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# Overview of Chlorine Dioxide

## What is Chlorine Dioxide?

Chlorine dioxide is a molecule consisting if 1 chlorine atom and 2 oxygen atoms. Abbreviated to **CLO²**.

- It has a molecular weight of 67.45.
- It is a gas at normal temperatures and pressures.
- It has a melting point of -59$^{o}$C.
- It has a boiling point of 11$^{o}$C
- It is yellowish / green and has an odour 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 pH.

- **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 GRAS 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 maximised 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 organisations 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/sanitising programme 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 (QUATS), 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 / oxidiser can make this claim hence chlorine dioxide can easily meet GMP, HACCP, 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 Odour 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 odour 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 $ClO_2$ with a simple tablet (Globalex patent) .
- 2009 Used to prevent against H1N1 flu.
- 2011 New patent to produce $ClO_2$ 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 Cryptosporidium. $ClO_2$ also improves taste and odour, 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. $ClO_2$ 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 A1 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.

## 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.

| | | |
|---|---|---|
| Bacteria | Leuconostoc mesenteroides | Tuberculosis |
| Blakeslea trispora | Listeria innocua ATCC 33090 | Vancomycin-resistant Enterococcus faecalis(VRE) |
| Bordetella bronchiseptica | Listeria monocytogenes F4248 | Vibrio strain Da-2 |
| Brucella suis | Listeria monocytogenes F5069 | Vibrio strain Sr-3 |
| Burkholderia mallei | Listeria monocytogenes LCDC-81-861 | Yersinia enterocolitica |
| Burkholderia pseudomallei | Listeria monocytogenes LCDC-81-886 | Yersinia pestis |
| Campylobacter jejuni | Listeria monocytogenes Scott A | Yersinia ruckerii ATCC 29473 |
| Clostridium botulinum | Methicillin-resistant Staphylococcus aureus (MRSA) | Viruses |
| Corynebacterium bovis | Multiple Drug Resistant Salmonella typhimurium (MDRS) | Adenovirus Type 40 |
| Coxiella burneti (Q-fever) | Mycobacterium bovis | Canine Parvovirus |
| E. coli ATCC 11229 | Mycobacterium fortuitum | Coronavirus |
| E. coli ATCC 51739 | Pediococcus acidilactici PH3 | Feline Calici Virus |
| E. coli K12 | Pseudomonas aeruginosa | Foot and Mouth disease |
| E. coli O157:H7 13B88 | Pseudomonas aeruginosa | Hantavirus |
| E. coli O157:H7 204P | Salmonella | Hepatitis A Virus |
| E. coli O157:H7 ATCC 43895 | Salmonella spp. | Hepatitis B Virus |
| E. coli O157:H7 EDL933 | Salmonella Agona | Hepatitis C Virus |
| E. coli O157:H7 G5303 | Salmonella Anatum Group E | Algae/Fungi/Mold/Yeast |
| E. coli O157:H7 C7927 | Salmonella Choleraesins ATCC 13076 | Alternaria alternata |

