Elementary Handbook of Water Disinfection

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TT 206/03

Water Research Commission

ELEMENTARY HANDBOOK OF WATER DISINFECTION

Prepared for the
Water Research Commission

by

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WRC Report No. TT 205/03

November 2003

Obtainable from:

Water Research Commission
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0031

The publication of this report emanates from a project entitled:
An Introduction to the Principles of Water Disinfection Processes
(WRC Project No. K5/770/1/01)

ISBN No. 1-86845-983-7

Printed in the Republic of South Africa

AUTHOR'S PREFACE

The aim of this Handbook is to provide readers with an introduction to the processes of water disinfection. The emphasis has been placed on chlorination and chloramination, these being the two processes most commonly encountered in South Africa. Discussions of the alternative processes of chlorine dioxide treatment, ozonation, mixed oxidants (mainly the Peroxone process), and ultraviolet irradiation are included.

The Handbook is intended for non-specialists in chemistry and microbiology and is aimed at introducing and establishing principles, and affording a basic understanding rather than providing specific information for running a water treatment plant, since such information is readily available elsewhere. Suggested sources for further reading on the various processes have been included. These should be consulted by interested readers who wish to improve their depth of understanding. A useful source of up-to-date information and reports of current work on water disinfection, if indeed a single source can be identified, is the *Journal of the American Water Works Association.*

This Handbook is an abridged and simplified version of a more extensive work titled, *Guide to the Chemistry, Biochemistry and Microbiology of Chemical Water Disinfection Processes* by F.H.H. Carlsson and P.W. Wade (Revised and Expanded Edition), Pretoria 1997, 188 + x pp. This is available on request from: Information Centre, CSIR / Environmentek, P.O. Box 395, Pretoria, 0001.

ACKNOWLEDGMENTS

The author acknowledges with gratitude the financial support of the WRC in executing this project. The following individuals are thanked for their contributions in reading the manuscript and offering helpful criticism. Any shortfalls are entirely those of the author.

Mrs APM Moolman..... Research Manager, Water Research Commission
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CHAPTER 1

INTRODUCTION

GENERAL OVERVIEW

In South Africa raw water is drawn from one or a combination of the following sources:

- □ Rivers
- □ Dams
- □ Groundwater

Before being pumped into the distribution network and being supplied to consumers, water passes through a purification works that may be large or small depending on the number of consumers it serves. This is necessary to render the water fit for human consumption and incorporates such processes as the removal of suspended solids and colour, but is particularly aimed at protecting the health of the consumers by killing any bacteria, viruses or parasites that may be present thus preventing the outbreak of waterborne diseases which are caused by these microorganisms.

Raw water may contain a variety of impurities which make it unsuitable for human consumption. These may include dissolved, suspended and colloidal solids, plant material, algae, bacteria, viruses and protozoan parasites. In the purification works, raw water undergoes treatment to make it conform to certain standards of purity as laid down by the water board, municipal, provincial or national guidelines or standards. These quality guidelines ensure that the water conforms to certain minimum requirements and is safe for human consumption.

Treatment consists of some or all of the following principal stages:

- □ *Screening and sedimentation*, to remove coarse particles on mesh screens and to allow the coarser suspended solids to sediment (settle).

- □ *Flocculation and coagulation*, to promote the settling of finer suspended and colloidal solids, usually with the aid of some flocculating agent such as alum.

- □ *Filtration*, most often through sand beds, to remove any remaining suspended solids, protozoan parasite cysts as well as certain larger bacteria.

- *Stabilisation* with lime in order to minimise corrosion and scaling of the distribution system.

- Other stages could include pre-chlorination or pre-ozonation after the screening and sedimentation step (to kill and thus aid coagulation and settling of algae), as well as post-treatment with activated carbon and/or membrane filtration, which would take place as the final stage after sand filtration.

The final stage before distribution is

- ***Chemical disinfection***, to kill any surviving pathogenic bacteria and viruses as well as to prevent re-growth of bacteria in the distribution system. This consists of treating the water with one or several chemical disinfection agents that will kill any harmful bacteria, viruses or, on prolonged treatment with the stronger oxidants, protozoan parasites that may be present.

What is disinfection?

Disinfection is the treatment of water, usually with one or more chemical agents that will kill all or most bacteria, viruses and parasites that give rise to gastro- intestinal illness, the most common symptom of which is diarrhoea. Such micro-organisms (bacteria, viruses and parasites) are referred to as *enteric organisms*.

Pathogenic bacteria are bacteria which are able to cause infection, not necessarily only enteric infections, but also others such as ear, nose and throat infections.
Whilst effective flocculation, sedimentation and filtration remove many of the micro-organisms present, chemical disinfection is necessary and mandatory in order to ensure water safe for human consumption. It serves to kill any bacterial pathogens, viruses and, provided the contact time is sufficiently long and the disinfectant is powerful enough, protozoan parasite cysts, that may have survived the preceding stages. These organisms can cause a variety of waterborne gastro-intestinal illnesses such as diarrhoea, dysentery, cholera and typhoid fever. Chemical disinfection is not optional but essential in providing safe drinking water and preventing the outbreak of serious waterborne diseases.

Often groundwater is used without any disinfection if it can be shown to be free from pathogenic micro-organisms. However, it is advisable to provide chemical disinfection in order to maintain the quality of the water in the distribution system as well as at the point of use where secondary infection may occur.

The chemical disinfection stage should never serve to compensate for deficiencies in the earlier treatment stages.
It is essentially a final, "polishing" step, designed to achieve what the other stages cannot, assuming that they are carried out optimally.

Chemical disinfection is also applied to treated water being discharged from sewage works. This is to prevent the possibility of discharge of pathogenic bacteria and viruses into watercourses that could pose a health hazard to water users. It is, also in such cases, a "polishing" step following sewage treatment by whatever processes may be applied such as trickling filters, activated sludge etc. There would be no purpose served by treating raw sewage with e.g. chlorine on account of the very high chlorine demands that this would show.

Disinfection agents

The most common disinfection agent for water of all types is *chlorine gas* which is injected into the water under pressure before it is distributed to consumers. Another common agent used most often in conjunction with chlorine is *monochloramine* which is generated by adding ammonia at some stage of the chlorination process, and known as *chloramination* or the *ammonia-chlorine* process. This serves to provide a longer lived, although weaker disinfectant, species than free chlorine, monochloramine, and thereby extend the active disinfection process into the distribution system and prevent the re-growth of harmful bacteria.

Disinfection processes other than chlorination are generally referred to as *alternative* processes and this designation usually includes chloramination.

These include, apart from chloramination, processes such as

- □ Chlorine dioxide treatment
- □ Ozonation
- □ Hydrogen peroxide treatment (with or without added ozone)
- □ Ultraviolet irradiation treatment

All these processes have particular, sometimes special, applications suited to certain conditions. More importantly, they are often combined with chlorination and chloramination or used sequentially to solve particular problems that may exist on certain plants drawing particular qualities of raw water. This is a modern trend in water disinfection.

FURTHER READING

CSIR DIVISION OF WATER TECHNOLOGY (1990) *Manual on Water Purification Technology* (Technical Guide K73) Denysschen, JH. (ed.), Pretoria. 178 pp + xiii.

DEPARTMENT OF WATER AFFAIRS AND FORESTRY (1997) *South African Water Quality Guidelines,* 2nd edn, **1**: Domestic Use, Government Printer, Pretoria, 198 pp.

SOUTH AFRICAN BUREAU OF STANDARDS (1984) *South African Standard.* Specification for Water for Domestic Supplies. SABS 241-1984, SABS, Pretoria, 15pp.

WHITE G C (1992) *Handbook of Chlorination and Alternative Disinfectants*, 3rd edn, Van Nostrand Reinhold Company, New York. 1308 + xiv pp.

CHAPTER 2

CHLORINATION

INTRODUCTION

The effectiveness of chlorine as a disinfectant for water and wastewater is beyond question as the practice has successfully been in place for most of this century. Modern urban life, certainly in the tropical and sub-tropical countries such as South Africa, would be nearly impossible without chlorination of water supplies. It is so well established that other disinfectants are often referred to as *alternative disinfectants.*

Chlorination of drinking water has been described as one of the single measures that has contributed the most to health in general in the industrialised countries. By means of this simple and cheap method it became possible, in the beginning of this century, to set completely new bacteriological health standards for drinking water particularly with respect to faecal pollution. The number of coliform bacteria, which are indicators of the presence of bacteria that cause gastrointestinal diseases such as diarrhoea, cholera and dysentery, in the treated water could be brought down to less than one thousandth of the number present in untreated water. The frequency of cases of typhoid fever also dropped drastically following the introduction of water chlorination. It has been said that chlorine has saved more lives than the antibiotic penicillin that revolutionised the treatment of bacterial infections in the early to mid-1940s.

Chlorine has saved more lives than penicillin

It is not surprising that it caused a stir in 1974 when it was discovered that, under certain conditions, the chlorination process could give rise to the formation of chloroform and other trihalomethanes (THMs) which, under certain conditions, are potential human carcinogens i.e. substances which have been shown to cause cancer in experimental animals. Thus, chlorination of water not only results in the killing of micro-organisms but may also contribute to the formation of substances which are potentially hazardous to human health. These substances are not restricted to the THM's and the list grows longer every year as new compounds are discovered. A very large number of these are classed as mutagens which are compounds that can potentially cause cancer.

However, it is doubtful whether chlorine disinfection will ever be completely superseded or generally discontinued. The benefits of chlorination are too great and the risks that exist from potentially adverse effects of chlorination by-products are overwhelmingly compensated for by the health benefits.

It is significant that in the case of the City of Amsterdam, to name but one example, where water chlorination has been discontinued in view of the health hazards of THM's, chlorination equipment is kept on stand-by for cases where alternative disinfection facilities (ozonation) may prove inadequate to provide drinking water free from coliform bacteria and to the reduce the total bacterial count.

CHEMISTRY OF CHLORINATION

It is not possible to correlate disinfection potency with the total analytical concentration of free chlorine (a measure of the amounts of hypochlorous acid and hypochlorite ions present) as, dependant on the pH, all the chlorine is not available to inactivate micro-organisms with equal facility. Hypochlorite ions are slower acting than hypochlorous acid.

Chlorine reacts rapidly with water to give hypochlorous acid, usually referred to as *free available chlorine*

Chlorination is most often carried out by injecting chlorine gas through the water. Chlorine reacts very rapidly to give hydrochloric (HCl) and hypochlorous (HOCl) acids according to the reaction below. Thus **free available chlorine** refers to hypochlorous acid and not to the actual chlorine gas (Cl_2) since the latter practically does not exist as a free species in solution on account of the very rapid reaction of chlorine with water, as follows:

$$Cl_2 + H_2O \rightarrow HCl + \mathbf{HOCl} \quad \text{..... (2.1)}$$

This equation and that below show that the concentration of hypochlorous acid, the principal disinfectant species, depends on the total chlorine concentration and the pH.

Disinfection potency depends on the chlorine concentration and the pH

The important part of equation 2.1 is the formation of hypochlorous acid which is the more rapidly acting and hence the more important disinfectant.

Hypochlorous acid exists in solution in equilibrium with hydrogen ions and hypochlorite ions as shown in equation 2.2, the proportions being governed by the concentration of hydrogen ions (H^+) which is expressed by the pH:

$$HOCl \rightleftharpoons H^+ + OCl^- \quad (2.2)$$

Hypochlorous acid partly dissociates into hydrogen ions and hypochlorite ions

Note: Essentially the same chemistry applies to other forms of chlorine such as sodium hypochlorite (household bleach, JIK®), calcium hypochlorite (HTH®) and to trichloroisocyanurate (stabilised chlorine, Chlor-Floc® etc.). These substances all afford hypochlorous acid in solution that dissociates according to Equation 2.2.

Table 2.1 gives the percentages of the free available chlorine present as hypochlorous acid at various pH values.

Table 2.1 Percentages of free available chlorine present as hypochlorous acid in aqueous solutions of chlorine gas, sodium or calcium hypochlorite at various pH values measured at 20°C.

pH	**% HOCl** (approx.)
5.0	99
5.5	98
6.0	97
6.5	**90**
7.0	**80**
7.5	**50**
8.0	25
8.5	10
9.0	3
9.5	2
10.0	0

This is an important table since the disinfectant potencies of hypochlorous acid and hypochlorite ion are very different, the former being a 100-fold more effective disinfectant species than the latter.

Hypochlorous acid is a more rapidly acting and effective disinfectant species than hypochlorite ion

It can be seen from Table 2.1, that at pH 7.5, the free chlorine is present as 50% hypochlorous acid and that the amount in solution decreases very rapidly with increasing pH. This is partly the reason why swimming pools, utilising chlorine disinfection, and where short bacterial killing times are of prime importance, are ideally maintained at between pH 7.2-7.6.

However, drinking water disinfection by chlorination is carried out at above neutrality, being stabilised at pH 8 ± 0.2. This is the general practice despite the presence of only 25% of the free chlorine as hypochlorous acid at this pH (Table 2.1). This pH is used in view of a major consideration being the prevention of erosion of concrete distribution pipelines. Short bacterial killing times are also not of prime concern since drinking water is allowed to stand before distribution giving the less potent hypochlorite ions a longer time to act.

With reference to Equation 2.1 it is seen that one molecule of hypochlorous acid (HOCl) is derived from one molecule of chlorine (Cl_2), but contains only one atom of chlorine. Thus, half of the chlorine is apparently "lost" as chloride ions when chlorine reacts with water.

There is, however, no loss in disinfection (oxidising) power since one molecule of chlorine has the same disinfection power as one molecule of hypochlorous acid.

The term *available chlorine* can be confusing, should be avoided and has no place in water treatment terminology

The term *available chlorine* can be confusing and has no place or indeed use in the field of water and water treatment terminology. It derives from the iodometric determination of the total oxidising power of chlorine or a chlorine containing compound. Therefore, the *available chlorine* is always twice the percentage by mass of the chlorine content of an oxidising compound such as hypochlorous acid, calcium or sodium hypochlorite.

The term *available chlorine* must not be confused with the terms *free available chlorine* or, preferably, *free chlorine residual*

The term *available chlorine* has a particular meaning and must not be confused with the terms *free available chlorine* or *free chlorine residual*. The latter two terms refer to the same thing, namely, *the total concentrations of hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) that occur in chlorinated water* according to Equation 2.2. It, therefore, gives no indication of the total concentration of the principal disinfectant, hypochlorous acid, present. This has to be determined with reference to the free chlorine residual and the pH value from Table 2.1.

The foregoing discussion pertains to the behaviour of chlorine in pure water. It is necessary to consider some of the reactions that can take place if common impurities are present which is almost always the case. The following discussion will deal with ammonia, the presence of which exerts the most profound influence on the course of water chlorination. Ammonia originates as the final product from the bacterial breakdown of a very wide range of nitrogen containing substances of animal and plant origin.

This gives rise to the *breakpoint phenomenon* which takes place due to the presence of ammonia and is a description of the process whereby chlorine reacts with ammonia in dilute aqueous solution.

