Overview of Chlorine Dioxide

What is Chlorine Dioxide?

- Chlorine dioxide is a molecule consisting if 1 chlorine atom and 2 oxygen atoms. Abbreviated to CLOT.
- It has a molecular weight of 67.45.
- It is a gas at normal temperatures and pressures.
- It has a melting point of -59'C.
- It has a boiling point of 11◦C

- It is yellowish / green and has an odor similar to that of chlorine.
- It is denser than air and is water soluble at standard temperatures and pressures up to 2500 ppm.
- It is explosive in air at concentrations > 10%
- It is prohibited from all form of transport, it is normally generated at the point of application.
- It will decompose in the presence of UV, high temperatures, and high alkalinity (> ph 12).
- Chlorine dioxide is not another form of chlorine. We can draw an analogue to hydrogen and hydrogen cyanide, they are both gases, have the same first name, but completely different properties. So too with chlorine dioxide and chlorine, indeed one molecule does make a big difference.

- Chlorine Dioxide is defined in the USA as having no elemental free chlorine" hence it does not chlorinate. It is because of this fact and the amazing chemistry of chlorine dioxide that it is slowly becoming an important tool in disinfection and oxidation in the world to-day.
- The physical and chemical properties of chlorine dioxide outline below will unravel its amazing capabilities.
- Chlorine dioxide does not dissociate in water.
- It stays as chlorine dioxide therefore its ability to operate as a disinfectant sanitizer is independent of p1-f.
- Chlorine dioxide is an oxidant with a low redox potential.
- It has a redox potential of +0.96 mV compared to chlorine of +1.36 mV. There is no relationship between redox and disinfecting efficacy.
- Chlorine dioxide has a few specific chemical reactions.
- From this property a number of very interesting properties are derived:
- It has a very low toxicity rating; indeed some formulations have GRA status.
- It is generally regarded as a "no irritant ".
- It is not corrosive as a pure chlorine dioxide solution.

- Its reactions are selective hence as an oxidant reagent consumption is maximized in the redox reaction not through side reactions.
- Chlorine dioxide has a very high efficacy against vegetative cells, for example, bacteria: fungi yeasts and molds; viruses; algae; and protozoa. It has little to no effect on human, animal and fish cells. It has been shown to have high efficacy against molluscs and acracides with unconfirmed reports suggesting some action against nematodes.
- From the above properties it is not surprising then to learn that " chlorine dioxide does not constitute a risk against the environment ".The Alliance for Environmental Technology (AET), is a group of 19 North American chemical manufacturers and forest product companies, established to promote proven and practical technologies to raise the environmental awareness has indicated that the "environmental risks of a modern paper mill using chlorine dioxide are INSIGNIFICANT."
- The low oxidation potential of chlorine dioxide means that it can penetrate biofilm and indeed chlorine dioxide has been proven as the MOST effective chemical against biofilm. This has now been recognized by numerous organizations eg. Institute of Food Technologists in their report entitled "Microbial Attachment and Biofilm formation-A Scientific Summary, July '94 Food Technology. It has been clinically demonstrated that the presence of biofilm is the critical step in the infection pathway of legionellae. A simple and elegant solution is available in chlorine dioxide to overcome the problems related to having biofilm in a system. In terms of legionella control the singles biggest problem is the formation of cysts, in the biofilm. Only chlorine dioxide and ozone have the capability of inactivating cysts!. Pulse dosing of a disinfectant is about a 1000 times more effective for biofilm control than low level continuous dosing.
- CAUTION, is advised when one is running disinfection/sanitizing program during which one is eroding away the biofilm---theory and practice are indeed different bed mates.
- Chlorine dioxide is a factor lower in dosage for the same efficacy against bacteria
- and fungi when compared against any other standard disinfectant like chlorine, iodine, bromine, hydrogen peroxide, quaternary ammonium compounds MATS), glutraladehyde, phenolic and peroxyacetic acid formulations.
- Finally, chlorine dioxide can be easily and accurately measured in the food plant,
- potable water plant and for environmental applications. No other disinfectant / oxidizer can make this claim hence chlorine dioxide can easily meet GMP, HACCP1 SQF or any other quality food safety management system or environmental system for consistency of performance.
- In conclusion, therefore we have a disinfectant / sanitizer which is an oxidant with few chemical reactions, no pH limitations, very low toxicity, worldwide approval for drinking water, very high efficacy against micro-organisms, has a strong and measurable residual. The product when applied at *use* concentration in water will not corrode equipment; will not produce an environment harmful to workers or consumers.
- Truly a wonderful product but it is not a magic bullet and it cannot solve all problems. We have examined the properties of chlorine dioxide that make it close to being the "ideal"' biocide, however, the fact that it is a gas which cannot be compressed without exploding seemingly reduces its availability to be used.

Chlorine Dioxide Timeline

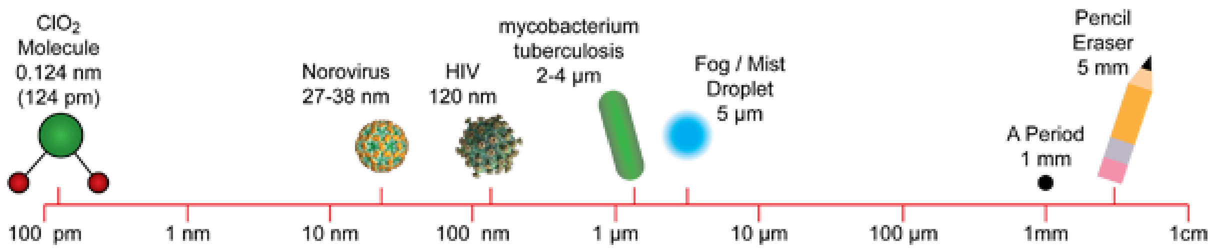
- 1811 first discovered by Sir Humphrey Davey.
- 1944 Fist commercial application. Used as a Biocide/Taste and Odor Control agent in domestic water at Niagara Falls in the USA.
- 1977 Three thousand municipal water systems achieving biological control using chlorine dioxide,

