

## Chapter 17

# Disinfection

### 17.1 INTRODUCTION

The purpose of disinfection of water or wastewater is to kill or remove pathogenic (disease-causing) organisms. The groups of organisms implicated in the transmission of water-borne diseases include viruses, bacteria, protozoa and helminths (worms). The more important microbial water-borne pathogens are listed in Table 17.1.

**Table 17.1** Microbial 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 histolytica	Amoebic dysentery
	Giardia lamblia	Diarrhoea
	Cryptosporidium parvum	Diarrhoea

Disinfection is a vital process in the production of drinking water and in the treatment of swimming pool waters. It is used to a much lesser extent in the treatment of wastewaters, where it may be applied, for example, to protect receiving waters used for bathing purposes.

The disinfection processes of significance in water and wastewater treatment can be classified in three categories:

- (1) Chemical disinfectants, the more important of which are chlorine, including its various compounds, and ozone; other chemical disinfectants include iodine, phenolic compounds and silver nitrate.
- (2) Physical disinfectants, such as heat and high frequency (UV) electromagnetic radiation.
- (3) Physical separation processes, such as centrifugation and membrane filtration.

### 17.2 DISINFECTION BY CHEMICAL AGENTS

In 1908 Chick showed that the rate of reduction of bacterial numbers by a disinfectant in a given contact time is proportional to the number of survivors at that time, i.e.

$$\frac{dN}{dt} = -K \cdot N \quad (17.1)$$

where N represents the number of living organisms, t denotes contact time and K is the rate constant or coefficient of lethality.

Equation (17.1) is generally referred to as 'Chick's Law'. Integration of equation (17.1) yields:

$$\ln\left(\frac{N}{N_0}\right) = -K \cdot t \quad (17.2)$$

where  $N_0$  is the initial number of microorganisms and N is the surviving number after a disinfectant contact time t.

It emerges that if the lethal action of a particular disinfectant on a microbial population obeys Chick's Law and if the coefficient of lethality is independent of N and t, then the plot of the logarithm of the fraction or number of organisms surviving against time will be linear. However, it should be noted that the number of disinfectant-microorganism combinations exhibiting exact conformity with Chick's Law is rather limited, since the coefficient of lethality is often time-dependent.

A time-dependent rate of kill may be expressed in the form:

$$\frac{dN}{dt} = -K \cdot N \cdot t \quad (17.3)$$

for which the integrated form is:

$$\ln\left(\frac{N}{N_0}\right) = -K \frac{t^2}{2} \quad (17.4)$$

It has been found that the biocidal action of the halogens and other oxidizing disinfectants rarely conforms to Chick's law, being more accurately represented by a time-dependent model, such as defined by equation (17.3).

### 17.3 DISINFECTION BY ULTRA VIOLET LIGHT

Ultraviolet (UV) light kills the vegetative and spore cells of microorganisms. It is also lethal to viruses. The lethality of UV light varies greatly with its wavelength. The bactericidal wavelength extends from 200 nm to 295 nm, with a maximum effect at about 254 nm.

The rate of devitalization of a population of microorganisms due to irradiation with ultraviolet light obeys Chick's Law. The coefficient of lethality, K, is a function of the radiation intensity:

$$K = K'I^n \quad (17.5)$$

Where K' is a constant, I is the radiation intensity, n is a constant, approximating to unity in value.

The intensity of radiation is reduced as it passes through an absorbing medium. This reduction can be represented as follows:

$$\frac{I}{I_i} = e^{-ax} \quad (17.6)$$

where  $I_i$  is the intensity of the incident radiation at the medium surface, I is the intensity after it has travelled a distance x into the absorbing medium (x is referred to as the light path) and a is a constant, which is sometimes called the 'linear absorption coefficient'.

The fraction  $I/I_i$  is known as the 'transmittance' or 'opacity', denoted by  $T$ ; hence equation (17.6) may be written in the form

$$\log \frac{1}{T} = 0.4343 ax \quad (17.7)$$

$\log (1/T)$  is known as the 'optical density' or 'absorbance' or 'extinction'.  $[0.4343 a]$  is called the 'extinction coefficient'.

It is at once apparent that the plot of extinction against light path will be linear and that the slope of this plot yields the extinction coefficient.