The *breakpoint* phenomenon in its simplest form is due to the presence of ammonia

Ammonia (NH_3) reacts with hypochlorous acid (HOCl) in dilute aqueous solution to form chloramines according to the following reactions:

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \quad \text{(Monochloramine)} \ldots\ldots (2.3)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad \text{(Dichloramine)} \ldots\ldots (2.4)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \quad \text{(Trichloramine)} \ldots\ldots (2.5)$$

The interrelationships of these reactions and the dependence on pH, contact time etc. is very complex. It is sufficient to state for the purposes of the present discussion that the predominant species is *monochloramine* with a trace of dichloramine.

Chlorine in the form of any of the chloramines is known as *combined chlorine* and any substance that leads to the consumption of chlorine is said to exert a *chlorine demand*.

Chlorine in the form of any of the chloramines is known as *combined chlorine* and any substance that leads to the consumption of chlorine is said to exert a *chlorine demand*.

In the absence of ammonia, the free chlorine residual would simply increase linearly with the amount of chlorine introduced into the water, as expected. However, in the presence of ammonia the above reactions come into play and the so-called *breakpoint* phenomenon, alluded to earlier, occurs.
For explanatory purposes it is useful to idealise the situation where the pH is near neutrality and the water contains no chlorine-reducing substances and no nitrogen containing matter other than ammonia. When chlorine is added to such water in separate, successive portions and the solutions are allowed to stand for time periods varying from several hours to a day or more, the curve shown in Fig. 2.1 is obtained.

The residual oxidising chlorine increases proportionately to the added chlorine dose until a chemical or molar ratio of added chlorine to initial ammonia concentration (i.e. one molecule of ammonia and one molecule of hypochlorous acid, according to Equation 2.3) of unity is reached at the so-called, hump (Fig. 2.1; Point A). There is essentially no breakdown of chloramines to free nitrogen over this range. Once the molar ratio of hypochlorous acid to monochloramine exceeds unity, a decrease in residual oxidising chlorine is found with increasing chlorine dosage.

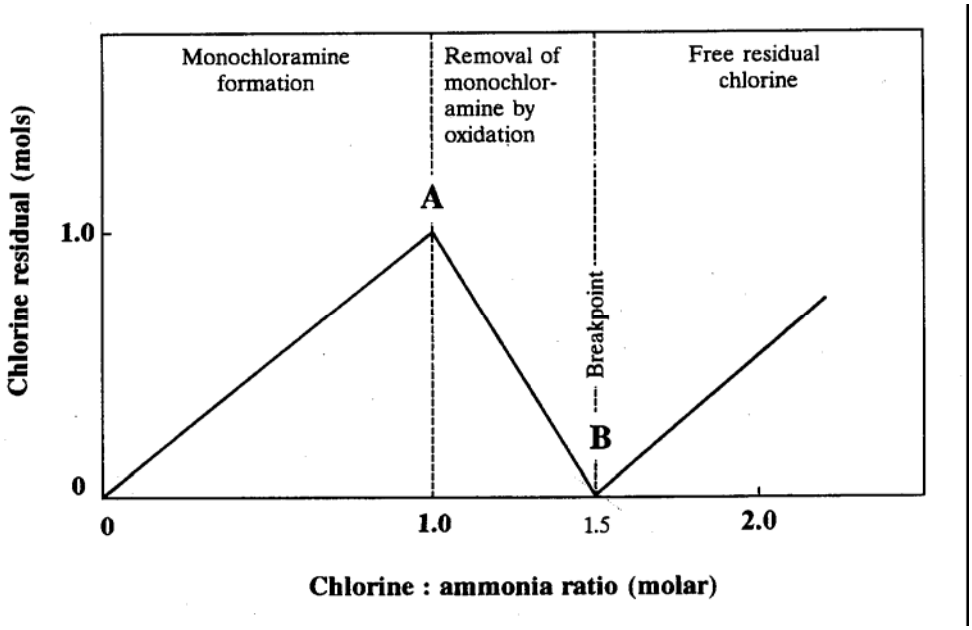

Fig. 2.1 Idealised curve of breakpoint chlorination

This is due to the chlorine which is added to exceed the 1:1 molar ratio as depicted in Equation 2.3, oxidising monochloramine to nitrogen which comes off and becomes part of the normal atmospheric nitrogen. This is equivalent to the removal of ammonia by oxidation. The reaction is depicted in Equation 2.6.:

$$2NH_2Cl + HOCl \rightarrow \mathbf{N_2\ (nitrogen)} + H_2O + 3H^+ + 3Cl^- \quad \text{.....(2.6)}$$

At Point B (Fig. 2.1), the *breakpoint*, essentially all the chlorine has been reduced after an appropriate contact time, and all the chloramine, originally present as ammonia, has been oxidised by chlorine to nitrogen. After the breakpoint (Fig. 2.1; Point B), a free residual of chlorine remains as hypochlorous acid and hypochlorite ions.

It is noteworthy that up to the so-called hump (Fig. 2.1; Zero to Point A), all the chlorine added is present as chloramines; principally monochloramine, according to Equations 2.1 to 2.3.

A more realistic depiction of the breakpoint phenomenon is given in Fig. 2.2.

This differs from the idealised picture on account of the complexity of the phenomenon where many competing side-reactions take place

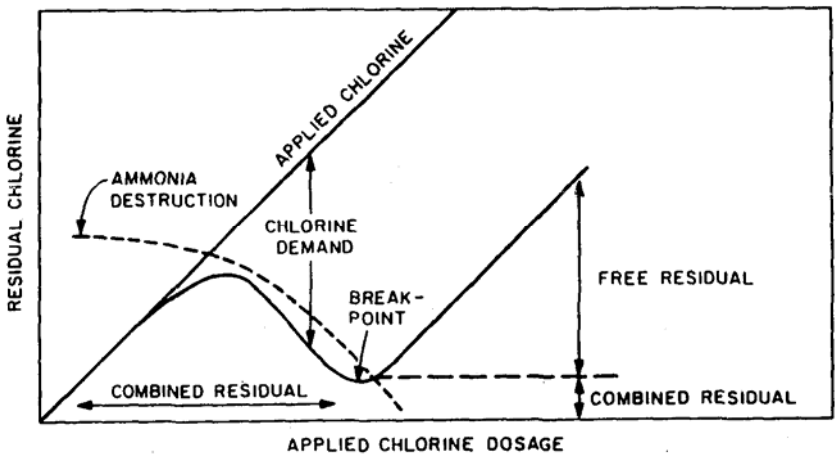

Fig. 2.2 Breakpoint chlorination presented more realistically

Simplistically, the breakpoint phenomenon can be accounted for by the following two reactions:

□ The formation of monochloramine from ammonia and hypochlorous acid (Fig. 2.1: Zero up to Point A):

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \quad \text{.....(2.3)}$$

□ The destruction (oxidation) of monochloramine by excess hypochlorous acid (Point A to Point B):

$$2NH_2Cl + HOCl \rightarrow N_2 \text{ (nitrogen)} + H_2O + 3H^+ + 3Cl^- \quad \text{.....(2.6)}$$

The second reaction (Equation 2.6) is presumed to occur whenever excess free chlorine remains after the formation of monochloramine. These equations may be added together to give the following, simplified net reaction, from which the theoretical chemical ratio of ammonia to free chlorine (hypochlorous acid) at the breakpoint of 3 : 2 or 1.5 : 1 can be deduced:

$$\mathbf{2}NH_3 + \mathbf{3}HOCl \rightarrow N_2 + 3H_2O + 3H^+ + 3Cl^- \quad \text{.....(2.3 + 2.6)}$$

This translates to a ***mass ratio*** of ammonia nitrogen to chlorine of 1 : 7.6.

An even further simplified picture of the reaction of ammonia and chlorine is given by the following Equation 2.7 where the ratio of 1 : 1.5 is again represented:

$$\mathbf{2}NH_3 + \mathbf{3}Cl_2 \rightarrow N_2 + 6HCl \quad \text{.....(2.7)}$$

Note: These reactions do not accurately represent the very complex mechanism of breakpoint chlorination but are sufficiently representative of reality to explain the overall process.

In water treatment, the process is known as *free residual chlorination* rather than breakpoint chlorination. The practical consequences are as follows:

- The chlorine residuals up to the hump (Fig. 2.1; zero to Point A) are all monochloramine i.e. *combined chlorine*. This is a relatively poor disinfectant, comparable in potency to hypochlorite ion (OCl^-) requiring contact times of 2h or more for effective disinfection.

- Between the hump (Point A) and the breakpoint (Point B) the added chlorine is consumed to convert (oxidise) the chloramine to nitrogen thereby ridding the water of ammonia.

- It is important to chlorinate to beyond the breakpoint otherwise it is not possible to maintain a stable free chlorine residual as the added chlorine is used up in breaking down combined chlorine (chloramines) to nitrogen.

- Beyond the hump (Point A) some dichloramine and trichloramine begin to form with increasing levels of hypochlorous acid. Dichloramine has a disagreeable "chlorine" taste and trichloramine a foul odour (both are eye-irritants which is an important consideration in swimming pool disinfection), whilst monochloramine has neither property. Because of tastes and odours this region of the curve must be avoided in water treatment.

- At or beyond the breakpoint, the combined chlorine residuals, consisting of di- and trichloramine will be at a minimum, although low residuals which may persist beyond the breakpoint are responsible for any unpleasant tastes and odours present.

- In practice, following free residual chlorination, the total (free and combined) chlorine residual should consist of 85-90% free residual chlorine, i.e. hypochlorous acid and hypochlorite ion.

The presence of *organic nitrogen*, being a more complex form of nitrogen than ammonia, severely impairs the process of free residual chlorination.

The presence of organic nitrogen severely impairs the process of free residual chlorination

The term *organic nitrogen* refers to nitrogen that occurs in various combinations in biological material, both plant and animal. It constitutes a large group of substances, but mainly proteins and their breakdown products: polypeptides and, ultimately, amino acids. Other forms are the nucleic acids and their breakdown products as well as excretion products such as urea, uric acid and creatinine. Many of these compounds are substituted by both chlorine (i.e form chloramines) and/or oxidised (i.e. to form nitrogen) and hence exert a *chlorine demand*.

This is a process that, in contrast to the substitution of ammonia by chlorine to form chloramines and the subsequent oxidation of chloramines by chlorine to nitrogen, may proceed very slowly, often over several days. Others form relatively stable organic chloramines, in the same way as does ammonia. These contribute to the **combined chlorine residual** represented by the region to the left of the breakpoint in the chlorination curves such as those of Figs. 2.1 or 2.2.

In severe cases, the curve will cease to display a well-defined breakpoint minimum and will instead approach a plateau shape. This is due to there being very little loss of nitrogen by oxidation owing to the stability of the organic chloramines to oxidation by chlorine. There is evidently also greater formation of foul smelling di- and trichloramines after the ill-defined or virtually non-existent breakpoint with the attendant taste and odour problems in drinking water.

In swimming pool disinfection, the incidence of bather eye irritation would also increase as a result of increased concentrations of di- and trichloramines.

Di- and trichloramines contribute to bad odours

The main practical significance of the presence of organic nitrogen is:

- It will not be possible to produce water having or even approaching a stable chlorine residual. This instability depends on the complexity of the nitrogenous materials as well as on their concentrations.
- Ammonia nitrogen can be destroyed by chlorination in 0.5 - 1h, and the amino group in 1 - 2h. The proteins and polypeptides are more resistant to oxidation by chlorine and their substitution by chlorine, followed by oxidation to nitrogen can continue for days.

SUMMARY

- The more rapidly acting and hence important disinfectant species in chlorination is hypochlorous acid. The hypochlorite ion is approximately 100-fold less effective within the same contact time.

- Hypochlorous acid is usually referred to as *free chlorine*, although strictly speaking, this term refers to both hypochlorous acid and hypochlorite ion in solution.

- It is important to maintain a pH close to 7 to optimise the disinfectant conditions. In practice, where other considerations are taken into account, the disinfection pH is stabilised at pH 8 ± 0.2, principally to protect concrete pipelines from erosion which occurs at lower pH.

- Monochloramine is a relatively ineffective disinfectant, comparable in potency to hypochlorite ions, requiring much longer contact times than hypochlorous acid.

- Free residual chlorination, i.e. chlorination to beyond the breakpoint, should always be practised.

- Organic matter should be removed as far as possible by flocculation, coagulation and/or sedimentation as its decomposition to yield "organic nitrogen" seriously impairs effective chlorination by making it very difficult to attain and maintain stable, free chlorine residuals.

FACTORS INFLUENCING INACTIVATION OF HEALTH-RELATED MICRO-ORGANISMS AND VIRUSES

In water disinfection we are concerned with, in order of decreasing size:

- protozoan parasite cysts, 6 - 10 μm
- bacteria, 1 - 3μm, and
- viruses, 0.01 - 0.1 μm

For convenience these will all be referred to as microbes.

Note: Protozoan parasites, as will be seen later, are resistant to most disinfection processes. If present, all or as many as possible of them should be removed by the initial filtration stage. On account of their large size relative to bacteria and viruses, this is usually successful if this stage is operated optimally.

The factors known to affect microbial inactivation by a particular disinfection process besides the concentration of the disinfectant and the contact time, include:

- □ Type of microbe
- □ Condition of the microbe (physiological state, prior conditions experienced)
- □ Physical state of the microbe (aggregation, suspended and attachment to surfaces)
- □ Water quality
- □ Engineering considerations (reactor design, mixing etc)

Type of microbe

In general the order of sensitivity to chlorination is as follows:

bacteria > viruses > protozoan parasites.

Condition of the microbe

The physiological state of a microbe can influence its response to disinfection and also whether it is able to be detected and quantified. Factors such as antecedent growth conditions, prior exposure to disinfectants, injury caused by environmental agents including chlorine disinfectants, and the methods or conditions used for assaying viability are all important.

Exposure to sub-lethal concentrations of chlorine may result in the selection of resistant survivors when these are afforded the opportunity to multiply and can lead to high resistance to disinfection. Resistant cells develop an exopolysaccharide slime layer which most probably results in resistance to chlorine oxidation.

This arises from the phenomenon known as the *viable but non-culturable* state, where bacteria exposed to chlorine disinfection may be incapable of growing on standard media but still be viable and virulent if they happen to be pathogens. Thus the number of viable microbes in chlorinated water may be greatly underestimated if only standard culture methods and media are used in viability assays.

Physical state of the microbe

Aggregation or clumping is the natural state for many waterborne microbes.
This reduces disinfection efficiency for purely physical reasons in that microbes inside aggregates are shielded from exposure to chlorine or any other disinfectant.

Aggregation need not be mutual but can be to any suspended, particulate matter such as cellular debris or faecal solids.

Most viruses in water are embedded in or otherwise associated with suspended solids and such association often interferes with virus inactivation.

A more important phenomenon is attachment to surfaces and biofilm formation. This provides the greatest resistance to disinfectants like chlorine The reasons are obvious in that a freely suspended microbe can be approached by disinfectant molecules from all sides, whereas in a biofilm the approach is limited to essentially one side and from a limited number of directions. The disinfectant also has to diffuse through the biofilm to reach the unexposed cells. The age of the biofilm also has an effect, presumably because older biofilms have developed thicker exopolysaccharide protective layers which protect them from the effects of disinfectants.

