

Chlorine Residual Boosting



in Distribution Water

There is no shortage to the available information in regard to disinfection methods from principle to application. Two common disinfection methods are to apply chlorine gas to the plant water, or to make the chloramine from ammonia and chlorine in the plant.

However, when it comes to the methods to increase, or boost, the low level of disinfectant in distribution water, information is scarce. This article is written especially for small utilities purchasing wholesale water containing chloramine in the distribution system and who find it necessary to boost the chlorine residual. It discusses boosting problems, solutions and actions to be taken in increasing low residual level (chloramine) using a simple device such as a pocket chlorine colorimeter.

This report will discuss four techniques in which a low level of chlorine in the distribution system can be increased by the free or combined chlorine.

- Free chlorine injection to free chlorine-containing water (recipient).
- Chloramine to chloramine.
- Ammonia and free chlorine to chloramine.
- Free chlorine to chloramine.

It is necessary to understand the boosting mechanisms and implementation methods as well as stability concerns of the newly formed chlorine disinfectant.

Before attempting to increase the chlorine residual level, the type of disinfectant (free or combined chlorine) at the intake of the boosting site must be known. One can obtain this type of information from the supplier. However, be careful because there is the possibility that plant discharge water already may be boosted by a wholesaler changing the chloraminated water into the free chlorine (breakpoint application). For example, the South Texas Water Authority (STWA) purchases Corpus Christi's water as a wholesaler to redistribute it to Driscoll (population 690), Bishop (3,500), Kingsville (25,000) and several other small utilities.

The disinfectant type (free or combined) also can be determined by methods such as amperometric titration, Hach's DPD reagents for free and total chlorine, the selective ion electrode for ammonia to distinguish between free and combined, and a peak and breakpoint search. The amperometric titration and selective ion electrode methods need lab equipment, so these tests cannot be carried out in the field.

The type of disinfectants in the water determines the type of disinfectant that

should be applied. There are no major problems in increasing the chlorine level when the same disinfectant is added to the boosting water. This is because there is no reaction between disinfectants (e.g., free to free chlorine and chloramine to chloramine) at the disinfection concentration level (1.0–4.0 mg/L) that is used for potable water. If someone adds the free chlorine to the monochloramine containing water, an oxidation-reduction reaction takes place to reach the breakpoint at an increasing chlorine dose (Figure 1).

Corpus Christi Water Disinfectant

At the City of Corpus Christi, the discharge water of the O.N. Stevens water plant contains chloramine as disinfectants (total chlorine: 3.5–4.0 mg/L, free: 0.1–0.2). This disinfectant (mainly, monochloramine) is formed as the result of feeding the raw water with liquid ammonium sulfate and chlorine gas, and second chloramination is to inject the same chemicals to the filtered water prior to the clear well. The finished water is prepared with conventional treatment processes (e.g., flocculation, sedimentation, sand or granulated activated carbon [GAC] filtration). Filtered sand and GAC water is blended prior to distribution.

The distribution system serves not only the inside city (the farthest sampling site is about 40–45 miles), but also extends to several small utilities (40 miles to the east and west) for wholesales. Well-established records show that the disinfectant dissipates (50 to 75 percent) at the distant sites from the plant, especially

during the summer season. The maximum temperature in the Corpus Christi distribution system is around 77° F while it is about 86°–88° F in plant basin waters.

Both free and combined chlorine are inherently unstable even in the buffered water.¹ Therefore, it would be natural to expect that disinfectants (free or combined) in the distribution system are more susceptible to dissipation. Distribution pipes may contain a few of the various factors responsible for inactivating the chlorine disinfectants. The dissipating disinfectant in the distribution system would compromise water quality, resulting in a microbial population increase, creating odor and taste problems and a high risk in microbial access to the tap.