- 1980's chlorine dioxide gradually replacing chlorine in many industries.
- Pulp and Paper industry as a bleaching agent.
- Industrial water treatment as a biocide and as an odor control agent.
- Food processing as a sanitizer.
- 1990's increasing used for the secondary disinfection of potable water.
- 2001 As the principal agent used in the decontamination of buildings in the United States after the anthrax attacks.
- 2005 Used after Hurricane Katrina to eradicate dangerous mold from house inundated by water from massive flooding.
- 2008 First patent to produce 010_2 with a simple tablet (Globalex patent) .
- 2009 Used to prevent against I-11N1
- 2011 New patent to produce 010_2 with a simple tablet — 2 years stability — 12% concentration (Globalex patent).

Chlorine Dioxide: The "Ideal" Biocide

- Chlorine dioxide is an extremely effective disinfectant, which rapidly kills bacteria, viruses, and Giardia, and is also effective against Cryptosporidi um. $C10_2$ also improves taste and odor, destroys sulfides, cyanides, and phenols, controls algae, and neutralizes iron and manganese ions. It is an effective biocide at concentrations as low as 0.1 ppm (parts per million) and over a wide pH rang. It is 10 times more soluble in water than chlorine, even in cold water. Unlike iodine, chlorine dioxide has no adverse effects on thyroid function. Chlorine dioxide is widely used by municipal water treatment facilities.
- The term "chlorine dioxide" is misleading because chlorine is not the active element. Chlorine dioxide is an oxidizing, not a chlorinating agent. $C10_2$ penetrates the cell wall and reacts with amino acids and the cytoplasm within the cell, killing the microorganism. Then by-product of this reaction is chlorite, which is harmless to humans.
- For the super performance characteristics, chlorine dioxide has been described as the "ideal" biocide. It is now included in many drinking water hygiene programs around the globe. Complete testing has confirmed the safety of chlorine dioxide. This includes extensive studies by the Environmental Protection Agency (EPA) and World Health Organization (WHO).
- Chlorine dioxide has been recognized by World Health Organization (WHO) as the most effective Al disinfecting reagent.
- Its usage was approved by Food and Drug Administration (FDA) and Environment Protection Agency (EPA).
- Its status is also seen in the Report of FAO Codex Alimentarius, Food additive details Chlorine Dioxide.
- Chlorine dioxide is approved and recommended by EPA as an environmental friendly drinking water additive to replace chlorine.
- Chlorine dioxide has been called the "ideal" biocide for a number of reasons:
- It works against a wide variety of bacteria, yeasts, viruses, fungi, protozoa, spores, mold, mildews, and other microbes.
- It exhibits rapid kill of target organisms, often in seconds.
- It is effective at low concentrations and over a wide pH range.
- It biodegrades in the environment
- Unlike chlorine, it does not generate harmful by-products.

MOLECULAR SIZE MATTERS



As can be seen in the chart above, the size of a chlorine dioxide gas molecule is 0.124 nm, much smaller than microorganisms and viruses, allowing the gas to easily penetrate into any areas where these microorganisms might be concealed.

Chlorine Dioxide Germicidal Spectrum

- Below table of some of organisms that chlorine dioxide has been tested with. Chlorine dioxide has proven effective at eliminating a wide range of organisms.

Biological Efficacy of Chlorine Dioxide

Bacteria	Ref.	Bacteria	Ref.
akeslea trispora	28	*E. coli O157:H7 G5303*	1
Brucella suis	30	*Erwinia carotovora (soft rot)*	21
Burkholderia mallei	36	*Franscicella tularensis*	30
Burkholderia pseudomallei	36	*Fusarium sambucinum (dry rot)*	21
Campylobacter jejuni	39	*Fusarium solani var. coeruleum (dry*	21
Clostridium botulinum	32	*Helicobacter pylori*	8
Corynebacterium bovis	8	*Helminthosporium solani (silver scurf)*	21
Coxiella burneti (Q-fever)	35	*Klebsiella pneumonia*	3
E. coli ATCC 11229	3	*Lactobacillus acidophilus NRRL B1910*	1
E. coli ATCC 51739	1	*Lactobacillus brevis*	1
E. coli K12	1	*Lactobacillus buchneri*	1
E. coli O157:H7 13B88	1	*Lactobacillus plantarum*	5
E. coli O157:H7 204P	1	*Legionella*	38
E. coli O157:H7 ATCC 43895	1	*Legionella pneumophila*	42
E. coli O157:H7 EDL933	13	*Leuconostoc citreum TPB85*	1