Water quality

The role of *particulate matter* in the water has been dealt with in the preceding section. Another case is when the particle is able to react with and consume free chlorine leading to reduced disinfection efficiency.

For a strongly oxidising disinfectant such as chlorine, *dissolved organic matter* reacts with and consumes the disinfectant. This results in a reduced disinfectant concentration reaching the microbes. Reaction products such as organic chloramines and other chlorinated organics have greatly reduced or no disinfection potency.

The presence of *inorganic ions*, in particular ammonia (NH_3), nitrite (NO_2^+), iron (as Fe^{2+}) and manganese (as Mn^{2+}), can interfere with the action of chlorine. The formation of the less efficient disinfectants, chloramines, has already been mentioned.

Nitrite will exert a chlorine demand in being oxidised to nitrate, and iron and manganese in being oxidised to their higher oxidation states.

The effect of pH on chlorination has been mentioned. A high pH favours the presence of hypochlorite ion which is a very much less effective disinfectant than hypochlorous acid. A pH of 7 and below favours the presence of hypochlorous acid.

The effect of *temperature* is that increased temperature produces higher rates of inactivation and *vice versa*.

It should be borne in mind that a higher temperature will increase the losses of hypochlorous acid to the atmosphere by volatilisation from open vessels.

Engineering considerations

Reactor design, mixing and other hydraulic considerations are important especially when the disinfectant is rapidly lost or consumed, or changes to a less active form as is the case when free chlorine forms chloramines.

Differences with regard to reactor design have been found particularly when comparing plug-flow (tubular) with mixed batch (backmixed) reactors. Disinfection of coliform bacteria is more rapid in the former type having highly turbulent flow and mixing times of 0.05 - 0.5s, than in the latter that employs mechanical mixing with mixing times of 5 -25s. The differences are due to greater initial inactivation by free chlorine in the plug-flow reactor due to shorter mixing times. In the batch reactor, however, the free chlorine initially present has less opportunity to disinfect bacteria and most of the disinfection is produced by the rapidly formed combined chlorine.

Further consideration of reactor design is beyond the scope of this Handbook and the reader is referred to texts such as White (1992).

MECHANISMS AND EFFICACY OF BACTERIAL VIRAL AND PROTOZOAN INACTIVATION BY CHLORINE

Bacterial inactivation

Hypochlorous acid penetrates the bacterial cell wall and the first site of interaction with the bacterium is the cell membrane. This leads to physical, chemical and biochemical changes resulting in permeability changes and leakage of essential macromolecules as well as early damage to genetic material.

The *bacterial membrane* is the Primary target of free chlorine

Hypochlorous acid, being small and electrically neutral, is able to penetrate the cell wall and subsequently the cell membrane, with ease. Interference with the activities of membrane bound enzymes takes place, the primary mode of action being oxidation of sulphydryl and thioether groups. The higher resistance of bacterial spores and acid-fast bacteria to chlorine is ascribed to the failure of hypochlorous acid to penetrate the bacterial cell wall and thus reach the cell membrane.

Viral inactivation

The primary site of action of chlorine on viruses is the nucleic acid and not the outer protein capsid although minor adverse changes to the latter take place.

The *viral nucleic acid*
is the primary target of free chlorine

Disinfection efficacy

The two forms of free chlorine in water i.e. hypochlorous acid and hypochlorite have different target sites and reaction mechanisms and may explain observed differences in sensitivities of various genera, species and strains of micro-organisms.

Chlorination is effective against most enteric microorganisms and viruses

Protozoan parasite inactivation

The inactivation of protozoan parasites, notably *Giardia* and *Cryptosporidium* spp., should any fail to be retained in the filtration process, is a much longer process and not generally considered as falling within the capabilities of the chlorination process. These organisms have a tough outer coat, almost impermeable to hypochlorous acid, rendering them very resistant to chlorine inactivation.

Disinfection efficacy is best summarised by consulting Table 2.2.

It is evident from Table 2.2 that bacteria and viruses are all killed within 2.5 min by 1 mg/ℓ of free chlorine, whilst the protozoan cysts require much longer contact times. This implies that efficient pre-treatment, in the form of e.g. slow sand filtration, is necessary. Good maintenance of these two steps is essential to ensure optimum efficiency.

Table 2.2 *Ct* values (Ct, mg/ℓ x minutes)* and contact times at 1mg/ℓ chlorine for 99% inactivation of various micro-organisms by free chlorine at pH 6 - 7 and 5°C (USEPA, 1989).

Microorganism	***Ct*** (mg.ℓ$^{-1}$.min)	**Contact time at 1 mg/ℓ, free chlorine**
E. coli	0.034 - 0.05	2 - 3 s
Poliovirus 1	1.1 - 2.5	1 - 3 m
Rotavirus	0.01 - 0.05	1 - 3 s
Coliphage f2	0.08 - 0.18	5 - 10 s
G. lamblia cysts	47 - >150	1 - 2.5 h
G. muris cysts	30 - 630	0.5 - 10 h

- The ability of a disinfectant to inactivate a microorganism is often expressed as the product of the disinfectant concentration (*C*, mg/ℓ) and the required contact time (*t*, min) at this particular concentration i.e. *C* x *t* or *Ct*, having units of mg.ℓ$^{-1}$.min.

FORMATION OF CHLORINATION BY-PRODUCTS

All natural waters contain a large number of organic compounds. Many of these are simple hydrocarbons but the major portion, by mass, consist of high molecular mass humic and fulvic acids or fragments thereof, derived from the decomposition of plant material. Particularly striking examples of this is the mountain water in the Western Cape and the western part of the Eastern Cape which is brown in colour due to these substances.

It is possible to reduce the total amount of organic matter in water by various treatment regimens but complete elimination is never possible. Therefore, when water is chlorinated there is always organic matter present that can form chlorinated organic compounds by substitution, *combined chlorine*, or can be oxidised by chlorine to nitrogen.

Since it was discovered in 1974 that trihalomethanes (THM's) are formed during the chlorination of water containing humic and fulvic acids, which under certain conditions are able to act as carcinogens, there has been a knowledge explosion on the subject of disinfection by-products (DBP's) and hundreds of additional chlorinated compounds have been identified derived from humic and fulvic precursors. Chlorination by-products are not restricted to THMs although these predominate, particularly *chloroform*. The amounts of THMs formed are determined by the quantities of organic matter present, the chlorine dose, contact time, temperature and pH.

Disinfection by-products need not all arise from the chlorination of humic material but can arise from other, man-made, lower molecular mass pollutants such as *phenols*, which are fairly common pollutants and readily chlorinated.
Table 2.3 lists some chemical species that have been identified

Typical concentrations of THMs (as chloroform) can be up to 100-200 µg/ℓ and in South Africa is on average, 45 µg/ℓ

Table 2.3 Chlorinated organic compounds identified as chlorination by-products

Class of Compound	Specific compounds
Trihalomethanes	Chloroform, etc
Haloacetonitriles	Dichloroacetonitrile, etc
Chlorinated aldehydes	2-Chloropropenal, etc
Chlorinated acetones	1,1-Dichloroacetone, etc
Chlorinated phenols	2-Chlorophenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol etc
Chlorinated acetic acids	Di- and trichloracetic acid etc

The mechanisms whereby these compounds are formed from humic and fulvic precursors are the subject of continuing investigations.

Typical concentrations of THMs (as chloroform) can be up to 100-200 µg/l and in South Africa the concentration is on average 45 µg/ℓ.

Carcinogenesis and mutagenesis are the major potential health risks

There is still much uncertainty as to the toxicological properties of the chlorinated disinfection by-products. However, the main adverse health effects are the potential cancer-causing properties i.e. *carcinogenicity* of the THMs and the potential for causing genetic changes i.e. *mutagenicity* of other substances, largely unidentified.

The uncertainty as to whether chloroform (and other THMs) really pose a significant cancer risk is illustrated by two extreme examples. On the one hand, e.g. the city of Amsterdam, The Netherlands, has stopped the chlorination of its water supply and introduced ozonation, whilst on the other, the World Health Organisation (WHO) has relaxed their guideline value for THMs (as chloroform) from 30 to 200µg/l. This may be an indication of the priorities of the WHO, whose guidelines are applied by many countries worldwide, and which realises that in many parts of the world the relative risks to life and general wellbeing associated with outbreaks of waterborne disease such as cholera and typhoid fever, far outweigh the minimal risks of contracting cancer after several decades of exposure to chlorinated water.

TASTES AND ODOURS

This section will consider the formation as well as the removal of tastes and odours as a result of water chlorination. The former phenomenon is undesirable, since it alters the otherwise, ideally, neutral taste and absence of odour, of drinking water.

Formation of tastes and odours

If a water is contaminated with some substance that, when chlorinated, gives rise to a product(s) that has an undesirable taste or odour and a low odour threshold concentration, then the disinfection process *per se* would have given rise to a taste or odour.

Natural amino acids are potent odour causing chemicals when oxidised to the corresponding aldehydes

These compounds, 2-methylpropanal, 3-methylbutanal and 2-methylbutanal arise as a result of the oxidation of valine, leucine and isoleucine, respectively. These amino acids are sometimes present as a result of the degradation of naturally occurring proteins.

The six naturally occurring amino acids: alanine, methionine, valine, phenylalanine, leucine and isoleucine are very powerful odour precursors during water disinfection by chlorine. The odorous compounds have been identified as the corresponding aldehydes: acetaldehyde, methional, isobutyraldehyde, phenylacetaldehyde, isovaleraldehyde and 2-methylbutanal, respectively. A dipeptide tested under the same conditions, L-tyrosyl-L-glutamic acid, induced intense odours closely resembling those found in surface waters described as "muddy-septic-river".

A very common source of taste and odour is the formation of chlorinated phenols from phenols which are common pollutants in certain regions. Chlorophenols impart a "medicinal" or "TCP" taste to water at very low concentrations.

Another source of odours is the formation of chloramines as a result of the presence of ammonia during chlorination.

This applies particularly to the odorous species, dichloramine and trichloramine formed near the breakpoint as discussed earlier in this chapter. It is, therefore, important to practise breakpoint or free residual chlorination and to avoid the region on the curve beyond the hump and near the breakpoint dip

Three very important taste and odour causing substances and their associated odours are **geosmin** (earthy), **methylisoborneol**, **MIB** (musty) and **dimethyltrisulphide** (onion, garlic, swampy).

In common with most of the compounds causing taste and odour problems in drinking water, these substances are metabolites produced by various micro-organisms including certain algal species. The microbiological processes producing them occur in streams and reservoirs and sometimes even in the treatment plant itself. The odour threshold concentrations for these substances are as low as a few ng/ℓ (1ng = 1/1 000 000 mg).

Removal of tastes and odours

Chlorine is ineffective in removing tastes and odours due to geosmin and MIB because the chemical structures of these substances are unreactive to the oxidative effects of free chlorine.

Chlorine removes tastes and odours by oxidation

Dimethyltrisulphide (fishy-swampy), on the other hand, is removed with >99% efficiency by a 2mg/ℓ dose of free chlorine and a 1- hour contact time.

The higher than normal chlorine concentrations often required to remove certain tastes and odours may result in higher than permitted/recommended concentrations of disinfection by-products. This dilemma can only be resolved by suitable pretreatment of a water, either by physical means or by using an alternative oxidant such as ozone (*see* Chapter 3).

The general principle, as in all other cases of water chlorination, is that impurities should be removed as completely as possible by physical means such as filtration and physico-chemical means such as flocculation and coagulation, before chlorination is undertaken. In this way taste and odour formation is minimised without having to sacrifice the advantages of chlorination.

ADVANTAGES AND DISADVANTAGES OF CHLORINATION

Advantages

- It is one of the most practical and economical disinfectants currently available.
- It can readily be compressed and transported in cylinders to the site of application.
- It can be supplied as a solution (sodium hypochlorite) or as a solid (calcium hypochlorite).
- The residual effect is very advantageous for the maintenance of water quality in the distribution system.
- It is the most appropriate disinfectant for use in emergencies.
- Apart from disinfection, chlorine has other practical functions such as the control of certain tastes and odours, control of algal and slime growth, the oxidation of inorganic compounds, and the improvement of coagulation.

Disadvantages

- Free chlorine residuals react with organic compounds to form disinfection by-products that have potentially adverse health effects.
- Chlorinated wastewater effluents adversely affect aquatic life on account of the stability of chlorinated compounds.
- The effectiveness of chlorination is strongly pH dependent and is low at alkaline pH values often prevalent in water treatment.
- Chlorination fails to remove odours due to the commonly occurring odourants, geosmin and MIB, and may itself cause taste and odour problems.

The various chlorine species differ with respect to disinfection potency

For enteric bacteria i.e. bacteria causing intestinal disease such as faecal coliforms, *E. coli, Salmonella* spp., *Shigella* spp., *Klebsiella* spp. and *Enterobacter* spp., the general order of disinfection potency, for equivalent contact times, is as follows:

$$HOCl > OCl^- = NHCl_2 > NH_2Cl$$

CONCLUSION

The advantages of chlorination as a means of providing safe drinking water, on the one hand, and the disadvantage inherent in the formation of potentially health hazardous chlorination by-products, on the other, is a subject that has been debated ever since the formation of THMs was discovered in 1974.

Much work has been done to evaluate the potential risks to human health posed by e.g. the THMs. Some critics of chlorination feel that the necessity and the benefits of chlorination are not discussed with the same stringency as the potential health risks posed by the THMs. The health risks associated with the THMs have not been proved beyond doubt, but neither have they been shown to be harmless. The necessity of chlorination of water, particularly in our situation, arises from the fact that it is impossible to attain an acceptable water quality using, e.g. slow sand filtration to remove contaminating micro-organisms.

Examples of European cities that have ceased chlorination of their water supplies and introduced alternative disinfectants are many. Here the conditions are very different and, to name but one reason, the distances over which they have to pipe disinfected drinking water are often shorter than in South Africa.

In outbreaks of waterborne diseases, such as cholera and typhoid fever, it can often be proved beyond doubt or the circumstantial evidence may be very strong, that these were due to the failure of the disinfection step, and not to some other cause.

Whatever point of view may be held on the benefits or otherwise of chlorination, it is clear that the disinfection step, such as chlorination should never serve the purpose of compensating for faulty or inadequate engineering design or other shortcomings at any stage in the water purification process. It is important to address the problem of water quality at the earliest possible stage. Short of going over to an alternative disinfectant, the solution to the problem of chlorination by-products lies in minimising the doses of chlorine applied after, as

far as possible, having removed the offending substances that lead to their formation.

It is doubtful whether a country such as South Africa could provide safe drinking water without chlorination. It is never a choice between microbial risks due to infection by contaminating micro-organisms, on the one hand, and chemical risks due to the toxicity of disinfection by-products, on the other. Both are important and neither should be neglected. However, the microbial quality should always be regarded as the first threshold in a multibarrier approach to the protection of water quality. Chlorination is of paramount importance in the crossing of this first threshold of quality.

The disinfection by-products should be approached in a responsible, balanced and realistic manner taking due cognisance of all the facts. We should refrain from advocating unrealistic regulations.

FURTHER READING ON CHLORINATION

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CHAPTER 3

CHLORAMINATION

INTRODUCTION

Two of the earliest reasons for using chloramination for primary water disinfection in preference to free chlorine, were that

- Chloramination gives rise to less problems with tastes and odours, and
- Chloramination results in a more stable disinfectant residual in distribution systems.

