CHLORINATION OF WATER

By

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PREFACE

This report entitled "Chlorination of Water" is submitted to Professor Quintin B. Graves to fulfill the necessary requirements for the obtaining of a Master of Science Degree from the School of Civil Engineering, Oklahoma Institute of Technology, Oklahoma A & M College.

One of the phases of sanitary engineering is that dealing with the treatment of water. Of the various physical and chemical processes employed, chlorination is one of the most important. This report discusses the reaction of chlorine with water and its impurities and the many factors affecting these reactions.

I would like to thank Professors Ren G. Saxton, Roger L. Flanders, Quintin B. Graves, and Nathan C. Burbank, Jr. for their assistance and criticism of this report.

Respectfully submitted,

Foster S. Burba

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CHLORINATION OF WATER

Chlorine has become a very widely used chemical for industrial purposes. Although less than seven per cent of the chlorine produced in the United States is used in the treatment of water, this is the most beneficial use to mankind. A great deal has been learned concerning the application of chlorine to water to make it safe (as well as desirable) for drinking purposes and other uses. Despite this, there are a number of misconceptions and misuses of chlorination. Research has revealed a great deal of information; but the number of factors influencing the efficiency of chlorination (especially as a bactericidal agent) has resulted in very little definite information as to the mechanics of the action and the influence of each factor. The principle factors influencing its use as a water disinfectant include:

time of contact
chemical characteristics of reactants
concentration of disinfectant
concentration of organisms
temperature

Chlorine is a very active element. It is the second member of the seventh column in the periodic table. Seven electrons surround the nucleus of the chlorine atom. It has a strong tendency to acquire an electron to complete its shell of eight electrons, therefore, it is a strong oxidizing agent. Because it is so active, chlorine always occurs in nature in a combined state and never as free or elemental chlorine. Chlorine may be liquified at room temperature at pressures ranging from five to ten atmospheres. Besides being rather economical, it is easy to transport. These characteristics, plus its solubility in water, (7,300 ppm at 68°F and one atmosphere), make it adaptable to the treatment of water.

PRINCIPLES OF WATER CHLORINATION

When chlorine is placed in water, it immediately undergoes hydrolysis to form hypochlorous acid. This reaction is virtually complete in less than a second even at 0°C temperature. This reaction is not complete in strong solutions but may be considered complete when occuring in the concentrations normally used in water treatment. For the time being, the ionization of hypochlorous acid to the chlorite ion will be disregarded. Hypochlorous acid reacts with any of a number of reducing agents in the water and the subsequent consumption of chlorine is termed chlorine demand. A chlorine atom plus an electron results in a neutral chloride particle or organic chloride and the chlorine loses its disinfecting power. Among the materials which render chlorine unavailable for disinfecting purposes are: inorganic iron, manganese, nitrogen dioxide, and hydrogen sulfide. Many waters contain organic materials which also exert a chlorine demand even though these impurities may be harmless to humans. A part of the organic material may include organisms some of which are pathogenic. To further complicate the possibilities of chlorine demand, ammonia, organic amines, and certain other nitrogen compounds may "tie up" the chlorine although the compound formed has a disinfecting potential. All of these possible reactions are influenced by a number of factors which will be discussed later. Generally, however, the living organisms are the last of these impurities to be affected by the chlorination process.

TWO TYPES OF CHLORINE RESIDUALS

In the treatment of water, the application of chlorine to water is controlled by the available chlorine residual in the water after a specified time interval. The two types of chlorine residuals are a combined available residual (commonly termed chloramine) and a free available chlorine residual.

A combined available chlorine residual is defined as a chlorine residual in which the chlorine present has combined with nitrogen compounds to form pure chloramines with ammonia or other chloramines and other chloro-derivatives with organic nitrogen compounds. The combined chlorine residual available in water is composed chiefly of pure chloramines due to the absence or near absence of organic nitrogen compounds. Therefore, chloro-derivatives of organic nitrogen compounds may be disregarded. Depending upon the pH of a solution, the two types of combined chlorine residuals available will be monochloramine (NH_2Cl) or dichloramine ($NHCl_2$) or a mixture of the two. Since most waters have a pH greater than 7.0, the chlorine residual available in water will be chiefly monochloramine.

