Chlorine dioxide generators can produce high levels of disinfection byproducts, but combining chlorine with chlorine dioxide can effectively disinfect water while keeping the level of disinfection byproducts low.

Impact of Mixing Chlorine and Chlorine Dioxide on Total Trihalomethane Formation: Part 1

By Douglas Rittmann, Ph.D., P.E., and Anthony Tarquin, Ph.D., P.E.

The 1986 amendments to the Safe Drinking Water Act[1] are challenging many water utilities to meet stricter water quality requirements. Two rules, the Surface Water Treatment Rule (SWTR)[2] and the Disinfection–Disinfection By-Products (D-DBP) Rule[3], are requiring utilities to implement more advanced technologies in water treatment. The Surface Water Treatment Rule emphasizes the need for utilities to meet minimum levels of disinfection for surface waters, whereas the Disinfection–Disinfection By-Products Rule limits the disinfectant byproducts. Therefore, utilities will have to implement a treatment approach that balances the benefits of disinfection against disinfection byproducts.

After the *Cryptosporidium* outbreak in Milwaukee during March 1993[4], many utilities immediately began investigating the possible use of more advanced disinfectants such as ozone and chlorine dioxide in order to combat the threat from the *Cryptosporidium* protozoan. Chlorine alone was not adequate to inactivate the new target organism. Most disinfectants produce disinfection byproducts causing a potentially long-term adverse health impact from cancer. Although chlorine has served the water industry well for about a century in safeguarding the public's health, it is relatively ineffective against *Cryptosporidium* and can cause excessive trihalomethanes (THMs) in distribution systems.[5] THMs were limited in drinking water in 1979 to 100 ppb (THM Rule) because of their potential carcinogenic properties.[6]

Although ozone is the strongest and most capable disinfectant against *Cryptosporidium*, it can produce excessive bromates, a potential carcinogen.[7] Chlorine dioxide also is capable of inactivating *Cryptosporidium* but not as well as ozone. However, there are concerns about its disinfection by-products such as chlorites, identified as causing hemalytic anemia, especially in 13 percent of black males.[8] In El Paso, Texas, the Umbenhauer/Robertson Water Plant is adding 2 mg/L of chlorine with 3 mg/L of chlorine dioxide in the same disinfection zone in order to minimize TTHM formation and maximize disinfection capability (Figure 1).

The primary purpose of this paper is to examine the impact of adding chlorine with chlorine dioxide on the formation of TTHMs. Laboratory and plant studies are presented to determine the impact of the addition of chlorine alone and in combination with chlorine dioxide on the formation of TTHMs. Since the Eka SVP-Pure Chlorine Dioxide Generator system is a chlorate-based technology and does not have chlorine or chlorite in its generator stock solution, it was used for testing.[9]

Laboratory Study Procedures

This project was carried out using laboratory studies. Analyses were performed at the El Paso Water Utilities Central Laboratory and an outside EPA-approved laboratory using proper QC/QA procedures. The raw water source for the studies was the Rio Grande River. This water was available for treatment during the period of March through September in El Paso. The raw water samples were dosed with chlorine dioxide solutions obtained from the chlorine dioxide generator utilizing a 40 percent sodium chlorate/50 percent hydrogen peroxide/78 percent sulfuric acid system (Figure 2). In order to evaluate the impact of adding chlorine with chlorine dioxide on disinfection byproducts, raw water samples were dosed with 1, 2 or 3 mg/L of chlorine dioxide and dosed with various amounts of chlorine ranging from 0 percent (chlorine dioxide alone) to 200 percent of the chlorine dioxide dose. After the sample sets were initially dosed with chlorine dioxide and chlorine, they were held for about 45 minutes. Then, all of the sample sets were equally dosed with 7 mg/L of chlorine and held for a 1-hour contact period in order to compare the effects of various combinations of chlorine dioxide and chlorine on TTHM formation.

Although chlorine has served the water industry well for about a century in safeguarding the public's health, it is relatively uneffective against* Cryptosporidium *and can cause excessive THMs in distribution systems.