Bacteria	Ref.
Leuconostoc mesenteroides	5
Listeria innocua ATCC 33090	1
Listeria monocytogenes F4248	1
Listeria monocytogenes F5069	19
Listeria monocytogenes LCDC-81-861	1
Listeria monocytogenes LCDC-81-886	19
Listeria monocytogenes Scott A	1
Methicillin-resistant Staphylococcus aureus (MRSA)	3
Multiple Drug Resistant Salmonella typhimurium (MDRS)	3
Mycobacterium bovis	8
Mycobacterium fortuitum	42
Pediococcus acidilactici PH3	1
Pseudomonas aeruginosa	3
Pseudomonas aeruginosa	8
Salmonella	1
Salmonella spp.	2
Salmonella Agona	1
Salmonella Anatum Group E	1
Salmonella Choleraesins ATCC 13076	1
Salmonella choleraesuis	8
Salmonella Enterica (PT30) BAA-1045	1
Salmonella Enterica S. Enteritidis	13
Salmonella Enterica S. Javiana	13
Salmonella Enterica S. Montevideo	13
Salmonella Enteritidis E190-88	1
Salmonella Javiana	1
Salmonella newport	4
Salmonella Typhimurium C133117	1
Salmonella Anatum Group E	1
Shigella	38
Staphylococcus aureus	23
Staphylococcus aureus ATCC 25923	1
Staphylococcus faecalis ATCC 344	1
Tuberculosis	3
Vancomycin-resistant Enterococcus faecalis (VRE)	3
Vibrio strain Da-2	37
Vibrio strain Sr-3	37
Yersinia enterocolitica	40
Yersinia pestis	30
Yersinia ruckerii ATCC 29473	31

Viruses	Ref.
Adenovirus Type 40	6
Calicivirus	42
Canine Parvovirus	8
Coronavirus	3
Feline Calici Virus	3
Foot and Mouth disease	8
Hantavirus	8
Hepatitis A Virus	3
Hepatitis B Virus	8
Hepatitis C Virus	8
Human coronavirus	8
Human Immunodeficiency Virus	3
Human Rotavirus type 2 (HRV)	15
Influenza A	22
Minute Virus of Mouse (Parovirus)(MVM-i)	8
Minute Virus of Mouse (Parovirus)(MVM-p)	8
Mouse Hepatitis Virus (MHV-A59)	8
Mouse Hepatitis Virus (MHV-JHM)	8
Mouse Parvovirus type 1 (MPV-1)	8
Murine Parainfluenza Virus Type 1	
Newcastle Disease Virus	8
Norwalk Virus	8
Poliovirus	20
Rotavirus	3
Severe Acute Respiratory Syndrome Coronavirus	
Sialodscryoadenitis (Coronavirus)(SDAV)	
Simian rotavirus SA-11	15
Theiler's Mouse Encephalomyelitis (TMEV)	
Vaccinia Virus	10

Algae/Fungi/Mold/Yeast	Ref.
Alternaria alternata	26
Aspergillus aeneus	28
Aspergillus aurolatus	28
Aspergillus brunneo-uniseriatus	28
Aspergillus caespitosus	28
Aspergillus cervinus	28
Aspergillus clavatonanicus	28
Aspergillus clavatus	28

Algae/Fungi/Mold/Yeast	Ref.
Aspergillus egyptiacus	28
Aspergillus elongatus	28
Aspergillus fischeri	28
Aspergillus fumigatus	28
Aspergillus giganteus	28
Aspergillus longivesica	28
Aspergillus niger	12
Aspergillus ochraceus	28
Aspergillus parvathecius	28
Aspergillus sydowii	28
Aspergillus unguis	28
Aspergillus ustus	28
Aspergillus versicolor	28
Botrytis species	3
Candida spp.	5
Candida albicans	28
Candida dubliniensis	28
Candida maltosa	28
Candida parapsilosis	28
Candida sake	28
Candida sojae	28
Candida spp.	5
Candida tropicalis	28
Candida viswanathil	28
Chaetomium globosum	7
Cladosporium cladosporioides	7
Debaryomyces etchellsii	28
Eurotium spp.	5
Fusarium solani	3
Lodderomyces elongisporus	28
Mucor circinelloides	28
Mucor flavus	28
Mucor indicus	28
Mucor mucedo	28
Mucor rademosus	28
Mucor ramosissimus	28
Mucor saturnus	28
Penicillium chrysogenum	7
Penicillium digitatum	3
Penicillium herquei	28
Penicillium spp.	5

Algae/Fungi/Mold/Yeast	Ref.
Phormidium boneri	3
Pichia pastoris	3
Poitrasia circinans	28
Rhizopus oryzae	28
Roridin A	33
Saccharomyces cerevisiae	3
Stachybotrys chartarum	7
T-mentag (athlete's foot fungus)	3
Verrucarin A	33

Bacterial Spores	Ref.
Alicyclobacillus acidoterrestris	17
Bacillus coagulans	12
Bacillus anthracis	10
Bacillus anthracis Ames	30
Bacillus atrophaeus	14
Bacillus atrophaeus ATCC 49337	31
Bacillus megaterium	12
Bacillus polymyxa	12
Bacillus pumilus ATCC 27142	12
Bacillus pumilus ATCC 27147	11
Bacillus subtillis (globigii) ATCC 9372	11
Bacillus subtillis ATCC 19659	31
Bacillus subtillis 5230	12
Clostridium. sporogenes ATCC 19404	12
Geobacillus stearothermophilus ATCC	
Geobacillus stearothermophilus ATCC	
Geobacillus stearothermophilus VHP	11
Bacillus thuringiensis	18

Chemical Decontamination	Ref.
Mustar	
Ricin Toxin	10
dihydronicotinamide adenine dinucleotide	24
microcystin-LR (MC-LR)	25
cylindrospermopsin (CYN)	25

Beta Lactams	Ref.
Amoxicillin	29
Amplicillin	29
Cefadroxil	29
Cefazolin	29

Beta Lactams	Ref.
Cephalex	
Imipenem	29
Penicillin G	29
Penicillin V	29

Protozoa	Ref
Chironomid larvae	27
Cryptosporidium	34

Protozoa	Ref
Cryptosporidium parvum Oocysts	9
Cyclospora cayetanensis oocysts	41
Giardia	34
Encephalitozoon intestinalis	27

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Disinfection By-Products of Chlorine Dioxide

