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Water Disinfection: A Review with Some Consideration of the Requirements of the Third World

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I. INTRODUCTION

The need to remove or destroy disease-producing contaminants in polluted drinking water has been evident since 1849, when Dr. John Snow suspected water of being the means of communication of cholera. He was able to prove this theory a few years later in 1854 when, in the celebrated affair of the Broad Street pump in London, he eliminated a local, but severe, outbreak of cholera simply by removing the handle from the pump supplying the suspect water.[1,2] Then, following the rapid development of the science of microbiology during the second half of the 19th century, it became quickly evident that the disease-creating substances were, in fact, living microorganisms largely in the form of bacteria and viruses. The need to eliminate these from drinking water supplies was now obvious.

Disinfection is the term normally applied to the activities associated with the destruction, or inactivation, of disease-producing microorganisms in water. The term implies the destruction — or inactivation — of only the disease-producing, or pathogenic, microorganisms and not necessarily the total destruction of all life within the water. This latter requirement would demand a process of sterilization which, except possibly for some applications of ozone, is not usually intended or achievable within the operational limits imposed with the use of most water disinfectants of concentration, taste and odor production, time and cost.

Although the developing employment of slow sand filtration, as the 19th century continued, greatly reduced the dangers to health associated with the use of polluted surface water sources, it was not until the early years of this century that the application of disinfectants to water supplies made possible the complete removal of the disease risk. Of these water disinfectants, it is chlorine, employed at perhaps 99% of water treatment works, which is the principal agent of success. It can be totally effective for the destruction of waterborne pathogenic microorganisms without creating other hazards to public health. Its nearest competitor is the powerful, but short-lived, ozone which is traditionally popular in France and other continental European countries. Other potable water disinfectants in use include chlorine dioxide, ultraviolet (UV) radiation, and iodine.

In the pursuit of pathogen-free drinking water, it would be unwise to rely entirely on the application of a disinfecting agent which may or may not, depending on type, dosage, contact time, and degree of pollution present, be able to destroy all harmful microorganisms. The effective total resolution of the problem requires the application of additional techniques which must include, whenever possible, the prevention of source pollution. Also, in those situations in which the use of lower quality waters for treatment is unavoidable, the long-term storage of the water prior to conventional treatment must be considered as one of the

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more important, if simple, techniques to employ. Particularly in these days of concern for the danger associated with the products of the reaction between chlorine and a variety of organics in water, the prevention of source pollution must be high on the list of imperatives for any responsible water supply organization. However, with the increasing demand for water, it is unavoidable that many sources of lower quality water have necessarily to be employed. In these situations, major improvements in water quality can be achieved as a result of long-term storage by which turbidity and color can be reduced, organic content lowered, ammonia oxidized, iron precipitated, and, of greatest importance, the count of intestinal bacteria radically decreased.[3] The benefits of storage will include simpler and more effective treatment and especially more assured disinfection.

All the normal techniques of water treatment remove, to some extent, potentially harmful microorganisms from water thus reducing, and making more certain of complete success, the role of the disinfection stage. Screening, chemical pretreatment, and sedimentation, filtration, softening, and activated carbon adsorption are all capable of removing microorganisms to a greater or lesser extent, although the very real ability of the activated carbon in this role is somewhat compromised by a possible periodic release of quantities of microorganisms following concentration and a chromatographic-style transport through the carbon bed. Slow sand filters will remove, if well designed and adequately operated, a very high percentage of intestinal bacteria and possibly, so long as the temperature is not too low, all of the viruses, while the processes of coagulation/flocculation/sedimentation are reported as being capable of removing rewardingly high percentages of viruses. Coret et al.[82] report the removal of between 31 and 90% of the initial virus count in the Seine River water following chemical pretreatment with a basic aluminium chloride. This reduction increased to between 90 and 99% by passage through the rapid sand filters operating at 5 m/h. Walsh and coworkers[83] found, in a laboratory investigation, that 99% of introduced *polio virus 1* became associated with formed alum floc at pH 7.0. Rao et al.[84] reported that more than 99% of the rotavirus could be removed by coagulation/flocculation/settling using either alum floc or ferric chloride. Ferric chloride floc removed only 14% of the polio virus in the same situation, but 74% of the *hepatitis A* virus, while alum floc removed 49% of the polio virus and 65% of the hepatitis A. In the same investigation, it was found that coagulation and settling followed by filtration removed between 98.4 and 99.7% of the total viruses. In addition, this research demonstrated a greater than 90% removal of *rotavirus* during the removal of magnesium hardness at pH 10.8 and 37°C.

Disinfecting agents fall into the following groups: (1) oxidizing agents; (2) cations of heavy metals; (3) quaternary ammonium and pyridine compounds; (4) gaseous agents; and (5) physical agents (heat, UV radiation, ionizing electromagnetic waves). Most of those employed in water treatment are oxidizing agents. In addition, UV radiation is moderately widely employed, especially for small water supplies, and silver has been used in a limited number of applications. The boiling of water is also a possible means of bringing about water disinfection for small quantities in areas where fuel is not a problem.

Water disinfectants are selected because of their ability to destroy effectively the causative organisms of waterborne diseases at concentrations, or dosages, which are harmless to the consumer while not creating undesirable taste and odor problems and by being within acceptable cost limits. Preferably, also, the disinfectant should be capable of providing residual protection for the water during the period between leaving the water treatment unit and arrival at the consumer. Few water disinfectants, if any, can achieve all these aims under all conditions of water quality. Even the paramount requirement of initial inactivation of pathogenic microorganisms can only be achieved by the correct combination of concentration and contact time. Presently, concerns over the long-term harmful effects to the consumer are beginning to influence the methods for the employment of chlorine in particular, and only two, or possibly three, disinfectants are capable of providing residual disinfection throughout a distribution system.

The incidence and death-rate from typhoid fever has been used as an indication of the efficacy of water treatment in general and of chlorination in particular. At the beginning of this century, the average death-rate from typhoid in the U.S. was as high as 36/100,000, resulting in the horrific figure of 25,000 deaths in 1900.[4] By 1910, this had decreased to 20/100,000 and by 1935,[11] following a dramatic improvement in water treatment processes and drinking water quality, it had dropped to only 3/100,000.[8] In 1960, fewer than 20 people died from typhoid in the whole of the U.S.[12] However, in addition to these figures, there has been observed what has become known as the Mills-Reincke phenomenon as these two researchers recorded that with the replacement of a polluted water supply by a pure supply the health of the general public improved to a level far beyond that associated just with the eradication of the hazard of typhoid and other waterborne diseases. These observations were supported by the work of Allan Hazen, who concluded that for every person who did not die from typhoid as a result of receiving a pure water supply three others were saved from death by other causes.[4]

A. Chick's Law and Concentration/Time Products

It is widely accepted, if only for convenience, that the rate of inactivation of microorganisms follows a first-order relationship dependent on the number of the particular microorganism under consideration on any occasion, i.e.,

$$\frac{dN}{dt} = -k \cdot N \qquad (1)$$

where N is the number of viable microorganisms present at any time t and k is a proportionality constant. Thus on integrating for $N = N_0$ at $t = 0$

$$\log_e \frac{N}{N_0} = -k \cdot t \qquad (2)$$

$$\frac{N}{N_0} = e^{-k \cdot t} \qquad (3)$$

This relationship is usually referred to as Chick's Law.[85]

Ideally, the plot of log N/N_0 against $k \cdot t$ should produce a straight line; that in most situations it fails to do so is a result of the peculiarities and nonuniformity of the microbial suspensions. The situation is confused by the failure of the microorganisms to behave as straightforward chemical reactants. Aggregation or clumping of the microorganisms can influence the results. There is also the necessity for the disinfectant to diffuse into the microbial cell in order to be effective and the situation is further complicated by the efficiency — or otherwise — of the mixing process and also by the loss of disinfectant as a result of extraneous reactions or by volatilization.[68] As a result, the failure to obey Chick's Law exactly is the rule rather than the exception.

From the beginning of investigations into rates of disinfection, it was obvious that the concentration/time relationship was of importance. In 1908, Watson[87] developed the empirical relationship

$$k. = C^n \cdot t \qquad (4)$$

which is now, not infrequently, referred to as Watson's Law. With this, t is again time and

C represents the concentration of the disinfectant while n is a constant called the coefficient of dilution and k_* is a further coefficient specific to the particular microorganism under specific conditions. When n = 1, both C and t are of equal importance and the C · t product is independent of the concentration of disinfectant employed. When n > 1, it is the concentration of the disinfectant which is the dominant factor and the C · t product declines as the concentration of the disinfectant increases. With n < 1, the exposure is more important and C · t values increase as the disinfectant concentrations increase. Morris[88] reported that evaluation of the constant n was only justifiable in those limited numbers of situations in which the experimental data conformed to Chick's Law.

However, the concentration/time product has been found to be a convenient and helpful method for judging the effectiveness of a disinfection action against a particular microorganism or of stipulating the important conditions for water disinfection. In 1980, the Safe Drinking Water Committee selected C · t values as the method of comparing biocidal efficacy. These values are now widely employed for assessing the relative efficiencies of different disinfectants and for expressing the different resistance of individual types of organism. In practice, the concentration (C) is usually quoted in terms of milligrams per liter (mg/l) and the time (t) in minutes.

Since the detection of the 100% kill is not realistic, it is normal to determine a C · t product for a specific percentage inactivation such as 99 or 99.9%. C · t products tend to increase with pH and vary inversely with the temperature of the water. Lippy[89] reported that with free-chlorine at pH 7.0 and for a 99% inactivation of protozoans that the C · t product declines from about 100 at 5°C to 35 at 15°C and to 15 at 25°C. At pH 8.0 and over the same temperature range, he reported that the C · t values came down from about 150 to 50 to 15. He further suggested, rather conservatively, that a viral C · t value will be about 12 between about 0 and 5°C and at a pH of between 7.0 and 7.5, while at 10°C and the same pH it will be about 8. These values, he reported, will rise to about 35 (0 to 5°C) to 22 (10°C) as the pH is increased to between pH 8.5 and 9.0. For his generalized viral values, Lippy based his figures on the requirements for the inactivation of the *Coxsackie A2 virus*, which he considered to be substantially more resistant than the *poliovirus*.

Lippy suggested for the disinfection of groundwaters with free chlorine that a minimum C · t product of between 15 and 30 should be considered to achieve the complete inactivation of any viruses that might be present. For surface water abstractions, particularly in situations where the temperature might be appreciably low and the presence of protozoans at the time of disinfection cannot be eliminated, he proposed a minimum C · t product of between 100 and 150.

C · t values generally indicate the weakness of combined chlorine as a disinfecting agent and the great strength of ozone. Most information, as would be expected, is available for the C · t values associated with *Escherichia coli* and for the viruses it is the *poliovirus 1* which is the most investigated. Generally, C · t values for free chlorine for the *poliovirus 1* are about 10 to 20 times greater than for *E. coli.*[68] Chlorine dioxide shows a slightly higher C · t value for *poliovirus 1* at pH 7.0 than chlorine, but the value decreases toward pH 9.0.[68] C · t values also indicate that chlorine dioxide is probably the best chlorine-based disinfectant against Giardia cysts.[21] (See Table 1.)

II. CHLORINE

A. History and Development

Chlorine exists widely and abundantly, especially as salts of sodium and potassium, and is produced as a dense gas by the electrolysis of sodium chloride. It is usually supplied under pressure in steel cylinders, drums, or tanks — to which it is not corrosive in the dry state — as a mixture of about 85% liquid and 15% gas, although for small or isolated communities chlorine is provided as sodium or calcium salts of hypochlorous acid.

Table 1
C · t Values for 99% Inactivation

Organism	Disinfectant	Temp.	pH	C · t value (mg · min/l)	Ref.
Escherichia coli	Free chlorine	5	6	0.045	409
E. coli	Free chlorine	5	10	0.84	409
E. coli	Free chlorine	23	7	0.014	21
E. coli	Chloramine	5	7	22	367
E. coli	Chloramine	5	9	113	367
E. coli	Chlorine dioxide	20	6.5	0.17	410
E. coli	Ozone	12	7	0.002	68
Poliovirus 1	Free chlorine	20	6	0.5—0.7	21
Poliovirus 1	Chloramine	25	9	216	367
Poliovirus 1	Chlorine dioxide	25	7	0.9	68
Poliovirus 1	Ozone	20	7	0.05	339
Giardia lamblia	Free chlorine	5	8	110	81
G. muris	Chloramine	15	7	848	68
G. muris	Chlorine dioxide	25	7	5.3	68

Karl Scheele, the Swedish chemist, is credited with the discovery of chlorine in 1774. As an upholder of the phlogiston theory, Scheele called the gas he had discovered dephlogistated muriatic acid, and it was not until some years later that Humphrey Davy suggested the name chlorine from the Greek word chloros for green. In 1785, Berthollet, working in the French town of Javel, dissolved chlorine in potassium hydroxide to produce a bleaching solution which is still known, in France, as Eau de Javel. In 1789, Charles Tennant, following extensive investigation, managed to produce a dry compound known, since then, as bleaching powder.[4]

It was as a bleaching powder that chlorine was initially employed for the disinfection of water, probably to counter an outbreak of typhoid at the Austria-Hungary naval base of Pola in 1896. Then, in the following year, it was used at Maidstone in England, again to counter an epidemic of typhoid, The first known continual use of chlorine as a water disinfectant was at the small Belgium town of Middekerke in 1902. This was followed by Ostend in 1903, where chlorine was generated from a mixture of oxalic acid and potassium chlorate. In England, the first continuous application of chlorine using bleaching powder was at the city of Lincoln where, between February 1905 and 1911, when a new water source became available, chlorine was employed to disinfect the contaminated water from the River Witham.

In the U.S. chlorine was first employed, indirectly, to assist water treatment when it was electrolytically generated in the sewage effluent at Brewster, NY, before discharge to the River Croton which formed part of the water source for New York City.[4] Chlorine was again used to disinfect the water supplied to the Chicago stockyards in 1908,[4-6] and also in 1908 a hypochlorite plant was commissioned to add chlorine to the water abstracted from the Rockaway River to serve Jersey City.[4,7] Then, in 1910, a major step forward in the application of chlorine for water treatment was taken when Major C. R. Darnall of the U.S. Army Medical Corps began experimenting with the storage of liquid chlorine under pressure in steel containers and developed the first practicable gaseous-chlorine chlorinator. Following this, the first full-scale application of gaseous chlorine to a public water supply scheme took place at Wilmington, DE, in February 1913.[4,8-10]

1. *Reactions*

When chlorine is added to water, both hydrolysis and disproportionation reactions commence

$$Cl_2 + H_2O = H^+ + Cl^- + HOCl \qquad (5)$$

Table 2
Percentage of Hypochlorous Acid and Hypochlorite Ion Present at Various pHs at 15°C

pH	HOCl (%)	OCl (%)
5	99.7	0.3
6	97.5	2.5
7	79.7	20.3
8	28.0	72.0
9	3.8	96.2

$$HOCl = H^+ + OCl^- \tag{6}$$

The quantities of each species present are governed by reaction concentrations, reaction rates and equilibria, pH, and temperature. Kinetic evidence[13-15] indicates also the participation of very low concentrations of the hypochlorinium ion, whose stability has been indicated by thermodynamic calculations[16]

$$Cl_2 + H_2O \rightarrow H_2OCl^+ + Cl^- \tag{7}$$

The existence of the chlorinium ion, however, in water is considered to be unlikely,[13,17] and the presence of molecular chlorine will only be of significance at high concentrations and at a very low pH.[18]

The hydrolysis constant for Reaction 1 varies with temperature from 1.5 × 10^{-4} at 0°C to 4.0 × 10^{-4} at 25°C, while the dissociation constant for Reaction 2 increases from 1.6 × 10^{-8} at 0°C to 3.2 × 10^{-8} at 25°C.[19] HOCl is a weak acid which dissociates increasingly as the pH increases. At any particular pH, the percentage distribution of the hypochlorite ion (OCl^-) and the undissociated hypochlorous acid can be determined from

$$\frac{[HOCl]}{[HOCl] + [OCl^-]} = \frac{1}{1 + \frac{K}{[H^+]}} \tag{8}$$

The percentages of the two forms present in an aqueous chlorine solution at 15°C are given in Table 2.

2. Biocidal Strengths of Hypochlorous Acid and Hypochlorite Ion

Although both the undissociated hypochlorous acid and the hypochlorite ion are disinfecting agents, the hypochlorite ion is far less effective than the undissociated acid. It has been suggested[4,20] that the OCl^- ion is only $^1/_{80}$ as powerful a bactericide (specifically *E. coli*) as the HOCl and only between $^1/_{500}$ and $^1/_{300}$ as effective as a cysticide[4,21] (specifically *Endamoeba histolytica*). Hence, the germicidal effect of chlorine in water is dramatically reduced as the pH rises above pH 7.0. Butterfield and co-workers[22] found that only 0.05 mg/l free chlorine was required to achieve a 100% kill of *E. coli* bacteria in 3.0 min at pH 7.0 and at between 2 and 5°C, while at pH 9.8 and the same temperatures, 0.72 mg/l of free chlorine required 10 to 20 min to bring about a complete kill. At the higher pH of 10.7, 60 min contact was necessary to achieve a 100% kill. These workers also noted that the pH effect was not so marked at higher temperatures. Dealing with the *Rota virus* SA-11, Rizet et al.[23] demonstrated a 99.9% inactivation at pH 6.0 with 0.2 mg/l free chlorine in 15 s, while 1.4 min was required to achieve the same result under otherwise identical conditions at pH 10. Jarroll[21] reported that at pH 6.0 and 15°C 2.5 mg/l of free chlorine required 10 min to inactivate Giardia cysts, but at pH 8.0 some still survived after 60 min. With Giardia cysts, Jarroll also reported a pronounced temperature effect in that at pH 7.0 nearly ten times the concentration of free chlorine was required to bring about a 99% inactivation in 20 min at 5°C as at 25°C.

B. Free and Combined Chlorine

In the literature, hypochlorous acid (HOCl) and/or the hypochlorite ion (OCl^-) in aqueous solutions are referred to as either "free residual chlorine" or as "free available chlorine," whereas once they are reacted with ammonia or N-organo compounds to form a series of lower oxidation potential compounds such as monochloramine (NH_2Cl), dichloramine ($NHCl_2$) or a variety of organo-N-chloro-compounds, the term employed is either combined chlorine, combined residual chlorine, or combined available chlorine. Combined chlorine, as these compounds will now be referred to in this review, is a less powerful disinfectant than free chlorine and is employed widely either intentionally or unintentionally in water treatment practice.

1. Reactions with Ammonia

Free chlorine in the form of hypochlorous acid reacts with any ammonia in water in the following way

$$NH_3 + HOCl = NH_2Cl + H_2O \tag{9}$$

$$NH_2Cl + HOCl = NHCl_2 + H_2O \tag{10}$$

$$NHCl_2 + HOCl = NCl_3 + H_2O \tag{11}$$

The formation of the monochloramine (NH_2Cl), the dichloramine ($NHCl_2$), and nitrogen trichloride (NCl_3) is dependent on pH, temperature, and, more importantly, the ratios of chlorine to ammonia present in the reaction. Reaction 9 is swift and proceeds at its fastest at pH 8.3. It is reported that for a 99% conversion the time taken at pH 8.3 is only 0.069 s, 0.2 s at pH 7.0, 147 s at pH 4, and at the high pH of 12, 33.2 s.[4,19,24,25] Reaction 10 is much slower except with pH values of less than 5.5.

In the pH range of 7 to 8 and with equimolecular concentrations of hypochlorous acid and ammonia [5:1 by weight], only the monochloramine will be formed. The dichloramine will be formed either as the ratio of HOCl to NH_3 increases toward 10:1 by weight or as the pH declines. Nitrogen trichloride may be formed as the hypochlorous acid to ammonia ratio increases upward toward 15:1 by weight. Jolley and Carpenter [19] state that no NCl_3 is formed above pH 7.5 and that at a pH of less than 3 only the nitrogen trichloride is formed. White[4] suggests that at very high HOCl to NH_3 ratios of about 25:1 NCl_3 can be found in water treatment plants at a pH as high as nine. However, with the conditions normally found in water treatment plants, it is the monochloramine which is predominantly formed.

