

The Practice of Chlorination: Application, Efficacy, Problems and Alternatives

Chlorination for disinfection of drinking waters has proven effective in the fight against waterborne pathogenic organisms since the middle to late 19th century.

In most cases, chlorination is still the least costly and often the best means to disinfect potable water supplies and control bacterial growth in the distribution system.

However, in the last decades of the century much concern has been raised about the potential formation of undesirable by-products of chlorination that could be possibly deleterious to health. Because of current concerns over such chlorination by-products, many water utilities in the industrialised world are changing chlorination practices to minimise potential risks associated with by-product formation and to reduce public objections to chlorine-related tastes and odours in treated waters.

In balancing the trade-offs associated with chlorination of drinking waters a difference in approach has arisen between the United States and many European countries.

Whereas the treatment practice in the United States is based upon disinfection followed by maintenance of a detectable chlorine residual in the distribution system in order to minimise biological growth, the practice in some European countries is based upon the production of a biologically stable water with little to no chlorine demand, and very low chlorine concentrations in the distribution system.

Water purveyors in many countries around the world are evaluating the fundamental differences between acute risks associated with waterborne disease epidemics and long-term risks associated with exposure to DBPs considered to be mutagenic in animal testing.

During chlorination of drinking waters, chlorine is typically introduced through the use of chlorine gas or liquid sodium hypochlorite.

Chlorine reacts with (oxidises) substances present in natural waters

such as organic material (including microbial cell wall substances) and inorganic materials. A combination of many factors control the effectiveness of disinfection including: disinfectant and disinfectant dose, disinfectant demand of the water, contact time, water pH, temperature, type of micro-organism (e.g. bacteria, viruses, protozoan cysts) and concentration of micro-organisms.

Alternative oxidants (e.g. ozone, chlorine dioxide) in place of chlorine have also become common to achieve disinfection and other water treatment goals including oxidation of reduced iron and manganese, or oxidation of odorous compounds such as sulphide.

The goal of water disinfection is to remove or inactivate waterborne pathogenic micro-organisms.

Disinfection is not synonymous with the sterilisation of water, in which all organisms are killed. In many disinfection regulations, total coliform bacteria are used as indicators or surrogates of faecal contamination to represent the possible presence of pathogenic organisms (e.g. *Escherichia coli*, *Salmonella typhi*).

The primary pathogenic micro-organisms targeted for inactivation include: bacteria, viruses and protozoan cysts (*Giardia lamblia*, *Cryptosporidium parvum*). The emerging challenge for disinfection practices has been the newly recognised presence of protozoan cysts and oocysts in surface water supplies; *Cryptosporidium* oocysts for example, are the cause of the disease called Cryptosporidiosis, which has been shown to be potentially life-threatening in weakened or immunocompromised individuals.

This position paper will provide an overview discussion on the practice of chlorination in water treatment. The discussion will cover the following topics: general chlorination practice, chlorine disinfection capabilities, by-product formation, current regulations and use of alternative oxidants for disinfection.

This publication is intended to give information on the global situation concerning Chlorination, but does not reflect the policies of the Individual or Associate Members of the IWSA.

INTRODUCTION

Ever since 1854, when Dr. John Snow showed the connection between the Broadstreet Well and the London cholera epidemic (1), protecting public health has meant keeping drinking water free of pathogens. In its early stages, drinking water treatment took the form of slow sand filtration. By the turn of this century however, chlorine disinfection came to play a more important role in controlling devastating waterborne disease epidemics around the globe than any other water treatment practice (2,3). In short, the practice of chlorination had nearly eliminated waterborne bacterial and viral diseases in many parts of the world.

In the last decades of this century, much concern has been raised about the potential formation of undesirable by-products due to chlorination that could be possibly deleterious to health. In 1974, scientists identified a correlation between chlorination and the presence of organohalides in drinking waters (4, 5). In the following years, additional chlorination by-products were identified, some of which were shown to exhibit carcinogenic properties in animal testing (6). In light of these findings, many countries established limits on the trihalomethane group of chlorinated organics in the 1980's (7), and since that time regulations have been proposed on other types of disinfection by-products (DBPs) (8,9).