A free available chlorine residual is defined as a chlorine residual which is present either as hypochlorous acid (HOCl) or as hypochlorite ion (OCl^-), or both, depending upon the pH of the water. This definition of free chlorine residual does not refer to molecular or free chlorine (Cl_2). Water containing molecular chlorine (Cl_2) must have a pH of 3.0 or less or have a chlorine concentration exceeding 1,000 ppm. Neither of these conditions occur in the normal treatment of water; therefore, free (molecular) chlorine is never encountered in water treatment practices. The term free chlorine residual is often incorrectly used in the place of free available chlorine residual wherein hypochlorous and/or hypochlorite ion are present.

A number of terms (such as pre, post, super, marginal, etc.) have been used to describe methods of chlorination procedures. Since there are basically two types of residuals, there can be only two definite types of chlorination—combined available chlorination (or chloramination) and free available residual chlorination.

> "Combined residual chlorination is the application of chlorine to water to produce with ammonia a combined available chlorine residual, and to maintain that residual through part or all of a water treatment plant or distribution system. The ammonia may be either added or occur normally in the water."[1]

> "Free residual chlorination is the application of chlorine to water to produce directly or through the destruction of ammonia a free available chlorine residual and to maintain that residual through part or all of a water treatment plant or distribution system."[2]

Heretofore, the treatment of water has frequently consisted of maintaining a chlorine residual with little regard as to the type of residual obtained. Each chlorination procedure has certain advantages (as well as disadvantages) which must be considered in determining the type best applicable to a certain water, water treatment plant, and distribution system.

INACTIVATION OF ORGANISMS IN WATER

The destruction of bacteria (and of other micro-organisms) by a substance is essentially the result of a chemical reaction between the active agent and some vital substance necessary to the functioning of the organism.

The pathogenic water borne organisms include:

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[1] Wallace and Tierman. Break-point Chlorination Manual.

[2] Ibid.

1. Enteric vegetative bacteria among which are Eberthella, Shigella, Salmonella, and Cholera.
2. Spore-forming bacteria such as Bacillus antracis.
3. Protozoa, the most important of which is Entamoeba histolytica.
4. Worms such as the cercariae or the schistosomes.
5. Viruses such as the virus causing infectious hepatitis.

Each of the above groups react differently to disinfectants which is one reason for the diffiuclty encountered in research concerning disinfection. Of the groups listed, the enteric bacteria are the most easily destroyed by the chlorination process whereas cysts of Endamoeba histolytica and bacterial spores seem to be the most resistant. Where cysts are found in water which is improperly filtered, a high concentration of chlorine is required for safe water. Little is known about viruses although they apparently are more resistant than enteric bacteria but not as resistant as cysts.

Satisfactory treatment of water is now a problem of great concern because many cities now use a source polluted by sewage. Hoskins[3] estimates that approximately 400 billion coliform bacteria are issued from a persons body each day through feces and urine. In a city with typhoid rate of 200 per 100,000 population, the sewage might contain 100 E. typhosa per milliliter. In areas of high E. histolytics endemicity (approximately 50%) ratios, it would be quite possible for each milliter of sewage to contain 10 cysts per milliliter of concentrated sewage. These and other pathogenic organisms (as well as a number of non-pathogenic organisms) should be either killed or removed by the treatment processes.

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[3] Fair, Morris, and Chang. Dynamics of Water Chlorination. Inter-Americana De Ingenieria Sanitaria, January, 1948.

The destruction of cells of minute organisms is not due to naescent oxygen as once was believed by water works men. Green of Columbia University believes that death results from a chemical reaction of hypochlorous acid with an enzyme system in the cell that is essential for the metabolic functioning of the organism. The enzyme is thought to be triosephosphate dehydrogenase which is essential for the utilization of glucose.

Laboratory tests indicate that the rate of diffusion of the active agent through the cell wall largely determines the rate of disinfection and relative efficiency of the agents. Therefore, it is not primarily the strong oxidizing power of hypochlorous acid which makes it a superior disinfectant—although that is essential. Rather, the small molecular size and electrical neutrality which allow the hypochlorous acid to pass readily through cell membranes are responsible.

The principle factors of disinfecting efficiency include:

1. Time of contact.
2. Concentration of organisms.
3. Concentration of disinfectant.
4. Temperature.
5. Nature of disinfectant.

In the consideration of time of contact of disinfectant with organism, Chick's Law[4] should hold.

Log $\frac{N}{N_0}$ = kt where $\frac{N}{N_0}$ is the fraction of the original number of organisms remaining at the time t and k is a proportional constant.

