

STRATEGIES AT CHARLESTON CPW FOR COMPLIANCE WITH DBP REGULATIONS

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ABSTRACT

Charleston Commissioners of Public Works (CPW) in Charleston, South Carolina, has traditionally accomplished control of disinfection byproducts (DBPs) through the use of chloramines in the distribution system and through the periodic addition of chlorine dioxide downstream of filtration. In order to further refine the strategy for DBP control, testing was performed during the summer in two separate years to assess the effect of pH during chlorine contact time prior to ammonia addition, and the effect of chlorine dioxide oxidation on the formation of trihalomethanes (THMs) and haloacetic acids (HAAs).

This paper will present the key results from the work at Charleston CPW, including the following:

- For many water quality conditions, operation at a lower pH during chlorine contact will assist Charleston CPW in meeting the Stage 1 Disinfection Byproducts Rule (DBPR) for THMs, with no significant increase seen in HAA5 formation.
- Water quality conditions, in particular elevated levels of bromide, appear to influence the effectiveness of pH adjustment as a method for minimizing THM formation.
- Chlorine dioxide addition prior to chlorine contact was effective in the reduction of THM formation during both test periods, a strategy that has worked effectively full-scale.

Ongoing work includes an evaluation of the use of chlorine dioxide in lieu of free chlorine for primary disinfection.

KEYWORDS

Disinfection byproducts, chlorine dioxide, trihalomethanes, haloacetic acids

INTRODUCTION

The Charleston CPW operates the 118 million gallon per day (mgd) Hanahan Water Treatment Plant (WTP). The Hanahan WTP obtains water from two sources; a river source and a sidestream reservoir of a river source. Both sources contain high levels of organics with low to moderate levels of alkalinity. The plant utilizes a conventional coagulation/flocculation/sedimentation process followed by dual media filtration. The plant operates two sets of filters and clearwells downstream of the sedimentation basins. One set is designated as the Stoney filters and clearwells and has a capacity of 92 mgd, and the second set is designated the Booker filters and clearwell and has a capacity of 26 mgd. Disinfectant contact time (CT) credit is achieved through the addition of free chlorine downstream of filtration prior to onsite finished water clearwells.

For the Stoney portion of the plant, prior to August 2002, the onsite clearwell consisted of a 5 million gallon (MG), oval cast-in-place structure (Stoney Clearwell No. 1). Disinfectant CT credit was achieved within Stoney Clearwell No. 1 in a pH range of approximately 8.3 to 8.7. Following Stoney Clearwell No. 1, additional chlorine was added along with ammonia to form chloramines for secondary disinfection.

In August 2002, CPW completed construction of a new five million gallon, circular prestressed concrete clearwell (Stoney Clearwell No. 3) to operate in series with the existing Stoney Clearwell No. 1. From August 2002 to approximately July 2003, CPW operated Stoney Clearwell No. 1 and Stoney Clearwell No. 3 in series. This approach offered added flexibility in obtaining CT credit for disinfection by allowing CPW to utilize a disinfection sequence in which free chlorine was added upstream of Stoney Clearwell No.1 and a lower pH (approximately 5.0) retained in Stoney Clearwell No. 1 to obtain CT credit. Following Stoney Clearwell No. 1, the finished water pH was adjusted to a pH of 8.3 to 8.7, and additional chlorine was added along with ammonia to form chloramines prior to Stoney Clearwell No. 3.

In July 2003, Stoney Clearwell No. 1 was shut down due to foundation failure. With Stoney Clearwell No. 1 out of service, Charleston CPW returned to operation of only one clearwell, with chlorine contact time occurring in Stoney Clearwell No. 3 at a pH of approximately 8.3 to 8.7.

For the Booker portion of the plant, the onsite clearwell consists of the Booker Clearwell, which is a 2.5 MG, circular cast-in-place clearwell. Disinfectant CT credit within the Booker Clearwell is achieved at a pH of approximately 5.0. Following the Booker Clearwell, caustic is added to raise the pH to approximately 8.3 to 8.7, and additional chlorine is added along with ammonia to form chloramines for secondary disinfection.

