Chlorine dioxide production systems

Handbook

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PREFACE

The purpose of this handbook is to illustrate in detail the world of chlorine dioxide (ClO_2), a gaseous substance increasingly used in water treatment. The manual outlines the features, benefits, applications, process, safety and environmental topics related to chlorine dioxide use.

Following a brief historical and general introduction about water treatment, the Handbook presents the chemical and physical characteristics of chlorine dioxide before moving on to an overview of the different processes by which chlorine dioxide can be produced, touching on the yield of reaction, with examples of efficiency calculations. This handbook focuses on the innovative underwater reactors developed by ISIA, a Grundfos-owned company fully integrated into Grundfos Water Treatment Solutions, meaning we are now highly specialised in delivering chlorine dioxide in large-scale applications.

Issues of safety and storage are discussed before moving on to the central part of the manual: the chemistry and the interaction between chlorine dioxide and inorganic and organic compounds.

Equipped with knowledge of chlorine dioxide characteristics, the reader can better understand the wide range of its applications for treatment of potable and industrial water, seawater, sewage systems (both liquid and gaseous). The final section deals with the correct – and accepted global standard – analytical method for measuring chlorine dioxide concentration in treatment solutions.

Grundfos and water treatment
Grundfos Water Treatment Solutions is a full-line supplier of tailored solutions for the entire water treatment process with the know-how and resources to handle any application in the field of dosing and disinfection technology. As specialists in chemical dosing and chlorination, Grundfos offers large scale, tailored applications of chlorine and chlorine dioxide in water treatment.

Grundfos has been a global leader in advanced pump solutions and a trendsetter in water technology for more than 60 years and turnover in 2013 was EUR 3.1 Billion. Today 2.5 million Grundfos pumps in operation collect water for 800 million people and our pump solutions distribute water to more than 600 million people. Grundfos is raising the bar for sustainable product solutions within energy efficiency and water, focusing on the entire product life cycle.

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Introduction

WATER TREATMENT NOW AND IN THE FUTURE
It is no secret that this century will be characterised by serious water-related problems, which will compound the energy issues from last century. The scarcity of water in relation to demand will affect how this resource is used both for irrigation purposes and as drinking water, together with the water requirements of industry.

To remedy this, it will be necessary to develop effective technologies for the extraction of water (locating and drilling) and to streamline the delivery from the source to the final consumer, but above all to maximise the water resource through the recycling and purification of polluted water.

On this last point, treatments aimed at recycling water can be divided into two macro-categories: domestic consumption and its use in continuous industrial processes. For domestic use, treatment is for drinking water related to natural surface water, or water obtained by boring, to provide water suitable for human consumption; and treatment of wastewater (rainwater or exhaust) which involve a series of physical-chemical and biological steps to render it usable for agriculture.

For industrial uses, water is involved in many processes and types of equipment, such as steam turbines, steam generators, heat exchangers, as well as in industrial chemical processes. Thanks to its chemical properties, water enables the reaction and dissolution of several substances, and its thermal characteristics make it a good carrier of heat.

The demand for water in industry is met by using surface water with low levels of salt and oxygen due to pollution, underground water containing more carbon dioxide, or much more rarely, water from the atmosphere which is typically corrosive because of the dissolved gas it contains. Depending on the state and size of contaminants, various treatments involving mechanical processes, physics or chemistry are therefore used to make the water fit for use in industrial processes.

The constraints on the availability of water resources as well as growing demand, both for domestic and industrial use, suggest that the ability to optimise exploitation will be of vital importance in all areas of water use. However, based on recent demand forecasts, it is very unlikely that a single form of optimisation will be sufficient. In this century the problem of desalination of sea water – and the treatment needed to make it usable – must also be solved efficiently.

THE HISTORY OF CHLORINE USE
Chemists began to experiment with chlorine and its compounds in the nineteenth century. In 1850, the English physician John Snow was among the first to use chlorine to disinfect water when he tried to sterilise the water supply of Broad Street in Soho after an outbreak of cholera.

In 1897, the pathologist Sims Woodhead used a decolourising solution to sterilise drinking water temporarily in Maidstone, Kent, UK following the outbreak of an epidemic of typhoid fever. The continuous chlorination of drinking water, however, began in England in the early years of the twentieth century and its success in reducing the number of victims of typhus led to the introduction of chlorine in the USA, where it was first adopted in Jersey City, New Jersey in 1908. Since then it has steadily been used more widely around the world.

APPLICATIONS OF CHLORINE DIOXIDE
Due to its chlorine component, chlorine dioxide is used in water treatment for domestic and industrial uses to eliminate bacteria, reduce unpleasant odours or flavours, and remove silt, mould and algae as well as to help remove iron and manganese from untreated water. Specifically for water purification, chlorine dioxide has the major advantage of ensuring clean water from the tap where the action of other disinfectants such as ozone, ultraviolet light and ultrafiltration, is only temporary.

This advantage is common to chlorine too; there is no doubt that chlorination has saved an invaluable number of lives and many experts remain sceptical of the assumption that the enormous benefits of chlorine-based or chlorine dioxide can be provided by alternative methods of disinfection.

However, chlorine dioxide has advantages compared to chlorine for the treatment of potable water. Chlorine dioxide:

• is not affected by hydrolysis
• is immediately effective and less downgraded in big networks and reservoirs
• does not produce bromates or THM, which are very hazardous as cancer promoters, a big concern for potable water plants – especially when using seawater distillation. Halogenated compounds such as TTHMs and bromate, being toxic, are also dangerous in outlet waters for animal species in the environment.

For industrial applications, it should be noted that some plants have tried to avoid the use of chlorine or chlorine dioxide and instead are starting to use alternative products such as ozone for primary sterilisation. However, it is known that since ozone breaks down quickly, it cannot be used to maintain sterility in distribution systems and therefore small doses of chlorine and other disinfectants still have to be added. Moreover, re-equipping plants is very expensive.

Compared to chlorine, chlorine dioxide:

• has a biocide activity that is constant over a wide pH range (6-9), making it suitable for a wide range of waters
• does not react with ammonia or urea, making it suitable for ammonia-rich waters or wastewater treatment and for fertiliser industries
• does not react with organic matter and oil, whenever present, making it suitable for refinery and desalination plants
• has a strong effect on anaerobic bacteria that reduce sulphate to sulphide.

In conclusion, the chlorination of water represents a simple solution both for domestic as well as industrial uses and it may be assumed that it will remain the cornerstone of the process of water purification for the near future. Chlorine dioxide is not only a simple but also an effective solution, and it is therefore the best alternative for the use of chlorine as an agent for water treatment.