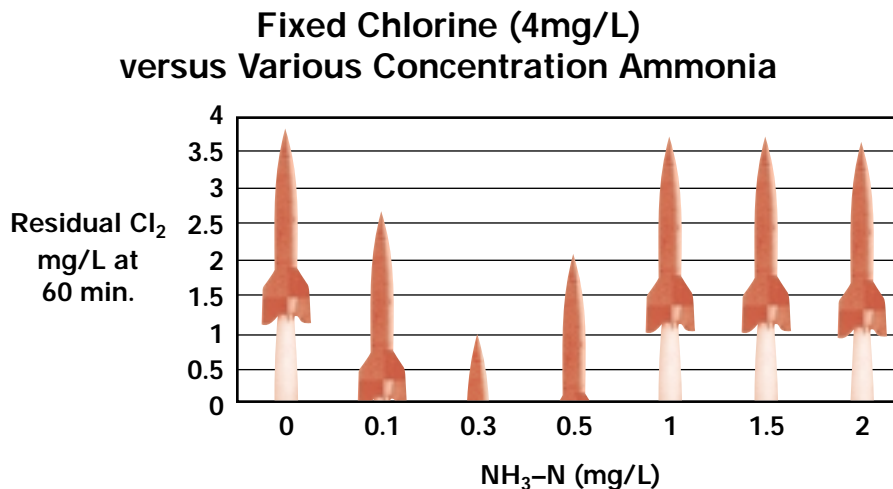
Dissipation Factors

The decomposition of disinfectants (free and combined chlorine) depends on various physico-chemical and biological factors.

- **Water quality parameters:** pH and alkalinity, nitrite, hydrogen sulfite, bromide (high concentration in Corpus Christi's raw water 0.2–0.8 mg/L) and DOC (dissolved organic carbon).
- **Environmental factors:** temperature, water supply retention time (distance from plant), distribution pipe quality, biofilm formation and abnormal conditions (e.g., boiling, icing and storing in a porcelain container).
- **Plant factors:** treatment condition (Cl/N), treatment chemicals (manganese and iron), GAC filter media to yield nitrite and nitrate due to bacterial nitrification and GAC particles with catalytic activity to chloramine (if filter media is GAC).

Chlorine decay factors such as icing, boiling and porcelain container storage

Figure 1: Near Breakpoint Chlorination



This graph indicates a slight change below 1.0 mg/L ammonia (Cl:N= 4:1) can reduce residual chlorine. pH 7.2, 0.3 mM, phosphate buffer.

have nothing to do with the daily plant and distribution operations, but knowing this information may lead to better water products. For example, some iced tea makers start with ice in which residual chlorine is depleted during ice formation, while some water becomes better tasting after storing in a cool porcelain container. Different factors must enhance decomposition of disinfectants in different mechanisms. The lowered disinfectant level at sampling sites may be the result from one factor, or in some cases, from the synergistic effects of decaying factors.

Dissipation in Corpus Christi

Reviewing the daily or monthly results of the residual level makes it possible to determine which factors may be involved in lowering disinfectant chloramine in the distribution system as well as in plant. For example, 1996 data in Corpus Christi showed that while nine daily distribution samples were normal (average residual:

3.9 mg/L, in the range 3.6–4.2), one exceptionally low residual level (0.8 mg/L) was found to be correlated to a high level of nitrite and nitrate. While some deviation from the average also can be found with this sample in chlorite and pH, it is not as significant as nitrite and nitrate.

