Break Point Chlorination

Introduction

Chemistry

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., NaOCl and $Ca(OC1l)_2$]. 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.

Chemistry

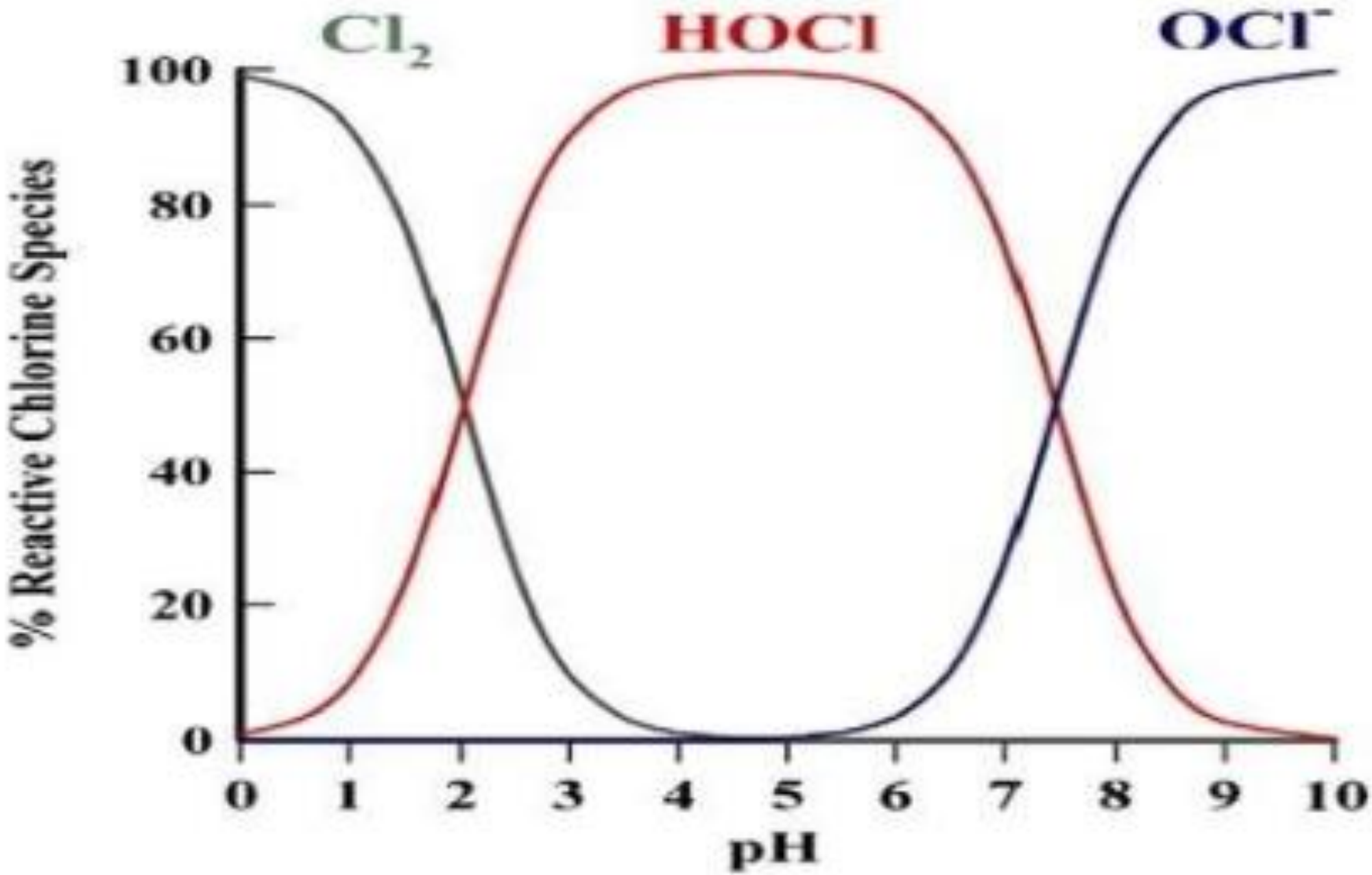
$Cl_2 + H_2O = HOCl + H^+ + Cl^-$

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

$Ca(OCl)_2 + 2H_2O = Ca^{2+} + 2HOCl + 2OH^-$

$NaOCl + H_2O = Na^+ + HOCl + OH^-$

The two chemical species formed by chlorine in water, hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) along with Cl_2 are commonly referred to as “free” or “available” chlorine.


Cl_2
HOCl
OCl^-
100
80
60
40
20
0
% Reactive Chlorine Species
0 1 2 3 4 5 6 7 8 9 10
pH

Chemistry

Cl_2 can be significantly at low pH values (below pH 2); while HOCl is dominant between pH 3 and 6. Between pH 6 and 9, the relative fraction of HOCl decrease, while the corresponding fraction of OCl^- increases. Generally disinfectant capabilities of HOCl are greater than that of OCl, especially at short contact times. The dissociation of HOCl 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.

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_2Cl), dichloramine ($NHCl_2$) and trichloramine or nitrogen trichloride (NCl_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.