Chemical and physico chemical characteristics

1.1 Physical properties

At room temperature, chlorine dioxide (ClO_2) is a gas denser than air, yellow-greenish in colour, and highly soluble in water. Its principal physical properties are provided in table 1 here below.

|		
Molecular weight	g/mol	67.457
Melting point	°C	-59
Boiling point	°C	+11
Density (liquid) at 0°C	kg/l	1.64
Density (vapor)	g/l	2.4
Critical Temperature	°C	153
Vapor pressure at 0°C	Torr	490
Dissolution heat in water at 0°C	kcal/mol	6.6
Evaporation Heat	kcal/mol	6.52

*Table 1*

1.2 Molecular structure and stability

The chlorine dioxide molecule, which is composed of one atom of chlorine and two atoms of oxygen, has an angular structure in which the length of the Cl-O bond is 1.47-1.48, while the size of the Cl-O angle is 117.7 degrees. ClO_2, with an uneven number of chlorine atoms and unpaired electron, may be considered to be a free radical with the following resonance structure:
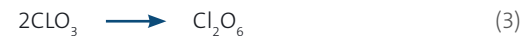
The chlorine dioxide molecule which contains 19 electrons in the valence layers of its atoms, in accordance with the Lewis theory on molecules with an uneven number of electrons, has paramagnetic properties. In the gaseous state, chlorine dioxide is highly unstable and breaks down if its presence in the air reaches concentrations higher than 10% in volume. Under the effect of temperature, ClO_2 gas will decompose in accordance to the following reaction:

$$ClO_2 \longrightarrow 1/2\ Cl_2 + O_2 + 98.2kJ \qquad (1)$$
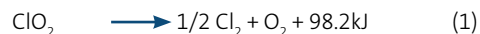
The decomposition of gaseous ClO_2 is accelerated by light, which is absorbed at a wavelenght of 365 nm. Photodecomposition, takes place in the following manner, in the case of dry ClO_2 in the gaseous state:

$$ClO_2 \longrightarrow ClO + O$$

$$ClO_2 + O \longrightarrow ClO_3$$

$$2ClO \longrightarrow Cl_2 + 0_2 \qquad (2)$$
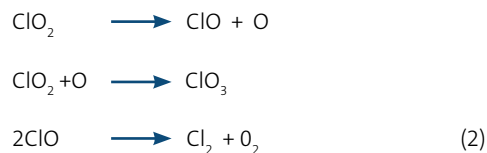
The chlorine trioxide ClO_3 in turn dimerises:

$$2CLO_3 \longrightarrow Cl_2O_6 \qquad (3)$$

Or else releases chlorine by thermal decomposition:

$$2ClO_3 \longrightarrow Cl_2 + 3O_2 \qquad (4)$$

In the presence of humidity, the photo decomposition of gaseous chlorine results in the formation of a mixture of acids: $HClO$, $HClO_2$, $HClO_3$, $HClO_4$.

1.3 Solubility and stability in aqueous solution

Chlorine dioxide is highly soluble in water, more than chlorine or ozone. The solubility of a gas is expressed by the concentration of dissolved gas in equilibrium, between its gaseous and its dissolved states. According to Henry's law, the quantity of gas dissolved in a given volume of liquid at constant temperature, is directly proporsional to the pressure exerted by the gas on that liquid:

$$Ceq = KH \times PG$$

Where:

Ceq is the concentration of gas dissolved in the liquid at equilibrium;
KH is Henry's constant (in function of the nature of the gas-liquid system and temperature under consideration);
PG is the partial pressure of the gas upon or above the liquid.

The graph in Figure 1 show the values of ClO_2 concentration at different temperatures and partial pressures.

The solubility of ClO_2 is not influenced by the potential presence of chlorine in the water.
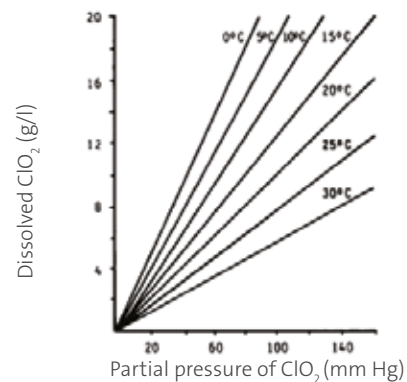
*Figure 1 : Solubility of chlorine dioxide in water.*

In the interval of pH values characteristic of drinking waters (i.e. 6-8), chlorine dioxide does not undergo hydrolysis, but remains in solution as dissolved gas, because the reaction:

$$2ClO_2 + H_2O \longleftrightarrow HClO_2 + HClO_3 \qquad (5)$$

is displaced to the left, and the equilibrium constant, at 20°C, stands at:

$$K= \frac{[HClO_2][HClO_3]}{[ClO_3]^2} = 1.2 \; 10^{-7}$$

In a basic environment, chlorine dioxide decomposes instead into chlorite and chlorate according to the reaction:

$$2ClO_2 + 2OH^- \longleftrightarrow ClO_2^- + ClO_3^- + H_2O \qquad (6)$$
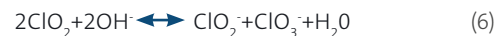
This reaction is not complete except at pH values above 11

where there is:

$$ClO_2 + e^- \longleftrightarrow ClO_2^-$$

$$2ClO_2 + 2OH^- \longleftrightarrow ClO_2^- + ClO_3^- + H_2O$$

1.4 Oxidising properties

Chlorine dioxide is an oxidant that can be reduced in a varity of ways, depending on the system conditions and the nature of the reducing agent. In aqueous solutions, the following reactions may occur with the respective E0 calculated at 25°C:

$$ClO_2 + e^- \longleftrightarrow ClO_2^- \qquad EO=0.95V$$

$$ClO_2 + 4e^- + 4H^+ \longleftrightarrow Cl^- + 2H_2O \qquad EO=0.78V$$

$$ClO_2 + 5e^- + 4H^+ \longleftrightarrow Cl^- + 2H_2O \qquad EO=1.51V \quad (10,11,12)$$
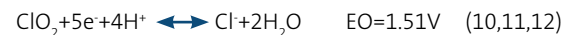
Both reactions depend on the pH values and (10) is usually the main one in case of drinking water. It should be noted that with protonisation of chlorite ion, chlorous acid is formed:

$$ClO_2^- + H^+ \longrightarrow HClO_2 \qquad (13)$$

which, in view of its oxidation potential, is considered to be a strong oxidant:

$$HClO_2 + 3H^+ + 4e^- \longrightarrow Cl^- + 2H_2O \quad EO=1.57V \quad (14)$$
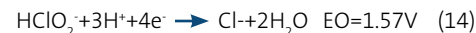
In table 2 the redox potential values (E_0) are shown for some types of oxidising chemicals normally involved in disinfection process.

Reactions	Readox Potential (Volt)
$HClO_2+3H^++4e^-=Cl^-+2H_2O$	1.57
$ClO_2+4H^++5e^-=Cl^-+2H_2O$	1.51
$HClO+H^++2e^-=Cl^-+H_2O$	1.49
$Cl_2+2e^-=2Cl^-$	1.36
$HBrO+H^++2e^-=Br^-+H_2O$	1.33
$O_3+2e^-=2Br^-$	1.24
$Br_2+2e^-=2\ Br^-$	1.07
$HIO+H^++2e^-=I^-+H_2O$	0.99
$ClO_2(aq)+e^-+2e^-=ClO_1^-$	0.95
$ClO^-+2H_2O+2e^-=Cl^-+2OH^-$	0.90
$ClO_2^-+2H_2O+4e^-=Cl^-+4OH^-$	0.78
$NH_2Cl+H_2O+2e^-=NH_3+Cl^-+OH^-$	0.75
$I_2+2e^-=2I^-$	0.54

Table 2: Standard Redox Potentials (E_0)

As can be seen from this listed series of redox potentials, chlorine dioxide does not react with bromides to form bromine, unlike ozone, chlorine and hypochlorite.

For further information concerning the reactivity of chlorine dioxide with halides, please refer to the chapter on "Reactivity with inorganics".