Griffin and Chamberlain,[32] working in the late 1930s, discovered that as chlorine was added in increasing amounts to water containing ammonia not only did the ammonia disappear (and reappear to some extent at high HOCl to NH_3 ratios) but that the residual chlorine initially increased, as was expected, then declined and finally increased again. He called the point of maximum reduction of the available chlorine the "break-point". His observation led to intensive investigations of the breakpoint phenomenon by Palin[25,26] in the U.K. and in the U.S. by a group at Harvard including Fair, Morris, Chang, and Weil.[27-31]

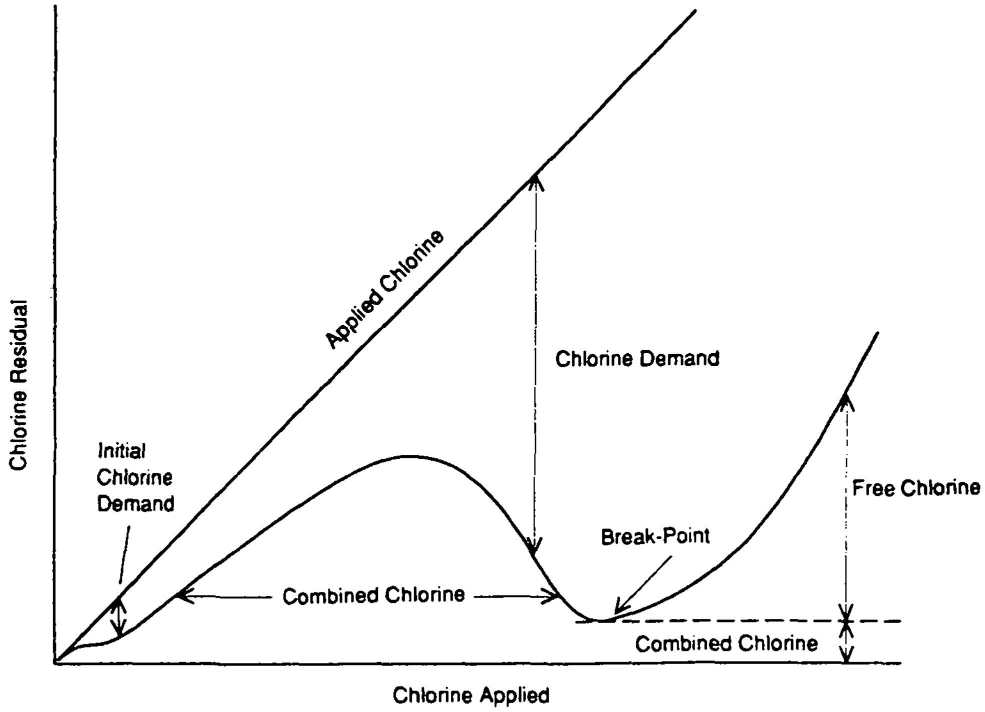

FIGURE 1. The breakpoint curve.

The breakpoint curve can be followed in Figure 1, which relates to a pH of 7.0 and a contact time of 2 h at 10°C. With the initial slope of the increasing chlorine residual, HOCl is reacting with ammonia to form only the monochloramine, until the ratio of HOCl to NH_3 reaches approximately 5:1, which corresponds with the peak of the curve. As the HOCl to ammonia ratio continues to increase, dichloramine is formed but as it is unstable, it proceeds to decompose according to

$$2NHCl_2 + H_2O \rightarrow N_2 + 3H^+ + 3Cl^- + HOCl \qquad (12)$$

which results both in a loss of ammoniacal nitrogen as N_2 and also of chlorine in the form of the negative chloride ion. The end-products from the breakdown of the chloramines in this section of the curve are not only nitrogen gas but include also some nitrous oxide and nitrate. The reactions involved may be substantially more complex than is indicated by Equation 8 and possibly involve the formation of the nitroxyl radical (NOH) as an intermediate.[4] Other reactions may occur at this time, including the formation of nitrogen trichloride and the disproportionation of monochloramine,[13] but at a neutral pH these will be only of minor significance, although White[4] refers to "nuisance" residuals of dichloramine and nitrogen trichloride which might be present under the breakpoint dip of the curve.

2. Reactions with N-Organo Compounds

Should N-organo compounds also be present in the water undergoing chlorination as well as ammonia, the reactions become somewhat more complex and the profile of the breakpoint curve is likely to be substantially modified.[27,32] The organic nitrogen compounds present will largely be of biological origin[4,13,33-35] and consist of proteins and the products of enzymic breakdown of proteins: protein → proteases → peptones → polypeptides → dipeptides → α amino acids. Further enzymic attack on the amino acids will produce ammonia and free fatty acids. The concentration of N-amino compounds in surface waters and some ground water may exceed by a substantial amount the concentration of ammonia present. However, with much of the protein present in a colloidal form, this may be largely removed prior to the addition of chlorine. The reaction with free chlorine, and with chloramine, will be electrophilic in nature and the rate of reaction will depend upon the nucleophilic nature of the organic nitrogen. As a result, the reaction rate between equimolar concentrations of HOCl and methylamine at 25°C is 60 to 70 times faster than for the production of monochloramine from ammonia[13,19,36,37] but the reaction between HOCl and the less basic amides is substantially slower.[13,38,39] Monochloramine is also an active agent for the transfer of chlorine to nitrogen to produce N-chloro-organics.[19]

The effective differences between the chlorination of organic nitrogen compounds and of ammonia are a matter of time, the complexity of the compounds produced, and the reduced loss of nitrogen.[4,26,40] Ammoniacal nitrogen is nearly totally lost as a result of breakpoint chlorination, while the result of the chlorination of the simple unsubstituted amino-N of many common amino acids is only the slow loss of nitrogen. Little nitrogen loss will be incurred as the result of the chlorination of proteins.[19] Because of this, there is a reduction in the dip of the curve, at the breakpoint, to create more of a shallow plateau,[26,27,32,40] and there will be a substantial increase in the combined chlorine existing together with the free chlorine. This combined chlorine will be made up of mono- and dichloramines and also perhaps a significant quantity of nitrogen trichloride, which may create an enhanced nuisance value in the treated water. With the likely presence of appreciably basic N-organic compounds in surface waters, the formulation of organic chloramines is likely to be significant, although White[4] suggests that they will quickly hydrolize and merely add to a system of unstable residuals with which a process of oxidation by chlorine would continue over a long period but with little loss of nitrogen.

3. Chloramines in Water Treatment and Their Biocidal Effect

The first observations of the germicidal effects of chloramines were made by Rideal while experimenting with the chlorine of sewage effluent at Guildford, England,[741-43] although chloramines were first applied to water treatment in Ottawa, Canada in 1917 by Race, who had been seeking an alternative disinfectant to sodium hypochlorite.[44-46] Later the same year, preformed chloramines were employed by the Denver Union Water Company[4,43] to control aftergrowth problems. Harold and Ward[48] of the Royal Army Medical Corps observed that the use of preformed chloramines prevented the formation of chlorophenol tastes, while Houston,[49] and then Adams[50] a little later, recognized that by adding ammonia at the same time as sodium hypochlorite the removal of "iodoform" tastes was achieved.

Interest in the ammonia/chlorine technique developed rapidly in the U.S. during the latter half of the 1920s and into the 1930s, principally to control the development of taste and odor,[4,51-54] with it also being employed to prevent algal growth in reservoirs and bacterial aftergrowth in distribution systems.[55-64] By 1938, 16% of municipal water supplies in the U.S. added ammonia at some stage in the treatment process.[43,65] However, interest declined with the understanding of breakpoint chlorination and with the shortage of ammonia during World War II.[4,43] By the early 1960s, less than 3% of municipal water suppliers were employing the technique,[66] although the concern associated with haloforms has recently revitalized its use.

Initially, Rideal[41,42] claimed that the phenol coefficient of chloramine was three times that of chlorine. This was soon proved to be incorrect.

Wattie and Butterfield[69] were the first to demonstrate that, in comparison with free chlorine, chloramines possessed only a limited bactericidal effect. They observed that at pH 8.5 and 25°C 0.14 mg/l free chlorine required only 5 min to bring about a 99% kill of *E. coli*, while it was necessary to employ 0.3 mg/l chloramine to achieve the same effect. Trask and co-workers[70] found that while 1.32 mg/l free chlorine required only 10 min to inactivate 99% of Theiler's mouse virus (FA) strain that 5.4 mg/l of chloramine required 30 min to achieve the same result. Similarly, while a 99% inactivation of polio virus 1, 2 and 3 and of cocksackie virus B1 and B5 required only 4 to 16 minutes with between 0.2 and 0.35 mg/l free chlorine at pH 7 to 9 and 25°C, a dosage of 0.6 to 1.0 mg/l chloramine would require between 2 and 8 hours. With the cysts of *E. histolytica*, it was demonstrated that a 99% inactivation was achieved with 3 mg/l of free chlorine at pH 8 while 8 mg/l chloramine was required to achieve the same effect. Butterfield concluded,[67] as a result of his extensive investigations into the relative biocidal properties of chloramines and free chloramine, that 25 times as much chloramine as free chlorine was required to bring about a similar kill of *E. coli* in a similar time or a contact time of between 60 and 144 greater at the same dose. Jarroll[21] suggested 25 to 100 greater concentrations are required than with free chlorine and Hoff[68] suggested an increase in contact time of between 25 and 100 times if similar doses are being applied.

Both the temperature effect and the effect of pH are reported as being pronounced.[67,68,72] The rates of inactivation due to chloramine increase as the pH declines. Esposito[72] demonstrated that with the reduction of pH the bactericidal effect increased, i.e., as the conditions for the presence of dichloramine improved. This could be due either to the possibly greater bactericidal efficiency of di- over the monochloramine, or it may be the result of the damaging effect of lower pHs on the microorganisms or, more likely, to the increasing presence of hypochlorous acid as the monochloramine hydrolyzes in more acid conditions.[68]

Blaser and co-workers,[194] using 1.0 mg/l monochloramine at pH 6 and a temperature of 25°C, achieved a 97.76% kill of *E. coli* (ATCC11229) in 15 min while with similar conditions, but at a pH of 8, less than a 91% kill was achieved. Butterfield[67] demonstrated the effect of temperature on the biocidal effectiveness of combined-chlorine in that he found at 2 to 6°C and pH 7.0 that a concentration of at least 1.2 mg/l was required with a contact time of 60 min to bring about the complete inactivation of *E. coli,* while at 20 to 25°C and the same pH complete inactivation was achieved with only 0.3 mg/l.

It is evident that some organic chloramines are able to exert a significant biocidal action. Researchers at the Department of Chemistry and Microbiology at Auburn University have intensively investigated the characterisitcs of one of these, 3-chloro-4, 4-dimethyl-2-oxazolidinone (compound 1), the bactericidal properties of which were first demonstrated by Kaminski et al.[74,75] This compound, although possessing appreciable biocidal properties, was judged[76] to be a poorer biocide than monochloramine under chlorine-demand-free conditions while being appreciably more stable in water with a significant organic content. At pH 4.5 and pH 7.0, it was not found to dissociate into free-chlorine, although this occurred to some slight extent at the higher pH of 9.0.[77,78] It was observed that compound 1 could, at a concentration of 2.5 mg/l (as Cl^-), achieve a complete kill of *Staphylococcus aureus* in demand-free water at pH 9.5 and 22°C in 60 min and in 240 min at 4°C. This was compared with the action of $Ca(OCl)_2$, [1.0 mg/l as total chlorine] which required 5 min at 22°C and 30 min at 4°C.[76] However, in water with a significant synthetic chlorine-demand, compound 1 (at 5 mg/l chlorine) was more effective at 4°C than the $Ca(OCl)_2$ at the same concentration of free chlorine. The long contact times required by the chloramine to inactivate effectively various bacteria was very substantially reduced by the addition of very small quantities of total chlorine (1:10 ratio of compound 1 to calcium hypochlorite; total chlorine 1.0 mg/l) with which it is suggested that there may be a synergistic effect.[79]

Remarkably, this organic-chloramine has been demonstrated by recent research[80] to be more effective in chlorine-demand-free water at 22°C than calcium hypochlorite, at pH 4.5, pH 7.0, and at pH 9.5, at inactivating the cysts of *Giardia lamblia* and those of *G. canis.* At 4°C in a synthetic chlorine-demand water, both compound 1 and chlorine were less effective than in demand-free water but the organic chloramine was still more effective than the chlorine. At 5 mg/l chlorine equivalent, compound 1 was demonstrated to inactivate cysts of *G. lamblia* and *G. canis* within 2 min at 22°C over the pH range 4.5 to 9.5 and within 10 min at 4°C. These results are appreciably superior to those for free chlorine obtained by Jarroll and co-workers,[81] who suggested 8 mg/l free chlorine was required over 10 min at 5°C to kill completely the cysts of *G. lamblia* at pH 6 to 7 and 30 min at pH 8.0. Kong and co-workers[80] suggested that these results indicated a different mechanism for the inactivation of cysts by compound 1 than by free chlorine. They suggested that because of the far weaker oxidizing potential of the organic-chloramine compared to free chlorine that it is able to penetrate more easily the thick walls of the cyst and there destroy crucial membrane enzymes rather than the less crucial enzymes on the walls of the cyst with which the chlorine may react.

C. Haloforms in Drinking Water

The possibility of health risks developing as a result of the formation of haloforms during water treatment was first suggested by Rook in the Netherlands in 1974[91] and was nearly immediately supported by Bellar and co-workers[92] in the U.S. The problem was then substantiated by a nation-wide survey in the U.S. by the Environmental Protection Agency.[93] The haloform reaction is defined[13] as "the successive replacement of hydrogen by halogen on the α-carbon to a carbonyl group, followed by eventual hydrolysis to produce a haloform and generally a carboxylate."

Apparently, there appear to be no short-term health risks associated with the presence of haloforms in drinking water but there is a strong suspicion that the carcinogenicity of these compounds may, over a long period, result in increased incidences of cancers of the gastrointestinal tract and also of the urinary tract.[99]

A study carried out by the National Cancer Institute[95] in the U.S. demonstrated that cancers were formed in rats which had been fed chloroform dissolved in corn oil at the high rate of between 90 and 180 mg/kg of body weight over a 78-week period. Then, in an epidemiological study, Cantor[96] investigated the association between the different cancers and haloforms in water, making use of the information contained in the National Organics Reconnaissance Survey and the Environmental Protection Agency's Region V Survey. From this work, a significant association was demonstrated between the presence of haloforms in water and bladder cancer. The correlation between cancer and haloforms was stronger with regard to brominated haloforms than with chloroform. Other surveys have demonstrated some relationship between cancer mortality and the use of river waters as the source of drinking water.[138,139]

Later, the National Academy of Sciences Safe Drinking Water Committee,[97] on reviewing 13 epidemiological studies, concluded that no causal relationship had been established between haloforms in drinking water and the incidence of cancers in the population. However, using much the same data, Hogan and co-workers[98] concluded, following a study in depth, that positive correlations did indeed exist between rectal-intestinal and bladder cancer mortality rates and the levels of chloroform in drinking water.[99]

In their extensive work concerned with the health aspects of organics in drinking water, which progressed well past the concern associated only with haloforms in drinking water, the researchers at the Water Research Centre (WRc)[106] concluded that by 1976 any epidemiological evidence then available was conflicting and controversial and justified further investigation. The ensuing epidemiological studies associated with this particular study did, however, reveal higher rates of cancers associated with drinking waters from upland supplies rather than from lowland supplies, and as upland supplies in the U.K. nearly invariably contain appreciable levels of humic material this must provide at least some tentative connection between levels of haloforms (following chlorination) and cancer. The conclusion of this section of WRc research of the work, that was only very indirectly concerned with haloforms in water, was that epidemiological studies had revealed no strong associations between water reuse and ill-health in the U.K., although, conversely, the results only provided weak reassurance that reuse is safe.

The WHO,[100] in establishing the guideline value of 30 μg/l for chloroform in drinking water, employed a multi-stage linear extrapolation model to the results of the NCI investigation into cancer production in rats and concluded that at this suggested level the incidence of cancer in the population would increase at a rate of less than 1 case in 100,000 in a lifetime. However, despite this assurance, it must be admitted that with the present state of knowledge the health significance of complex mixtures of organic chemicals, including haloforms, produced as byproducts as a result of the use of chlorine in water treatment is largely unknown.[18]

Haloforms occur in drinking water largely as a result of chlorination during water treatment. Stetler and co-workers[132] found less than 1 μg/l of haloforms in a source water receiving the effluents from several wastewater treatment plants but an average total haloform concentration of 338 μg/l in the treated water when prechlorination was practiced.

In their investigation into the health aspects of organics in drinking water, Fawell and co-workers[18,94] found that chlorination made a significant contribution to the mutagenicity found in drinking water, with only occasionally mutagenicity being demonstrated in raw water samples.

Haloforms are created apparently by the reaction of free chlorine with natural humic substances, particularly with humic and fulvic acids derived from peat. The presence of treated municipal and industrial wastewater in the raw water may have some influence on haloform production but it is likely to be only limited. Also, algae possibly have a strong influence on the production of haloforms, but the effect is probably more associated with the chlorination of the products of algal metabolism than with the algal cells.[104] Pilkington[104] reported that algal extracellular compounds are less reactive than the natural color compounds for the formation of haloforms. Chlorophyll itself appears to be only a minor source of these compounds.[104] Greene and Fadzeau[107] reported that with upland water in Scotland showing color levels up to 250° Hazen the total THM level of the chlorinated water was often considerably in excess of the maximum MAC level of 200 μg/l. A correlation has been observed between haloform production and the total organic matter present[13,91] in water, and Fawell et al.[106] report a correlation between the mutagenicity observed with TA 98 strains of *Salmonella typhimurium* and the total organic carbon (TOC).

Chloramines produce considerably fewer haloforms than free chlorine.[104,105] Fleischacker and Randtke[103] reported that combined chlorine always produces less "non-purgeable organic chlorine" than free chlorine but that the amounts produced may still be significant, under some conditions, in relation to restricted standards such as the Swiss maximum requirement for TOC of 25 μg/l. With relatively high concentrations of monochloramine present, an appreciable rate of autodecomposition has been noted and the free chlorine again present must add to the possibility of haloform formation.[36,102,103] Bromides in water in the presence of free chlorine make a significant contribution, via the formation of hypobromous acid, to the formation of total haloforms,[18] and the bromoforms created are possibly more significant from a health hazard point of view than their chlorine counterparts.

Acetone, which has a well-established chloroform reaction,[13] was initially considered as a source of haloforms in water but it has since been concluded that the levels of acetone are too low to be of significance.[108] Hydroquinone, catechol, resorcinol, and pyrogallol were also considered.[91] However, the substrate structure considered most likely to result in the production of haloforms is the 1,3-dihydroxybenzene (resorcinol) configuration in the humic acid and fulvic acid molecules which contains two hydroxyl or ketonic groups meta or beta to each other.[33,91,108,109] Rook[91] calculated that the chloroform yield from these acids would involve only between 0.2 and 0.8% of the total carbon present.

The reaction rates between chlorine and humic material to create organohalides are influenced by pH, temperature, time, and ratio of chlorine to organics.[94,103] The chlorination of organic species is generally held to increase as the pH decreases[13] and Fleischaker and Randtke[103] found that the production of non-purgeable organic chlorine increased dramatically in the presence of free chlorine as the pH declined. However, haloform reactions such as those which take place between chlorine and humic and fulvic acids are base catalyzed and the rate increases with increasing pH.[13,110] Fleischaker and Randtke[103] observed a 100% rate of increase in $CHCl_3$ formation between pH 3 and pH 11. They also recorded an increase in chloroform formation with free chlorine and fulvic acid at pH 7.0 as the temperature was increased from 3 to 30°C.

It is not only haloforms which can be formed with the chlorination of water, and, according to the type of organics present and the concentration of chlorine employed, either substitution, addition, or oxidation reactions may occur.[13,18,111,112] Similar reactions will take place in the presence of bromides to produce the bromine analogues of the chlorine compounds. Also, it is not only the humic substances in water that react with chlorine but many other organic compounds including, particularly, amino acids and bound amino acids in proteins and peptides, which are common constituents of surface water. The products of the chlorination of amino acids are numerous, including chloroform, and also include substances shown to be mutagenic to the TA100 strain of *S. typhimurium*.[18,106]

The principal problem with the isolation and identification of both precursors and products of chlorination reactions in water is the limitation of the existing techniques of recovery and analysis. Even with the advances made over the last 2 decades, principally with the use of gas chromatography coupled to mass spectroscopy, perhaps only about 20% of the organics in water can be identified. Chloroform and dichloro- and trichloroacetic acids apparently account for over 50% of the adsorbable organic halogen[18,113-115] produced during the chlorination of humic substances, although de Leer and co-workers[116] identified more than 100 products of these reactions. Of this large number of products identified, the presence of many had been demonstrated by previous workers,[113-120] but, in addition, de Leer and co-workers[116] found various chlorinated carboxylic acids and ω-cyano-alkanoic acids together with a range of trichloromethyl chloroform precursors including:

$\mathrm{Cl_3C \cdot CH(OH) \cdot COOH}$
$\mathrm{Cl_3C \cdot C \cdot CH_3(OH) \cdot COOH}$
$\mathrm{Cl_3C \cdot CH(OH) \cdot CH_2 \cdot COOH}$
$\mathrm{Cl_3C \cdot CH(OH) \cdot C \cdot Cl_2 \cdot CH_2 \cdot COOH}$
$\mathrm{Cl_3C \cdot CH(OH) \cdot C \cdot Cl_2 \cdot CH \cdot Cl \cdot COOH}$
$\mathrm{Cl_3C \cdot CO \cdot CH = CH \cdot COOH}$
$\mathrm{Cl_3C \cdot CO \cdot CH = C(CH_3) \cdot COOH}$
$\mathrm{Cl_3C \cdot CO \cdot C(COOH) = C \cdot Cl \cdot COOH}$
$\mathrm{Cl_3C \cdot CO \cdot C(COOH) = C(COOH)_2}$
$\mathrm{Cl_3C \cdot CO \cdot CCl = CCl \cdot CH_2 \cdot COOH}$

Fawell and co-workers[106] published a list of compounds which are produced during water treatment chlorination (Table 3). Most of these have humic substances as their precursors but several are derived from amino acids and proteinaceous material.

1. Mutagenicity and Health Significance

The health significance of compounds produced as a result of the chlorination of water supplies is still very largely unknown. To a great extent, this is the result of the very low concentrations at which these compounds exist in water. Because of this, there is no practicable way in which they can be tested on mammals with any realistic expectation of carcinogenic properties being revealed. Hence, it has been found necessary to develop short-term, *in vitro* bacterial screening tests to establish whether or not the compounds concerned possess mutagenic properties. These tests allow the chemicals under consideration to react with the DNA of target bacteria and, possibly, produce mutations. A great deal of work has been carried out which has demonstrated [121] that there exists a good correlation between the

Table 3
Compounds Produced during Water Treatment Chlorination

Benzaldehyde*
Benzyl cyanide*
Bromochloroacetonitrile
Bromochloroiodomethane
Bromochloronitromethane
Bromodichloroacetonitrile
Bromodichloromethane
Chlorohydroxybenzyl cyanide*
Dibromoiodomethane
Dichloroiodomethane
Nitrotrichloromethane
Bromodichloronitromethane
Bromoform
Chloral
Chlorodibromoacetonitrile
Chlorodibromomethane
Chlorodiiodomethane
Chloroform*
Dibromoacetonitrile
Dichloroacetonitrile*
Dichloronitromethane

- * Products derived from amino acids or proteinaceous material.