Pure water absorbs UV light. Natural and wastewaters may well contain a variety of molecular and ionic species that absorb UV light. The absorption coefficient is a function of the concentration of the absorbing species. The relationship between transmittance and concentration was shown by Beer, in 1852, to take the form (for a single absorbing species)

$$T = e^{-a'c} \quad (17.8)$$

where  $a'$  is a constant and  $c$  is the concentration of the absorbing species.

Combining equations (17.7) and (17.8) gives the 'Beer-Lambert Law', which expresses the relation between transmittance, light path and concentration of the absorbing material:

$$T = e^{-a''c x} \quad (17.9)$$

where  $a''$  is a constant.

It follows that

$$\log \frac{1}{T} = 0.4343 a'' c x \quad (17.10)$$

where  $0.4343 a''$  is called the 'specific extinction coefficient'.

It is important to note that the magnitudes of  $a$ ,  $a'$ , and  $a''$  are functions of the radiation wavelength and may well be significantly dependent on other factors, such as temperature.

For the purposes of water disinfection, UV light emanates from a source and penetrates the water bulk. Hence, the rate of kill varies throughout the water depth. An average coefficient of lethality can be computed by means of the relation

$$K_{avg} = \frac{\int_0^x K dx}{x} \quad (17.11)$$

Combining equations (17.5), (17.6) and (17.11) and assuming  $n$  to have unit value, the average coefficient of lethality is found to be

$$K_{avg} = \frac{K'I_i}{x} \left[ \frac{1}{a} - \frac{e^{-ax}}{a} \right] \quad (17.12)$$

This average coefficient of lethality can then be incorporated into equations (17.2)-(17.4), inclusive.

Light-scattering particles will also reduce the intensity of electromagnetic radiation. However, the effect of such particles on the light intensity dose not lend itself to a generalised mathematical treatment since their ability to scatter light is a function of many variables such as the size, shape and

the chemical nature of the particle. A mathematical treatment is further complicated by the fact that light-scattering particles may also absorb light.

## 17.4 DISINFECTION BY HEAT

Disinfection by heat also obeys Chick's Law. The rate constant analogous to the coefficient of lethality is a function of the thermal resistance of the target organism. It is important to note that the vegetative and spore cells of the same organism may well differ considerably, the spore cells being far more resistant to thermal devitalization. The situation is further complicated by the fact that the rate constant, being temperature-dependent, will vary with time since the disinfection procedure will involve increasing the temperature, holding the temperature at a fixed level and then cooling the system.

Milk pasteurisation is an example of disinfection by heat. The temperature range used is usually 60-80 °C. The required exposure time at 60 °C is about 20 minutes; it decreases with an increase in temperature.

## 17.5 DISINFECTION BY SEPARATION PROCESSES

Microorganisms are sometimes removed from fluids, both gases and liquids, by filtration using very fine filters (refer Chapter 6 for discussion of the disinfection effectiveness of membrane filtration, including the removal of the protozoan pathogens, *Cryptosporidium* and *Giardia*).

A reduction in the bacterial content of natural and wastewaters may be accomplished by processes where the primary function is to remove suspended particulate matter. Such processes include screening, sedimentation, dissolved air flotation, sand filtration and centrifugation. Chemical coagulation also effects a significant removal of bacteria through their entrapment by the associated flocculation process.

## 17.6 DISINFECTION WITH CHLORINE

### 17.6.1 Chlorine properties (White, 1986)

Chlorine (Cl<sub>2</sub>) is a greenish-yellow gas which can readily be compressed to form a clear amber-coloured liquid. It vaporizes readily at normal atmospheric pressure and temperature. It has a critical temperature (the temperature above which it can only exist as a gas) of 144 °C and a critical pressure (the vapour pressure at critical temperature) of 7.712 MN m<sup>-2</sup> absolute. On gasification at °C and 1 atm, its volume expands by a factor of 457.6. Liquid chlorine has a density of 1468 kg m<sup>-3</sup>, while gaseous chlorine has a density of 3.21 kg m<sup>-3</sup> at 1 atm and 0 °C (i.e. about 2.48 times that of air). It is highly soluble in water (ca. 1% by weight at 10 °C), as may be seen from the solubility data given in Table 1.6.