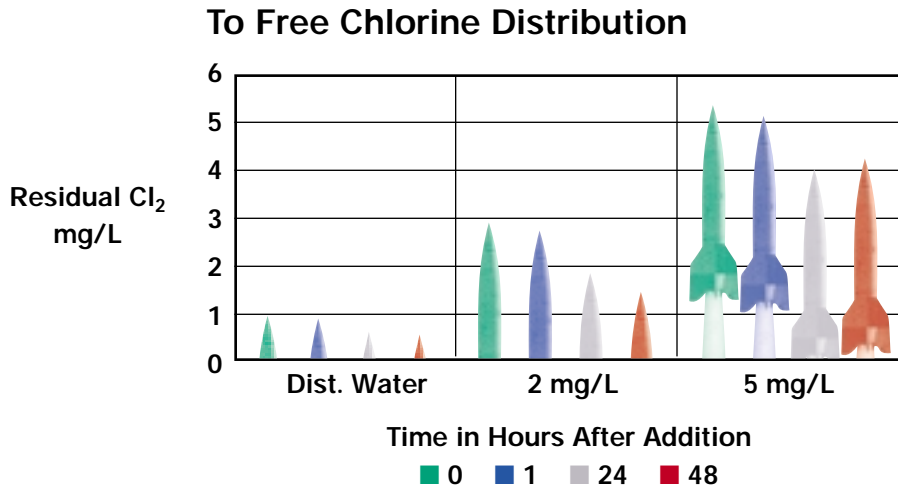
An effect of the water supply retention time can be seen in the distant sampling sites. The chlorine residual of sampled water in North Padre Island (40–45 miles from plant) is about half as low as the downtown area (5–20 miles) especially during warmer months (May to November in Corpus Christi). In addition to long retention time, the distribution water to the island flows in the pipe installed under the shallow bay for 10 miles. Therefore, the high temperature of bay water (77–86° F) also is a contributing factor for dissipation during the summer season.

In some cases, monthly distribution system results can be used to trace back the relationship between a low residual level at the tap and plant operation. During February and June 1996, twelve GAC filter beds were introduced to replace sand filters, while the rest of the filters were not modified. Thereafter, the distribution water became a blended one with sand and GAC filtered water.

In April 1996, two months after the first six GAC filter installments, the chlorine residual decreased over the entire city with some

Suggested Selection of Dosing Chemicals			
Injecting Chemicals			
Type of Disinfectant in Water	Free Chlorine	NH ₃ ⁺ Chlorine	Chloramine
Free chlorine	Yes	No	No
Combined Chlorine (Chloramine)	Breakpoint Chlorination	Injection Order	Yes

Figure 2: Free Chlorine Boosting



Boosting the free chlorine of the distribution water (Mathis, Texas) with free chlorine. The exogenous free chlorine, 2 and 5 mg/L were supplemented to increase residual in the distribution water. Mathis's water is of surface sources.

results falling below 0.5 mg/L. The temporary removal of all GAC filtration operation with air scouring and thus switching to all sand filters restored the entire distribution system back to the normal level (3.0–3.5). This operational change suggests that GAC has an involvement in lowering the chlorine residual in far distances away from the plant.

It was reported in a previous paper on chloramine decay² that the plant water with GAC filtration showed significant chloramine decay in a few days, much faster than the water with the sand filter. An interesting observation also was made on the existence of GAC particles on the bacteriological membrane filter (Gelman, 47 mm, 0.45 mu) with plant GAC water. The Ingleside water utilities, user of Corpus Christi water (40 miles to east), reported the same observation, suggesting

that GAC particles can be carried a considerable distance from the plant.

In water treatment, operation and plant structures also can lead to a loss of disinfectant. Unexpected low chlorine residual levels can be found in the basin water after chloramination. This is due to a high ratio (CL/N) at the breakpoint level. It would result simply from a low supply of ammonia. Nitrification in the GAC media converts free and combined ammonia into nitrite that inactivates monochloramine in the distribution system.³ Service pipes between basins and laboratory taps in the plant can create a problem in determining chlorine residual in the basins especially when there is a low chloramine level in the basin and during the warmer season. The nitrifying bacteria are colonized in the pipes to convert monochloramine into

ammonia by nitrite produced during nitrification, reducing the monochloramine level at the tap. The nitrification in the service pipe compromise the residual level at the basins. As the result, the chlorine level measured by operator at the tap may not be the same as basin water.

Prior to boosting, it is a good idea to check which causative agents might be involved in lowering residual. However, at this moment there have been no systematic studies attempted that elucidate chloramine decay occurring during flow from the plant (effluent residual, 4.0 mg/L) to utilities (e.g., Kingsville, 45 miles, 0.1–0.5 mg/L).

