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Title: **DRINKING WATER DISINFECTION USING CHLORINE THEORY AND PRACTICE**

Authors: Professor T J Casey, Aquavarra Reseach Limited
Peter O'Reilly, Fingal County Council

Aquavarra Research Limited
22A Brookfield Avenue
Blackrock
County Dublin
Ireland
www.aquavarra.ie

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DRINKING WATER DISINFECTION USING CHLORINE THEORY AND PRACTICE

INTRODUCTION

This paper presents a discussion of process engineering issues related to the use of chlorine and its compounds for the production of pathogen-free drinking water. The following abstract from the World Health Organisation Drinking Water Guidelines (WHO, 1993) provides an appropriate context for the subject matter covered: "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 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."

The foregoing WHO comment encapsulates the primary reasons for careful regulation of chlorine use in drinking water preparation. There is also the not insignificant secondary reason that there is consumer resistance to drinking mains water that tastes of chlorine residues; where such taste problems exist, consumers are likely to consider bottled water more wholesome than the mains supply. The potentially long-term adverse health effects of organo-chlorine compounds are now well recognised. As a consequence, drinking water standards contain mandatory limits for the concentrations of these substances. The requirement for compliance with such quality standards constitutes the effective control on the upper limit of chlorine dose in drinking water application.

While effective disinfection is an essential treatment step in the production of most public water supplies, it does not on its own guarantee microbiologically safe water at the consumer's tap. The management, operation and integrity of the water distribution infrastructure also play an important role.

The first part of the paper presents an overview of the principles and process engineering considerations relating to drinking water disinfection as used in current water supply practice. The second half of the paper presents a practical illustration of these principles, using the Fingal County Council water supply coming from the Liffey waterworks at Leixlip as an illustrative case study.

WATER-BORNE PATHOGENS

The contamination of surface and groundwater drinking water sources by pathogens arises from the ingress of residues derived from the faeces and urine of infected humans and animals. As such reservoirs of infection exist in all human and animal populations, the risk of water contamination is always there. Diseases which are naturally transmitted between vertebrate animals and man are classified as zoonoses (Palmer et al., 1998). Significant waterborne Zoonotic pathogens include Cryptosporidium, Giardia, Salmonella and Eschericia coli O157.

The waterborne pathogens of main concern in the water supply context are listed in Table 1, categorised in the microbiological groupings of viruses, bacteria and protozoa. There are also a number of parasitic helminthic pathogens, such as those causing Bilharzia and Schistosomiasis, which are of great significance in tropical regions but are not of significance in the water supply context in Ireland.

The protozoan pathogens merit special comment because of their environmental persistence and resistance to disinfection processes.

Cryptosporidiosis was only identified as a human infection as recently as 1976 (Coop et al.). The causative organism, Cryptosporidium parvum, is a small protozoan obligate parasite. Infection, which results from the ingestion of environmentally resistant oocysts, shed in the faeces of an infected person or animal, causes self-limited diarrhoea in immunocompetent human beings but potentially chronic or life-threatening diarrhoea in immuno-compromised patients, particularly those with acquired immunodeficiency syndrome

(AIDS). The main animal sources of infection are thought to be scouring calves or lambs. Contaminated drinking water is a potential transmission route for human infection. There is some uncertainty as to the infective dose (Craun et al., 1998). Haas and Rose (1995) proposed an action level of 10-30 oocysts/100l within and above which a waterborne disease outbreak is possible. The small size of the oocysts (5 μm) allows them to pass through some treatment systems, and their resistance to chlorination enables them to enter distribution systems in a viable state. The stable cool conditions found in surface waters favour survival of the oocyst, which may be viable for many months.

