Chlorine Chemistry For Water and Waste Treatment

SEVERN TRENT SERVICES

Disinfection Products

Dosage - The amount of chlorine added to the water. Usually expressed as parts per million (ppm), that is, pounds of chlorine per one million pounds of water. Can be equivalently expressed as milligrams per liter (mg/l).

Demand - The amount of chlorine used up or consumed by bacteria, algae, organic compounds and some inorganic substances like iron and manganese. Chlorine demand is time dependent since many of the reactions are not instantaneous and need time to be carried to completion. Normally expressed as ppm (mg/l).

Residual - The amount of chlorine remaining in the water at the time of measurement. Since chlorine demand is time dependent so is chlorine residual. Normally expressed as ppm (mg/l).

DOSAGE - DEMAND = RESIDUAL

NOTE: Since dosage, demand and residual are normally expressed as parts per million, the following formula will be helpful:

English: lb/day = gpm x ppm* x 0.012
where lb/day = pounds per day chlorine feed
gpm = gallons per minute water flow
ppm = dosage in parts per million

Metric: kg/h = l/s x mg/l* x 0.0036
kg/h = m^3/h x mg/l*x 0.00
where kg/h = kilograms per hour
l/s = liters per second
m^3/h = cubic meters per hour
mg/l =milligrams per liter
*ppm = mg/l

Free Chlorine Residual - When chlorine dissolves in water, a mixture of hypochlorous and hydrochloric acids is formed:

$Cl_2 + H_20$ ------> HOCI + HCI (Eq. 1)
Hypochlorus Acid; Hydrochloric Acid

Actually, the HCI always completely dissociates into hydrogen and chloride ions:

$HCI \text{ -----> } H^+ + Cl^-$

The hypochlorous acid only partially dissociates (because it is a so-called "weak acid ") into hydrogen and hypo-chlorite ions: $HOCI \text{ -----> } H^+ + OCI^-$

The extent of this dissociation is pH dependent. In slightly alkaline solution (pH 7.5) the chlorine is equally divided between the two forms (see Fig. 1). As the water becomes more alkaline (higher pH), more and more hypochlorite is formed. At pH 10 all chlorine exists as hypochlorite. The reverse is true as solutions become more acidic (pH below 7) with increasing amounts of hypochlorous acid being formed. At pH 5 chlorine exists solely as HOCI.

In either the HOCI or OCI^- form, chlorine is called FREE CHLORINE RESIDUAL. As far as killing power toward bacteria is concerned the HOC, existing at lower pH values is more effective.

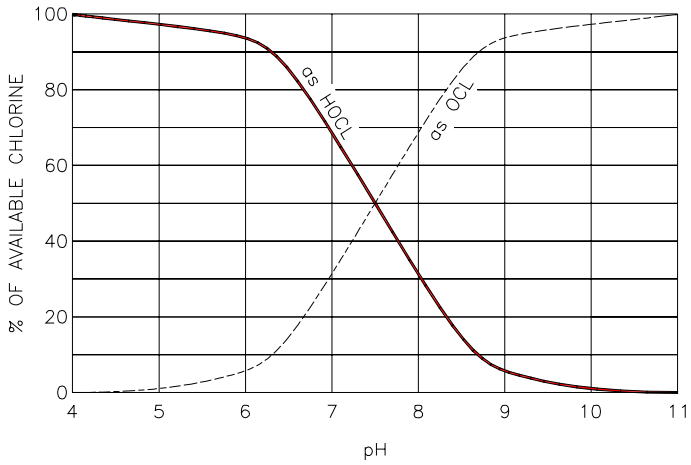

Figure 1 - Relationship between HOCl and OCI^- at various pH values

Combined Chlorine Residual - If the chlorinated water contains ammonia or certain amino (nitrogen based) compounds, as is the case with sewage, additional compounds called chloramines are formed. The possible reactions between HOCI and ammonia are as follows:

$NH_3 + HOCI \text{ -----> } H_2O + NH_2CI$ (Monochloramine)

$NH_3 + 2HOCI \text{ -----> } 2H_2O + NHCI_2$ (Dichloramine)

$NH_3 + 3HOCI \text{ -----> } 3H_2O + NCI_3$ (Nitrogen Trichloride)

These reactions occur essentially instantaneously and are pH dependent. At pH levels above 8.5 only mono-chloramine is formed, below this, mixtures of mono and dichloramine result, and below pH4.2 only nitrogen trichloride exists.