Enhancement of Chlorine Residual in Distribution

Free to Free

The lowered level of free chlorine easily can be increased by adding with the same free chlorine. A test was conducted with the distribution water containing free chlorine. It was determined that the recovery of added free chlorine was 1.9 mg/L recovered (95 percent) to spiked 2.0 free chlorine, and 4.4/spiked 5.0 (88 percent recovery) at 60 minutes after adding free chlorine to chlorinated distribution water in Mathis, Texas. The result (Figure 2) indicates that almost all free chlorine added was recovered, and there seems to be no interaction between boosting free chlorine and the preexisting monochloramine. It also was found that daily dissipation of chlorine residual occurs at room temperature both in the municipal water as well as the boosted water. This type of slow chlorine dissipation is normal, especially in the free chlorine.

Chloramine to Chloramine

This type of boosting should not induce any interaction between dosing and pre-existing monochloramine due to the same chemical nature. The test results (Table 1A) show that the addition of the premade monochloramine (4.5 mg/L) increases chlorine residual in the distribution water at the expected rate and without significant residual decline for a few days after boosting. An expected increase also was found with the chloramine of distribution water when premade chloramine was as low as 1–2 mg/L. The rapid decline of chlorine residual after its addition did not take

Table 1A: Boosting Low Chloramine by Premade Chloramine and Disinfectant Stability

Sample	Cl ₂ (Sampled)	Cl ₂ (Before Cl)	Post Boosting Time in Hours			
			0	5	24	48
D89	1.9	0.28	4.2	4.4	3.9	3.5
D92	2.0	1.0	5.2	5.0	4.3	4.4
D94	3.6	0.48	4.6	4.7	4.3	3.8
D95	4.1	1.9	6.0	5.8	5.4	5.4
D96	3.7	1.3	5.4	5.2	5.2	4.8
P-Buffer		0	4.5	4.6	4.5	3.9

Samples were collected and stored in refrigerator on 12/13/00, and boosted on 12/27/00 with 4.5 mg/L chloramine.

place as found in the breakpoint application because of the same disinfectants.

The problem is selecting the dosing monochloramine concentration to apply (stock solution of premade monochloramine). A low concentration (100–200 mg/L) of stock chloramine cannot be used for extensive dilution, because the dilution factor is only 25–50 to increase by 4 mg/L in boosted water. A concentration as high as 1,000–4,000 mg/L may be appropriate for a larger dilution, thus it can be diluted to increase by 4 mg/L with a dilution factor (x250–x1,000). Five gallons of chloramine stock in deionized water (4,000 mg/L) can be added to 5,000 gallons of water to be boosted. However, boosting with chloramine must be completed within 4–5 hours after preparation due to the instability of high concentrations of chloramine during storage. Our test results indicate that 95–96 percent of chloramine prepared at such a high concentration dissipates in 24 hours at room temperature (73° F) as well as in the refrigerator (41° F).

Ammonia and Chlorine to Chloramine

The monochloramine is made in the water treatment plant by either injecting ammonia into the raw water followed by chlorine injection or injecting ammonia into the already chlorinated water. There is no strict consensus in the injection order to form monochloramine. However, some plants believe by applying the chlorine followed by ammonia, it allows the free chlorine to disinfect plant basin water for a short time during flocculation.

If the chloramine level of chloraminated water increases, it is critical to inject ammonia at first so that the subsequent free chlorine can interact with free ammonia to change into the monochloramine. The ammonia should be dispersed to an even concentration in the pipe or tank with accurate dosing before chlorine injection. Table 1B shows that boosting also can be carried out in expected increase by applying free chlorine and free ammonia to the distribution water with lowered chloramine.