This was not substantiated by Butterfield[5] who found it to vary with

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[4] Ibid.

[5] Ibid.

t^2 rather than t. This may have been due to: a combination of slow diffusion through the cell wall of the disinfectant and a rate of killing which is dependent upon the concentration of disinfectant inside the wall. Or, it may be that there are three to four active centers which must all be destroyed before the organism is killed.

Not much is known about the effect of concentration of organisms upon the efficiency of disinfection.

The changes in disinfection efficiency with the concentration of disinfectant may be expressed by[6]: $C^n t = k$ where C is the concentration of disinfectant.

t is the time necessary for a constant percentage of the organism to be destroyed.

n is a constant (the concentration exponent).

With high values of n, the efficiency of the disinfectant decreases as it is diluted. With low values of n, time (t) becomes more important.

As temperature increases, the rate of disinfection also increases.

CHEMISTRY OF CHLORINATION

As previously stated, chlorine undergoes hydrolysis when added to water:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (1)$$

This reaction is virtually complete within a very short period of time. The hypochlorous acid (HOCl) is the main disinfecting agent as will be discussed later.

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[6] Fair, Morris, Chang, Weil, and Barden. The Behavior of Chlorine as a Water Disinfectant. American Water Works Association, 1948.

The hypochlorous acid ionizes as shown:

$$HOCl \rightleftharpoons H^{+} + OCl^{-} \qquad (2)$$

Equation (2) is essentially an instantaneous, reversible process. The Equilibrium Equation is as follows:

$$\frac{(H^{+}) \quad (OCl^{-})}{HOCl} = K$$

( ) stands for activity, which is approximate equal to the molar concentration of the enclosed substance. K is the ionization constant, dependent only upon the temperature of the solution. Values of K for various temperatures are shown in Table No. 1.

Table No. 1[7]

°C	°F	$K(10^{-8})$
0	32	2.0
5	41	2.3
10	50	2.6
15	59	3.0
20	68	3.3
25	77	3.7

Rearrangement of the Equilibrium Equation gives:

$$\frac{(OCl^{-})}{(HOCl)} = \frac{K}{(H^{+})}$$

Thus, the relative amounts of hypochlorous acid and hypochlorite ion present in a solution are a function of the hydrogen ion concentration.

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[7] *Ibid.*

Table No. 2[8]

pH	HOCl %	Free Chlorine, ppm necessary for one ppm HOCl
4	100.000	1.000
5	99.700	1.003
6	96.800	1.033
7	75.200	1.330
8	23.300	4.300
9	2.900	34.000
10	0.300	331.000
11	0.030	3,300.000

Hypochlorites extablish this same ionization equilibrium in water. Calcium hypochlorite dissolves in water as follows:

$$Ca(OCl)_2 \rightleftharpoons Ca^+ + 2\ OCl^-$$

The hypochlorite ions combine with H ions from the water to form hypochlorous acid.

$$H^+ + OCl^- \rightleftharpoons HOCl$$

This is the reverse of the previous ionization process. Hence, at the same pH, chlorine solutions and hypochlorite solutions must have the same disinfecting efficiencies.

FORMATION OF CHLORAMINES

The action of chlorine solutions is further modified by the reaction of hypochlorous acid with substances common to water. Of these, ammonia and many organic amines combine with the hypochlorous acid to form chloramines. The oxidizing capacity of the chlorine is retained by the chloramines and permit recording of residual chlorine by the common tests. However, the molecular nature of the chlorine is changed with a resultant

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[8] Ibid.

different disinfecting power.

Formation of Chloramines:

$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O$ monochloramine

$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O$ dichloramine

$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O$ nitrogen tri-chloride

The rate of reaction in the first step is very much dependent upon the pH of the solution. The maximum reaction rate occurs at a pH of 8.3 and decreases at higher and lower pH values. The relative proportions of monochloramine and dichloramine are affected not only by the pH of the solution but also by the excess ammonia present.

$$2\ NH_2Cl + H \rightleftharpoons NH^+_4 + NHCl_2$$

The disinfecting efficiency of a solution will vary with the $NHCl_2 : NH_2Cl$ ratio just as a change in $HOCl:OCl^-$ will do.

Table No. 3 illustrates how the monochloramine:dichloramine ratio varies with pH for a certain chlorine:ammonia-nitrogen ratio.

