CHLORINE RESIDUAL IN WATER SYSTEMS

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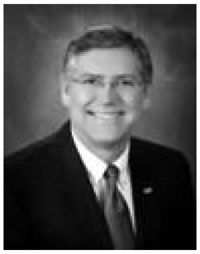

The injection of chlorine in public water systems as a disinfectant has been one of the great public health advances in modern times. Because of its required use, relative to other parts of the world, the United States has all but eliminated the waterborne diseases which take such a toll on human life and productivity elsewhere. While chlorine is not the only disinfectant available for water purification, it is certainly the most widespread, as it is highly effective and generally the least expensive.

Chlorine is normally applied as part of the treatment process prior to pumping into the distribution system. As a multi-use treatment chemical, chlorine can be applied for oxidation of organic and inorganic contaminants, substitution reactions with certain chemicals and, of course, disinfection.

Beyond its use within the treatment plant, United States regulations have long considered it necessary to carry a chlorine residual into the distribution system in order to maintain the integrity of the water while being delivered to the customer. The putative objectives of carrying a chlorine residual are as follows:

- Inactivate microorganisms in the distribution system
- Indicate variance in distribution system water quality
- Control biofilm growth.

There are perennial professional debates about how and whether these objectives are achieved, but regulations are clear that the residual is to be maintained.

Types of Chlorine Residual

Actually, chlorine residual is a generic term which covers a number of different forms of chlorine that remain in the water. It is important to carefully define these different forms, because they have different germicidal properties. Because chlorine is a chemical in aqueous solution, in order to discuss these different forms, it is necessary to briefly sketch the primary chemical reactions.

Most water plants introduce chlorine through a chlorinator which safely transfers chlorine gas into the water. Because chlorine gas is highly toxic, most chlorinators limit the chlorine injection rate to approximately 3500 mg/L so that the probability of chlorine degassing is very low. The hydrolysis reactions of chlorine gas into aqueous solution proceeds according to the following simplified equations:

$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$ where HOCl: Hypochlorous acid

$HOCl \rightleftharpoons H^+ + OCl^-$ where OCl^-: Hypochlorite ion

As might be expected from equations of this form, chlorine functions as a weak acid in water. The speciation can be estimated using the equations:

$$\frac{[H^+]\,[Cl^-]\,[HOCl]}{[Cl_2]} = 4\times10^{-4}$$

$$\frac{[H^+]\,[OCl^-]}{[HOCl]} = 2.7\times10^{-8}$$

It can then be seen that these dissociation equations are in dynamic equilibrium. The proportion of the chlorine which exists as HOCl versus OCl^- in pure water is dependant on the temperature and pH of the water. Of course, any background demand or reactions will be satisfied before the residual is established. In other words, when chlorine is applied to the water it will immediately react with other substances in the water which are amendable to oxidation, such as manganese or sulfides, and thus be removed. After those reactions occur, the chlorine that remains will be available as a residual.

Some Chlorine Reactions of Interest

Because chlorine is such a strong oxidizer, it reacts with a wide range of chemicals. Some of these initial reactions involve organic materials which, when reacting with chlorine, may form compounds that are potentially carcinogenic. These compounds are generally classified as Disinfection By-Products (DBP). State and federal regulations limit the levels to which they can exist in drinking water. The regulations focus on trihalomethanes (THM) or haloacetic acids (HAA5) as primary indicators of this occurrence. The specific chemicals forming these groups are:

a) Total THM: chloroform, bromodichloromethane, dibromochloromethane, and bromoform and

b) Haloacetic acids – 5: monochloroacetic acid, dichloroacetic acid, trichloroacetic acid monobromoacetic acid and dibromoacetic acid

The reason that DBPs have become a topic of concern is that some toxicological and epidemiologic studies have identified a number of these parameters as being carcinogenic in animals or associated with cancer (primarily bladder cancer) in epidemiological meta-analyses.

Another reaction of interest is the one between chlorine and ammonia. This is highlighted for several reasons. First, ammonia is an indicator of contamination, as well as a contaminant itself, at sufficient doses. Therefore, any time that ammonia is found, the source and concentration distribution should quickly be traced. Chlorine is an effective means of dealing with ammonia in limited concentrations.

Second, somewhat paradoxically, ammonia is sometimes mixed with chlorine to form chloramines, which are in turn used as another form of disinfection residual. This is because chloramines are more stable in distribution systems and are desirable because of the tendency to form fewer disinfection byproducts. Chloramines exist in three forms given by the equations below. These reactions typically proceed in stepwise fashion depending on the available hypochlorous acid. Monochloramines are the preferred form of use in water systems due the potential for taste and odor problems associated with dichloramine and nitrogen trichloride.

