TwinOxide compared to Chloramine

TwinOxide is using a combination of powders (A & B) to produce a 0.3% Chlorine Dioxide Solution. Chlorine Dioxide and Chloramine may appear to be similar, based on names associated with Chlorine. However this is far from the truth, they are entirely different molecules, and they have significantly different characteristics and properties, and will disinfect water through different mechanisms.

A lot of material and data has been published on Chloramine and Chlorine Dioxide. Collation and correlation of this material can be used to compare and contrast Chlorine Dioxide and Chloramine when used as disinfectants, biocides or sterilizers, which is the content and objective of this Bulletin.

TwinOxide does have all 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.

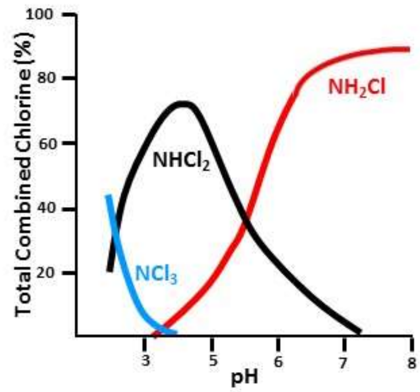
Chloramine has been used as a disinfectant in treatment of drinking water since 1the early 1990s. Chloramine is effective at killing many of the microorganisms commonly found in water, and is effective, although not as effective as Chlorine Dioxide, at controlling biofilm. Unlike Chlorine Dioxide, Chloramine does in fact support the growth of biofilm inside the distribution system surfaces.

Chloramines are products of the reaction between Ammonia and Chlorine, or Hypochlorite, or more correctly Hypochlorous Acid obtained from the hydrolysis of Chlorine Gas or Hypochlorites in aqueous solution. There are three Chloramines, Monochloramine (NH_2Cl), Dichloramine ($NHCL_2$) and Trichloramine or Nitrogen Trichloride (NCl_3). The molecule(s) produced depends upon the ratio of Chlorine, as Cl_2, to Ammonia, as NH_3, used as reactants, Equations (i), (ii) and (iii), and pH of the reactant solution.

$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$	(Cl2:NH3 3-5:1)	(i)
$NH_3 + 2HOCl \rightarrow NHCl_2 + 2H_2O$		(ii)
$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$	(Cl2:NH3 5-7:1)	(iib)
$NH_3 + 3HOCl \rightarrow NCl_3 + 3H_2O$		(iii)
$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$	(Cl2:NH3 >7:1)	(iiib)

Chloramines also have a "preferred pH", *Figure 1.*
Monochloramine is a different chemical from Dichloramine and Trichloramine. Dichloramine and Trichloramine are Chloramine compounds sometimes found in and around which can cause skin, eye, and respiratory problems. These chemicals are not Monochloramine is a different chemical usually linked to drinking water.

Figure 1
Distribution of Chloramines with pH



Chloramination

The practice of using Chloramines to disinfect water is known as Chloramination. Chloramination can be performed in two ways. The Chloramine can be pre-prepared and added, as Chloramine solution, to the water to be treated. The other technique is to Chlorinate the water to be treated and then, at a later stage, add Ammonia to the water, at a correct Chlorine to Ammonia ratio, to form the required Chloramine. In this case, the Chloramine is a Secondary Disinfectant, and this technique is the one normally used to Chloraminate Drinking Water.

Chloramines are weaker oxidizing agents than Chlorine or Chlorine Dioxide and much slower to kill microorganisms, by a factor of 2000 times slower. Therefore, Chloramines require significantly greater contact time and/or higher concentrations than Chlorine Dioxide, which is reflected by the Ct values shown in Table 1.

For this reason, the preferred method to Chloraminate Drinking Water is to initially rapidly disinfect the water with Chlorine, and then add Ammonia to form Monochloramine. The slower, but much more persistent Monochloramine can maintain some biocidal protection of the Drinking Water and distribution pipework for a long time, several days and/or along several kilometers of distribution pipework.

Although this is a beneficial technique with respect to efficiency or speed of kill, it imparts some of the negative aspects of using Chlorine or Hypochlorite as a disinfectant, namely the production of harmful, and *in all cases* carcinogenic, Disinfection By-Products (DPBs).

Disinfection By-Products

Chlorine forms many Chlorinated Organic by-products, including Trihalomethanes (THMs), Halo-acetic Acids (HAAs) and Mutagen-X. 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.

One of the principal benefits of Chloramine is that its use reduces the overall levels of these regulated contaminants compared to Chlorine. Chloramine generally produces a lower amount of THMs and HAAs, than Chlorine. However, if Chloramine is used as a secondary disinfectant, the initial Chlorination of the water will produce THMs and HAAs if there is organic matter in the water.

Chloramine also forms N-nitrosodimethylamine (NDMA), a Nitrosamine that has been identified as a probable human carcinogenic, and, Cyanogen Chloride (CNCl), which is rapidly metabolized to Cyanide in the body. Other by-products that may be formed, in small amounts, are Haloketones, Chloropicrin or Nitrochloroform, Haloacetonitriles, Aldehydes and Chlorophenols.

It is well known that Hydrazine is produced by the reaction between Monochloramine and Ammonia. Hydrazine is a potent carcinogen and is classified by the EPA as a probable human carcinogen with a 10^{-6} risk level of 10 ng/L in drinking water

Chlorine Dioxide does not form any THMs or HAAs. 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.