Reactions with Ammonia

$NH_3 + HOCl = NH_2Cl + H_2O$; pH 4.5 to 8

$NH_2Cl + HOCl = NHCl_2 + H_2O$; pH 4.5 to 8

$NHCl_2 + HOCl = NCl_3 + H_2O$; pH < 4.5

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

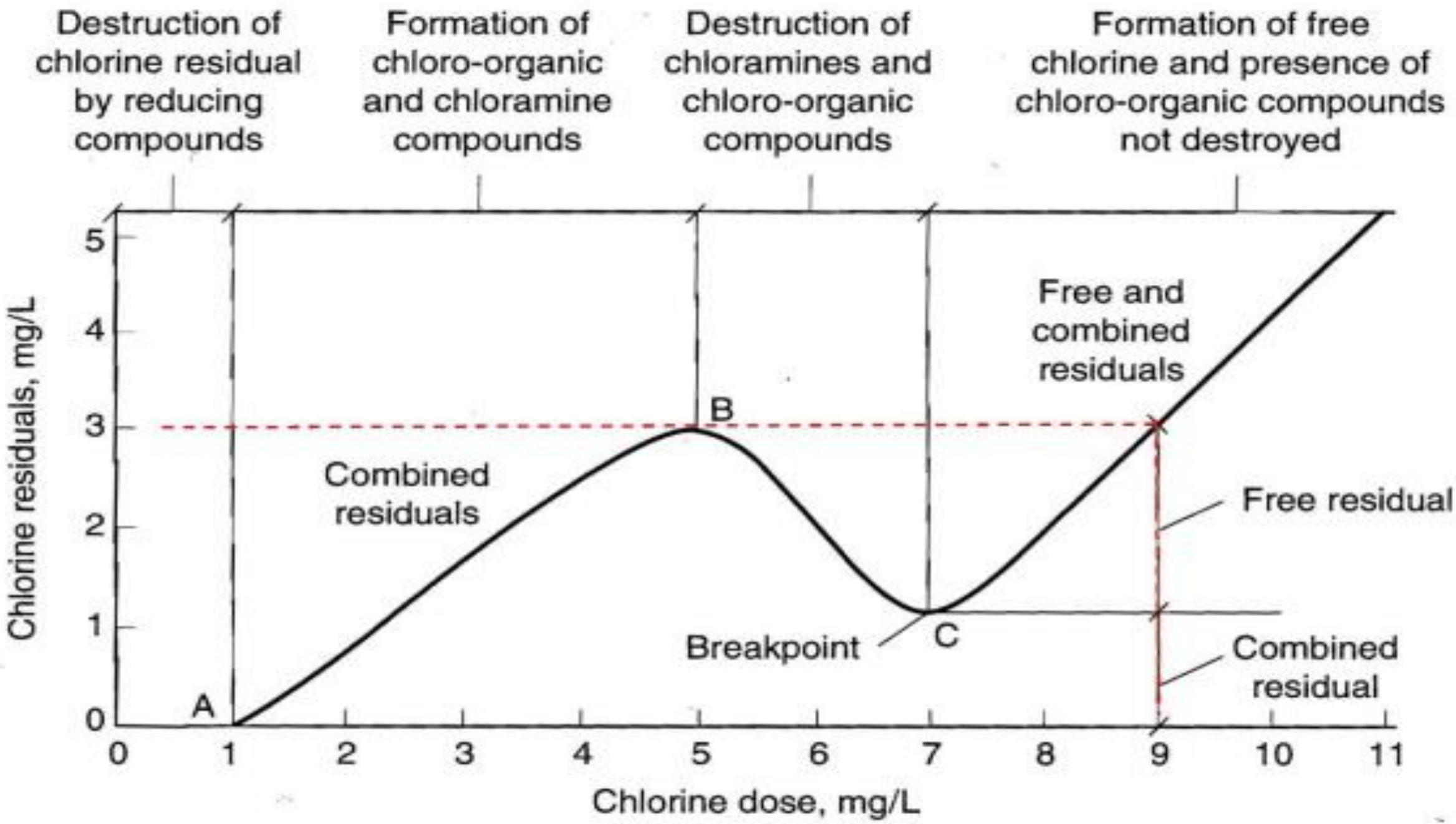
Chlorine combines with various reducing agents and organic compounds thus increasing the chlorine demand which must be satisfied before chlorine is available to accomplish disinfection. Fe^{2+}, Mn^{2+} ,NO_2^-, and H_2S are examples of inorganic reducing agents present in water supplies that will react with chlorine. Chlorine can react with phenols to produce mono-, di- or trichlorophenols, which can impart tastes and odors to waters, Chlorine also reacts with humic substances present in water to form trihalomethanes (THM).

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 as shown in following figure.

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 as shown in following figure. But 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 “no demand line” or “zero demand line”.


Destruction of chlorine residual by reducing compounds
Formation of chloro-organic and chloramine compounds
Destruction of chloramines and chloro-organic compounds
Formation of free chlorine and presence of chloro-organic compounds not destroyed
Chlorine residuals, mg/L
Chlorine dose, mg/L
Free and combined residuals
Combined residuals
Free residual
Combined residual
Breakpoint
A
B
C
0
1
2
3
4
5
6
7
8
9
10
11

Break Point Chlorination

$3\ Cl_2 + 2\ NH_3 = N_2\ (g) + 6H^+ + 6\ Cl^-$

$4Cl_2 + NH_3 + 3H_2O = 8Cl^- + NO_3^- + 9H^+$

Addition of chlorine beyond point C 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".

Environmental Significance

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 is 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 and Apparatus

Procedure

Calculation

Residual chlorine (mg/L) = mL of 0.025N sodium thiosulfate used x M.F.

$$\textbf{M.F.} = \frac{\text{Normality of } N_2S_2O_3 \text{ X Equivalent wt.of } Cl_2 \text{ X } 1000}{\text{mL of sample taken}}$$

Graph

Discussion

Assignment