Break Point Chlorination

As chlorine is added, it is consumed by chemical reaction with the net effect of a rise in chlorine concentration. The slope will depend on addition rate and reaction rate. For the usual rates of addition, the reaction rate will suddenly speed up so that the concentration of chlorine falls. This is explained by the ease with which chlorinated compounds accept more chlorine. In other words, the rate of addition of the first atom of chlorine is relatively slow, but rates are greater for further reaction because chlorinating potentiates reactivity. When most of the reactions with chlorine are complete, the addition of more chlorine results in a permanent residual. A reasonable time for the experiment is 30 minutes. The point at which the concentration returns to an upward slope is termed the ***breakpoint***. There may be no breakpoint observed for certain waters because different organic compounds react at various rates.

http://www.youtube.com/watch?v=3rXZg6VDVRQ

Chloramines / Combined Chlorine

If you smell "chlorine", coming from your water, what you really smell are combined forms of chlorine, also called chloramines. Chloramines are chemical compounds formed by chlorine combining with nitrogen containing contaminates in the water. These, are still disinfectants, but they are 40 to 60 times less effective than free available chlorine.

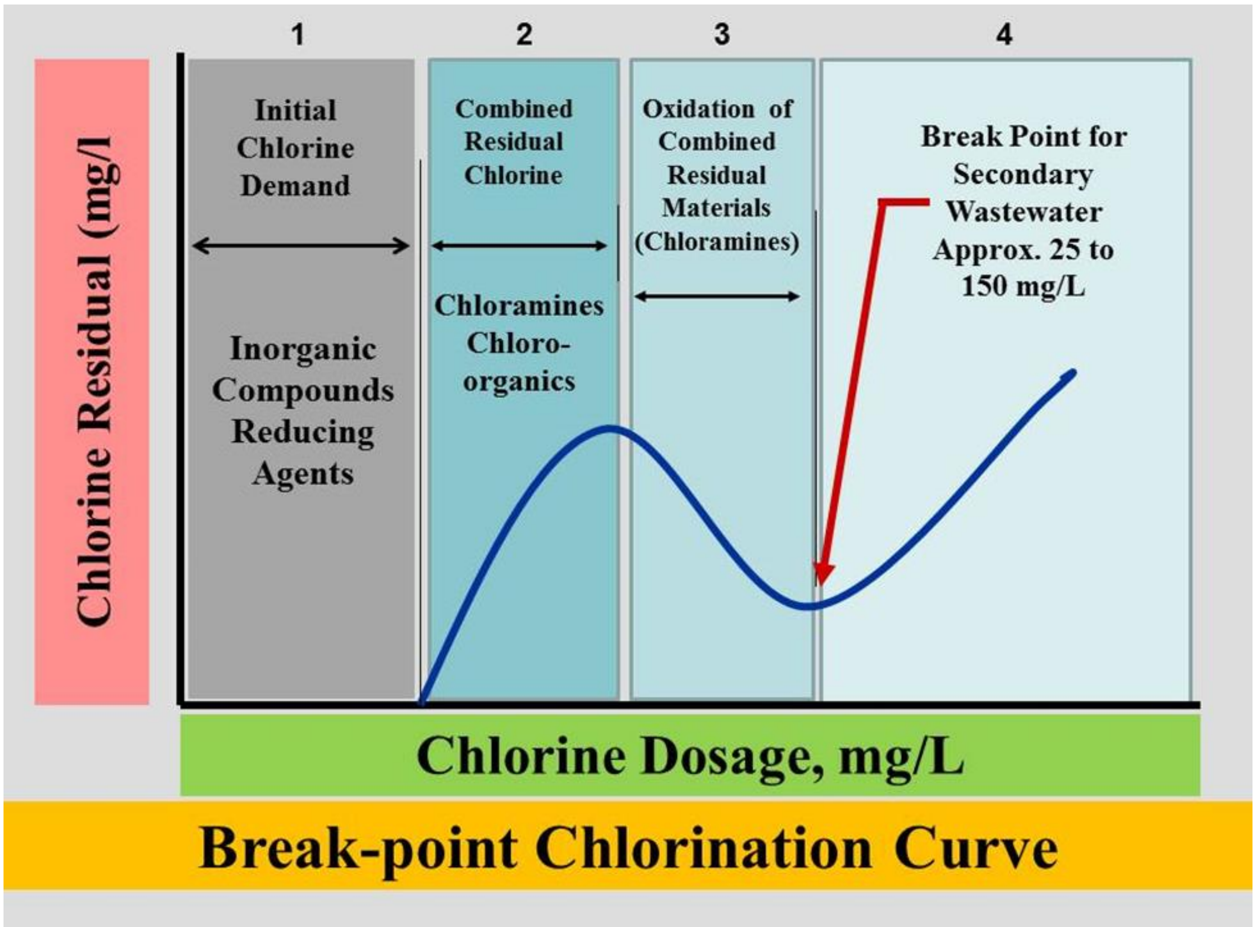
Three types of chloramines can be formed in water - monochloramine, dichloramine, and trichloramine. Monochloramine is formed from the reaction of hypochlorous acid with ammonia. Monochloramine may then react with more hypochlorous acid to form a dichloramine. Finally, the dichloramine may react with hypochlorous acid to form a trichloramine. Trichloramines cause the "chlorine" smell and hang in the air directly above the water level, often causing competitive or frequent swimmers to have asthma like symptoms. High levels of chloramines will also cause corrosion to surfaces and equipment. The trichloramines are especially irritating to the eyes, nose and lungs.