Table No. 3

Equilibrium Chloramine Distribution at a Chlorine to Ammonia-Nitrogen - Weight Ratio of 5:1.

pH	Chlorine as Dichloramine (%)
5	84
6	62
7	35
8	15
9	6

TWO TYPES OF AVAILABLE CHLORINE RESIDUALS

As was stated earlier, hypochlorous acid combines with ammonia and certain organic amines present in water, the oxidizing capacity of which is rather weak. It is slow in killing bacteria under most conditions as compared with a free available chlorine residual. For residuals of the same magnitude and normal pH waters, a combined available chlorine residual requires for certain bacteria 100 times the contact period necessary for this same bacterial kill by a free available chlorine residual. For certain bacterial kill within a given time and in a normal pH water, the required magnitude of the combined available chlorine residual is approximately 25 times that of free available chlorine residual. In the higher pH ranges (above 9.4) the combined available chlorine residual kills more readily than does a free available chlorine residual of the same magnitude.

Combined available chlorine residual will not oxidize manganese compounds although it will oxidize ferrous to ferric compounds.

Combined available residual will not oxidize many taste and odor producing substances. This may be advantageous in that ammonia may be added to water prior to the addition of chlorine and "tie up" this active agent before it reacts to certain harmless odor producing compounds which are present in certain waters. In certain waters of high organic content, free residual chlorination may be prohibitive by cost but with combined residual chlorination may be feasible economically.

A combined available chlorine residual is unaffected by sunlight. It may, however, be partially removed by aeration––especially so if the residual is dichloramine.

Since a combined available chlorine residual is a weak oxidizing agent, it retains its availability in water for a long period of time (as compared with a free residual). The chloramines react either very slowly or not at all with certain organic compounds contained in the water or on the objects which come in contact with the water containing the chloramines.

Chloramines have been widely used to control chlorophenol tastes and odors. This requires careful control whereby the chlorine is united with ammonia before it has an opportunity to react with the phenols. This is done by adding ammonia before chlorine to the water. In certain other instances, chlorine is added prior to filtration and then ammonia is added after the filter to "tie up" the residual before sending the water to the distribution system. This is often done when: the ratio of length of system to water pumped is large; the treatment plant is a great distance from consumers; the distribution system contains harmless organic growths which would react with a free chlorine residual to give undesirable tastes or odors; or the system contains a large storage capacity. It is necessary to maintain exact controls over both the chlorine and ammonia fed to any water. If an excess of ammonia is placed in the water, it (as well as the ammonia freed by the normal reaction of chloramines) will be available as food for the growth of organisms. In this way, chloramines may be detrimental to a system.

The formation of monochloramine (NH_2Cl) and dichloramine ($NHCl_2$) is dependent upon the pH of the solution. The optimum pH for monochloramine formation is 8.3 with dichloramines formation favorable at the lower pH values although dichloramines may be formed above pH 8.3.

As reported in Public Health Reports (Feb. 8, 1946) the bacterial properties of chloramines with 193 series of tests performed within the limits which might be encountered within the range of practical treatment. are as follows:

Of the 193 tests:

32 were performed at 2°-6°C temperature range at pH 8.5

- 12 with Escherichia coli
- 12 with Eberthella typhosa
- 8 with Shigella sonnei

143 were performed at 20°-25°C within the pH ranges of 6.5 to 10.5

- 26 with Escherichia coli
- 24 with Eberthella typhosa
- 24 with Shigella sonnei

18 were performed at 20°-25°C with Escherichia coli in waters of pH 7.0, 8.5, and 10.5 with the available chlorine residual constant at 0.3 ppm and the nitrogen content varied so that chlorine:ammonia ratios ranging from 1:1 to 1:25 were obtained.

Results of the 193 tests:

INFLUENCE OF RESIDUAL AND EXPOSURE TIME

Regardless of the temperature of water or its pH, the amount of chloramine present and the length of contact time had a marked affect on the results. Without exception, an increase in the amount of chloramine present increased the rate of kill of E. coli, and any increase in exposure time likewise increased the extent of kill. However, marked increases in the extent of kill were not observed in 60 minutes of exposure at temperatures of 2°-6°C with less than about 1.2 ppm residual at pH 8.5, and 1.5 ppm residual at 9.5. At the higher temperature range, 20°-25°C, residuals of about 0.3 ppm and 0.6 ppm, respectively, were required to obtain approximately the same kill. Tests show that at a pH of 8.5, and at 2°-5°C, the influence of the time of exposure chloramine and the amount of chloramine present, produced approximately the same effect on the rate and extent of kill of these two genera as was observed for E. coli. The same is true at the higher temperature, 20°-25°C when the residuals were 0.9 ppm or more. At lower residuals, strains of S. sonnei tested appeared to be slightly more resistant than E. coli.

