CHLORINE DIOXIDE

What You Can't Tell From the Name

While chlorine dioxide has chlorine in its name, its chemistry is radically different from that of chlorine. It has to do with the way electrons interact with one another. As we all learned in high school chemistry, we can mix two compounds and create a third that bears little resemblance to its parents. For instance, by mixing two parts of hydrogen gas with one of oxygen - liquid water is the formed. We should not be misled by the fact that chlorine and chlorine dioxide share a word in common. The chemistries of the two compounds are completely different

Chlorine dioxide and chlorine – because of their fundamentally different chemistries – react in distinct ways with organic compounds, and as a result generate very different by-products. It's this difference that explains the superior environmental performance of chlorine dioxide in a number of industrial applications.

Chlorine and chlorine dioxide are oxidising agents – electron receivers. Chlorine has the capacity to take in two electrons, whereas chlorine dioxide can absorb five. This property, along with the complex but well-known ways chlorine combines with certain organic materials, to form chlorinated organics that cause numerous environmental problems, explains the superiority of chlorine dioxide based products.

Aromatic compounds have atoms arranged in rings and they may have other atoms, such as chlorine, attached to these rings, to form a chlorinated aromatic. Within the group of chlorinated aromatics, which can be toxic to some organisms, are the infamous dioxins.

Chlorine dioxide's behaviour as an oxidising agent is quite dissimilar. Instead of combining with the aromatic rings, chlorine dioxide breaks these rings apart. In addition, as the use of chlorine dioxide increases, the generation of chlorinated organics falls dramatically. Chlorine dioxide's chemistry also explains why it is such an effective oxidant, or bleaching agent. It's 2.5 times more powerful than chlorine gas, and also much more selective.

In water treatment applications, chlorine dioxide, because of its more powerful action, has broad spectrum activity over a wide range of micro-organisms, and has the ability to penetrate biofilms, and other heavily contaminated areas, where chlorine treatment is simply not effective. Because of its increased efficiency, far less of the chlorine dioxide product need be used, eliminating waste, and reducing handling costs and risk

Chlorine dioxide has been shown to be, more powerful, easier to use, and more environmentally friendly than equivalent chlorine treatments

What is Chlorine Dioxide?

Chlorine Dioxide is a molecule consisting of 1 Chlorine atom and 2 oxygen atoms. Abbreviated to ClO_2.

- 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 2500ppm.
- 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(>pH12).

Chlorine Dioxide Timeline

- 1811 first discovered by Sir Humphrey Davey.
- 1944 First 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 sanitiser.
- 1990's Increasing used for the secondary disinfection of potable water.

What advantages does Chlorine Dioxide have over Chlorine?

- Chlorine Dioxide is a more powerful oxidant.
  It undergoes 5 changes in its oxidative nature. Chlorine is only capable of 1. It is therefore 2.6 times more powerful per ppm.

- Chlorine Dioxide acts only by oxidation. Chlorine will combine to produce harmful Chlorinated by-products, e.g. Chlorinated phenols, THM's, Dioxins etc. Many of these by-products are recognised carcinogens.

- Like Chlorine, Chlorine Dioxide is soluble in water. It however does not hydrolyse to form acid. Chlorine Dioxide is therefore less corrosive.

- The properties of Chlorine are very pH dependant, Chlorine Dioxide is effective at all pH's below 12.

- Chlorine has been found to be ineffective against complex organisms, e.g. cysts and protozoa. Chlorine Dioxide has been found to be effective against a wide range of organisms.

- Chlorine cannot be used at elevated temperatures (>40^{o} C) as it tends to dissociate evolving Chlorine Gas. Chlorine Dioxide does not dissociate as readily at elevated temperatures.

- Chlorine does not remove Biofilm. Chlorine Dioxide Does.

What is Stabilised Chlorine Dioxide and what are the advantages?

- Scotmas are the producers of solutions which contain Stabilised Chlorine Dioxide in a buffered state (pH 9). These solutions contain up to 5% (50,000ppm) Chlorine Dioxide.

- Stabilised Chlorine Dioxide solutions may be transported by road, sea and air.

- There is no capital outlay on generation equipment enabling small volume use of Chlorine Dioxide.

- Stabilised Chlorine Dioxide can become "Activated" Chlorine Dioxide by simple processes.
  Elevated Temperatures > 60^{o} C
  The addition of an acid.
  The addition of Chlorine.
  Or any combination of the above.

- Approved by the Drinking Water Inspectorate for the addition to potable water.

Further Approvals for the use of Chlorine Dioxide are;

- 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 environments. (Pending)

- EPA bactericidal approval as a dental pumice disinfectant.

- EPA approval for a terminal sanitising rinse for food contact surfaces in food processing plants, and in restaurants, dairies, bottling plants and breweries.

- EPA approval for disinfectant of environmental surfaces such as floor, walls and ceilings 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 disinfectant of water systems found aboard aircraft, boats, mobile vehicles, off-shore drilling rigs, etc.

- EPA approval for treatment of stored potable water, at 5 ppm, for drinking water.

- EPA approval for general disinfection and deodorization of animal confinement buildings, such as poultry, swine, barns and kennels.

- EPA approval for the disinfection and deodorisation of ventilation systems and air conditioning duct work.

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.