From Health Aspects of Organics in Drinking Water, WRC Report 231. 1986.

ability of chemicals to produce mutations in specific bacteria and their capacity to create cancers in animals undergoing toxicity tests. Strangely, however, despite its proven ability to produce cancers in animals, chloroform itself is not mutagenic.

The most widely employed bacterial screening test is the Ames Salmonella/Microsome Mutagenicity Assay[18,122,123] which employs strains of *S. typhimurium* which have been genetically modified to increase their sensitivity to mutagens. This test can be carried out in the presence of a mammalian liver extract (rat liver S9 fraction) so as to simulate an animal's metabolism. In its detailed work concerned with the health hazards of organics in drinking water, the WRc employed initially a development of the Ames test called the fluctuation test, developed by Green and co-workers,[124,125] and more recently the microtiter fluctuation assay.[126,127] These are more sensitive than the standard Ames test and more suitable for the study of water.[128,129] More recently still, mammalian cell test systems have been employed to test the mutagenicity potential of water samples.[18,130] Preliminary concentration and fractionation of organics in water have been achieved by employing methanol extractions of freeze-dried samples followed by adsorption onto a macroreticular resin (XAD-2) and solution with diethyl ether.[18,106] Using these concentration/fractionation techniques followed by bacteria mutagenicity screening tests, a substantial increase in TA 100 strain activity was demonstrated following chlorination.[106] In addition, during the investigation at the WRc, naturally occurring compounds were chlorinated in aqueous solution, subjected to concentration using the XAD/diethylether technique and tested for mutagenicity. Results indicated that humic acids and amino acids make significant contributions to the mutagenicity developed in water as the result of chlorination.[106]

2. Haloform Prevention and Removal

The investigation carried out by the WRc revealed a nonlinear correlation between chlorine dose and TA 98 mutagenicity, while linear regression analysis revealed a far stronger correlation between chlorine dose and TA 100 activity. With samples taken directly from a water treatment works, no mutagenicity was demonstrated for the samples prior to chlorination, but substantial mutagenicity was shown in samples taken after chlorination. This work supported the findings of other researchers, such as Kool and co-workers,[131] and Loper and co-workers,[170] that there is a pronounced relationship between chlorination and mutagenicity.

Since it is the chlorination of water during treatment that gives rise to the overwhelming proportion of the haloforms in the finished water, their control can be achieved only by modification of the techniques of water treatment and, in particular, of the processes of disinfection. The removal of formed haloforms is possible, but it is difficult, expensive, and somewhat chancy. Air-stripping can be moderately effective, but a large air/water ratio will be required to remove even the more volatile chloroform while the less-volatile compounds will be increasingly difficult to strip. Granulated activated carbon is able to remove haloforms, but their affinity for the activated carbon is appreciably less than that of other competing organics. As a result, more frequent — and costly — rejuvenation of the carbon will be necessary. An additional disadvantage of GAC is the possibility of chromatographic effects in the column resulting in the release, into the treated water, of sudden flushes of concentrations of haloforms.[104] However, as a result of the relative volatility of the formed haloforms, boiling of the finished water offers a distinct possibility of removing, or radically reducing, the concentration of these compounds on a small scale. It is important to appreciate that much — prehaps most — water that is consumed, is done so following heating, usually to the boiling point. Investigations at the WRc revealed that prolonged boiling in an open vessel removed the majority of the organics detectable by GC-MS and that when experiments were conducted with specific compounds such as chloroform, dibromochloromethane, bromoform, and trichloroethylene approximately 50% of these was removed by boiling.[106]

Storage of river water prior to chlorination also appears to have some beneficial effects with regard to removing precursors of mutagenic activity, although the period of storage may have to be appreciable. The WRc demonstrated that water storage over a limited period at the ambient temperature did nothing to reduce mutagenic activity following chlorination but that storage for a 60-day period substantially reduced the post-chlorine level of mutagenicity.[106]

It is possible to modify conventional water treatment practices in order to reduce the production of haloforms. It is also useful to be aware that some conventionally accepted techniques can play a major role in haloform prevention. Alum treatment is reported[133] to remove 70 to 80% of humic material from Finnish surface waters. Also, alternative disinfection techniques employing chlorine dioxide or ozone in place of prechlorination have been demonstrated as being able to reduce substantially the formation of organohalides, but Hiisvirta[133] was concerned that the use of ozone was likely to increase appreciably the microbial growth either in the plant or in the distribution system as a result of the partial degradation of humic substances into more easily assimilable compounds.

If chlorine is to be employed in situations in which the development of haloforms is both a strong possibility and a pronounced concern, then it is essential, as far as is possible, to avoid high dosages, high pHs, high temperatures, and prolonged contact times. This, in particular, means dispensing with superchlorination applied at an early stage in the treatment. This is not only because at this stage, prior to coagulation/flocculation/sedimentation, there are likely to be more precursors in the water but because of the relatively high chlorine concentration in contact with the water over a significant period. Stetler and co-workers[132] recorded that a 27% reduction in total haloforms was achieved by moving the point of chlorination downstream from prior to the addition of the coagulating/flocculating chemicals to following the sedimentation stage and a 48% reduction was achieved if the addition of chlorine was delayed further until after the filtration stage. In Finland,[133] a combination of high levels of humic substances together with the use of heavy prechlorination dosing, employed to reduce sliming and to improve coagulation, resulted previously in haloform concentrations of regularly between 100 and 400 μg/l with a highest value of 1400 μg/l. These high levels were reduced by 75% simply by eliminating pre-chlorination.

The employment of combined chlorine in place of free chlorine will also substantially reduce the formation of haloforms and, on occasion, nearly eliminate them, but the employment of combined chlorine as the only form of disinfection will bring into question the ability of the process to inactivate all potentially harmful microorganisms. Dechlorination, using a variety of agents, has been found to be effective[106] in substantially reducing both

TA 98 and TA 100 mutagenicity in treated water. This presumably means that the dechlorinating agents are reacting with the compounds creating mutagenicity. Low level re-chlorination was found to restore the activity to the TA 100 strain but not to the TA 98 strain of *S. typhimurium,* while chloramination of totally dechlorinated water resulted in a lower activity than with re-chlorination.[106]

The realization in Finland that the high levels of humic material in the surface waters, coupled with pre-chlorination at a relatively high dosage (10 to 20 mg/l chlorine), was resulting in unacceptably high levels of haloforms led to attempts to reduce these high concentrations by modifying the treatment process. As already noted, the abandonment, or drastic reduction, of pre-chlorination succeeded in reducing the haloform production by about 75% but this resulted in high total plate counts in the finished water and led to concern about the possibility of the growth of even pathogenic microorganisms in the filters. This risk had already been demonstrated by Geldrich and co-workers[134] and Allen,[135] and in Finland in 1978[133,136] there had been an outbreak of allergic alveolitis of which the suspected cause was *Actinomycetes growing in both the filter and in the distribution system* — additional chlorination in the network being only practiced in Helsinki.

On the whole, the procedure adopted in Finland to reduce the haloform level has been to employ smaller and smaller doses of chlorine at the distribution stage but efforts have been made also to increase the removal of organics prior to chlorination. Careful adjustment of the pH combined with careful control of the addition of chemicals at the coagulation/flocculation stage have resulted in some improvement, and pilot plant tests using two-stage coagulation — initially using a ferric salt and then alum — have demonstrated a reduction of the $KMnO_4$ value from 10 to 15 mg/l following the conventional alum coagulation to a level of 5 to 10 mg/l after the two-stage treatment. Some doubts have been cast on the practice of chlorinating at a reduced pH in order to lower the production of haloforms because the formation of nonpurgeable organic chlorine problems[103] and mutagenicity[137] have been demonstrated as being higher at a reduced pH.

The problems created by haloforms and other organic-chlorine compounds are real and the concern to reduce their levels in drinking water is fully justified. Although, at this stage relatively little is known about the organic compounds present in low concentrations in treated water and much remains to be discovered concerning their effects on the population over extended periods, it has now been sufficiently demonstrated that a hazard exists. Measures to reduce this hazard are therefore fully warranted. However, in attempting to reduce this lesser hazard, there is some possibility of not paying sufficient attention to the major hazard, i.e., disease-producing microorganisms in drinking water. The removal or destruction of pathogenic organisms is the principal aim of water treatment. This fact cannot be too greatly emphasized and great care must always to be taken that any modifications to the treatment process that may be considered to reduce the level of haloforms must never, in any circumstances, compromise the major aim of producing water free from disease-producing organisms. This is a fact which must always be borne in mind, particularly in the developing world, where concern about production of haloforms must be very, very secondary to that of the complete disinfection of the water.

D. Techniques of Chlorination

There exist basically four different approaches to the application of chlorine to water at a treatment plant. These are (1) simple (or marginal) chlorination, (2) ammonia-chlorine (or chloramine) treatment, (3) superchlorination/prechlorination followed by dechlorination, (4) break-point (or free residual) chlorination. Palin[171] classed the first two of these techniques as forms of combined residual chlorination and the latter two as free residual chlorination, although it could be argued that with high-quality water the available chlorine with technique No. 1 could be present as free chlorine.

Simple, or marginal, chlorination can be defined as the addition of chlorine to water, at a low rate, as a regular controlled dose. This approach to chlorination is usually employed with waters of a persistent high quality — often groundwater — and the chlorine is added purely as a precautionary measure, particularly to safeguard it through the distribution system. It is frequently the only form of treatment applied and usually at low concentrations of only 0.2 to 0.5 mg/l. There are dangers and disadvantages associated with the approach, but these will only become meaningful if the water quality is not continually high. These dangers are (1) low security as the dose is limited; (2) the possible disappearance of the chlorine from the water before it reaches the consumer; (3) taste and odors may be imparted to the water if even trace quantities of some compounds — particularly phenols — are present; (4) odors and tastes already present in the water will not be destroyed.

Obviously this approach is only acceptable if the raw water is not subject to fluctuations of bacterial content, does not contain phenolic substances, and never contains products of algal metabolism or decay.

E. Ammonia/Chlorine Process

As discussed earlier, the ammonia/chlorine process (chloramine) has a long and well-documented history in water treatment, with the process reaching the peak of its popularity during the 1930s in the U.S. Traditionally, this process has been employed either to avoid the creation of taste and odors in the treated water or in order to provide long-term residual disinfection in the distribution system. More recently, it has been favored as a means of avoiding the creation of haloforms in water without reducing significantly the disinfection of the water.

The presence of chloramine in water, as opposed to that of free chlorine, is often favored because the combined chlorine does not react with phenolic compounds to produce chlorophenolic tastes and because, being less reactive than free chlorine as an oxidizing agent (E° hypochlorite — 1.49 v, E° monochloramine — 0.75 v) and hence less likely to be rapidly reduced in treated water, it will continue to exist in water for far longer periods. In addition, chloramine is now also valued as it will not normally (or only very slowly) react with humic materials to produce haloforms. If combined chlorine is to be employed with the intention of avoiding the creation of tastes and odors in water, it is essential that the ammonia be added before the chlorine and always be present in excess. With this in mind, it is necessary to be aware that a ratio (by weight) of ammonia to chlorine of 1:4 represents an excess of ammonia, although in these particular situations it would be more normal to operate at a ratio of 1:3. On the other hand, if combined chlorine is to be employed merely to provide a long-lasting residual disinfection capability for the water following treatment, the ammonia is not added until the end of the process, thus allowing the chlorine to have been present as free chlorine for an appreciable period. If, however, the object of employing the ammonia/chlorine technique is the prevention of excessive haloform formation, then it might be considered suitable either to allow only combined chlorine to be in contact with the water at any time or to permit a limited period of free chlorination followed quickly by the additional ammonia.[132]

As discussed previously, the microbiocidal action of combined ammonia is recognized as being far weaker than that of the undissociated hypochlorous acid. It has been suggested[143] that in many treatment plants this does not represent a major disadvantage as much free chlorination is carried out at a relatively high pH in the presence of the weak hypochlorite ion as opposed to the strong hypochlorous acid. Tetlow and Hayes[140] suggested that the use of combined chlorine does little to prevent the development of heterotrophic bacteria in the distribution system and record, during the summer months in England, plate counts (22°C/3 days) frequently in excess of 20,000/ml. They point out that these counts include members of the *Pseudomonad* and *Aeromonad* groups of which the *Pseudomonads* are undesirable in water delivered to the food and drink industry and to hospitals, while *Aeromonas hydrophilla* has been linked with outbreaks of gastroenteritis. These workers also highlighted the possibility of nitrate formation in the distribution systems as a result of chloramination.

Mitcham and co-workers[144] investigated operational conditions in a treatment process employing initially lime-soda softening following by pre-chlorination and flocculation. They pointed out that the presence of free chlorine through the softening stage produced conditions very favorable for the formation of haloforms. In their investigation, they compared two treatment streams, one in which free chlorine was employed (1.0 mg/l) and the other in which the free chlorine was replaced by 1.5 mg/l combined chlorine (0.45 mg/l ammonia added). As well as a reduction of haloforms being produced from about 100 µg/l to an average of 20 µg/l, they reported that the combined chlorine was practically as effective as free chlorine for the removal of *E. coli* and *Fecal streptococci*. With the viral units in the raw water varying from an average of 0.4 to 17.4/l, only one sample in ten was found to contain viable viruses following treatment with combined chlorine, compared with none for the free chlorine. In the removal of the troublesome crustaceans *Bosmina* and *Cyclops* prior to sand filtration, Mitcham and co-workers found that free chlorine was more effective at destroying the *Bosmina* while combined chlorine was more effective at controlling the *Cyclops* together with the nauplii of the *Cyclops*.

In a study in which various microorganisms were added to waters containing a substantial chlorine demand, in order to simulate the effect of cross connections in a distribution system, it was found[145] that 0.7 mg/l initial free chlorine inactivated 99.9% of the coliform bacteria in 30 min, while 0.9 mg/l initial combined chlorine only inactivated 90% after 2 h. Similar results were obtained for *Shigella sonnei* and *Salmonella typhi*, while between 1.0 and 1.5 log reductions of *polio virus 1* and *bacteriophage f2* were achieved by both the free and the combined chlorine systems after a 2-h exposure.[43,145] However, Hejkal and co-workers[146] found that, again with waters containing an appreciable chlorine demand, more than four times the concentration of combined chlorine compared with that of free chlorine was required to inactivate *polio virus* at pH 8.0.

In comparing published results recording the efficacy of chloramines, Wolfe et al.[43] concluded that there exist serious discrepancies between results from laboratory-scale work and those obtained in the field. These discrepancies they considered to be the result of three factors:

1. The relative resistance of microorganisms existing in natural waters and those specifically cultured in the laboratory
2. The different methods of applying the disinfectant in the two dissimilar situations
3. The criteria for evaluating the effectiveness of the disinfectant

In support of the first factor, Wolfe and co-workers cited the work of Carson and co-workers,[147] Favero and Drake,[148] Schaffer and co-workers,[149] and Ward and co-workers,[150] which generally reported naturally occurring microorganisms as having been more resistant to disinfection than laboratory-cultured organisms. Wolfe and co-workers[43] also suggested that in most laboratory experiments in which combined chlorine was employed that the chloramines were preformed before addition and thus free chlorine was never in contact with the microorganisms while, in the field situation, there would be a short, destructive contact period between the free chlorine and the microorganisms before the chloramine reaction had gone to completion. In support of this claim, they quoted the work of Hoff and Geldreich,[151] Hoathen,[152] Houghton,[153] Selleck and co-workers,[154] Holwerda,[155] Kruse and co-workers,[156] Mackenzie,[157] and Schmelkes.[158]

At the Sjaelso[159] water treatment works in Denmark, chlorination with preformed chloramine at the rate of 0.1 to 0.2 mg/l has been incorporated into the final stage of the treatment

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process in order to prevent the formation of haloforms by eliminating any chance of contact between free chlorine and the water. However, it is considered necessary at Sjaelso to ensure initially the inactivation of all viruses and other potentially harmful and resistant microorganisms by the addition of about 2 mg/l ozone prior to treatment with biologically active activated carbon. All the chloramine employed in the final process is preformed in a separate reaction tank in which the ammonia is always in excess, although so controlled that there is only a concentration of 0.01 to 0.02 mg/l ammoniacal nitrogen in the treated water.

The reasons for the preformation of the chloramine in this situation are not only to avoid the possibility of limited haloform production in the main water stream, but also so as to be able to control the conditions of the reaction to prevent the possibility of formation of dichloramine and nitrogen trichloride. The ratio of chlorine to ammonia used is approximately 3.5:1, and at a concentration of 1000 mg/l the ammonium sulfate and hypochlorite (stabilised with NaOH) mixture has a pH of 9.0 at which the formation of other than monochloramine is avoided.

With this system, it is found that the monochloramine in the distributed water reduces from 0.2 to 0.05 mg/l in about 16 h, although the rate of reduction depends on such factors as temperature, pipe materials, the deposits in the pipework, and the ratio of surface to ground water in the final product, as well as retention time.

Some concern about the possible health affects has been reported, although there is not a great deal of information available on this subject. It is known that chloramines are lethal to aquatic invertebrates and to fish in very low concentrations.[43] The mechanism of this toxicity is methemoglobinemia. Sub-lethal effects include limitation in growth and in reproductive activity.[43] Also, people undergoing long-term hemodialysis have been reported as developing anemia when exposed to water containing chloramines.[160-162] It is possible that the chloramines diffuse through the reverse osmosis unit.[160]

There is some evidence that monochloramine is weakly mutagenic[163] and also that it is capable of producing chromosomal aberrations in plants. A U.S. EPA project reported the formation of skin papillomas on mice in some of their investigations with chloramine[164,165] and a study by the National Toxicology Program demonstrated increased mitotic figures, cellular hypertrophy, and bizarre chromatin patterns in the liver cells of mice which had been subjected to between 200 and 400 mg/l of chloramine over a 90-day period.[43,166] However, more recent investigations involving mice,[167] monkeys,[168] and human males[169] have demonstrated no evidence of methemoglobinemia or of any changes in hematological characteristics. It is possible that the monochloramine is not absorbed into the blood stream or even that the liver and kidneys are able to carry out routine detoxification and produce readily excretable products.[43,167]

F. Pre-Chlorination/Superchlorination

The term superchlorination is applied to the addition of a relatively heavy concentration of chlorine to the water under treatment, normally to produce a presence of free chlorine. Superchlorination is invariably followed by some form of de-chlorination. Increasingly, superchlorination has come to be employed with lower quality surface waters and the amount of chlorine added may vary, according to the quality of the water, from as relatively little as 3 to 4 mg/l to as much as 20 mg/l. Pre-chlorination is the addition of chlorine — usually at a relatively high concentration — as a preliminary step in the treatment of water. The terms superchlorination and pre-chlorination are frequently accepted as being nearly synonymous. However, pre-chlorination does not necessarily infer the production of free chlorine, which is implied by superchlorination. It is possible, on occasion, to have a system of pre-chlorination utilizing as much as 17 mg/l chlorine added without free chlorine being produced.

De-chlorination is employed to reduce the chlorine content at the end of the treatment process to a level sufficient to maintain a residual disinfecting action throughout the distribution system, and also to a level acceptable to the consumer. Sulfur dioxide is commonly employed for the de-chlorination process at the rate of about 0.9 mg/l SO_2 for 1.0 mg/l of chlorine removed

$$SO_2 + H_2O \rightarrow H_2SO_3 \tag{13}$$

$$H_2SO_3 + HOCl \rightarrow H_2SO_4 + HCl \tag{14}$$

Sulfur dioxide will also remove combined-chlorine residuals

$$H_2SO_3 + NH_2Cl + H_2O \rightarrow NH_4HSO_4 + HCl \tag{15}$$

Other de-chlorinating substances such as sodium sulfite and sodium metabisulfite can also be employed[4] and activated-carbon treatment will always remove chlorine.

Until recent years, the process of superchlorination had been becoming very popular with the water industry but with the increasing awareness of the problems of haloform production the general tendency has been either to eliminate the practice entirely or to control it more thoroughly both to reduce the rate of chlorine application and the period of contact. Tetlow and Hayes[140] suggested that the reasons for employing prechlorination are

1. The provision of a supplementary disinfection stage, which is considered to be particularly relevant to direct river abstractions
2. The control of freshwater mussels in raw water pipelines and storage tanks
3. The avoidance of slimes and filamentous algal growths within treatment units
4. To enhance the removal of algae and zooplankton from eutrophic waters at the clarification and filtration stages of treatment
5. The oxidation of ferrous sulfate coagulant

Hiisvirta[133] reported that high dosages of 10 to 20 mg/l of chlorine at the pre-chlorination stage had been employed traditionally in Finland principally to prevent sliming and in order to improve coagulation as well as, to some extent, the prevention of microbial growths in the filters. This practice, as noted above, has since been radically modified, with pre-chlorination having either been dispensed with entirely or employed only periodically. Stetler and co-workers[132] reported the original practice, at a small water-treatment plant in Michigan, of adding 7 to 10 mg/l chlorine prior to chemical pretreatment. Again, this practice has been modified, to reduce the produciton of haloforms. Hubbs and Olthius[141] reported on a successful modification, in the treatment of water from the Ohio River, from pre-chlorination at the inlet to the reservoir to a mere 10 min at 0.8 to 1.4 mg/l free chlorine before the addition of ammonia between the coagulation and the softening basins. Ficek and Bull[142] noted that delaying chlorination reduced algae/slime control, taste and odor control, and the oxidation of iron and manganese as well as making it difficult to maintain sludges in an aerobic condition. They advocated the use of potassium permanganate to overcome these problems.