Giardia is the most common human pathogenic intestinal parasite with a worldwide distribution (Thompson, 1998). Giardia infection, which is caused by the ingestion of Giardia cysts, is the most frequently diagnosed water-borne disease (Levine et al., 1990). While humans are likely to be the main reservoir of infection, animals also constitute an additional source, hence Giardia infection, like Cryptosporidiosis, is classified as a zoonosis

Table 1
Water-borne Pathogens

Biological group	Organism	Disease or Symptoms
Viruses	Polio virus	Poliomyelitis
	Hepatitis A virus	Infectious hepatitis
	ECHO virus	Fever, diarrhoea
	Cocksakie virus	Vomiting, etc.
	Rotavirus	Gastro-enteritis
	All enteric viruses	Minor malaise
Bacteria	Vibrio cholera	Cholera
	Salmonella typhi	Typhoid fever
	Salmonella paratyphi	Paratyphoid fever
	Other salmonellae	Gastro-enteritis
	Shigella spp.	Bacillary dysentery
	Leptospira spp.	Fever, jaundice etc.
	Legionella pneumophila	Respiratory illness
	Escherichia coli	Gastroenteritis
Protozoa	Entamoeba hystolytica	Amoebic dysentery
	Giardia lamblia	Diarrhoea
	Cryptosporidium parvum	Diarrhoea

DRINKING WATER REGULATIONS

Statutory Instrument 439 of 2000 sets out the disinfection-related quality standards for drinking water in Ireland in compliance with the requirements of 1998 EU Drinking Water Directive (98/83/EC). The provisions of SI 439 that relate to disinfection are set out in Table 2.

Table 2
SI 439 of 2000 - disinfection-related parameters

Parameter	Units	Parametric value
Escherichia coli (E.coli)	Number/100 ml	0
Coliform bacteria*	Number/100 ml	0
Enterococci	Number/100/ml	0
Clostridium perfringens*	Number/100 ml	0
Colony count at 22°C*		No abnormal change
Total trihalomethanes (TTHM)	μg/l	100

*indicator parameters

In the United States drinking water quality is regulated under the Safe Drinking Water Act (SDWA) of 1974, which gives the responsibility for setting drinking water standards to the US Environmental Protection Agency (USEPA). The US drinking water standards relating to disinfection are set in USEPA regulations known as the microbial-disinfection byproduct (M-DBP) rules. The following provisions of the 1998 M-DBP rules are of relevance in the current context (Brass, 2000):

- The TTHM limit was reduced from 100 µg/l to 80 ug/l
- The limit for the sum of 5 haloacetic acids (HAA5) was set at 60 µg/l
- Disinfectant residual limits: chlorine 4 mg/l; Chloramines 4 mg/l; Chlorine dioxide 0.8 mg/l
- Cryptosporidium: goal of zero contamination level; 2-log removal by filtration required for surface waters

DISINFECTION

The process goal in the disinfection of drinking water is to eliminate the risk of transmission of waterborne disease to consumers. It constitutes an essential treatment step in situations where there is a risk that drinking water may contain pathogens. Clearly, this is invariably the case where the water is abstracted from a surface water source. Many groundwaters, however, are pathogen-free and can meet drinking water microbial regulation requirements without the need for a disinfection step. Nevertheless, in some countries there is a legal requirement that all public water supplies are disinfected, irrespective of their microbial status. The overall situation in this regard within the EU is summarised in Table 3.

Table 3
Legal requirement to disinfect drinking water in EU Member States (Hydes, 1998)

Country	Surface water supplies	Groundwater supplies
Austria	Yes	No
Belgium	No	No
Denmark	Yes	No
Finland	No	No
France	Yes	No
Germany	No	No
Greece	No	No
Ireland	No	No
Italy	No	No
Luxembourg	No	No
Netherlands	Yes	No
Portugal	Yes	Yes
Spain	Yes	Yes
Sweden	No	No
G. Britain	Yes	Yes
Switzerland	No	No

The principal drinking water disinfectants in current use are chlorine and its compounds, ozone and UV radiation. Chlorine is mainly used as gaseous chlorine (Cl_2) or hypochlorite solution but also in the form of chlorine dioxide (ClO_2) and in combination with ammonia (chloramination). The choice of drinking water disinfectant in EU Member States is summarised in Table 4.