Considerable debate has developed in the international arena regarding the benefits and detriments of chlorine application in water treatment, particularly with regard to the suitability of water treatment alternatives in industrialised and developing countries. In light of the potential (country-specific) health risks associated with water treatment, attention should be paid to the fundamental difference between the acute risks associated with waterborne disease epidemics and the long-term risks of exposure to disinfection by-products considered to be mutagenic in animal testing. Although chlorine disinfection is a critical water

treatment step in the developing world, many water utilities in the industrialised world are changing chlorination practices to minimise potential risks associated with formation of chlorination by-products and to reduce public objections to chlorine-related tastes and odours in treated waters. It is important that such changes be designed, at a minimum to achieve the same level of disinfection of potential pathogens.

Although the management of DBP formation is often characterised as a problem of managing “disinfectants” and by-product “precursors”, by-product formation is not necessarily or exclusively the result of disinfection. In fact, by-products may be generated by the addition of any number of chemical oxidants (e.g., chlorine, ozone, chlorine dioxide) to natural waters to achieve a number of different water treatment goals. Application of chemical oxidants may be designed to achieve treatment goals that may include: inactivation of bacteria, viruses or protozoa, oxidation of reduced iron and manganese, or oxidation of odorous compounds such as sulphide. Given the range of oxidant applications in water treatment, the term oxidation by-product (OBP) may be more appropriate than the term DBP in providing more accurate etiology of by-product formation.

This position paper will focus mainly on the practice of chlorination in water treatment. The discussion will cover the following topics: general chlorination practice, chlorine disinfection capabilities, by-product formation, current regulations, and use of alternative oxidants for disinfection.

GENERAL PRACTICE

Traditional Practice

The following terms are commonly used to describe the various ways chlorine has been used in drinking water treatment:

- **Prechlorination** - The addition of chlorine at the beginning of the treatment process to oxidise inorganics (iron, manganese, sulphides, etc.), to remove taste and odours, to enhance the coagulation process and to reduce algae growth on process units.
- **Primary Disinfection** - The addition of chlorine to protect against potential pathogens in the source water, often accomplished by achieving a certain product of chlorine residual concentration [C] and contact time [T]. The product of C*T (in units of mg*min/L) is often used as a criterion of disinfection dosing practice for inactivation of certain waterborne pathogens in the United States and other countries.
- **Breakpoint Chlorination** - The practice of using chlorine to oxidise ammonia and other chlorine demanding materials present in the water, such that a free chlorine residual is detected.
- **Residual Chlorination** - The practice of maintaining a chlorine residual in the water throughout the water distribution system to protect against degradation of water quality due to biological growths, cross-connections, accidental contamination, etc.
- **Superchlorination** - The practice of using very high levels of chlorine for a short period followed by dechlorination. Is useful in removing colour, iron, manganese, certain macroinvertebrates, among other things.
- **Facilities Disinfection** - The practice of introducing a fairly high chlorine residual for a short time to disinfect new facilities or in old facilities that have been repaired before they are put in service. Examples might be new or repaired water mains or storage reservoirs. This practice is also used periodically as a way of controlling or preventing recurrent water quality problems, especially in water storage reservoirs.
- **Intermittent Chlorination** - The practice of introducing chlorine for a short time periodically to control growths in pipelines, intakes etc. Intermittent chlorination is sometimes practiced in treatment plants that do not use chlorine ahead of clarification in normal operations.

Chemical Technologies Used

Chlorine is generally introduced into the water through the use of chlorine gas, liquid sodium hypochlorite or calcium hypochlorite. These products are designed to provide disinfection and produce a free chlorine residual. Occasionally ammonia is also introduced to produce combined chlorine (chloramines), which provides a longer-lasting but less powerful form of chlorine residual. The following discussions expand on each of these options.