The ratio (Cl:N) of 2:1 may be appropriate with the input ammonia concentration in the distribution water; 1.5–2.0

Table 1B: Boosting Low Chloramine by Ammonia and Free Chlorine and Disinfectant Stability

Sample	Cl ₂ (Sampled)	Cl ₂ (Before Cl)	Post Boosting Time in Hours		
			0	5	24
D90	3.1	1.5	4.3	4.3	4.4
D91	2.6	1.3	4.7	4.8	4.5
D97	3.6	0.94	4.8	4.3	4.2
P-Buffer		0	4.0	4.0	3.6

Additional chloramine was made in the low residual distribution water by adding ammonia (1.0 mg/L), and followed by the free chlorine (4.0 mg/L). The ratio of input chemical is 4:1 (Cl:N). The distribution water used had been kept in refrigerator for 15 days before boosting.

mg/L as NH₃-N with chlorine dosing 3.0–4.0 mg/L. If NH₃ dosing is set below 1.0, it increases the risk to reach the breakpoint if there is even slight operational difficulty where the formed monochloramine is converted into the nitrogen or nitrogen oxide gas. Therefore, it may be safe to stay within the range of 1.5 and 2.0 mg/L of ammonia (Figure 1).

Free Chlorine to Chloramine (Breakpoint Chlorination)

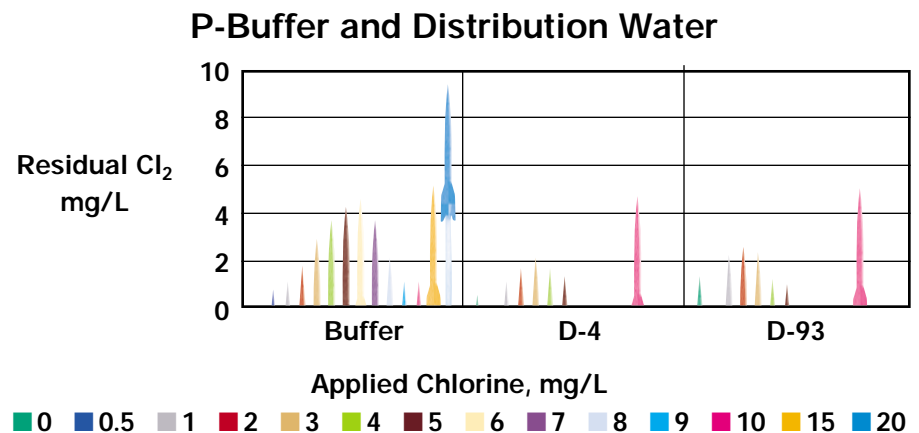
If the water to be boosted is chloraminated or with combined ammonia, increasing the dose of free chlorine first results in an increase in the chlorine residual, then a decline after peakpoint after reaching the breakpoint (Figure 3). It changes the residual chlorine mode from chloramine to free chlorine. The resulting

free chlorine is not only more bactericidal but also virocidal (100–500 times as effective as monochloramine).

This method is especially appropriate after a hurricane or heavy rain. This type of breakpoint application would decrease the risk of possible contamination from the outside. The dosing amount of the free chlorine is to be determined to make it possible to implement the breakpoint application to the chloraminated distribution water of Corpus Christi.

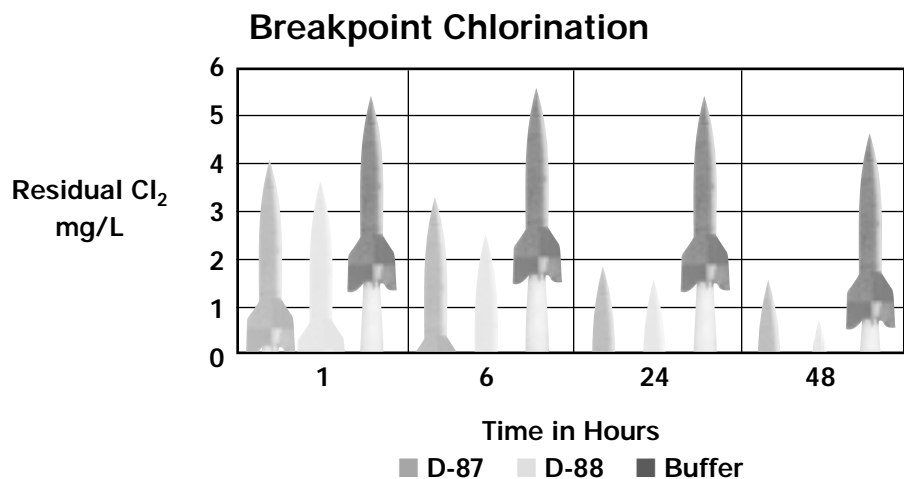
Figure 3 is the breakpoint curve prepared in the laboratory with the phosphate buffer (pH 7.2, at 23° C, NH₃-N=1.0 mg/L), indicating the peakpoint at Cl:N = 6:1, and breakpoint at 10:1. In the Corpus Christi plant, the chlorine gas is injected into the presedimented water with a 4:1 ratio, the yield is almost all in