Chlorine Comparison

Chlorine has been used as a water disinfectant for many decades, and many people are familiar with its use in water disinfection systems - so why change? We list below a number of advantages that chlorine dioxide treatments have over chlorine based systems:

Chlorine		Chlorine Dioxide	
Does not remove biofilm		Will remove biofilm and thus clean tanks and pipes	
Produces unwanted by-products including carcinogens		Does not form chlorinated by-products	
Is corrosive and unpleasant to handle		Is much less corrosive than chlorine. Does not hydrolyse to form an acid	
Already Banned in certain parts of Europe and the USA		Is rapidly replacing chlorine in many of these areas	
Is pH Dependent and very ineffective above pH 7		Is not pH dependent (<pH 11)	
Is ineffective against complex organisms (e.g.: Cysts & Protozoa)		A very broad spectrum kill *	
Limited oxidative effect against various chemical contaminants. Forms chlorinated phenols		Destroys phenols (without forming chlorinated phenols) specific destruction of Hydrogen Sulphides. Destruction of a wide range of chemical contaminants #	
Neutralisation required before dumping to the foul drain		Because no unwanted by-products are formed, and will have a lower residual after use, no neutralisation normally required	
Cannot be used at temperatures above 40^oC due to the release of chlorine gas		Effective at higher temperatures - does not disassociate as rapidly as chlorine	
Increased disinfection time and more service work required to combat high bug counts		Cost savings in labour and use efficiency outweighs the additional chemical costs	

* Includes aerobic, non-aerobic, gram positive & gram negative bacteria, spores, viruses, fungi, cysts and protozoa

\# Includes iron, manganese and other metallics, phenols, trichlorophenols, Hydrogen Sulphides and Sulphides. Refer to Scotmas Systems's ClO_2 reactivity booklet for further information and for specific reactivity rates for particular contaminants

Chlorine Dioxide Mode of Action

Background

Many Scotmas products are based around chlorine dioxide. A powerful biocide, chlorine dioxide has a number of advantageous properties outlined below:

The antimicrobial activity of chlorine dioxide is extremely broad spectrum. It is highly effective against gram negative and gram positive, aerobic and anaerobic, spore forming and non spore forming pathogenic and saprophytic bacteria. This includes bacterial spores, one of the most resistant forms of microbial life to disinfection. The viricidal activity may actually exceed its bactericidal potency. Chlorine dioxide is also effective against molds and yeasts -. both categorized as fungi. It is exceedingly active against acid tolerant bacteria, such as the infamous E. Coli O157:H7. This broad spectra also includes organisms such as algae and protozoans, including Cryptosporidium, Microsporiclium and Giardia lamblia.

As impressive as this list of microorganisms vulnerable to chlorine dioxide is, it is interesting to note the organizations that actually produced this data on chlorine dioxide. Much of the early work was done or compiled by the US EPA’s Division of Drinking Water, in an effort to discover the best replacement for chlorine in water treatment applications. After over 12 years of research, beginning in 1976, their overall recommendation endorsed the use of chlorine dioxide for drinking water applications.

Other researchers interested in chlorine dioxide technology have done numerous comparisons with standard disinfection compounds, such as chlorine, quaternaries, iodine, peroxide, peracetic acid glutaraldehyde, and others. Dr. Ralph Tanner in 1989 published the first broad based comparison in the Journal of Industrial Microbiology. Stabilized chlorine dioxide was shown to be far superior overall in scope and speed of kill, using test bacterial and fungal organisms. In-house commissioned studies also reflect this pronounced antimicrobial activity, with 5 log reductions (99.999%) within 30 to 60 seconds against Listeria, E. coli, Pseudomonas, Salmonella, Staphylococcus and Streptococcus among many others. This type of documentation is never completed, and our product development is ongoing.

As mentioned earlier, the primary chemical reaction of chlorine dioxide based compounds is through oxidation. There are other oxidants in the marketplace. Why is chlorine dioxide’s oxidation any better than, say, peroxide? The answer is that chlorine dioxide’s oxidation is more selective, in that it is highly reactive with certain amino acids that make up proteins, the structural and enzymatic components of life. Two of these amino acids are aromatic, tryptophan and tyrosine, and two contain sulphur in their structures, rnethionine and cysteine. As nature will have it, these amino acids contain easily abstracted electrons, a prerequisite for rapid reactions with chlorine dioxide. The “dug” structures in aromatic molecules contain clouds of electrons, while the sulphur containing molecules have the natural electronegativity of sulphur to promote the donation of electrons to chlorine dioxide. While the reactions of chlorine dioxide with the aromatic amino acids are probably responsible for the observed destruction of cellular structural components, the reactions with the sulphur containing amino acids are more likely responsible for the rapid cell death of the microorganisms, The enzymes found within all cells mediate practically all biochemical reactions within a living cell. These include respiration, metabolism, cellular repair, active transport of materials in and out of the cells and protein synthesis, just to mention a few. These enzymes are proteinaceous and are composed of many strands of polypeptides, which are chains of linked amino acids. These chains of amino acids are held together in a rigid three-dimensional shape by disulfide bonds cross linking the chains together where two sulphur containing amino acids from two different locations come into close contact. In order for enzymes to perform their function as catalysts for biochemical reactions, they must have a particular shape. IT the disulfide bonds are broken (oxidized), the shape is altered and the enzyme loses its specificity, causing toss of that particular biological function. The simultaneous loss of respiration, metabolism, cellular repair, and cell component synthesis is a rapidly fatal condition.

In general, microbes have two differing cell types, prokaryotic and eukaryotic structures. Most bacteria have the more simplistic prokaryotic cell type, where enzymes are located just inside the cellular membrane. These locations come under oxidative attack almost immediately from chlorine dioxide and therefore these cell types are most rapidly destroyed. Fungi and protozoa are of the eukaryotic cell type, where their enzyme systems are located deeper within the cell structure and therefore are slightly more resistant to rapid destruction. Bacterial spores have many layers of protective material surrounding them and therefore are more resistant. For example, a vegetative bacterial cell may require only 30 seconds exposure to chlorine dioxide for cell death to occur, while its spore form may require 5 minutes. Fungal spores are not nearly as protected as bacterial spores and show very little resistance to chlorine dioxide