- The disinfection by-products (DBPs) of chlorine dioxide reactions are chlorite ($C10_{2-}$) and chlorate ($CI0_{3-}$) and eventually chloride (Cl*). The fate of any DBPs depends largely on the conditions at the time, concentration, temperature and the presence of other molecules.
- Generally, it is the concentration of chlorite residuals that is the "monitored" DPB of chlorine dioxide. Modern generation systems are able to monitor the downstream residual DBP and adjust the dose rate to ensure that environmental limits are not breached. In special cases, downstream reactions can be used to remove excess chlorite residual from the water stream.
- It is important to note that the DPBs of chlorine dioxide are easily managed with the correct experience and advice, and do not present nearly the same scale of problems as found with other biocide. Unlike ozone, chlorine dioxide does not oxidize bromide ion (Br_{-}) to bromate ion ($Br0_{3-}$). Additionally, chlorine dioxide does not produce large amounts of aldehydes, ketones, or other DBPs that originate from the ozonization of organic substances.
- Approvals and Registrations for the use of Chlorine Dioxide
- USA Environment Protection Agency (EPA)
- EPA approval for disinfectant / sanitizer with applications in food processing plants.
- EPA approval for disinfectant of environmental surfaces such as floor, walls and ceiling in food processing plants, such as poultry, fish, meat, and in restaurants, dairies, bottling plants and breweries.
- EPA approval for a terminal sanitizing rinse for food contact surface in food processing plants, such as poultry, fish, meat, and in restaurants, dairies, bottling plants and breweries.
- EPA approval for a sanitizing rinse of uncut, unpeeled fruits and vegetables, at 5 ppm followed by a potable tap water rinse.
- EPA approval for bacteriostatic in ice making plants and machinery.
- EPA approval for treatment of stored potable water, at 5 ppm, for drinking water.
- EPA bactericidal and fungicidal approval for hard non-porous surfaces in hospitals laboratories and medical environments.
- EPA bactericidal and fungicidal approval for instruments in hospital and dental environment (Pending).
- EPA bactericidal approval as a dental pumice disinfectant.
- EPA approval for general disinfectant and deodorization of animal confinement building, such as poultry, swine, barns and kennels.
- EPA approval for the disinfection and deodorization of ventilation systems and air conditioning duct work.
- Food and Drug Administration (FDA)
- FDA approval as a terminal sanitizing rinse, not requiring a water rinse, on all food contact surface.
- United States Department of Agriculture (USDA)
- P-1 approval for bacterial and mold control in federally inspected meat and poultry processing plants for environmental surfaces,

- 0-2 approval **as** terminal sanitizing rinse not requiring a water flush, on all food contact surfaces in food processing plant.
- 3-0 approval for washing fruits and vegetables that are used as ingredients of meat, poultry **and** rabbit products by a potable water rinse.
- G-5 approval for cooling and retort water treatment.
- EU Codex Alimentarius
- For use as an anti-microbial for incidental contact on food or surfaces that the food comes into contact with.

UK Government

- Approved by the UK Secretary of State for the Environment under Regulation 25 (1)(a} of the Water Supply (Water Quality) (Amendments) Regulations 1991 (also in Scotland).
- Approved as a disinfectant for service reservoirs, distribution, mains and waterworks apparatus.
- Approved as a disinfectant and taste and odor control product for use in water that is supplied for drinking, washing, cooling and food production purposes on condition that the combined concentration of chlorine dioxide, chlorite and chlorate does not exceed 0.5 ppm entering supply.
- Approved as a disinfectant by the Minister of Agriculture, Fisheries and Food and the Secretaries of State for Scotland and Wales for the Purposes of the Diseases of Animals (Approved Disinfectant) Order 1978 (As Amended) with corresponding approvals in Northern Ireland and Eire.
- Approved for the Control of legionellae.
- Approved by H5 (GPO for "The Control of legionellae including Legionnaires Disease" and MISC 150 the Technical Supplement to HS(G170 "The Control of legionellae in Hot and Cold Water Systems".

Modes of Action of Chlorine Dioxide

Micro biocide Action

- Chlorine dioxide is a stronger disinfectant than chlorine and chloramine. Ozone has great micro biocide effects, but limited residual disinfection capability. Recent research in the United States and Canada demonstrates that chlorine dioxide destroys enteroviruses, E. colt amoebae and is effective against cryptosporidium cysts (Finch et al., 1997).
- Chlorine dioxide exists in the water as $C10_2$ (little or no dissociation) and thus is able to permeate through bacterial cell membranes and destroy bacterial cells (Junli et. Al, 1977b). its action on viruses involves adsorbing onto and penetrating the protein coatof the viral capsid and reacting with the viral RNA (An RNA virus is a vim that has RNA (ribonucleic acid) as its genetic material. This nucleic acid is usually single-stranded RNA (ss1NA), but may be double-stranded RNA (dsRNAIL Notable human diseases caused by RNA viruses include SAPS, influenza, hepatitis C.. West Nile fever, polio and measles,.

- The ICTV classifies RNA viruses as those that belong to Group II, Group 'V or Group V of the Baltimore classification system of classifying viruses, and does not consider viruses with DNA intermediates in their life cycle as RNA viruses. Viruses with RNA as their genetic material but which include DNA intermediates in their replica don cycle are milled retroviruses, and comprise Group VI of the 3altimore classification. Notable human retroviruses include HIV-1 and HIV-2, the cause of the disease AIDS
- Another term for RNA viruses that explicitly excludes retroviruses is rihnovirus.l.
- As a result, the genetic capability of the virus is damaged (Junli et. Al, 1977x). In comparison to chlorine, chlorine dioxide can be more effective as a disinfectant due to the fact that chlorine exists in the water as HOCL or OCL-, As a result, bacterial cell walls are negatively charged and repel these compounds, leading to less penetration and absorption of the disinfectant into the membranes.

