

Impact of Chlorine Dioxide on TTHMs Reduction in Drinking Water
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Introduction

In 1974, chloroform, a trihalomethane (THM) species, was identified from pre-chlorination and later established as a potential carcinogen by USEPA (1). As a result, researchers and utilities began evaluating chlorine dioxide as a replacement for chlorine in pretreatment disinfection. At the 1978 20th Annual Public Water Supply Engineers' Conference, enough was known to suggest that primary disinfection by chlorine dioxide would be an acceptable alternative to the use of chlorine (2). In 1979, the American Water Works Company showed that disinfecting with chlorine dioxide reduced TTHMs in the range of 59-90 percent (3). After the potential carcinogenic effects from TTHMs were established and alternative treatment methods were available, the USEPA promulgated, in 1979, the maximum contaminant level (MCL) for TTHMs at 0.10 mg/L based on an annual running average. After the establishment of the TTHMs MCL, the Louisville Kentucky Water Company (4) and the Kentucky-American Water Company in Lexington (5) chose chlorine dioxide as a necessary treatment modification for reducing trihalomethane formation. Other studies and water plants, in the 1980s, confirmed that chlorine dioxide could limit TTHMs while providing primary disinfection, oxidizing taste and odor compounds, oxidizing iron and manganese and improving color removal. Chlorine dioxide's use as a pre-oxidant also allowed the application of chlorine at a later stage in the treatment train after significant amounts of TTHM precursors were removed by coagulation and filtration (6-9).

Chemistry of Chlorine Dioxide

About 50 to 70 percent of the chlorine dioxide gas reacted with natural organic matter (NOM) in water result initially in chlorite formation by the following reduction half-reaction (10):



Because chlorite is limited in drinking water to 1.0 mg/L, the maximum chlorine dioxide dosage in the plant has been limited to about 1.4 mg/L. During the 1990s, M. H. Griese et al introduced a new technology of chlorite reduction by ferrous chloride or ferrous sulfate. He determined, in bench-scale testing, that 0.3 mg/L of chlorite could be reduced by 1.0 mg/L of ferrous iron as Fe in the water treatment process (11). Chlorite oxidized the ferrous ion to the ferric ion form, which became a strong coagulant while lowering the chlorite level. In 1993, this new process was implemented on a plant-scale basis at the 40 mgd Canal Plant in El Paso Texas (12). With the chlorite reduction capability, the Canal Plant raised its chlorine dioxide dosage to 3.0 mg/L in order to lower TTHMs more and increase its disinfection capability to meet the threat from

Cryptosporidium sp. Bench scale and plant tests verified that 2.0 mg/L chlorine dioxide dose was required to obtain significant reduction of TTHM precursors (humic and fulvic acids) (13,14). At lower chlorine dioxide doses, TTHM reduction depended primarily on the elimination of the chlorine dose and/or reduction of the contact time in pretreatment.

Chemistry of TTHMs Formation

There are six major contributing factors to TTHM formation. They are: 1. chlorine dose; 2. total organic carbon (TOC) level; 3. contact time; 4 water temperature; 5 pH; 6. bromide. An increase in any one or more of these parameters increase TTHM levels in water. Therefore, it is not surprising that the highest TTHM levels normally occur during the summer months when water temperatures, TOC levels, and chlorine demands (doses) are the highest. On the other hand, if chlorine dioxide replaced chlorine in pretreatment, then lower TTHM levels result in the distribution system because the chlorine dose has been eliminated and the contact time reduced. If the chlorine dioxide dose was raised to 2.0 mg/L or higher with chlorite reduction by ferrous ion, then additional TTHM precursors are removed to facilitate even lower TTHMs. For example, the El Paso Water Plant showed 40% reduction of maximum TTHM levels when 1.4 mg/L chlorine dioxide dose replaced pre-chlorination. However, when the water plant raised the chlorine dioxide dose to 3.0 mg/L, an additional 20% reduction (.030 mg/L) of TTHMs was achieved (13-15). Since raw water quality parameters vary, one should expect that individual results will vary but the basic principle of TTHM reduction by chlorine dioxide is a consistent expectation in any raw water quality.

Chemistry of Chlorine Dioxide versus Other Oxidants

Chlorine dioxide is superior to other oxidants in reducing TTHMs' formation on an equal dosage basis. It is readily soluble in water and remains in solution as dissolved gas in the pH range of 2 to 10. It does not hydrolyze to any appreciable extent like chlorine, which causes TTHMs and is weaker as an oxidant and disinfectant especially with increasing pH levels. Ozone increases the biodegradable dissolved organic carbon (BDOC) level in the distribution system, which may cause re-growth problems and higher TTHM levels. A consensus has emerged that ozone oxidation alone is relatively ineffective in controlling halogenated DBP precursors (16-18). Chloramines, the weakest disinfectant, form some TTHMs in pretreatment but chlorine dioxide will not. However, when chloramines are used in the distribution system, they are effective in minimizing TTHM formation where longer contact times are necessary. Therefore, chlorine dioxide use in pretreatment with chlorine/chloramines in the distribution system is an excellent combination for obtaining maximum disinfection capability with minimum TTHM formation potential (14,19).

Application of Chlorine Dioxide

Chlorine dioxide is produced on site from two chemicals (Purate[®] and 78% Sulfuric Acid) using an Eka Chemicals Inc. SVP-Pure[®] Generator. The chlorine dioxide solution should be applied at a point in the water treatment process where uniform mixing is

possible. It is recommended that the feed point should be well below the water level or at a point where volatilization of the chlorine dioxide gas is prevented. Also, chlorine dioxide should not be fed with lime or powdered activated carbon at the same location.

SVP-Pure[®] ClO₂ Generator



About the Author

Dr. Douglas Rittmann has a PhD in Environmental Science and Engineering from the University of Texas at El Paso and he is a registered professional engineer in Texas. He has more than 35 years experience in water and wastewater utility operations. In 1993, he developed the first plant use of ferrous chloride to reduce excessive chlorite levels at El Paso Texas.

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