Chlorine gas has a characteristic penetrating and pungent odour and is quite toxic. It is irritating and corrosive to the respiratory tract, eyes and skin. Exposure to low concentrations of chlorine gas (1 to 10 ppm) may cause sore throat, coughing, and eye and skin irritation. Exposure to higher levels could cause burning of the eyes and skin, rapid breathing and pain in the lung region. Exposure to even higher levels can produce severe eye and skin burns, lung collapse and death.

### 17.6.2 Aqueous chemical reactions

When chlorine is added to water, the following chemical reactions (Snoeyink and Jenkins, 1980) occur:



where HOCl is hypochlorous acid, HCl is hydrochloric acid and OCl<sup>-</sup> is the hypochlorite ion.

At ordinary water temperatures, this reaction reaches equilibrium within a few seconds. In dilute solutions and pH levels above 4, the reaction is pushed towards the right, resulting in very little chlorine remaining as chlorine gas in the water. The corresponding equilibrium expression is

$$\frac{[\text{HOCl}][\text{H}^+][\text{Cl}^-]}{[\text{Cl}_2]} = K_s = 4.5 \times 10^{-4} \text{ at } 20^\circ \text{C} \quad (17.14)$$

where the square brackets denote molar concentration.

Hypochlorous acid is a weak acid, the degree of dissociation or ionization being given by

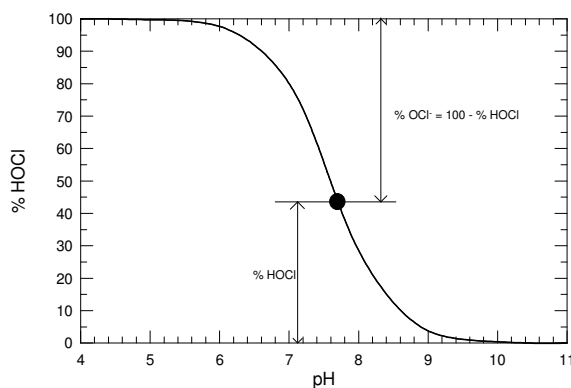
$$\frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} = K_i = 2.5 \times 10^{-8} \text{ at } 20^\circ \text{C} \quad (17.15)$$

K<sub>i</sub> is known as the ‘ionization’ or ‘dissociation’ constant.

Dissociation of hypochlorous acid reaches equilibrium virtually instantaneously. It is at once apparent from equation (17.15) that the degree of dissociation is pH-dependent. It should be noted that K<sub>s</sub> and K<sub>i</sub> are temperature-dependent.

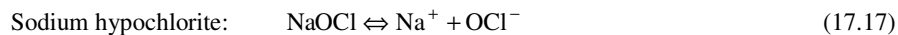
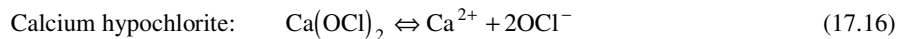
Chlorine gas and hypochlorous acid are potent germicidal agents. The hypochlorite ion also exerts a lethal effect but it is not as potent as the former species. Since very little chlorine remains as chlorine gas in water, the principal disinfecting action of chlorine is associated with hypochlorous acid.

Chlorine existing in water as hypochlorous acid and hypochlorite ion is defined as ‘free available chlorine’. The relative distribution of hypochlorous acid and the hypochlorite ion is very important since the former is about 40-80 times more efficient as a disinfecting agent than the latter. Fig 17.1 shows their relative amounts as a function of pH, as determined by the equilibrium equation (17.15).



**Fig 17.1** Dissociation of hypochlorous acid as function of pH

Hypochlorous acid is also produced when hypochlorites such as calcium hypochlorite and sodium hypochlorite are dissolved in water:

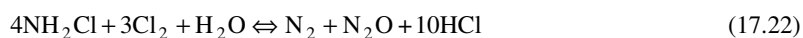
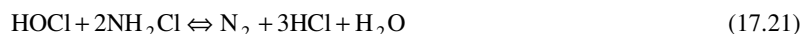


A certain fraction of the hypochlorite ions will combine with hydrogen ions to produce hypochlorous acid. Equilibrium will be established in accordance with equation (17.15). Thus, the same equilibria are established in water whether elemental chlorine or hypochlorite is employed. The important distinction is the resultant pH and hence the relative amounts of hypochlorous acid and hypochlorite ions existing at equilibrium. Chlorine tends to reduce the initial pH, whereas hypochlorite salts tend to raise it.

