Tech Brief

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Chlorination

By **Lorene Lindsay**, NDWC Engineering Scientist

Summary

Beginning with its use for the Jersey City drinking water supply in 1908, chlorination has been the most commonly used disinfection technique for public drinking water. Chlorine provides good disinfection and is effective against a wide range of pathogens in drinking water. Recently, however, many water treatment plants have altered their disinfection strategies because of regulation changes concerning disinfection byproducts. Nevertheless, chlorination remains the most cost-effective and reliable disinfection method available.

What is chlorine?

Chlorine is greenish-yellow in its gaseous form and is 2.5 times heavier than air. It is extremely corrosive and will react violently with organic substances. For example, when petrochemicals are mixed with chlorine, they produce a dangerous explosive. Stored chlorine must be kept away from all sources of organic chemicals, and it must be protected from sunlight, moisture, and high temperatures.

Chlorine's corrosive nature requires that systems use special materials on all chlorination equipment. Systems must use corrosion-resistant piping, valves, and metering equipment and keep this equipment free from contaminants, including oil and grease.

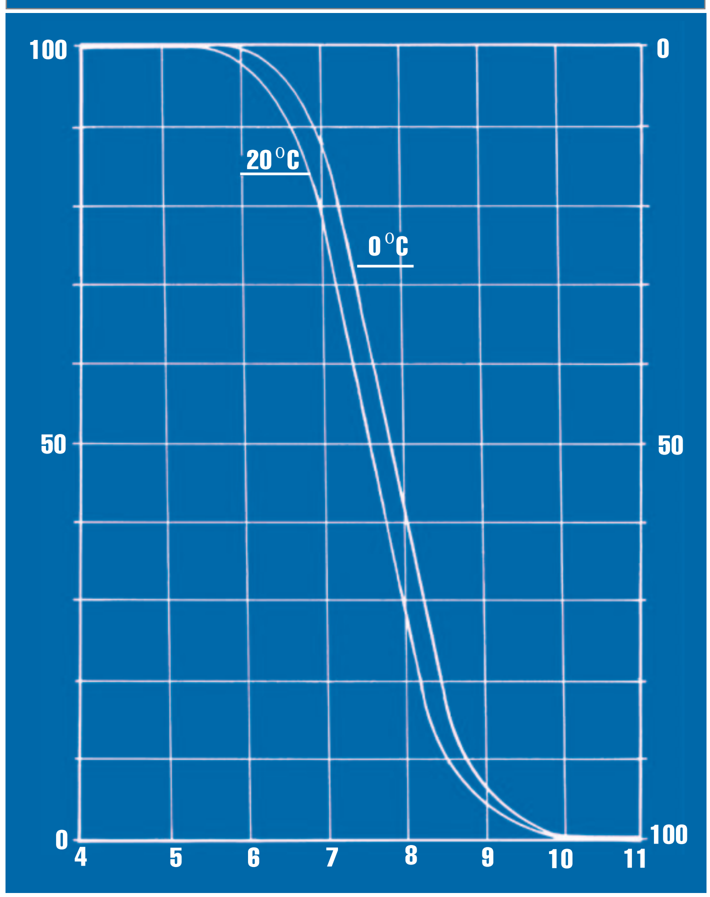
All operators who use chlorine should have chlorine safety training. If they use gaseous chlorine, they should have special safety equipment, such as an SCBA [self-contained breathing apparatus] on hand. Operators should also make sure that all personnel are trained to use the equipment and respond to a leak. The SCBA must be stored near but outside the chlorine room. (For more information about chlorine safety, see the fall 1998 issue of *On Tap* for the article "Chlorine Safety: Know What You're Doing.")

Forms of Chlorine

Chlorine is a strong, oxidizing agent that systems may use as a liquid or gas. Either form is stored and used from gas cylinders under pressure. The chlorine cylinders may be 150-pound, ton, or rail-tank car size. Small drinking water systems commonly use 150-pound cylinders.

Systems may use either calcium hypochlorite or sodium hypochlorite. Calcium hypochlorite may be a solid or powder and provides 65 percent available chlorine. Calcium hypochlorite is more stable than other forms of chlorine. Sodium hypochlorite comes in a liquid solution of five to 15 percent chlorine. Both calcium hypochlorite and sodium hypochlorite can be

Figure 1 - Relationship between hypochlorous acid (HOIC), hypochlorite ion (OCI) and pH