In order to dispense with pre-chlorination, or to minimize its unwanted effects, Tetlow and Hayes[140] advised that the following actions would be necessary:

1. The control of eutrophication in storage reservoirs by the addition of ferric sulfate to pumped river in-flows
2. The replacement of the cheaper ferrous sulfate as a coagulating/flocculating agent with ferric sulfate in order to minimize the use of chlorine

3. The use of chlorine dioxide as a substitute preoxidant in place of chlorine
4. Severely reducing the chlorine contact time
5. Reducing pre-chlorination doses so that free chlorine is never present
6. Employing ozone coupled with biological treatment

G. Free-Residual (or Breakpoint) Chlorination

This process, obviously, is a controlled form of superchlorination in which sufficient chlorine is added to a wtaer to overcome all the chlorine demand and to provide a small residual of free chlorine to act as an effective disinfectant. As White[4] points out, it is widely referred to as breakpoint chlorination, although it is truly a mechanism that produces free residual chlorination. It is a process that can be most readily carried out with a raw water, the quality of which does not change noticeably over an appreciable period of time.

If the water under treatment contains merely ammonia and no organic nitrogen, then there should be little difficulty encountered with this process at a neutral, or higher, pH. The breakpoint then can be illustrated adequately by the equation

$$2NH_3 + 3Cl_2 = N_2 + 6H^+ + 6Cl^- \tag{16}$$

in which all the ammonia is destroyed and the nitrogen is lost as gas. The chlorine demand with this will be 7.6 g of chlorine for every gram of ammoniacal nitrogen, although in practice, because of the presence of other chlorine-demand materials, the Cl_2:N ratio will probably be appreciably higher.

However, should there be a substantial concentration of organic nitrogen compounds in the water, the situation may be appreciably different. Because of the speed of the reactions, ammonia can be readily destroyed by chlorine and the majority of the nitrogen released, but with organic nitrogen the reaction will be much slower and may not be completed in the normal time of contact available in the water treatment process. According to White,[4] the reactions may go on for days and even weeks.

As discussed previously, the presence of organic nitrogen results in a reduction of the depth of the breakpoint dip following the initial combined-chlorine hump in the breakpoint curve. This is due to continuing reaction between monochloramine and dichloramine and the limited loss overall of nitrogen.[4] The raising of the breakpoint dip to become nearly a plateau indicates the presence of a larger proportion of mono- and dichloramines, as well as a variety of N-chloro compounds which will usually show up on analysis as dichloramines, although they usually lack any appreciable disinfection qualities. As the Cl_2:N ratio increases to about 20:1, nitrogen trichloride will probably be formed. In such a situation, complete de-chlorination may be necessary, followed by re-chlorination with ammonia-chlorine in order to prevent obnoxious tastes and odors.

H. Mechanisms of Inactivation

The mechanism of destruction of vegetative bacterial cells appears to be primarily the disruption of the cytoplasmic membrane and the inhibition of the enzymic activity associated with it. Respiration is impaired, the selective permeability of the membrane destroyed, and irreparable damage is done to the metabolic functions.[43,179-181] Chang[172] stated that respiration took place in the vicinity of the cell wall both with simple sugars and allied compounds on the surface and with the essential enzymes, co-enzymes, and H^+ carriers on the inside adjacent to the membrane. This makes the respiratory function extremely vulnerable to powerful oxidizing agents with which destruction of the metabolic systems is so fast and so extensive that affected bacteria cannot be expected to recover.[173]

Green and Stumpf[174] reported that the oxidation of glucose in a bacterial cell was inhibited by the presence of chlorine and they suggested that this was due to the breakdown in the first stage of the oxidation process involving the enzyme triosphosphate dehydrogenase. They supported this hypothesis by demonstrating that the enzyme, when extracted from rabbit skeletal muscles, was in fact inhibited by chlorine. Skidal'skaya[75] also reported the decreased dehydrogenase activity in bacterial enzyme systems when subjected to chlorine. Knox and co-workers[176] demonstrated the reduction of activity in the presence of chlorine of certain sulfhydryl enzymes including triosephosphate dehydrogenase, d-amino acid oxidase, and transaminase. Doetsch and Cook[177] reported that the cytoplasmic membrane was the site of respiration enzymes such as succinic dehydrogenase. Venkobachar and co-workers[178] demonstrated the marked decrease in succinic dehydrogenase activity in a crude extract of *E. coli* in the presence of chlorine. This they suggested was due to the oxidation of the sulfhydryl groups to disulfide. However, these workers also found that the operation of the important ATP-ase, also localized in the cytoplasmic membrane, was not affected by bactericidal concentrations of chlorine, nor was the activity of catalase affected.

Bringman,[182] using an electron microscope found no change in the bacterial cell wall following chlorination, but Friberg,[183] using ^{32}P-labeled bacteria, observed leakage through the cell wall of cellular components after chlorination. Venkobachar and co-workers concluded from their investigation[179] that the first step of the interaction between chlorine and *E. coli* is with the cytoplasmic membrane and that the zeta potential, permeability, and oxidative phosphorylation, all of which are important properties of the membrane, are affected by chlorination. Both oxygen uptake and phosphate uptake were affected by even low-level chlorination, but with the phosphate uptake being more considerably affected at low chlorine levels than the oxygen uptake. The zeta potential was found to reduce as the chlorine dosage increased, coming down from -40 to about -23 mV with 1000 μg/l of chlorine. In addition, leakage of cytoplasmic material was recorded, with RNA being observed even following small dosages of chlorine (100 μg/l), although the presence of DNA was only detected after high doses were applied.

Haas and Engelbrecht[181] proposed an answer to the question as to what are the lethal lesions caused by chlorine by suggesting both disruption to the cell membrane and physical damage to the DNA of the cell as being the causative effects. They rejected the theory of respiratory damage as the sole lethal lesion and cited the work of Stuart and co-workers[184] and McFeters and Camper[185] in support. The likelihood of cell-membrane disruption was supported by the release of UV-absorbing material such as proteins and nucleic acids from the cells of *E. coli, Candida parapsilosis,* and *Mycobacterium fantuitum,* as observed by Haas and Engelbrecht,[181] following chlorination. The research of several workers[188-193] has demonstrated physical damage to the DNA of cells by chlorination, and both Rosenkranz[186] and Shih and Lederberg[187] observed that bacterial mutations, deficient in DNA repair enzymes, were increasingly sensitive to both chlorine and chloramines. Haas and Engelbrecht[181] employed the Ames tests to correlate mutagenicity with chlorine-induced inactivation and suggested that the lethal action, possibly involving strand scission or cross-linkages, created damage to the DNA and inhibited replication.

Ingols[190] surmised that bacterial inactivation due to chloramines (and to chlorine) was largely the result of chemical modification of hemin (ferroprotoporphyrin) which is found in many important proteins such as cytochrome, catalase, and peroxidase. Wolfe and co-workers[43] cite the work of Shih and Lederberg[187] to support the case for the modification of DNA as a source of inactivation, but suggest that cellular death as a result of monochloramine may be due to a variety of nonspecific actions such as oxidation of reduced enzymes, chlorination of amino acids, and even hydrolysis of fatty acids. As a consequence, they suggest that no single mechanism or site may be the ultimate cause of bacterial inactivation but rather a series of reversible or irreversible steps.

I. Inactivation of Viruses

Chang,[172] in his study of modern concepts of disinfection in 1971, suggested that inactivation of a virus was a result of the denaturing of the protein capsid and that the nucleic acid core could remain unaffected. Anson and Stanley[242] had previously demonstrated that the necessary denaturing of the capsid of the tobacco mosaic virus with iodine had to proceed considerably beyond the oxidation of the R–SH group to the S–S stage if the virus were to be inactivated. Since this necessary denaturing is far more difficult than the destruction of R–SH and of other H-carriers, Chang's suggestion that the need for virucidal residuals to be at least 20 to 70 times higher than is required for bacterial inactivation is explained.

However, some time later Olivieri and co-workers[195] reported that it was the reaction between free chlorine and the viral genome that caused the initial lethal damage. They found that the activity of viral RNA extracted from the f2 coliphage paralleled the activity of the intact virus when chlorinated at various pHs. They also reported that at pH 10.0 the inactivation of f2-RNA was more rapid than that of the intact virus. They attributed the slowness of the reaction with the intact virus at this pH to the difficulty of the OCl^- ions to penetrate the protein barrier protecting the RNA.

Dennis and co-workers referred to the work of Hayatsu and co-workers,[196] Hoyano and co-workers,[197] Patton,[198] Jolley,[199] Prat and co-workers,[200] Dennis[201] himself, as well as that of Olivieri et al.,[195] to support his contention that it is the RNA of the f2 coliphage which initially reacts, with lethal results, with free chlorine. As further support, they demonstrated that all the nucleotides comprising RNA, with the exception of uridine monophosphate, undergo reactions with hypochlorous acid with the loss of their characteristic absorption bands at 250 to 280 nm. As a conclusion to this work, they claimed a positive correlation between the rate of consumption of HOCl by nucleotides and the rate of inactivation of viruses by HOCl.

In apparent contradiction to the work of Dennis and co-workers, Tenno and co-workers,[202] after investigating the effect of chlorine on Type 1 *polio virus*, claimed that inactivation was achieved by reaction with the protein coat and even after quite prolonged chlorine/virus contact that there was no evidence of the RNA being affected. Tenno and co-workers[202] suggested that although inactivation was achieved by reaction with the protein coat this did not result in any detectable change in the structure of the virus nor did it affect the reactivity of the RNA, although there was no evidence that ingestion of the still infectious RNA could result in human infection. Degradation of the protein, they suggested, would only occur following prolonged and multiple reactions between the protein capsid and the HOCl. Interestingly, Tenno and his team put forward the suggestion that lack of agreement between their results and those of Dennis and co-workers could be ascribed to the use of the f2 coliform virus by the latter group. Although the overall morphology of the *polio virus* and that of the f2 are simliar, the structural organization of the protein and nucleic acid in the animal virus is substantially different from that of the bacterial virus and the modes of infection by the two viruses are also significantly different. This cast doubt, they suggested, on the validity of employing a bacterial virus as a model to study the effects of disinfection on a human enteric virus.

Alvarez and O'Brien[203] reported that iodine in the form of HIO reacts with the protein coat of the *polio virus* and inactivates it by reducing its ability to adsorb onto host cells. On the other hand, they found that although chlorine dioxide is capable of reacting with the protein this disinfectant primarily inactivates viruses as a result of damage to the RNA and that in this mechanism it is decidedly superior to chlorine. They also reported that a separation of the RNA from the capsid appears to be a general phenomenon of enterovirus inactivation by halogens, although the act of separation does not appear, of itself, to result in inactivation. Working with the DNA-containing *Parvovirus* H-1, Churn and co-workers[243] supported the contention that the inactivating reactions are initially between the chlorine and the capsid rather than between the chlorine and the nucleic acid. From their work, it would appear that the effect of chlorine is not to cleave the capsid polypeptides but rather to rearrange the linkages with a consequent reduction in the adsorptive capabilities of the virus to the host cell. As much as 5 mg/l chlorine was required to rupture the viral capsid so that the DNA protruded like a tail-like extrusion while remaining attached to the capsid.

The controversy as to the precise mechanism of chlorine inactivation of viruses is apparently continued with the action of chloramines, which Olivieri and co-workers,[204] experimenting with the f2 bacteriophage, reported as reacting with RNA fragments while Fujioka and co-workers[205] considered that the chloramines reacted primarily directly with the protein coat. Wolfe and co-workers[43] point out that, as is undoubtedly the case with free chlorine, the inactivation of viruses with chloramines depends greatly on virus type and disinfection concentration.

III. OZONE

Ozone used as a water disinfectant is the only real competitor to the employment of chlorine. Although not greatly employed in North America or in the U.K., ozone is extremely popular in continental Europe where it is used extensively for a wide range of purposes in the water industry as well as for water disinfection.

A. History and Properties

Ozone is an allotropic form of oxygen existing as the molecule O_3 instead of O_2. It is a highly unstable, toxic gas with a boiling point (atmospheric pressure) of $-112°C$ and a density 1.5 times that of oxygen. It is the most powerful oxidant employed as a water disinfectant withan oxidation potential (at 25°C and unit hydrogen ion concentration) of 2.07 v compared with that for hypochlorous acid of 1.49 v, 0.75 v for chloramine, and 1.25 v for chlorine dioxide.[276] Its use in water treatment is a result of its highly electrophilic characteristics. Ozone will attack most metals, except platinum and gold, and gaseous mixtures containing more than about 9% ozone will readily deteriorate. Hence, it is always produced on site as required.

The solubility of ozone in water compared to that of oxygen is reported variously as 10 times,[276] 13 times,[277,278] and 20 times[279] greater. Kinman[280] has reported an ozone solubility of 575 mg/l at 20°C and 775 mg/l at 10°C.

Ozone was first discovered in 1785 by the Dutch philosopher van Marum, who also reported the characteristic odor which he noticed in the vicinity of his electrostatic machine. The name ozone, from the Greek word ozein — to smell — was suggested by Schonbein in 1840. Modern day ozonators are all derived from the apparatus developed in 1857 by Werner von Siemens in Germany.[279] The use of ozone in water treatment was first demonstrated by de Meritens in France[277,279] in 1886, who showed that polluted water could be sterilized by dilute ozone in air. Ohlmuller[276,280] in 1892 reported that ozone could inactivate cholera and typhoid bacteria and also anthrax spores. A few years later, the possibility of destroying all spore-forming bacteria[282] and of eradicating all pathogenic and saprophytic microorganisms likely to be present in water was demonstrated.[283] From the results of a pilot-scale plant operated at Martinikenfield in Germany, Frölich was able to report in 1891 on the effective bactericidal properties of ozone in water treatment. The first full-scale plant to employ ozone disinfection was commissioned at Oudshorrn in the Netherlands in 1893. This was followed in 1901 and 1902 by ozone units at Wiesbaden and Paderborn in Germany. Then in 1906 ozone was first employed at Nice in France where it has been used continually to the present day.[277,279]

B. Reasons for Employing Ozone

Ozone in water treatment may be viewed principally as a bactericide and virucide, but it is selected and employed also for a variety of other purposes which include the removal of color, the destruction of taste and odor, the removal of unwanted organics from the water, the decomplexing and oxidation of soluble iron and manganese salts, and the enhancement of flocculation.

By 1978, there were approximately 1040 water treatment plants worldwide employing ozone of which the vast majority were in France, Switzerland, Federal Republic of Germany, and Austria.[279] Of these countries, France, Switzerland, and Austria principally employ ozone for the destruction of bacteria and viruses with the removal of taste being also of considerable importance, particularly in France. In Germany, the principal reason for the use of ozone was stated in a survey[290] to be the destruction of organic material, with taste removal being next, followed by virus inactivation. In the U.K. and The Netherlands, color removal is the prime reason for using ozone, with disinfection action being secondary.

Ozone is effective in removing color in that it readily cleaves carbon-carbon double bonds in colored molecules.[285] It has been found to be particularly useful at removing the yellowish color of humic compounds present in much raw water gathered from upland regions in the U.K.[286] Schalenkamp[284] reported a reduction of 50% of the color intensity with a dose of 1.0 mg/l and 70% with 5.0 mg/l O_3. Experience in the U.K. with color removal from water abstracted from Lakes Windermere and Ullswater suggest that color intensities of up to 50 Hazen units (H.U.) can be dealt with and that color intensities of 20 to 30 H.U. may be readily reduced to less than 5.0 H.U., with dosages of 1 to 2 mg/l O_3, but that lesser removal rates may result in the later return of up to 50% of the removed color.

Ozone, when employed to reduce taste and odor in water, appears to be particularly effective against hydrogen sulfide and phenolic compounds — especially non-chlorinated phenols[277] — although its reaction with alicyclic taste — and odor — producing compounds such as geosmin and methylisoborneol is reported as only being slow.[299] The oxidation of phenol by ozone proceeds initially through the production of di- and trihydroxyaromatic compounds and quinones, with the application of heavier doses breaking the aromatic ring to form aliphatic acids. Eisenhauer[287] isolated hydroquinone, catechol, p-quinone, cis-muconic acid, oxalic acid, and fumaric acid during the ozonation of phenol until ultimately 4 mol ozone had been used to every one of phenol. Both inorganic iron and manganese salts are oxidized by ozone to higher valency states, with iron being later hydrolyzed, coagulated, and precipitated; manganese eventually precipitates out as manganese dioxide. In addition, humic complexes of these metals can be destroyed prior to the oxidation of the metal ions. Overzealous ozonation employing high residuals and long contact periods can produce the pink color of permanganate, which should not be allowed to enter the water distribution system, although it will nearly certainly be reduced slowly to $Mn(OH)_4$ and then precipitated as MnO_2 should it do so.[277,290]

Claims are made that ozone is able to assist appreciably in the coagulation and flocculation stage of water treatment. Schalenkamp[284] claimed that the optimum dose of ozone to assist these processes lies somewhere between 1.0 and 5.0 mg/l, obviously depending on the characteristics of the water and coagulant/flocculant employed. He warned, however, that dosages in excess of 5.0 mg/l might result in entirely the reverse of the required action being achieved. Rice et al.[277] suggested that the presence of a strong oxidizing agent will reduce the surface charge of those small particles creating turbidity so that they more readily flocculate. In addition the oxidation of ferrous (Fe^{2+}) ions present will result in the production of a specific coagulating agent. Ozone is used at some European treatment plants, together with hydrolized aluminium chloride, to enhance flocculation, sedimentation, and eventual clarification. Klein and Brown[289] suggested that up to 50% of the flocculant can be saved as a result of ozonation and reported that the off-gas from the main ozonation which may still, sometimes, contain from 5 to 15% of the original ozone can be employed at the flocculation stage. Rice et al.[277] elucidated the term microflocculation, which refers to the hydrogen-bonding formed between the polar carboxylic acids, aldehydes, ketones, alcohols, etc. which are created by the ozonation of larger, less polar molecules. The result of this hydrogen-bonding is the formation of vastly higher molecular weight compounds which, in the presence of polyvalent metallic cations, will readily flocculate out. It has also been reported[290-292] that water treatment works abstracting water from the Oise and Seine Rivers in France are able to reduce substantially the level of flocculant employed by the use of pre-ozonization.

It is found that C=C double bonds are most easily broken by the application of ozone with the formation of shorter chain-length carboxylic acids, aldehydes, and ketones. The end products of ozone reaction with complex organics in water are not necessarily, or usually, carbon dioxide and water.[289] Schalenkamp[284] reported a major increase in the concentration of aldehydes and ketones in ozonated water by a factor of about 10 following conventional dosages of about 1.0 mg/l ozone and by as much as 30 following a heavy dose of 5.0 mg/l ozone. The principal compounds found were heptanal, octanal, nonanal, and decanal. Schalenkamp and others[277,286,289] pointed out the advantages of using granular activated carbon (GAC) following the employment of ozone to reduce the concentration of simpler biodegradable compounds produced by the process. Compounds containing aromatic groups are more readily oxidized by ozone than aliphatic materials, with rings being broken to produce aliphatic compounds. Gilbert[293-295] demonstrated that aromatic compounds containing sulfonic acid groups are less readily oxidized by ozone than those without them. Gilbert[295] also reduced by 1.0 kg the COD content of partially polluted wtaers by the addition of 1.2 kg ozone. Rice et al.[277] reported that pesticides in water vary appreciably in their reaction to ozone. Malathion, parathion, phosalone, and aldrin are readily oxidized to destruction, while DDT, PCBs, PCP, and endosulfan react only slightly. Heptachlor is oxidized quantatively to heptachlorepoxide which itself withstands further destruction and is itself a very toxic material.[296] Miller et al.[279] reported that most pesticides are destroyed by a combination of ozone and UV radiation but at higher dosages and longer contact periods than would normally be employed in a water treatment plant.

1. Ozone and Haloforms

Haloforms are hardly affected by ozone, although a limited air-stripping may occur as a result of the use of a large air/ozone to water ratio.[279] No oxidation by ozone of haloforms was reported by Love and co-workders,[297] even with concentrations of as high as 25 mg/l O_3, and no oxidation effect of chloroform in tapwater was reported by the same workers even following a 48-h contact with 10 mg/l O_3. Similar results have been reported by Peyton and co-workers[300] and Hoigné and Bader.[301] Some limited oxidation of chloroform has been reported as the result of employing UV radiation together with ozone.[297] Georgeson and Darimi[298] reported an approximately 24% reduction in haloform potential by 1.0 mg/l O_3, while Klein and Brown[289] stated that although humic and fulvic acids are oxidized by ozone the oxidation products are still potential haloform precursors.

