TwinOxide compared to Chlorine

TwinOxide is using two powders to produce a 0.3% Chlorine Dioxide Solution. Because both Chlorine Dioxide and Chlorine contain the word or chemical Chlorine, many people think that the two molecules are similar. This is far from the truth, they are entirely different molecules, have significantly different characteristics and properties, and disinfect water through different mechanisms.

A lot of material and data has been published on Chlorine and Chlorine Dioxide. Collation and correlation of this material can be used to compare and contrast Chlorine Dioxide and Chlorine when used as disinfectants, biocides or sterilizers, which is the content and objective of this Bulletin. TwinOxide exhibits all of the attributes of Chlorine Dioxide, and provides some additional benefits with respect to Health, Safety, Environmental and Capital Expenditure, compared to Chlorine Dioxide produced by generators.

Chlorine is probably amongst the oldest disinfectant used for treatment of drinking water. Chlorine is effective at killing many of the microorganisms commonly found in water, and is relatively low cost, which, ignoring other issues related to the use of Chlorine, makes it look very favorable. Chlorine Gas is very poisonous and hazardous to handle. Sodium Hypochlorite, which is less hazardous, is often used as a biocide.

Main comparisons of Chlorine and Chlorine Dioxide can be broadly classified into a few main categories.

Disinfection By-Products

Following concerns over reaction products formed when using Chlorine in waters containing organic compounds and organic matter, Drinking Water Regulations were revised in 1974. While disinfecting with Chlorine, and with Bromine or Iodine, or Halogens in general, reaction products that form, known as Disinfection By-Products (DBPs), are Halogenated Organic Molecules, broadly categorized as Trihalomethanes (THMs), Halo-acetic Acids (HAAs) and Mutagen X (MX). These are known to be toxic, and harmful to humans. THMs, HAAs and MX's have been linked to cancer, miscarriages, stillbirths and birth defects. The cancer potency of Mutagen X is 170 times greater than that of chloroform.

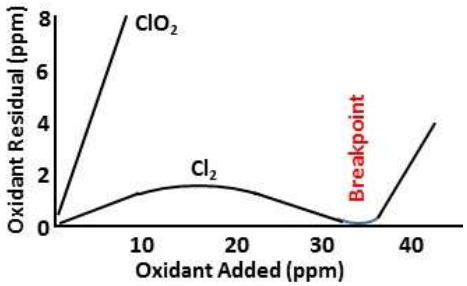
Chlorine reacts with Ammonia and Ammoniacal Compounds to form Chloramines, which creates a large Chlorine Demand, requiring the use of significantly higher concentrations of Chlorine in order to obtain a Free Chlorine

Residual. Chloramines are also biocidal but in the order of 80 to 200 times less efficient, or slower, than Chlorine.

Chlorine Dioxide does not react with Ammonia so Ammonia and Ammoniacal Compounds in the water to be treated does not create a Chlorine Dioxide Demand and higher Chlorine Dioxide concentrations are not required.

The profile of residual obtained versus dosage for Chlorine and Chlorine Dioxide, Figure 1, is similar for both highly polluted waters and waters containing Ammonia. The point where a Free Residual Chlorine Concentration is finally obtained is known as the Breakpoint and application of this technique is called Breakpoint Chlorination.

Figure 1
Measured Residual versus Dosage in Polluted Water



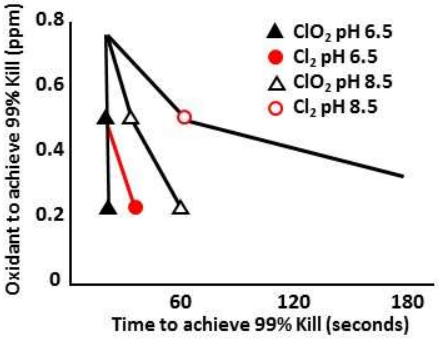
The main potential concern with regard to Disinfection By-Products produced by Chlorine Dioxide are probably Chlorite and Chlorate Production. The amount of Chlorite and Chlorate produced depends upon the original purity of the Chlorine Dioxide Solution used and the Concentration used, which is related to the strength of the solution and target Chlorine Dioxide Residual. Laboratory tests have shown that a nominal 0.3% Chlorine Dioxide Solution produced from TwinOxide Components A and B contained 3800 ppm Chlorine Dioxide, 480 ppm Chlorite and 528 ppm Chlorate.

World Health Organization (WHO) regulations stipulate a maximum Total Chlorite and Chlorate concentration in Drinking Water of 0.7 ppm. Disinfection of Drinking Water with TwinOxide® 0.3% Chlorine Dioxide Solution is significantly lower than WHO specifications and limitations for Chlorite and Chlorate concentration.