- **Chlorine Gas** - Available in a pressurised liquid form stored in a wide range of sizes, from small pressurised steel cylinders to railroad tank cars of liquid. Chlorine gas is a hazardous substance and is highly toxic when it is inhaled. The storage area should be well ventilated, preferably by forced ventilation. Safety standards have made use of chlorine gas more difficult; however, this is the most common and least expensive form of chlorine dosing
- **Sodium Hypochlorite** - Available as an aqueous solution or bleach. Sodium hypochlorite is usually manufactured off-site by the combination of chlorine gas and sodium hydroxide; however, it can also be produced on-site by electrolysis of sodium chloride solution. Measures must be taken to provide storage of solutions in plastic or glass vessels and provide protection against external heat and radiation from the sun, and occasional confirmation of hypochlorite concentration must be performed to determine the hypochlorite decay over time. Although sodium hypochlorite is usually more expensive than chlorine gas, it raises fewer safety issues, and is commonly used for disinfection in densely populated areas.
- **Solid Calcium Hypochlorite (High Test Hypochlorite, or HTH)** - Available in granular form or in tablets (70% available chlorine). This chemical is rarely used to provide continuous chlorination in current practice for any but small water plant operations; however, calcium hypochlorite is very popular for facilities disinfection.
- **Chloramines** - Combination of chlorine and ammonia. Ammonia is available as a commercial aqueous solution or as a pressurised gas; any form of chlorine may be used. Chloramines are less efficient as biocides as compared to free chlorine, but react to form fewer organic by-products and are often used as a residual disinfectant in the United States. However, the use of chloramines for residual disinfection in the distribution system is not considered acceptable practice in many European countries due to concern over the impacts of potential chloramine discharge on aquatic life.

AQUEOUS CHLORINE CHEMISTRY

When chlorine gas is dissolved in water it reacts rapidly to form hypochlorous acid (HOCl) and hydrochloric acid (HCl) as shown in Equation 1 in Table 1 below:

Table 1 - Hydrolysis of Chlorine Gas (or Chlorination Reactions)

Chlorination Reaction	Equation
$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$	(1)
$HOCl \rightleftharpoons H^+ + OCl^-$	(2)

The formation of hypochlorous acid (Equation 1) is often considered the most important reaction in water chlorination, and the complete reaction occurs within a few tenths of a second. Hypochlorous acid is a “weak” acid, which means it tends to undergo partial dissociation to form hypochlorite ion (OCl⁻) as shown in Equation 2. Together, the sum of hypochlorous acid and hypochlorite ion concentrations in aqueous solution is referred to as Free Available Chlorine. Molecular chlorine is also considered to be free available chlorine, but it is not usually found in detectable concentrations at the pH of most water treatment practices.

The partitioning of the free available chlorine between hypochlorous acid and hypochlorite ion is a function of both pH and temperature (10), as shown in Figure 1 below. A higher proportion of free available chlorine is present as hypochlorous acid at lower pHs. Because hypochlorous acid is a stronger oxidant than the hypochlorite ion, a pH of 7 is often sought as a goal for disinfection conditions. It happens that this pH is also beneficial for the oxidation of ammonia by chlorine.

Chlorine reacts with (oxidises) other substances present in natural waters such as organic material and inorganic materials, which may include but

organic chloramines, which have little disinfecting capabilities. All components of Chlorine Demand must be expressed in terms of equivalent chlorine (as Cl₂ mg/L), in order to quantify chlorine demand relative to the chlorine dose.

Chlorine that reacts with traces of free ammonia in the raw water may produce concentrations of inorganic chloramines, which may include monochloramine or dichloramine, and in some cases, small concentrations of trichloramine (Equations 3, 4 and 5). The series of complex reactions between inorganic ammonia and chlorine are collectively referred to as breakpoint chlorination (Simplified equations provided in Table 2). These reactions are largely dependent upon contact time, pH, temperature, concentration of chlorine and ammonia, and initial chlorine to ammonia ratio. The initial reaction (Equation 3) demonstrating conversion of hypochlorous acid (HOCl) to monochloramine (NH₂Cl) occurs most rapidly at pH 8.3 when the ratio of chlorine to ammonia is equimolar. The reactions involving formation of dichloramine and trichloramine (Equations 4 and 5) are much slower than the monochloramine reaction, requiring much higher molar ratios of chlorine to ammonia and a lower pH range. Dichloramine is not a stable molecule, and will quickly decompose to N₂ and HOCl. Dichloramine and trichloramine may also contribute a disagreeable odour and/or bitter taste to the water.