C. Reactions of Ozone in Water

The reaction of ozone in water is apparently a very complex affair. Weiss[302] proposed the intermediaries of the hydroperoxyl and hydroxyl radicals and Alder and Hill[303] suggested the presence of the HO_3^+ ion. Later Gorbenko-Germanov and Kozlova[304,305] were able to confirm the presence of the ozonide radicals and superoxide ions in strongly alkaline solutions. Thomas[306] reported the development of hydrogen peroxide from hydroxyl radicals. The hydroxyl radical was then reported as reacting with the hydroxyl ion[307] to create the oxide radical which would react with oxygen[307] to form the ozonide ion. As a result of this work, together with that of Czapski and co-workers,[309-311] Norrish and Wayne,[312] and Demore,[313] Peleg[314] postulated the following stages for ozone decomposition in aqueous solution

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$$O_3 + H_2O \rightarrow O_2 + 2OH$$

$$O_3 + OH \rightarrow O_2 + HO_2$$

$$O_3 + HO_2 \rightarrow 2O_2 + OH$$

$$OH + OH \rightarrow H_2O_2$$

$$OH + H_2O \rightarrow H_2O + O_2$$

$$OH + OH^- \rightarrow O^- + H_2O$$

$$O^- + O_2 \rightarrow O_3$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

Of the reactive products available, he selected the hydroxyl radical (E_o — 2.8 v) as being probably the principal germicidal agent.

Later work by Hoigné and co-workers,[315-317] and Hart and co-workers[318,319] elucidated a complex chain mechanism involving single-election and atom transfers associated with the hydroxyl radical, together with the HO_2, HO_3, HO_4 radicals and the O_2^-, O_3^-, and OH^- ions with the chain mechanism being capable of initiation by a number of substances such as hydroxide, hydroperoxide, formate, ferrous ions, and even humic substances. In pure water, the chain will repeat frequently, with hundreds of ozone molecules being decomposed by a single initiation step. In natural water, the cycle can be stopped by the trapping of the hydroxyl radical by carbonate/bicarbonate or by natural humic substances and, of course, as a result of radical-radical coupling. The bicarbonate ion is capable of extending the half-life of ozone in water by a factor of 10. Glaze and co-workers[320] emphasized, however, that the ozonation reactions with other substances may involve direct reactions with ozone as well as via the hydroxyl radicals. At high pH levels, the effectiveness of ozonation processes may be reduced as the carbonate ion is a far more effective trapper of the hydroxyl radical than even the bicarbonate ion and, in addition, direct ozonation is not known to occur at a pH of greater than 10.3.

Ozone reacts only very slowly with ammonia in water — if at all. Keenan and Hegemann[321] suggested that it is only under alkaline conditions that the oxidation of ammonia occurs. Hoigné and Bader,[322] who investigated thoroughly the reactions of ozone with ammonia, reported, also, that the oxidation only occurred when relatively high concentrations of the NH_3 molecule prevail, i.e., that the NH_4^+ form is not attacked. Below pH 9.0, it is the ozone molecule which initiates the reaction for which the rate constant is very low. Above pH 9.0, it is the free radical $OH^\cdot$ which commences the oxidation, and this is often inhibited by the presence of other free radical consumers such as carbonate, organics in solution, and hydrogen peroxide. Hoigné and Bader[322] concluded that ammonia will only interfere at all with the other reactions of ozone should it be present in an appreciable concentration.

D. Production of Ozone

For use in water treatment, ozone is prepared by passing dry air through a silent electric discharge

$$O_2 + 2(e) \rightarrow 2O^- + \text{heat}$$

$$2O^- + 2O_2 \rightarrow 2O_3$$

Modern ozonation installations will consist of (1) air blower, (2) dust filter, (3) air compressor, (4) air cooler, (5) air drier, (6) ozonator, and (7) ozone injection and contact unit. In addition, there will probably be some system for the destruction of waste ozone before the off-gases are passed to the atmosphere. Since ozone is extremely toxic, the destruction of any remaining ozone in the waste gases is normally considered to be essential, although with small plants discharge from a tall stack and massive dilution is sometimes employed. Other techniques that can be employed include reinjection or reintroduction, destruction by heat, adsorption into activated carbon, and catalytic reduction.[288] Schalenkamp[284] recommends a thermic/catalytic device like that employed at the Zurich water treatment works for inexpensive and effective destruction of the ozone from waste gases.

Wet air passing into the ozonator will result in the production of oxides of nitrogen and hence in tastes in the treated water, in excessive corrosion, and in the too rapid decomposition of the formed ozone. Formation of nitric acid, as a result of excessive moisture, will create cracking of the dielectrics,[323] and the presence of oil and dust in the air being ozonized can result in sparking damage.[324] Air drying is accomplished by the use of refrigerator chilling and/or the use of desiccant (activated alumina or silica gel) down to an operating dew point lower than −50°C.[323,324] The ozone is created between large electrodes (usually tubes, sometimes plates) separated by air and a (glass) dielectric operating at about 15 kV. It is essential that the heat created by the process be quickly dissipated to avoid too rapid decomposition of the formed ozone. Total power requirements for the production of ozone from air vary from about 22 to 31 kWh/kg ozone produced[324] and the ozonated air will contain between 1 and 3% O_3. The ozone in the airstream can be dissolved into the water either by means of porous diffusers (teflon, ceramic, stainless steel), packed bed (ceramic material) contactors, injection and mechanical stirring, or by motor-driven turbine contactors. With porous diffusers, a bubble size of 2 to 3 mm will be adequate when injected into a depth of between 5 and 6 m employing a counter-current flow system. Transfer efficiency will depend upon bubble size, temperature, diffuser depth, and initial ozone concentration and will commonly be about 80%, although 95% may be achieved using turbo-mixers which require additional power.

One of the disadvantages with the application of ozone is the difficulty in obtaining more than a low concentration into the water being treated. Although the solubility of ozone in water is many times higher than that of oxygen, because the ozone is only produced in low concentrations (about 2%) in the ozonated air, it is difficult to achieve a concentration in water of much more than 1.0 to 2 mg/l. Fortunately, this is sufficient for most disinfection purposes, although the dosage applied needs to be related to the water quality (i.e., the immediate ozone demand) and to the residual that will be still available after several minutes. Hoigné and Bader[325] reported that ozone is rapidly destroyed in the aqueous environment and that the half-life, which will depend on the nature of the water, will generally be of the order of several dozens of minutes. Rice et al.[277] quoted Wynn and co-workers[327] as reporting a half-life of 165 min in distilled water at 20°C but considerably less in solutions containing oxidizable material. Majumbar and Sproul[328] suggested an ozone half-life in water of between 20 and 30 min.

1. Germicidal Effects of Ozone

Vegetative bacteria are readily destroyed by ozone in water. Dosages of between 0.5 to 1.5 mg/l to produce a residual of 0.1 to 0.2 mg/l after 5 min have been suggested as being more than adequate.[289] A concentration of ozone of 0.19 mg/l over 5 min was sufficient to kill all vegetative *Bacillus cereus*, *B. megaterium*, and *E. coli*, while the spores of *B. cereus* and *B. megaterium* required between 2.03 and 2.29 mg/l O_3 over a 5-min period to be destroyed.[329]

Ozone is widely accepted as being the best virucide available in conventional water treatment,[330] although it can be effective also against other organisms such as the cercariae of *Schistoma mansoni*, which Masschelein[331] reported as being inactivated by 0.9 mg/l O_3 in 6 min. Newton and Jones[332] reported the near total destruction of the cysts of *E. histolytica* between 1 and 3 min with between 0.5 and 1.0 mg/l O_3. The cysts of *G. lamblia* were found to be inactivated by 99% at between 0.03 and 0.15 mg/l O_3 between 1.06 and 5.5 min at pH 7 and 25°C and in about the same time by between 0.11 and 0.48 mg/l O_3 at 5°C. For chlorine, the comparable figures were 1.5 mg/l and under 10 min at 25°C and 2.0 to 4.0 mg/l and 40 to 45 min at 5°C.[333,364] The same workers reported a 99% inactivation of *poliovirus 1* by 0.15 mg/l O_3 within 0.5 min at 20°C and pH 7.2 and in 1.45 min at 5°C. A 99% reduction of *E. coli* only required 0.065 mg/l O_3 over 0.33 min at pH 7.2 and 1°C. Kessel and co-workers reported the total inactivation of a nonpurified viral suspension of *poliovirus* in 2.0 min by as little as 0.05 mg/l O_3. Coin and co-workers[334,335] reported a greater than 99% inactivation of poliomyelitis virus types 1, 2, and 3 within 4 min at an ozone residual of 0.4 mg/l. Polio viruses held in triple distilled water were reduced by greater than 99% after 2.5 min with an initial dose of 1.27 mg/l O_3 reducing to 0.23 mg/l,[328] while for biolgoically treated wastewater a similar reduction was achieved in the same time with an initial 1.38 mg/l O_3 reducing to 0.2 mg/l. Roy and co-workers[336] found that when maintaining an ozone residual of 0.15 mg/l at 20°C and pH 7.2 there was a decreasing order of resistance of *poliovirus 2* > *echovirus 1* > *poliovirus 1* > *coxsackievirus* B5 > *echovirus* 5 > *coxsackievirus A9*, with the maximum difference in effect being about 40-fold. The time for a 99.9% inactivation of *coxsackie A9* was about 10 s.

Boyce and co-workers,[339] investigating the virucidal action of ozone in the presence of bentonite clay, reported a greater than 99.7% reduction in active *coxsackievirus A9* within 20 s at as little as 0.02 mg/l O_3, with no retardation of the action due to the presence of bentonite turbidity being recorded despite a 13% adsorption of the viruses onto the clay particles. They also reported a greater than 97% inactivation of *poliovirus (sabin type 1)* within 10 s with 0.2 mg/l O_3 when using between 9.7×10^{-1} and 1.3×10^{2} PFU/ml. In addition, concentrations of *E. coli* of between 9.4×10^{7} and 3.6×10^{8} CFU/100 ml were consistently reduced by at least 99.9% within 10 s by between 0.038 to 0.53 mg/l O_3. Total inactivation was usually achieved after 30 s.

The idea of a threshold level of ozone in water has appeared quite widely in the literature,[276,280,328,337,338] the concept being that there exists a concentration above which ozone is efficacious as a water disinfectant and below which its power is either non-existent, or at best, very reduced. Perlman,[338] working in Paris, suggested a threshold of 0.7 mg/l O_3. Ingols and co-workers[337] suggested a threshold value of 1.0 mg/l O_3 for the inactivation of *poliovirus* in distilled water with two distinct rate mechanisms existing one above and one below the threshold. Lawrence and Cappelli,[276] citing the work of Bringman, suggested a level somewhat lower than 0.1 mg/l. The concept fairly obviously resulted from the ozone demand of the waters under consideration and the consequent lack of correlation between initial dosage and the residual remaining after a limited time. Kinman took issue with this concept in his review of 1975.[365]

Farooq and co-workers[340] investigated the bactericidal effect of the ozone bubbles in a reactor by continually removing any ozone residual as it was formed. An appreciable but not excessive effect was recorded which was attributed by the authors to direct contact, especially as the bubble reached the surface. A significantly greater, if not remarkably so, destruction of both *M. fortuitum* and *C. parapsilosis* was recorded for ozone bubbles in contact with an ozone residual as compared with the residual on its own.

The germicidal action of ozone is little affected by pH, certainly less so than with chlorine,[276] although Leiguarda and co-workers[341] demonstrated a rather reduced effect of ozone against *E. coli* and *Clostridium perfringens* at pH 8.0 as compared with pH 6.0. Conversely, Farooq and co-workers[340] reported a decreasing bactericidal effect of ozone with increasing pH against *M. fortuitum* using the same rate of ozone application, although the residuals declined with increasing pH. Further investigations employing constant residuals at pH 5.7, 7.0, 8.5, and 10.1 revealed no pH effect at all. These workers concluded that any effect of pH noticed was more the result of the faster decomposition of ozone at higher pHs[342] — probably being the result of the catalytic effect of the OH^- ions as proposed by Hewes and Davison[343] — than to the pH per se. However, Wickramanayake and co-workers[344] were able to demonstrate some limited decreasing effect of ozone against the cysts of *G. munis* as the pH was increased from 7.0 to 9.0 at constant O_3 residuals.

Rice et al.[277] suggested that the bactericidal effect of ozone is little affected by temperature, although Sommerville and Rempel[345] have stated that the ozone disinfection action depends upon temperature as well as concentration, contact time, and efficiency of contact. Leiguarda and co-workers[341] reported that temperature did not affect the bactericidal efficiency of ozone, and Kinman[280,365] found little difference in the rate of destruction of total bacteria between 0, 2, 5, 7, 20, and 30°C. Similarly, Zeff and co-workers,[347] as cited by Farooq et al.,[346] reported only insignificant temperature effects on the destruction of *Streptococcus faecalis, Klebsiella pneumoniae,* and *Ancanthamoeba castellanii.* Conversely, Farooq and co-workers[346] reported a significant temperature effect in the inactivation of *M. fortuitum* in the range between 9 and 37°C with a constant ozone residual of about 0.6 mg/l. This effect produced only about a 60% inactivation after 40 s from an initial count of 3.1 to 4.02 × 10^5/ml at 9°C and an approximate 0.2% survival at 37°C.

2. Advantages and Disadvantages

Ozone possesses some very obvious advantages for use in the water industry, particularly that of being a most powerful bactericide and viricide, but associated with these important advantages there exist some very real disadvantages, especially perhaps those of cost and lack of residual disinfecting power. The advantages and disadvantages may be summarized as

	Advantages		Disadvantages
1.	Powerful disinfection action readily removing spores, cysts, bacteria, and viruses	1.	High cost (equipment and production)
2.	Pronounced improvement in organoleptic qualities of water	2.	Elevated skill levels required for operation
3.	Removal of iron and manganese	3.	High reactivity results in low selectivity (i.e., only to be used with good quality water)
4.	Destruction of color	4.	Toxicity of reactant
5.	Little evidence of production of potentially dangerous breakdown products	5.	Low solubility under operational conditions
6.	Produced on site and hence avoids problems associated with transport and storage of dangerous chemicals	6.	No residual disinfecting action
		7.	Measurement difficulties

IV. ULTRAVIOLET RADIATION

UV radiation comprises a section of the electromagnetic spectrum with wavelengths between 15 and 400 mm of which it is only the section between about 200 and 310 nm which is microbicidal, with a definite lethal intensity peak existing at about 255 nm. On either side of the peak, both at shorter and longer wavelengths, the germicidal potential of the radiation falls off quite dramatically.[206,209,220,229] Mechsner[206] suggested that, within this waveband, radiation at about 295 nm causes sunburn; those of about 260 nm will create conjunctivitis in man; those with a wavelength between 280 to 300 nm give rise to vitamin

D; and the longer wavelengths of 300 of 400 nm give rise to skin browning. More systematically, UV radiation is divided into: UVa — 400 nm to 315 nm; UVb — 315 nm to 280 nm; UVc — 280 nm to 200 nm. The UV region below 200 nm is strongly absorbed by air and is often referred to as vacuum-UV.[220]

The adverse effects on cells result primarily from photochemical damage to nucleic acids — particularly to DNA — which absorb strongly at or about 260 nm. Energy dissipation reportedly causes disruption of unsaturated bonds which appears to produce a progressive lethal biochemical change.[230] Johansen and Myhrstad[207] reported that lethal, or sub-lethal, effects are caused by damage to proteins, nucleic acids, and nucleic acid components of which it is the purine and pyrimidine bases that absorb particularly strongly in this range, with the most frequent effect being the production of thymine dimers. Secondary effects may include DNA strand breakages, as well cross-linking between DNA and DNA strands, between DNA and proteins, and between RNA and proteins. In addition, hydrates may be coupled to DNA molecules disturbing the genetic code and hence DNA replication. Some cellular changes may also occur, including reduced DNA synthesis as a result of dimer production, reduced RNA and protein synthesis, and reduced mitosis as a result of protein damage.

The germicidal effect of UV radiation in sunlight was first discovered by Downes and Blunt in 1877,[203] and in 1901 Hewitt developed a mercury vapor arc lamp for the effective production of UV radiation. The later discovery that quartz possessed a high transparency in the UV range coupled with a low coefficient of expansion and high melting point enabled it to be employed as a near-ideal envelope for UV lamps and much encouraged the research into and application of UV radiation for water disinfection.[209] Jepson[209] credits Cernovodeau and Henri,[214] working at Marseilles in 1910, as being the first people to use UV for the disinfection of water. UV installations to treat drinking water on ships have been in use since 1916, but reports of problems with these continued for some time.[233-235] Between 1916 and 1928, there were at least four water treatment plants employing UV disinfection in the U.S. although, in competition with the rapidly growing popularity of chlorine in water treatment, UV never established any popularity, basically as a result of reliability and maintenance problems and cost.[209] Research continued, however, into the application of UV radiation as a germicidal agent, and in 1929 Gates[210] published the results of his work using monochromatic radiation into the germicidally effective wave ranges of UV and later the association was made between the lethal wavebands and absorption by nucleic acids. Oda,[211] Stiff,[212] and Koller[213] all individually reviewed the literature on the subject.

A. Factors Affecting Disinfection by UV Radiation

The disinfection of water by UV radiation depends upon a number of factors. Principally, these are the emission spectrum of the UV source, the intensity of the irradiation and the period of exposure, the sensitivity of the various microorganisms involved, and the performance of the reactors. The intensity of the irradiation will be affected to some extent by the aging of the UV source and also, to a considerable extent, by the quality of the water, which in this case relates to the transparency of the water under treatment to the lethal wavelengths of the UV radiation.

The relationship between UV radiation intensity and its absorption is governed by Lambert's Law, i.e., equal fractions of the incident radiation are absorbed by successive layers of equal thickness of the light-absorbing material. For solutions, there is also Beer's Law, which states that equal fractions of the incident radiation are absorbed by equal changes in concentration of the absorbing substance in a path of constant depth, i.e.,

$$\frac{dI}{db} = kI \qquad (17)$$

and

$$\frac{dI}{dc} = k'I \tag{18}$$

therefore on integration

$$I = Ioe^{-kb} = I_0 10^{-ab} \tag{19}$$

for Lambert's Law and

$$I = Io \cdot e^{-k'c} = I_0 10^{-a'c} \tag{20}$$

for Beer's Law, where I_0 is the intensity of the incident radiation; I is the intensity of the radiation after passage through thickness b of absorbing material; k is the absorption coefficient; a is the molar absorptivity (sometimes the extinction coefficient); c is the concentration of the solution. Lambert's Law is always obeyed and Beer's Law is obeyed for most dilute solutions.

Combining the laws gives

$$I = I_0 \cdot 10^{-a \cdot b \cdot c} \tag{21}$$

and

$$I_{absorbed} = I_0(1 - 10^{-a' \cdot b \cdot c}) \tag{22}$$

thus

$$\log \frac{I_0}{I} = a' \cdot b \cdot c = d \text{ (optical density)} \tag{23}$$

and the intensity of radiation (I) is measured in milliwatts per square meter. The optical density of water being irradiated by UV light will depend largely on turbidity, color, and the organic content of water. Humic acid, phenol, lignin sulfate (effluents from paper mills), and iron[219] will all absorb UV radiation at the critical 255-nm wavelength. The variation in the absorption of UV light with water quality was investigated by Luckeish and Holladay[216] during their work to adapt the new type of germicidal UV lamp to water treatment. Then, in the early 1950s, Gilchreas and de Lalla[217] investigated limiting values of turbidity and color to UV treatment, and Huff and co-workers[218] measured the relative transmission of UV radiation through waters of varying color, turbidity, and bacterial density.[209]

The germicidal effectiveness of UV radiation can be represented by the survival ratio (N/N_0), which can be approximated at any given time by an exponential function

$$\frac{N}{N_0} = \exp(-k'' I_{effect} t) \tag{24}$$

in which N = initial count of specific species of microorganism; N0 = final count of specific species of microorganism; I_{effect} = effective irradiation (J/m^2); t = time (seconds); k" = constant depending on sensitivity of the specific species; $I_{effect} \times t$ = exposure (J · s/m^2). The practical consequence of this log function is that if it is wished to decrease the survival ratio from 0.1 to 0.01 then the exposure will have to be doubled.

Table 4 Approximate Dose Requirement to Achieve a Survival Ratio of 0.1 at 253.7 nm

Microorganism	Dose (J/m²)
Bacteria	
Escherichia coli	30
Eberthella typhosa	21
Salmonella enteritis	40
Shigella dysenteriae	22
Staphylococcus aureus	26
Bacillus subtilis	70
B. subtilis (spores)	120
Yeasts	
Saccharomyces ellipsoideus	60
Torula sphaerica	23
Algae	
Green algae	3600—6000
Protozoa	
Paramecium	640—1000
Mold spores	
Aspergillus amstelodami	667
A. niger	1320
Cladosporium herburum	600
Penicillium digitatum	440
Rhizopus nigricans	1110

From The basic principles of UV-disinfection of water, *Ozone Sci. Eng.*, 9, 299, 1987. With permission.

Since there is considerable variation in the sensitivity of microorganisms to UV radiation, the constant k″ will possess a range of values depending on which microorganism is under consideration. Spores, cysts, and algae are particularly difficult to inactivate with UV, and Mechsner[206] reported that the relative sensitivity of various bacteria is in the order *Salmonella* spp. > *Shigella* spp. > *E. coli, Streptococcae* > *Bacterium prodigiosum, Pseudomonas fluorescens* > *Bacillus proteus* ≫ *Bacillus* spores. Generally, Gram-positive bacteria containing a thick capsule are more difficult to inactivate than the thinner-walled Gram-negative bacteria. Viruses possess sensitivities to UV similar to many bacteria. Algae may require hundreds of times more energy than bacteria to bring about their destruction. Table 4, presented in a simplified form from the paper by Meulemans,[220] gives typical values for the exposure necessary to bring about a survival ratio of 0.1. Should a survival ratio of 0.0001 be required, for example, it would be necessary to multiply the stated exposure by a factor of four. Normally, a minimum exposure of between 160 and 250 J/m², depending on the country, is considered to be sufficient.