Comparison of the Effect of 1 mg/L of ClO_2 and Chlorine Doses on TTHMs

The results of these tests are shown in Figure 3. As illustrated, the raw sample dosed with 7 mg/L chlorine alone, held for 1-hour contact time, forms about 42 ppb of TTHMs. The 1 mg/L chlorine dioxide dose with 0 percent chlorine had insignificant reduction in TTHMs. This is to be expected because the initial chlorine dioxide demand (< 1 minute time) of the Rio Grande River water is usually between 1.5 mg/L and 2.0 mg/L (i.e., there seems to be insufficient dosage to cause a long enough contact time of the chlorine dioxide with TTHM precursors to cause a significant reduction in TTHMs). However, when chlorine is added with the 1 mg/L of chlorine dioxide dose, the TTHM levels are reduced at the 33 percent, 66 percent and 100 percent chlorine levels. At the 150 percent and 200 percent levels, the TTHMs are higher than the 0 percent chlorine and raw TTHM levels. The results imply that the chlorine

Figure 1: Umbenhauer/Robertson Water Plant Flow Schematic

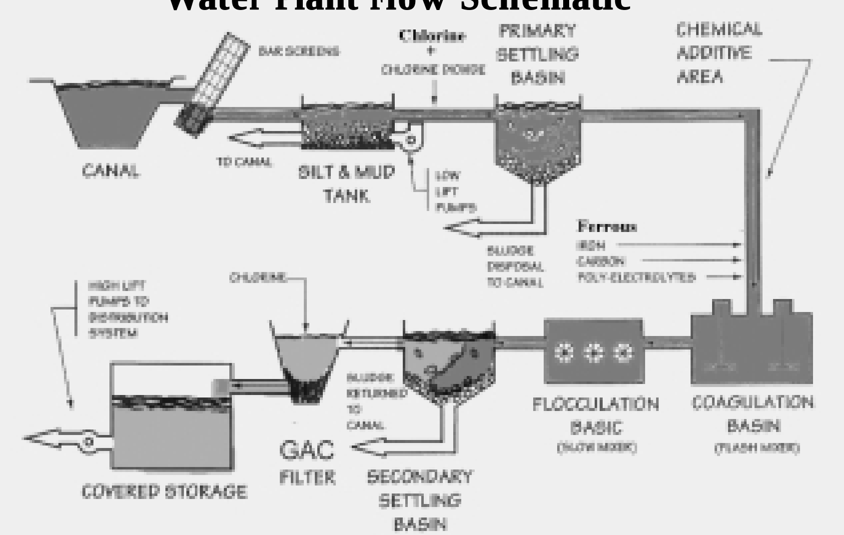


Figure 2: Eka SVP Pure Chlorine Dioxide Generator

with 1 mg/L chlorine dioxide is participating in TTHM reduction by possibly reforming chlorine dioxide with the chlorite by product of chlorine dioxide degradation.

Since most water plants dose at the 1 mg/L chlorine dioxide level, the perception from most water professionals is that chlorine dioxide at this concentration can only prevent TTHM formation, not reduce TTHMs. However, in this testing, it has been shown that TTHM reduction can be accomplished by adding chlorine with chlorine dioxide, even at the 1 mg/L dosage level. When the chlorite byproduct level is exceeded by the amount of the chlorine necessary to reform chlorine dioxide, the excess chlorine will participate in forming higher TTHMs. This also implies that chlorine is able to reduce the chlorite byproduct levels in order to form chlorine dioxide. As shown in the next section, the chlorite and chlorate levels were analyzed at various percent chlorine dosages to determine if the chlorine was reducing chlorite.

Chlorine Effect on Chlorite and Chlorate at 1 mg/L Chlorine Dioxide Dose

In Figure 4, the chlorite and chlorate levels versus chlorine levels from 0 percent to 200 percent are plotted for the same samples depicted in Figure 3. At 0 percent chlorine, the chlorite level is highest at 0.46 mg/L while the chlorate level is 0.19 mg/L. As the chlorine dosages are increased, the chlorite levels decrease and the chlorate levels are rather flat. The overall reduction in chlorite was about 0.10 mg/L (0.46 mg/L to 0.36 mg/L). The chlorate level increase was negligible at about 0.03 mg/L (0.19 mg/L to 0.22 mg/L). Therefore, it seems reasonable that the chlorite reduction is principally caused by the sequence of reactions with chlorine to reform chlorine dioxide, ultimately being reduced to chloride. If the chlorine level exceeds the amount needed by the chlorite level for reforming chlorine dioxide, the amount of the chlorine not needed for chlorite oxidation will participate in forming TTHMs. This may be the reason for the lowest TTHM level at about 66 percent chlorine and the subsequent increase in TTHMs at the 100 percent, 150 percent and 200 percent chlorine dosages.