Effect of pH

The efficacy of Chlorine, mainly related to "speed of kill", is pH dependent, being slower and requiring higher concentrations in higher pH waters, typically Alkaline Water. Chlorine Dioxide is of the same efficacy over a wide pH range of pH 4 to 10. This can be interpreted as Chlorine Dioxide being a better or more efficient biocide than Chlorine in Alkaline Waters or water above a pH of about 7.5. This is not to say Chlorine does not work in high pH waters, just that it if less efficient as judged by "speed of kill", Figure 2.

Figure 2
Efficiency at pH 6.5 and pH 8.5



The reason for this is that Chlorine hydrolyses in water, the hydrolysis product, Hypochlorous Acid (HOCl) dissociates to Hypochlorite Ions (OCl-). The Hypochlorous Acid and Hypochlorite Ions are in equilibrium, the equilibrium reaction, Equation (ii), moves to the right, that is increased concentration of Hypochlorite Ions, as the pH increases.

$$Cl2 + H2O \rightarrow HOCl + HCl \quad \text{(ia)}$$

$$NaOCl + H2O \rightarrow HOCl + NaOH \quad \text{(ib)}$$

$$HOCl \rightleftarrows H+ + OCl- \quad \text{(ii)}$$

Chlorine Dioxide is a solution of Chlorine Dioxide Gas in water and does not hydrolyze.

Biocidal Efficiency

There are several parameters that may be used to compare the "strength" or "efficacy" of a biocide. One of these, "speed of kill" is illustrated in Figure 2.

In terms of Oxidation Capacity, Chlorine Dioxide is 2.6 times greater than Chlorine. This is derived from the fact that in the redox reaction for Chlorine Dioxide, Chlorine Dioxide accepts a total of 5 electrons, Equations (iii), (iv) and (v).

$$ClO2 + e- \rightarrow ClO2- \quad \text{(iii)}$$

$$ClO2- + 4H+ + 4e- \rightarrow Cl- + 2H2O \quad \text{(iv)}$$

$$\text{Overall, } ClO2 + 4H+ + 5e \rightarrow Cl- + 2H2O \quad \text{(v)}$$

In the redox reaction for Chlorine, Chlorine only accepts 2 electrons, Equation (vi).

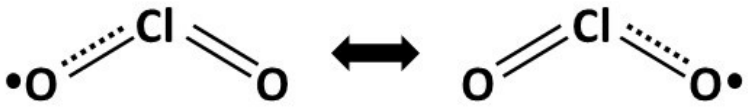
$$Cl2 + 2e- \rightarrow 2Cl- \quad \text{(vi)}$$

Taking Atomic and Molecular Weights, Chlorine Dioxide contains 52.56% Cl, which, taking into account the 5 electron change, equates to 263% Available Chlorine. Chlorine is, by convention, taken as 100% Available Chlorine, which makes Chlorine Dioxide more than 2.6 times the Oxidation Capacity of Chlorine.

These comparisons suggest that Chlorine Dioxide is reduced to Chloride, and during this reaction it accepts 5 electrons. The Chlorine atom remains, until stable chloride is formed. This explains why no chlorinated substances are formed. When Chlorine reacts, not only does it accept electrons but also takes part in addition and substitution reactions. During these reactions, one or more Chlorine atoms are added to the foreign substance, hence the formation of Chlorinated Compounds.

This mode of action highlights the major difference in the mechanism of microbiological control by Chlorine Dioxide and Chlorine. As an oxidizing agent, Chlorine Dioxide is very selective due to unique one electron exchange mechanisms, or free radical electrophilic (i.e. electron-attracting) abstraction, typically behaving like a Free Radical.

Chlorine dioxide attacks the electron-rich centers of organic molecules. One electron is transferred and Chlorine Dioxide is reduced to Chlorite (ClO2-). The mechanism of Chlorine is by oxidative substitution or addition, hence production of Chlorinated By-Products such as THMs, HAAs, etc.



By comparing the oxidation strength and oxidation capacity of different disinfectants, one can conclude that chlorine dioxide is effective at low concentrations. Chlorine Dioxide is not as reactive as Chlorine and only reacts with Sulfuric substances, Amines and some other reactive Organic substances. In microbiology Amines or Amino type compounds are molecules such as Amino Acids, Proteins and Enzymes, all of which are important in the metabolism and biochemical reactions of Microorganisms. Chlorine Dioxide destroy or inactivates these molecules, thus disrupting the metabolism and results in mortality of the organism.