1. Possible Recovery from Inactivation

Microorganisms may be considered to be resistant to UV radiation if the DNA is heavily protected (as with spores of fungi and bacteria) or if the nucleic acid region is small (as for some viruses) or, most importantly, if they possess the faculty for reactivation. Microorganisms subjected to an insufficient exposure may reactivate themselves from about 60 and 100 min after the irradiation.[207] The mechanisms of reactivation are either photorepair, dark repair, or both. Photorepair, which is enzymically regulated and becomes increasingly effective with increasing temperature, takes place in visible light or in the near-UV region

(>320 nm).[207,223,224] Dark repair is primarily a matter of excision and post-replication repair (PRR) of which the latter may be of greater importance for the survival of microorganisms.[207] Excision repair operates before replication by removing the UV-induced dimers and filling the spaces with new nucleotides.[225-227] PRR, which is independent of excision repair and is similar to genetic recombination, operates as the name suggests following DNA replication. There is a possibility of induced mutations with dark repair following inadequate irradiation.[228-230] The need to protect UV-irradiated water from sunlight is evident,[207] as is the requirement to design for overdose. Angehrn[236] does not believe that reactivation and repair processes are possible under operational conditions and suggests they can only be brought about under laboratory conditions utilizing increased temperature and extended exposure to light of greater than 300-nm wavelength. Mechsner[206] cites Träger[241] in reporting that no cases of reinfection resulting from photorepair mechanisms have been proved in effectively treated drinking water.

B. UV Sources

The original source of UV radiation was the high-pressure mercury vapor lamps which emitted only about 3% of the power input as UV and which were decidedly polykymatic in that the range of emission peaks covered much of the UV spectrum as well as parts of the visual.[206,236] The high operating temperature of high-pressure lamps also results in a significant absorption by mercury vapor of UV radiation produced in the 250 to 260-nm range. The sole operational advantage of high-pressure lamps appears to be their compact size, although relatively high UV-intensities can be achieved at high power inputs.

Currently, it is the low-pressure mercury vapor light operating on the same principle as the fluorescent light, but without the phosphor coating and with a quartz envelope, that is widely employed. Radiation is produced by passing a current of a suitable voltage between two electrodes in a tube containing an inert gas together with a small amount of mercury, which when stimulated produces a characteristic emission. Unlike the band spectrum of a hot solid body, a gas or metal vapor emits its radiation as line spectra, and the lower the pressure, the fewer and sharper the lines produced. Up to about 40% of the electrical energy input is achieved as UVc radiation, of which about 90% may be at the 253.7-nm line.[206,236] Current consumption may be as low as 0.5 W/cm length of the lamp, with the input to output UV ratio increasing substantially if this figure should exceed much more than 1.0 W/cm.[236] Mercury vapor will also emit a small proportion of its output at a wavelength of about 186 nm, which possesses the potential to ionize oxygen to produce ozone and nitric oxides in air. This line is removed by special types of quartz glass envelopes which retain all emissions of less than 200 nm. The quartz envelope retains, in all, between about 5 and 7% of the emitted energy. Low-pressure lamps, unlike the higher-pressure sources, may be stopped and started at will. Tubes are subject to aging as a result of the deposit of burnt-off electrodes on the inner quartz surface, which decreases the UV emission. Conventionally, a maximum working life of about 3000 h has been adhered to, although Angehrn[236] suggests an operational life in excess of 7000 h without the UV emission dropping below 80%.

The UV treatment units normally consist of narrow stainless steel cylinders containing one or more UV lamps with their longitudinal axes parallel to that of the chamber. Lamp lengths may be as little as about 300 mm, and contact periods between water and irradiation might be as short as 1.0 s or less. Maximum water distance to be traversed by the radiation is about 100 mm, although this might be substantially less. Flow rates per lamp per irradiation chamber vary greatly from less than 7 to more than 140 m^3/h. Essentially, a photocell is situated on the cylinder wall to record the intensity of radiation received. Should this intensity drop below a predetermined minimum, the unit is automatically closed down. For this reason, it is always necessary to mount two or more units in parallel.

1. Examples of UV Installations

Jepson[209] described a 55-W output UV disinfection unit operating in the early 1970s at a remote village in Derbyshire, U.K., of the following dimensions and rating:

Flow	7 m³/h
Annular area	5480 mm²
Annular length	394 mm
Annular volume	2.16 l
Irradiated length	394 mm
Exposure time (av.)	1.11 s
Average direct intensity in irradiated volume	0.90 mW/mm

Trials[237] using a similar unit treating brook water known to be periodically heavily polluted and subject to substantial variations in turbidity and organic content produced the following results.

	Raw water	Treated water
Highest recorded *E. coli* count/100 ml	1600	0
Lowest recorded *E. coli* count/100 ml	4	0
Highest plate count (3 days at 20°C)	4020	395
Lowest plate count (3 days at 20°C)	230	0

Another study[236,238] carried out with water with a relatively high UV absorption (36% over 100 mm) taken from Lake Lucerne and initially treated by rapid sand filtration demonstrated that over a 4-month period in 1959 the number (MPN) of *E. coli* in the irradiated water was consistently below 1/100 ml and the number of saprophytic bacteria always less than 10/100 ml. A more recent 11-month investigation of rapid-sand filtered water from the River Ruhr[236,239] utilizing the whole operating span of the 36 W UV lamps of 9900 h revealed that, with the raw water coliform count varying between 5×10^2 and 5×10^3/100 ml, no coliforms were discovered in the 48 tests of the treated water.

Warne and Sachoux[221] reported on the relatively large-scale, fully automated Thames Water installation at Hambledon, U.K., with a present capacity of 5500 m³/day. This treatment unit consists of eight parallel lines of UV chambers, each of which containing two chambers in series and each chamber incorporating a medium-pressure mercury vapor lamp. The pairs of chambers are automatically opened and closed as required, particularly in response to an upstream analyzer which continually measures the transparency of the water prior to UV irradiation. Should insufficient lines be available at any time, a telemetric signal is sent to the distant control room to reduce the flow to the unit. The maximum power requirement at a flow of 2300 m³/h is 40 kW. Lamps are changed after between 3000 and 4000 h of operation and the outside of the quartz envelope is only infrequently cleaned. The whole treatment unit only occupies 42 m². Light chlorination is applied at the outlet to provide some residual disinfection.

2. Advantages and Disadvantages of UV Treatment

The principal advantages of the Hambledon UV unit are suggested as being ease of maintenance, low installation costs, low operational costs, small size, and perfect security. Overall, the advantages of UV disinfection can be listed as

1. Satisfactory disinfection (both bacteria and viruses inactivated)
2. No alteration to the chemical composition of the water
3. No addition of taste and odor

4. No production of potentially harmful chemicals
5. No induced aftergrowth as a result of the partial breakdown of large organic molecules
6. Low installation and operational costs
7. Low maintenance requirements
8. No danger from overdosing
9. No chemical handling
10. Limited space requirements
11. Few corrosion problems
12. Ease of automation
13. Limited contact time hence no reaction tank required
14. Ease of operation

V. CHLORINE DIOXIDE

Chlorine dioxide exists as a red, highly unstable liquid boiling at 11°C to form an unstable yellowish-green gas possessing a disagreeable, irritating odor not unlike that of chlorine and not dissimilar from ozone. The odor becomes apparent at about 17 ppm and is irritating at a concentration of about 45 ppm.[4] The sensitivity of chlorine dioxide precludes its bulk manufacture and transport and hence it is invariably prepared on site. At room temperature and with a partial pressure of 300 mm, it will dissolve in water to about 2.9 g/l. It does not react with water. The principal uses of chlorine dioxide are for the bleaching of kraft pulps, for bleaching and dye-stripping in the textile industry, for the bleaching of flour, fats, and oils, and increasingly in the water industry.

Chlorine dioxide is normally prepared by the reaction of either acid or chlorine with a strong sodium hypochlorite solution in a packed column

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 2H_2O + 5NaCl \qquad (25)$$

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \qquad (26)$$

The classic route in the water industry is to react a strong chlorine solution of at least 500 mg/l with a concentrated stream of sodium chlorite containing more than 300 mg/l. In theory, this allows for a 25% greater yield of chlorine dioxide from the expensive sodium hypochlorite than with the acid reaction. The theoretical stoichiometric requirement of chlorine to sodium hypochlorite is only 0.39:1, but an excess of chlorine of even as high as 1:1 both prevents the potentially toxic salt getting into the water supply and creates the necessary conditions for a rapid conversion and a 100% yield of the chlorine dioxide.

With an oxidation potential of only 1.15 compared with 1.49 v for hypochlorous acid, chlorine dioxide is obviously not a more powerful oxidant than chlorine in aqueous solution. However, it does possess about 2.5 times the oxidizing power of chlorine

$$ClO_2 + 5e^- \rightarrow Cl^- + 20''$$

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

i.e., once the difference in molecular weights has been taken into consideration, it is reported as having 263% available chlorine, although this oxidizing capacity is not usually fully employed and the chlorine dioxide (ClO_2) is only normally reduced to chlorite (ClO_2').[4]

In the water industry, chlorine dioxide has been widely employed for the removal of taste and odor, being particularly effective against phenols, and will destroy any formed chlorophenols in the water.[4] It is reported[369] as being successful in the removal of tastes and odors due to algae and phenol but as not being particularly effective against "musty" river taste or oils. White[4] reported that it has been employed to remove "musty" tastes and "fishy" tastes as well as tastes and odors produced by *mallomonas*, *anabena*, *asterionella*, synura, vorticella, and actinomycetes. It is also reported as not being effective against the color created by peat in the water[369] and, indeed, the presence of color is reported[348] as strongly reducing the effectiveness of chlorine dioxide in water especially at pH 6.5.

At higher pHs, chlorine dioxide is reported as disproportionating

$$2ClO_2 + 2OH' \rightarrow H_2O + ClO_2' + ClO_3' \qquad (27)$$

to create both the chlorite and chlorate ions.[203,349] It is also reported as being a superior disinfectant at high pHs than at low pHs.[348-350,354,355,358] Alverez and O'Brien,[203] while investigating the effect of chlorine dioxide on *poliovirus 1*, considered the possibility that the enhanced virucidal effect of chlorine dioxide with increasing pH may be a result of the disproportionation of the ClO_2 molecule, with the chlorite and chlorate ions being possibly responsible for the increased virucidal activity. However, since they appreciated that chlorite is a product of many reactions of chlorine dioxide with organic compounds, they progressed to the consideration that it was the chlorate which was the more likely of the two disproportionation products to be primarily effective under these conditions. This explanation did not appear to be totally tenable in light of the low (5%) disproportionation reported for chlorine dioxide at pH 10,[351] so Alvarez and O'Brien concluded that the increase in virucidal effect as a result of increasing pH was to some large extent due merely to the increased sensitivity of viruses to chlorine dioxide at higher pHs.

The possibility of the existence of a different mechanism of attack at pH 6.0 to that at pH 10 was also put forward, with the RNA being suggested as being the primary target of the ClO_2 at the lower pH. The chlorine dioxide appears to react also with the protein coat, but inactivation apparently occurs at near normal pHs as a result of the reaction with the RNA. This RNA/ClO_2 reaction probably impairs the ability of the viral genome to act as a template for RNA synthesis.[203]

Moss and Olivieri,[349] working with the f2 bacterial virus, also reported an increased inactivation as the pH increased from pH 5.0 to pH 9.0. In addition, they were able to demonstrate that the disproportionation products of chlorine dioxide exhibited no virucidal activity and cited in support the work by Emerich[352] which indicated that the autolytic degradation of chlorine dioxide occurs too slowly below pH 10 for the products to have any real effect. Moss and Olivieri concluded that all the virucidal effects observed were due purely to the undissociated chlorine dioxide and that the enhanced effect with increasing pH was merely a function of a change in reactivity between the viral components and the chlorine dioxide with increasing pH and was definitely not the result of any reaction with other oxychlorine species.

On comparing the virucidal effectiveness of iodine and chlorine dioxide, Alvarez and O'Brien reported that the chlorine dioxide is a more effective virucide than iodine and that the ClO_2 is more destructive of the RNA of the *poliovirus 1* than chlorine. Brett and Ridgeway[348] considered that under normal conditions of operation in water treatment chlorine dioxide is seldom a superior disinfectant to chlorine. Rizet and co-workers[353] reported that 0.1 mg/l of chlorine at between pH 5.0 and pH 6.0 at 5°C will bring about a 4-log inactivation of *rotavirus* SA-11 in 15 s but at pH 10, 1.4 min would be required for the same effect, while 0.5 mg/l ClO_2 at pH 10 and 5°C was able to inactivate the same high percentage of the virus in less than 15 s. Bernarde and co-workers[354,356] claimed that chlorine dioxide is a slightly superior bactericide in aqueous solution than hypochlorous acid. Hettche and Ehlbeck[359] reported that chlorine dioxide was more effective against the *poliomyelitis* virus than either chlorine or ozone, while Bedulvich and co-workers[360] found that ClO_2 possessed a higher bactericidal efficiency than chlorine against *E. coli*, *Salmonella typhosa*, and *Salmonella paratyphi*.

Ridenour and co-workers[357,358] concluded as a result of their investigations that chlorine dioxide was at least as effective as chlorine and that its germicidal reactions were relatively unaffected by pH. A little later, Ridenour and Armbruster[358] demonstrated that a concentration of chlorine dioxide of less than 0.1 mg/l destroyed *Eberthella typhosa*, *Shigella dysenteriae*, and *Salmonella paratyphi B* at temperatures between 5 and 20°C and at a pH value greater than 7, always within a 5-min period. They also reported an improvement in efficiency as the temperature increased. Other workers[361,362] have demonstrated that in a no-demand situation and within a 2-min contact period dosages of chlorine dioxide of 0.2, 0.4, 0.6, and 0.8 mg/l would inactivate the *poliovirus 1* by 0.5-, 1.5-, 2.0-, and 3.5-log units, respectively.

Hoff,[68] on the basis of C · t values, concluded that chlorine dioxide at pH 7 was a somewhat inferior disinfectant to free chlorine at pH 6, but he suggested that the disinfecting efficiency increased threefold as the pH increased from 6.0 to 9.0. Hoff quotes figures from Cronier, Scarpino, and Brigano[350,366-368] to demonstrate a C · t reduction from as high as 3.6 (5°C) and as little as 0.9 (25°C) for pH 7 to 0.35 at 21°C for pH 9.0. Hoff also found the Q10 value for chlorine dioxide to be about 2. Jarroll reported unpublished data from Rubens and co-workers demonstrating that the C · t product for *G. muris* in the presence of chlorine is 30 times higher than with chlorine dioxide.

Dosages of chlorine dioxide employed in the water industry are usually at a rate below 1 mg/l. As a result of concern about suggested toxicity of chlorite and chlorate in drinking water, the U.S. EPA[362] in 1978 recommended a maximum combined concentration of 0.5 mg/l for chlorine dioxide and chlorite. Savoir et al.[370] reported a maximum concentration at the Tailfer water treatment works in Belgium of 1.6 mg/l, and Dowling[369] reported a dosage of 0.25 mg/l ClO_2 in conjunction with up to 1.0 mg/l Cl_2 at the Huntingdon water works abstracting water from the River Dee to supply the City of Liverpool. This latter combination was found to be superior to the previous practice of superchlorination employing 4.9 mg/l Cl_2 followed later by 0.5 mg/l sulfur dioxide.

One of the principal advantages of using chlorine dioxide in the water industry is its lack of reaction with ammnonia.[4,353,363] Obviously, this reduces considerably the oxidation demand with ClO_2 in water and allows for its more limited — yet equally efficacious — dosing into rather lower quality surface waters. Chlorine dioxide does, however, react with other subtances in abstracted surface water. Oehler and co-workers[372] reported that chlorine dioxide will react with small quantities of humic acid in water with a production of chlorite equivalent to the ClO_2 consumption. Both the consumption of chlorine dioxide and the production of chlorite increased with increasing temperature and pH. With lake water, both the consumption of chlorine dioxide per unit value of organic carbon and the production of chlorite was less than with straight humic acid in water but still appreciable. No haloforms were discovered following treatment of lake water with 2.0 mg/l ClO_2.

Tan and co-workers[371] mixed 7 m*M* of amino acids and peptides with equimolar concentrations of chlorine dioxide for 4 h at 25°C and pH 6 in the dark and discovered that only 6 of the 21 amino acids, together with the 3 peptides tested, reacted. Amino acids containing sulfur or an aromatic ring had previously been found to be most reative with ClO_2.[373] The reaction products from the three peptides and from two of the six amino acids (hydroxyproline and tyrosine) were discovered to exert mutagenic activity toward both tester strains of TA 98 and TA 100 in the presence of rat liver S9 mix.

As already recorded, Oehler and co-workers[372] were unable to detect haloforms following a dosage of 2 mg/l ClO_2 to a specific lake water. This inability to produce haloforms with chlorine dioxide appears to be the conclusion of most researchers into the subject. Symons et al.[381] reported that the use of chlorine dioxide does not result in the formation of suspected carcinogens such as haloforms. Miltner[384] reported that chlorine dioxide does not create haloforms, nor will it remove them if already present.[385] Savoir et al.[370] cited the work of five workers[376-378] to support their contention that no volatile organochlorides like haloforms are produced by chlorine dioxide. In addition, Savoir et al. claimed that the chlorine which is nearly invariably present together with chlorine dioxide in water treatment produces fewer haloforms than a similar concentration of chlorine on its own. However, Lin and co-workers[393] apparently demonstrated that just the opposite effect occurred when a Cl_2/ClO_2 mixture was employed with the hydroxylated derivative of benzoic acid, which has been assumed to be a model of part of the humic acid molecule, to produce a chloroform concentration greater than that obtained with an equivalent concentration of chlorine. Other authors have found that ClO_2 produces 5 to 20 times fewer haloforms than chlorine.[375,377,380] In the absence of chlorine, no haloforms were detected in water from the River Meuse in Belgium, even when treated with concentrations of chlorine dioxide as high as 20 mg/l.[368]

Because chlorine dioxide, as a result of the common practice of production, is nearly invariably dosed into water together with chlorine, there still does exist some definite danger of haloform production unassociated with any possible reaction between the ClO_2 and haloform precursors present in the water. One way of removing this problem is to add ammonia to the water in sufficient quantity to react with the free chlorine prior to the addition of the ClO_2/Cl_2 disinfecting agent. Conversely, mineral acid may be employed for the ClO_2 production in place of the chlorine.

A. Toxicity of Chlorine Dioxide

Perhaps the principal concern with the use of chlorine dioxide in water treatment is the possible toxicity of the chlorite ion produced. In 1982, the AWWA Committee[362] reporting on disinfection of water stated that "data are still unavailable to evaluate fully the possible health effects of the products formed when chlorine dioxide reacts with organic materials present in a water supply." It was the presence of chlorate and chlorite, and particularly the latter, which was of concern. White[4] affirmed the general acceptance of the production of chlorite being the principal end-product of chlorine dioxide reactions in water. Myhstad and Samdal[382] reported the complete conversion of added chlorine dioxide to chlorite in 35 min. White[4] cites Dodgen and Taube[383] as reporting the rapid rate of exchange between chlorine dioxide and chlorite. Miltner[384] demonstrated that the primary products resulting from the presence of chlorine dioxide in surface water included chlorites and chlorates, which were present at 50 and 30%, respectively, of the ClO_2 demand. In addition, Dodgen and Taube[383] described the slow disappearance of free chlorine in the presence of chlorine dioxide with the production of the chlorite ion.

By means of orally administered chlorine dioxide, Abdel-Rahman and co-workers[385] demonstrated hematologic changes and inhibition in the testicular uptake of ^3H-thymidine in rats. Moore and Calabrese[386] reported on the effect of chlorine oxides on glucose-6-phosphate dehydrogenase. Abdel-Rahman et al.[385] investigated the effects of chlorine dioxide and metabolites on the cellular glutathione (GSH) system in rat, mouse, and chicken blood. Heffernan and co-workers[388,389] reported *in vitro* damage created by $NaClO_2$ to erythrocytes and demonstrated a dose-dependent oxidative stress produced by $NaClO_2$ in rats. Abdel-Rahman and co-workers[385] described the ClO_2-associated kinetics of red cell GSH depletion and intravascular hemolysis in rats and chickens. However, Michael et al.,[390] in a prospective epidemiological study, failed to demonstrate any clinicopathological effects of chlorine dioxide in the water supply on human volunteers. In particular, no thyroid effects were found in serum of these volunteers consuming about 1 mg/l ClO_2.

Bercz and co-workers,[391] at the U.S. EPA Health Effects Research Laboratory in Cincinnati, employing pure ClO_2 (no Cl_2, OCl′), reported that chlorine dioxide is a potent inhibitor of thyroid synthesis at the very high dose of 9 mg/kg/day. They also verified the findings of Hefferman et al.[389] and Moore and Calabrese[386] of oxidation stress-induced methemoglobinemia and anemia in rats. Bercz and co-workers concluded that the thyroid-inhibiting effect of chlorine dioxide appears to be significant and at that time of unknown explanation and meriting further research.