Oxidant Action

- The oxidant action of chlorine dioxide often improves the taste, odor, and color of water. Chlorine dioxide reacts with phenolic compounds, humic substance, organics, and metal ions in the water.
- For example, iron is oxidized by chlorine dioxide so that it precipitates out of the water in the form of iron hydroxide. The precipitate is then easily removed by filtration.
- $CI0_2 + 5Fe(HCO_3)_2 + 3\ H_20 = 5\ Fe(011_3 + 10\ Cl_2 + +$
- Chlorine dioxide reacts with organics, typically by oxidation reactions, and forms few Because of its radical structure, chlorine dioxide has a particular reactivity - totally different from that of chlorine or ozone. The latter behave as electron acceptors or are
- chlorinated organic compounds. Free chlorine, in the presence of organic precursors can form trihalomethanes (TWA's) and other halogenated compounds (Aieta and Berg, 1986).
- Phenolic compounds presents in drinking water are due mainly to contamination from industrial sources. Such molecules, even when present in concentrations of micrograms per litre, give an unpleasant odor and taste. Chlorine dioxide reacts rapidly with phenols. This reaction may vary in different systems.
- The formation of quinones or chloroquinones
- The breaking of the aromatic ring and the formation of aliphatic derivatives.
- Humic acid, a THM precursor, is oxidized by chlorine dioxide thus minimizing halogenated compound formation in secondary treatment (Aieta and Berg, 1986)
- Function of Chlorine Dioxide
- Chlorine dioxide can be used as a Disinfectant, Sanitizer, Tuberculocide, Virucide, Fungicide, Algaecide, Slimicide, and Deodorizer.
- Chlorine dioxide is a powerful oxidizing biocide and has been successfully used as a water treatment disinfectant for several decades in many countries. Rapid progress has been made in the technology for generation of the product and knowledge of its reactivity has increased with improved analytical techniques. Chlorine dioxide is a relatively stable radical molecule. It is highly soluble in water, has a boiling point of 110°C, absorbs light and breaks down into $C10_3$" and CI_-. Because of its oxidizing properties chlorine dioxide acts on Fe_{2+}, Mn_{2+} and NO_2" but does not act on CI, NR_{i+} and Br" when not exposed to

light. These ions are generally part of the chemical composition of natural water.

- electrophilic, while chlorine dioxide has a free electron for a homopolar bond based on one of its oxygen. The electrophilic nature of chlorine or hypochloric acid can lead, through reaction of addition or substitution, to the formation of organic species while the radical reactivity of chlorine dioxide mainly results in oxycarbonyls. Generally chlorine dioxide rapidly oxidizes phenol type compounds, secondary and tertian·, amines, organic sulphides and certain hydrocarbon polycylic aromatics such as ben7opyrene, anthracene and benzoathracene. The reaction is slow or non-existent on double carbon bonds, aromatic cores, quinionic and carboxylic structures as well as primary amines and urea.
- The oxidizing properties and the radical nature of chlorine dioxide make it an excellent virucidal and bactericidal agent in a large pH range. The most probable explanation is that in the alkaline media the permeability of living cell walls to gaseous chlorine dioxide radicals seems to be increased allowing an easier access to vital molecules. The reaction of chlorine dioxide with vital amino acids is one of the dominant processes of its action on bacteria and viruses.
- Chlorine dioxide is efficient against viruses, bacteria and protozoan clumps usually found in raw water. A rise in pH level further increase its action against f2 bacteriophages, amoebic clumps, polioviruses and anterovirus. It is efficient against Giardia and has an excellent biocide effect against Cryptosporidia which are resistant to chlorine **and** chloromines. It has been demonstrated that $CI0_2$ has greater persistence than chlorine. In a recent report for dosages 3 times lower than those of chlorine at the station outlet, the residual of $CI0_2$ used alone was always higher than that of Cl_2 which also required 3 extra injections of chlorine in the distribution system.
- The reduction of bad tastes and odor with $CI0_2$ is the result of the elimination of algae and on the negligible formation of organs-chlorinated derivatives. The latter formed under chlorination give rise to very unpleasant odours. By its action on dissolved organic materials, without the formation of organic halogen compounds, $C10_2$ limits problems of taste and color. In addition the low dosages used in post disinfection are an advantage. When chlorine dioxide replaces chlorine in a system it may take up to 15 days for the benefits of the change to become apparent. Changes should be made gradually to avoid problems of a sudden release of slime into the system.

Markets & Applications

Chlorine dioxide has a wide range of applications including:

Human Water Systems

- Treatment of Potable Water for Human Consumption
- Water Storage Systems Aboard Aircraft, Boats, RV's and Off-Shore Oil Rigs
- Municipal Well Waters

- Swimming Pools &Spas Industrial
- Industrial water treatment
- Cooling and process water microbiological control
- Wastewater disinfection
- Cooling Towers
- Treatment of Ventilation Systems
- Mollusk control
- Odors control
- Iron and manganese removal
- Phenol oxidation
- Cyanide destruction
- Paper & pulp
- Influent Water Disinfection
- Backup on generators failures
- White water slimicide
- Iron Control
- Bleaching of specialty papers
- Oil & gas
- Microbiological control of oil wells and bores
- Sulfide destruction
- Pipeline and tank cleaning
- TI-IM control
- Taste and odor control

Public Places

- Hospitals
- Microbiological control
- Lower risk of MRSA
- Cleaning
- Legionella prevention and control
- Hotels & leisure centers
- Disinfection of water system
- Biofilm removal in water system