The unavailability of ammonia during World War 2, led to the decline in popularity of the process in the U.S. A resurgence of interest took place in the middle 1970's when it was found that free chlorination of raw surface waters could give rise to the formation of the potentially health hazardous THMs. A further reason was that chloramination is the cheapest of the *alternative* drinking water disinfection processes. However, the process has disadvantages in that laboratory studies have shown that monochloramine requires considerably longer contact times in order to inactivate pathogenic organisms than does free chlorine. Recent toxicological studies have indicated that there may also be potential human health risks associated with exposure to chloramines.

This chapter will consider the chemistry of chloramination as well as the microbicidal actions including the efficacies and the mode of action of the process. The toxicology of chloramines and the formation of any by-products will be considered including the formation and removal of tastes and odours. Advantages and disadvantages with respect to other disinfection processes will be listed.

In contrast to some parts of the U.S., in South Africa, chloramination is not employed for primary disinfection of drinking water, but only to provide a residual disinfectant concentration that will persist in the distribution system and prevent bacterial regrowth following chlorination.

CHEMISTRY OF CHLORAMINATION

Much of the chemistry associated with chlorination applies also to chloramination; particularly the section dealing with the reactions of chlorine in the presence of ammonia and the associated breakpoint phenomenon.

The process of chloramination is also referred to as *Combined Residual Chlorination* or the *Ammonia-Chlorine Process*, and is based upon the reactions of free residual chlorine (hypochlorous acid) with ammonia to form mainly monochloramine, as described previously:

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \quad \text{(monochloramine)} \quad (3.1)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad \text{(dichloramine)} \quad (3.2)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \quad \text{(trichloramine)} \quad (3.3)$$

These reactions are governed mainly by pH and the chlorine to ammonia ratios. The speciation with respect to pH and the conditions given, can be expressed graphically as in Fig. 3.1.

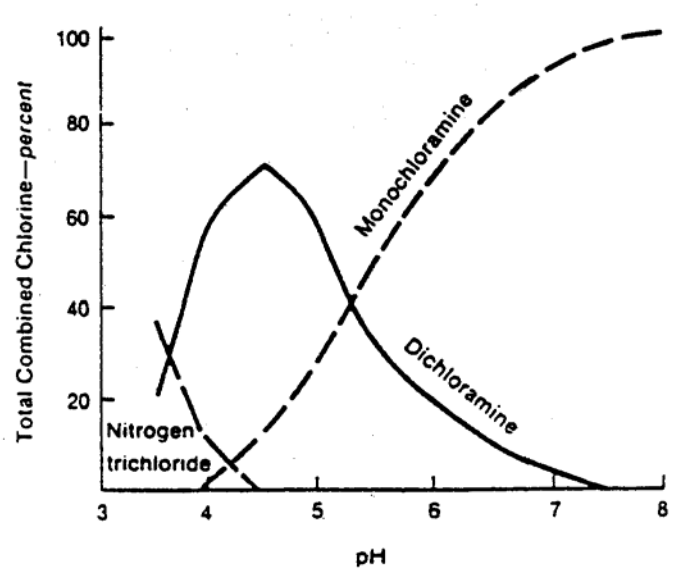

Fig. 3.1 Distribution of chloramine species with pH.

2.5 mg chlorine/l; 0.5 mg ammonia nitrogen/l; contact time = 2h.

(Wolfe *et al.*, 1984; *reproduced with permission*)

Monochloramine is produced rapidly in the pH range 7 - 9 and most readily when the molar ratio, Cl_2:N is $\leq$ 1:1 ($\leq$5:1, by mass). This corresponds to the region up to the "hump" on the

breakpoint curve as given in Figs. 2.2 and 2.3. From Fig. 3.1 it can be seen that, in the pH range 6 - 9, which is that most frequently encountered in public water systems, monochloramine is the predominant species in chloraminated water.

Monochloramine is the predominant species in chloraminated water

The only important breakdown (hydrolysis) reaction of monochloramine is the reverse of Equation 3.1, which occurs with a half-life of ca. 10h. It is also important not to exceed the 1:1 molar ratio of Cl_2 : N (5:1, mass ratio) since this moves the process beyond the hump in the breakpoint curve into the region of monochloramine decomposition by excess free chlorine.

The formation of di- and trichloramine is undesirable

The formation of dichloramine and trichloramine is undesirable, since these species impart an unpleasant "chlorine" taste to drinking water at concentrations of 0.8 mg/ℓ and 0.02mg/ℓ, respectively. Therefore, it is important to control the Cl_2 : N ratio to prevent it from rising above 1:1 (5:1, by mass) and to regulate the pH, keeping it at least above 7, according to Fig. 3.1. However, dichloramine forms very slowly at pH 7 - 9, the normal conditions of water treatment, and does not pose a problem unless the pH falls to below 5.5. Trichloramine forms only at pH values below 4.4 and at Cl_2 : N molar ratios of $\geq$1.5:1 ($\geq$7.6:1, by mass), i.e. at the breakpoint.

The presence of nitrogenous organic compounds interferes with the process of chloramination

The presence of materials with a chlorine demand will interfere with the process. This particularly applies to nitrogenous organic material such as proteins, peptides and amino acids. Chlorine binds to these more rapidly than to ammonia and gives rise to organic chloramines with little or no microbicidal activity.

FACTORS INFLUENCING INACTIVATION OF HEALTH-RELATED MICRO-ORGANISMS AND VIRUSES BY CHLORAMINATION

The factors known to affect the efficiency of microbial inactivation by a particular disinfection process apart from disinfectant concentration and contact time include:

- □ Type of microbe
- □ Condition of the microbe (physiological state, prior conditions experienced)
- □ Physical state of the microbe (aggregation, suspended matter and attachment to surfaces)
- □ Water quality
- □ Engineering considerations (reactor design, mixing etc)

Type of microbe

In general, the order of sensitivity to chloramination is as follows:

Bacteria > viruses > bacterial spores, acid-fast bacteria and protozoan cysts.

Sensitivities can differ even within bacterial species; different isolates of the same bacterium, e.g. *Escherichia coli*, having differing sensitivities.

This is important because it is not always possible to predict disinfection efficacy on the basis of the behaviour of indicator organisms on account of the differences in sensitivity to disinfectants between indicator organisms and various pathogens.

Condition of the microbe

The physiological state of a microbe can influence its response to disinfection and also whether it is able to be detected and quantified. Factors such as earlier growth conditions, prior exposure to disinfectants, injury caused by environmental agents including disinfectants, and the methods or conditions used for assaying viability are all important.

Physical state of the microbe

Aggregation or clumping is the natural state for many waterborne microbes. This reduces the disinfection efficiency for purely physical reasons in that microbes inside aggregates are shielded from exposure to monochloramine or any other disinfectant. Aggregation need not be mutual but can be to any suspended, particulate matter such as cellular debris or faecal solids. Most viruses in water are embedded in or otherwise associated with suspended solids and that such association often interferes with virus inactivation.

A more important phenomenon is attachment to surfaces and biofilm formation. This provides the greatest resistance to disinfectants. The reasons are obvious in that a freely suspended microbe can be approached by disinfectant molecules from all sides, whereas in a biofilm the

approach is limited to essentially one side and from a limited number of directions. The disinfectant also has to diffuse through the biofilm to reach the unexposed cells. The age of the biofilm also has an effect, because older biofilms have developed thicker exopolysaccharide layers which protect them from the effects of disinfectants.

Cells associated with the hepatitis A virus are more resistant to inactivation by chloramination than the dispersed virus.

Water quality

The role of *particulate matter* in the water has been dealt with in the preceding section. Another case is when the chemical constituents of the particle are able to accept chlorine from the monochloramine. This will result in a reduced disinfectant concentration reaching the microbes and the presence of reaction products such as organic chloramines and other chlorinated organics that have greatly reduced or no microbicidal activity.

The effect of *pH* on the microbial inactivation by monochloramine is such that it is more effective at pH 6 - 7 than at 8 - 10 . However, *Giardia muris* cysts are more sensitive to monochloramine at pH 9 than at pH 6 or 7.

The effect of *temperature* is such that increased temperature produces higher rates of inactivation and *vice versa*.

Engineering considerations

Reactor design, mixing and other hydraulic considerations are probably less important in the case of chloramination since the disinfectant is not lost, consumed or changed to a less active form, as rapidly as is the case with free chlorine. Long contact times are implicit and an accepted part of the process, particularly if it is being used as a method of primary disinfection. In South Africa contact time in the reticulation system is the crucial factor. Since these are almost invariably long on account of the extensive systems such as in Gauteng, the chloramine has adequate time to perform its intended task.

MECHANISMS AND EFFICACY OF BACTERIAL, VIRAL AND PROTOZOAN CYST INACTIVATION BY CHLORAMINATION

Preformed monochloramine applied in the laboratory may act differently from the *in situ* process used in the field

Laboratory studies

The mechanisms whereby monochloramine exerts its microbicidal action appears to be less well-defined than is the case for free chlorine. It is important to realise that the dosing of preformed monochloramine, the method used in laboratory studies, may act differently from processes whereby monochloramine is formed during the actual disinfection process. The latter mode is by far the most common in water treatment.

The issue is clouded by the fact that during the "in process" formation of monochloramine, short-lived intermediates, such as highly reactive and hence highly microbicidal free radicals or free chlorine may form. These species exert a considerable degree of disinfection potency. Therefore, laboratory studies using preformed monochloramine would not necessarily be good indicators of field performance where chloramine is formed *in situ*.

Monochloramine can enter the cell and react with proteins and nucleic acids

The mechanisms of *bactericidal* action are probably similar to those of free chlorine. These mechanisms were outlined in Chapter 2. Recent work on *E. coli* has shown that the primary action of monochloramine is not to destroy or severely disrupt the integrity of the bacterial membrane and it is probable that these differences arise as a result of the distinct chemical properties of chloramines. Furthermore, no single lesion is responsible for bacterial cell death but monochloramine targets primarily amino acid residues implying that the disinfectant action involves proteins or protein mediated processes which includes a host of enzymatic reactions within the cell.

Amino acids are converted to chloramines and cysteine sulphydryls are oxidised to the disulphide, cystine. Free chlorine exerts a much more powerful action, tending to oxidise, deaminate and hydrolyse such compounds. Monochloramine also, irreversibly, destroys hemin, an essential prosthetic group in enzymes such as cytochromes, catalases and peroxidases, all of which occur widely in micro-organisms and which are essential for many

crucial functions of bacteria. Monochloramine induces breaks in the DNA, the primary genetic material, of *Bacillus subtilis.* This also implies that monochloramine can penetrate the cell-membrane and enter the cell.

Viral inactivation takes place as a result of changes to either the capsid protein or the RNA

Reports on mechanisms of *viral* inactivation by monochloramine are few. Chloramine destroys the integrity of the RNA, the genetic material essential for replication, of f2 coliphage, whereas poliovirus is inactivated by a primary mechanism involving the coat (capsid) protein. It is probable that these differences may be dependent on virus type and disinfectant concentration.

Protozoan cysts are highly resistant to chloramination

No reports on the mechanism of *protozoan cyst* inactivation are available. These are very resistant to inactivation by chloramination with the exception of *Giardia* which are less so.

According to laboratory studies, chloramines are considerably less microbicidal than free chlorine. Indicator bacteria such as *E. coli*, faecal coliforms, total coliforms and total (HPC) bacteria (total plate count) as well as pathogens such as *Salmonella* spp. and *Shigella* spp. show that residuals of up to 1 - 2 mg/ℓ and contact times of hours are needed to bring about appreciable inactivation. Viruses, such as HAV, rotavirus, coliphage MS2 and poliovirus require *Ct* products of the order 10^2 - 10^3 $mg\ell^{-1}$.min (*see* footnote to Table 2.2).

In view of the slow inactivation of health-related microbes by monochloramine, the process should not be used for primary disinfection unless the source water is of very good quality. This question never arises in South Africa since chloramination is used exclusively for secondary disinfection.

Field studies

As a contrast to the laboratory data, several instances of field applications of chloramine for primary disinfection have been described where chloramination has been shown to be effective as a primary disinfection process:

Chloramination has been shown to be effective in the field

The following are instances of the field use of chloramination quoted from the literature and are intended to serve as illustrations:

- Chloramination in conjunction with coagulation, sedimentation and filtration reduced coliform counts from 10^5/ℓ in raw water to nearly zero. The incoming water (pH 7.0 - 7.3) was dosed with 1.6 mg/ℓ chlorine and enough ammonia to give a Cl_2 : N mass ratio of 3:1.

- Post-ammoniation with ammonium sulphate (1.8 mg/ℓ Cl_2; Cl_2:N: :3:1; pH 8.3) which resulted in a 52% decrease in total plate count compared to the use of free chlorine.

- Concurrent addition of ammonia and chlorine (1.5-1.8 mg/ℓ) produced a monthly average total bacterial count of less than 50/ml in finished water. No coliforms were detected in the finished water.

- Chloramines (1.5 mg/ℓ; Cl_2 : N::3 : 1; pH 7.9 - 8.9) were as effective as free chlorine in reducing coliform counts, *E. coli*, faecal streptococci and enteric viruses. Furthermore, chloramines were more effective in killing certain zooplankton crustaceans.

- On changing from chlorination to chloramination as the primary mode of disinfection, whereas chlorination produced water where 84.1% of samples were free of total coliforms; 94.7% free of *E. coli*; and 78.2% showed less than 100/ℓ total bacterial count, chloramination afforded the following percentages: 100; 99.6; 95, respectively. In addition the frequency of isolation of *Naegleria* spp., *N. fowleri, Aeromonas* spp., heterotrophic iron bacteria and fungi, were all reduced. The improvements were attributed to relative stability of chloramines in the distribution systems.

In the first four cases, lower levels of total THMs were reported than were produced by free chlorine. The last report made no mention of these levels. These findings bear out the effectiveness of chloramines as primary disinfectants and motivated the USEPA, in 1979, to rescind its earlier ban on chloramination as an alternative process for primary disinfection and instead recommend that the process only be used on a case-by-case basis after adequate laboratory and pilot-scale trials had been performed.

Chlorination and chloramination have been compared for controlling bacterial regrowth when used for secondary disinfection. Both reduce growth in the distribution system, but the chloraminated water has a lower total bacterial count, fewer positive coliforms, less taste and odour and a more stable disinfectant residual.

Viruses are potentially problematic in their resistance to chloramination

Waterborne viruses can sometimes cause problems when monochloramine is used as a primary disinfectant. Monochloramine alone is not capable of reducing a virus count 100-fold (2-log reduction of coliphages), unless impracticably long contact times are employed.

Discrepancies between laboratory and field chloramination can be explained

The discrepancies between the laboratory and field results are explained on the basis of the following differences:

- The relative resistance of laboratory grown organisms and naturally occurring organisms.
- The method of application of the disinfectant under laboratory and field conditions.
- The criteria for evaluating the efficacy of the disinfectant.