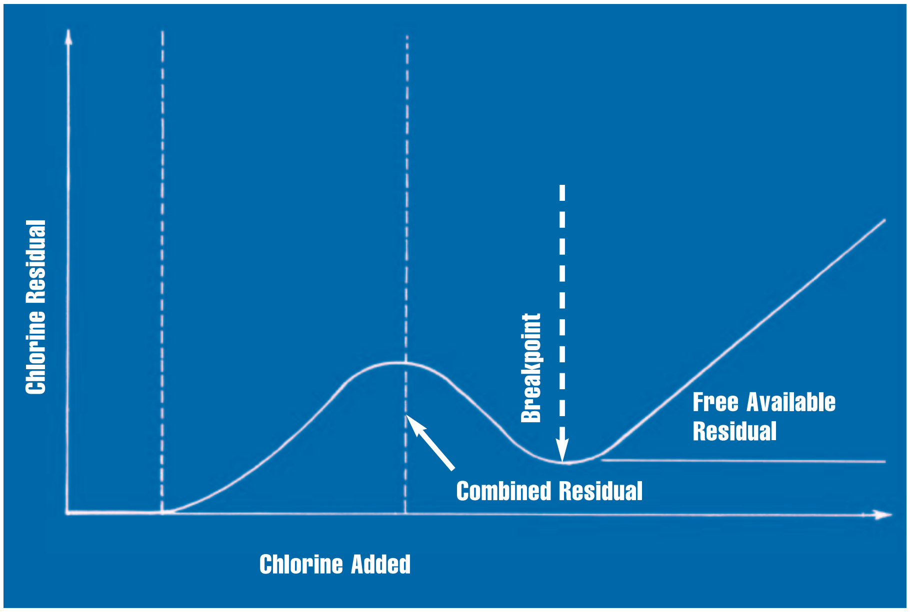
Source: Water Plant Operation, Volume 1, *California State University, Sacramento, CA Dr. Ken Kerri, Project Director* fed using a liquid solution tank with a small chemical feeder pump.

Storing Chlorine

A drinking water system should always have a one- to two-week supply of chlorine on hand, and many plants keep a 30-day supply. Calcium hypochlorite is more stable than other forms of chlorine and may be stored for up to a year. Sodium hypochlorite should not be stored for more than one month. If a system stores more than 2,500 pounds of chlorine onsite, a risk assessment and an emergency response plan are required.

A risk assessment requires that the facility determine the worst-case scenario for an accidental release. If the worst-case scenario could affect the general public, a prevention program must be developed. The prevention program should include identification of hazards, written operating procedures, training, maintenance, and accident investigation. If employees from the system respond to a leak, the system must develop an emergency response plan and submit it to the U.S. Environmental Protection Agency (EPA). The public also must have access to this plan.

Figure 2 - Breakpoint Chlorination Curve



Source: Water Plant Operation, Volume 1, *California State University, Sacramento,CA Dr. Ken Kerri, Project Director*

Chlorine Reactions in Water

Chlorine mixed with water forms hypochlorous and hypochlorite ions. The hypochlorous ion is a more effective disinfectant and is formed in greater concentration at lower pH values. At pH 7.3, the hypchlorous and hypochlorite ions will be present in equal numbers. The hypochlorite ion predominates above pH 8.3 and is not as effective as a disinfectant. For this reason, better disinfection occurs at a lower pH. The graph shown in Figure 1 displays the relationship between different forms of chlorine over a range of pH.

Chlorination should be applied after treatment to remove the precursors that combine with chlorine to form the trihalomethanes and haloacetic acids that EPA now regulates. Some water treatment systems have begun using chlorine, ultraviolet (UV), or ozone as a primary disinfectant, then using chloramines as a secondary disinfectant to minimize the production of disinfection byproducts.

Chlorine Demand

Because chlorine is a strong oxidant, it combines with many other substances in the water, including inorganics, such as ferrous iron, hydrogen sulfide, and ammonia. This reaction is instantaneous, and no disinfection occurs until the chlorine has combined with the organic and inorganic substances present in the water. The substances with which chlorine combines exert a demand on the chlorine that must be satisfied before a free-chlorine residual is formed. The free-chlorine residual produces the most effective form of disinfectant and is a measure of the hypochlorous and hypochlorite ions.

Chlorine also combines with ammonia that may be present to form chloroamines. The chloroamines provide disinfection, but the process is much slower. A longer contact time is required for complete disinfection to occur. The chloroamines are part of the combined chlorine residual and will provide disinfection but at a slower rate than free chlorine.

Chloramines do provide a longer disinfection contact time and are very beneficial in the distribution system where monochloramine, dichloramine, and trichloramine continue to kill microorganisms and extend the effective contact time.

The total residual chlorine is the sum of the combined and free residuals:

Total residual, milligrams per liter (mg/L) = combined residual, mg/L
\+ free residual, mg/L

For example, if the free chlorine residual is 1.0 mg/L and the combined residual is 2.0 mg/L, then the total residual is 3.0 mg/L.