Thanks to its radical structure, ClO_2 functions first as an electron receiver and thus as an oxidant, unlike chlorine and hypochlorous acid which not only act as oxidants, but also stimulate addition and substitution reactions (and, therefore, chlorination reactions). For chlorine dioxide, the reactions are mainly numbers (10,11,12), while, for chlorine and hypochlorite they are:

$Cl_2 + H_2O \longleftrightarrow HClO + HCl$

$HClO + H^+ + 2e^- \longrightarrow Cl^- + H_2O$

$HClO + RH \longrightarrow HClO + RH$

$Cl_2 + RH \longrightarrow RCl + HCl$

(15,16,17,18)

In general, chlorinating action of chlorine and, therefore, also of hypochlorous acid, has been neglected for a long time. Today, however, a great attention is being devoted to this aspect in the field of drinking water treatment, owing to the difficulties arising from formation of halogenated organic and bromate by-products in disinfection treatments.The problem of chlorinated organics, in particular the THM one (trihalomethanes), has reached such relevance that a statement was issued as early as 1975, at the Oak Ridge Congress in Tennessee, on the need to find alternatives to chlorine in the treatments of water disinfection; this necessity was reiterated by influential scholars, B. Hileman among others, with his paper on "The chlorination question". Subsequently the danger of halogenated organics was confirmed, and extensive researches were undertaken to better understand the mechanism of their formation, and the possibility of their being conveyed and accumulated along the food chain.

Additional information on the danger of disinfection by-products from chlorine and hypochlorite will be provided in the chapter "Reactivity with organics".

On site generation of chlorine dioxide

Since chlorine dioxide is a relatively unstable gas, it cannot be compressed and liquefied, and must, therefore, be generated "on site" dissolved in water. Diluted solutions of chlorine dioxide (from 1 to 3 g/l) however may be safely handled and are stable over time. Summarising chlorine dioxide may be obtained by either oxidising chlorite or reducing chlorate.

2.1 Generation from chlorate

Generation from chlorate is generally adopted when large quantities of chlorine dioxide are needed (in the order of more than one ton per day, as in case of pulp bleaching or in industrial production of sodium chlorite) since it requires rather complex equipment and may create problems in terms of by-products, investments and operations.

There are two categories of generating process from chlorate which differ with respect to operating conditions, reaction by-products and purity of obtained chlorine dioxide.

From an economic standpoint, the feasibility of the process depends upon the possibility of reusing the by-products. Below are the principal reactions of the two processes for the generation of chlorine dioxide, starting from chlorate:

$$2ClO_3^- + 4HCl \longrightarrow 2ClO_2 + Cl_2 + 2H_2O + 2Cl^- \qquad (19)$$

which leads to the formation of ClO_2 and Cl_2 in a molar ratio of 2/1, and:

$$2ClO_3^- + H_2SO_4 + SO_2 \longrightarrow 2ClO_2 + 2HSO_4^- \qquad (20)$$

which is accompanied by the following secondary reaction, with the formation of chlorine:

$$2ClO_3^- + 5SO_2 + 4H_2O \longrightarrow Cl_2 + 2HSO_4^- + 3H_2SO_4 \qquad (21)$$

2.2 Generation from chlorite

The processes for generating ClO_2 from chlorite are definitely the first choice in the field of water treatment. Starting from chlorite, chlorine dioxide may be obtained either through the action of chlorine or through a strong acid.

2.3 Generation from chlorite and chlorine

There are two processes for the production of chlorine dioxide by means of oxidation of sodium chlorite with chlorine: the first uses chlorine in aqueous solution in the form of hypochlorous acid, while the second uses chlorine in molecular gas form. The first systems for the production of chlorine dioxide consists in pumping a sodium chlorite solution into a chlorine aqueous solution. The two solutions reacted as follows:

$$2NaClO_2 + Cl_2 \longrightarrow 2ClO_2 + 2NaCl \qquad (22)$$

Grundfos uses such a reaction to produce large quantity of chlorine dioxide as antifouling agent in power stations, which use sea or fresh water for their cooling system (once through or recirculating). When chlorinated water is already present in the plant, with a simple modification we convert chlorine into chlorine dioxide.

2.4 Generation from chlorite and hydrochloric acid

This process is most commonly used in the field of drinking water disinfection given the reliability of its operation. The special generator developed and called **"chlorine dioxide under water generating system"** fulfils the most diversified requirements in terms of usage, safety, reliability, yield, purity of ClO_2 solution and ease of conduction. The preparation of chlorine dioxide is effected through the acidification of chlorite according to the reaction:

$$5Cl_2^- + 4H_3O^+ \longrightarrow 4ClO_2 + Cl^- + 6H_2O \qquad (23)$$

The most common method of producing chlorine dioxide uses sodium chlorite and hydrochloric acid according to the reaction:

$$\mathbf{5NaClO_2 + 4HCl} \longrightarrow \mathbf{4ClO_2 + 5NaCl + 2H_2O} \qquad (24)$$

The principal reaction may be accompanied by the followings secondary reactions:

$$4HClO_2 \longrightarrow 2ClO_2 + HClO_3 + HCl + H_2O$$

$$5ClO_2^- + 2H^+ \longrightarrow 3ClO_3^- + Cl_2 + H_2O$$

$$4ClO_2^- + 4H^+ \longrightarrow 2Cl^2 + 3O_2 + 2H_2O \qquad (25,26,27)$$
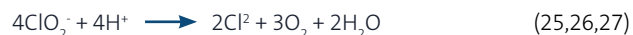
The chlorine dioxide solution which is obtained may, therefore, contain chlorine and chlorates, in addition to the expected chlorides. Appropriate generator (as in case of the Grundfos under water generating system) and operating conditions make it possible to produce solutions of ClO_2 without Cl_2 and with only small quantities of chlorate (less than 1%). Moreover high yields may be obtained with an output of chlorine dioxide as close as possible to the theoretical one of 4 moles of ClO_2 per 5 moles of $NaClO_2$. With the Grundfos generating system a yield of about 95% against 80-85% with the classic generator found in the market is guaranteed.

Molecular Structure of Chlorine

Cl

Atomic symbol: Cl
Atomic number: 17
Atomic number: 35.453
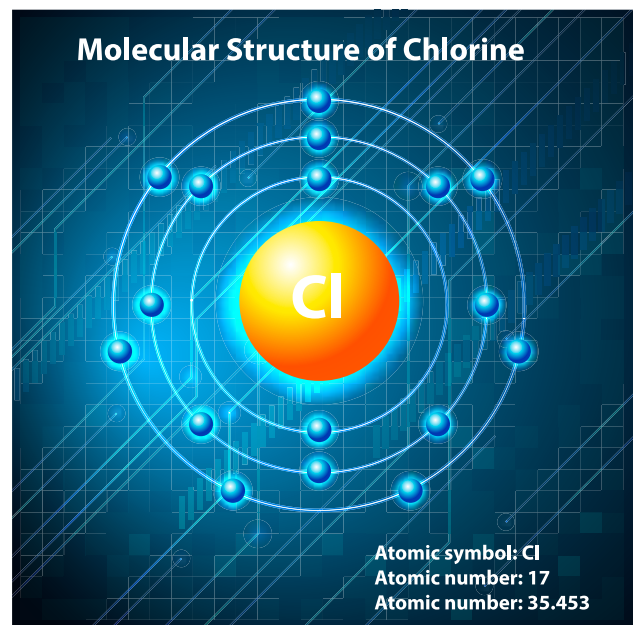
2.5 Grundfos generating system

After years of study Grundfos developed a special chlorine dioxide generator, which works "under water". It means that the formation of chlorine dioxide takes place only in the water and it is not present in any other part of the plant. We can say 100% safe generator because there is no possibility for chlorine dioxide to be relased from the water. Therefore we always have a very diluted solution (normally 1,000 mg/l) and never ClO_2 gas. Moreover, in normal generator you can find in the market, chlorine dioxide is generated into a reaction chamber having a big volume, for instance, to generate 10 kg/h the volume is 70 liters, in our generator the volume to generate the same quantity is 0.2 liter only. As you can understand, the task linked to releasing chlorine dioxide depends strongly on the hold-up you have at the site in any moment.