In comparison to Chlorine, less Chlorine Dioxide is required to obtain an effective residual disinfectant. It can also be very effective when a large amount of Organic Matter is present in the water to be treated, such as in polluted Waste Waters.

Efficiency and "speed of kill" are related to the concentration of active disinfectant used. This leads to an important concept that a lethal Concentration (C) of disinfectant must be maintained for a given Contact Time (t). This is known as the CT Value with units typically mg minute/liter or ppm minute, or, mg hour/liter or ppm hour/liter.

CT Value = C x t .....(vii)

Table 1

CT Values to obtain a 99% Kill

Guidelines for Drinking-water Quality, Third Edition Incorporating the First and Second Agenda, Volume 1 Recommendations, World Health Organization, 2008, page 140.

Organism	**Monochloramine**	**Chlorine Dioxide**
Bacteria	$CT_{99\%}$ 278 PPM / Minute	$CT_{99\%}$ 0.19 PPM / Minute
Virusses	$CT_{99\%}$ 430 PPM / Minute	$CT_{99\%}$ 2.8 PPM / Minute
Giardia (protozoa)	$CT_{99\%}$ 1000 PPM / Minute	$CT_{99\%}$ 7.3 PPM / Minute
Cryptosporidium	Not Killed	$CT_{99\%}$ 40 PPM / Minute

Test Conditions	Bacteria NH_2Cl 1-2°C, pH 8.5 ClO_2 1-2°C, pH 8.5	Giardia NH_2Cl 15°C, pH 6-9 ClO_2 25°C, pH 7-7.5
	Viruses NH2Cl 15°C. pH 6-9 ClO2 10°C. pH 7-7.5	Cryptosporidium NH_2Cl 22°C, pH 8 ClO_2 22°C, pH 8

Biofilm Control

Chlorine Dioxide is one of few biocides that is efficient and effective in the control and removal of Biofilm.

Chlorine Dioxide is a better disinfectant than Chlorine because Chlorine Dioxide effectively controls and removes biofilm. Chlorine or Sodium Hypochlorite do not accomplish biofilm control and removal as effectively as Chlorine Dioxide because Chlorine has difficulty penetrating the Biofilm, and, the organic content of the Biofilm reacting with the Residual Chlorine or creating a Chlorine Demand, makes the Chlorine or Sodium Hypochlorite less effective killing organisms associated with the Biofilm. Chlorine Dioxide is dissolved Chlorine Dioxide Gas and can penetrate the slime layer protecting the bacteria in a biofilm. Because it is a powerful oxidizing agent it 'dissolves' the slime layer and kills the exposed bacteria.

Corrosion

There is a false belief that Chlorine Dioxide is corrosive to metals. This is untrue, Chlorine Dioxide is not corrosive to metals.

The misconception is based on the fact that Chlorine Dioxide Solutions prepared using a Chlorite/Acid technique in a Chlorine Dioxide Generator has a very low pH <<1 and is therefore very acidic. This is because excess acid, compared to the stoichiometric requirement, Equation (viii), is used to increase the yield of Chlorine Dioxide in the generator.

$$5NaClO2 + 4HCl \rightarrow 4ClO2 + 5NaCl + 2H2O \qquad \text{(viii)}$$

The stoichiometric requirement based on Equation (viii) is, to produce 1 gram of Chlorine Dioxide, 1.676 gram of Sodium Chlorite and 0.54 gram of Hydrochloric Acid, or, required is 0.32 gram of Hydrochloric Acid for every 1 gram of Sodium Chlorite. In generators, a mixture of 7.5% Sodium Chlorite and 9% Hydrochloric Acid, or, 25% Sodium Chlorite and 30-36% Hydrochloric Acid Solutions are used. In practice, equal volumes of the relevant Sodium Chlorite and Hydrochloric Acid solutions are used. As can be seen from Table 2, the amount of HCl used to improve the yield from the reaction can be 3.75 times that required stoichiometrically.

So, it is the actual Chlorine Dioxide Reactant Solution that is corrosive because it is very acidic, and the acidity is in the form of Hydrochloric Mineral Acid, the chloride ions of which are in themselves corrosive to many metals.