The total chlorine demand must be satisfied and then the addition of more chlorine will produce a rapid increase in free-chlorine residual. Figure 2 illustrates how the chlorine residual is produced as more chlorine is added. The point at which the free-chlorine residual begins to rise in direct proportion to the amount of chlorine added is called the breakpoint. At the breakpoint, the chlorine demand has been satisfied, and the addition of more chlorine produces a free-chlorine residual in a one-to-one ratio. Most water treatment systems try to produce a free chlorine residual of 0.6 mg/L in the finished water and maintain at least 0.2 mg/L total residual in the distribution system.

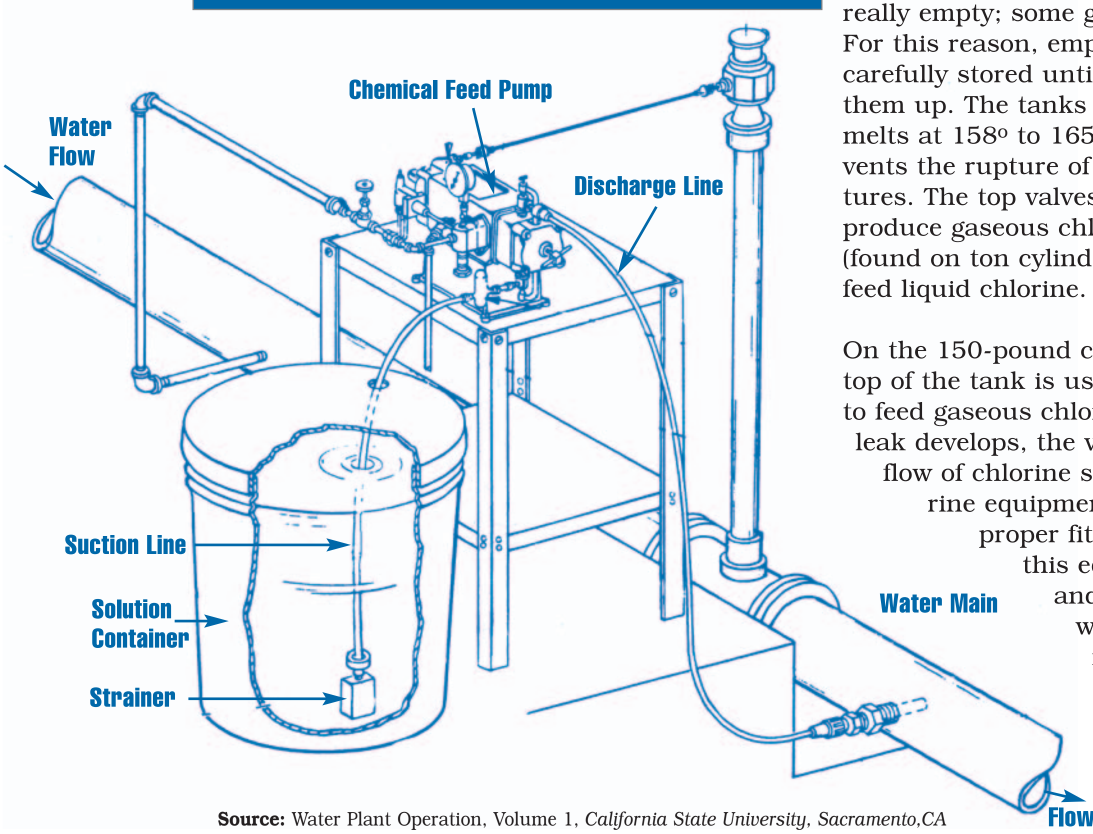
Chlorine Dose

The required chlorine dose can be calculated by determining the desired residual, the volume of flow, and chlorine demand. For example, to treat 1 million gallons per day (MGD) of water and produce a chlorine residual of 0.6 mg/L with water having a 1.0 mg/L chlorine demand, the chlorine dose rate in pounds per day would be calculated as follows:

Chlorine, pounds/day = Vol. MGD x 8.34 lbs/gal x total concentration, mg/L

= 1.0 MGD x 8.34 lbs/gal x 1.6 mg/L
= 13.3 lbs per day

Figure 3 - Hypochlorinator



Source: Water Plant Operation, Volume 1, *California State University, Sacramento,CA*
Dr. Ken Kerri, Project Director

Using this example, the chlorination feed equipment should be calibrated to provide a dose of 13.3 pounds of chlorine per day. When gaseous chlorine is used, the chlorine cylinder should be set up on a scale, and the total pounds per day should be recorded.