THE TOXICOLOGY OF CHLORAMINES

Low levels of chloramines are acutely toxic to a variety of aquatic organisms. The mechanism of toxicity is the oxidation of haemoglobin to methaemoglobin resulting in haemoglobinaemia leading to anoxia and death. Sub-lethal effects include reductions in growth rate, oxygen consumption and reproductive activity.

Methaemoglobin production is also observed in haemodialysis patients exposed to chloramines through dialysis equipment. However, elevated levels of oxidised haemoglobin are not detected in mice or humans who have orally ingested chloramines.

The cancer causing properties (carcinogenicity) of chloramines is a matter of conjecture.

Monochloramine probably induces effects via an indirect mechanism, such as nutritional deficiencies, rather than a direct toxicological effect on specific organs and tissues.

The expected human exposure levels, based on daily water intake, are far below the levels associated with adverse effects in rodents and could never disqualify the use of chloramines for water disinfection. Monochloramine also produces a far lower level of THMs, giving it an obvious advantage.

This area has been identified by a group from the American Water Works Association participating in a project designated *Drinking Water and Health in the Year 2000,* as one requiring attention in the near future.

FORMATION OF CHLORAMINATION BY-PRODUCTS

One of the principal reasons for the use of chloramination in preference to free chlorine is that lower levels of the potentially health hazardous THMs are formed. This advantage offsets the disadvantage of low disinfection potency under certain circumstances. This has been borne out by several comparative studies where the formation of THMs was reduced by up to 80% compared to the use of free chlorine. This property is thus well established and beyond dispute.

Another aspect has to be considered. As mentioned previously, chloramine can chlorinate organic compounds such as peptides and amino acids by *substitution,* whereas the action of free chlorine is much stronger, tending to *oxidise, deaminate* and *hydrolyse* in addition to chlorination by substitution under certain conditions. Although the action of chloramines is mild, it has to be ascertained whether or not they form by-product substances which may be as harmful, or more so, than are the THMs.

The extent of THM formation has been found to be dependent on the stage at which the chlorine and ammonia are applied to form chloramines. Contact between chlorine and organic material should be minimised. Thus, either pre-ammoniation or the concurrent addition of ammonia and chlorine should be practised. Pre-chlorination with the subsequent addition of ammonia leads to higher levels of THMs.

TASTES AND ODOURS

Free chlorine removes some tastes and odours by virtue of its oxidising power. If, therefore, chlorine is replaced by chloramine, whose oxidising power is considerably less, then certain taste and odour causing substances remain unchanged.

Chloramine is ineffective in completely removing the common culprits, methylisoborneol and geosmin, although in both cases it is marginally better than free chlorine.

Chloramine is as effective as free chlorine in removing dimethyltrisulphide to an extent of >99%.

Chloramine is equally as effective as free chlorine in producing the corresponding odorous aldehydes from valine, leucine, isoleucine and phenylalanine, respectively.

Chloramination produces fewer tastes and odours partly because, in generating monochloramine only, the breakpoint region is avoided, whereas this is not the case in chlorination. This means that di- and trichloramine are not formed, eliminating one of the sources of taste and odour encountered with chlorine.

Another reason is that chloramines are less prone to give rise to the odoriferous chlorophenols formed on chlorination of small quantities of phenols that may occur in water.

ADVANTAGES AND DISADVANTAGES OF CHLORAMINATION

Advantages

- Taste and odour problems are reduced.
- Chloramines are more stable in the distribution system than is free chlorine, and are able to reduce algal growth in reservoirs and bacterial regrowth in distribution systems.
- The formation of THMs is appreciably reduced.
- The overall cost of application and maintenance is relatively low; chloramination being the cheapest of the alternative disinfection methods.

Disadvantages

- The effective level of monochloramine may be reduced in water by the preferential reaction of the combined chlorine with certain organic compounds such as amino acids, resulting in a reduction in the level of monochloramine while the measured total chloramine concentration remains unchanged.
- Laboratory studies show that pathogenic bacteria, viruses and protozoa are inactivated much more slowly by monochloramine than by free chlorine.

- Certain tastes and odours that require the strong oxidising power of free chlorine for their elimination, are not removed.

- Low levels of chloramines have been shown to be acutely toxic to a variety of aquatic organisms.

- There is growing concern about the potential human health risks associated with exposure to monochloramine, which has been found to be a weak mutagen and thus a potential cancer-causing agent.

CONCLUSION

There is always a price that has to be paid when a particular disinfection process is used in preference to another. In the case of chloramination, THM formation is decreased but longer contact times are needed for proper disinfection. Longer lived residuals are obtained in the distribution system but the chloramines are possibly more toxic to man and aquatic life than is free chlorine. There is, therefore, no ideal disinfection method that can be applied to give perfect disinfection with no attendant risks to those consuming the water.

The U.S. attitude is cautious in the use of chloramination as a primary method of disinfection, although the practice is widespread in that country and even the national watchdog, the USEPA, has been persuaded to rescind its regulations regarding the use of chloramination as a means of primary disinfection. However, for the process to be effective as a primary means of disinfection, the source water has to be of good quality and efficient pre-treatment in the form of filtration, coagulation and sedimentation have to be carried out.

In South Africa it is not used for primary disinfection, but serves only to maintain an active chlorine residual in extensive reticulation systems.

The primary reasons for opting for disinfection by chloramination is to avoid taste and odour problems associated with chlorination, such as the chlorination of phenols, to reduce the formation of THMs, and to provide a more stable residual in the distribution system. In South Africa, post-chloramination is gaining in popularity and is practised by two of the largest regional water boards: Rand Water and Umgeni Water,in order to provide the needed disinfectant residual in their vast distribution networks.

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CHAPTER 4

ALTERNATIVE DISINFECTANTS

INTRODUCTION

The processes that will be considered in this chapter will be:

- □ Chlorine dioxide treatment
- □ Ozonation
- □ Mixed oxidant processes, principally Peroxone
- □ Ultraviolet irradiation treatment

CHLORINE DIOXIDE TREATMENT

The use of chlorine dioxide has become increasingly popular in recent years not only for the treatment of drinking water, primarily as a disinfectant, but also for minimising tastes and odours, and for the oxidation and removal of iron and manganese compounds. It is not used in South Africa to any significant extent or at all.

As a result of increasingly stringent regulations abroad, governing the presence of THMs in drinking water, it is one of the alternative disinfectant options open to suppliers of drinking water. If the chlorine dioxide is not generated with excess chlorine, THMs are not formed in the presence of humic substances. This also applies to other disinfection by-products such as haloacids and haloacetonitriles. However, there are possible adverse health effects from the by-products, *chlorite* and *chlorate*. Chlorine dioxide is particularly applicable to the removal of tastes and odours associated with phenols.

The use of chlorine dioxide in drinking water treatment has been reviewed in the South African context by Juby (1992).

CHEMISTRY OF CHLORINE DIOXIDE TREATMENT

Chlorine dioxide is very soluble in water, 5-fold more than chlorine. In contrast to the latter, it does not react with water (hydrolyse) but remains as a dissolved gas.

Chlorine dioxide is not produced commercially due to its instability and explosive nature, but is generated on-site, oxidatively from sodium chlorite. Three methods can be used.

The chlorine-sodium chlorite method has two variants

Aqueous chlorine-sodium chlorite method

This method is based on the following reaction:

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \quad (4.1)$$

Two methods have been developed to keep the pH below 3, which serves to maximise the yield of chlorine dioxide. In the first method the chlorine is added in 2 - 3 molar excess over the stoichiometric requirement. The sodium chlorite solution is then pumped into the chlorine (hypochlorous acid) solution and is allowed to react to form chlorine dioxide according to Equation 4.1. A side-reaction can occur under these conditions to form chlorate ion, particularly if high molar excesses of chlorine are used:

$$2ClO_2 + HOCl + H_2O \rightarrow 2ClO_3^- + 2H^+ + HCl \quad (4.1.1)$$

A competing reaction may also take place to form chlorate ion:

$$NaClO_2 + Cl_2 + OH^- \rightarrow NaClO_3 + HCl + Cl^- \quad (4.1.2)$$

A subsequent development utilises hydrochloric acid to lower the pH. This results in only about 7% excess chlorine in solution, which is important for the prevention of THM formation.

Gaseous chlorine-sodium chlorite method

This method was patented in 1981 and is also based on the reaction of Equation 4.1. It consists in reacting chlorine gas with concentrated sodium chlorite solution under vacuum.

The reported yields are >95% and <5% free chlorine is present in the chlorine dioxide solutions.

The acid-sodium chlorite method does not utilise free chlorine

This method does not utilise free chlorine and is based on the following reaction:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \quad (4.2)$$

In the absence of free chlorine it would not be expected that any should be present in the final chlorine dioxide solution. However, in practice, 4 - 7.5% may be formed as a result of side-reactions.

The hypochlorite - acid sodium chlorite method is based on the generation of HOCl

This process is based on the generation of hypochlorous acid from the acidification of a hypochlorite, which then reacts with sodium chlorite and excess hydrochloric acid to form chlorine dioxide, according to the following reactions:

$$Ca(OCl)_2 + 2HCl \rightarrow CaCl_2 + 2HOCl \quad (4.3)$$

$$HOCl + 2NaClO_2 + HCl \rightarrow 2ClO_2 + 2NaCl + H_2O \quad (4.4)$$

The stoichiometry of Equation 4.4 indicates that 1 mol of sodium chlorite forms 1 mol of chlorine dioxide. As in the case of the chlorine-sodium chlorite method, this process uses less chlorite than the acid-sodium chlorite method, resulting in lower costs.

Plants for generating chlorine dioxide by the chlorine-sodium chlorite methods are more common than those employing acid activation on account of the ease with which existing chlorination facilities can be retrofitted with equipment for generating chlorine dioxide.

Chlorine dioxide is an oxidising and not a chlorination agent

Chlorine dioxide does not chlorinate, but acts primarily as an oxidising agent, being reduced to chlorite according to Equation 4.5.

$$ClO_2 + e \rightarrow ClO_2^- \quad \text{.....(4.5)}$$

Any changes at the molecular level due to chlorine dioxide alone are oxidative in nature, with chlorite as one of the products.

MECHANISM AND EFFICACY OF BACTERIAL, VIRAL AND PROTOZOAN CYST INACTIVATION BY CHLORINE DIOXIDE

As with chlorine and chloramination, the order of sensitivity to chlorine dioxide is

Bacteria > Viruses > Protozoan parasite cysts

The factors influencing the disinfection by chlorine dioxide are also as described for the previous two processes that have been considered.

Chlorine dioxide is equally or more effective than chlorine as a disinfectant

Table 4.1, summarises data published by the USEPA on the efficacy of chlorine dioxide.

Table 4.1 *Ct** values for 99% inactivation of various micro-organisms with chlorine dioxide at 5°C (Lykins *et al*., 1990).

Micro-organism	***C.t*** (mg.ℓ^{-1}.min)
E. coli	0.4-0.75
Poliovirus 1	0.2-6.7
Rotavirus	0.2-2.1
Phage f2	ND
G. lamblia cysts	26**
G. muris cysts	7.2-18.5
Cryptosporidium parvum oocysts	78***

* See footnote to Table 2.2
** 99.9% inactivation at pH 6-9 and 5°C
*** 90% inactivation at pH 7 and 25°C
ND No data

Chlorine dioxide is an efficient inactivator of indicator bacteria such as coliforms and some bacterial pathogens e.g. *Legionella pneumophila.* Faecal streptococci, *Clostridium perfringens*, viruses e.g. coliphage f2 and MS2, poliovirus 1, rotavirus SA11 and hepatitis A, and protozoan cysts such as *Giardia muris* and *G. lamblia*, and *Naegleria gruberi*, are all

more resistant to inactivation than are coliforms, particularly at low pH levels. Under worst case conditions the *C.t* values for the inactivation of enteric viruses and protozoan cysts in clean water are in the range 1-20 $mg.\ell^{-1}.min$.

Generally, chlorine dioxide is more microbicidal than free chlorine, but concerns about the toxicities of its by-products may mitigate against its usefulness as a drinking water disinfectant.

The mechanism of inactivation of bacteria by chlorine dioxide involves the outer membrane

The mechanism whereby chlorine dioxide inactivates bacteria has not been completely elucidated.

Gross bacterial damage involving significant leakage of bacterial membrane does not occur. The action involves a loss of permeability control with accompanying subtle changes in the membrane properties.

Chlorine dioxide has also been found to be effective in controlling the growth of biofilms, thought to be as a result of its oxidative action on the slimy polysaccharide protective coating that some micro-organisms produce in order to attach themselves to surfaces to form biofilms and in order to protect themselves once they have formed biofilms.

The target for viral inactivation by chlorine dioxide is the capsid protein

The mechanism of action of chlorine dioxide on viruses strongly favours a reaction with the viral protein outer coat. Bacteriophage f2 is affected to the extent that its ability to attach to the host cell is inhibited. For poliovirus, the prevention of the complete uncoating or penetration of the particle seems to be the reason why the virus is inactivated.

The mechanisms of inactivation of protozoan cysts appear to be oxidative and probably involves chemical damage once chlorine dioxide has penetrated the polysaccharide cyst wall.

REMOVAL OF INORGANIC COMPOUNDS

Chlorine dioxide is commonly used to oxidise iron and manganese in water to forms that enable removal by settling.

Manganese (II) is oxidised to manganese (IV), which forms insoluble manganese dioxide, as follows:

$$2ClO_2 + 5Mn^{2+} + 6H_2O \rightarrow \mathbf{5MnO_2}\downarrow + 12H^+ + 2Cl^- \quad \text{.....(4.5)}$$

The oxidation of iron(II), shown as the bicarbonate, to the insoluble ferric hydroxide, proceeds as follows:

$$ClO_2 + 5Fe(HCO_3)_2 + 3H_2O \rightarrow \mathbf{5Fe(OH)_3}\downarrow + 10CO_2 + Cl^- + H^+ \quad \text{.....(4.6)}$$

Chlorine dioxide has been used in situations where iron removal was not the primary purpose, but where iron-bearing waters promote the growth of iron bacteria in the distribution system.

TOXICOLOGY OF CHLORINE DIOXIDE DISINFECTION

Chlorine dioxide and its products, chlorite and chlorate are such that, according to current knowledge, the risk to humans is minimal to non-existent if chlorine dioxide disinfected water is ingested.

FORMATION OF CHLORINE DIOXIDE TREATMENT BY-PRODUCTS

Some of these by-products have been mentioned previously, such as chlorite and chlorate. Chlorine dioxide is a very strong oxidising agent that reacts with organic material to produce a variety of oxidation products. Under the conditions of drinking water disinfection, limited formation of by-products has been observed. Most of these have not been studied except for formaldehyde and acetaldehyde, formed from amino acids, which have been found to be cancer producing (carcinogenic) in some animal studies. Quinones and benzoquinones can form from several substrates of humic and fulvic origin found in source waters and also from phenol and chlorophenols. In fact, chlorine dioxide reacts with the normal THM precursors and renders them unreactive or unavailable for THM formation.

The minimisation of THM formation using chlorine dioxide is effective if it is used as a pre-disinfectant even though chlorine may be used as the final disinfectant. Chlorine dioxide treatment following flocculation and filtration is much more effective than treating raw water.

