Fact Sheet 1 of 3

Chlorine and chloramine residual basics

Introduction

The most important consideration in delivery of safe drinking water is ensuring that it is free of contamination by microbial pathogens. Following adequate source protection, treatment and primary disinfection, water should be safe for consumer consumption, however, before reaching consumers, water must travel through distribution systems. Recontamination of water by microbial pathogens can occur during transport via a number of pathways including failure of distribution system infrastructure allowing ingress, and growth of ubiquitous pathogenic species in pipes and storages. While distribution systems are carefully managed to address these hazards, it is not possible to completely eliminate their occurence. Therefore an additional barrier is commonly required in distribution systems for consumer protection.

Maintenance of a chemical disinfectant residual (ie secondary disinfection) is the practice of dosing a chemical disinfectant (in Australia, chlorine or chloramines) at,or downstream of water treatment facilities to generate an excess or 'residual' concentration to remain in the water during reticulation.

A disinfectant residual provides protection (some disinfecting power) against the ingress of contaminating material into the distribution system, and inhibits the growth of ubiquitous microbial species that degrade reticulation infrastructure and water quality, and contribute to disinfectant residual decay.

Commonly used terminology

Chlorination - is the dosing of chlorine to water. Chlorination can be used in either primary or secondary disinfection.

Chloramination - is the dosing of chlorine and ammonia to water to form inorganic chloramines (target species monochloramine) as a disinfection agent.

Primary disinfection – is the application of a disinfectant to water at a concentration and contact time that will inactivate pathogenic microbial species from source water. It is the disinfection process taking place prior to water entering the distribution network. Water should never be supplied to consumers without undergoing primary disinfection.

Secondary disinfection - usually refers to both the application and maintenance of a chemical disinfectant residual (chlorine or chloramine) to previously disinfected water for distribution to consumers.

Chlorine/chloramine decay - is the loss of chlorine and chloramine in distributed water as it passes through the reticulation system. Chlorine and chloramine are lost through reaction with compounds in water, autodecomposition and through reaction with distribution system infrastructure and contaminants.

Chlorine/chloramine demand - is the chlorine or chloramine consuming power of a substance or water. Waters that contain a large amount of chlorine/chloramine reactive substances will have a high chlorine/chloramine demand.

Free chlorine - is the concentration of 'free' uncombined chlorine in water. It is measured as the sum of the concentration of chlorine in the form of hypochlorous acid (HOCl) and hypochlorite ion (OCl -). In chlorinated systems, secondary disinfection involves the implementation of a chlorine residual barrier. The chlorine residual is the concentration of free chlorine.

Total chlorine - concentration in water is the total of combined and uncombined (free) chlorine. The formation of combined chlorine occurs when free chlorine and ammonia occur in solution together to form chloramines.

Residual - in the context of secondary disinfection, is the concentration of chemical disinfectant present in the water as it leaves the water treatment facility and circulates through the distribution system. During treatment, the chemical disinfectant has been added in excess of the amount required for primary disinfection to leave a residual concentration behind. The maintenance of this disinfectant residual throughout the network is the purpose of secondary disinfection.

C.*t* factor - is used in primary disinfection to determine the concentration and contact time of a disinfectant required to inactivate pathogenic microbial species. C.*t* is usually calculated as the product of the disinfectant concentration (mg/L), measured at the end of the contact time, multiplied by contact time (minutes). It is subsequently reported in mg/L.min. Different microorganisms require different C.*t* values to achieve the same log removal. Similarly, higher C.t values will be required for higher degrees of log removal of an individual species. The C.*t* required to inactivate bacteria and viruses is lower than that required for inactivation of protozoan and amoebic pathogens. How the C.*t* factor is calculated, and C.*t* values for inactivation of various pathogens is available in the ADWG (NHMRC, 2011).

Log removal - is calculated from the percentage removal or inactivation of microorganisms by a given process. For the disinfection of pathogens, log removal = log10 (concentration of viable pathogens before disinfection divided by the concentration of viable pathogens after disinfection). For example 99.9 % reduction is equivalent to 3 log removal.

Basic chlorine chemistry

When chlorine gas is dosed to water, free chlorine is produced as hypochlorous acid (HOCl)

$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^-$

Where sodium or calcium hypochlorites are used for dosing, free chlorine is formed through production of hypochlorite ions OCl-.

$NaOCl \rightarrow Na^+ + ClO^-$ $\quad$ $Ca(OCl)_2 \rightarrow Ca_2^+ + 2ClO^-$

HOCl and ClO^- (sometimes written as OCl^-) exist in equilibrium in solution (below), and the concentration of HOCl and ClO^- are referred to as 'free chlorine'.

$HOCl \leftrightarrow H^+ + ClO^-$ $\quad$ (Free chlorine in water)

Free chlorine reacts with organic and inorganic species in water and inactivates microbial pathogens. When free chlorine is used for disinfection and residual maintenance the key disinfectant species targeted is HOCl, as this is a considerably more effective disinfectant than ClO^-.

The proportion of each species formed is pH dependent, with higher pH favouring formation of OCl^-, and lower pH favouring formation of HOCl. To ensure a significant proportion of free chlorine is present in the form HOCl, the pH of water in chlorinated supplies should be maintained below 8 and preferably, lower than 7.5.

What chlorine residual to target?

As a minimum, detectable free chlorine should be present at the end of the distribution network (>0.1 mg/L).

0.2 mg/L is the minimum concentration recommended, however free chlorine residual targets should be developed for individual distribution systems on a risk management basis.

For instance, where specific hazards of concern are present (eg regrowth of pathogenic microbial species), minimum target residual concentrations may need to be higher (eg 0.5 mg/L needed to control *Naegleria fowleri*).

Basic chloramine chemistry

Chloramine formation occurs when chlorine and ammonia occur together in solution. These reactions are stepwise, with monochloramine (NH_2Cl) initially formed, and di- and trichloramines ($NHCl_2$ and NCl_3 respectively) formed under certain conditions.

$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$ $\quad$ Monochloramine formation

$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$ $\quad$ Dichloramine formation

$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$ $\quad$ Trichloramine formation

Although dichloramine and trichloramine are more effective disinfectants than monochloramine, they are responsible for undesirable tastes and odours in water, which are unpalatable to consumers. Hence, utilities target optimal formation of monochloramine for disinfection. Monochloramine is preferentially formed at pH >8 and at chlorine and ammonia-N ratios between 3:1 and 5:1.

Monochloramine is a weaker disinfectant than chlorine, but has the advantage of greater persistence (slower decay) than chlorine in distribution systems. It also generally produces lower concentrations of disinfection by-products (DBPs), although the use of chloramination will result in the formation of some DBPs not present in chlorinated systems, such as N-Nitrosodimethylamine (NDMA).

What monochloramine residual to target?

As a minimum, detectable monochloramine should be present at the end of chloraminated distribution networks (>0.1 mg/L), however higher concentrations than this are recommended for the protection of chloraminated supplies.

In chloraminated systems, monochloramine concentrations will need to be higher to control biofilm growth (2 mg/L minimum) and reduce the risk of nitrification (0.5 mg/L minimum recommended for nitrification control), as well as specific pathogens of concern (0.5 mg/L minimum to control *Naegleria fowleri*).

In systems where chloramines are being used for primary and secondary disinfection, chloramine dose rates will need to be based on achieving minimum C.*t* prior to contact with the first customer, if this isn't already achieved at the time the water leaves the treatment facility.

Reference: Chow C, Cook D and Mussared A (2014) Guidance manual for the maintenance of chlorine and chloramine residuals. WaterRA Project 1064