TwinOxide® generates Chlorine Dioxide from Chlorite through oxidation by peroxysulfate in an acidic solution, Equation (ix). Sodium Bisulfate is used to create the acidic medium, it does not produce sulfuric acid.

$$7ClO2^- + HSO5^- + 5HSO4^+ \rightarrow 6ClO2 + Cl^- + 6SO42^- + 3H2O \qquad \text{(ix)}$$

Table 2
Mass Balance of Chlorine Dioxide Production in Generators

Precursor Concentration	7.5% NaOCl 9% HCl	25% NaOCl 30% HCl
NaOCl in 100 ml precursor	7.5 g	25 g
Required HCl	2.42 g	8.05 g
Actual HCl used in 100 ml precursor	9.0 g	30 g
NaOCl:HCl (Stoichiometric 0.32)	1.2	1.2
Excess HCl in 200 ml reaction solution	6.58 g	21.95 g
Excess HCl in 1 litre reaction	32.92 g	109.73 g
Molecular Weight of HCl	36.5	36.5
HCl Molarity = Hydrogen Molarity $[H^+]$	0.90 M	3.01 M
$pH = -\log_{10}[H^+]$	pH 0.04	pH -0.48

The TwinOxide 0.3% Chlorine Dioxide Solution is about pH 2, the same pH as Lemon Juice or Vinegar and much higher than that of the Chlorine Dioxide reaction solution produced in generators. The main cations in TwinOxide® 0.3% Chlorine Dioxide Solution are Sulfate ions, which are much less aggressive or corrosive to metals than the Chloride in generator Chlorine Dioxide reaction solutions. Overall, it can be expected that the TwinOxide® 0.3% Chlorine Dioxide Solution is much less corrosive to metals than Chlorine Dioxide Solutions produced in generators from a Chlorite Acid technique.

Spectrum of Biocidal Efficiency

Chlorine, Sodium Hypochlorite and Chlorine Dioxide are all effective for controlling Bacteria, Fungi and Yeast. However, Chlorine Dioxide tends to be more efficient and effective for controlling Algae, Pathogens, Viruses, Spores and Biofilm. Control and eradication of Biofilm is fundamental for minimizing the Risk of Legionnaires Disease, as is required by many Authorities, particularly in Cooling System, and, Hot and Cold Water Systems. Control of Biofilm can also minimize the potential for Microbiologically Influence Corrosion (MIC).

TwinOxide® 0.3% Chlorine Dioxide Solution

With the exception of Corrosion, TwinOxide® 0.3% Chlorine Dioxide Solution exhibits the characteristics, properties and efficacy of Chlorine Dioxide, as mentioned above. TwinOxide® 0.3% Chlorine Dioxide Solution has some other benefits compared to Chlorine Dioxide produced by other techniques.

Other techniques use concentrated liquid precursors. In the event of a leak or spillage, the liquids will spread, unless they are used and stored within a containment bund. Spread and flow of a liquid oxidizing precursor may allow the oxidant to come in contact with reducible and/or flammable material and can result in combustion and fire. Spread and flow of a liquid Mineral Acid precursor may result in corrosion of material it comes in contact with, and in the case of come metals this corrosion can liberate Hydrogen. The TwinOxide® technique uses solid, powdered precursors which are less likely to spread in the event of spillage, Figure 3, and they are not in the same reactive form as liquid precursors.

Figure 3
Spillage of Liquids and Powders

Leakage of Solution | Spillage of Solution | Spillage of Solid

At concentrations >0.8% Chlorine Dioxide (8000 ppm ClO2) aqueous solutions, with a gas phase, can be explosive. Although several safety features are installed on Chlorine Dioxide Generators to avoid such high and dangerous Chlorine Dioxide Solution concentrations being produced, such as incorrect ratio of the feed of the precursors and/or failure on the dilution water supply, the risk is probably greater than with the TwinOxide® solid precursor technique. With the TwinOxide method the two precursors are added to a volume of water. The weights of the two solid components is fixed for a given specified volume of water or volume of 0.3% Chlorine Dioxide Solution being prepared. Therefore, one would have to add the contents of the component containers to a volume of water that is only 37.5% or about one third of the prescribed volume of water. This is unlikely to happen unless deliberately engineered. TwinOxide has developed a preparation and dosing unit, called TODD (TwinOxide Dual Dosing) , which has water level sensors on the Preparation Tank, linked to a pre-programmed Programable Logic Controller (PLC). Prior to preparation and addition of the contents of the component containers, the PLC will control the volume of water added to each Tank and ensure the correct prescribed volume is added to “fill” the tank. This will ensure the correct volume of water is always present in each dosing Tank at the start of the preparation procedure, and avoid preparation of a solution that is significantly higher than 0.3% ClO2

The cost of equipment required to prepare and dose a TwinOxide 0.3% Chlorine Dioxide Solution is always significantly lower than the cost of a Chlorine Dioxide Generator. (1:1000)