EFFECT OF VARIATION IN HYDROGEN ION CONCENTRATION (UPON CHLORAMINES)

When E. coli were exposed to the same residuals at pH 7.0 and 8.5 with a 100 per cent kill used as a criterion, 2 to 6 times (average 3.4) longer exposure periods were required at pH of 8.5. Further increase in pH (8.5 to 9.5) required approximately another two fold to four fold increase in the exposure time. Similarly, to obtain a 100 per cent kill of E. coli in the same exposure interval at pH 8.5 required 1.5 to 3 times (average 2.3) the residual needed at pH 7.0. Further shift of the pH from 8.5 to 9.5 again required a 1.3 fold increase in residual.

EFFECT DUE TO TEMPERATURE DIFFERENTIATION (UPON CHLORAMINES)

Results were obtained on a temperature differentiation of 20°C (2°-6° and 20°-25°C) and showed the following: upon a basis of 0 per cent survival and at pH values of 7.0 and 9.5, approximately nine times the exposure time of the higher was required at the lower temperature with a given concentration of chloramine. With the same exposure time, approximately 2.5 times as much chloramine was needed to produce a 100 per cent kill at the lower temperature.

VARIATIONS IN GENUS RESISTANCE

In this study, the chloramine resistance of two strains each of four genera: Eschericia, Aerobacter, Pseudomonas, and Eberthella and thirteen strains of one genus, Shigella, was investigated.

At pH 7.0 A. aerogenes were definitely the most resistant and S. dysenteriae the least resistant of the five genera studied. At pH 8.5, S. dysenteriae gain was the most sensitive and the other genera tested (including S. sonnei) all showed approximately the same resistance. At pH 9.5, the trends were about the same as at pH 7.0 and 8.5, with the exception that S. dysenteriae, though still remaining the most sensitive genus at the lower chloramine residual, appeared to be more resistant with the largest concentration, 1.8 ppm.

EFFECT OF EXCESS NITROGEN

In water at pH values of 7.0 and 8.5, there is a definite tendency for the larger amounts of nitrogen to reduce slightly the percentage of kill.

In water at pH 10.5, increased amounts of nitrogen after long periods of exposure appeared to enhance rather than to reduce the percentage of kill. With chlorine:nitrogen ratios in which the nitrogen exceeds the chlorine by seven times or more, the effect on the vactericidal efficiency of the chloramine produced was not marked. In waters of pH 7.0 to 8.5, the efficiency decreased slightly with nitrogen increases. In waters of pH 10.5, the efficiency increased slightly with nitrogen increase.

FREE RESIDUAL CHLORINATION

Free residual chlorination has been defined as the type of chlorination wherein a free available chlorine residual is maintained through a part of or all of the water system.

Free available chlorine is a strong oxidizing agent and it acts on bacteria very quickly. Often, normal concentrations kill bacteria in less than three minutes contact time. As previously mentioned, the killing time depends (among other things) upon the pH of the solution. This time is greatly increased at a pH of 9.4 and above. (In this higher pH range, the chloramine treatment is considered by many to be more effective than free available residual chlorination.)

Since free available chlorine is a strong oxidizing agent, it is used in the control of many tastes and odors. It will not, however, eliminate all tastes and odors. In certain instances, a free chlorine residual will intensify the taste and odor in the water. (An example of this is a water which contains phenolic compounds.)

Free available chlorine residual will oxidize iron and manganese compounds to insoluble products. In being used for this purpose, the chlorine should be added at or before the flash mix (and never behind the filters) in order that the insoluble compounds formed will be deposited in the sedimentation basin and on the filters. Both iron and manganese are more insoluble at a certain pH value and their removal will be affected by the addition of lime and alum. This must be taken into consideration if coagulating chemicals are to be used also.