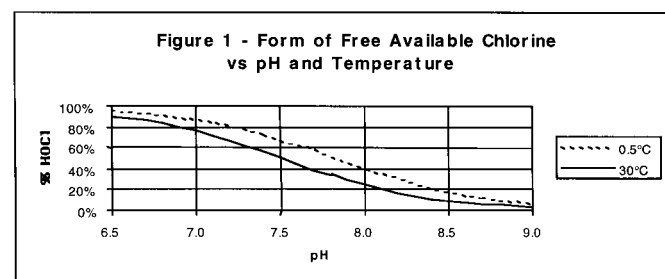
By accounting for the components of chlorine identified in Equations 1 through 5 (with all components expressed as equivalent chlorine in mg Cl₂ per litre), the original chlorine dose can be accounted for in the following manner:

Table 2 - Breakpoint Chlorination Reactions

Breakpoint Reactions	Equation
$HOCl + NH_3 \rightleftharpoons NH_2Cl + H_2O$	(3)
$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O$	(4)
$NH_2Cl + HOCl \rightleftharpoons NCl_3 + H_2O$	(5)

$$\text{Chlorine Dose} = \text{Free Available Chlorine} + \text{Combined Chlorine} + \text{Chlorine Demand}$$

In this equation, the organic and inorganic chloramines are called Combined Chlorine. Each component of this chlorine dose equation must be expressed in terms of equivalent chlorine as: mg/L as Cl₂.



are not limited to reduced metals, sulphides, bromide ions, and organic and inorganic nitrogenous compounds. The amount of chlorine consumed during reactions with dissolved or suspended substances is referred to as the Chlorine Demand. In the presence of reduced metals for example, chlorine oxidation will promote formation of oxidised metal precipitates. In the presence of bromide-containing waters, hypobromous acid will be formed through the oxidising action of chlorine; the bromide ion also contributes to the Chlorine Demand. Chlorine may be consumed by reaction with organic amines to form

CURRENT TECHNICAL ISSUES

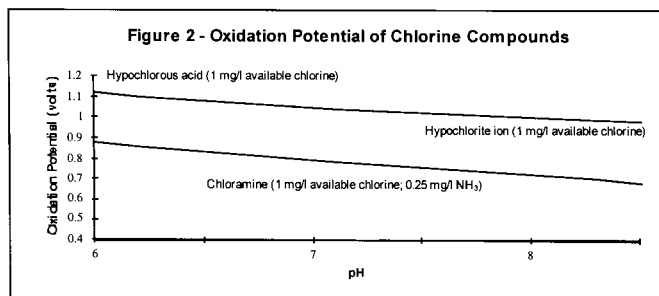
Disinfection Efficacy of Chlorine

The goal of water disinfection is to remove or inactivate waterborne pathogenic micro-organisms. Disinfection is not synonymous with the sterilisation of water, in which all organisms are killed. The primary pathogenic micro-organisms targeted for inactivation include: bacteria, viruses and protozoan cysts (*Giardia lamblia*, *Cryptosporidium parvum*, *Cyclosporida* and *Cyclospora*).

A combination of many factors control the effectiveness disinfection (10), including:

- Disinfectant and disinfectant dose;
- Oxidant/disinfectant demand of the water (several demand factors listed above);
- Time of contact between the micro-organisms and the disinfection agent;
- Water temperature;
- pH of the water during disinfection;
- Nature of the micro-organism (e.g., bacteria, viruses, protozoan cysts);
- Concentration of micro-organisms.

It is generally agreed that hypochlorous acid is a more effective disinfectant than hypochlorite ion and chloramines for two primary reasons: 1) hypochlorous acid (HOCl) is better able to penetrate bacterial cell walls than hypochlorite due to its charge neutrality; and 2) hypochlorous acid is a more effective oxidant, as shown by the different oxidation potential values in Figure 2 below (10).