Abdel-Rahman and co-workers[385] gave water containing ClO_2, ClO_2', and ClO_3' to rats over a 12-month period and reported decreased osmotic fragility in all groups; this was probably related to the formation of disulfide bonds between membrane elements and hemoglobin, causing precipitation of hemoglobin. GSH was decreased following exposure to ClO_2, ClO_2', and ClO_3'. This is consistent with the protective role of GSH against damage by oxidants already reported.[392] Rats drinking water containing ClO_2, ClO_2', and ClO_3' over a 9-month period were reported as exhibiting depressed red blood cell counts, hemoglobin concentration, and packed cell volumes. In addition, ^3H-thymidine studies revealed ClO_2, ClO_2', and ClO_3' induced diminished DNA synthesis in testes, kidneys, and liver but not in the small intestine which was the site of the administration. Interestingly, the small intestine would have therefore been exposed directly to ClO_2 while the other organs would only have been exposed to the metabolites in circulation. Ozawa and Kwan[379] found evidence of protective hemastatic when employing electron spin resonance spectroscopy to detect a short-lived ascorbate radical when chlorine dioxide was reacted with ascorbic acid. They concluded that ascorbic acid is a suitable agent for the detoxification in the body of any ClO_2 remaining in treated drinking water. However, the reaction between chlorine dioxide and ascorbic acid results in the production of ClO_2' or $HClO_2$.

VI. IODINE

As far as disinfection of potable water is concerned, iodine must be the last of the conventional disinfectants to be considered as it is undoubtedly the least used, if for no other reason than that of cost. Weight for weight, the cost of iodine is about 20 times that of chorine. There exists little likelihood of iodine ever being adopted as a principal disinfectant at any major water treatment works, but that is not to say that it does not posses a significant potential as a potable water disinfectant nor that it cannot be extremely valuable in certain distinct situations. However, these situations are, and are likely to remain, those of disaster after-effects and of small and isolated supplies.

Iodine is a blue-black element with a melting point of 113.5°C and a boiling point of 184.4°C; it is normally obtainable in the form of crystals and is extracted commercially either from Chilean nitrate-bearing earth (caliche) or from seaweed. It will volatilize to produce a blue-violet gas with an irritating odor. It is the heaviest of the halogens, with an atomic number of 53 and an atomic weight of 126.9. It is also the least soluble and the least hydrolized in water. Iodine possess valences of 1, 3, 5, and 7, with the monovalency being the most common. The oxidation potential $(I_2 + 2e' \rightarrow 2I')$ is only 0.54 at 25°C compared with that of chlorine of 1.39 V. Care is always necessary in handling iodine because contact with the skin can produce lesions.[244,245]

The disinfecting action of iodine in wounds has been recognized since early in the 19th century. In 1827, Lugol demonstrated that its solubility in water increased in the presence of potassium iodide[247] (Lugol's solution) and iodine has been included in the U.S. Pharmacopeia since 1830 in the form of aqueous or hydroalcoholic solutions.[248] Vergnoux[249] was apparently the first to employ iodine for drinking water treatment during World War I, and later Hitchens[250] recommended its use to the U.S. Army in 1922. Then, during World War II, the work of Fair and his group at Harvard University[251] advanced the use of iodine in water treatment and resulted in the development of globaline tablets. Following this up, Chang and Morris[252] published their important study which proved the effectiveness of iodine

Table 5
The Effect of pH on the Proportion of Reactive Iodine Agents in Water (0.5 mg/l Titratable Iodine in the Presence of Iodide)

pH	I_2 (%)	HOI (%)	OI^- (%)
5	99	1	0
6	90	10	0
7	52	48	0
8	12	88	0.005

against bacteria, viruses, and cysts and demonstrated its superiority to chlorine against cysts of *E. histolytica*.

In 1945, the U.S. Public Health Service in the Manual of Rural Water Supply and Sanitation[253] recommended the use of iodine for emergency water treatment, and in 1962 the U.S. Public Health Service tentatively approved its use on a regular basis at no more than 5 mg/l.[248]

By 1965, iodine was already authorized for use as a swimming pool disinfectant in ten states, and Ehlers and Steel[254] were recommending it for the disinfection of individual water supplies.

The solubility of iodine in water is limited and is significantly affected by temperature, so that at 20°C a saturated solution will contain 290 mg/l whose concentration rises to 4450 mg/l at 100°C. In an analogous manner to that of chlorine in water, but to a much more limited extent, the dissolved iodine hydrolyzes to form hypoiodous acid

$$I_2 + H_2O = HIO + H^+ + I'$$

The hydrolysis constant is 3×10^{-13} mol/l at 25°C. There is then some very limited dissociation of the hypoiodous acid. As a result, at normal temperatures and in a usual pH range, there are two disinfecting agents present in the water: elemental iodine and hypoiodous acid. The concentration of the hypoiodous ion (OI') is never significant. The relative percentages of these agents present at various pHs is illustrated in Table 5, adapted from Chang.[255]

Chang[255] reported that at pHs above 8.0 the HIO was partially unstable and would decompose to form the hypoiodate (HIO_3)

$$3HIO + 2OH' \rightarrow HIO_3 + 2H_2O + 2I' \qquad (29)$$

but Black and Kinman demonstrated that the amount of hypoiodate produced was insignificant. The formation of the periodide (I_3') in the presence of iodine and iodide is also possible but is again insignificant in iodated drinking water.[248] Chang[255] also mentioned another form of titratable iodine — the iodophors — in which iodine is loosely bound with non-ionic detergent. This material is more soluble, less corrosive, and less volatile than iodine but possesses a reduced microbicidal action.

Both forms of iodine in water — the elemental iodine and the hypoiodous acid — are distinctly germicidal, with the iodine being found to be more effective against cysts and spores and the hypoiodous acid more effective as a viricide. Chang[172] suggested that the greater cysticidal effect of iodine is due to its ability to diffuse readily through the cyst wall; its diffusibility being more important than its oxidizing power in this particular situation. Chang also suggested that I_2 is two to three times as cysticidal[255] and six times as sporocidal as HOI,[172] while the HIO is more than 40 times[256] as virucidal as I_2. It was demonstrated

Table 6
Time Taken in Seconds for 99.99% Destruction at 3 to 4°C Using a Dose of 1.0 mg/l Iodine

	Escherichia coli	*Aerobacter aerogenes*	*Pseudomonas aeruginosa*	*Streptococcus faecalis*	*Staphylococcus aureus*
pH 5.0	60	60	120	180	45
pH 7.0	81	60	110	336 (est.)	50
pH 9.0	210	180	180	1080 (est.)	320 (est.)

After Reference 245.

that a residual of 3.5 mg/l elemental iodine would destroy cysts of *E. histolytica* in 10 min at 25°C.[174] Kinman and co-workers[248] reported that only 0.55 mg/l or iodine in water was required to kill 1 × 10[6] *E. coli* in 1 min at 20°C. Under the same conditions, they found that the same effect was achieved by 0.56 mg/l of chlorine in 30 s. Hence, they argued that on an atom-to-atom basis nearly four times as many chlorine atoms will only manage the same result in half the time as with iodine. Kahn and Visscher,[267] concerned with the disinfection of personal water supplies in the wilderness, pointed out that it had been demonstrated that a dose of 3 to 5 mg/l iodine will destroy amoebae and their cysts, bacteria and their spores, as well as algae and enteroviruses, in 15 min or less at 25°C and within 20 to 30 min in water near to 0°C.[260,265,266]

The effect of iodine on various microorganisms has been investigated. McKee and co-workers[257] investigated the effects of iodine on *P. aeruginosa*, Carroll[258] investigated the effect on *Micrococcus pyrogenes*, and the effects on *Leptospira* were investigated by Chang and co-workers.[252,259] Other microorganisms investigated with reference to the effect of iodine include viruses,[252,259,260] *E. histolytica*,[252,255,259] *Streptococcus faecalis*,[262,263] *Aerobacter aerogenes*,[252,262] *E. coli*,[252,258,262,264] and *Salmonella* spp.[252,262]

On the whole, pH in the range 6.0 to 9.0 has no great influence on the effectiveness of iodine in water as a microbicidal agent, although any effect is more noticeable at lower rather than higher temperatures.[262] However, Taylor and Butler[268] reported that iodine was most effective at pH 9.0 against the *poliovirus*. Rather differently, Karalekas and co-workers,[246] working with six different bacterial genera, reported a noticeable, if not pronounced, reduction in effect as the pH was increased from 5.0 to 7.0 to 9.0, although generally the differences reported between the effects at pH 5.0 and 7.0 may not have been statistically significant. They recorded that when employing 1.0 mg/l initial dose of iodine at 3 to 4°C no viable *E. coli* cells were recovered after 1.5 min at pH 5.0, although some viable cells were still evident after 5.0 min at pH 9.0. More systematically, they reported that a 4-log destruction of *E. coli* (3 to 4°C) took 60 s at pH 5.0, 81 s at pH 7.0, and 210 s at pH 9.0. Similar, but by no means identical, results were reported for the other test bacteria, as is illustrated in Table 6.

Ellis and van Vree,[269] working with *E. coli* and fecal streptococci, reported a declining effect of iodine as the pH was increased from pH 7.0 to 8.5. They also reported a noticeable decline in effect as the turbidity (provided by river silt) of the test solutions increased up to 100 NTU, although in each case they found the effect of increasing pH and increasing turbidity to be more pronouced with chlorine than with iodine. Under none of the conditions of pH and turbidity investigated did they find that 1.0 mg/l iodine was capable of reducing the initial counts of bacteria of between 2000 and 17,000/100 ml *E. coli* and between 200 and 600/100 ml fecal streptococci to a level acceptable in potable water. Chlorine at 1.0 mg/l was only capable of producing water of a potable standard at the lowest pH investigated and at the lower turbidities. With 2.0 mg/l iodine, there was always an effective, but rarely total, removal of the fecal indicator organisms at the lower pHs and at the lower turbidity levels investigated but, again, this removal declined with increasing pH and turbidity. Despite the poor quality waters employed in the investigation, dosages of 4.0 and 8.0 mg/l iodine were always effective in producing water of an approximate potable quality under all the conditions employed.

One of the most significant characteristics of iodine as a water disinfectant is its lower aptitude compared to chlorine to react with impurities in the water. The iodine demand of waters is always substantially lower than the chlorine demand.[270] Certainly, at the low concentrations employed in water treatment, iodine is relatively unreactive. Iodine in dilute aqueous solutions does not react with phenols to produce taste- and odor-forming compounds. Hunter and Budrow[271] found that iodine in dilute aqueous solutions does not react with pure phenol, although under anhydrous conditions it is possible to iodinate sodium phenolate. Perhaps, even more importantly, iodine does not react with ammonia in water to form iodamines.[170,270] Chang and Morris[252] found that iodine and urea up to concentrations of 5 mg/l had no effect on the disinfecting capability of iodine. Also, these two researchers reported that natural color in water — simulated by the addition of weak tea — did not produce an iodine demand. Kinman and co-workers[248] found carboxylic acids to be generally quite stable towards iodine.

As might be expected with such a subjective parameter, opinions concerning taste and odor vary considerably. Black and co-workers[273] reported that taste problems were found with 1 mg/l HIO, while previously it had been reported[270] that it was not possible to detect 1 mg/l elemental iodine by odor or color, although at 1.5 mg/l some people were able to detect a faintly sweet taste which was definitely not a truly iodine taste and which was not objectionable. In limited tests carried out with iodine in distilled water, the author has found usually little response until 4 mg/l, although the more sensitive subjects report a taste and odor at 2 mg/l. Chang and Morris[252] reported that 8 mg/l imparts a faint-to-distinct taste and that 15 mg/l produced a distinct-to-decided taste. Kahn and Visscher[267] suggested that a concentration of about 8 mg/l iodine is "less than palatable."

The problem of how to add iodine to water depends largely on whether the supply concerned is relatively large or small. At a municipal or institutional level, Black and co-workers[273] suggested three different methods. First, they suggested vaporization of solid iodine crystals by the controlled addition of heat. Or, as an alternative, passing water through a bed of iodine in order to saturate it and then adding the saturated solution containing a known iodine concentration to the water supply at a controlled rate. This is the technique that was employed for the extended investigation involving prison inmates at Lowell, FL. The third possibility is to add an excess of an oxidant such as chloramine to water already containing the iodide ion so that the iodide is quantitatively oxidized to iodine. Particularly for swimming pool water, this third technique appears to offer distinct advantages as the same iodine may be used repeatedly as it is consecutively oxidized/reduced and oxidized once again by the addition of a cheaper oxidant. This also appears to be a suitable method for ensuring a residual disinfection action to protect water adequately in extended distribution systems. Black and co-workers[270,273] reported that HIO in the presence of chloramine persisted longer than just the HIO. In one sample iodine alone persisted for only 17 h, but in the presence of 0.5 mg/l chloramine there was an iodine residual even after 68 h.

On a smaller scale either for individual residences or for personal drinking water, it is possible to add iodine as a saturated aqueous solution, although it is important to be aware of the appreciable variation in iodine solubility with temperature and of the longer contact time required as the temperature declines. Kahn and Visscher[267] suggested that if a near-saturated solution in contact with iodine crystals is held at body temperature then 10 ml/l of water to be treated will provide a sufficient dose of 4 mg/l iodine. At 20°C, this aliquot will have to be increased to 13 ml and to 20 ml at 3°C, with a minimum 15-min contact time being required. They suggested that half the dose but with an increased contact time of 40 min will improve the palatability of the treated water without reducing the protection. Eight drops of a 2% tincture of iodine to a quart of water has also been suggested.[266] Kahn and Visscher[267] also indicated that for the traveller simple iodination of water is superior to the use of p-dichlorosulphamoyl benzoic acid (Halazone) which possesses only a low solubility together with relatively short shelf life and is of limited use at higher pHs or with polluted water.

During World War II a team at Harvard University, working with a contract from the Office of Scientific Research and Development, formulated the globaline tablet which liberates about 8 mg of elemental iodine to water. The active constituent of the tablet is tetraglycine hydroperiodide resulting from the reactions between elemental iodine, potassium iodide, glycine, and hydrochloric acid. In addition to the tetraglycine hydroperiodide, the tablet also contained some sodium acid phosphate and a small amount of talc.[274] Treatment of personal drinking water at the rate of one tablet per liter will destroy all amoebic dysentery cysts, enteric bacteria, as well as the infective cercariae of schistosomiasis within 10 min in most waters and within 20 min in cold water.

Ever since treatment of drinking water supplies with iodine became a realistic and practical possibility following the work carried out by the Harvard group during the war, there has existed some continuing concern over the possibility of harmful physiological effects through the long-term ingestion of iodated water. These concerns have largely been satisfied as the result of two extended-period tests. The first of these involved U.S. service personnel in the Marshall Islands between 1949 and 1950[274] and the second — a much more extensive and rigorous investigation — in prison populations in Florida.

The Marshall Islands investigation was carried out at the naval installation on Uliga Island in the Majuro Atoll between the 1st November 1949 and the 30th April 1950. The investigation was not concerned with the microbiocidal efficiency of iodine in water but merely with any possible toxic effects of iodine consumed over an extended period and, as the water supply was already chlorinated, a sufficient amount of sodium iodide was added to yield an iodine concentration equivalent to, or in excess of that used in field purification processes. Although iodide was added to the whole water supply of the naval station, detailed clinical data were obtained from a group of only 24 servicemen. During the first 16 weeks of the investigation, the average intake per person per day of iodide was approximately 12 mg, which was increased to 19.2 mg for the final 10 weeks. No evidence of weight loss, failure of vision, cardiovascular damage, altered thyroid activity, anemia, bone marrow depression, or renal irritation was found among the subject group. Nor was any evidence of sensitization to iodine, unusual skin diseases, impaired wound healing, or defective resolution of infections discovered during the test period.

The team at the University of Florida began its work in 1958 by investigating the effectiveness of iodine as a disinfectant for swimming pool water.[275] Then, in 1963, it progressed to public water supplies when two water systems serving three prisons with a total population of 750 persons at Lowell, FL, were selected for investigation with regard to the use of iodine as a water disinfectant. Generally, 1 mg/l iodine was added to the water, with short periods at 5 and 0.3 mg/l. A test group of 133 inmates was assessed twice before iodine was applied to the water, four times during the first 10 months and again after 37 months, although by that time the size of the test group had declined to 29 persons. Throughout this period, the serum thyroxine concentrations of the test group personnel remained unchanged and there was no evidence of hypersensitivity or other adverse effects resulting from iodine. More importantly, there was also no evidence of impaired thyroid function. In all, the long-term evidence from Lowell was that 1 mg/l iodine was able to disinfect adequately the water supply and that no evidence was produced that an extended-period ingestion of iodine in water had been deleterious to health.[248,274]

VII. T

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VII. TURBIDITY AND DISINFECTION

Turbidity in water undergoing disinfection is not a factor of major concern in most modern water treatment works. These are designed and operated, to a large extent, to remove such turbidity and to produce a water which is sparkling and clear. However, with smaller installations, with which the filtration stage may either be of lower efficiency or occasionally nonexistent, turbidity at the time of disinfection is a factor that must be considered. Turbidity of the water undergoing disinfection must particularly be a factor of concern in the developing world where low quality waters are not infrequently treated purely by chlorination. In addition, turbidity developed within the distribution system as a result of the sloughing-off of developed biofilm can give rise to concern in some situations.[396]

The evidence for bacteria attached to solids in water is well documented,[397-401] as is the affinity of viruses for suspended particles.[402-406] Symonds and Hoff[406] demonstrated the connection between solids in water and disease-producing organisms. Carlson and co-workers[402] and Schaub and Sagrik[403] reported that viruses have a natural affinity for solids in water and may be found adsorbed to solids consisting of clay or of fecal matter. Berg[405] suggested that most viruses in water are associated with solid matter. In 1978, Hoff[404] made the important point that the influence of turbidity on the disinfection process depended more on the type of turbidity rather than its density. He reported that inorganic clay or alum floc created little interference with chlorine disinfection but that cell-associated viruses and coliforms associated with naturally occurring solids were more prone to escape the disinfecting action.

Le Chevallier and co-workers[401] reported a major influence of turbidity in the form of naturally occurring stream sediment on chlorine disinfection. With a turbidity of 13 NTU and at 10°C and pH 7, a chlorine dosage of 2.5 mg/l associated with a chlorine demand of 1.9 mg/l brought about only a 20% inactivation of coliforms in 1 h whereas at 1.5 NTU the inactivation was complete. These researchers, working in the Pacific Northwest region, reported that disinfection efficiency was influenced by turbidity, by the chlorine demand, and by the season. The seasonal effect is due to the increase in the TOC concentration in the summer months. A statistical model, developed through multiple linear regression, predicted, with a constant chlorine dosage, an eight-fold decrease in disinfection efficiency with a turbidity increasing from 1.0 to 10 NTU.

The organic content of both the water and the suspended matter has a profound effect on disinfection efficiency. Hoff[404] reported little protection was afforded to *poliovirus 1* from HOCl by inorganic suspensions but considerable protection was provided by organic suspensions such as cell debris. Chang and Morris[252] found that clay turbidities of up to 500 mg/l had little effect on disinfection by iodine but, strangely, fine sand did influence the disinfection to some extent. Ellis and van Vree,[269] employing turbidity created by natural stream sediment, found that increasing the turbidity in stages up to a maximum of 100 NTU reduced both the effect of iodine and of chlorine. Gevandian and co-workers[407] demonstrated, with a water containing 50 mg/l kaolin and 25 mg/l lactoalbumin, as much as 50 mg/l O_3 was required to inactivate poliovirus but without the organic addition, yet still with the kaolin, only 0.16 mg/l O_3 was required for full inactivation.

The disinfection action of chlorine on the f2 bacteriophage was reported by Staggs and co-workers[408] as being somewhat retarded by the presence of clay turbidity but as still being rapid. According to Hoff[404] and Walsh and co-workers,[83] alum flocs provides little protection to either bacteria or viruses. Working with ozone and alum floc turbidity and with the *poliovirus 1* tightly associated with the floc, 0.012 mg/l O_3 brought about a 99.95% inactivation of unabsorbed poliovirus together with 99.97% inactivation of floc-associated virus (5 NTU) within 20 s. Similar results were reported for *E. coli* and the f2 bacteriophage, although the results with the bacteriophage were less clear. Boyce and co-workers,[339] also investigating the effect of ozone on turbidity, demonstrated a total lack of effect on both *poliovirus 1* and *coxsackievirus A9* by 5 NTU created by bentonite. Also, with *E. coli*, the presence of bentonite turbidities (5 NTU) produced no noticeable effect, although the very small proportion of *f2 bacteriophage* (2%) adsorbed onto the bentonite was afforded some degree of protection.

A. Bacterial Survival in Protozoa

Many workers have reported the ability of bacteria — including pathogenic bacteria — to survive and multiply within protozoa.[429-432] It has been demonstrated that the cysts of *G. microti* contain intracellular bacteria.[14] The ability to survive in these situations has also been linked with pathogenicity. Enhancement of the virulence of strains of *Legionella* has been demonstrated during periods of ingestion. It has been suggested that the ability to survive within a protozoan may be a demonstration of preadaptation for the invasion of human hosts. Survival rates of bacteria within protozoa depend on the rate of digestion, which is in its turn influenced by temperature and bacteria type. Endocytobiotic relationships have also been reported between bacteria in ciliates and flagellated algae.[434] Relationships have been reported as including cytoplasmic and endonuclear colonization of protozoa by bacteria.

Since protozoa are appreciably more difficult to kill than free bacteria, ingestion within a protozoan offers a route whereby the effects of normal levels of chlorination may be avoided. The ciliate *Tetrahymena pyriformis* was reported by King and co-workers[433] to have survived exposure to 4 mg/l free chlorine for 30 min at 25°C and pH 7.0. The amoeba *Ancanthamoeba castellani* survived exposure to 10 mg/l free chlorine for 24 h. All the amoeba held in more than 4 mg/l free chlorine encysted but were later recoverable. The encystment of the carrier protozoa has been suggested as protecting bacteria from stress conditions due to osmotic pressure, desiccation, and increased temperature.[432] Ingestion by ciliates was demonstrated to increase the resistance of bacteria to chlorine by between 30- and 120-fold. A 99% inactivation of *K. pneumoniae* within the amoeba *A. castellani* was only achieved after 120 min at 25°C and pH 7 with 10 mg/l of free chlorine.

