

Technical Memorandum

To: Municipal Treatment Plant Manager/Consulting Engineer
From: Dean Gregory
Date: February 9, 2008
Re: Impact of ClO_2 on TTHM/HAA-5 formation at a South Carolina treatment facility

Project Description and Findings

This memorandum summarizes the findings of a bench-scale study of the impact of chlorine dioxide (ClO_2)—added as a pre-oxidant—on TTHM/HAA-5 formation in finished water from a South Carolina water treatment facility. The treatment facility currently applies free chlorine for primary disinfection. In order to minimize TTHM/HAA-5 formation in the distribution system, ClO_2 was investigated for use as a pre-oxidant—where it can destroy TTHM/HAA-5 precursors as well as taste and odor compounds—and, potentially, as an alternative disinfectant. In previous studies, over a wide range of raw water quality, ClO_2 has been shown to be very effective for oxidizing TTHM/HAA-5 precursor compounds and reducing formation in the distribution system. Another potential advantage of using chlorine dioxide for pre-oxidation would be a reduction in post-chlorine usage, which would further reduce TTHM/HAA-5 formation.

The overall objective of this project was to determine the impact of ClO_2 , applied to the raw water as a pre-oxidant, on TTHM and HAA-5 formation in finished water. The major findings include:

The application of chlorine dioxide to the raw water can significantly reduce TTHM/HAA-5 formation in the WTP clearwell/distribution system. Compared to the control process (no pre-ox.), chlorine dioxide doses of 0.75 and 1.25 mg/L reduced the TTHM level by 28 and 61 percent, respectively (Figure 1). HAA-5 levels were reduced by 39 and 48 percent for the same doses.

Overall, the rate of chlorine dioxide decay in the raw water is relatively low. Typical applied doses for pre-oxidation should be in the range of 0.6 – 0.9 mg/L (Figure 3).

Compared to the control process (no pre-ox.), the use of chlorine dioxide as a pre-oxidant can reduce post-chlorine usage by 15 – 25 percent.

Experimental Approach and Methods

Water quality. Table 1 provides water quality data for the raw water sample. The water was shipped overnight in a cooler to CDG laboratory facilities in Arvada, CO. Upon its arrival, the water was immediately stored in a refrigerator until the experiments were commenced.

Table 1. WTP raw water quality.

Constituent	Raw
pH	6.31
Alkalinity (mg/L as CaCO ₃)	19
Total Organic Carbon (mg/L)	2.41
Turbidity (NTU)	4.66
Temp. used for all experiments (°C)	20

Simulated distribution system experiments. The impact of the following three pre-oxidation scenarios on TTHM/HAA-5 formation was examined in simulated distribution system (SDS) experiments:

Control process in which no pre-oxidant was used. Following the coagulation-flocculation-sedimentation processes a post-chlorine dose of **2.0 mg/L** was applied.

ClO₂ as a pre-oxidant (dose = 0.75 mg/L), followed by coagulation-flocculation-sedimentation and chlorination (**1.75 mg/L**).

ClO₂ as a pre-oxidant (dose = 1.25 mg/L), followed by coagulation-flocculation-sedimentation and chlorination (**1.50 mg/L**).

For scenarios 2 and 3 the ClO₂ was added 3 minutes prior to the coagulant, which also allowed lower post-chlorine doses to be used. Following the final application of chlorine, a 5-day holding period--in the dark, at pH = 6.8 ± 0.05 and T = 20°C--was provided prior to collecting TTHM/HAA-5 samples. Free chlorine residuals were measured after 24 hours and again after 5 days.

Coagulation/flocculation/sedimentation processes. A standard 2-L jar test apparatus was used to simulate the full-scale coagulation/flocculation/sedimentation processes. After the rapid mix stage (30 sec. @ 300 rpm), a three-stage tapered mixing energy flocculation process was used (15 min. @ 48, 32, and 18 rpm, respectively), followed by a 30-min. settling period. A PACl dose of 17 mg/L was used for all samples. The coagulation pH was 6.05 ± 0.05. For the SDS phase of the experiments the pH of three samples was adjusted to 6.7. TOC samples were collected after the settling period and analyzed by the UV/persulfate method (Standard Methods 5310 C).