In many disinfection regulations, total coliform bacteria are used as indicators or surrogates of faecal contamination to represent the possible presence of pathogenic organisms (e.g. *Escherichia coli*, *Salmonella typhi*). For example, in bacterial studies where 99% (2-logs) inactivation of the indicator organisms: coliform bacteria is achieved by an appropriate combination of disinfectant concentration (C) and contact time (T), the assumption is made that a corresponding inactivation of harmful bacteria would be achieved for the same or lower CT value. In studies of virus inactivation, enteroviruses (e.g., poliovirus) have been shown to be more resistant to free chlorine than enterobacteria, and may require CT values 10 to 100 times higher than required for the same inactivation of *E. Coli*. The inactivation of bacteria and virus with chlorine has been studied and is well documented (12). Examples of the germicidal effectiveness (2-log inactivation at 5°C) of free chlorine (98% to 83% HOCl) and preformed chloramine (NH₂Cl) against three microbial species are provided in Table 3 below (11, 12).

The emerging challenge for disinfection practices has been the newly

Table 3 - CT Ranges for 2-log Microbial Inactivation by Disinfectants at 5°C²

Chlorine Species Concentration (mg/L as Cl)	<i>E. coli</i> Bacteria	Poliovirus	<i>Giardia</i> <i>muris</i> cysts
Free Chlorine (pH 6 - 9)	0.034-0.05	1.1-2.5	30-630
Chloramine (pH 6 - 9)	95-180	768-3740	1400

² - concentration values expressed as mg/L; inactivation based upon 10 minutes of contact time; adapted from Morris (1975) (12, 13, 14).

recognised presence of protozoan cysts and oocysts in surface water supplies. In the case of these protozoa, CT values for 99% inactivation of *Giardia* cysts have been reported to be 50-100 times higher than those required for inactivation of poliovirus, and 500-10,000 higher than for *E. coli* (as shown in Table 3).

Cryptosporidium oocysts are the etiologic agent for the disease called *Cryptosporidiosis*, which has been shown to be potentially life-threatening in immunocompromised individuals. There are little data available on the inactivation of these organisms by chlorine or other oxidants; however, initial indications suggest that chlorine and chloramines are relatively ineffective biocides when employed for inactivation of *Cryptosporidium* oocysts.

Formation of By-Products

Oxidation by-products (and disinfection by-products) are compounds that form during water treatment as a result of reactions between raw water constituents and the introduced oxidant (or disinfectant). They can be divided into three main categories:

- substances provoking potentially deleterious effects in higher living organisms (toxic, genotoxic, carcinogenic compounds);
- assimilable organic carbon (predominantly aliphatic acids and aldehydes) stimulating microbiological growth in the treated water; and
- compounds producing objectionable tastes and odours, such as organohalides (e.g., chlorophenolic compounds). Objectionable tastes and odours are also derived from natural microbial intracellular substances (e.g., methylisoborneol and geosmin) that are sometimes liberated by chlorine oxidation; however, chlorination of geosmin may promote formation of even more odoriferous substances.

The first category of OBPs/DBPs represents the most significant health concern resulting from chlorination. The chlorinated OBPs/DBPs may be grouped as shown in Table 4 below. Health risks associated with these compounds have been assessed and will be discussed in the following section with regard to drinking water

guidelines for DBP concentrations.

Table 4 - Principle Chlorination By-Products

Family of Compounds	Chlorinated Constituents of Concern ³
Trihalomethanes (THMs)	chloroform and bromodichloromethane
Halogenated carboxylic acids	dichloro- & trichloroacetic acid
Halogenated ketones	dichloro- & trichloropropanone
Halogenated aldehydes	trichloroacetaldehyde
Halogenated acetonitriles	dichloroacetonitrile

³ - Brominated species of these families of compounds may also warrant health concerns.

The formation of chlorinated by-products, both speciation and concentration strongly depend on the following characteristics of the raw water and of the treatment process:

- Total chlorine dose;
- Chlorination contact time (free chlorine contact time);
- Water temperature;
- pH of the water during chlorination;
- Total organic carbon (TOC) content and its character (as an indicator of DBP precursor material);
- Bromide concentration of the raw water;
- Pre-treatment method (i.e., alternative non-chlorine oxidants or biological treatment with post-filtration chlorination only).

Current and Proposed Regulations

World Health Organisation (WHO)

The WHO made the following statement in the second edition of its "Guidelines for Drinking Water Quality", 1993 (9): "Disinfection is unquestionably the most important step in the treatment of water for public supply. The destruction of microbiological pathogens is essential and almost invariably involves the use of reactive chemical agents such as chlorine, which are not only powerful biocides but also capable of reacting with other water constituents to form new compounds with potentially long-term health effects."

