Course Number : CE 332
Course Name : Environmental Engineering Lab
Course Credit : 1.50

Experiment No. 13
Residual Chlorine and Chlorine Demand: Break Point Chlorination

INTRODUCTION

Chlorination of public water supplies and polluted waters serves primarily to destroy or deactivate disease-producing microorganisms. The practice of disinfection with chlorine is widely practiced. Chlorination may produce some adverse effects including taste and odor problem. In recent years, chlorination has been found to produce trihalomethanes (THMs) and other organics of health concern (THMs are suspected human carcinogens). Thus, use of alternative disinfectants, such as chlorine dioxide and ozone that do not cause this particular problem, is increasing.

CHEMISTRY OF CHLORINATION

Disinfectant capabilities of chlorine depend on its chemical form in water, which in turn is dependent on pH, temperature, organic content of water, and other water quality factors. Chlorine is used in the form of free chlorine [e.g., chlorine gas] or as hypochlorites [e.g., NaOC1 and $Ca(OCl)_2$]. Chlorine applied to water either as free chlorine or hypochlorite initially undergoes hydrolysis to form free chlorine consisting of aqueous molecular chlorine, hypochlorous acid and hypochlorite ion.

$$Cl_2 + H_2O = HOC1 + H^+ + Cl^- \quad (1)$$
$$NaOC1 = OC1^- + Na^+ \quad (2)$$
$$Ca(OC1)_2 = 2\,OC1^- + Ca^{2+} \quad (3)$$
$$HOC1 = H^+ + OCl^- \quad (4)$$

The relative proportion of these "free chlorine" forms is pH and temperature-dependent. Figure 1 shows a distribution diagram for the various chlorine species (Cl_2, HOC1, OCl^-) over a broad pH range.

Figure 1 shows that Cl_2 can be significant only at low pH values (below pH 2); while HOC1 is dominant between pH 3 and 6. Between pH 6 and 9, the relative fraction of HOC1 decreases, while the corresponding fraction of OCl^- increases. The dissociation of HOC1 is also temperature dependent. The effect of temperature is such that at a given pH, the fraction of HOCl will be lower at higher temperatures. Generally, the disinfectant capabilities of HOCl are greater than that of OCl, especially at short contact times (Montgomery, 1985).

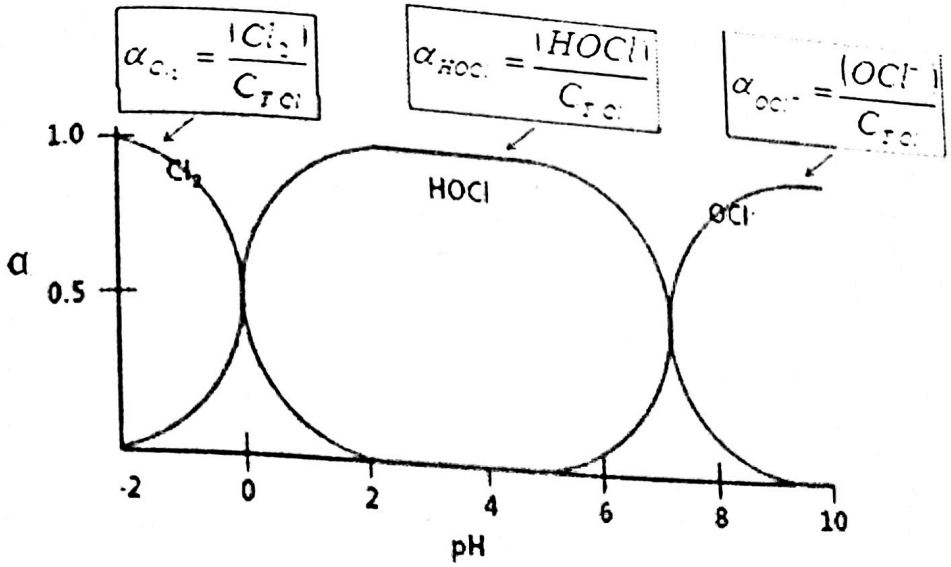


Figure 1: Distribution diagram for chlorine species at 25°C (Total Chlorine, $C_T = 10^{-3}$ M)

Reactions with Impurities in Water:

Reactions with Ammonia: Free chlorine reacts readily with ammonia and certain nitrogenous compounds to form what are collectively known as "combined chlorine". The inorganic chloramines consist of three species: monochloramine (NH_2C1), dichloramine ($NHC1_2$) and trichloramine or nitrogen trichloride ($NC1_3$). The presence and concentrations of these combined forms depend on a number of factors including the ratio of chlorine to ammonia-nitrogen, chlorine dose, temperature, pH and alkalinity.

$$NH_3 + HOC1 = NH_2C1 + H_2O \quad (5)$$
$$NH_2C1 + HOC1 = NHC1_2 + H_2O \quad (6)$$
$$NHC1_2 + HOC1 = NC1_3 + H_2O \quad (7)$$

In addition to chlorinating ammonia, chlorine also reacts to oxidize ammonia to chlorine-free products (e.g., nitrogen gas and nitrate) as shown below.

$$3\,Cl_2 + 2\,NH_3 = N_2(g) + 6\,H^+ + 6\,Cl^- \quad (8)$$
$$4\,Cl_2 + NH_3 + 3\,H_2O = 8\,Cl^- + NO_3^- + 9\,H^+ \quad (9)$$

The mono- and dichloramines have significant disinfecting power and are therefore of interest in the measurement of chlorine residuals. Combined chlorine in water supplies may be formed in the treatment of raw waters containing ammonia; chlorinated wastewater effluents, as well as certain chlorinated industrial effluents normally contain only combined chlorine.