Agricultural

- Horticulture
- Disinfection of irrigation water
- Cleaning of irrigation system
- Treatment of Agricultural Storage Facilities
- Treatment of Horticulture Work Area and Benches
- Treatment of Horticulture Pots and Plats
- Treatment of Horticulture Cutting Tools
- Treatment of Horticulture Bulbs
- Treatment of Greenhouse Glass, Walkways and Under Benches
- Treatment of Evaporative Coolers
- Treatment of Retention Basins and Ponds

- Treatment of Decorative Pools, Fountains and Water Displays
- Vegetables & fruit washing/processing

Food Processing

- Sanitizing Food Contact Surfaces
- Sanitizing Non-Food Contact Surfaces
- Sanitizing Food-Processing Equipment
- Ice Making Plants and Machinery
- Ice Manufacture
- Canning Retort and Pasteurizer Cooling Water
- Stainless Steel Transfer Lines, Hydro coolers and Pasteurizer
- Washing fruit and vegetables
- Washing fish and seafood
- Washing meat, poultry and processing equipment
- Extend shelf life and freshness of non-processed fruits and vegetables
- Process water for canned and frozen packaging
- Control of bacteria growth and bio fooling
- Control of salmonella and legionella
- Disinfection lines, holding tanks and other equipment
- Disinfect in beverage and water systems and lines
- Reduction of ammonia nitrogen concentration in recycled water
- Cleansing and rinsing of bottles
- Disinfect in beverage and water systems and lines
- CIP (Cleaning In Place)

Livestock

- Treatment of Drinking Water
- Disinfection of Animal Confinement Facilities
- Treatment of Animal Transport Vehicles
- Deodorization of Animal Holding Rooms, Sick ROOMS and Work Rooms
- Control of Odor and Slime Forming Bacteria in Animal Confinement Facilities
- Disinfection of Poultry Chiller Water / Carcass Spray
- Treatment of Egg Room
- Treatment of Hatching Room
- Treatment of Incubator Room
- Treatment of Tray Washing Room and Loading Platform
- Treatment of Chick **Room,** Chick Grading Box and Sexing Room
- Hand Dip for Poultry Workers
- Shoe Bath Use

Aquaculture

- Live Fish Transport: Transport Water, Disease treatment during holding
- Disease prevention treatment
- Fish larval rearing

- Prawn larval rearing
- Spraying in feeds
- Treatment of diseases
- Fishing boats/Wholesale/Retail
- Dipping de-scaled and gutted fish
- Spray / Dipping on fish and prawns
- In sorting / grading water for prawns
- Ice manufacture
- Disinfection of display cabinet

Frequently Asked Questions of Chlorine Dioxide

Has chlorine dioxide been used before?

- Chlorine dioxide has been recognized as an effective biocide for decades, and is used in a range of hygiene-related applications worldwide. Municipal water systems have used chlorine dioxide to treat drinking water for over 50 years.

Why couldn't I use chlorine dioxide before?

- Prior to various chlorine dioxide delivery agent products, expensive mechanical generators or relatively impure "stabilized' solutions were the only ways to make chlorine dioxide. The expense of capital equipment and the corrosiveness of the lower quality solutions prohibited the development of many horticultural applications.

Is chlorine dioxide safe?

- The Niagara Falls New York water treatment plant first used chlorine dioxide for drinking water disinfection in 1944. Currently, there are approximately 400 — 500 water treatment plants in the United States and over 1000 in Europe utilizing $CI0_2$ to purify municipal drinking water systems. Numerous studies have shown chlorine dioxide, when used at the appropriate concentrations, has no adverse health effects, either by skin contact or ingestion.

Is chlorine dioxide toxic?

- Fifty years of worker experience has demonstrated that $CI0_2$ is a safe compound when handled properly. World-wide, nearly 4.5 million pounds per day of chlorine dioxide are used in the production of pulp and paper. However, as with any and all disinfectant chemicals, if handled improperly, or consumed internally or absorbed or subjected to prolonged exposure, 010_2 can be toxic. However, it is also this toxicity that makes 010_2 a good water disinfectant agent.

Is chlorine dioxide environmentally friendly and does it create harmful by-products?

- Chlorine dioxide is far more environmentally friendly than other oxidizing biocides and disinfectants including chlorine and bromine. Substituting chlorine dioxide for chlorine eliminates the formation of toxic halogenated disinfection by-products including trihalomethanes (TWO and other chlorinated compounds that are harmful to the environment. In fact chlorine dioxide actually helps to remove substances that can form trihalomethanes. The disinfection is by oxidation as chlorine dioxide does not have either addition or substitution reactions associated with its chemistry.

What methods are used to detected chlorine dioxide?

- Chlorine dioxide can be detected in several ways. Some of these methods such as DPD, Amperometric, and loclornetric are standardized, widely accepted and used.

Is Chlorine Dioxide expensive?

- When compared to the cost of chlorine, the cost of $CI0_2$ is lower comparing efficiency and high range disinfection. However in those instances in which chlorine is not the preferred regulatory or environmental alternative, 010_2 is a very attractive alternative. The costs are also less than that of other alternatives like ozone which can also be used for water treatment.

Can Chlorine Dioxide be stored safely?

- No because explosive gas in the air (10%). Globalex provide a safety solution to produce "just in time".

What legal provisions does chlorine dioxide carry?

- Chlorine dioxide has a number of legal provisions by different states list in the follow table.