| | | |
|---|---|---|
| Erwinia carotovora (soft rot) | Salmonella choleraesuis | Aspergillus aeneus |
| Franscicella tularensis | Salmonella Enterica (PT30) BAA-1045 | Aspergillus aurolatus |
| Fusarium sambucinum (dry rot) | Salmonella Enterica S. Enteritidis | Aspergillus brunneo-uniseriatus |
| Fusarium solani var. coeruleum (dry rot) | Salmonella Enterica S. Javiana | Aspergillus caespitosus |
| Helicobacter pylori | Salmonella Enterica S.Montevideo | Aspergillus cervinus |
| Helminthosporium solani (silver scurf) | Salmonella Enteritidis E190-88 | Aspergillus clavatonanicus |
| Klebsiella pneumonia | Salmonella Javiana | Aspergillus clavatus |
| Lactobacillus acidophilus NRRL B1910 | Salmonella newport | Aspergillus egyptiacus |
| Lactobacillus brevis | Salmonella Typhimurium C133117 | Aspergillus elongatus |
| Lactobacillus buchneri | Salmonella Anatum Group E | Aspergillus fischeri |
| Lactobacillus plantarum | Shigella | Aspergillus fumigatus |
| Legionella | Staphylococcus aureus | Aspergillus giganteus |
| Legionella pneumophila | Staphylococcus aureus ATCC 25923 | Aspergillus longivesica |
| Leuconostoc citreum TPB85 | Staphylococcus faecalisATCC 344 | Aspergillus niger |
| Aspergillus ochraceus | Mucor flavus | Bacillus megaterium |
| Aspergillus parvathecius | Mucor indicus | Geobacillus stearothermophilus ATCC 12980/7953 |
| Aspergillus sydowii | Mucor mucedo | Geobacillus stearothermophilus VHP |
| Aspergillus unguis | Mucor rademosus | Bacillus thuringiensis |
| Aspergillus ustus | Mucor ramosissimus | Chemical Decontamination |
| Aspergillus versicolor | Mucor saturnus | Mustard Gas |
| Botrytis species | Penicillium chrysogenum | Ricin Toxin |
| Candida spp. | Penicillium digitatum | dihydronicotinamide adenine dinucleotide |
| Candida albicans | Penicillium herquei | microcystin-LR (MC-LR) |
| Candida dubliniensis | Penicillium spp. | cylindrospermopsin (CYN) |
| Candida maltose | Phormidium boneri | Beta Lactams |
| Candida parapsilosis | Pichia pastoris | Amoxicillin |
| Candida sake | Poitrasia circinans | Amplicillin |
| Candida sojae | Rhizopus oryzae | Cefadroxil |
| Candida spp. | Saccharomyces cerevisiae | Cefazolin |
| Candida tropicalis | Stachybotrys chartarum | Cephalexin |
| Candida viswanathil | T-mentag (athlete's foot fungus) | Imipenem |
| Chaetomium globosum | Bacterial Spores | Penicillin G |
| Cladosporium cladosporioides | Alicyclobacillus acidoterrestris | Penicillin V |
| Debaryomyces etchellsii | Bacillus coagulans | Protozoa |
| Eurotium spp. | Bacillus anthracis | Cryptosporidium parvum Oocysts |
| Fusarium solani | Bacillus anthracis Ames | Chironomid larvae |
| Lodderomyces elongisporus | Bacillus atrophaeus | Microsporidia |
| Mucor circinelloides | Bacillus atrophaeus ATCC 49337 | Encephalitozoon intestinalis |

## Disinfection By-Products of Chlorine Dioxide

The disinfection by-products (DBPs) of chlorine dioxide reactions are chlorite ($ClO_2^-$) and chlorate ($ClO_3^-$) 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 oxidise bromide ion ($Br^-$) to bromate ion ($BrO_3^-$). Additionally, chlorine dioxide does not produce large amounts of aldehydes, ketones, or other DBPs that originate from the ozonisation 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 sanitising 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 sanitising 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 deodorisation of ventilation systems and air conditioning duct work.

### Food and Drug Administration (FDA)

- FDA approval as a terminal sanitising rinse, not requiring a water rinse, on all food contact surface.

### United States Department of Agriculture (USDA)

- P-1 approval for bacterial and mould control in federally inspected meat and poultry processing plants for environmental surfaces.
- D-2 approval as terminal sanitising rinse not requiring a water flush, on all food contact surfaces in food processing plant.
- 3-D 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 odour 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 HS (G)70 for "The Control of legionellae including Legionnaires Disease" and MISC 150 the Technical Supplement to HS(G)70 "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. coli, amoebae and is effective against cryptosporidium cysts (Finch et al., 1997).

Chlorine dioxide exists in the water as $ClO_2$ (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 coat of the viral capsid and reacting with the viral RNA (An RNA virus is a virus that has RNA (ribonucleic acid) as its genetic material. This nucleic acid is usually single-stranded RNA (ssRNA), but may be double-stranded RNA (dsRNA). Notable human diseases caused by RNA viruses include SARS, influenza, hepatitis C, West Nile fever, polio and measles.
The ICTV classifies RNA viruses as those that belong to Group III, Group IV 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 replication cycle are called retroviruses, and comprise Group VI of the Baltimore 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 ribovirus.).

As a result, the genetic capability of the virus is damaged (Junli et. Al, 1977a). 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, odour, and colour 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.