Reactions with Other Impurities: Chlorine combines with various reducing agents and organic compounds thus increasing the chlorine demand which must be satisfied before chlorine is available to accomplish disinfection.

Fe^{2+}, Mn^{2+}, NO_2^-, and H_2S are examples of inorganic reducing agents present in water supplies that will react with chlorine. Chlorine can react with phenols to produce mono-, di-, or trichlorophenols, which can impart tastes and odors to waters. Chlorine also react with humic substances present in water to form trihalomethanes (THMs, e.g., chloroform, bromoform, etc.) which are suspected human carcinogens (Note: According to USEPA, maximum allowable level of THMs in drinking water is 100 µg/L).

Break Point Chlorination:

If chlorine is added to water containing reducing agents and ammonia (either naturally present or added to water to produce combined chlorine), a hump-shaped breakpoint curve is produced.

The different segment of the curve is described below:

a. If the water is free of ammonia and other compounds that may react with chlorine, the application of chlorine will yield free available chlorine residual of same concentration. This is denoted by the *"no demand line"* or the "zero demand line".

b. Chlorine first reacts with reducing agents such as H_2S, Fe^{2+}, Mn^{2+} and develops no measurable residual as shown by the portion of the curve from A to B.

c. Addition of chlorine beyond point B results in forming mainly mono- and di-chloramines. With mole ratios of chlorine to ammonia up to 1:1 [i.e., Cl_2:NH_3-N = 1:1], both mono and di-chloramines are formed. Chloramines thus formed are effective disinfectants.

d. Further increase in the mole ratio of chlorine to ammonia result in formation of some trichloramine and oxidation of part of ammonia to N_2 and NO_3^- (see Eq. 8, 9). These reactions are essentially complete when 1.5 mole of chlorine has been added for each mole of ammonia nitrogen originally present in water [i.e., Cl_2:NH_3-N = 1.5:1]. This is represented by the portion of the curve from C to D.

e. Addition of chlorine beyond point D would produce free chlorine residuals and is referred to as *"breakpoint chlorination"*. In other words, chlorination of water to the extent that all ammonia is converted to N_2 or higher oxidation state is referred to as *"breakpoint chlorination"*.

