quality. The fourth edition of the WHO Guidelines for drinking-water quality builds on over 50 years of guidance by WHO on drinking-water quality, which has formed an authoritative basis for the setting of national regulations and standards for water safety in support of public health.

The WHO guideline values for chlorine and chloramine are conservative as no adverse effect level could be determined in the associated study. The guideline maximum values for free chlorine is 5 mg/l and for monochloramine is 3 mg/l. These levels are greatly in excess of the residuals of chlorine and monochloramine that are used in water treatment and supply in the UK.

Key considerations

When a water supply company formulates its primary disinfection policy, and how to maintain an adequate residual in the distribution system, there are a number of microbial and chemical factors which need to be taken into consideration, as detailed below.

Inactivation of Pathogens

In the UK, disinfection is always carried out on public water supplies by applying one or more processes, to remove or inactivate waterborne pathogens, including viruses, bacteria and parasitic protozoa, which may be present in sources of drinking water.

Disinfection, utilising free chlorine, is most commonly used in the UK because it is highly effective at inactivating many harmful viruses and bacteria. Chloramination as a primary disinfection process is not normally undertaken as chloramines require very long contact times to achieve satisfactory inactivation of pathogens and disinfection of the water.

Further information on the disinfection of water may be found in CIWEM's PPSs on 'Disinfection of water supplies' and 'Chlorine disinfection of water supplies in the UK'.

Disinfection by-products

The reaction between chlorine or monochloramine and certain types of organic substances naturally present in some sources of drinking water may lead to the formation of disinfectant by-products (DBPs), such as trihalomethanes (THMs), haloacetic acids (HAAs) and N-nitrosodimethylamine (NDMA).

There are a number of factors which influence the rate and degree of THM formation, including, concentration of organic matter, pH, temperature and chlorine residual. Typically, free chlorine residuals in the distribution system may result in higher concentrations of most DBPs than those distribution systems which utilise a chloramine residual. Disinfection using chloramination typically results in very low concentrations of THMs but may produce very low concentrations of N-nitrosodimethylamine (NDMA).

Water companies in the UK and Europe have a legal requirement to ensure that the disinfection process minimises the formation of all disinfectant by-products without compromising the effectiveness of disinfection.

Specifically, concentrations of THMs in drinking water are regulated in the UK by the Water Supply (Water Quality) Regulations and enforced by the Drinking Water Inspectorate. The legal limit of total chlorinated and brominated THMs in drinking water in UK is 100 µg (micrograms) per litre. It should be noted that guideline values and regulatory limits for disinfection by-products vary from country to country.

Some research indicates there is a possibility that certain DBPs (e.g. individual THMs and NDMA) may be carcinogenic. This category "possibly carcinogenic" is used for agents for which there is inadequate evidence of carcinogenicity in humans but there may be evidence in experimental animals.

Maintaining microbial safety in distribution systems

A chlorine residual in distribution is used to preserve the microbiological quality of drinking water during supply and provide some protection in the event of ingress of pathogens.

If bacteriological concerns arise in long distribution systems, then the addition of free chlorine in the form of reactive chlorination may be needed to minimise the potential impact to public health. In a chlorinated system this can be achieved quickly and efficiently with minimal disruption to the customer. Chlorine is dosed into the affected pipeline or chlorine is increased at the source works. This targets the bacteriological issue and the potential bacteriological event is eliminated quickly.

In a chloraminated distribution system, elimination of bacteriological issues may be more challenging as the chloramine residual is weaker, however there is some evidence to indicate its persistence may help to minimise long term microbial growth (biofilms) with certain distribution systems.

Poor control of the chloramination process may result in an excess of ammonia, this contributes to nitrification in the distribution system which can rapidly cause the decay of the monochloramine residual. Nitrification of distribution systems should be carefully monitored and controlled through the assessment of nitrite residuals and nitrite/nitrate ratios. It should be noted both these parameters are required to be sampled and reported in compliance with the Water Supply (Water Quality) Regulations in England and Wales.

It is essential that there is a holistic approach to the management and maintenance of the distribution system to maintain an adequate chlorine or chloramine residual and to safeguard the water quality at the customer tap.

Taste and odour

Free chlorine or chloramine residuals have the potential to cause taste and odour concerns and consumer perception and acceptability of the taste/ odour threshold is variable.

In general the taste/odour threshold of a free chlorine residual is lower than a chloramine residual, depending on the dose. If the chloramination process is poorly controlled it may result in di- or trichloramines which may impart a strong taste or odour to the water.

Free chlorine or chloramine residuals in the distribution system should not mix and should be clearly segregated, the mixing of these two forms of chlorine residual can result in significant taste and odour issues. There may be certain circumstances where free chlorine must be added as an emergency measure to protect public health, in this instance there may be taste and odour issues arising although the safety of the water is not compromised.

Summary of key issues associated with free chlorine and chloramines

Issue	Chlorine (free)	Monochloramine
Biocidal properties	Very effective	Not very effective
Effective against viruses	✓	✓
Effective against bacteria	✓	✓
Effective against Giardia and/or Cryptosporidium	×	×
Good longevity of residual	Moderately good	Very good
Can be mixed with free chlorine	✓	×
Can be mixed with chloramines	×	✓
Use after UV	✓	✓
Use after ozone	✓	✓
Can be used with chlorine dioxide	✓	✓
Potential THM issues	✓	×
Potential nitrification issues	×	✓
Potential corrosivity issues in distribution	✓	✓

Further information

AWWA Research Foundation and USEPA. 2007. Long-Term Effects of Disinfection Changes on Water Quality AWWA. Chapter 3, Chlorine to Chloramines.

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Government of Canada. 2011. Guidelines for Canadian Drinking Water Quality: Guideline Technical Document: N-Nitrosodimethylamine (NDMA), Available here

Water Supply (Water Quality) (England and Wales) Regulations 2016

World Health Organisation. 2003. Chlorine in Drinking Water. Background document for development of WHO Guidelines for Drinking water quality

World Health Organisation 2017. 'Guidelines for Drinking Water Quality' 4th Edition

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Note: CIWEM Policy Position Statements (PPS) represents the Institution's views on issues at a particular point in time. It is accepted that situations change as research provides new evidence. It should be understood, therefore, that CIWEM PPS's are under constant review and that previously held views may alter and lead to revised PPS's. PPSs are produced as a consensus report and do not represent the view of individual members of CIWEM.