Since a free available chlorine residual has the ability to kill many types of bacteria, its value from the health standpoint is important. This type of residual may be important economically. Harmless bacteria and slime growths may clog pipes and reduce the flow of water. Too, these growths may cause corrosion of the pipe (steel is very susceptible to corrosion). A number of plants have found it economically feasible to chlorinate the raw water with any or all of the following benefits? prevent clogging of raw water line; aid coagulation; and insure a greater margin of safety as a result of longer chlorine contact time.

A free available chlorine residual is rapidly dissipated by sunlight but it is not easily aerated from water.

Putting free available residual chlorination into practice is a relatively simple matter providing the chlorinator has adequate capacity to satisfy the maximum chlorine demand plus an allowance for the desired residual. The amount of chlorine required is influenced primarily by the amount of ammonia in the water. After chlorine is added to a water containing ammonia, chloramines are formed rapidly. Then, if there is a sufficient amount of chlorine present, these chloramines are slowly destroyed and only then can a free residual persist. In testing for chlorine residual and interpreting results, consideration of time elapsed is important. Within about two minutes after chlorination, all chloramine formation is about complete. At five minutes after chlorination, much of the chloramine is still present along with the excess free available chlorine. Twenty minutes after chlorination, most of the total residual will consist of a free available residual.

A comparison of free available residual and combined available chlorine residual by W. W. Streeter[9] (1943) is as follows: Tests on suspensions of coliform bacteria showed that a marked difference existing between the bactericidal power of free available chlorine residual and combined available residual. With a "free" residual, concentrations as low as 0.05 ppm killed all of the coliform bacteria within two or three minutes. The same concentration of chloramines required forty to ninety minutes to produce the same killing effect.

In the tests conducted by Streeter with a 0.05 ppm free available chlorine residual showed the following effect as a result of pH variation: with a pH of 8.0, the killing rate was one-half that of a similar test at a pH of

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[9] Streeter. <u>Progress Report on Studies of Water Chlorination</u>. American Water Works Association. April, 1943.

6.0-7.0. At a pH of 9.0, the killing rate was only one-third of that in the pH range 6.0-7.0.

Tests by Fair[10] indicate that in a time of thirty minutes, dichloramines were found to be 60 per cent as effective a hypochlorous acid. In a solution of the same pH, monochloramines were found to be 22 per cent as effective as hypochlorous acid. Because of the formation of relatively ineffective hypochlorite ion by free available chlorine at high pH values, chloramines actually are more efficient cysticidal agents than free chlorine. In tests of the spores of B. anthracis, dichloramines were found to be 15 per cent as effective a hypochlorous acid (in thirty minutes contact time) and monochloramines had no marked affect upon the organisms. With enteric bacteria, a dichloramine concentration 80 to 100 times that of hypochloric acid is required for a 50 per cent kill in one minute.

BREAK-POINT CHLORINATION

Possibly the most widely discussed chlorination process is break-point. Break-point chlorination has been considered by many persons to possess magicla powers in allaying water treatment ills. It has solved many problems but has definite limitations.

Until about 1938, water chlorination consisted of maintaining a residual with little if any regard as to the type of residual. The results were irregular and often contradictory. This uncertainty was due to the inability of treatment men to differentiate between the types of residuals as well as their inability to prove that chlorine residual was present. Careful laboratory analysis revealed that, with increased chlorine dosages, available

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[10] Fair, Morris, and Chang, _op. cit._, January, 1948.