Figure 3: 1 mg/L Chlorine Dioxide vs. Percent of Chlorine Doses

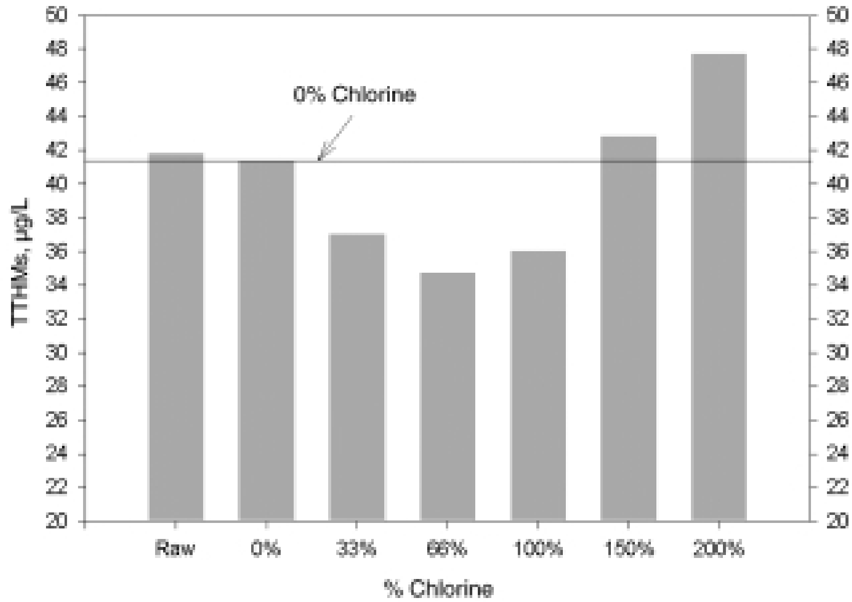
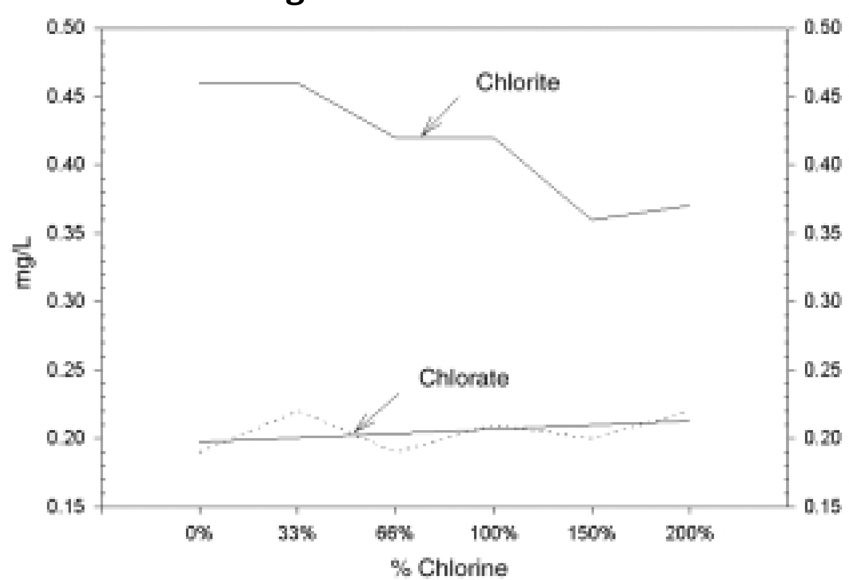


Figure 4: Chlorine Effect on Chlorite and Chlorate at 1 mg/L Chlorine Dioxide Dose



Part 2 will appear in the September issue and will present conclusions about the study.

Acknowledgments

Thanks are extended to the El Paso Water Utilities/Public Service Board for funding and making their facilities available to complete this study. Special thanks go to Richard Wilcox for his invaluable contributions and outstanding laboratory work in analyzing our samples.

For a list of references, please go to www.waterinfocenter.com.

About the Authors:

Douglas Rittmann, Ph.D., P.E., is a water/wastewater consultant and a lecturer at the University of Texas at El Paso Civil Engineering Department. He was previously the division manager for the El Paso Water Utilities.

Anthony Tarquin, Ph.D., P.E., is a professor in the Department of Civil Engineering at the University of Texas at El Paso.