TASTES AND ODOURS

One of the reasons often given for the choice of chlorine dioxide as a water disinfectant is that it does not give rise to tastes and odours as readily as free chlorine. This probably applies to chloramine formation under conditions of sub-breakpoint chlorination, a phenomenon that

does not occur with chlorine dioxide, and also to the fact that chlorine dioxide does not react to chemically substitute chlorine onto organic compounds in water. Instead, it acts as a strong oxidising agent. Thus, if water containing phenolic compounds is treated with chlorine dioxide, the odoriferous and medicinal tasting, chlorophenolics are not formed as is frequently the case with free chlorine treatment.

The oxidising power of chlorine dioxide is inadequate to destroy the structural integrity of geosmin and MIB. In contrast, trimethyltrisulphide, is completely destroyed by chlorine dioxide.

ECONOMICS

Some indications of cost can be given. Each case of potential application of chlorine dioxide has, however, to be judged on its merits and peculiar circumstances.
Sodium chlorite currently has to be imported from Germany, although the infrastructure for local production exists.
In South Africa the cost of chlorine dioxide per kg is 4-15 times higher than chlorine, depending on the method used for generation, and the source of chlorine.

ADVANTAGES AND DISADVANTAGES OF CHLORINE DIOXIDE TREATMENT

Advantages

- It is a very effective microbicide, being inferior to ozone and superior or at least equal to free chlorine.
- It can exert its action relatively independently of pH conditions.
- It is able to remove iron and manganese by oxidation to insoluble forms.
- THM formation is minimised so it can be used to advantage where the formation potential is high.
- Tastes and odours are not formed from chlorine dioxide, and chlorinated odorants, such as chlorophenols, are not formed.
- The stability in the distribution system is better than free chlorine but inferior to chloramines.

- It does not react with ammonia and can be used in situations where the chlorine demands are high.

Disadvantages

- The health effects of chlorite and chlorate are uncertain at present, but the indications are that neither they nor any of the products of reaction with organic components present either acute or chronic health risks.

- It is unable to oxidise two of the major odourants, geosmin and MIB.

- Costs of treatment are often considerably higher than with chlorine.

- It is more volatile than chlorine

- It is photosensitive and will break down to chlorite if exposed to sunlight.

- It has to be produced from an imported feedstock, sodium chlorite.

CONCLUSION

It is doubtful whether chlorine dioxide treatment will supersede chlorination in this country. However, there is an increased tendency toward applying several processes on the same plant. Chlorine dioxide has a niche for its application in South Africa which could lead to the local manufacture of sodium chlorite becoming a viable proposition.

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OZONATION

Ozone has been used for drinking water disinfection in France since 1906. Interest in the USA was only generated following the discovery in 1974 that chlorination of surface waters led to the formation of THMs. There are currently about 1500 plants worldwide that have adopted ozone disinfection; among them cities such as Budapest, Düsseldorf, Los Angeles, Montreal, Moscow, Paris and Zürich.

In South Africa the Western Transvaal Regional Water Company and Umgeni Water appear to be the only water boards employing ozonation on a full scale, but for pretreatment rather than for post-disinfection.

Ozone is a much more powerful disinfectant than chlorine but can form chemical by-products. The chemistry of ozone as a water disinfectant and its efficacy as a microbicide have been thoroughly investigated. Particular advantages claimed are that tastes and odours are improved, that otherwise recalcitrant substances are oxidised to more readily biodegradable forms, and that it exerts a microflocculation effect.

CHEMISTRY OF OZONATION

Ozone (O_3) is a triatomic molecule, being an allotropic modification of oxygen which is diatomic (O_2).

The behaviour of ozone in water is complex, dependent on the pH conditions and, to some degree, uncertain. It is not the intention to discuss the various theories of the aqueous chemistry of ozone.

Ozone is electrically generated by corona discharge

The only method of commercial importance used for ozone generation in water treatment and disinfection is the process using a strong alternating current electric field to produce corona discharge in the feed gas, which is usually air that has been filtered and dried. Using air produces nitrogen oxide by-products which are undesirable. These can be minimised by e.g. decreasing the residence time of the air in the corona discharge and increasing the pressure at which the ozone is generated. Most commercial reactors, however, only produce about 0.5 kg of nitrogen oxides for every 100 kg of ozone generated. Technical aspects of transfer of the ozone into the water are very important but irrelevant to the present discussion.

Both the mechanism and kinetics of the dissociation of ozone in water are uncertain. Possible species formed when ozone makes contact with water are: O_3, $OH\cdot$, $HO_2\cdot$, O^-, O_3^- and possibly the free oxygen atom if the ozone decomposes before reacting with the water.

At high pH ozone not only acts by the direct reaction of O_3 but by the formation and action of the hydroxyl radical, $OH\cdot$, one of the most reactive of the oxygen species. The formation of the various species when ozone decomposes can be represented as a cyclic chain process, depicted in Fig. 4.1.

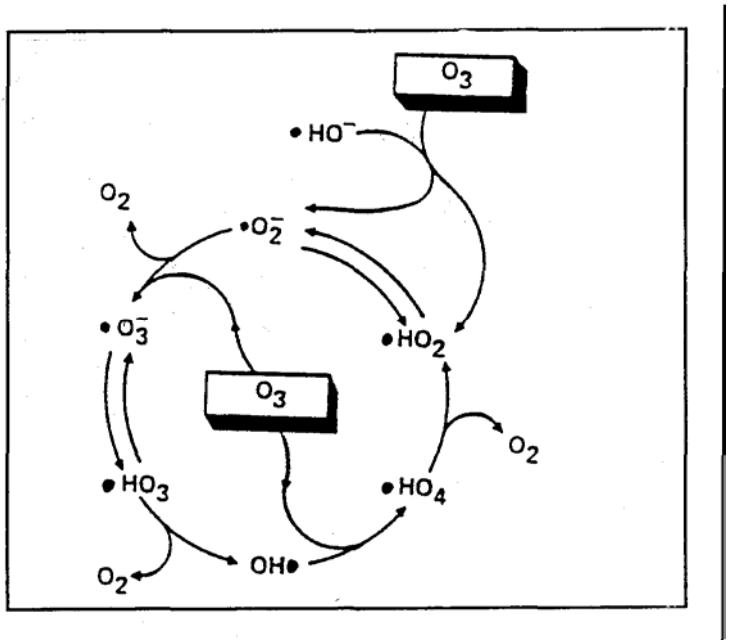

Fig. 4.1 Cyclic chain mechanism of the decomposition of aqueous ozone initiated by hydroxyl radicals. (Glaze, 1986; 1987; *reproduced with permission*)

This chain mechanism can be initiated by a base such as hydroxyl ion (Fig. 4.1) or, as depicted in Fig. 4.2, by hydrogen peroxide, either added directly or produced by the action of light on ozone.

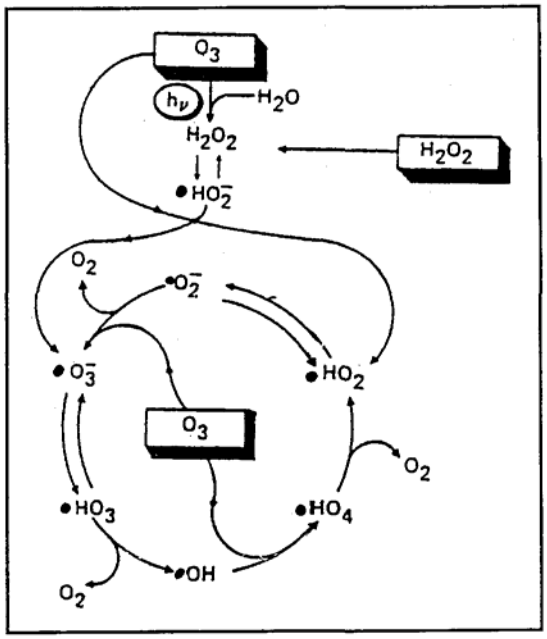

Fig. 4.2 Cyclic chain mechanism of the decomposition of aqueous ozone initiated by UV radiation or by the addition of H_2O_2.
(Glaze, 1986; 1987; *reproduced with permission*)

In both cases, the essential feature of the chain decomposition mechanism is the formation of the hydroxyl radical, one of the most reactive of the oxygenated species. Therefore, the reactions of organic compounds with ozone should be viewed not only in terms of the chemistry of the O_3 molecule, but also in terms of the chemistry of the hydroxyl radical, OH·.

An important feature of the decomposition of ozone is the formation of the highly reactive, hydroxyl radical

Ozone has one of the highest oxidation potentials known, being 2.07 V in acidic and 1.24 V in basic solution. However, the OH· radical has an oxidation potential of 2.8 V ($[H^+] = 1.0$ **M**). This strongly suggests that the OH· radical may be the species responsible for the very strong microbicidal action of ozonated water, not the free O_3 itself.

In water treatment, ozone probably never reacts according to classical chemistry

In water treatment applications, it is doubtful whether ozone ever acts purely according to the classical chemical reactions. In addition to the classical reactions, there will be parallel reactions often interacting with the classical reactions and usually involving free radicals, particularly the hydroxyl radical.

Ozone reacts classically, or nearly so, when it acts:

- In the oxidation of metal ions.
- In the oxidation of activated aromatic substances, such as phenol.
- In addition reactions to carbon-carbon multiple bonds.

These reaction-rates are severely depressed by the presence of electron-withdrawing groups such as halogens. Ozone also does not react with aliphatic compounds other than those that have easily oxidisable groups such as aldehydes and ketones that will be oxidised to the corresponding carboxylic acids.

Ozone has been used to oxidise sulphides to sulphate, nitrites to nitrate, cyanide to cyanate, and some detergents and pesticides to less toxic organic species.

The following reactions result from free radical mechanisms (Fig. 4.1) and are not due to the classical reactions of ozone:

- The hydroxylation of aromatics, such as humic and fulvic material. This results in activation and further classical reaction by ozone.
- The hydroxylative dechlorination of e.g. atrazine.
- The reaction with secondary amines to produce primary amines, such as in the de-ethylation of atrazine.

The free radical processes are promoted by the products of the classical reactions, especially the superoxide ion, OH^{2-}, but also by water contaminants such as metal ions.

One of the important advantages of ozone is that it not only acts as a microbicide but can also destroy humic and fulvic acids and many man-made organic pollutants. It can also oxidise iron and manganese to the insoluble hydroxide and oxide, respectively. In cases where pollutants are not destroyed they may at least be converted to more readily biodegradable forms.

MECHANISMS AND EFFICACY OF BACTERIAL, VIRAL AND PROTOZOAN CYST INACTIVATION BY OZONE

Ozone is the *most* efficient disinfectant

Indicator bacteria such as coliforms and pathogens such as *Salmonella* spp. are very sensitive to ozone inactivation unless the water contains a high ozone demand.

By comparison faecal streptococci and myobacteria are more resistant to ozone as is the case with viruses and protozoan cysts. Rotavirus and *G. lamblia* cysts are inactivated >99% at *C.t* products of <1. Virus inactivation in sewage effluents is much less efficient in view of the high ozone demand of such water. Ozone appears to be the most efficient disinfectant for inactivating protozoan cysts.

Data published by the USEPA summarises some of the more important data. These are depicted in Table 4.2.

Table 4.2 *Ct** *values* for 99% inactivation of various micro-organisms with ozone at pH 6-7 and 5°C (Lykins *et al*., 1990; USEPA, 1989).

Microorganism	***Ct*** (mg.ℓ^{-1}.min)
E. coli	0.02
Legionella pneumophila	0.5-1.5
Poliovirus 1	0.1-0.2
Rotavirus	0.006-0.06
Phage f2	ND
G. lamblia cysts	0.5-0.6
G. muris cysts	1.8-2.0
Cryptosporidium parvum oocysts	5-10**

* See footnote to Table 2.2
** 99% inactivation at pH 7 and 25°C
ND No data

These values bear out the general observation that ozone is the most efficient disinfectant of all.

The disinfection potency of ozone may be influenced by several factors

Poliovirus type 1 and Cocksackievirus A9 are inactivated at similar rates when adsorbed to *particulate matter*. However, Bacteriophage f2 is inactivated more strongly in the presence of particulate matter.
With strong oxidants such as ozone, *dissolved organic matter* can react with and consume the disinfectant, reducing its concentration and, hence, its efficiency. Pre-ozonating secondary effluent increases the rate of inactivation of Poliovirus Type 1 on account of pre-ozonation satisfying the ozone demand of the wastewater organics.

The presence of *inorganic ions* can influence disinfection by ozone. The degree of nitrification of treated wastewater influences the efficiency of inactivation of coliphages and indicator bacteria. The presence of carbonate/bicarbonate increases the inactivation of Poliovirus type 1, ten-fold. The presence of bicarbonate prevents the hydrolysis of ozone to the less virucidal hydroxyl radical. The hydroxyl radical is also effectively trapped by bicarbonate ions, thus waters of high alkalinity may not be favourable for the action of hydroxyl radicals. Bicarbonate ions are known as hydroxyl radical scavengers.

The microbial inactivation mechanisms of ozone involve classical and free radical reactions

Given the chemical reaction mechanisms, *via* the classical pathway of addition to carbon-carbon double bonds and the free radical mechanism involving principally the hydroxyl radical, it is possible to inactivate all or most bacteria, viruses and protozoan cysts.

The bacterial cell wall is vulnerable to attack by the highly reactive hydroxyl radicals. The bacterial membrane is also vulnerable to oxidation processes through ozone adding to double bonds in unsaturated fatty acids present in membrane phospholipids. Any membrane proteins would also be targets of oxidation by either or both mechanisms. Destabilisation of the cell wall and membrane would expose important intracellular functions to further action by both mechanisms.

Viruses would be expected to have their coat proteins oxidatively modified by the reactive hydroxyl radicals, possibly destabilised and degraded, thereby exposing the nucleic acid component i.e. the genetic material, to further action of ozone and hydroxyl radicals.

Protozoan cysts, which are normally very resistant to disinfectants such as chlorine and chloramines are destroyed by ozone (Table 4.2). The cyst wall is reactive to hydroxyl radicals and to ozone itself.

FORMATION OF OZONATION BY-PRODUCTS

Much less work has been done on ozonation by-products than is the case with chlorination by-products.

The principal ozonation by-products are aldehydes

The principal products formed from the ozonation of surface waters appear to be aldehydes, particularly formaldehyde and heptanal. Many other products are formed at lower levels including carboxylic acids and possibly aliphatic and alicyclic ketones. The origins of these are as diverse as natural organics including unsaturated fatty acids, and xenobiotic aromatics. Carboxylic acids can originate from aldehydes and ketones.

Ozone is the disinfectant least prone to the formation of mutagenic by-products

The health effects of ozonation by-products have also not been well investigated. Some aldehydes are known to have adverse effects on the liver and some unsaturated aldehydes can block protein and DNA synthesis, among other effects. None of those associated with the ozonation of water appear to exert significant toxic effects at concentrations expected to be found after ozonation of water. However, aldehydes are often odourants and this will be discussed in the next section.

Examination of ozonated waters using the Ames mutagenicity test shows that ozone is the disinfectant least prone to forming mutagenic by-products which are indicative of substances with the potential of being cancer producing.