As a result of the potential long-term health effects associated with DBPs, the WHO forwarded guideline values for a certain number of threshold toxic substances, that could form during chlorination of water (Table 5). These guideline values have been based on

scientifically proved specific NOAELs (no adverse effect levels) or LOAELs (low adverse effect levels) and on uncertainty factors varying from 1,000 to 10,000.

European Union (EU)

The European Commission of the EU made the following remarks concerning disinfection by-product formation in the explanatory memorandum of the proposal for a Council Directive (COM 94/612 final) as a revision of the existing drinking water Directive 80/778/EEC: "The immediate and direct threat to health, and even to life, presented by pathogenic organisms in water makes it unthinkable that disinfection should be given up. The parametric values proposed for disinfection by-products are therefore not so strict that disinfection

Table 5 - WHO Guidelines and EU Standards for Chlorination By-Products (10)

Compound	WHO Guideline Values (µg/l)/	EU Values (µg/l)
Dibromochloromethane (CHBr ₂ Cl)	100	
Bromoform (CHBr ₃)	100	
Dichloroacetic acid	50	
Trichloroacetic acid	100	
Trichloroacetaldehyde	10	
Dichloroacetonitrile	90	
Dibromoacetonitrile	100	
Trichloroacetonitrile	1	
Chlorite	200	
Hydrogen Peroxide		100
	<u>Proposed Maximum⁴</u>	
Chloroform (CHCl ₃)	200	40
Bromodichloromethane (CHBrCl ₂)	60	15
Bromate (BrO ₃ ⁻)	25	10
2,4,6-Trichlorophenol	200	

⁴ No WHO threshold values were set for these four substances; however, proposed maximum concentrations were set based on probable carcinogenicity, with an excess lifetime (70 years) cancer risk of 10⁻⁵.

is compromised.”

The European Commission proposed interim concentration standards for only a few of the DBPs identified by the WHO; comparisons are provided in Table 5 above. The EU parameters were chosen based upon demonstration of some level of carcinogenicity towards tested animals. For regulatory compliance, the concentration

limits identified by the EU must not be exceeded at the outlet from the treatment plant; future standards may also be established for maximum contaminant concentrations as measured in the distribution system.

US Environmental Protection Agency (EPA)

The US EPA has proposed new standards on the concentration of total THMs and haloacetic acids (HAAs) in the distribution system, as a part of Stage 1 of the Disinfectant/Disinfection By-Product Rule (D/DBPR). According to these standards, the maximum total concentration of THMs allowable in the distribution system would be reduced from 100 to 80 µg/l and a standard set for HAA(6) concentration of 60 µg/l. With regard to other DBPs, the USEPA Maximum Contaminant Level (MCL) proposed for bromate (10 µg/l) is lower than the WHO guideline (25 µg/l), and equivalent to the EU standard.

Issue of Chlorine Residual in the Distribution System

A contrast exists between the approach taken in the United States and some countries in Europe in their approaches to maintaining microbial water quality in the distribution system. The treatment practice in the United States, is based upon maintenance of a detectable chlorine residual in the distribution system in order to minimise biological growth, prevent regrowth, provide some protection against local accidental contamination and minimise biologically-related corrosion in the distribution system (11). To this end, the US EPA has set goals for minimum chlorine residual concentrations in the distribution system: minimum free chlorine residual (Cl₂) of 0.2 mg/l, and minimum combined chlorine residual (predominantly NH₂Cl) of 1.0 mg/l. These minimum goals may be compared with the maximum guideline values set by the WHO: maximum free chlorine residual of 5 mg/l and maximum monochloramine residual of 3 mg/l.

some parts of Europe is based upon reduction and in some cases elimination of chlorine residuals from the distribution system. Water treatment instead focuses on production and distribution of a biologically stable water with effectively no chlorine demand. To this end, the strategy of some European water purveyors is to reduce the concentrations of assimilable organic carbon (AOC) in the treated water before it enters the distribution system and to maintain a high quality distribution network, such that the potential for contamination introduced into the distribution system is very low. However the strategy of producing a biologically stable water and minimising chlorine residuals in the distribution system is not accepted practice in all European countries. Many continue to argue that maintaining a residual disinfectant concentration in the distribution system is also an effective means of controlling biofilm growth.