Table 4
Drinking Water Disinfection in EU Countries
(Breach & Patsch, 1998)

	At	Be	Dk	De	Es	Fl	Fr	GB	Gr	Ir	It	Nl	Pt	Sw
Cl_2	•••	•••	•	•••	•••	•••	••	•••	•••	•••	•••	••	•••	•••
O_3	•	•		••	••	•	••	•		•	•	•••		
UV	•	•		•		•		•				•		
ClO_2	•	•		•••			••	•		•	•••			•
ClAm					••	•						••		••

••• dominant •• common • occasional

Chlorination

When chlorine is added to water it reacts almost instantly to form hypochlorous acid (HOCl) and hydrochloric acid (HCl). Hypochlorous acid is the active disinfectant agent. It is a weak acid which undergoes partial dissociation to form hypochlorite ion (OCl^-), the degree of dissociation increasing with the water pH. The sum of the HOCl and OCl^- concentrations is referred to as the Residual Free Chlorine. Molecular chlorine is also considered to be free available chlorine, but it is not found in detectable concentrations within the normal drinking water pH range.

Chlorine is a strong oxidising agent and hence reacts with other substances present in natural waters such as organic matter and inorganic substances that are amenable to oxidation such as reduced metal ions, sulphides, bromide ions and organic nitrogenous compounds. The chlorine consumed by such reactions is referred to as the Chlorine Demand of the water and is expressed in terms of equivalent chlorine (mg/l as Cl_2). It should be noted that the Chlorine Demand uptake of chlorine generally takes place over a period of time, during which the residual free chlorine is being reduced in concentration, as illustrated in Fig 1.

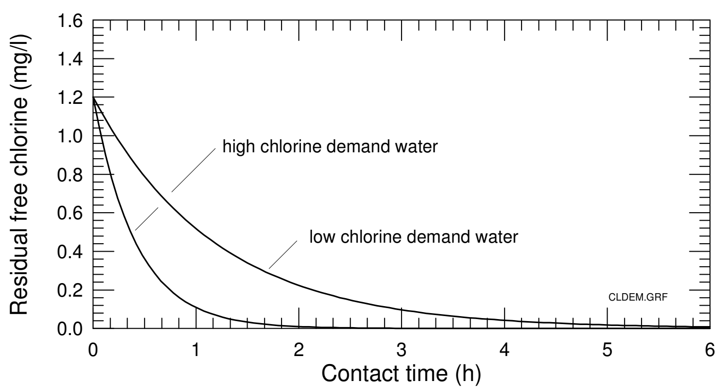

Fig 1 **Residual free chlorine decay rate**

The free chlorine decay rate can be approximately modelled (Chua, 1996) as an exponential rate process represented as:

$$C_t = C_0 e^{-kt} \qquad (1)$$

where C_t (mg/l) is the residual free chlorine after a contact time t (min), C_0 is the applied chlorine dose and k is the rate constant (min^{-1}). The rate constant k can be estimated as follows:

$$k = \frac{-\ln \frac{C_t}{C_0}}{t} \qquad (2)$$

Chlorine also reacts with free ammonia in water to form inorganic chloramines (monochloramine, dichloramine and trichloramine), which are also active disinfectants, but less potent than free chlorine. These reactions are dependent upon contact time, pH, temperature and chlorine to ammonia ratio. The sum of these secondary disinfectants is referred to as Combined Chlorine.

Thus, the chlorine dose added to water may be accounted for as follows:

Chlorine Dose = Residual Free Chlorine + Combined Chlorine + Chlorine Demand

where each component is expressed in terms of equivalent chlorine (mg/l as Cl_2).

A number of factors influence the disinfection effectiveness of chlorine, including:

- applied dose
- chlorine demand of the water
- contact time
- water temperature
- water pH
- species of microorganism (bacteria, viruses, protozoan cysts).
- concentration of micro-organisms

It is generally agreed that HOCl is a more effective disinfectant than OCl^-. At pH 6.5 free available chlorine exists almost entirely as HOCl, while at pH 9.0 it is almost completely dissociated to the OCl^- form. Hence, chlorination is considered to be more effective at an acid pH than at an alkaline pH.