TASTES AND ODOURS

A particular feature of ozonation as a disinfection process is that tastes and odours of waters are minimised. This is generally true, although in some cases ozonation gives rise to tastes and odours, consistent with the formation of aldehydes as described in the previous section.

Ozonation and granular activated carbon are effective in removing musty odours from water that had contained blue-green algae and which had been chlorinated. Ozone is effective in removing odours due to MIB and geosmin but at the relatively high dosage of 4 mg/ℓ. Ozone is less

effective in oxidising these two problem substances than is Peroxone (*see* next section). Ozonation also removes musty, earthy, fishy and muddy tastes, but not plastic and astringent odours, from water that has been chlorinated. On the other hand, it is often found that compounds are formed that give rise to odours described as orange-like, fruity, sweet, fragrant, sour and plastic.

Orange-like odours originate from heptanal, hexane, methyl ethyl benzene and phenyl acetaldehyde. Fruity odours are identified with C_8, C_{11} and C_{14} aldehydes as well as phenyl acetaldehyde. Sweet odours originate from C_{15}-C_{22} alkanes. An oxidant odour is associated with heptanal and C_3-C_{10} aldehydes and a fragrant odour with nonanal.
Sour odours are associated with trimethylcyclohexane, and plastic odours with 4-methyl-2,6-di-*t*-butylphenol, 1-ethoxypropane and 2-methyl-2-ethoxypropane.

Several aldehydes and some unidentified compounds are formed on ozonation of surface waters containing fulvic acids. These have been identified as *n*-heptanal, *n*-decanal, phenyl acetaldehyde, vanillin and several unidentified compounds. They impart odours variously described as pungent, sweet and nauseous. Several organic acids are formed, but their concentrations decrease on repeated ozonation, indicating their destruction.

In controlling off-flavours in drinking water, ozone is superior to chlorine and chlorine dioxide, and inferior only to Peroxone.

ECONOMICS

With the availability of cheap electric power in South Africa, ozonation may be an attractive alternative disinfectant to chlorine. Calculations have been performed by Van Leeuwen (1992) and the results quoted by Juby (1993). The cost of generating ozone taking everything into account including amortisation of capital was R5.50/kg in 1991 compared to a cost of chlorine generation of R3.30/kg (*see also* Table 4.4, below).

ADVANTAGES AND DISADVANTAGES OF OZONATION

Advantages

- It is the most effective water disinfectant known and, unlike the others, is effective against protozoan parasite cysts without having to allow unpractically long contact times.

- Iron and manganese can be removed by oxidation to insoluble forms.

- □ It can be used where THM formation potential is high.

- □ It can destroy the native structures of humic or fulvic acids and many man-made pollutants or at least render them more biodegradable.

- □ Certain tastes and odours are removed very effectively.

- □ The likelihood of generating mutagenic by-products is very low.
- □ Generation costs are not prohibitively high and require no special raw materials.

Disadvantages

- □ Although certain tastes and odours are removed, ozonisation can give rise to the formation of odorous compounds such as certain aldehydes.

- □ Ozonation will not remove odours due to principal odourants such as MIB and geosmin except at high doses.

- □ The stability in the distribution system is low, necessitating post-chlorination.

CONCLUSION

It is doubtful whether ozonation will completely supersede chlorination in South Africa. There is an increased tendency to apply several disinfection processes on the same plant to overcome certain disadvantages of individual processes. Ozonation may well have a role to play here. As mentioned, ozonation is applied by the Western Transvaal Regional Water Company and by Umgeni Water, both major suppliers of potable water. With our supply of cheap electrical power, the way is probably open to more widespread application of the process.

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MIXED OXIDANTS: PEROXONE

Unlike the other alternative disinfection processes, hydrogen peroxide treatment alone is not used on a large scale. It is, however, used on a large scale in conjunction with other disinfectants such as ultraviolet radiation and ozone, particularly the latter. In this case it is known as the *Peroxone* process which is becoming popular in many parts of the world. Hydrogen peroxide is also used for the remediation of surface water where e.g. spillages have occurred or where algae or water plants have exerted adverse effects on watercourses. It is also used for swimming pool shock treatment not only to oxidise organic matter, but also to enhance the bactericidal action of other bactericides.

Hydrogen peroxide is produced in South Africa by Alliance Peroxide under the trade name Hyprox®. This company has produced a useful information brochure which provides a valuable background on the manufacture, applications and uses of hydrogen peroxide.

CHEMISTRY OF HYDROGEN PEROXIDE PROCESSES

The use of hydrogen peroxide is ecologically very desirable since the decomposition products are only water and/or oxygen. The following sections will consider hydrogen peroxide alone followed by the Peroxone process.

Hydrogen peroxide

Hydrogen peroxide has three important chemical properties:

- *It is an oxidising agent*

  $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ .....(4.8)

  $H_2O_2 + 2e^- \rightarrow 2OH^-$ .....(4.9)

- *It is a reducing agent*

  $H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$ .....(4.10)

- *It can disproportionate into water and oxygen in an intermolecular redox reaction*

  $2H_2O_2 \rightarrow 2H_2O + O_2$ .....(4.11)

Hydrogen peroxide can act as an oxidising agent, a reducing agent, and

can disproportionate into water and oxygen

The non-catalysed decomposition of hydrogen peroxide to water and oxygen is strongly exothermic and proceeds with the formation of hydroxyl radicals and singlet oxygen, both highly reactive species. The radical mechanism of decomposition is as follows:

$H_2O_2 \rightarrow 2OH\bullet$ ..... (4.12)

$OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet$ ..... (4.13)

$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2$ ..... (4.14)

$HO_2\bullet + OH\bullet \rightarrow H_2O + O_2$ ..... (4.15)

The initial reaction is rate determining and the decomposition of pure hydrogen peroxide proceeds at a very rapid rate.

The decomposition is accelerated by small quantities of a very large number of substances both in solution and in the solid state such as dust and dirt, vessel surfaces and, in particular, heavy metal ions such as Fe^{2+}:

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet$ ..... (4.16)

Hydroxyl radicals can also be formed by photolysis with ultraviolet light at 200-280 nm:

$H_2O_2 + \text{UV-light} \rightarrow 2OH\bullet$ ..... (4.17)

This has the advantage over the Fe^{2+} catalysed reaction that two radicals are formed per hydrogen peroxide molecule but is, unfortunately, only applicable to flocculated and filtered water on account of the high absorptivity of raw water at these wavelengths.

The other very reactive species that can be formed is *singlet oxygen* in a stoichiometric reaction with hypochlorite:

$OCl^- + H_2O_2 \rightarrow Cl^- + H_2O + {}^1O_2$ ..... (4.18)

Singlet oxygen is much more reactive than ground state triplet oxygen and behaves like an electrophilic olefin in that it can react with conjugated dienes and enter into (2+2) cycloaddition with electron-rich olefines.

The *Peroxone* process

The Peroxone process is based upon various ratios of hydrogen peroxide and ozone, generally around 0.5 : 1, by mass. This gives rise to the species depicted in Fig. 4.2 in the previous section.

The action of the process is based to a large extent on the formation of highly reactive hydroxyl radicals according to the scheme depicted in Fig. 4.3.

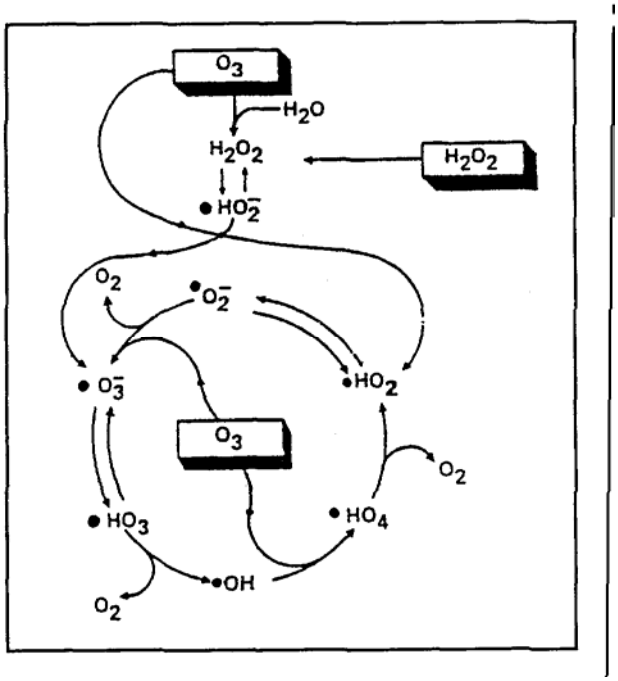

Fig. 4.3 The radical species formed in the Peroxone process (Glaze *et al*., 1986, 1987; *reproduced with permission*)

This may be simplified as follows:

$$H_2O_2 + 2O_3 \rightarrow 2HO\bullet + 3O_2 \quad (4.19)$$

The chemistry of the process has not yet been fully elucidated but the reactivity of the hydroxyl radical plays a major part in the various reactions such as the degradation of harmful organic compounds at least to more biodegradable forms, the oxidation of undesirable inorganic ions, and the microbicidal action on bacteria, viruses and protozoan cysts.

Hydrogen peroxide-based processes have been applied to removing chemical contaminants from water.
Peroxone is the most effective and the most widely used mixed oxidant process

Many of the hydrogen peroxide associated processes are useful for removing chemical contaminants from water, e.g.:

- The treatment of dyestuff and agrochemical containing effluent with hydrogen peroxide followed by activated carbon adsorption.
- Hydrogen peroxide alone is ineffective as an oxidant to remove manganese from water which is high in organic compounds.

- Hydrogen peroxide in the presence of ultraviolet radiation is an effective way of removing organics and a range of potential environmental pollutants from water applied to the production of highly purified water.

- The removal of the Ames mutagen (potential cancer causing agent) "MX" (*3-chloro-4-(dichloromethyl)-5-hydroxy-2[5H]-furanone*) is effective using hydrogen peroxide in the presence of Fe^{2+} ions. As described, this is a way of generating hydroxyl radicals.

The combination of *ozone and hydrogen peroxide* (Peroxone) is the most effective and, hence, the most widely used method:

- The action of Peroxone on various organic compounds in solution is effective in oxidising, particularly, certain carbonyl compounds formed in ozonation which are stable towards ozone.

- The presence of hydrogen peroxide accelerates the oxidative action of ozone on tri- and tetrachloroethylene present in polluted groundwater by virtue of the presence of hydroxyl radicals, but carbonate or bicarbonate act as radical scavengers that inhibit the reactions. Further work on a pilot scale indicate this to be a cost-effective method of controlling the common chlorinated organics found in groundwater.
  An H_2O_2/O_3 mass ratio of 0.5 yields higher VOC oxidation rates and the most efficient use of oxidants compared to other ratios when tested on groundwater contaminated with chlorinated organic compounds.

- The radical scavenging effect of alkalinity (bicarbonate) in water has been confirmed for the removal of dissolved organic carbon (DOC) from humic water.

- Using Peroxone as a final disinfectant is effective in reducing THMs by 30% compared with the use of ozone alone.

- Several pesticides such as dichlorvos, atrazine and simazine are more effectively

decomposed using Peroxone rather than ozone alone.

□ Peroxone removes most organic micropollutants and pesticides in drinking water for which it is most suitable. The products of the oxidation process are removed using one or more biological filtration steps.

MECHANISMS AND EFFICACY OF BACTERIAL, VIRAL AND PROTOZOAN CYST INACTIVATION BY HYDROGEN PEROXIDE-BASED PROCESSES

Hydrogen peroxide alone is not a viable alternative to chlorination in water treatment since it is a poor water disinfectant, and is highly unlikely to win a place as a primary disinfection agent. The reason is that the process needs an appropriate catalyst which has not yet been found.

Hydrogen peroxide alone is a poor water disinfectant

"Free" hydrogen peroxide would have to be used at concentrations exceeding 1000 mg/l in order to be an effective water disinfectant; 1000 mg/ℓ is required to reduce viable *Legionella pneumophila* by 99% in 30 minutes, and 100-300 mg/ℓ is required to completely kill off the same population in 24 hours. Even stabilised hydrogen peroxide used in swimming pools needs to be used at 60-100 mg/ℓ and allowed to act overnight at least.

The reason for this resistance is the ubiquitous presence, in bacteria, of the enzyme, *catalase*, which catalyses the disproportionation of hydrogen peroxide according to Equation 4.11, acting as a natural defence mechanism.

The Peroxone process is the most common application of mixed oxidant disinfection

The most important studies done on the bactericidal action of hydrogen peroxide and ozone have been carried out at the Metropolitan Water District of Southern California who first gave the name, Peroxone, to the process.

The bactericidal (against *E. coli*) activity of Peroxone is greatly affected by the ozone dose, the H_2O_2:O_3 ratio, contact time, source water quality, and the type of microorganism present.

Peroxone is less potent than ozone at all ratios if the contact times are 5 minutes or less, particularly at ratios between 0.5 - 0.8.
In contrast, the virucidal (against MS2 Coliphage) potency of Peroxone is comparable at all ratios. Heterotrophic bacteria are the most resistant to Peroxone.

Regardless of the source water, >4.5 logs of *E. coli* and MS2 Coliphage (virus) are inactivated at an applied ozone dosage of 2.0 mg/ℓ when the $H_2O_2 : O_3$ ratio is $\leq$ 0.5.

However, the Peroxone process must be optimised for each source of raw water in order to achieve the optimum effectiveness as a disinfectant.

Peroxone is an effective microbicidal process against bacteria, viruses and protozoan cysts

In the disinfection of *Giardia muris* cysts seeded onto surface water supplies, Peroxone and ozone are comparable in potency at an $H_2O_2 : O_3$ ratio of 0.2. A minimum inactivation level of 2 logs is usually achieved at an ozone residual of $\geq$ 0.65 mg/ℓ irrespective of the source water, temperature, turbidity or contact time. Results for inactivation of total or heterotrophic bacteria are similar to those for *Giardia* up to about 2.8 logs. Thus, total or heterotrophic bacteria may be useful indicators of *Giardia* cyst inactivation under some conditions.

Ozone-hydrogen peroxide mixtures (doses of 2 mg/ℓ O_3 and 0.6, 1.0, or 1.6 mg/ℓ H_2O_2), rapidly inactivate both hepatitis A virus and MS2 Coliphage virus at pH 6-8.

Thus, Peroxone is an effective water disifection process against bacteria, viruses and protozoan parasite cysts.

The mechanisms of action of hydrogen peroxide-based processes partly depend on the high reactivity of the *hydroxyl radical*

An important species partly responsible for the disinfection potency of ozone is the hydroxyl radical. This is also the case with Peroxone but, as was seen, the microbicidal efficacy is also dependent on the ozone residual. There is some dispute about the microbicidal efficacy of Peroxone. Despite the higher oxidising power the hydroxyl radical appears to be a less potent bactericide than ozone. This could be related to the short lifetime of the hydroxyl radical

rendering it unable to penetrate certain bacterial cell-walls. The efficiency with which it inactivates viruses is as a result of their simpler structure and where the capsid protein can be degraded. In certain cases penetration and reaction with the genetic material is also possible.

FORMATION OF BY-PRODUCTS

Reports dealing with the Peroxone process do not mention the formation of any by-products. This is not the case with ozonation where common by-products are aldehydes of various kinds which are mainly responsible for different odours. The higher oxidising power of Peroxone is such that any by-products of this nature are oxidised further and destroyed in the process.