When chlorine is added to water containing natural or added ammonia, the latter reacts with hypochlorous acid to form various chloramines:



The distribution of the reaction products is governed by pH, temperature, time and the initial  $\text{Cl}_2:\text{NH}_3$  ratio. The situation is complicated by the fact that as additional amounts of chlorine are applied, the chloramines are eventually destroyed. Thus, the chloramines will exist while ammonia is in excess but are destroyed when chlorine is in excess. The following reactions lead to the destruction of the chloramines:



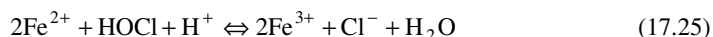
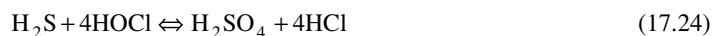
( $\text{N}_2\text{O}$  is nitrous oxide)

The chloramines are effective disinfecting agents but are not as potent as hypochlorous acid.

Chlorine also reacts with organic nitrogen to form compounds analogous to the products formed when it combines with free ammonia.

Chlorine which is in chemical combination with ammonia or organic nitrogen is commonly designated as 'combined available chlorine'.

Free chlorine readily oxidizes reduced inorganic substances such as hydrogen sulphide, nitrites, iron and manganese (in the ferrous and manganous forms):

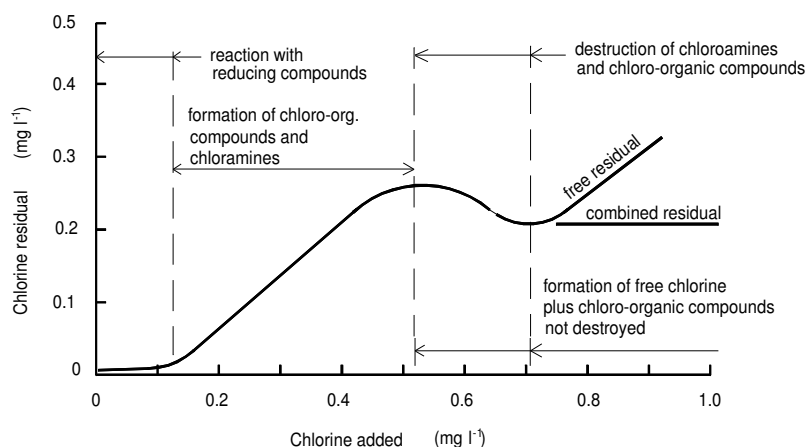


Chloramines do not enter vigorously into these reactions.

The various substances that react with chlorine as it is added to water are said to exert a 'chlorine demand'. The above inorganic species, which readily react with chlorine, are said to constitute an 'immediate chlorine demand'. A plot of the chlorine residual against the amount of chlorine added is presented in Fig 17.2.

‘Combined residual chlorination’ practice involves the application of chlorine to water to produce, with natural or added ammonia, a combined available chlorine residual with the objective of maintaining a residual through part or all of a water treatment plant or distribution system.

‘Free chlorination’ practice involves the addition of chlorine to water to produce, either directly or through the destruction of ammonia, a free available chlorine residual and to maintain that residual through part or all of a water treatment plant or distribution system.



**Fig 17.2** Correlation of chlorine residual and chlorine dose

### 17.6.3 Chlorine compounds

The chlorine-releasing compound used in water/wastewater treatment plants include chlorine gas, calcium hypochlorite, sodium hypochlorite, and chlorine dioxide. While chlorine gas is still widely used at waterworks, there has been a trend towards the more general use of hypochlorites due to the hazardous nature of chlorine gas.

Calcium hypochlorite is available commercially in either a ‘dry’ (solid) or a ‘wet’ (dissolved) form. Because the solid material is relatively stable under proper storage conditions, it is often favoured over the wet form. Because hypochlorite is a strong oxidizing agent it should be stored in a cool, dry location in corrosion-resistant containers and away from other chemicals.