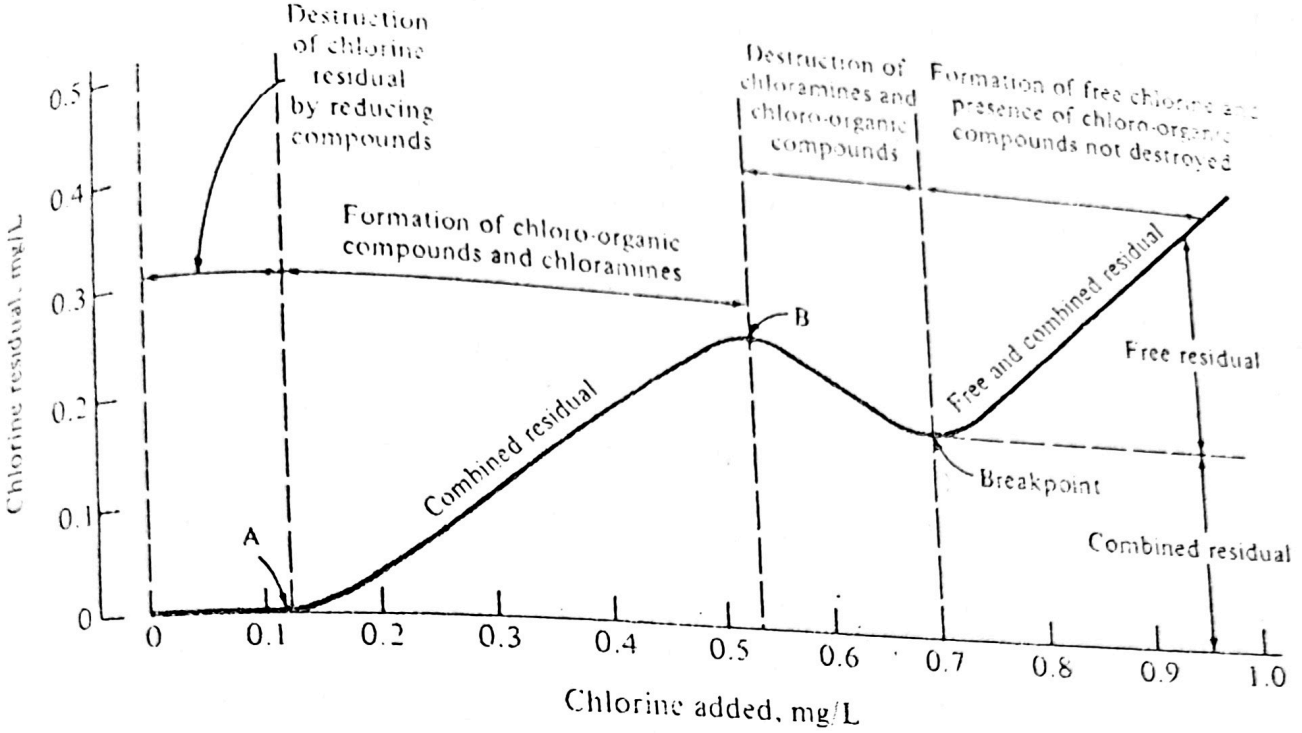


Figure 2: Generalized curve obtained during breakpoint chlorination (Source: Peavy and Rowe, 1985)

Breakpoint chlorination is required to obtain a free chlorine residual for better disinfection if ammonia is present in a water supply. While free chlorine residuals have good disinfecting powers, they are usually dissipated quickly in the distribution system. For this reason, final treatment with ammonia if often practiced to convert free chlorine residuals to longer-lasting combined chlorine residuals. The difference between the amount of chlorine added to the water and the amount of residual chlorine (i.e., free and combined available chlorine remaining) at the end of a specified contact period is termed as *"chlorine demand"*.

REAGENTS:

1. Starch Indicator
2. Standard 0.001N Sodium thiosulfate
3. Potassium Iodine crystal
4. Cone. Hydrochloric Acid
5. Chlorine water

APPARATUS:

1. Erlenmeyer flask (250 ml) : 1 no.
2. Bottle (8-oz) : 6 nos.
3. Beaker (250 ml) : 1 no.
4. Measuring cylinder : 1 no.
5. Dropper : 1 no.
6. Stirrer : 1 no.

PROCEDURE:

1. Place 200-ml portion of the water to be chlorinated in each of six 250-mL flasks.
2. Add required quantity (as instructed by your teacher) of "chlorine water" (stock solution of bleaching powder in water) in each of the flasks. The chlorine content of the "chlorine water" (determined earlier in the laboratory) would be provided to you by your teacher. Calculate the chlorine dose for each of the six flasks.
3. Shake each flask gently and allow to stand for 30 minutes.
4. Determine residual chlorine of water from each flask by the starch-iodine method as described below:

Starch-Iodine Method:

The starch-iodine method is based on the oxidizing power of free and combined chlorine residuals to convert iodide ion into free iodine as shown below.

$$Cl_2 + 2I^- = I_2 + 2\,Cl^-$$

I_2 + starch → blue color (qualitative test for the presence of Chlorine)

In the starch-iodine method, the quantity of chlorine residuals is determined by measuring the quantity of iodine released by titration with a reducing agent sodium thiosulfate ($Na_2S_2O_3$). The end point of titration is indicated by the disappearance of blue color.

$$I_2 + 2\,Na_2S_2O_3 = Na_2S_4O_6 + 2\,NaI$$

Or,
$$I_2 + 2\,S_2O_3^{2-} = S_4O_6^{2-} + 2I^-$$

The procedure to be followed in the laboratory is described below:

(a) Place 200 ml of the sample in an Erlenmeyer flask. Chill to 20^0C or lower by immersing the flask in a bath of ice-water.
(b) Add a small crystal of potassium iodine and 1 mL of concentrated hydrochloric acid to the water.
(c) Add 1 ml of starch solution to the water. A blue color shows the presence of chlorine in the water.
(d) Titrate the solution with standard sodium thiosulfate ($Na_2S_2O_3$) solution until the blue color just disappears.
(e) Record the quantity (in mL) of sodium thiosulfate ($Na_2S_2O_3$) solution used.

CALCULATION:

Residual chlorine (mg/L) = mL of 0.001N Sodium thiosulfate used × Multiplying Factor (MF)

where, MF = normality of $Na_2S_2O_3$ × equivalent wt. of Cl_2 × 1000 / (ml of sample taken)
$= 0.001 \times 35.45 \times 1000/200 = 0.1773$

ASSIGNMENT QUESTIONS

(1) What are the major disadvantages of chlorination? Name some of the alternate disinfectants.

(2) You would like to perform chlorination to a water sample with pH 7.5. At this pH, what would be the relative proportions of HOC1 and OCl^- (see Figure 1). What kind of change in pH would you propose in order to increase the relative proportion of HOC1, which is a better disinfectant?

(3) Schematically draw a "chlorine residual" versus "chlorine dose" curve for a water sample with no ammonia or organic matter.