Chloramines can usually be eliminated from the water by performing breakpoint chlorination with chlorine or super oxidation with a non chlorine oxidizer. Ultraviolet systems and ozone systems are effective at reducing chloramines in water.

Breakpoint chlorination

Break point chlorination is adding enough chlorine to eliminate problems associated with combined chlorine. Specifically, breakpoint chlorination is the point at which enough free chlorine is added to break the molecular bonds; specifically the combined chlorine molecules, ammonia or nitrogen compounds. It takes a ratio of chlorine to ammonia atoms of 7.6 to 1 to reach breakpoint, other contaminants (i.e. bacteria, algae) are also present that must be oxidized, so 10 times the amount of combined chlorine must be added. When sufficient free chlorine (FC) is added to water, the inorganic chloramines are converted to dichloramine, then to nitrogen trichloride, and then to nitrogen gas. Any excess chlorine leftover will become the chlorine residual (FC).

The graph below shows what happens when chlorine (either chlorine gas or a hypochlorite) is added to water. First (between points 1 and 2), the water reacts with reducing compounds in the water, such as hydrogen sulfide. These compounds use up the chlorine, producing no chlorine residual.



Achieving Breakpoint Chlorination

To achieve the breakpoint, the free chlorine (FC) added to the water must be about ten times the amount of combined chlorine (CC). This is an “all or nothing” process. Not adding enough chlorine to reach breakpoint will make the problem even worse as the result is the formation of more chloramines and re-dissolving of chloramines back into the tank. Continual “shocking” but not reaching breakpoint will result in the tank reaching a point of no return. Partial or complete draining of the tank and refilling with fresh water may be the only remedy at this point

Calculating Amount of Chemical to Achieve Breakpoint Chlorination

The DPD test does not measure combined chlorine (CC) directly, it measures free chlorine (FC) in Step 1 and total chlorine (TC) in Step 2. Total Chlorine is the sum of free chlorine and combined chlorine. Therefore combined chlorine is the difference between total chlorine and free chlorine. CC = TC – FC.

The first step in determining the necessity of a shock treatment is to determine the level of combined chlorine.

Using the D.P.D. testing kit, test for **free chlorine (FC)** and **total chlorine (TC)**. After completing the water test, you subtract the free chlorine reading from the total available chlorine reading, the result indicates the **combined chlorine (CC)** or chloramine level in the water.

For example:

Combined Chlorine = Total Chlorine - Free Chlorine

2.3 mg/L (TC) measured from test kit - 1.5 mg/L (FC) measured from test kit = 0.8 mg/L CC.
If the water has no chloramines, the answer to the subtraction will be zero (0) and a shock treatment is not needed. This is a desirable level. After determining the level of combined chlorine in the tank water, the operator must determine the breakpoint chlorination for that value.

The breakpoint chlorination value is 10 times the combined chlorine (CC) level.

For example: 0.8 mg/L (CC) from the above example × 10 = 8 mg/L of chlorine to achieve breakpoint.

Taking into account the free chlorine already in the tank, chlorine will have to be added to the level of 8 mg/L.

Determine the Amount of chemical to add*:

Example**: Calculate the chemical change to achieve Breakpoint Chlorination in 60,000 gallon TANK with FC of 1.5 mg/L and TC of 2.3 mg/L. What would be the amount of calcium hypochlorite needed if the chlorine source is 67% Calcium Hypochlorite:

STEP 1: Determine the amount of Combined Chlorine (CC)

Total Chlorine (TC) – Free Chlorine (FC) = Combined Chlorine (CC)

2.3 mg/L – 1.5 mg/L = **0.8 mg/L**

STEP 2: Calculate the breakpoint Chlorination (BPC) amount

Breakpoint (BPC) = CC × 10

0.8 × 10 = **8.0 mg/L**

STEP 3: Determine the desired change amount

Desired Change = BPC – FC

8.0 mg/L – 1.5 mg/L = **6.5 mg/L**

Lbs = Volume (V) (MG) x 8.34 ls/gallon x Concentration (mg/l)

= 60,000 gallons/1,000,000 gallons/million
= 0.06 MG

= 0.06 MG x 8.34 x 6.5 mg/l

= 3.25 lbs of pure chlorine

Since the source of chlorine is from 67% Calcium Hypochlorite then

$$= \frac{3.25 \text{ lbs}}{0.67}$$

= 4.85 lbs of Calcium Hypochlorite