King and co-workers not only demonstrated the survival of bacteria within specific protozoa, but also suggested that as a result of the temporary nutrient-rich and protective microenvironment vulnerable and fastidious bacteria may be maintained in greater abundance on release. In all, there is little doubt that the protection of bacteria, under the conditions of normal chlorination, has been adequately demonstrated in the presence of such protozoa that are not uncommonly found in distribution networks.

Within a distribution system, microorganisms have been demonstrated as existing in and on tubercules removed from the inside of the water pipes,[420] and the scanning electron microcope has revealed profuse bacterial growth on the inside of such pipes.[421] Particle-containing water in distribution systems has also been demonstrated to have microorganisms associated with the particles which, however, go undetected in the bulk water phase.[422]

This possible source of coliforms has been suggested[423-426] for sudden increases in these organisms in distributrion systems where cross-connections can be ruled out. In particular, the sloughing of biofilm from the distribution system has been suggested[427] as the reason for an outbreak of coliforms, not suppressed by heavy chlorination, in the bulk water at Muncie, IN. It is possible that attached bacteria become more resistant to chlorination than free bacteria and this hypothesis is apparently borne out by the work of Herson and co-workers,[427] who reported an appreciable if not great increase in the resistance of *E. cloacae* associated with sloughed-off iron particles.

VIII. DISINFECTION OF POTABLE WATER IN THE DEVELOPING WORLD

When considering the problems of potable water disinfection, or more generally, of potable water treatment in the developing world, it must be emphasized initially that the term "developing world" is very elastic and one that can be extremely misleading. Those countries which are usually referred to as being part of the developing world vary enormously in their level of economic and technical development. At the one end of the scale, there are those countries with highly developed commercial and industrial sectors, well-established secondary and tertiary education systems, good communications, and a well-developed ability to improvise adequately when apparently essential equipment is not available. At the other extreme, there are countries in which the already minimal economic achievement is totally overburdened by natural or political disasters, where communications are appalling, technical and tertiary education nearly nonexistent, and the agricultural and industrial base so limited that the provision even of the simplest techniques of water supply is only achieved through external aid, and the operation and maintenance of these is a continuing nightmare. All this makes generalization concerning the developing world extremely risky, sometimes inappropriate, and not infrequently insulting. The ensuing comments do not apply to all countries, but they occur to some extent in most, although the extent of the problem will vary considerably from place to place.

Also, before commencing an analysis of the problems, it is of importance to emphasize that it is the provision of appreciable quantities of water — not necessarily of what would normally be assumed to be of a potable quality — that is initially of more importance than the provision of high-quality drinking water. The fecal-oral and water-washed classes of disease, as defined by Cairncross and Feachem,[411] are reduced to a greater extent by the provision of sufficient water to a community than by the supply of potable quality water. It has been suggested[412] that whereas water availability to a community will reduce the diarrheal morbidity by 25% and adequate excreta disposal by a further 22%, the provision of potable quality water will only increase these figures by a further 16%.

A. The Problems

The disinfection of potable water supplies is a topic that for the so-called developed world can be regarded satisfactorily as being a sufficiently separate section of water treatment to be considered on its own. This is not so in much of the developing world, where the disinfection stages are those which are either most frequently misemployed or under-employed or commonly not operating at all. In the author's experience, it is the disinfection stage of any potable water treatment plant which is by far the most likely either to be operating inadequately or to be out of operation at any given time. Hence, disinfection must be considered largely as an integral part of all the water treatment processes employed, so that in the consideration of potable wter disinfection in the developing world it is necessary to include all the techniques of water treatment; and if any individual technique does not assist appreciably in the removal of pathogen organisms, its validity in any particular situation must be questioned.

The reasons for the failure of the disinfection stage and for the associated widespread inability to effectively treat potentially potable water supplies are manifold and must include the nonavailability of adequate funds — particularly foreign currency — to support the construction and, even more importantly, the operation of treatment works. However, shortage of money does not cover, by any means, the whole of the problem. Difficulties associated with water treatment in the developing world also encompass problems with training, provision of appropriate treatment techniques, shortage of spares and chemicals, nonstandardization of equipment and transport, distribution problems, the lack of effective support and administration units, and particularly operation and control. Of these, it is perhaps the latter which contributes most widely to the failure of many treatment works to provide adequate quality water.

It is not uncommon in the developing world to discover well-designed and constructed water treatment plants which are not, however, operating adequately. The difficulties may frequently arise from lack of mechanical or electrical spares, shortage of chemicals, or inadequate staff training. However, even in the absence of these particular problems, widespread difficulties are encountered as a result of what is not infrequently the principal barrier to effective water treatment, i.e., the lack of adequate supervision by plant managers and higher-ranking authority. Take this in conjunction with another major problem, i.e., the lack of support by an experienced and disciplined administration unit, and the operational standards quickly decline until very little in the way of adequate water treatment is being achieved. Failure to achieve adequate supervision is not infrequently the result of lack of personal discipline on behalf of the supervisors and those responsible for supervising the supervisors, but is equally commonly the result of lack of specialist training and experience of senior engineers and other professionals, who are then most reluctant to lose face by demonstrating their ignorance to the work force in such situations. An office then becomes, for many a senior engineer, a citadel from which one must never move without danger of losing status.

1. Bottled Waters

Before progressing to an examination of disinfection of water in the developing world, it is of interest to consider one further factor that militates against the provision of a potable quality water, i.e., the marketing of bottled water. Bottled water, packaged and marketed in a sophisticated manner, provides for the professional classes of many countries a supply of "safe" drinking water, although it might be that the faith in the quality of the product is somewhat unfounded. However, these bottled supplies are widely believed to be entirely suitable to serve as the drinking water for the community — if they can be afforded. Of course, the majority of the population cannot afford the cost of the continuing supply of bottled water. However, with the educated and vocal few who are capable of influencing events now being satisfied with the availability of good quality drinking water, the driving force to effect a radical improvement in the quality of town's supply is severely blunted and continuing progress is slow.

B. Removal of Pathogenic Organisms

Potable water disinfection, in those regions under considration, can be realistically considered more as the continuing removal of pathogenic organisms by a series of separate water treatment techniques than at one particular and vulnerable stage. Most, if not all, water treatment techniques remove some — but seldom all — of the potentially harmful organisms. As discussed earlier in this review, efficient[82-84] coagulation and flocculation are surprisingly effective at removing viruses in particular, although the subsequent rapid sand filtration technique rarely does much to enhance the process. However, the coagulation/flocculation/sedimentation stages and the rapid sand filtration stage represent techniques which are not only demanding in terms of initial and continuing cost but which also demand for their effective operation an appreciable level of technical skill. These requirements are not infrequently in very short supply and hence chemical pretreatment and rapid sand filtration can rarely be considered as appropriate treatment techniques.

The techniques of water treatment which can be widely regarded as being appropriate to the level of economic development and the availability of technical skills are those of long-term storage, river bank filtration, and slow sand filtration. To these three might be added the prevention of source pollution.

On a village scale, the prevention of source pollution might merely involve controlling the access of cattle to the vicinity of the well, both to prevent direct pollution by fecal matter and indirect pollution in the form of a massive addition of nitrate to the aquifer. These aims are readily achieved by ensuring the provision of good surface and subsurface protection for the bore-hole, provision for cattle watering at some distance, the adequate covering of a hitherto open well, and the provision of a suitable water-lifting device. A system in which a camel or donkey is used to lift the water bucket from a deep well is hardly satisfactory if each time it is raised the rope trails among the feces deposited around the well.

On a larger scale, the prevention of source pollution for a surface water abstraction is obviously a much more complex requirement possibly only achieved as a result of specific legislation and the creation of a specialist surface water pollution control organization. However, bearing in mind that most surface water pollution in the developing world emanates from newly developed industry or, more rarely, from recently installed water-borne sewerage systems at major towns, the problem is not insurmontable and anything that may be achieved in alleviating source pollution can add considerably to the likelihood of the provision of "safe" potable water.

Storage of water over an appreciable period, which may have to be in excess of 60 days or more, can be an effective means of radically reducing the bacterial count and the concentration also of other potentially harmful microorganisms. Such a technique is known to be effective,[3] although insufficient work has been done to relate reduction in pathogens to such factors as temperature, retention period, water quality, water depth, intensity and duration of sunlight, and design of the storage reservoir. The drawbacks of this form of treatment include the difficulty in adequately protecting the storage reservoir from cattle pollution and pollution by the local population. The latter is critical particularly in areas in which a system of sanitation has not been provided, and illustrates the importance in all situations of combining the provision of a water supply with the provision of a suitable, and acceptable, sanitation system. A further and perhaps more intractable problem associated with long-term storage is the possibility of the development of algal blooms with all the difficulties associated with them for further treatment and for the provision of a palatable drinking water.

Infiltration of river water through the silt and gravel of the river bank or river bed, to be abstracted via either infiltration galleries or broad, shallow wells, is a widely practiced technique either for the partial treatment or for the total treatment of the abstracted water.[395,416–419] Depending upon the river water quality, the characteristics of the bank, the distance traversed, and the rate of abstraction, the water can be of a surprisingly good quality and containing few, if any, indicator organisms. It is a technique that is particularly widely practiced in the Indian sub-continent.

Over the last decade and more, so much has been published[428] to advocate the use of slow sand fitration in the developing world that few water treatment specialists can be unaware of its great potential. Adequately designed and operated slow sand filters can ensure the removal of all cysts, spores, and viruses from the raw water and the nearly complete removal of all harmful bacteria. Necessitating only a relatively simple design, being capable of construction largely with local material and local labor, requiring only low-level technical support, and being so effective in the removal of pathogenic organisms, the slow sand filter must be considered as the obvious choice for the treatment of surface waters in the developing world unless powerful, local reasons can be assembled to counter it.

Even more simple than slow sand filtration is the filtration of water through a muslin cloth. Yet this is all that is required to remove the cyclops host of Guinea worm *(Dracunculus medinensis)*, and if only in the regions in which this disease is endemic, all water could be passed through a simple cloth filter before drinking, the disease could be eradicated. The prevalence of this disease must again emphasize the superiority of ground water sources to surface water sources in regions in which adequate water treatment, let alone disinfection, cannot be guaranteed.

C. Disinfection

Although the point has been stressed that in many regions of the Third World, in which low technical skills, shortage of finance together with an underdeveloped tradition of occupational discipline are endemic, that the provision of a separate disinfection stage in a water treatment unit is not necessarily desirable and may well prove to be dangerously counterproductive, there will always exist many situations in which some form of disinfection will have to be incorporated as an essential and frequently the only form of treatment. Such forms of water disinfection must always be designed to be as simple, as robust, and as undemanding of maintenance as is possible.

The boiling of water for household supplies is, on occasion, advocated for the rendering safe of domestic supplies. This is an obvious and effective technique but one difficult to apply when lack of health education deprives the (invariably) woman of an adequate incentive as to why she should carry through, continually, a time-consuming and apparently unnecessary task. In addition, in much of the developing world, fuel shortage is one of the principal problems of domestic life and it is unlikely that households would welcome the profligate use of wood for such a (to them) questionable purpose.

At the other extreme, the use of ozone is totally out of the question for any but the largest water treatment works in those countries of the Third World in which financial and technical development has been most pronounced. Those who advocate such techniques[394] are not only not reacting responsibly to the requirements of the poorer countries but verge on demonstrating the least acceptable face of the developed world's water industry to the Third World. In the same manner, the proposed use of UV radiation could possibly invite a similar blast of disapproval and whereas it is most unlikely that the widespread employment of UV radiation would ever be advocated the reliability of the installed equipment could make it a possibility for a strictly limited number of small communities where a reliable power supply is available, in which finances are not too limiting, and where the necessary maintenance can be supplied.

Iodine is unlikely ever to be widely employed as a water disinfectant, principally because of its cost, on any but the smallest units. Its value in water treatment lies primarily in disaster situations, where its peculiar ability to disinfect the low quality surface waters[245,249-251,264,266,267] which would be all that would be available, together with its ease of transport and simplicity of application, make it an obvious choice. The regular use of iodine in some situations should not necessarily be dismissed out of hand despite its cost as it does possess a potential for small and isolated comunities that have to rely upon polluted surface water and for which more sophisticated treatment processes may not be practicable. In such situations, application could best be achieved by the addition of measured quantities of a saturated solution. In the same manner, adequate disinfection of well water could be achieved without having to rely on the changing and diminishing chlorine content of the usual chloride of lime. An advantage with the use of iodine must be the development of a distinctive taste as the dosage surpasses the required concentration.

However, despite the availability of other disinfectants and as a result of its availability, limited cost, and general ability to destroy those microorganisms responsible for waterborne diseases, it is upon chlorine that one must largely rely in the developing world as in the developed world. One must merely adapt to different sources and simpler techniques of application. The principal difference is that in the developing world it is on the employment of "solid" chlorine in the form of bleaching powder or calcium hypochlorite that one must rely even for treatment units appreciably larger in size than those for which these sources of chlorine would be considered as being suitable elsewhere. With the exception of large water treatment works serving relatively sophisticated communities where the necessary technical skills and supervision are constantly available, the use of gaseous chlorine should never be considered. Besides, even in these situations, a reserve supply of HTH is nearly essential in case of any breakdown in the system of supply.

The use of sodium hypochlorite solution is not encouraged as a result of problems of transport, limited available chlorine, and rapid loss from an open container. Calcium hypochlorite, which is widely available commercially as HTH, would appear to be a near ideal source of chlorine. Its high level of available chlorine, long storage life, low-loss rate even after the containers are opened, and the absence of an irritating powder all tend to make it a most suitable source of chlorine for water treatment. However, its cost mitigates strongly agaist its use in most Third World situations and it is therefore upon bleaching powder (chloride of lime) that one is forced to rely.

Bleaching powder is readily, and relatively cheaply, available in all developing countries and is manufactured in many. It must be the preferred source of chlorine. Its principal disadvantage is the rate at which chlorine is lost once the container is opened and it is not unknown for an operator to be seen carefully measuring out the stipulated amount of powder to make up a standard chlorine solution but using a supply of bleaching powder from which all chlorine has long since fled.

Chloride of lime is usually employed by making up a standard solution of 2 to 3% available chlorine, allowing the sediment to settle, and decanting the liquid into a dark bottle from which it can be dosed into the water supply. The initial problem, as already suggested, is the uncertainty concerning the chlorine content of the solid source. The next is to ensure a constant rate of addition of the solution to the water. Various simple, constant head devices are available[393] of which the aspirator with inlet air-tube penetrating to the bottom of the container in such a manner that the head across the delivery is independent of the liquid level is the simplest. Other devices making use of a flexible delivery tube suspended under a float are reliable so long as the flexible tubing is not damaged. Slightly more sophisticated arrangements make use of a secondary dosing tank controlled by a ball-cock. Messrs. Wallace and Tiernan market a reliable self-powered batch doser. This employs a cup, impelled by a float in the slowly filling dosing tank, rising through the strong chlorine solution toward a static piston which eventually displaces a controlled volume of the hypochlorite into a siphon-operated, self-emptying batch tank.

Other, more sophisticated solution-dosing pumps are also available for larger installations where maintenance may be less of a problem. However, even in these situations, it is necessary that the equipment be of the simplest possible design, robust, and with a ready availability of easily interchangeable spares. In its excellent book concerned with the disinfection of rural and small water supplies, the WHO (European Office)[395] recommends that hypochlorite dosing pumps possess:

1. A simple operating principle
2. Simple and robust construction
3. Few and slow-moving working parts
4. Minimal sliding friction
5. Positive mechanical drive to the displacer
6. Small unswept volume
7. Access to valves without opening the pumping chamber
8. Design that provides for ease of cleaning and replacement of renewable parts

Disinfection of village wells can be achieved on a daily basis by the direct addition of a calculated amount of the solid chloride of lime or of the solution. Disinfection over an extended period is managed by the use of pot or double-pot diffusers containing a mixture of coarse sand and bleaching powder[409,412,413] (together with, sometimes, sodium hexametasphophate to prevent hypochlorite interaction with hardness blocking the diffuser holes). These diffusers which will maintain a disinfection action over days and even weeks have been demonstrated to be effective in many parts of the world including Southern Portugal.[395] A disadvantage is that there will be a delay after the introduction of pot diffusers before the hypochlorite has spread through the well water. This can be overcome by adding some hpochlorite solution to the well at the same time as the pot diffuser is introduced.

I. The Designer's Role

The provision of good-quality drinking water in the developing world is best ensured by avoiding sophistication in works design. Simplicity and reliability must be the key words that the designer must at all times bear in mind and, above all, it is necessary to always appreciate the vulnerability of the disinfection stage. For this particular reason, the selection of all treatment processes must be directed principally toward the removal or destruction of pathogenic organisms. Even without an operating disinfection stage, it is essential that the treatment works be able to supply a water largely free from harmful microorganisms. In addition, it must be remembered that a treatment works that relies to a large extent on the use of dosed chemicals for effective treatment represents a distinct public health hazard in much of the Third World.

At all times, a water treatment works designer in the developing world has to be aware of the necessity to comply with the following requirements:

1. Simplicity of design
2. Use of local materials
3. Non-reliance on imported mechanical and electrical spares
4. Non-reliance on imported chemicals
5. The necessity to be operable by low-level technical assistance
6. The ability to produce a "safe" water even if the disinfection stage fails

APPENDIX 1

A. Chlorine Concentration in Water

In water disinfection, the concentration of chlorine in water is invariably reported in terms of milligrams per liter, but with the initial hydrolisis reaction being represented in terms of

$$Cl_2 + H_2O \rightarrow HCl + HOCl \qquad (1)$$

There is the possibility of some confusion as to which chlorine is being referred to, i.e., the mass per liter added as the two-atom molecule Cl_2 or the one of these atoms that is found in the active oxidizing compound HOCl. To quickly elucidate this, it is necessary to revert to basic principles, i.e., oxidation is a loss of electrons, e.g.,

$$Fe^{2+} - (e) \rightarrow Fe^{3+} \qquad (2)$$

and as a compound is oxidized, the oxidant is equivalently reduced, i.e., it gains electrons, e.g., chlorine reacts oxidatively as

$$Cl_2 + 2(e) \rightarrow 2Cl^- \qquad (3)$$

and in so doing is reduced and two electrons of reducing (oxidizing) power are consumed by a molecule of chlorine or 1 mol of reducing (oxidizing) power is consumed by $^1/_2$ mol chlorine or one unit of oxidizing power is produced by $^1/_2$ mol chlorine (71/2 = 35.5 g).

Hypochlorous acid reacts oxidatively as

$$HOCl + H^+ + 2(e) \rightarrow H_2O + Cl^- \qquad (4)$$

so that 2 mol of electrons are consumed for each mol of HOCl, or one unit of oxidizing power is produced by $^1/_2$ mol HOCl ($^1/_2 \times 52.5 = 26.25$). However, since chlorine reacts in water according to Equation 1, the oxidizing power available in the 1 mol of HOCl is identical to the oxidizing power available in the 1 mol of chlorine. Hence, chlorine concentration in water can adequately be represented in terms of milligrams per liter of the chlorine added.

APPENDIX 2

A. Available Chlorine

The term available chlorine is widely employed in the water treatment industry to indicate the relative amounts of chlorine in different products which are present for the disinfection of water. The availability of chlorine in a compound is traditionally determined by the amount of iodine released when it is mixed with potassium iodide in an acidic solution. However, the availability is perhaps best represented in terms of the basic oxidation reactions. For example, when a chlorine molecule is reduced, two electrons are required for the reaction

$$Cl_2 + 2(e) \rightarrow 2Cl^- \qquad (5)$$

i.e., one electron per mole is consumed for each 71/2 = 35.5 g of molecular chlorine as it is reduced to chloride ions. The chloride ion represents the ultimate fate (or sink) of the chlorine as its oxidative power is spent.

With sodium hypochlorite (NaOCl)

$$NaOCl + 2H^+ + 2(e) \rightarrow Cl^- + Na^+ + H_2O \qquad (6)$$

i.e., one electron per mol consumed for each $^1/_2$ mol of the sodium hypochlorite reduced, i.e.,

$$\frac{74.5}{2} = 37.25 \text{ g NaOCl}$$

Hence, comparing NaOCl with Cl_2 in its capacity to consume electrons (i.e., act as an oxidizing agent) per equivalent mass

$$\text{NaOCl is } \frac{35.5}{37.25} \times 100 = 95.3\% \text{ as effective as chlorine}$$

Hence, sodium hypochlorite is reported as possessing 95% available chlorine.

With calcium hpochlorite — $Ca(OCl)_2$ — one electron is consumed for each $^1/_4$ i.e., 143/4 = 35.75 g of $Ca(OCl)_2$. Hence, the percentage available chlorine is given as

$$\frac{35.5}{35.75} \times 100 = 99.3\%$$

HTH is not pure calcium hypochlorite and hence is normally represented as possessing 70%

available chlorine. Rather more strangely, hypochlorous acid (HOCl) which requires two electrons per mol and with a molecular weight of 52.5 has a percentage available chlorine of 35.5/26.25 × 100 = 135.2%. While chlorine dioxide (ClO_2) reacting as

$$2ClO_2 + 8H^+ + 10(e) \rightarrow 2Cl^- + 4H_2O \tag{7}$$

has a percentage of available chlorine of 263!

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