Biocidal Efficiency

Of the three Chloramines, Monochloramine is the most effective disinfectant. When the pH of the water is 7 or higher, Monochloramine is the most abundant Chloramine. The pH value does not interfere with or affect the effectiveness of Chloramines. Chlorine Dioxide is of the same efficacy over a wide pH range of pH 4 to 11, in summation the pH of the water does not affect the efficiency of either Monochloramine or Chlorine Dioxide. Because Monochloramine is a weak oxidizer and slow, significantly higher concentrations of Monochloramine are required, compared to Chlorine Dioxide, for the same percentage mortality or reduction of viable microorganisms, as illustrated in Table 1.

The mode of action highlights the major difference in the mechanism of microbiological control by Chlorine Dioxide and Chloramine. 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 (ClO_2^-).

Chloramines, like Chlorine, are Oxidizing Agents, and can kill bacteria by penetration of the cell wall and blockage of their metabolism. Monochloramine reacts directly with Amino Acids in bacterial DNA. During deactivation of microorganisms, Chloramines destroy the shell which protects a virus.

Efficacy 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 .... (iv)

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

Corrosion and Degradation of Materials

There is a false belief that Chlorine Dioxide is corrosive to metals. This is untrue, Chlorine Dioxide, at use concentration as a biocide or disinfectant is not corrosive to metals or elastomers.

Chloramines have been implicated with corrosion of Copper and Lead domestic water pipes and the degradation of Rubber

The misconception levied on Chlorine Dioxide 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 (v), is used to increase the yield of Chlorine Dioxide in the generator.

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \qquad (v)$$

The stoichiometric requirement based on Equation (v) 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 (vi). Sodium Bisulfate is used to create the acidic medium, it does not produce sulfuric acid.

$$7ClO_2^- + HSO_5^- + 5HSO_4^+ \rightarrow 6ClO_2 + Cl^- + 6SO_4^{2-} + 3H_2O \qquad \text{(vi)}$$

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.

Here is evidence that when some water systems switch to chloramines, there is a concurring increase of Lead concentration in drinking water, perhaps because Chloramines can cause Lead to leach from pipes, fixtures, and solder. Leaching of Lead can be from Lead Pipes, Lead Soldering and from so called "Lead Free" Brass Plumbing Parts. Lead leached by Chloramine can cause Lead Poisoning, which can neurological damage, health problems and even death in young children.

Chloramine can cause pinhole pitting in Copper pipes. Leaks from the pinholes can cause Mold to grow, and the Mold can be toxic to humans and can endanger the health of individuals, often permanently.

In general, elastomers have performed well in water distribution systems. However, with the switch from chlorine to chloramines, an increase of Elastomer failures, particularly Rubber, has been noted, with the switch to Chloramination for disinfection of Drinking Water. Chloramine can cause corrosion or degradation of Rubber Plumbing Parts. Damaged or degraded Rubber parts need to be replaced with Chloramine resistant parts such as synthetic polymer. Degradation or corrosion of Rubber can be spotted as early as 6 months after Chloramine has been added to the water supply. Signs of corrosion can be seen when small black specks appear in the water from plumbing parts.

The thousands to tens of thousands of dollars of damage and plumbing repair costs caused by Chloramine are passed on to property owners.

Spectrum of Biocidal Effectiveness

Chloramine and Chlorine Dioxide are all effective for controlling Bacteria, Fungi and Yeast. However, Chlorine Dioxide tends to be the 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 Systems, and, Hot and Cold Water Systems. Control of Biofilm can also minimize the potential for Microbiologically Influence Corrosion (MIC). Both Chloramine and Chlorine Dioxide can control Biofilm, again, Chlorine Dioxide being the more efficient. Chlorine Dioxide can also remove Biofilm from surfaces.

Preparation and use of Chloramine and Chlorine Dioxide

Chloramination involves the use of Chlorine Gas or Sodium Hypochlorite solution and gaseous Ammonia or concentrated Ammonia solution. Gaseous Chlorine and gaseous Ammonia can pose serious health and safety risks and need careful handling. Chlorine gas would need a Chlorinator which incurs significant capital and maintenance costs. Although concentrated aqueous solutions of Ammonia may pose a little less potential health and safety hazards than gaseous Ammonia, they give rise to Ammonia fumes which can be hazardous and the solution can cause serious burns if splashed on the skin. Sodium Hypochlorite is less hazardous than Chlorine gas, but still poses some potential health and safety concerns. However, much larger volumes, about 6 to 12 times more, Sodium Hypochlorite would be required compared to Chlorine gas. Sodium Hypochlorite solution decompose, the rate of degradation depends on Hypochlorite concentration, pH of the solution, temperature of the solution, concentration of certain impurities which catalyze decomposition and exposure to light.

To ensure that Monochloramine s produced, strict and accurate control of the Chlorine: Ammonia ratio is required.

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 to produce Chlorine Dioxide 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 2, and they are not in the same reactive form as liquid precursors.

At concentrations >0.8% Chlorine Dioxide (8000 ppm ClO_2) 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.

Figure 2
Spillage of Liquids and Powders

Leakage of Solution — Spillage of Solution — Spillage of Solid

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.

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

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