APPLICATION OF pH ADJUSTMENT AND CHLORINE DIOXIDE FOR DBP CONTROL

In August 2001 and August 2002, Black & Veatch performed bench-scale testing to assess the effect of pH adjustment and chlorine dioxide addition on the formation of

THMs and HAAs in filtered water. This bench-scale testing was performed to assess options for pH adjustment that became available with the construction of Stoney Clearwell No. 3. This construction offered added flexibility in obtaining CT credit for disinfection in the Stoney portion of the plant by allowing CPW to utilize a disinfection sequence in which free chlorine could be added upstream of Clearwell No.1 and a lower pH retained in Clearwell No. 1 to obtain CT credit. Following Clearwell No. 1, the finished water pH could be adjusted to a pH of 8.3 to 8.7, and additional chlorine added along with ammonia to form chloramines prior to Clearwell No. 3. The potential benefits of reduced pH values during contact with free chlorine (i.e., in Clearwell No. 1) include more effective disinfection with free chlorine and a corresponding greater log removal credit for disinfection, and potential reduction in the formation of THMs, since formation of THMs is typically reduced at lower pH values. One concern with this revised mode of operation is the potential for increased formation of HAA5 at the lower pH value in the first clearwell, since HAA5 formation is typically greater at lower pH values.

For the bench-scale testing, chlorine contact, both with and without prior chlorine dioxide addition, was assessed at various pH levels to simulate the effect that clearwell pH has on the formation of DBPs. The testing was conducted by collecting a sample of combined filter effluent and adjusting to the desired pH (pH values between 5.0 and 8.3 were analyzed) prior to chlorine contact for a time period simulating the full-scale chlorine contact time in the onsite Clearwell No. 1. For the chlorine dioxide studies, a chlorine dioxide dose of either 0.5 mg/L or 1.0 mg/L was added to the sample prior to the addition of chlorine. At the end of the period of chlorine contact, the final pH was adjusted to match the full-scale finished water pH, and ammonium chloride and additional chlorine were added to form chloramines to match the full-scale finished water combined chlorine concentration.

Simulated distribution system analyses of THM and HAA formation were performed to assess the effects of time of travel within the distribution system. A series of samples were drawn from each test condition and were incubated for 1-, 3-, and 7-day time periods. These provided simulated distribution system analyses of THM and HAA formation to assess the effects of time of travel within the distribution system. An initial THM and HAA sample was also withdrawn for each treatment scenario.

The bench-scale testing results from the two weeks of testing indicated that chemically decreasing the pH during chlorine contact will decrease THM formation in the finished water for many of the raw water quality conditions that occur. Decreasing the pH during chlorine contact did not cause any significant increase in the formation of HAA5 during either week of testing.

Water quality conditions influence the effectiveness of pH adjustment as a method for minimizing the formation of THMs. One water quality factor that appears significant is the bromide concentration, with elevated bromide levels in the raw water appearing to decrease the effectiveness of pH adjustment during chlorination for control of THMs. The bromide level in the raw water for the first week of testing was 0.16 mg/L, and the bromide level in the raw water for the second week of testing was 0.28 mg/L. The

increased bromide concentration during Week 2 affected the speciation of THMs formed. During Week 1, the most heavily chlorinated species, chloroform and bromodichloromethane, constituted over 60 percent of the THMs. During Week 2, the most heavily brominated species, bromoform and chlorodibromomethane constituted almost 80 percent of the THMs.

The elevated bromide levels during the second week of testing also coincided with an increased yield of THMs per amount of total organic carbon (TOC) present. Higher specific yields were seen during the Week 2 testing when compared to the Week 1 testing. For Week 1, the combined filter effluent TOC value was 3.2 mg/L, with seven-day THM formation values of 46 to 64 $\mu\text{g/L}$ at the various pH levels, indicating yields of 14 to 20 $\mu\text{g THMs/mg TOC}$. For Week 2, the combined filter effluent TOC value was 1.2 mg/L, with seven-day THM formation values of 63 to 77 $\mu\text{g/L}$, indicating yields of 52 to 64 $\mu\text{g THMs/mg TOC}$. This greater yield can be partially explained by the higher percentages of brominated species, which have higher molecular weights, formed during the Week 2 testing. However, even when calculated on a molar basis as opposed to a weight basis, the increased yields during Week 2 are still evident.

In addition to the effects on the initial formation of THMs, the increased tendency to form the more heavily brominated THMs under the higher bromide conditions in Week 2 appears to have resulted in a degree of continued THM formation following the addition of ammonia to form chloramines. This condition contrasted with the tendency of ammonia addition to quench further THM formation over time during Week 1. These results have implications regarding the potential for a degree of additional THM formation in the distribution system under some water quality conditions when higher bromide levels are present.