Sodium hypochlorite is commercially available as a 15% w/w aqueous solution. The rate of decomposition tends to increase with increasing concentration and is affected by exposure to light and heat. It must be stored in corrosion-resistant containers and in a cool place.

Sodium hypochlorite may also be produced on-site by electrolysis of a sodium chloride solution. A low-strength hypochlorite solution is produced, typically containing less than 1% w/w hypochlorite. The process has the merit of effectively eliminating the chemical handling hazards associated with the chlorination process.

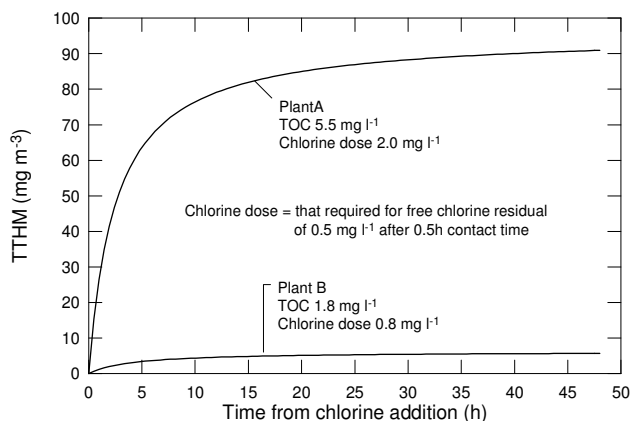
Chlorine gas is supplied in liquefied form in high-pressure cylinders. As noted earlier (section 17.6.1) chlorine gas is an extremely corrosive and poisonous gas. Being heavier than air, adequate exhaust ventilation must be provided at floor level. Chlorine storage and chlorination equipment rooms should be sealed off from the rest of the plant and should be accessible only from out-of-doors. It is recommended that a fixed-glass viewing window be included in an inside wall. Fan controls and gas masks should be located at the entrance to the room. Dry chlorine gas and liquid chlorine can be handled in black wrought iron piping but chlorine solution is very corrosive and should be handled in rubber-lined or tough plastic piping with diffusers of hard rubber. The gas cylinders in use should be mounted on platform scales set flush with the floor so that loss of weight can be used as a positive record of chlorine dosage.

Chlorine dioxide ( $\text{ClO}_2$ ) is used in place of gaseous chlorine in situations where reactions between the latter and certain trace organic compounds, such as phenolic compounds, give rise to bad taste or odour in drinking water. Chlorine dioxide is a reddish-yellow gas at ambient temperature ( $10^\circ\text{C}$ ) and is highly soluble in water (see Table 1.7). It is produced by reaction between chlorine and sodium chlorite:



#### 17.6.4 Trihalomethane formation

As shown in Fig 17.2, when chlorine is added to water it reacts with dissolved organic compounds to form a variety of chloro-organic compounds. As noted in section 7.4 of Chapter 7, organohalogen compounds as a group are listed as dangerous to living organisms. The trihalomethanes (THMs) are of particular concern in the context of drinking water disinfection by chlorination. They are formed from the reaction of *free* chlorine and naturally occurring humic substances in water. The THMs have the general formula  $\text{CHX}_3$ , where X can be Cl, Br or I. Chloroform ( $\text{CHCl}_3$ ) is of particular concern in drinking water because it is a suspected carcinogen. The brominated species which may be formed include dichlorobromomethane ( $\text{CHCl}_2\text{Br}$ ), dibromochloromethane ( $\text{CHClBr}_2$ ) and bromoform ( $\text{CHBr}_3$ ). The total THM concentration (TTHM) in chlorinated drinking water is a function of the organic precursor concentration and the chlorine dose used, as illustrated in Fig 17.3. This data set is taken from a study of THM formation in Irish drinking water supplies (Chua, 1996), being the highest and lowest values measured. It will be noted that the water from plant A has a higher TOC and, hence, a higher chlorine demand than plant B. These factors combine to produce a much higher TTHM generation in the water from plant A than in the water from plant B.