Normal chlorine dioxide generator and "Underwater generating system" comparison:

Considered parameters	Normal ClO$_2$ generator	Grundfos ClO$_2$ generator	advantages
Volume of reaction chamber for 10 kg/h ClO$_2$ production	70 liters	0.2 liters	Less ClO$_2$ quatity means, in general, less risk
Location of reaction chamber	In the atmosphere	Always under water: inside the main water line or into a by-pass	In any kind of event, ClO$_2$ is never released in the atmosphere
Pipe line from the generator to ClO$_2$ injection point	2-3 inch pipe containing a solution of about 20,000 mg/l of ClO$_2$ stretching from generator to the injection point	1-inch pipe containing water stretching from reagents pumping station to the injection point. (the reagents line are installed inside the water pipen in order to prevent any kind of leakage)	No risk due to breakage of pipe. No releasing of chemicals in any kind of event
Yield of reaction	80-85%	95 % ± 2	Less by-products such as chlorite ions
Reagents consumption	HCl 7.3 kg per 1 kg of generated ClO$_2$	HCl 5.4 kg per 1 kg of generated ClO$_2$	Saving of material (it is because normal generator needs 300% HCl of the stoichiometric request)
Spare parts and maintenance	Very special and specific mechanical spare parts are required	Free market availability of mechanical spare parts	L ow cost and less repairing time
Generation flexibility	Very high flexibility: if a 10 kg/h generator is installed, the minimal ClO$_2$ quantity to generate is 5 kg/h	Very high flexibility: if a 10 kg/h generator is installed, the minimal ClO$_2$ quantity to generate is 0.5 kg/h	Possibility to manage ariable water flow rate with only one generator

systems, suitable for every installation conditions, by applying customers design and construction standards or its own standards.
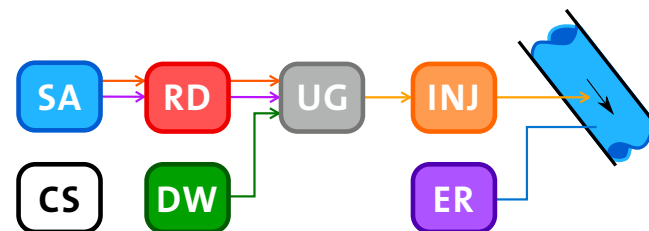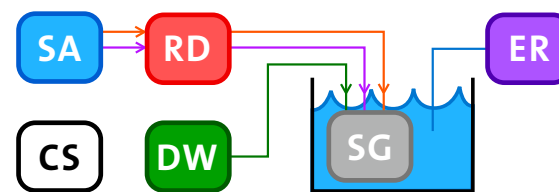

Diagram for a system dosing ClO$_2$ in a pipe

SA - Storage Area
RD - Reagents Dosing Area
DW - Dilution Water Area
UG - U-type Generator
SG   - Submerged Generator
INJ - ClO$_2$ Injection Area
CS   - Control System
ER   - EasyaReadox

Diagram for a system dosing ClO$_2$ in a basin

Referring to the schematic picture here above, our chlorine dioxide generating systems can be divided in three different sections:
• Storage area (SA);
• Dosing area (RD+DW);
• Generating, injection and analysis area (UG/SG+INJ+ER).

1) The **storage area** is mainly composed by:
• One or more tanks for each reagent (opportunely designed depending on the plant chemicals consumption, horizontal or vertical tank, GRP material);
• Loading section (pneumatic or electrical pumps, local or remote control system);
• Instrumentation (level, flow, PH, pressure);
• Acid vapours cut down (fume trap);
• Safety equipment (shower, eye washer, Personal Protection Equipments);
• Facilities (Civil basement, Tank ladders, piping support, tank insulation, cable trays, etc etc);
The piping material can be different, according to customer requirements: C-PVC, U-PVC, U-PVC+GRP.

2) Depending on the plant ClO$_2$ demand, we provide **reagents dosing area** in different configuration:
• Complete redundancy (2 skids for 1 dosing point);
• Partial redundancy (3 skids for 2 dosing points);
• Single (1 skid for each dosing point);
• Other configuration on demand.

Grundfos skid solutions characteristics are:
• Pre-installation in a container;
• PP frame;
• Painted steel support;
• Normal or special pump type;
• Instrumentation (flow, pressure, level);
• Leakage containment basin with detector (PP);
• Piping material: C-PVC, U-PVC.

All the reagents dosing area and the related equipments are installed in a container in order to protect them and to let the operator work in a safe and clean place. The container is configurable with lights, A/C or heater, service sockets, fan, service sink, office or laboratory. Using the Grundfos container solution, the dosing area will be pre-installed and tested together with the Control System at the workshop, reducing the time and cost for the site activities.

Moreover, this configuration does not decrease the operator safety because the chlorine dioxide is formed only inside the reaction chambers installed outside the container.

As shown in the picture in the previous page, Grundfos developed two different reaction chambers type depending on the injection that has to be provided: U-type (UG) or submerged (SG) generator.

Dilution water is a must in the chlorine dioxide production process, for the safety point of view. The dilution water line is designed to guarantee always no more than 1 g/l concentration of chlorine dioxide during the action. For safety reasons, there is always at least a double redundant instruments on this line (flow meter, flow switch) connected to the Control System. Depending on the plant design and water availability, the dilution water can be pumped, filtered or both.

Submerged Generator:

This configuration is the safest solution for the Chlorine Dioxide generation, because the two chemicals and dilution water are carried from the dosage area up to the injection point separately and protected. The generator is always submerged into the water basin so the client will have a ClO$_2$ presence always only underwater. The generator is protect by a fibreglass cover. This type of generator is provided with a diffusion system for the chlorine dioxide in order to distribute it in the water and increase the efficiency. With this technology there is no limit for the generator capacity, even if the generator volume is always extremely smaller than a normal one.

U-Type Generator:

Where using the submerged generator is not possible, the Grundfos solution is the u-type generator providing a chlorine dioxide solution for every kind of plant. In this case, the reaction chamber is not submerged by the water to treat, but the reaction chamber is installed close to the dosing area. With this configuration the chlorine dioxide solution can be injected in existing pipelines or buffer tank, where the submerged generator cannot be installed. From the u-type reaction chamber, the chlorine dioxide solution is pumped by injection centrifugal pumps (titanium made).

By using U-type generators, the chlorine dioxide has to be carried from the reaction chamber up to the injection point, by using a pumping station. In this way Grundfos technology can satisfy any customer requirement (for example, the ISIA system can inject the chlorine dioxide on high pressurised lines).

This pumping station is commonly pre-installed in the container with the Control System and the Dosing area.

Control system:

Grundfos offers several types of solutions for the Electrical Power and Control System, due to its experience all over the world, with different standard and specifications. All the plant can be managed by using PLC and Human Machine Interface (HMI) that will be configured providing the best user-friendly interface but, at the same time, the safest program. The Control System in pre-installed in the container, together with the dosage area and it is tested at the workshop, reducing the costs for the installation at site.

Easyareadox:

Easyareadox consist of an online monitoring system of an oxidant biocide treatment used in industrial water treatment, which is capable of estimate, by an electrochemical probe the first biofouling growth (biofilm) and the presence of oxidising agents (chlorine dioxide). This instrument will help to decide the number and duration of shots, and chlorine dioxide dosage rate in order to optimise the dosing strategy.