The use of chlorine dioxide prior to chlorination was effective for reduction of THM values during both weeks of testing. Similar results have been observed in the full-scale plant at pH 8.3. The bench-scale results indicate that chlorine dioxide is effective at doses of 1 mg/L, with less effect seen at doses of 0.5 mg/L. Some bench-scale reduction in HAA5 values was generally seen with chlorine dioxide addition, although the reduction was less than that seen for THMs. Due to the limited full-scale HAA5 data, it is difficult to observe a full-scale trend for HAA5 as a function of ClO_2 dose.

One additional observation made from the bench-scale testing results is that the HAA9 values for both weeks of testing without ClO_2 addition were substantially greater than the HAA5 results. In addition, the HAA9 data followed the expected trend of increased formation with decreasing pH, a trend that was not seen in the regulated HAA5 values.

These bench-scale results indicate that operating at a lower pH during the period of free chlorine contact in the first clearwell will assist Charleston CPW in meeting the Stage I DBPR for THMs, while not significantly increasing HAA5 formation under many of the water quality conditions encountered. This reduction in pH for control of TTHMs may not eliminate the periodic use of ClO_2 , but should reduce its use. Similar results were also seen in the full-scale plant during the period when both Stoney Clearwell No.1 and

Stoney Clearwell No. 3 were in service, which allowed the WTP to operate at a lower pH during chlorine contact in the first clearwell.

CHLORINE DIOXIDE FOR PRIMARY DISINFECTION

With the Stoney Clearwell No. 1 out of service, Charleston CPW has returned to operation of only one clearwell, with chlorine contact time occurring in Stoney Clearwell No. 3 at a pH of approximately 8.3 to 8.7. Since this mode of operation has led to higher levels of THMs and HAA5 during certain periods of the year and certain water quality conditions, Charleston CPW is considering other options for obtaining CT credit while minimizing DBP formation in the finished water.

One option that is currently being evaluated is the use of chlorine dioxide or a combination of chlorine dioxide and chloramines for primary disinfection at the Hanahan WTP. For several years, CPW has applied chlorine dioxide to the filtered water to reduce the formation of DBPs, but has traditionally achieved all CT credit with the use of free chlorine in onsite clearwells.

Since the Hanahan WTP is a conventional surface water treatment plant, it has been granted credits for 2.5-log removal of *Giardia* cysts and 2-log removal of viruses by filtration. The addition of a disinfectant must be able to achieve 0.5-log inactivation of the *Giardia* cysts and 2-log inactivation of viruses for a total of 3.0-log inactivation of *Giardia* cysts and 4.0-log inactivation of viruses. For chlorine dioxide, unlike chlorine or chloramines, the controlling microorganism is dependent on temperature; below 10° C, a higher CT for virus inactivation is required; above 10° C, a higher CT is required for *Giardia* cyst inactivation.

The preliminary evaluation indicates that, based on the available detention times for both the Stoney and Booker portions of the plant, chlorine dioxide alone or in combination with chloramines may be a viable option for obtaining CT credit at the Hanahan WTP at the current temperatures and rated flows. The most feasible option for the use of chlorine dioxide appears to be the application of chlorine dioxide upstream of the filters, with a chlorine dioxide residual maintained through the filters to, and including, the onsite clearwells. Following the onsite clearwells, ammonia and free chlorine would be added to form chloramines for secondary disinfection.

A second option, which utilizes both chlorine dioxide and chloramines for primary disinfection, is the application of chlorine dioxide upstream of the filters and maintenance of a chlorine dioxide residual through the filters to the entrance of the onsite clearwells. Ammonia and free chlorine could then be added prior to the onsite clearwell with a chloramine residual maintained in the onsite clearwells and into the distribution system. This option appears feasible for temperatures above 20° C, which is typically seen during the months of May through September.

Both of the options involving chlorine dioxide and chloramines will be effective for controlling THM and HAA formation. The main constraints for any option utilizing

chlorine dioxide will be to maintain the chlorine dioxide dosage at less than 1.25 mg/L to minimize concerns with formation of chlorite and to maintain the chlorine dioxide residual leaving the plant at a level less than approximately 0.2 mg/L to minimize concerns with odors in the distribution system related to the chlorine dioxide, the most common of which are kerosene/cat urine odors seen with new carpet.