Figure 3: Breakpoint Chlorination at Corpus Christi



Samples stored in the refrigerator for 40 days (D4) and 7 days (D93) with low level of residual: 0.16 and 1.4 mg/L prior to breakpoint chlorination (23° C). Total chlorine residual was measured at 30 min. The phosphate buffer used is supplemented with 1 mg/L NH₃-N.

Figure 4: Chlorine Stability



Samples treated with 10 mg/L of free chlorine were studied 48 hours for decay. Ammonia (0.3 mg/L) was added to phosphate buffer for the control breakpoint chlorination. The following data are date of sampling and water chlorine residual prior to boosting. Ammonia assay was not made.

D87	3.5	(sampled, 12/13/01)	1.6 (boosting, 12/27/01)
D88	3.7	(" , ")	0.7 (" , ")

the form of monochloramine with little free chlorine (3 to 5 percent).

AWWA Manual M20 on water chlorination⁴ and Hach Application Note 123, monitoring chloramination⁵ extensively discuss the chemical process of breakpoint chlorination with ammonia specification. The total ammonia (free + combined) level does not change with increasing chlorine dosing until peakpoint (Cl:N=5.5:1), thus, free ammonia (NH₃+NH₄) starts to decrease, as the combined ammonia (NH₂Cl) increases stoichiometrically. An addition of a dechlorinating agent like sodium thiosulfate converts chlorine-combined ammonia or monochloramine into free ammonia. Therefore, there is no change in the total ammonia concentration. The combined ammonia interacts with injecting Cl₂ and HClO between peakpoint and breakpoint to yield N₂, NO₂ and N₂O that evaporates into atmosphere. As a result, the total ammonia is almost to zero. Therefore, there is no reaction possible between chlorine and ammonia at this breakpoint (Cl:N=9.3:1).

The distribution water to be boosted still contains some residual chloramine and free ammonia from the plant discharge (Driscoll 30 miles, average total chlorine residual during winter: 1.0–1.5 mg/L;

Bishop: 0.5; and Kingsville: 0.1–0.5). All utilities boosting chlorine further down the line have problems measuring the ammonia due to difficult access to various equipment such as SIE (Selective Ion Electrode) needed. Therefore, it is not practical to differentiate ammonia in the supplied water, but it is possible to make a breakpoint chlorination with the distribution water. Figure 3 shows that distribution water with a low level of total chlorine after several weeks in a refrigerator can respond with a typical peak and breakpoint at the dosing chlorine at 10 mg/L. Both samples (D4 and D93) reached the residual 4–5 mg/L after breakpoint without any information on ammonia specification and concentration.

Table 2 shows how several distribution waters with different low residual levels were treated with breakpoint chlorination. It was found that the samples treated by free chlorine (10 mg/L dosing) resulted in a post breakpoint residual in the range of 2.9–4.0 mg/L regardless of initial levels. These results indicate that the breakpoint chlorination with the distribution water occurred without any supplement of ammonia at a certain free chlorine dose (in this case 10 mg/L) without any knowledge of ammonia concentration. These results provide users with a

suggestive boosting concentration dose by which the resultant free chlorine concentration is in the range of 3–4 mg/L.