In contrast, the water treatment approach that has been adopted in

Alternative Methods of Disinfection

In the last twenty years, an increasing emphasis has been placed on application of alternative methods of disinfection, primarily due to the resistance of *Cryptosporidium* oocysts to traditional disinfectants and to the formation of undesirable by-products in the chlorine disinfection process. These methods can be divided into two categories of disinfection: chemical methods (ozone, chlorine dioxide) and physical methods (UV irradiation, membrane filtration).

Alternative Methods Of Chemical Disinfection

Ozone is a strong oxidant and a powerful germicidal agent. In water treatment systems, it may be used as a pretreatment or an intermediate oxidation process. Ozone has been shown to be an effective disinfectant of protozoan cysts (both *Giardia* and *Cryptosporidium*) (14, 15). As such, the CT values required for 2 log inactivation of *Giardia* cysts are much lower than required by the US EPA for other disinfectants, as shown in Table 6 (14, 15, 16). Table 6 represents a summary of cyst inactivation data collected from several sources. All reported data are for 2-log (99%) inactivation at 22°C.

In most cases, ozone is not employed as a postdisinfectant (except with very low TOC waters) because it can potentially produce a considerable amount of assimilable organic carbon, which promotes bacterial regrowth. Furthermore, ozone does not provide an active disinfectant residual in the distribution system. Although ozonation does not generate THMs, HAAs or other chlorinated by-products, it does produce aldehydes and can produce bromate when applied to bromide-containing raw waters under specific conditions. (Refer to bromate contaminant standards in Table 5.)

Chlorine Dioxide is a more powerful oxidant than free chlorine or chloramines, and has lower CT values for *Giardia* inactivation, as shown in Table 6 (16, 17). As an oxidant, chlorine dioxide has been used primarily to reduce taste and odour problems and to eliminate dissolved iron and manganese in raw waters. Furthermore, ClO_2 has been used in a number of European countries (e.g., Germany, Switzerland, France, Belgium, Netherlands) with the aim of reducing the concentration of disinfectant residual in the distribution network and the finished water concentration of many regulated DBPs. Although use of chlorine dioxide does generate not THMs or HAAs, reluctance to general use has developed due to the concerns with potential health effects from the

presence of chlorite and chlorate in treated waters. (Refer to chlorite contaminant standards in Table 5.)

Table 6 - CT Values for 99% Reduction in Cyst Concentration at 20°C

Disinfectant	<i>Giardia</i> (CT) ⁵	<i>Cryptosporidium</i> (CT) ⁵
Free Chlorine	40	N/A
Chloramines	500	N/A
Ozone	0.2	8
Chlorine Dioxide	10	80

⁵ Inactivation CT in units of mg*min/L; N/A = not acceptable; (14, 15, 16).

It is important to emphasise the fact that all chlorine disinfectants (free chlorine, chloramines or chlorine dioxide) have an additional value in water treatment that results from their persistence as an active disinfectant residual in the distribution system. In general, chloramine residuals are more persistent than free chlorine residuals and the latter are, in turn, more persistent than chlorine dioxide residuals.

Physical Methods Of Disinfection

UV Irradiation has appeared to be a good disinfectant for selected bacteria; however, in it has not yet proven to be reliably effective for removal of protozoan cysts, zooplankton and macroinvertebrates. The germicidal effects of UV irradiation are derived from photochemical damage to the RNA and DNA in the cells of a micro-organism; however, the resistance of waterborne micro-organisms against UV irradiation depends upon the cellular repair mechanisms available. For some bacterial organisms, the damage to DNA can be repaired through a process called photo-reactivation. Because UV irradiation does not provide residual disinfectant action in the distribution system, it is not considered to be a suitable postdisinfectant. UV irradiation is not currently associated with DBP formation or formation of other deleterious disinfection by-products.

Microfiltration and Ultrafiltration Membranes are promising treatment processes for drinking water applications because of their proven capabilities for removal of protozoan cysts and oocysts. Microfiltration (nominal pore size 0.2 µm) has been demonstrated to achieve absolute removal of protozoan species. Ultrafiltration (molecular weight cut-off between 1,000 and 100,000 Daltons) has been demonstrated to achieve absolute removal of protozoa, as well as significant removal of viruses (greater than 6-log removal) (18).