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O$$ (monochloramine)

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O$$ (dichloramine)

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O$$ (nitrogen trichloride)

Nomenclature for Chlorine Residual

As mentioned, chlorine is active and exists in a number of different forms which have different disinfection potentials. This is further complicated by the fact that chlorine residuals can be developed using chlorine dioxide and sodium hypochlorite. Therefore, it is necessary to develop a nomenclature for classifying these forms to assure that appropriate disinfection occurs. The most common forms of chlorine residual referenced in technical literature and in environmental regulations are listed below.

Free Available Chlorine Residual: concentration of hypochlorous acid and hypochlorite ions existing in chlorinated water.

Free Chlorine Residual: refers to a chlorinated water in which at least 85% of the total measured chlorine residual is hypochlorous acid.

Combined Chlorine Residual: refers to the chlorine residual that consists of chloramines.

Total Chlorine Residual (or Total Available Chlorine) is the sum of Free Available Chlorine Residual and Combined Chlorine Residual.

The term "Available Chlorine" is sometimes used in technical literature and can be confused with the terms mentioned above. The term, rather than referring to a specific concentration in water, refers to the oxidizing power of the compound tested. It is possible that the term could be used in conjunction with a compound that doesn't contain chlorine at all in that it is computing the equivalent oxidizing power of the compound related to chlorine. White (1999) believes the term should be discontinued because it can be confused with the legitimate term "free available chlorine."

Causes of Chlorine Residual Decay

Once water has exited the treatment plant and entered the distribution system, it can not be assumed that the chlorine residual will remain constant. Water system operators know that, in reality, the level and form of the chlorine residual is variable throughout the distribution system. This loss of disinfectant residual can weaken the barrier against microbial contamination which can occur within the distribution system. Many people assume that because the distribution system remains under positive pressure that intrusion into the system isn't likely to occur. However, this is not necessarily true.

Contamination can enter the system by cross-connections or pipe line breaks. Cross-connection control programs are required by the State of Florida (Chapter 62-555.360 FAC), however, complete compliance is difficult to achieve. Pipe breaks or construction intrusion are usually followed quickly by line disinfection, but often times there is a lag between the initiation of the event and final disinfection of the system. These events can result in consumption of chlorine residual which serves as both an indicator of contamination and an agent to fight the results of contamination.

Chlorine residual will also decay "naturally" within the system as a result of reaction of chlorine with materials in or on the pipe wall. This can be either the pipe material itself or biofilms or sediment at the pipe surface. The ability to predict this chlorine loss is difficult due to the variable physical characteristics of pipes within the distribution system (e.g., age, construction material, diameters, encrustation, etc.) To simplify the process, most designers assume that the chlorine residual decays as a first order reaction. The fundamental characteristic of this assumption is that "contact time" is the primary variable driving the decay. Decay coefficients can be estimated by laboratory tests, but again there is variance within the system. What is observed, however, is that water age can be significantly correlated to chlorine residual decay. Recall that water age is the amount of time that water remains in the distribution system after it leaves the water plant. Knowledge of water age within various zones of the distribution system can be a useful tool in monitoring chlorine residual in the field.

Controlling and maintaining chlorine residual can be challenging. As mentioned above, a number of communities are switching to chloramines (combined chlorine) as a disinfectant rather than free chlorine. Combined chlorine is less reactive and therefore more stable within the system. While this means that it is a less powerful disinfectant, it does persist in the distribution system better and therefore can be a more reliable secondary disinfectant.

Communities with a progressive approach to maintaining a reliable in-system chlorine residual many times will undertake a program of pipe replacement and flushing. Florida water system rules require quarterly flushing of dead end lines, but a more proactive program looks for other areas too. An intelligent flushing program does not promote indiscriminant water use. Rather, the city's computer model (extended period simulation) is used to identify the locations and most efficient means of flushing. This activity should be done in conjunction with the community water conservation plan so that water is not unnecessarily wasted.

In conclusion, chlorination of drinking water has been a key factor in the dramatic reduction of waterborne disease in the United States. Secondary disinfection in the form of maintaining a chlorine residual within the distribution system is important. The chlorine residual can take several forms with have different disinfection (oxidation) potentials, decay rates and byproduct formation. Chlorine residuals vary from point to point within a distribution system as a result of chlorine decay. This occurs for a number of reasons and water system operators must monitor their system and take a proactive approach to maintaining an adequate residual while not over-chlorinating or over-flushing.

References:

White, G. C. (1999). Handbook of Chlorination and Alternative Disinfectants (4th ed.). John Wiley & Sons, Inc. New York, NY.

Mays, L.W. (2000). Water Distribution Systems Handbook. McGraw-Hill. New York, NY.

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