The product of residual free available chlorine and contact time, designated as the "CT value", is an important disinfection process parameter. CT (mg.min/l) is quantified as the area under the C curve on Fig 1. If the chlorine decay rate is modelled as a first order rate process, the CT value is given by:

$$CT = \frac{C_0}{k} \qquad (3)$$

The influences of water temperature and pH on the CT value required for microbial inactivation are illustrated in Figs 2 and 3. Further data are given in the Water Treatment manual on Disinfection published by the EPA (1998).

Of the three predominant pathogen species in water supplies, i.e. bacteria, viruses and protozoan cysts, the latter are by far the most resistant to all forms of disinfection. 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 times higher than for E. coli. There are little data available on the inactivation of Cryptosporidium oocysts by chlorine or other oxidants. However, the available evidence suggests that chlorine and chloramines are relatively ineffective biocides for these oocysts, highlighting the importance of processes such as chemical coagulation and sand filtration in providing a barrier to their progression into supply. It would appear that the risk of Cryptosporidium breakthrough in the conventional treatment of surface waters is quite low – there have been no reported instances of waterborne Cryptosporidiosis in Ireland, where over 70% of the population is supplied with drinking water of surface water origin. Despite this favourable record, it is important to note that experience elsewhere (Mazounie et al., 1998) would indicate that poor performance of conventional coagulation/filtration processes could lead to a Cryptosporidium oocyst breakthrough.

The USEPA Surface Water Treatment Rule (SWTR) of 1989 requires that WTWs achieve an overall minimum 3-log reduction/inactivation of Giardia cysts and a 4-log removal/inactivation of viruses (Shaw & Regli, 1998). These efficiencies are assumed being achieved if WTWs employ soecified technologies which meet design and operating criteria and water quality performance measures. All systems are required a minimum continuos disinfectant residual of at least 0.2 mg/l at the entry point to the distribution system, and a detectable residual in at least 95% of the measurements taken throughout the distribution system.

SWTR states that properly operated chemical coagulation/filtration should provide a 2-log to 2.5-log reduction in Giardia cysts and a 1-log to 2-log reduction in viruses. On this basis, the disinfection process should achieve a minimum 1-log reduction in Giardia cysts and a 2 log removal of viruses. The CT values required to achieve these inactivation goals, as set out in the SWTR, are plotted on Fig 2 (Giardia cysts) and Fig 3 (viruses), as a function of water temperature and pH. It will be noted from these plots that CT increases with pH but is reduced with increasing temperature.
Based on the foregoing considerations, it is concluded that a CT value in the range 50-60 mg.min/l is a safe target range for conventional surface water treatment where chlorination is preceded by a well-operated chemical coagulation/sand filtration process combination.

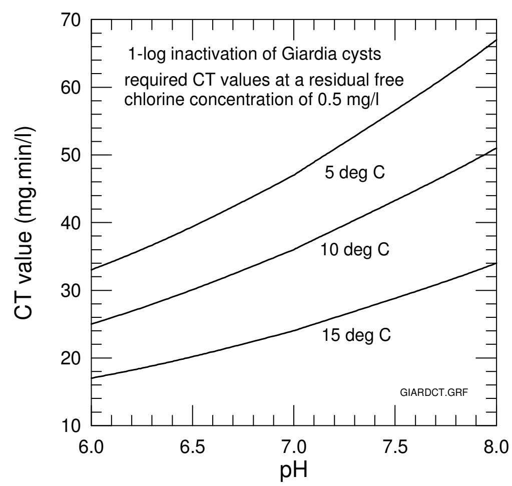

Fig 2 **Inactivation of Giardia cysts by free chlorine**
(US EPA, 1991)