Summary

Chlorine has proven its effectiveness for decades in the fight against waterborne pathogenic organisms and is in most cases still the least costly and often the best means to comply with bacteriological standards in the distribution system. However, because of current concerns over DBPs and public perception of taste and odour, water purveyors are currently considering alternatives to chlorine disinfection. In review of the alternatives to chlorine for disinfection, attention should be paid to the fundamental difference between risks of epidemics of waterborne disease and those associated with carcinogenic or mutagenic effects from exposure to chlorination by-products. In the case of waterborne disease, there is a long history of disease-causing epidemics affecting thousands of individuals around the world. In the case of long-term chemical exposure to chlorination

by-products, risk assessment has been based on effects observed in animal testing which have been extrapolated to the human population (with conservative assumptions). In light of these trade-offs, water suppliers should carefully consider the potential increase in risk of microbiological disease that may be associated with changes in disinfection practices that are designed to reduce chlorination by-product formation. The recommendation may also be made that water purveyors should recognise the importance of watershed protection as a means of maintaining high quality water supplies and reducing the need for disinfection at the treatment facility.

References

- (1) Huisman, L., 1974, Slow Sand Filtration, World Health Organisation, Geneva.
- (2) Rosenau, M., 1935, Preventative Medicine and Hygiene, 6th ed. Appleton-Century, NY, NY.
- (3) Baker, M., 1948, The Quest for Pure Water, AWWA.
- (4) Fair, G. Geyer, J. and Okun, D., 1966, Water Supply and Wastewater Engineering, Volume 2. Water Purification and Wastewater Treatment, John Wiley & Sons, NY, NY.
- (5) Bellar, T., Lichtenberg, J., and Kroner, R., 1974, "The Occurrence of Organohalides in Chlorinated Drinking Water," Journal of the American Water Works Association, 66:703.
- (6) Rook, J., 1974, "Formation of Haloforms during Chlorination of Natural Water," Water Treatment and Examination, 23:234.
- (7) Symons et al, 1975, "National Reconnaissance Survey for Halogenated Organic," Journal of the American Water Works Association, 67:634.
- (8) U.S. EPA, 1994, "National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts," Federal Register 59 FR 38668.
- (9) World Health Organisation: Guidelines for drinking-water quality (second edition): vol. 1 Health criteria and other supporting information. Geneva, 1993.
- (10) White, G. C., 1986, Handbook of Chlorination, Van Nostrand Reinhold, NY, NY.
- (11) Hoff, J. C., 1986, Inactivation of Microbial Agents by Chemical Disinfectants, EPA/600/2-86/067.
- (12) Morris, J. C., 1975, "Aspects of the Quantitative Assessment of Germicidal Efficiency", Disinfection: Water and Wastewater, J. D. Johnson (Editor), Ann Arbor Science, Ann Arbor, MI.
- (13) Safe Drinking Water Committee, 1980, "The disinfection of drinking-water", in: Drinking Water and Health, vol. 2, National Academy Press.
- (14) Finch, G. et al, 1994, Ozone Disinfection of Giardia and Cryptosporidium, American Water Works Association Research Foundation, Denver.
- (15) Finch, G., et al, 1993, "Ozone Inactivation of Cryptosporidium parvum in Demand-Free phosphate Buffer Determined by In Vitro Excystation and Animal Infectivity", Appl. and Env. Micro. V59:4203.
- (16) Rubin, A., undated, "CT products for the inactivation of Giardia cysts by chlorine, chloramine, iodine, ozone and chlorine dioxide," obtained for USEPA office for research.
- (17) Trussell, R. R., 1995, "The Changing Role of Oxidation and Disinfection", Anforderungen an die Aufbereitung von Oberflachenwasser zu Trinkwasser aus mikrobiologischer Sicht, Proceedings of Mulheimer Wassertechnischen Seminar, Duisburg, Germany.
- (18) Jacangelo, J. G., Patania, N. L. and Laine, J. M., 1992, "Low Pressure Membrane Filtration for Particle Removal", AWWA Research Foundation, Denver, CO.