When using a solution tank of calcium hypochlorite or sodium hypochlorite, the equation above must be modified because the amount of chemical used is not 100 percent chlorine. In the case of a hypochlorite solution that is 65 percent available chlorine, the dose of hypochlorite needed to produce 13.3 pounds per day of chlorine would be 20.5 pounds per day (13.3 pounds per day/0.65). The hypochlorinator must be calibrated to feed 20.5 pounds of calcium hypochlorite per day.

The contact time and dose are extremely important to achieve good disinfection. A contact time of 30 minutes is a minimum, and the contact time may need to be increased at low temperatures or higher pH to achieve the same level of disinfection if the dose remains constant. A higher chlorine dose may allow for a shorter contact time, but that may not be the best way to optimize the disinfection process.

Chlorination Equipment

As previously stated, the cylinders used for gas or liquid chlorine are made of steel, and the chlorine is under pressure. Operators must remember that the chlorine cylinders are never really empty; some gas will remain in the tank. For this reason, empty chlorine tanks must be carefully stored until the manufacturer picks them up. The tanks have a fusible plug that melts at 158° to 165° F. The fusible plug prevents the rupture of the tank at high temperatures. The top valves on a chlorine cylinder produce gaseous chlorine, and the lower valves (found on ton cylinders and rail tank cars) will feed liquid chlorine.

On the 150-pound cylinder, the valve on the top of the tank is used with a vacuum system to feed gaseous chlorine into the water. If a leak develops, the vacuum is broken and the flow of chlorine stops. The threads on chlorine equipment are unique, and only proper fittings may be used with this equipment. New gaskets and washers should be used when a new cylinder is put into service, and the chlorine valve is designed to provide maximum discharge with only one revolution. This safety feature allows a rapid shut-off for the cylinder if a leak develops. Many plants use an automatic shutoff safety valve to provide more protection against the accidental release of chlorine. Never use a wrench larger than six inches when working on a chlorine cylinder. Small leaks in the 150-pound cylinder may be repaired with Emergency Kit A, which contains different types of repair plugs and clamps that are specific for the 150-pound cylinder. Likewise, if ton cylinders are being used, then Emergency Kit B is required, which contains different types of repair plugs and clamps that are specific for the one-ton cylinder.

Chlorine leaks may be detected using a rag soaked in ammonia. To find a leak, pass the ammonia-soaked rag slowly over the chlorine piping. If a leak is present, the ammonia will combine with the chlorine and form a white cloud. Using an ammonia spray bottle is not recommended because if the leak is large, a large white cloud will form that may impair vision. Many leaks occur at the valve and may be stopped by tightening the packing gland around the valve.

Calcium hypochlorite, or sodium hypochlorite, is more commonly used to treat flows of 100,000 gallons per day or less. The hypochlorinator is composed of a solution tank, chemical metering pump, storage tank, and associated piping. Figure 3 shows the basic set-up for a hypochlorinator. The hypochlorinator requires mixing and filling the solution tank, usually on a daily basis. The hypochlorinator equipment is less expensive than gas feeder equipment. The upkeep and maintenance for solution feeders is easier to perform but requires more frequent attention. The suction feed line from the solution tank has a tendency to clog and should be checked frequently. The solution tank and the screen on the suction line should be cleaned monthly or quarterly, as needed.

The chlorine feed solution is extremely corrosive so all materials must be corrosion resistant and checked for evidence of failure. The liquid chlorine solution from calcium hypochlorite or sodium hypochlorite is easier to work with than gaseous chlorine, but the solution is still very hazardous.

Chlorine Testing

The only acceptable method for chlorine testing is DPD, [N,N-diethyl-p-phenylenediamine]. This method requires the addition of DPD to the sample and then measuring the intensity of color production in a colorimeter. Always check the expiration date on the DPD and protect it from high temperatures. Chlorine samples must be collected and analyzed immediately. No holding time or sample preservation is acceptable for chlorine samples. Agitation and sunlight will destroy chlorine in the sample, so field-testing kits should be used when taking samples from the distribution system.

Samples of drinking water should be tested for both free and combined chlorine residual. Personnel should collect samples from several locations throughout the distribution system, including the farthest point to ensure that adequate chlorine residual is maintained. The number and frequency of samples required depends upon the volume of drinking water produced. The Surface Water Treatment Rule requires some systems to provide continuous chlorine residual testing. The price of in-line monitoring equipment and keeping this equipment in good working order may be a significant expense for small water treatment systems.

Chlorination provides good disinfection to protect drinking water supplies from pathogens. For small drinking water systems, chlorination is the least expensive form of disinfection available in either the gaseous, solid, or liquid form. However, chlorine is a dangerous, corrosive chemical that requires special handling, storage, and use procedures. The challenges for many small systems are to provide chlorine safety training, minimize the production of disinfection byproducts, and still supply safe drinking water at a reasonable cost.

Where can I find more information?

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