TASTES AND ODOURS

Whereas ozone gives rise to certain tastes and odours mainly as a result of the formation of aldehydes, this does not occur with hydrogen peroxide or Peroxone. The oxidising power of these two substances is such that, in the former case, no odourants are formed owing to the relatively weaker action of hydrogen peroxide compared to ozone, whilst in the latter case, they are formed but are oxidised further and ultimately destroyed by the strong action of Peroxone.
Hydrogen peroxide alone is mostly ineffective in destroying common odourants such as MIB and geosmin, but not dimethyltrisulphide. Peroxone requires a significantly lower dosage of ozone to oxidise MIB and geosmin compared to ozone alone. Peroxone is moderately more effective than ozone in removing odours from filtered water.

An ozone dose of 2 mg/ℓ at a H_2O_2/O_3 mass ratio of 0.2 is comparable to the effects achieved with an ozone dose of 4 mg/ℓ in destroying 80 - 90% of MIB and geosmin concentrations.

ECONOMICS

Various chemical treatment costs based on the amortised capital costs (8% over 10 years) and the overhead and maintenance costs are available. This comes to an estimated treatment cost for the Peroxone process of US$ 46.00 per 1000 m^3 (= 1.0 Ml). Ozonation costs calculated on the same basis are US$ 40.00 per 1000 m^3.

In South Africa ozonation was estimated to be 67% more expensive than chlorination in 1991. This renders the Peroxone process an estimated 80% more costly than chlorination, i.e. approaching twice as expensive. It is, therefore, unlikely to replace chlorination in the short term except in cases where particular problems exist that may be solved by applying the Peroxone process.

ADVANTAGES AND DISADVANTAGES OF PROCESSES INCORPORATING HYDROGEN PEROXIDE

Advantages

- All of the advantages listed for ozonation apply to Peroxone.
- It is more effective in removing tastes and odours than ozone, removing the problem odour-causing substances, MIB and geosmin.
- Additional odourants do not appear to be formed as in the case of ozone.
- It is possible to destroy many more organic pollutants than is possible with ozone.

Disadvantages

- The process is relatively expensive and necessitates transporting hydrogen peroxide, a hazardous substance, to the site of application.

CONCLUSION

As with ozonation, it is doubtful whether any hydrogen peroxide based process such as Peroxone will supersede chlorination for general use in South Africa within the foreseeable future, except for special applications under exceptional circumstances. An advantage is that there is a local manufacturer of hydrogen peroxide, *Alliance Peroxide*, and also that electrical power is relatively cheap in South Africa. The process may have an application as pretreatment, prior to chlorination, for water with a high potential for forming THMs. As alluded to earlier, there is an increased tendency for disinfection plants to make use of several processes in tandem in order to overcome certain disadvantages of individual processes in dealing with their raw waters.

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ULTRAVIOLET IRRADIATION

Ultraviolet (UV) irradiation was first used for potable water disinfection in France in 1910. It has only come into its right in the last fifteen years when its advantages as an alternative disinfectant to chlorine have come to be appreciated. It has found more application to small volume water supplies and is a relatively low cost technology suited to communities which cannot afford the capital costs of ozonation or who do not have the skilled personnel to operate such installations. However, it has also been applied on a large scale to larger volume water sources where the raw water is of a suitable high quality. It is also used to disinfect sewage plant effluent before this is returned to the environment e.g. The Daspoort Sewage Works, Pretoria.

The basic principle of the process is to circulate the water to be disinfected past the sources of UV radiation in such a way as to get maximum exposure to the UV radiation. Generally water is passed through a shallow tank in which the tubes are mounted, transversely or longitudinally, in such a way that the thinnest possible water layer passes the UV source, thus ensuring maximum penetration.

The formation of disinfection by-products does not take place since radiation levels are relatively too low to allow this to happen. An obvious disadvantage of the process is that no residual disinfection potency exists after the irradiation is discontinued.

This section will consider the photochemistry of the process, the mechanisms of microbial inactivation, removal of tastes and odours, the economics of the process as well as advantages and disadvantages.

PHOTOCHEMISTRY OF DISINFECTION BY UV IRRADIATION

Ultraviolet radiation

The designation, ultraviolet, is given to the band of the electromagnetic spectrum immediately outside the violet end of the visible band but above the X-ray band. The UV thus spans the wavelength range from 100-400 nm. The ranges of interest are the three bands designated A,B and C and which have significantly different biological effects:

UV-**A**	315 - 400nm
UV-**B**	280 - 315nm
UV-**C**	200 - 280nm

The optimal microbicidal wavelength is 255 nm, corresponding very closely with the strong absorption band of the nucleic acids in the region of 260 nm.
This will be covered in more detail when the mechanism of disinfection is discussed.
Wavelengths below 200nm are of little biological significance since radiation in this range of the spectrum is absorbed by very short pathlengths in air.

The optimal microbicidal wavelength is 255nm

Sources of UV-radiation

Ultraviolet radiation is typically generated in electrically powered, low pressure mercury discharge arcs, enclosed in quartz envelopes that do not transmit short wavelength UV i.e. < 240 nm. This cutoff prevents the formation of undesirable photolysis products of certain organics and inorganics whilst recognising that UV-radiation of this wavelength is in any case relatively ineffective in deactivating micro-organisms since high energy UV-radiation has a very small penetration depth.

Factors affecting the UV-disinfection process

The efficiency of the UV-disinfection process depends on the effective dosage of radiation applied. The dosage required to achieve a certain level of bacterial inactivation is dependent on the conditions. Bacterial kill is primarily a function of the total dosage of UV-radiation and not on the intensity.

Bacterial and viral kill are functions of applied dosage, not intensity

The relationship between the dosage and the intensity is given by the following simple relationship:

$$D = I.t$$

where D is the dosage ($\mu Ws.cm^{-2}$)
I is the intensity ($\mu W.cm^{-2}$)
t is the exposure time (s)

Dosages may be expressed in different units according to local practice or preference.

Major water quality factors affecting the transmission of UV-radiation are:

- □ Dissolved organic substances which are able to absorb UV-radiation.
- □ Suspended solids (turbidity) which scatters UV-radiation.

Dissolved, UV-absorbing substances attenuate the energy of the UV exponentially as the pathlength

Changes in water quality and water depth have an influence on the disinfection efficiency because the decrease in the transmittance of the water due to dissolved matter reduces the radiation flux. Both influence the disinfection exponentially because of the decreased intensity of radiation reaching its target according to the Beer-Lambert Law as follows:

$$I = I_o e^{-\alpha d}$$

where I_o is the incident intensity
I is the intensity at depth d
d is the water depth penetrated
α is the absorption coefficient pertaining to the wavelength absorbed and the water quality.

Where a specific, absorbing, organic substance is present, the decrease in the intensity is expressed as follows:

$$I = I_o e^{-\varepsilon c d}$$

where, ε is the molar extinction coefficient of the substance, and
c is its concentration (mol/ℓ).

Suspended matter decreases the incident radiation by light scattering rather than by absorption. In practice, this means that pretreatment of the water is necessary unless it is of a very high quality.

Pretreatment of water is usually necessary prior to UV-disinfection

This may have to be intensive and costly such as e.g. using activated carbon to remove organics or it could be less costly, necessitating filtration through membranes. This fact is cited below as

one of the major disadvantages of UV-disinfection.

MECHANISM AND EFFICACY OF BACTERIAL, VIRAL AND PROTOZOAN CYST INACTIVATION BY ULTRAVIOLET RADIATION

Mechanism

When micro-organisms are exposed to UV-radiation of the correct wavelength and, hence, energy, the radiation has to penetrate, successively, the cell wall, the cell membrane and the protoplasm in order to reach the nucleus. Here structural change occurs in the primary genetic material i.e. the DNA. The DNA carries primary genetic information and is essential for controlling protein synthesis and, hence, the replication of the organism.

The structural change brought about by exposure to UV-radiation consists in the dimerisation of the nucleotide base, thymidine, as well as disruption of carbon-carbon and carbon-nitrogen double bonds. This leads to the cross-linking of DNA chains, disruption of hydrogen bonding and a consequent impairment of normal function of chain separation during the replicative process. While the microorganism is still metabolically active, the inability to replicate is the property prerequisite for infectivity. RNA is unaffected since thymidine occurs only in DNA.

Since DNA is present in all living organisms including the bacteria, protozoan parasite cysts and transitional forms such as viruses, it follows that all micro-organisms and viruses should be vulnerable to the germicidal effects of UV-radiation. This is the case except there is wide variation among different types.

UV-radiation damages DNA by dimerising thymidine

It is possible for organisms to undergo repair after having been damaged by UV-radiation in the manner detailed above. One manner is by exposure to higher wavelength radiation in the UV-A/visible region. This can lead to a photochemical reversal of the dimerisation reaction and restoration of the viability of the bacterium. Another mechanism is the so-called *dark repair* which is an enzymatic process initiated by the organism itself if only one DNA strand has been broken and it is able to repair the damage using the complementary second strand.

DNA repair is promoted by exposure to visible light

If the number of lesions introduced by the UV-radiation is large, at least five, then it follows that

the organism is unable to repair the damage. This emphasises the importance of delivering adequate doses of radiation to minimise sub-lethal damage.
It has also been established that UV- radiation fluxes sufficient for water disinfection do not lead to breakdown of high molecular weight substances that could act as easily metabolised nutrients for bacterial regrowth. These would include biopolymers such as alginic acid from algae and extracellular polysaccharides from bacteria.

Effectiveness for different organisms

No point-of-use disinfection treatment should be used in the case of water so polluted as to require extraordinary measures for purification to drinking standards. This is particularly true for UV-disinfection because of shielding of micro-organisms from the bactericidal radiation by particulate matter or by the presence of large numbers of micro-organisms.

In Canada, the suggested raw water quality cutoff is 1000 total coliforms/mℓ and 100 faecal coliforms/mℓ

In Canada, a country that widely utilises UV-disinfection, an upper limit of 1000 total coliforms/100mℓ or 100 faecal coliforms/100mℓ has been suggested as the cutoff counts above which UV disinfection should not be considered.
As expected, different micro-organisms display different susceptibilities to the disruptive effects of UV-radiation. Organisms the size of bacteria and smaller, such as viruses are susceptible to UV-radiation at very similar doses. When the organism becomes larger, such as protozoan parasite cysts or oocysts which are also encased in UV-absorbent coatings or, in the case of some viruses, which have double stranded RNA, then even higher UV-doses are required. The order of susceptibility to inactivation by UV-radiation is as follows:

Multiplying bacteria > Viruses > Bacterial spores > Protozoan parasite cysts/oocysts
It is evident that most pathogenic bacteria and enteric viruses are readily killed at reasonable dosages. The resistance of protozoan cysts is a problem common to all disinfection processes except ozonation and Peroxone. However, being large, they are usually removed by coagulation, sedimentation and filtration in the initial stages of the water purification process.

Some of these doses are listed in Table 4.3.

Table 4.3 Ultraviolet dosages ($mW.cm^{-2}$) required for 90 and 99.99% inactivation of various pathogenic micro-organisms (Cairns, 1992 Groocock, 1984; Myhrstad, 1980; Sobsey 1989).

Organism	Inactivation	
	90%	99.99%
Salmonella typhimurium	8.0	15.2
Salmonella enteritides	4.0	7.6
Salmonella paratyphi	3.2	-
Salmonella typhi	2.1	-
Shigella paradysenteriae	1.68	3.4
Escherichia coli	3.0	6.6
Pseudomonas aeruginosa	5.5	10.5
Staphylococcus aureus	5.0	6.6
Streptococcus faecalis	4.4	-
Legionella pneumophila	-	30
Poliovirus	7.5	20-30
Rotavirus	11.3	25
Coliphage	3.6	6.6
Protozoan parasites (various)	60 - 200	-

TASTES AND ODOURS: MUTAGENICITY

Ultraviolet treatment is not able to remove tastes and odours. Radiation of the bactericidal wavelength is not of sufficiently high energy to be able to achieve this, since it has to bring about the degradation of chemical structures.

On the other hand, UV- irradiation will also not lead to the formation of undesirable tastes and odours since there are no chemical agents involved in the disinfection process, such as in the case of chlorine.

Here the formation of chloroorganics, particularly, chlorophenols, is an ever present possibility if phenols occur as pollutants. There is also no evidence that UV-disinfection leads to the formation of mutagenic (i.e. potentially cancer causing) by-products formed as a result of the degradation of other substances.

ECONOMICS

Ultraviolet disinfection applied on a large scale is more expensive than chlorination. Capital and maintenance costs amount to four times the corresponding cost for a chlorination facility. However, as can be seen in Table 4.4, this only applies to large water treatment plants.

A comparative set of figures representing total annual costs of disinfection, applying to the US but, nevertheless, giving a reasonable idea of the relative costs of UV-treatment compared with other processes, are given in Table 4.4.

Table 4.4 Total annual costs of disinfection by various processes (US cents/m^3)

Disinfection Process	**PLANT CAPACITY (m^3/day)**		
	400	**200**	**20**
Chlorination	4.50	7.90	68.4
UV- irradiation	14.0	19.0	57.6
Ozone	17.4	25.3	190
Chlorine dioxide	22.6	29.2	138

It is evident that, for a small treatment plant (20 m^3/day), UV-treatment is marginally cheaper than chlorination, but the latter becomes more cost-effective as the capacity of the treatment plant increases.

The figures for chlorine dioxide treatment are not applicable to South Africa as the raw material has to be imported and, as a consequence, is very expensive.

ADVANTAGES AND DISADVANTAGES OF ULTRAVIOLET DISINFECTION

Advantages

- The bactericidal effect is rapid and there is no risk of overdosage.

- The system is low maintenance apart from the arcs having to be changed when they weaken and sleeves having to be kept free of deposits.

- □ Automation is easy.

- □ The water constituents undergo very little chemical change and no disinfection by-products are formed; in particular, no trihalomethanes.

- □ There are no residual chemicals to give rise to tastes and odours.

- □ Contact times can be easily adjusted by modifying flow-rates and hence providing for resistant organisms in the influent water.

Disadvantages

- □ Pretreatment is frequently necessary.

- □ Electric power is required.

- □ There is no disinfectant residual to prevent bacterial regrowth in the distribution system.

- □ Unallowed for deterioration of influent water quality can overwhelm the unit but this applies also to chemical disinfection units.

- □ Running costs are generally higher than those of chlorine disinfection plants and the process is expensive for larger plants.

CONCLUSION

In general, the data on inactivation of micro-organisms show that the effectiveness is reduced by suspended particles and dissolved organic substances in water. Although most actively growing bacteria are inactivated efficiently (>99.9%) by the recommended minimum UV-dose of 16mW-s/cm^2, higher doses are required for enteric viruses (Table 4.3). Protozoan cysts can be regarded as falling outside the area of applicability of UV-disinfection on account of their extreme resistance.

Difficulties in accurately determining the applied UV-dose and in cleaning and maintaining UV-lamps in the facility, the lack of disinfectant residual and relatively high costs for large-scale application have limited the process to mostly small-scale water disinfection systems.

FURTHER READING ON ULTRAVIOLET DISINFECTION

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