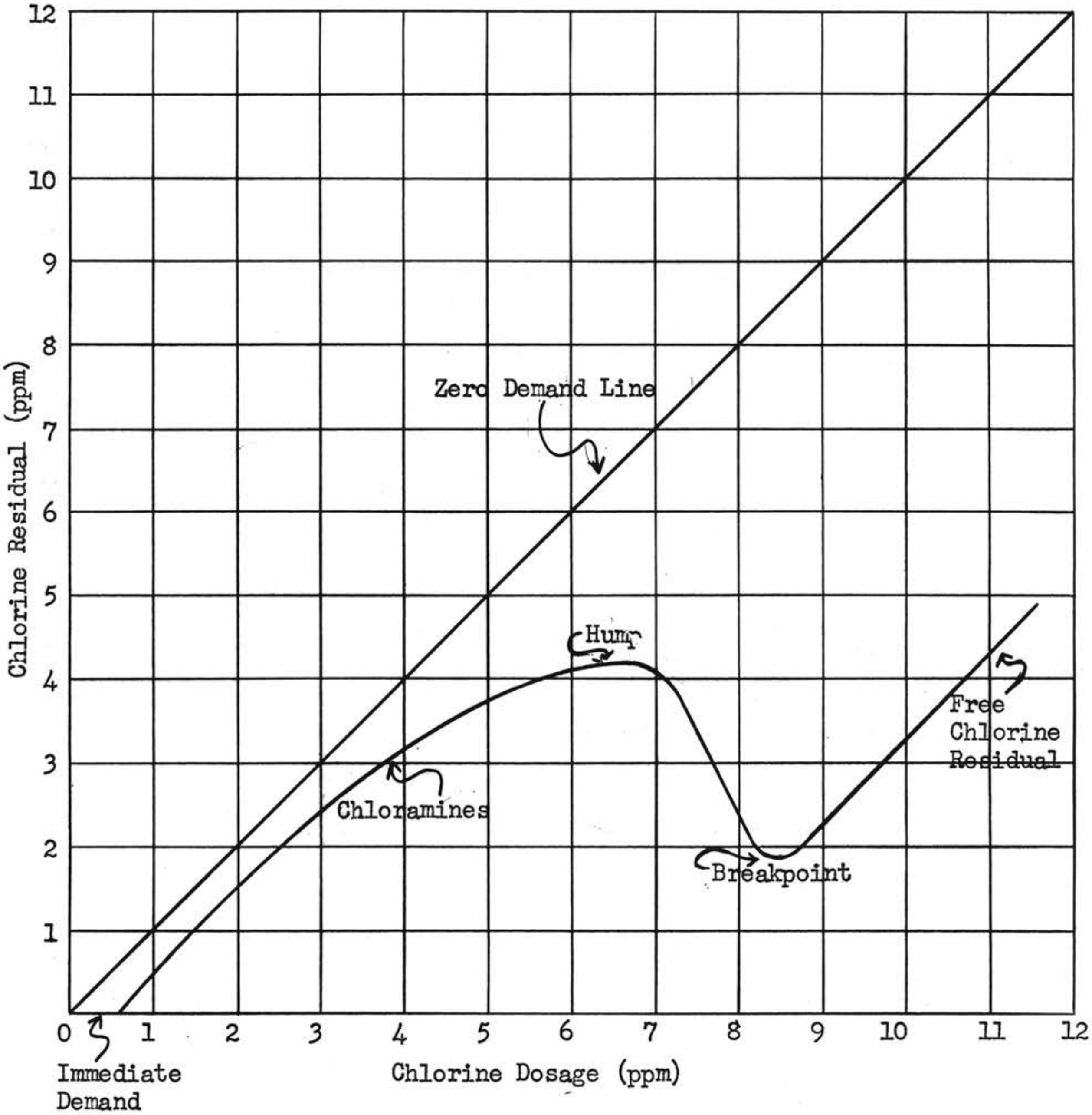
Chlorine Residual (ppm)
0
1
2
3
4
5
6
7
8
9
10
11
12
Chlorine Dosage (ppm)
Zero Demand Line
Hump
Chloramines
Breakpoint
Free Chlorine Residual
Immediate Demand

Figure 1

chlorine residuals increased to a certain point for a water, decreased, then increased again with additional dosages. The term break-point chlorination was applied to this process. Extended studies revealed that the available residual present past the break-point was a free one.

In the first portion of the above break-point curve, the ammonia or organic amines exert a demand upon the hypochlorous acid with a resultant formation of chloramines. Very little is known concerning break-point chlorination and the products of the reactions are uncertain. Possibly, the active chlorine is reduced to chloride and the ammonia-nitrogen is oxidized to a + 1 valence state, corresponding to N_2O.

Streeter found the reactions between chlorine and ammonia were very rapid at pH values of 7 and above, but were progressively retarded at pH values below 7. Where these reactions are retarded, free uncombined chlorine may be present for short periods of time.

Experiments with break-point chlorination show:

1. The rate of reaction is strongly dependent upon the pH of the solution.
2. One of the substances concerned in break-point process is probably dichloramines.
3. The rate of reaction is only slightly dependent upon the temperature of the solution.
4. The rate of reaction is very dependent on the total concentration of disoolved salts.