The electrical signal is correlated to the biological micro-fouling growth upon the surface and the system (pipe ,lines, heat exchangers, etc.). The electronic instrumentation of system can be connected to be the control system so it is possible to check the instant and the historical trend of an electrical signal (mV) coming from the electrochemical probe.
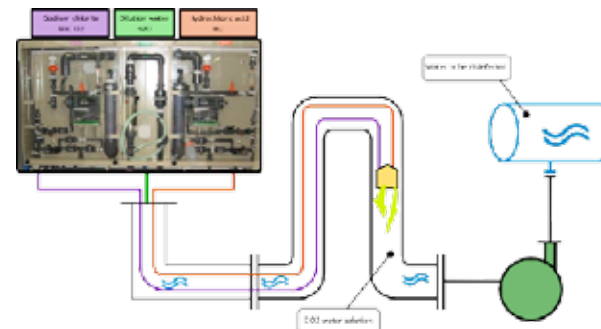
2.6 Generator yield

The yield or efficiency of a generator is determined by the ratio between the quantity of produced chlorine dioxide and the theoretical amount of production based on the stoichiometry of the earlier described reaction:

$$5NaClO_2 + 4HCl \longrightarrow 4ClO_2 + 5NaCl + 2H_2O$$

$$1.676\ g\ + 0.54g \longrightarrow 1g\ + 1.08g + 1.133\ g$$
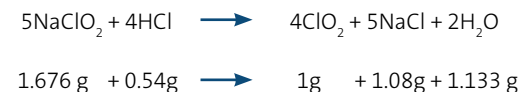
A theoretical conversion of 100% occurs when 1.676 g of $NaClO_2$ yield 1 g of ClO_2.

The theoretical stoichiometric ratio $R = HCl/NaClO_2$ is equal to 0.54/1.676 = 0.32, while the one used in practice may vary from 0.85 to 1.2; thus, 1 g of $NaClO_2$ for instance is made to react with 1 g of HCl (instead of 0.32 g).

The efficiency of the generator (η) is calculated in the following manner:

$$\eta = \frac{ClO_2 \text{ produced}}{ClO_2 \text{ theoretical}} \cdot 100 \text{ (N.28)}$$

where:

- "produced ClO_2" is the real concentration in g/l or mg/l of chlorine dioxide determined by analysis;
- "theoretical ClO_2" is the sum, always in g/l or mg/l of chlorine dioxide actually generated and the chorine dioxide which have been produced, if all the chlorite had reacted completely and/or had not formed any Cl_2 and $NAClO_3$ in accordance with to the following reactions:

$$2ClO_2^- + 6e^- + 8H^+ \longrightarrow Cl_2 + 4H_2$$

$$2ClO_2^- + H_2O \longrightarrow ClO_3^- + 2e^- + 2H^+ \qquad (29,30)$$

From the results of the analyses, and taking into account the stoichimetry of the reactions 28,29,30, the conversion of ClO_2 is thus calculated from the unreacted portions of sodium chlorite, sodium chlorate and chlorine which were formed, by applying the following formulae:

ClO_2 FROM UNREACTED $NaClO_2$= mg/l $NaClO_2 \cdot$ 0.5966

ClO_2 FROM ClO_2 = mg/l $ClO_2 \cdot$ 1.522

ClO_2 FROM $NaClO_2$ = mg/l $NaClO_2 \cdot$ 0.5071

Formula for the efficiency of the generator thus becomes:

$$\eta = \frac{A}{A + B + C + D} \cdot 100$$

Where:

A = ClO_2 produced effectively

B = ClO_2 corresponds to the portion of unreacted chlorite

C = ClO_2 corresponds to the portion of chlorite that formed chlorine

D = ClO_2 corresponds to the portion of chlorite that formed chlorate

The efficiency of the generator can be still calculated in a different way starting with the following data:
- flow of dilution water at the outlet of the generator,
- flow of sodium chlorite solution,
- concentration of sodium chlorite solution.

As indicated in "example of generator yield calculation", the efficiency of the generators currently on the market, properly maintained and operating with good quality reagents, is around 80-85%, whilst the Grundfos underwater generating system guarantees around 95%.

EXAMPLE OF GENERATOR YIELD CALCULATION:

It is possible to calculate the efficiency of a generator by using the following data:
• Flow of diluting water at the outlet of the generator, expressed in l/h (a);
• Flow of sodium chlorite solution, expressed in l/h (b) and concentration, expressed in g/l (c);
Concentration of chlorine dioxide, expressed in g/l, results of the analysis (d).

The efficiency of the generator is determined by means of the following formula:

$$\eta = \frac{\text{produced } ClO_2}{\text{theoretical } ClO_2} *100 = \frac{E}{F} \cdot 100$$
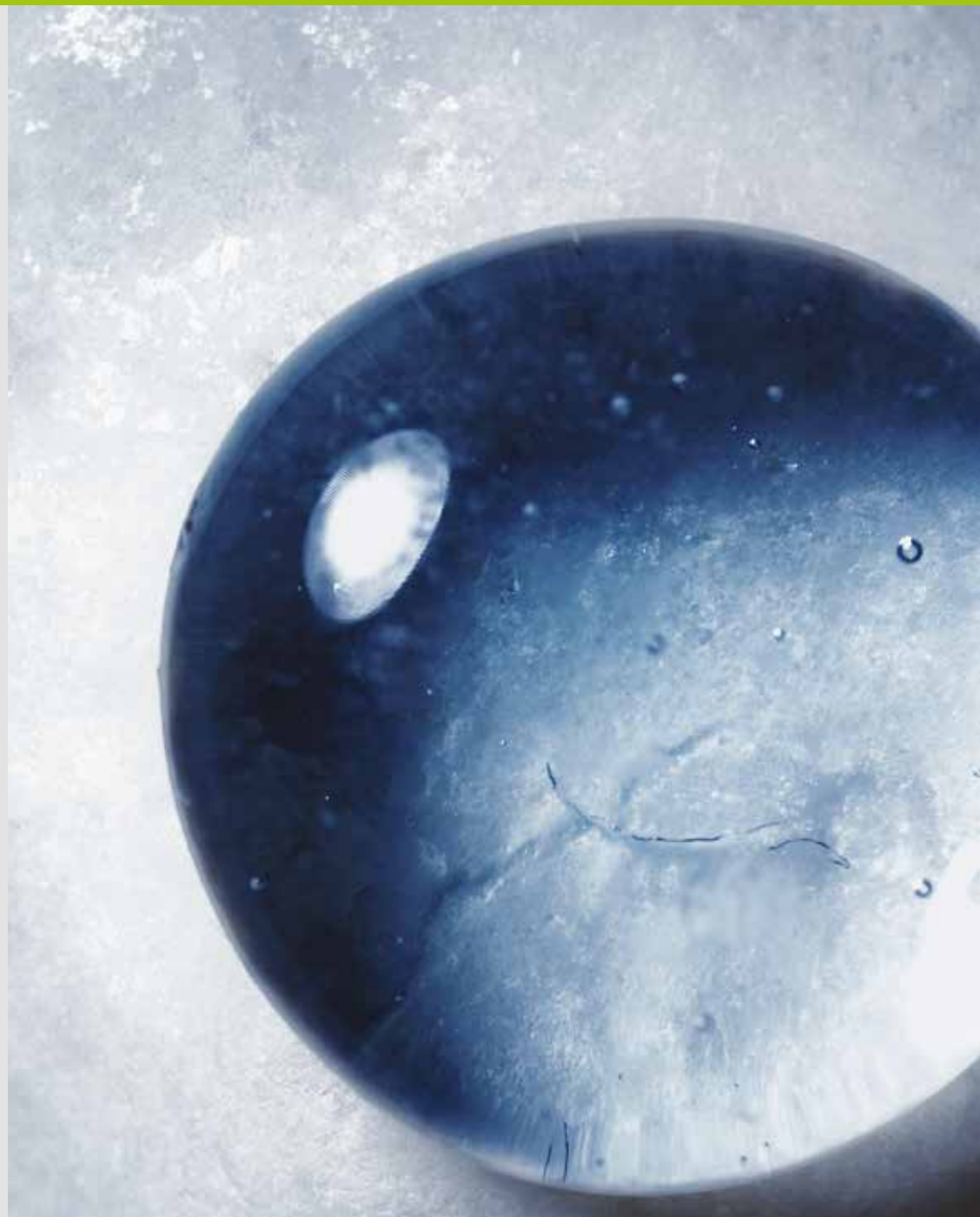
Where:

• E is the production of ClO_2 at the generator outlet, expressed in g/l;

• F is the theoretical quantity of ClO_2, expressed in g/l

The theoretical quantity of ClO_2 is as follow:

$$F = \frac{b*c}{1.676} = ClO_2(g/h)$$

While the production at the generator outlet is as follows:

$$E = d*a = ClO_2(g/h)$$

Safety recommandation for reagents storage

3.1 Chlorine dioxide

Chlorine dioxide is produced and used in the form of aqueous solution, as explained in the section entitled "on site generation of chlorine dioxide".

Safety problems are, in fact, related to the explosive properties of chlorine dioxide when its concentrations in the air is greater than 10% in volume as shown in the figure:

Chlorine dioxide in the gas state vapour pressure mbar %volume
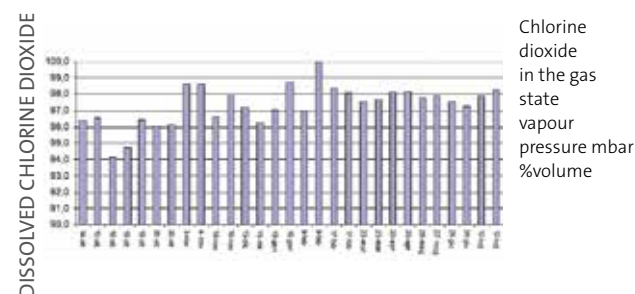
The graph shows the correlation between the concentration of chlorine dioxide solution and the percentage of chlorine dioxide in the air in equilibrium with that solution, at different temperatures. For this reason, every effort must be made to prevent the formation of gas pockets.

For safety reasons the Grundfos Underwater generating system is designed to operate avoiding any formation of chlorine dioxide gas. Is allowed only in a submerged small reaction chamber in order to avoid any releasing of chlorine dioxide in the atmosphere. On the contrary, in the classic generators found in the market, the reaction takes place in a big reaction chamber (about 100 times more than the Grundfos reaction chamber) placed in the work place with consequent possibility of chlorine dioxide realising in case of any odd event.

The Grundfos generator is equipped with systems of dosage and measurement for the reagents and the diluting water. The Grundfos system is able to shut down the operation in case of anomalies (for example, the lack of one of the reagents). The safe limit of exposure in the work place (TLV-TWA) is 0.1 ppm. The equipment for generation and distribution of chlorine dioxide, in case of classic generator, must, therefore, be installed only in locations provided with adequate ventilation where chlorine dioxide in air detector is operating. In the Grundfos underwater generating system all mentioned above is not strictly required as in the work place is installed only the reagents pumping station and no chlorine dioxide generation takes place there.

3.2 Hydrochloric acid

Hydrochloric acid is a fuming liquid when present in concentrations of above 20% in volume. It is a strong acid which attacks most metals and release hydrogen. In addition to individual protection of people assigned to its handling (suitable gloves, footwear, and masks-shower must be provided for washing in case of spills or overflows in the proximity of the storage tank). Hydrochloric acid, delivered in bulk, is usually discharged by means of a centrifugal pump made in plastic material with a suitable mechanical seal or magnetically driven. In the last case, particular attention should paid to the protection of the pump against the "dry" functioning (level switches, pressure switches) and against a functioning with plugged discharge. When added to sodium chlorite in concentrated solution, it causes an immediate release of chlorine dioxide which, if it is not vented, can cause the tank break-down. The risks of such accidents happening are usually linked to a accidental exchange of nozzles at the storage tanks during unloading when reagents are being delivered.

It is, therefore, advisable to arrange to have nozzles of two different diameters for the unloading of two different reagents, or else to have control devices such as pH-meter with alarm that shuts off the discharge pump. The pipe of hydrochloric acid can be made of plastic material as the valves. It is preferable that critical piping either under pressure or at risk of impact, as well as connecting tubes, are made of plastic reinforced with fibreglass. Storage tanks can be made of bis-phenolic or vinyl type polyester (GRP) that is an aging material and should be replaced every 10 years. For small storages, polyethylene (PE) may be used with better results, while for large tanks (switches capacity of over 10 cubic meters) polyvinylchloride (PVC) renforced with polyester (PVC+GRP) is also used. The using of polyester must absolutely be avoided, in case of use of hydrochloric acid contaminated with hydrofluoric acid which, by corroding the fibreglass reinforcement of the tank, could cause its collapse. The storage tank must be fitted with an overflow pipe which also functions as a vent, and level gauge monitor to safely handle loading operations.

A fume trap or a scrubber, installed on the vent line, wash the acid gas from the vent. The tank must be housed in a containing basin with a volume equal to that of the reservoir itself plus 10%, and lined with acid-proof material (rubber-based bitumen, tiles, polyester or painting).

3.3 Sodium chlorite

This product is usually marketed in aqueous solution and, thus, in the form of a clear pale-yellow liquid with a slight odour of chlorine. Sodium chlorite is an oxidant and must not therefore come into contact with organic materials such as rubber, paper, straw, or timber, due to their flammability, or with heat sources. When mixed with acids, it causes the formation of ClO_2 which may be dangerous for the container, as well as for safety of personnel. For safety reasons, the use of sodium chlorite solutions is preferred than of powder. The solutions offer several advantages: they are easier to handle, getting rid of irritating dusts and risk of error in preparation for the use. In addition, sodium chlorite solution are not classified as "oxidants".

Materials which are compatible with chlorite solution are: PVC, polyethylene, bis-phenolic polyester, vinylester, AISI 316 or better, 316 L stainless steel. Storage tank can be made of all of these materials; it is economical for large containers to use bis-phenolic polyester, externallypainted to avoid deterioration. The construction characteristic of the containing basin and storage tank are the same as those indicated for hydrochloric acid, except for acid-proof lining, not necessary. In addition, personal protection equipment shall be weared (gloves, goggles, proper protective garments).
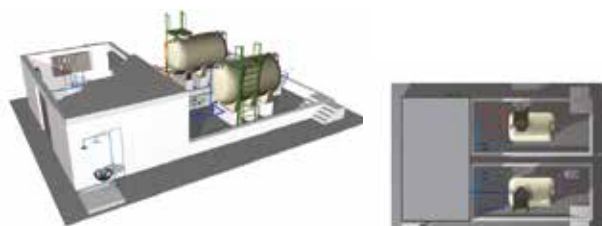
3.4 Consumption and storage of reagents

The consumption of reagents and the relative dimensions of their storage tanks are in function of the dosage of chlorine dioxide and the flow of the water to be treated. As an example, the storage volumes for the reagents are estimated for the use of ClO_2 in the post-disinfection treatment of a medium waterworks.