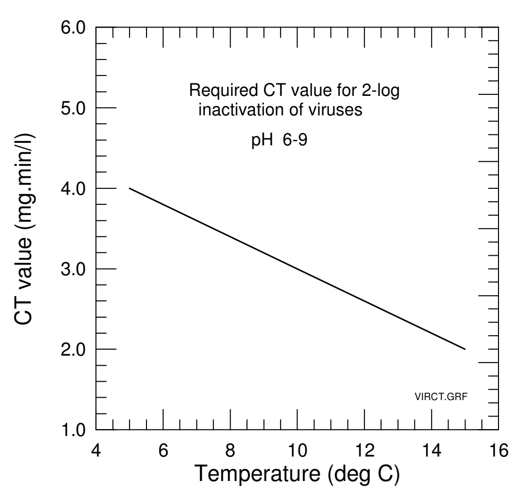

Fig 3 **Inactivation of viruses by free chlorine (US EPA, 1991)**
(US EPA, 1991)

Chlorination by-products

Apart from the fact that chlorine sometimes imparted a bad taste to drinking water, its liberal use for disinfection purposes went unquestioned until the 1970's when improving analytical techniques revealed the production of a variety of disinfection by-products (DPBs). The DPBs of main concern arising from chemical disinfection of drinking water are listed in Table 5. The presence of substances such as trihalomethanes (THMs) in drinking water gives rise to public health concern because of a possible carcinogenic link. For this reason, there has been a progressive tightening of drinking water standards in respect of the limit value for total THM (TTHM) in drinking water.

Table 5
Disinfection By-products

Disinfectant	DPBs
Gaseous chlorine	THMs & other halo-organics
Hypochlorite	THMs & other halo-organics Bromate Chlorate
Chlorine dioxide	Chlorite Chlorate
Ozone	Bromate Oxy acids
Chloramination	Nitrite

Disinfection: process design considerations

The key process design parameter for disinfection by chlorine is the product of residual free chlorine concentration x contact time (CT, mg.min/l). WHO (1992) recommends a minimum RFC concentration of 0.5 mg/l after 30 minutes contact at pH 7, for waters with turbidity of less than 1 NTU. The greater the chlorine demand of a water, the higher will be the initial dose required to achieve a particular residual at a target contact time. The chlorine demand characteristics of 12 major Irish urban water supplies, all based on surface water sources, were evaluated in a study by Casey & Chua (1997). These waters, after laboratory treatment by chemical coagulation and filtration, were chlorinated at the applied chlorine dose required to provide an RFC value of 0.5 mg/l after a contact time of 30 minutes. The resulting chlorine dose varied in the range 1.1–2.0 mg/l. The TTHM concentration produced after 24-hour contact time varied in the range 22-55 μg/l. The same study found that the TTHM concentration increases roughly in proportion to chlorine dose and also increases with contact time. It is therefore inevitable that high TTHM levels are produced where the target operational RFC is set at a high level. The experimental evidence would suggest that generally TTHM generation in chlorinated surface waters is not limited by organic matter availability. Thus, where drinking water TTHM levels in excess of 100 μg/l are reported, the prime cause is very probably the use of exceptionally high chlorine dose levels.

A number of EU Member States have a statutory requirement for disinfection of drinking water, as indicated in Table 2. Drinking Water Regulations in Austria, Spain and Portugal include prescribed limits for disinfectant residuals, as indicated in Table 6. It is noteworthy that German Drinking Water Regulations (1990) specify limits for both chlorine dose and chlorine residual for those WTWs where disinfection is necessary. The specified German limit values are given in Table 7.

Table 6
Legally required disinfectant residuals
(Hydes, 1998)

Country	Disinfectant	Leaving WTW	At tap
Austria	Chlorine (free) Ozone Chlorine dioxide	0.3-0.5 >0.1 >0.05	<0.3 <0.05 <0.2
Portugal	Chlorine	-	0.2
Spain	Chlorine (free) Chlorine (combined)	- -	0.2-0.8* 1.0-1.8*

*depending on pH

Table 7
Disinfectants and DBPs according to the German Drinking Water Regulations
(Hambsch, 1998)

Disinfectant	Target range after 2h contact time (mg/l)	Maximum dose (mg/l)	Limit value after treatment (mg/l)
Chlorine	0.1-0.3	2.0*	0.3* free chlorine 0.01* THM
Chlorine dioxide	0.05-0.2	0.4	0.2 Chlorine dioxide 0.2 Chlorite
Ozone	-	10	0.05 Ozone 0.01 THM
Silver	-	-	0.08 Silver

*maximum addition of chlorine may be increased to 6 mg/l, limits after treatment are then 0.6 mg/l free chlorine and 0.025 mg/l THM, if the microbial standards cannot be obtained otherwise or if ammonium temporarily interferes with disinfection.