$ClO_2 + 5Fe(HCO_3)_2 + 3\ H_20 = 5\ Fe(OH)_3 + 10\ Cl_2 + Cl^- + H^+$

Chlorine dioxide reacts with organics, typically by oxidation reactions, and forms few chlorinated organic compounds. Free chlorine, in the presence of organic precursors can form trihalomethanes (THM'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 odour and taste. Chlorine dioxide reacts rapidly with phenols. This reaction may vary in different systems.
(1) The formation of quinones or chloroquinones
(2) 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 oxidising 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$^{o}$C, absorbs light and breaks down into $ClO_3^-$ and $Cl^-$. Because of its oxidising properties chlorine dioxide acts on $Fe^{2+}$, $Mn^{2+}$ and $NO_2^-$ but does not act on $Cl^-$, $NH_4^+$ and $Br^-$ when not exposed to light. These ions are generally part of the chemical composition of natural water.

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 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 oxidises phenol type compounds, secondary and tertiary amines, organic sulphides and certain hydrocarbon polycylic aromatics such as benzopyrene, 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 oxidising 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 $ClO_2$ 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 $ClO_2$ 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 odour with $ClO_2$ is the result of the elimination of algae and on the negligible formation of organo-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, $ClO_2$ limits problems of taste and colour. 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
- THM 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 Flats
- 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

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# 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 $ClO_2$ 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 $ClO_2$ 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, $ClO_2$ can be toxic. However, it is also this toxicity that makes $ClO_2$ 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 (THMs) 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 Iodometric are standardized, widely accepted and used.

**Is Chlorine Dioxide expensive?**
When compared to the cost of chlorine, the cost of $ClO_2$ is lower comparing efficiency and high range desinfection. However in those instances in which chlorine is not the preferred regulatory or environmental alternative, $ClO_2$ 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 | U.S.A | 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 | U.S.A | EPA | Food processing plants, breweries, restaurants, environmental disinfection; Hospitals, labs and non-empty rigid surface equipment sterilization and removal mildew |
| 1989 | U.S.A | EPA | Storage water disinfection; Livestock, disinfection and deodorizing |
| 1988 | Japan | Ministry of Food Health | 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 and sterilization |
| 1996 | China | Ministry of Health | Food additives, fruits and vegetables Preservation |
| 2002 | U.S.A | 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 (THMs) 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 | $ClO_2$ | 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 40 °C | Activity increased | Result is best in 26-60 °C | No | No |
| PH Range | No effect | Alkaline | Acidic | Acidic | No effect | Alkaline | No effect |
| Anion Soap Compatibility | No | Yes | No | Yes | yes | Yes | No |
| Activity of Residue | No | Yes | No | Yes | No | Yes | No |
| Toxicity or Discomfort | No | No | Yes | Yes | Yes | Yes | Yes |
| Damage to Surface | No | No | Yes | No | Yes | Yes | No |
| Kill the Bacteria | Most | Part | Most | Most | Yes | Most | Most |
| Kill the Spores | Yes | Part | Part | No | Yes | Yes | No |
| Kill 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 trihalomethanes (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 hypochlorus 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 odour, colour, bad taste, phenols reduction, iron and manganese reduction

Disadvantages:

- decomposes in sunlight
- must be generated on-site

**What is the difference between $CLO^2$ generator and tablets?**

**Generators:**

• the generators are efficient for spot treatment in water. First step treatment or 2nd 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”. $ClO^2$ gas is explosive when it is in contact with air (10%).

Tablets:

• the tablets produce a sharp level of $CLO^2$ in small or big water volumes. They realise 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 give 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 realised 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:

I. For iodometric analysis
$2ClO_2 + 2I^- \rightarrow 2ClO_2^- + I_2$

2. Oxidation of iron
$ClO_2 + FeO + NaOH + H_2O \rightarrow Fe(OH)_3 + NaClO_2$

3. Oxidation of manganese
$2ClO_2 + MnSO_4 + 4NaOH \rightarrow MnO_2 + 2NaClO_2 + Na_2SO_4 + 2H_2O$

4. Oxidation of sodium sulfide
$2ClO_2 + 2Na_2S \rightarrow 2NaCl + Na_2SO_4 + S$

5. Oxidation of nitrogen oxide pollutant
$2NO + ClO_2 + H_2O \rightarrow NO_2 + HNO_3 + HCl$

6. Gas phase reaction with fluorine
$F_2 + 2ClO_2 \rightarrow 2FClO_2$

7. In alkaline solution
$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$

8. Aluminum, magnesium, zinc & cadmium react with $ClO_2$
$M + xClO_2 \rightarrow M(ClO2)x$

9. Disproportionation of chlorite depends upon chlorides present, pH, and ratio of ingredients
$4ClO_2^- + 4H+ \rightarrow Cl- + 2ClO_2 + ClO_3^- + 2H+ + H_2O$ $5ClO_2^- + 4H+ \rightarrow 4ClO_2 + Cl^- + 2H_2O$