The change from combined to free available residual is not a sharp one. It is quite possible to have both types of residuals present in a water over a rather wide range of dosage. Even though a break-point test were made for a certain water to be treated in a plant, it would be very difficult to satisfactorily apply the results to plant operation. A simple definition[11]

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[11] Wallace and Tiernan, op. cit.

is "break-point chlorination is the application of chlorine to water containing ammonia to produce a free available chlorine residual which is 85 per cent of the total residual." Break-point chlorination may be applied to a plant without first making either a test for ammonia content or a jar test to find the breaking point for that particular water.

In starting break-point chlorination at a plant, at least two testing places should be selected as control points and the chlorine dosage varied until the desired free available chlorine residual is present in the finished water. Point number one should be at a place which will permit approximately twenty minutes contact time of chlorine with water. Point two should permit a check of the finished water. The amount of residual required at point number two is determined by the residual necessary in the distribution system and to obtain a safe water.

A number of experiments were performed by Streeter to investigate some of the properties of break-point chlorination. The free available chlorine residuals and the available chloramine residuals each were determined by three methods: orthotolidine (O-T), starch-iodide, and electrometric. Several points were taken along break-point residual curves and the bactericidal rates observed. The highest killing rates along the pre-break-point chlorination section of the curve occurred at the crest where the indicated concentration of chloramine was the greatest. Although these bactericidal rates were high in comparison with the lower chloramine values, they were very low as compared with those immediately following the break-point where free available chlorine residual began to appear. This bactericidal value coincided with the oxidation-reduction potential reading which showed a sharp upturn at the break-point. The chlorine:ammonia ratio influenced the bactericidal effect as follows: Complete bacterial kill ranged from about five hours with ratio of 1:1 or below to about two minutes with a ratio of 11:1 or more. Ratios from 7:1 up to 12:1, when observed on the downward limb of the break-point curve, showed a more active killing power than ratios of 5:1 or less, although higher O-T residuals were present in the latter case.

TEST FOR AVAILABLE CHLORINE RESIDUALS

Ortho-tolidine is the most widely used reagent for determining available residuals. It is easy to use, economical, and requires very little time to determine a chlorine residual in water. It also may be used to differentiate between a free available residual and a combined available (or chloramine) residual. A recent addition to this test is the use of a secondary reagent "sodium arsenite" which makes possible the determination of "interfering agents". These are compounds in the water which indicate a false chlorine residual when the determination is made with ortho-tolidine only.

At water temperatures of $60^{\circ}F$ or less, the combined available chlorine residual develops a color slowly with ortho-tolidine reagent (O-T). If 5.0 ml of O-T per 100 ml of water sample is used and the O-T is 15 per cent acid by volume, the maximum color development with the combined available chlorine residual will be obtained in about five minutes (at a temperature of $60^{\circ}F$ or below). At all water temperatures, the free available chlorine residual will almost immediately develop a color with O-T reagent. This reaction and subsequent color development will take place within about five seconds even in waters having a temperature just above freezing. Thus, one difference between a combined and a free chlorine residual is their reaction with ortho-tolidine at low temperatures.

To make a control test to determine the amount of free chlorine residual and combined chlorine residual in a water, arsenite may be used. Arsenite destroys both types of chlorine residuals, but not the color which had developed (between the chlorine and O-T) prior to the addition of arsenite. Thus, if arsenite is added before O-T to a water containing an available chlorine residual, the arsenite destroys the chlorine which has not reacted with ortho-tolidine at that instant. If both types of residuals are present in a water free of any interfering agents, each residual may be determined as follows: 0.75 ml of ortho-tolidine is added to a 15 ml sample and 0.25 ml or arsenite is added five seconds later. The chlorine residual determined with a comparator is the amount of free available chlorine residual. To another cell, 0.75 ml of O-T is added to a 15 ml of sample and the comparator reading is the total available chlorine residual. The difference between total and free residual is the combined available residual.

One disadvantage of ortho-tolidine in testing for a chlorine residual in water is that the O-T combines with certain interfering agents to produce a color like that produced by chlorine even though available chlorine may not be present in the water. The amount of interference caused by these compounds (manganic manganese, ferric iron, and nitrates), may be determined with arsenite in the comparator test and allowances made accordingly. When arsenite is placed in water, it has no affect upon the color already produced with O-T which has been added to a water containing one of these interfering agents. Therefore, if arsenite is added before ortho-tolidine to a water sample, the available chlorine is "tied up" by the arsenite and any color produced with the subsequent addition of O-T is due to one or more of these interfering agents.

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