**Fig 17.3** Formation of trihalomethanes in drinking water

As may be noted from Fig 17.3, the THM concentration continues to increase over a relatively long period following chlorination. Following a decreasing rate curve, THM growth may be represented by a hyperbolic function of the form:

$$\text{TTHM}_t = \text{TTHM}_{\max} \left( \frac{t}{t_{50} + t} \right) \quad (17.29)$$

where  $t_{50}$  is the contact time (h) required to reach 50% of  $\text{TTHM}_{\max}$ . As plotted in Fig 17.3,  $t_{50}$  was 2.52h for plant A water (high THM water) and 4.17h for plant B water (low THM water).

THM formation can be significantly reduced by:

- (a) the removal of organic precursors (colour-causing humic substances) by chemical coagulation prior to chlorination.



- (b) A reduction chlorine dose.
- (c) The addition of ammonia to form chloramines in place of free chlorine (so-called chloramination).

### 17.6.5 Chlorination practice in drinking water treatment.

Chlorination practice in drinking water production is governed by the requirement to produce a finished water that meets the prevailing drinking water standards both in respect of microbiological quality and chloro-organic residuals. The microbiological quality requirement is generally deemed to be met if testing shows zero concentrations of total coliforms, faecal coliforms, faecal streptococci and sulphate-reducing clostridia (WHO, 2004; EU Directive 98/83/EC, 1998).

The disinfection effectiveness of chlorination depends on the chlorine dose and the chlorine contact time. As shown in Fig 17.2, chlorine reacts with organics and inorganics, thereby reducing the residual free chlorine (RFC) available for disinfection. The product of the RFC concentration and contact time gives the process CT-value, which is probably the best measure of the disinfection potential of a chlorination process. Fig 17.4 illustrates a typical RFC/time decay curve – the CT-value being the area below the curve. The CT-value can be approximated with reasonable accuracy (Chua, 1996) by assuming an exponential decay rate for RFC and using the 2h RFC value to define the decay rate constant:

$$C_t = C_0 e^{-kt} \quad (17.30)$$

Hence

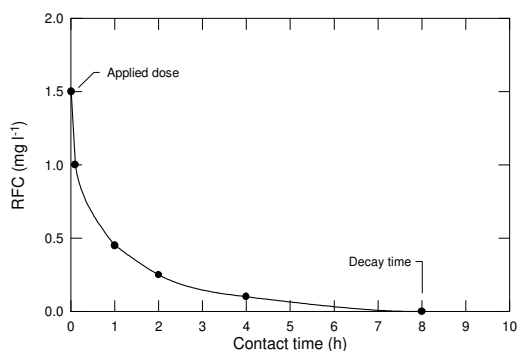
$$k = 0.5 \ln \left( \frac{C_0}{C_2} \right) h^{-1} = \frac{\ln(C_0 / C_2)}{120} \text{ min}^{-1}$$

where  $k$  is the decay rate constant,  $C_0$  is the initial RFC value and  $C_2$  is the RFC value after 2h contact time. The CT-value is found by integration over time:

$$CT = \int_0^{\infty} C_0 e^{-kt} dt = \frac{C_0}{k}$$

Hence

$$CT = \frac{120 C_0}{\ln \left( \frac{C_0}{C_2} \right)} \text{ mg l}^{-1} \text{ min} \quad (17.31)$$



**Fig 17.4** Typical chlorine decay curve

The WHO Drinking Water Guidelines (2004) recommend a minimum RFC of 0.5 mg l<sup>-1</sup> after 30 min contact time at pH 7 for waters with a turbidity less than 1 NTU. It should be noted that the use of a standard chlorination rate defined in this way does not result in a standard CT-value. In a series of tests

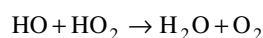
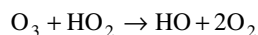
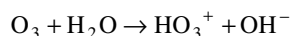
using the WHO guideline chlorination on 12 different drinking waters, which had been pre-treated by chemical coagulation/filtration processes, the CT-values were found (Chua, 1996) to vary in the range 48-136 mg l<sup>-1</sup> min. Because of the variation in the initial decay rate for different waters, it is preferable to regulate chlorination by specifying the RFC after a longer contact period than 30 min, say 2h. Equation (17.31) may then be used to calculate the corresponding CT-value. For waters that have been pre-treated by chemical coagulation/filtration, a CT-value of 50 mg l<sup>-1</sup> min should be adequate for drinking water disinfection.