Time	State	Approved Bureau	Usage Range
1992	—	WHO	Drinking Water Disinfection
1985	USA	FDA	Food Processing Equipment Sterilization
1985	EU	European Commission	Drinking Water Disinfection., food industry; medical.. livestock husbandry, aquaculture, environment and public areas disinfection and sterilization
1987	Germany	—	Drinking Water Disinfection
1987	UK	Ministry of Health	Drinking Water Disinfection., hospital, livestock aquaculture, environment and public areas disinfection and sterilization
1987	USA	EPA	Food processing plants, breweries, restaurants, environmental disinfection; Hospitals, labs and non-empty rigid surface
1989	USA	EPA	Storage water disinfection: Livestock., disinfection and
1988	Japan	Ministry of Food	Drinking Water Disinfection
1987	Australia	Ministry of Health	No 926 food Additives, food Bleacher
1987	China	Ministry of Health	Food industry, medical, pharmaceutical, livestock husbandry, aquaculture, environment and public areas disinfection
1996	China	Ministry of Health	Food additives, fruits and vegetables Preservation
2002	USA	FDA	Food processing equipment, pipe, crafts and arts equipment, especially in milk processing plant
2005	China	Ministry of Health	Drinking Water Disinfection
2011	Brazil	Ministry of Health	Drinking Water Disinfection, Food industry., Storage water disinfection,, Livestock

Can chlorine dioxide be used in combination with other disinfectants?

- Yes. Chlorine dioxide is often used in combination with chlorine in municipal drinking water plants in order to reduce the amount of trihalomethanes and HAAs that would be formed if chlorine were used alone. Chlorine dioxide is added as the primary disinfectant in order to remove a number of oxidisable compounds without forming chlorinated DBPs, while chlorine is added at low levels in order provide a residual biocide for use in the disinfection system.

Is chlorine dioxide different to chlorine?

- Yes. While chlorine dioxide has chlorine in its name, its chemistry is radically different from that of chlorine. Chlorine dioxide is not "chlorine in disguise". Both chlorine dioxide and chlorine are oxidizing agents. They are electron receivers. Chlorine has the capacity to take in two electrons, whereas chlorine dioxide can absorb five. This is why chlorine dioxide is far more effective than chlorine as a disinfectant. Environmentally, chlorine dioxide is friendlier to the environment than chlorine. Chlorine dioxide does not form toxin trihalomethanes (THIV1s) or other chlorinated compounds that are harmful to the environment and associated with chlorine, sodium hypochlorite and hypochlorous acid.

What the difference between chlorine dioxide with other disinfectants?

Characters	CIO	Chlorhexidine	Chlorine / Hypochlorite	Phenol	Aldehyde	NaOH	Alcohol
Resistance to Organic	Good	Ordinary	poor	General	good	good	General
Activity in Hard water	Yes	Yes	Yes	No	Yes	Yes	Yes
Affect High Temperature	Result is best in 5-69 ◦C	No	Activity decreased below 441)◦C	Activity Increased	Result is best in 26-fi4℃	No	No
PH Range	No effect	Alkaline	Acidic	Acidic	No effect	Alkaline	No effect
Anion Soap Compatibility	No	Yes	No	Yes	yes	Yes	Na
Activity of Residue	No	Yes	No	Yes	No	Yes	Na
Toxicity or Discomfort	No	No	Yes	Yes	Yes	Yes	Yes
Damage to Surface	No	No	Yes	No	Yes	Yes	Na
Of the Bacteria	Mast	Part	Mast	Most	Yes	Mast	Mast
Kill the Spores	Yes	Part	Part	No	Yes	Yes	No
Ulf the Viruses	Yes	No	Part	Part	Yes	Yes	Part

How much is the Permissible Exposure Limit of chlorine dioxide?

- The Occupational Safety and Health Administration (OSHA) has set safe exposure limits of 0.3 ppm (0.9 mg/m_3) for 15 minutes and a time-weighted average of 0.1 ppm (0.3 mg/m_3) for 8 hours of contact with chlorine dioxide gas.

What are advantages and disadvantages of chlorine dioxide?

Advantages:

- Effective against a wide variety of bacteria, yeasts, viruses, fungi, protozoa, spores, molds, mildews, Cryptosporidium, algae and is more potent than chlorine over a short contact time
- Destroys biofilms
- Effective over wide pH (3.5 to 11)
- Biodegradability in the environment
- Prevents trihalometha nes (THM's) and bromate formation
- Does not chlorinate organics
- Readily dissolves in water and does not react with ammonia
- Does not react with water to form free chlorine and hypochiorus acid
- Does not react with water to form free chlorine
- Is less corrosive than chlorine
- Selective oxidation reactions
- Cheaper than Ozone and more effective for odor, color, bad taste, phenols reduction, iron and manganese reduction

Disadvantages:

- Decomposes in sunlight
- Must be generated on-site

What is the difference between Clo2 Generators and Tablets?

Generators:

- The generators are efficient for spot treatment in water. First step treatment or 2_{n6} step. The CLO_2 cannot stay into the water and naturally the gas goes away quickly. The gas is produced by a reaction with 2 powders or with a liquid.
- The mix must be very sharp to have a good production gas. Also the qualities of chemicals components are determinant to have a stable production. It is not always the case and the generators are operational for big volumes water treatment.

- Once the gas is produced it must insert without delay into the water to be treated. The modulation on production is not "Just in Time **and on** demand". $CI0_2$ gas is explosive when it is in contact with air (1094)

Tablets:

- The tablets produce a sharp level of $C1.0_2$ in small or big water volumes. They realize the gas in 3 minutes.
- The tablets don't equipment or investment to produce the gas.
- The gas produced is made by chemical reaction and the bubbles have only some micron diameter; also it gives a resident factor. The gas can travel with the water and operate into the network or tanks. The disinfection is preserved from recontamination after treatment.
- The tablets don't energy to produce gas and can be used in many places.
- The tablets can easily be transported and the storage is possible for years.
- Easy to produce gas without risk. The operators are exposed because the gas is only realized into the water.
- The tablet is not inflammable and not dangerous to manipulate.
- Economic because gas resident many days (spend when in touch with needed)
- Only Globalex tablets produce CLO_2 only.