Chloramines collectively are called COMBINED CHLORINE RESIDUAL and have a much lower bactericidal effectiveness than Free chlorine residual.

Total Chlorine Residual - The sum of free and combined chlorine residual equals the TOTAL CHLORINE RESIDUAL.

FREE + COMBINED = TOTAL

NOTE: Methods are available for both laboratory and continuous measurement of Free Chlorine Residual and Total Chlorine Residual. Combined Chlorine Residual must be determined by subtracting Free residual from Total.

Available Cl_2 - The term “available “chlorine is commonly used. It means, simply, the concentration of chlorine in any of its oxidized forms that is available for disinfection or other oxidizing reactions. Thus, it is correct to term chloramines as combined available chlorine and hypochlorite and hypochlorous acid as free available chlorine. Once available chlorine oxidizes something, it is reduced to the chloride ion (Cl^-) and it is no longer ”available". Normally expressed as ppm (mg/l).

NOTE: By definition, chlorine gas is 100% available even though it forms equal amounts of oxidized chlorine and reduced chloride when dissolved in H_2O (see Eq. 1).

Breakpoint Chlorination

Theory - When sufficiently high chlorine dosages are applied to waters containing ammonia and ammonia compounds, different reactions will occur resulting in the destruction of the ammonia and the formation of a free chlorine residual. Fig. 2 shows what typically occurs with increasing chlorine dosages for water containing ammonia.

Low chlorine dosages result in the formation of mono and dichloramine and are depicted as increasing residual on the left end of the curve. The peak of the curve occurs when all of the free ammonia is used up forming chloramines. With excess chlorine due to higher dosages, the chloramines are unstable and destruction occurs due to one or both of the following reactions:

$$2NH_2Cl + HOCl \text{ -----> } N_3 + H_2O + 3HCl$$

$$NH_3Cl + NHCl_2 \text{ -----> } N_2 + 3HCl$$

This accounts for the downward sloping portion of the curve on the right side of the peak. When the dosage reaches approximately 8 to 10 times the ammonia concentration (the theoretical ratio is 7.6 but side reactions also occur) the “breakpoint “ is reached indicating that all the ammonia compounds have been destroyed. Further increases in chlorine dosage result in the formation of free chlorine residual. Complete destruction of ammonia seldom occurs at breakpoint and some chloramines invariably persist in the presence of free chlorine.

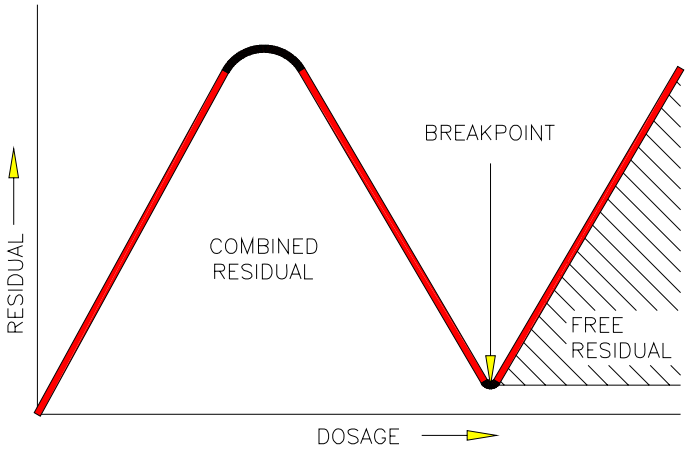

Figure 2 - Breakpoint Curve

Design improvements may be made without notice.
Represented by:

Severn Trent Services
3000 Advance Lane Colmar, PA 18915
Tel: 215-997-4000 • Fax: 215-997-4062
Web: www.severntrentservices.com
E-mail: marketing@severntrentservices.com