Calculations applied for CT credit at the plant have thus far been based on the step-change method. The step-change method is the simplest and most widely used method for calculation of CT. With this method, the residual at the end of the contact time is assumed to be the residual at the beginning and throughout the contact time. However, with disinfectants that have a relatively fast decay like chlorine dioxide or ozone, this method also can underestimate the true exposure of the disinfectant to potential pathogens. The use of a decay constant and subsequent use of an integrated method that accounts for the decay could provide a significant increase in disinfection credit when considering chlorine dioxide as a primary disinfectant.

Given the reactivity of chlorine dioxide, the use of an integrated method to determine CT credit will be appropriate if good decay constants can be developed for the decay of chlorine dioxide within the plant. Some bench-scale work has been performed, and full-scale samples are currently being taken to try to develop a database for determination of a decay constant for chlorine dioxide downstream of the filters. This approach has a greater advantage during warmer periods when the rate of decay is greatest. Application during colder periods may prove to be less advantageous due to the slower rate of change in chlorine dioxide concentration.

SUMMARY

At the Hanahan WTP in Charleston, South Carolina, control of disinfection byproducts has traditionally been accomplished through the use of chloramines in the distribution system, and through the periodic addition of chlorine dioxide downstream of filtration. With the promulgation of the Stage 1 DBPR, and the pending Stage 2 DBPR, Charleston CPW has been investigating different ways to refine and improve their strategy for DBP control. The options investigated include the use of pH control during chlorine contact and the addition of chlorine dioxide prior to chlorine contact. In addition, evaluations are currently underway to consider chlorine dioxide or a combination of chlorine dioxide and chloramines in lieu of free chlorine for primary disinfection.

Bench-scale testing was performed during two separate summer periods to assess the effect of pH adjustment and chlorine dioxide addition on the formation of THMs and HAAs in filtered water. Chlorine contact, both with and without prior chlorine dioxide addition, was assessed at various pH levels to simulate the effect that clearwell pH has on the formation of THMs and HAAs. The results of this bench-scale testing indicated that:

- Chemically decreasing the pH during chlorine contact will decrease THM formation in the finished water for many of the raw water quality conditions that occur.

Decreasing the pH during chlorine contact did not cause any significant increase in the formation of HAA5 during either week of testing.

- Water quality conditions influence the effectiveness of pH adjustment as a method for minimizing the formation of THMs. Elevated bromide levels in the raw water corresponded to a decrease in the effectiveness of pH adjustment during chlorination for control of THMs. The increased bromide concentrations during the second week of testing affected the speciation of THMs formed and increased the amount of TTHMs formed (per amount of organics present).

In addition to the effects on the initial formation of THMs, the increased tendency to form the more heavily brominated THMs under the higher bromide conditions in the second week of testing appears to have resulted in a degree of continued THM formation following the addition of ammonia to form chloramines. This condition contrasted with the tendency of ammonia addition to quench further TTHM formation over time during the first week of testing. These results have implications regarding the potential for a degree of additional THM formation in the distribution system under some water quality conditions when higher bromide levels are present.

- Chlorine dioxide addition prior to chlorine contact is effective in the reduction of THM formation. Results from both weeks of testing indicated that chlorine dioxide is effective at doses of 1 mg/L, with less effect seen at doses of 0.5 mg/L.

In assessing the effect of these observations on disinfection practices at the Hanahan Water Treatment Plant, some limitations are indicated for applying the strategy of pH adjustment during chlorination under certain water quality conditions. However, this remains a key tool for cost effectively meeting disinfection byproduct (DBP) regulations under most water quality conditions. Depending on the time of year and the levels of organics and bromide in the raw water, this strategy may need to be supplemented with other strategies such as chlorine dioxide addition.

Ongoing work includes evaluation of the use of chlorine dioxide in lieu of free chlorine for primary disinfection. The preliminary results from these evaluations indicate that the use of chlorine dioxide applied pre-filtration and maintained through the onsite clearwells may be a viable option for obtaining CT credit at the temperatures and current rated capacity of the plant. In addition, the use of chlorine dioxide applied pre-filtration and maintained to the entrance of the onsite clearwells, with ammonia and free chlorine added prior to the onsite clearwell with a chloramine residual maintained in the onsite clearwells and into the distribution system appears to be a feasible option for temperatures above 20° C (typically seen during the months of May through September).