I0. With hydrogen peroxide as a reducing agent in commercial production of chlorite
$2ClO_2 + H_2O_2 + 2NaOH \rightarrow 2NaClO_2 + 2H_2O + O_2$

11. A highly colored complex is formed when $ClO_2$ is dissolved in an aqueous solution of barium chlorite $ClO_2 + ClO_2^- \rightarrow Cl_2O_4$

## Organic Reactions:

I. With organic compounds in water → aldehydes, carboxylic acids, ketones & quinones

2. With olefins → aldehydes, epoxides, chlorohydrins, dichloro-derivatives, and chloro-and unsaturated ketones.

3. With ethylenic double bonds → ketones, epoxides, alcohols

4. With benzene → no reaction

5. With toluene → $Ch_3$, $CH_2Cl$, $CH_2OH$

6. With anthracene 45o → anthraquinone, l, 4-dichloroanthracene

7. With phenanthrene → diphenic acid, 9-chlorophenanthrene

8. With 3, 4-benzopyrene → quinones, traces of chlorinated benzopyrene (no longer considered carcinogenic)

9. With carboxylic and sulfonic functions → no reaction

10. With aldehydes → carboxylic acids

11. With ketones → alcohols

12. With aliphatic amines primary → slow or no reaction
secondary → slow or no reaction
tertiary → rupture of CN bond, no N-oxides formed

13. With triethylamine
$H_2O+(C_2H_5)_3N + 2ClO_2 \rightarrow (C_2H_5)_2NH + 2ClO_2^- + CH_3CHO + 2H^+$

14. With phenol → P-benzoquinone, 2 chlorobenzoquinone

15. Excess $ClO_2$ with phenol → maleic acid, oxalic acid

16. With thiophenols → sulfonic acids

17. With tocopherol → demethylated derivatives

18. With saturated acids → no reaction

19. With anhydrides → no reaction but catalyzes hydrolysis

20. With amino acids: glycine, leucine, serine, alanine, phenylalamine, valine, hydroxyproline, phenylaminoacetec, aspartic, glutamic acids→ little, or no reaction

21. With amino acids containing sulfur → reactive

22. With methionine → sulfoxide → sulfone

23. With aromatic amino acids → reactive

24. With tyrosine → dopaquinone, dopachrome

25. With tryptophan → idoxyl, isatine, indigo red, trace chlorinated products

26. With thiamine → slow reaction

27. With keratin → hydrosoluble acids

28. With carbohydrates CHO and $CH_2OH$ → carboxylic functions

29. With vanillin pH4 → monomethyl ester, _-formylmuconic acid

30. With pectic acid → mucic acid, tartaric acid, galacturonic acid

31. With chlorophyll and plant dyes → color removed.

32. With latex and vinyl enamels → delays polymerization

33. With napthaline → no reaction

34. With ethanol → no reaction

35. With biacetyl → acetic acid, carbon dioxide

36. With 2,3-butaneodiol → acetic acid, carbon dioxide

37. With cyclohexene → aldehydes, carboxylic acids, epoxides, alcohols, halides, dienes, ketones

38. With maleic acid → no reaction

39. With fumaric acid → no reaction

40. With crotonic acid → no reaction

41. With cyanides → oxidized

42. With nitrites → oxidized

43. With sulfides → oxidized

Hydrocarbons of longer chain length than $C_8$ are the most oxydable by $ClO_2$. The organic compounds most reactive with $ClO_2$ are tertiary amines and phenols. Unsaturated fatty acids and their esters are generally oxidized at the double bond.

## $ClO_2$ 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, amido and imido groups, HO groups in alcohols and HO acids, free or esterified $CO_2H$ groups in mono and polybasic acids, nitrile groups, the $CH_2$ groups in homologous series, ring systems such as $C_6H_6$, $C_{10}H_8$, cyclohexane, and the salts of $C_5H_5N$, quinoline and piperidine.

Most aliphatic and aromatic hydrocarbons do not react with $ClO_2$ under normal water treatment conditions, unless they contain specific reactive groups.

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. $ClO_2^-$, chlorite, the reduction product of $ClO_2$, 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 dioxide.