## 17.7 DISINFECTION WITH OZONE

Ozone (O<sub>3</sub>) is a powerful disinfecting agent. It is used for drinking water disinfection and for air de-odourization in wastewater pumping stations and in sludge handling facilities.

It is a blue gas having a characteristic, but not unpleasant, odour. It is formed from oxygen (O<sub>2</sub>) by passing a silent electric discharge through air. Care must be taken to avoid the formation of an electric arc which could cause deterioration of the electrodes and produce nitrous vapours. This is ensured by using dry air and by covering one or both of the electrodes with a glass dielectric. The voltage applied between the electrodes is generally in the range 8-15 kV. At a frequency of 50 cycles per second, the production of ozone per square metre of discharge area is of the order of 14 mg s<sup>-1</sup> (i.e. 50 g h<sup>-1</sup>) and the power consumed is 1 kW. This output is doubled if a frequency of 500 cycles per second is used, an important factor in large installations. The ozone output decreases with increasing temperature. Consequently, the electrodes must be kept as cool as possible; this is usually achieved by circulating water or oil.

The concentration of ozonised air is typically in the range 5-10 g m<sup>-3</sup>. To sterilise 1 m<sup>3</sup> of reasonably clear water, from 0.5 to 1.0 g of ozone is needed. Greater quantities are required if the organic content of the water is significant. Neutral salts and hydroxyl ions accelerate ozone decomposition, which in pure aqueous solution occurs as:



The free radicals HO<sub>2</sub> and HO retain great oxidizing potential, and they are reactive with many common impurities such as metal salts and organic matter.

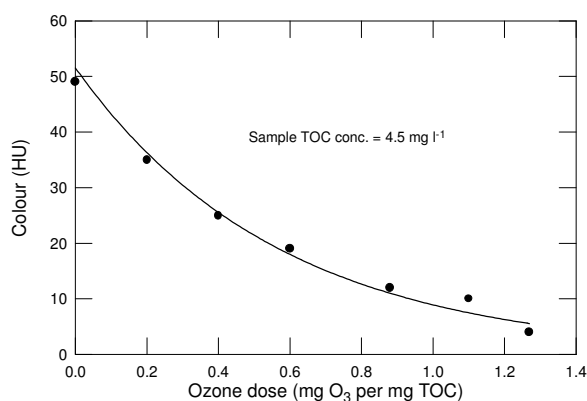


Fig 17.5 Colour reduction by ozone (Casey and Chua, 1995)

Since ozone has a low solubility in water (see Table 1.7) and its concentration (and therefore partial pressure) is low in the air or oxygen stream in which it is carried, an efficient gas-water contacting

system must be used for its dissolution. The ozonized air or oxygen stream is introduced through a submerged diffuser system or by means of a packed bed gas-water dissolution system, using materials that are chemically non-reactive with ozone.

Because of its strong oxidizing capacity, ozone can be used to remove natural colour from water by a bleaching action. An example of the bleaching action of ozone on water colour is given in Fig 17.5.

## REFERENCES

- Casey, T. J. and Chua, H. K. (1995) *Trihalomethanes in drinking water*, paper presented to the Water & Environmental Section, Institution of Engineers of Ireland, Dublin.
- Chua, H. K. (1966) *Trihalomethane Precursor Control in Drinking Water Treatment*, PhD Thesis, Department of Civil Engineering, University College Dublin.
- EU Directive (1998) *The Quality of Water Intended for Human Consumption*, 98/83/EC, Brussels.
- Snoeyink, V. L. and Jenkins, D. (1980) *Water Chemistry*, John Wiley & Sons, New York
- White, G. C. (1986) *Handbook of Chlorination*, van Nostrand Rheinhold, New York.
- WHO (2004): *Drinking Water Guidelines*, 3<sup>rd</sup>. Edition, WHO, Geneva.

## Related reading

- AWWA (1986) *Water Chlorination, Principles and Practice*, American Waterworks Association, Denver, Co 80235, USA
- Jolley, R. L. (1990) *Water Chlorination, Chemistry, Environmental Impact and Health Effects*, Vol. 6, Lewis Publications.