It is also noteworthy many German water supplies are operated without a chlorine residual – a 1991 survey of 1000 German WTWs found that 50% operated without a chlorine residual. Hambsch (1998) stated the following requirements for conversion to operation without disinfection residual:

1. The water to be distributed (prior to final disinfection) has to meet the microbiological standards of the drinking Water Regulation.
2. Furthermore, the water to be distributed must not have a high bacterial regrowth potential, i.e. it should not contain organic substances which are easily biodegradable (assimilable organic carbon, AOC) and can serve as nutrients for the small amount of bacteria which is always present. If AOC is present, long residence times in the water system can cause bacterial regrowth, which could possibly exceed the guidance values for heterotrophic plate counts in the water system or at the tap respectively.
3. In the system, the pressure must be high enough to prevent bacteria entering the pipe. This includes technical measures as specified in DIN 1988 (Technische Regeln fur Trinkwasser-Installationen, TRWI). In order to prevent sedimentation and the excessive formation of biofilms, the tanks and mains must be cleaned regularly.
4. Finally, it must be pointed out that the water distribution system should not consist of materials, which release organic substances to the water, which could cause bacterial growth at the surfaces or in the water.

A similar design approach is adopted in the Netherlands (van der Kooij et al, 1998) and also in Switzerland (Klein & Forster, 1998). It is noteworthy that the water supplies for Amsterdam and Zurich have both been operated without a disinfection residual in the distribution system for more than a decade.

CHLORINATION PRACTICE IN IRELAND

All public water supplies in Ireland are disinfected. Public supplies are predominantly based on surface water sources. Water treatment invariably comprises alum coagulation followed by rapid gravity sand filtration with disinfection by gaseous chlorine. While there are no established design norms in place for the determination of chlorine dose, the Irish EPA has produced a comprehensive Manual on Disinfection (EPA 1998), which is a valuable reference for the design and operation of drinking water disinfection systems.

There is very limited published information on drinking water chlorination practice in Ireland. The annual EPA reports on drinking water quality do not include information on water treatment. The reported data on the microbiological quality of drinking water delivered by public supplies confirms that the disinfection processes employed are effective in producing safe drinking water. While the data on DBPs contained in these reports are somewhat limited, there is evidence of high THM levels in some supplies.

In a limited once-off survey, carried out as part of a research study into THM formation, the chlorine dose applied at 12 Irish WTWs was found (Chua, 1996) to vary in the range 0.7-3.0 mg/l. (average 1.55 mg/l). The associated chlorine decay time was measured and the corresponding CT range was estimated to be 55-800 mg.min/l. Hence, it is concluded that most WTWs operate a chlorination regime having a CT value well in excess of the requirement for disinfection (CT 50-60 mg.min/l). In WTW practice, the control of chlorine dosing is automated to achieve a target residual after a set contact time. The residual and contact time vary from WTW to WTW, resulting in the very wide operational CT range already noted.

These findings suggest that the adoption of a standard chlorine dose determination procedure would probably lead to a reduction in the range of chlorine dose used in drinking water production in Ireland. For example, the WHO has set, as a Guide Level, a residual free chlorine concentration of 0.5 mg/l after a contact time of 30 minutes for treated waters, where the pH is less than 8. When this chlorination regime was applied to the waters taken from the 12 Irish WTWs, referred to in the previous paragraph, the required chlorine dose range was found to be 1.1-2.0 mg/l, while the decay time ranged from 4 to 10 hours. As already noted in Section 2.4, the German drinking water regulations specify a free chlorine residual in the range 0.1-0.3 mg/l after a contact time of 2 hours, subject to a maximum chlorine dose of 2 mg/l. The specification of a residual at 2 hours is preferable to a specification at 30 minutes, as it provides a more reliable control of the CT value

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