Chlorine dioxide demand/decay. A chlorine dioxide stock solution was produced using a CDG bench-scale chlorine dioxide generator. The solid sodium chlorite/chlorine gas process produces

chlorine dioxide gas that is virtually 100 percent pure. The concentration of the stock solution was approximately 3000 mg/L throughout the period of experiments. Demand/decay experiments were conducted using raw water. For each experiment ClO_2 residuals were measured over time, from $t =$ zero to $t = 20$ minutes (or until the residual reached zero). Applied doses were 0.5, 1.0, and 1.5 mg/L. The Lissamine Green B method was used to measure ClO_2 residuals.

Results and Discussion

TTHM/HAA-5 formation. The results of the SDS experiments, showing TTHM/HAA-5 formation during a 5-day free chlorine contact period, are presented in Figure 1. Compared to the control process, chlorine dioxide doses of 0.75 and 1.25 mg/L decreased the TTHM concentration from 36 to 26 and 14 $\mu\text{g/L}$, respectively (reductions of 28 and 61 percent). HAA-5 levels were reduced by 39 and 48 percent. These data clearly indicate that chlorine dioxide will oxidize a significant fraction of both TTHM and HAA-5 precursor compounds in the raw water. In addition to TTHM/HAA-5 reduction, the application of ClO_2 as a pre-oxidant will provide other treatment process benefits such as reducing T&O compounds, manganese oxidation, and optimization of particle removal during coagulation-sedimentation-filtration.

Figure 1. TTHM/HAA-5 formation in finished water for three different pre-oxidation processes. Temperature = 20°C, pH = 6.7, contact time = 5 days, TOC level of the three samples ranged from 1.51 – 1.66 mg/L.

TOC removal. The TOC residual in the three samples was measured following the sedimentation process. In the case of the 1.25 mg/L dose, the application of chlorine dioxide to the raw water improved TOC removal by approximately 9 percent (Figure 2). These results are typical for low-TOC waters such as the sample from this South Carolina WTP.

Figure 2. TOC removal for the control and pre- ClO_2 processes. PACl dose = 17 mg/L, coagulation pH = 6.05 \pm 0.5.

Chlorine dioxide demand/decay. Chlorine dioxide decay rates for three applied doses in raw water are shown in Figure 3. Overall, the chlorine dioxide demand was relatively low in this source, as evidenced by the fact that, for a typical water treatment dose of 1.0 mg/L, the initial demand was only 0.3 mg/L and after a 20-min. contact period a relatively high residual of 0.46 mg/L remained. These results were expected, given the relatively low TOC concentration of this water (2.41 mg/L). In

addition to providing time for the reaction with DBP precursors to occur, this low decay rate suggests that chlorine dioxide could be used to obtain disinfection credit (CT) in the raw water, which would in turn allow the post-chlorine dose to be reduced.

Figure 3. Chlorine dioxide demand/decay in raw water. Applied doses are shown. Temp. = 20°C, TOC = 2.41 mg/L, pH = 6.5.

Impact of pre-oxidation process on chlorine residual. Chlorine residuals in the three samples were measured 24 hours and 5 days after post-chlorination (Figure 4). Overall, these data indicate that the application of ClO₂ will significantly lower the post-chlorine demand, as evidenced by the fact that the 5-d residual in the ClO₂ = 0.75 mg/L sample was significantly higher than that of the control despite the higher initial dose applied to the latter (2.0 vs. 1.75 mg/L). These results also show that a higher pre-oxidation dose of ClO₂ can further reduce post-chlorine demand.

Figure 4. Free chlorine doses and residuals during the SDS experiments. Temperature = 20°C, pH = 6.7.

Chlorite ion formation. Chlorite ion residuals, measured approximately 4 hours after each demand/decay experiment, are shown in Figure 5. The residuals ranged from 59 – 65 percent of the applied ClO₂ dose, which is typical. It should be noted that, due to removal mechanisms such as destruction by UV radiation and adsorption/reduction in the filtration process, full-scale chlorite ion residuals in finished water are generally lower than the residuals shown here. These results indicate that a dose of approximately 1.6 mg/L could be used without exceeding the chlorite ion MCL of 1.0 mg/L.

Figure 5. Chlorite ion formation vs. chlorine dioxide dose in raw water. Full-scale residuals are typically lower than bench-scale results.