EXAMPLE OF CHLORINE DIOXIDE CONSUMPTION CALCULATION:

Consumption of chlorine dioxide

Dosage of ClO_2 = 0.25 mg/l
Flow of water to be treated = 5,400 m^3/h
Consumption of ClO_2 = 0.25 x 5,400 = 1,350 g/h = 1.35 kg/h

Consumption of reagents

To produce 1kg of ClO_2 (with a generation yield of 95%) using concentrated solutions of:

• 25% $NaClO_2$ (306 g/l d (15°C) = 1.22 kg/l) and
• 32% HCl (371 g/l d (15°C) = 1.16 kg/l)

The consumption of reagents is:
HCl = 6 l
$NaClO_2$ = 6 l

With a weight ratio,
R = HCl/$NaClO_2$ = 0.95 (theoretical R = 0.32), equal to a 300% excess of HCl compared to that required stoichiometrically.

Reactivity with inorganics

4.1 Iron and manganese

As indicated by the redox potentials of the Fe_3+/Fe_2+ and Mn_4+/Mn_2+ systems, that is:

$Fe_3^++e^- \longleftrightarrow Fe_2^+$ Eo=0.77V

$Mn_4^+ + 2_e^- \longleftrightarrow Mn_2^+$ Eo=0.37V

and by the redox potential of the system ClO2/ClO2- E0 = 0.95 V, the Fe_2^+ and Mn_2^+ ions are oxidised by chlorine dioxide with the formation, respectively, of ferric hydroxide and manganese dioxide which, being only very little soluble, precipitate.
The oxidation-reduction reactions at pH 7 are the following:

$ClO_2+Fe_2^- \longrightarrow Fe_3^++ClO_2^-$

$Fe_3^++3OH^- \longrightarrow Fe(OH)_3$

and

$2ClO_2+Mn_2^++2H_2O \longrightarrow 2ClO_2^-+MnO_2+4h+$

There is complete reduction to Cl- when pH values are greater than 7. The theoretical consumptions of ClO_2 are:

1.2 mg of ClO_2 per mg of Fe_2^+
2.45 mg of ClO_2 per mg of Mn_2^+

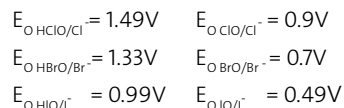There is also an advantage in the fact that the oxidation rate by chlorine dioxide to oxidise iron and manganese and, thus, extract them from water by precipitation, is exploited particularly in the treatment of water intended for human consumption. The presence of these ions in fact, alters the organoleptic properties of the waters conferring to them a substantially unpleasant flavour and odour.

Furthermore, a significant presence of iron causes an excessive proliferation of ferrobacteria in the distribution systems of drinking water.

4.2 Halides

The standard potentials of semi-reactions of halides, and their related oxidants, are:

$E_{O\ HClO/Cl^-} = 1.49V$ $E_{O\ ClO/Cl^-} = 0.9V$

$E_{O\ HBrO/Br^-} = 1.33V$ $E_{O\ BrO/Br^-} = 0.7V$

$E_{O\ HIO/I^-} = 0.99V$ $E_{O\ IO/I^-} = 0.49V$

which, compared with the potential of ClO_2/ClO_2^- ($E_0 = 0.95$ V), indicate that chloride and bromides cannot be oxidised by chlorine dioxide. No oxidation of bromide and therefore no formation of brome and consequently bromate, allows chlorine dioxide to be used in desalinated water disinfection where hypochlorite and chlorine promote large amount of bromate formation. Bromate is limited by Law to 10 ppb because suspected cancer promoter in humans.
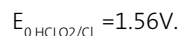
Iodides are oxidised according to the reaction:

$$2ClO_2^- + 2I^- \longrightarrow I_2 + 2ClO_2^-$$

In acid environments, iodides are rapidly oxidised by chlorites:

$$ClO_2^- + 4I^- + 4H^+ \longrightarrow 2I_2 + Cl^- + 2ClO_2^-$$

The oxidising agent in this case is probably chlorous acid ($HClO_2$) whose redox potential is

$E_{0\ HCLO2/Cl} = 1.56V$.

4.3 Cyanides

Cyanides are oxidised into cyanates by chlorine dioxide according to the reaction:

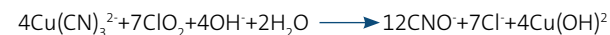$$CN^- + 2ClO_2 + 2OH^- \longrightarrow CNO^- + 2ClO_2^- + H_2O$$

with theoretical consumption of 5.19 mg of ClO_2 per mg of CN^-. The subsequent oxidation of the cyanates occurs at acceptable rate only under slightly acid conditions (pH=6) according to the following reactions:

$$2CNO^- + 6ClO_2 + 2H_2O \longrightarrow 2CO_2 + N_2 + 6ClO_2^- + 4H^+$$

$$10CNO^- + 6ClO_2 + 4H^+ \longrightarrow 10CO_2 + 5N_2 + 6Cl^- + 2H_2O$$

In the case of cyanides of bivalent metals (for example, Zn_2^+ and Cd_2^+) the reaction is:

$$Me(CB)_4^{2-} + 8ClO_2 + 10OH^- \longrightarrow 4CNO^- + 8ClO_2^- + Me(OH)^2 + 4H_2O$$

With cyanides of copper (Cu^+), a different reaction takes place, since the chlorite ion also takes part in the oxidation:

$$Cu(CN)_3^{2-} + 7ClO_2 + 8OH^- \longrightarrow 3CNO^- + 7ClO^{2-} + Cu(OH)_2 + 3H_2O$$

$$4Cu(CN)_3^{2-} + 7ClO_2 + 4OH^- + 2H_2O \longrightarrow 12CNO^- + 7Cl^- + 4Cu(OH)^2$$

$$5Cu(CN)^{2-}_3 + 7ClO_2 + 12OH^- \longrightarrow 15CNO^- + 7Cl^- + 45Cu(OH)_2 + H_2O$$

The oxidation of cyanides of nickel and cobalt is fairly difficult, while cyanides of iron are not oxidised In this case, the chlorine dioxide acts by oxidising only the metal that forms complex, that is, by transforming ferrous cyanide into ferric cyanide.

4.4 Nitrites and sulfides

Chlorine dioxide is able to oxidise nitrites according to the reaction:

$$2ClO_2 + NO_2 + H_2O \longrightarrow 2ClO_2^- + 2H^+ + NO_3^-$$

and sulfides according to the reaction:

$$2ClO_2 + 2\,S^{2-} \longrightarrow 2Cl^- + SO_4^{2-} + S$$
$$2ClO_2 + 5e^- \longrightarrow Cl^-$$
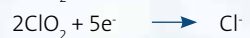
In the reaction with sulfides some involve the maximum oxidative capacity of chlorine dioxide.

Reactivity with organics

As a general rule, chlorine dioxide in highly diluted solutions reacts with the different dissolved substances according to 2nd order kinetics of the following type:

$V = K[ClO_2] * [solute]$

where:

- V is the reaction rate, expressed in 1/[M]s, where [M] is the molar concentration;
- K is the rate constant;

By the rate constant $kClO_2$ reported in the figure, it may be inferred that the reactivity of chlorine dioxide it elevated with:

- phenols, neutral secondary and tertiary amines, and organo-sulfurs,

while it is practically nil for:

- unsaturated organics aromatics with slightly activated or inactivated groups, ketones, quinines,

and

- carboxylates,
- ammonia, primary amines, urea and most amino acids.
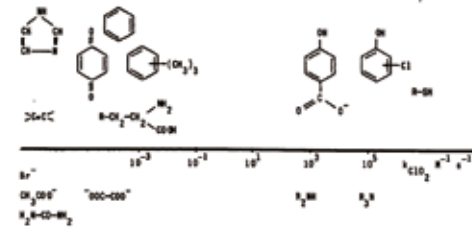
reactivity scale of chlorine dioxide, compared to some organic compounds.