Inorganic Reactions:

- For iodometric analysis
- 20102 + 21->20102-+ 12
- Oxidation of iron
- C102 + FeO + NaOH + H2O -> Fe (OH)3+ NaC102
- Oxidation of manganese
- 20102 + Mn O4 + 4NaOH MnO: + 2NaC102+ Na2SO4 + 2H20
- Oxidation of sodium sulfide 20102 +
  2Na23 -) 2NaCI + Na2SO4 + 3
- Oxidation of nitrogen oxide pollutant 2N0 +
  0102+ H2O - NO2 + HNO3+ HCI
- Gas phase reaction with fluorine F2 +
  2C102 2FC102
- In alkaline solution
- 20102 + 20H- -) 0102- + 0103 - + H2O
- Aluminum, magnesium, zinc & cadmium react with 0102 M +
  xC102-10(C102)x
- Disproportionation of chlorite depends upon chlorides
- present, pH, and ratio of ingredients
- 40102 - + 4H+ Cl- + 20102+ CI03- + 2H+ + H20 50102 - + 4H+ -
  40102+ CI -+ 2H20

- With hydrogen peroxide as a reducing agent in commercial production of chlorite 20102 + H202+ 2NaOH -) 2NaC102 + 2H20 + 02
- A highly colored complex is formed when 0102 is dissolved in an aqueous solution of barium chlorite C102+ 0102- -) C1204

Organic Reactions:

- With organic compounds in water -p aldehydes, carboxylic acids, ketones & quinones
- With olefins aldehydes, epoxides, chlorohydrins, dichloro-derivatives, and chloro-and unsaturated ketones.
- With ethyienio double bonds -) ketones, epoxides, alcohols
- With benzene -) no reaction
- With toluene -) Ch3, CH2CI, CH2OH
- With anthracene 45o anthraquinone, I, 4-dichioroanthracene
- With phenanthrene diphenic acid, 9-chlorophenanthrene
- With 3, 4-benzopyrene quinones, traces of chlorinated benzopyrene no longer considered carcinogenic)
- With carboxylic and sulfonic functions —) no reaction
- With aldehydes —) carboxylic acids
- With ketones —) alcohols
- With aliphatic amines primary —> slow or no reaction secondary —) slow or no reaction tertiary —) rupture of CN bond, no N-oxides formed
- With triethylamine
- H20+(C2H5)3N + 2CI02—) (C2F15)2NH + 2CI02- + CH3CHO + 2H+
- With phenol P-benzoquinone, 2 chlorobenzoquinone
- Excess C102 with phenol —) maleic acid, oxalic acid
- With thiophenols sulfonic acids
- With tocopherol demethylated derivatives
- With saturated acids —) no reaction
- With anhydrides —> no reaction but catalyzes hydrolysis
- With amino acids: glycine, leucine, serine, alanine, phenylalamire, valine, hydroxyproline, phenylaminoacetec, aspartic, glutamic acids—) little, or no reaction
- With amino acids containing sulfur —) reactive
- With methionine sulfoxide —) sulfone
- With aromatic amino acids reactive
- With tyrosine dopaquinone, dopachrome
- With tryptophan idoxyl, isatine, indigo red, trace chlorinated products
- With thiamine —) slow reaction
- With keratin hydrosoluble acids
- With carbohydrates CHO and CH2OH —) carboxylic functions
- With vanillin pH4 —) monomethyl ester, _.-formylmuconic acid
- With pectic acid —) mucic acid, tartaric acid, galacturonic acid
- With chlorophyll and plant dyes color removed.
- With latex and vinyl enamels delays polymerization
- With napthaline —) no reaction
- With ethanol —) no reaction

- With biacetyl acetic acid, carbon dioxide
- With 2,3-butaneodiol —› acetic acid, carbon dioxide
- With cyclohexene —> aldehydes, carboxylic acids, epoxides, alcohols, halides, dienes, ketones
- With maleic acid no reaction
- With fumaric acid —> no reaction
- With crotonic acid —) no reaction
- With cyanides —> oxidized
- With nitrites oxidized
- With sulfides oxidized
- Hydrocarbons of longer chain length than **CB** are the most oxydable by 0102. The organic compounds most reactive with C102 are tertiary amines and phenols. Unsaturated fatty acids and their esters are generally oxidized at the double bond.

Clo2 DOES *NOT* REACT WITH:

- hippuric acid, cinnamic acid, betaine, creatine, alanine, phenylalanine, valine, leucine, asparaginic acid, asparagine, glutaminic acid, serine, hydroxyproline, taurine, aliphatically combined NH2 groups, arnido and imido groups, I-10 groups in alcohols and HO acids, free or esterified CO2H groups in mono and polybasic acids, nitrile groups, the CH2 groups in homologous series, ring systems such as C61-16, CioHs, cyclohexane, and the salts of CslisN, quinoline and piperidine.
- Alcohols are resistant at neutral pH, but under conditions of very low pH, high temperatures or high concentrations, alcohols can react to produce their corresponding aldehydes or carboxylic acids. C102 - , chlorite, the reduction product of CI02, although a less powerful oxidant, is used to react with many malodorous and highly toxic compounds such as unsaturated aldehydes, mercaptans, thioethers, hydrogen sulfide, cyanide and nitrogen dioxidide.