These results were obtained from Corpus Christi distribution water that had been kept in the refrigerator for weeks with low residual. Most of the samples (70–80 percent) retain the total ammonia without any significant loss even after a month. We do not have any information on ammonia specification and concentration, but at the distant sampling site very low chloramine often was associated with loss of total ammonia. However, it may be very different from the water sample stored in the refrigerator in which the chloramine is converted into free ammonia during storing. This suggests that chloramine decay may occur in different mechanisms. Therefore, it is necessary for each utility to obtain a chlorination curve with the field water prior to boosting and determine a dosing concentration for the breakpoint chlorination.

Stability of Breakpoint Chlorine Formed in the Distribution Water

Table 1 (A & B) shows that there is no significant decay for a few days in the chloramine that is formed by the addition or formation in the distribution water.

The chlorine residual after breakpoint is the free chlorine. This newly formed free chlorine was investigated with respect to chlorine residual stability over the time and temperature expected during storage. This study can be accomplished by following the formed free chlorine residual level for a few days at room temperature. Figure 4 shows that the water is so unstable that more than half the chlorine residual dissipated within 24 hours.

A rapid decline after breakpoint also was found with the Robstown's distribution water where the finished water is prepared by the same source water (Nueces River) without GAC filtration. This kind of instability was not found in breakpoint chlorination with a phosphate buffer. No further study was made on instability mechanisms of free chlorine residual at breakpoint application. However, this observation corresponds favorably with

the field report by operators in Kingsville and Driscoll that free chlorine after boosting declined significantly during storage for 24 to 48 hours. The Kingsville operator reported that the boosted water contained 3.5 mg/L free chlorine but declined to 0.5–2.0 mg/L in 24 hours in the clear well.

This type of decline after boosting (whatever agents responsible) causes problems in maintaining the chlorine level during tank storage. If retention time is 24 hours during storage with initial free chlorine level 5.0 mg/L and 2.0 at 24 hours, the CT value would be 2,880 (1,440 × 2.0). This is sufficient enough to inactivate viruses as well as bacteria. Therefore, it is necessary not only to have good information as to the breakpoint application but also to conduct a test for residual dissipation of boosted water. If the boosted water shows an abnormal rapid dissipation in chlorine residual in 6–24 hours (e.g., 5.0 to 0.2), it is necessary to find the factors responsible.

The results and interpretations in this article are based on test results exclusively with Corpus Christi's water. These suggestions can be useful as a guide when our wholesale users find it necessary to boost residual. If some utilities want to boost with the distribution water for an emergency or low residual problem during the warmer season, it would be a proactive practice to conduct tests as described here with their own distribution water including a stability check. The results will give some direction for boosting before implementation.

Reference

1. Ozekin, S., R.L. Valentine, and P.J. Vikesland (1995) Technol. Conf. Proceedings, pp. 1,441–1,448, AWWA, Denver, Colo.
2. Tokuno, S., (1999), *Water Engineering & Management*, January, 1999, pp 16–21.
3. Tokuno, S., (1997), *Water Engineering & Management*, February, pp 22–25.
4. *AWWA Manual M20 on Water Chlorination Principles & Practices*, (1973), pp 20–34.
5. Hach Application Note 123, *Monitoring Chloramination Using APA 6000*, Loveland, Colo.

About the Author:

Shin-ichi Tokuno is a microbiologist with the Water Utilities Laboratory in the City of Corpus Christi, Texas.

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Table 2: Breakpoint Chlorination with Distribution Water

Sample	Chlorine Residual (mg/L)	
	Before Chlorination	60 min After Chlorination
D89	0.25	4.0
D90	1.4	3.0
D91	1.1	3.6
D92	0.82	2.9
D93	0.57	3.2
D94	0.33	3.6
D95	1.6	3.5
D96	1.1	3.4
D97	0.86	3.4
P-Buffer	0	8.5

The distribution samples were collected on 12/13/00, stored for four days in the refrigerator and conducted for breakpoint chlorination test with free chlorine dose (10 mg/L). P-buffer is phosphate buffer: pH 7.2, 0.3 mM, without ammonia.

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