5.1 Aliphatic compounds

Unsaturated compounds

Chlorine dioxide reacts very slowly with unsaturated hydrocarbons. Studies have been carried on the reaction mechanism in highly concentrated solutions. It was noted, for instance, that the oxidation of cycl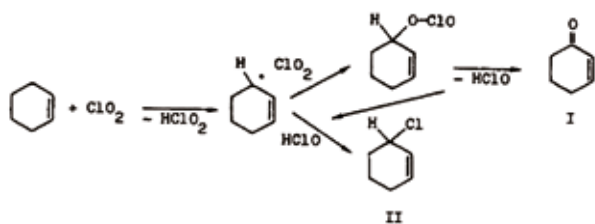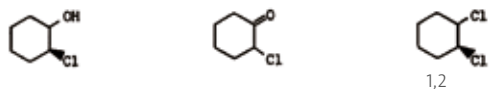ohexene by chlorine dioxide led to the formation of cyclohexanone and 3-chlorocyclohexene through a mechanism which involves an allylic radical:

Other identified products are typical of chlorination, probably due to the action of hypochlorous acid released by ClO_2, on cyclohexene and cyclohexanone:

2 chlorocyclohexane 1 olo   2 chlorocyclohexane 1 one   1,2 dichlorocyclohexane

5.2 Aromatics

The reactivity of chlorine dioxide with aromatics usually depends on the presence of active groups in the chain.

As may be seen from the data in the Table concerning concentrated solutions, the reactivity of chlorine dioxide, as evaluated by the demand for ClO_2, is nil for such molecules as nitrobenzene.

compounds	ClO_2 Demand moles moles^{-1} (pH 7.9-8.3)		
	1 mn	1h	24h
NH₂	2,4	3,1	3,4
N(CH₃)₂	2,6	3,6	5,6
N(C₂H₅)₂	2,2	3,6	5,2
OH NH₂	4,5	5,9	6,8
OH NH₂	4,0	6,2	7,0
NH₂ OH	1,9	2,0	2,0
NO₂			0
OH NO₂	5,2	6,6	7,0
OH NO₂	5,6	6,1	6,8
NO₂ OH	5,5	5,7	6,2
N			0
N	1,5	2,0	2,0

5.3 Phenols and phenolic derivatives

The presence of phenols in drinking water is due to contamination from industrial sources. Such molecules, even when present in concentrations of micrograms per liter, gives an unpleasant odour and taste to the water. As mentioned before, phenols react rapidly with ClO_2; the kinectis constant for phenol at 25 °C in a neutral environment is k = 2÷4 104 [M]-1 s-1. The action of chlorine dioxide on phenolic derivatives may vary with the formation of different compounds. There can be:

1) the formation of quinones or chloroquinones,
or
2) the breaking of the aromatic chain, with the formation
   of aliphatic derivatives.
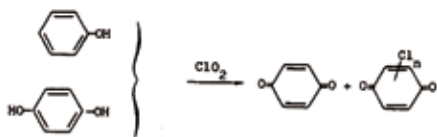
1)The first case refers to monophenols non-substituted in para position, and hydroquinones: Although the action of chlorine dioxide is primarily that of an oxidant, in this case it may be accompanied by a slight chlorination with formation of chlorinated organics.
2)The second case concerns mono-phenols with the carbon atom replaced in para position (i.e. p-cresol), di-phenols, and tri-phenols with the hydroxyl groups in or tho- or meta- positions (i.e. resorcinol, pyrogallol, and the like):

carboxylic acid + CO_2 + ..
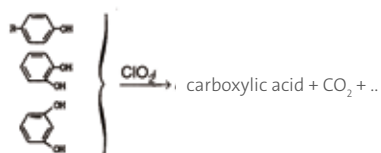
The breaking of the aromatic chain through oxidation on the part of ClO_2 leads to the formation of carboxylic acids and CO_2.

5.4 Monocyclic aromatics

The results of studies conducted on the oxidation of aromatics by chlorine dioxide are reported in Table 4, which lists the oxidation products identified so far for some monocyclic aromatics. N-Heterocyclics N-heterocyclics consist of a chain in which one of the carbon atoms is replaced by an atom of nitrogen.

5.5 N-Heterocyclics

Pyrrole

It is present in the structure of many natural compounds, such as chlorophyll and hemoglobin. Chlorine dioxide is very active in the presence of pyrrole, and certain oxygenated and chlorinated compounds have been identified through the products of oxidation. The break-down of the pyrrolic ring and the consequent deactivation of the chlorophyll enable chlorine dioxide to become effective in the control of algae growth.

compounds   Identified products

Table 4

5.6 Pyridine

It is a compound from which nicotinic acid is derived, a crucial component of the coenzyme NAD (nicotinamide adenine-dinucleotide) which is responsible for cellular respiration. Pyridine is a stable molecule with which chlorine dioxide does not react.

5.7 Atrazine and simazine

Atrazine and simazine, used in agriculture as herbicides, have been found as pollutants in groundwaters. Chlorine dioxide reacts very slowly with these compounds.

Polycyclic aromatic hydrocarbons (PAH), that is the clorine dioxide capability to oxidise, has been studied and compared with that of chlorine. The results, reported in Table 5, show that, in contrast with the slight reactivity of naphthalene and fluoranthene, the other PAH are rapidly oxidised by chlorine dioxide, which appears to be more selective than chlorine. Chlorine dioxide, in fact, functions essentially as an oxidant, while chlorine may produce addition or substitution reactions with subsequent formation of chlorinated organics. Because of this, the oxidation of anthracene and benzopyrene occurs much faster with chlorine dioxide than with chlorine. The reaction products are quinones and phenols, as well as traces of chlorinated compounds.

Hydrocarbon	ClO_2	Cl_2
Benzopyrene	0.17	17
Anthracene	0.15	60
Benzanthracene	1	30
Pyrene	90	-
Benzopyrene	200	20
Naphtalene	No reacton	400
Fluoranthene	No reaction	900

Table 5
PAH concetration: 1-10 g/l Disinfectant concentration: 1mg/l

5.8 Disinfectant properties

Chlorine dioxide has excellent bactericidal, virucidal, sporicidal and algicidal properties and, because of this, it is used to disinfect water and to inhibit the growth of algae. The oxidising and disinfecting properties of chlorine dioxide remain practically unchanged over a wide range of pH (from 4 to 10), unlike chlorine and bromine, whose active forms are considerably affected by the pH, as shown in Figure 16.

The graphs in Figure 17 show the effectiveness of some disinfectants in destroying 99 % of two different populations at 15 °C: of E. coli (a) and Poliovirus 1 (b). The graphs indicate that in the inactivation of Poliovirus 1, the effectiveness of chlorine dioxide at pH 7 is more or less equivalent to that of chlorine at pH 6 in the form of hypochlorous acid (HClO); while chlorine appears to be more effective than ClO_2 in inactivating E. coli. In the form of hypochlorite ion (ClO⁻) and of chloramine ($NHCl_2$, NH2Cl), chlorine appears to be less effective in both cases. The assessment of a disinfectant's efficiency is usually based on the concept of "concentration per duration" (C • t), in other words, on the basis of the concentration of the disinfectant in use and the contact time needed for the inactivation of selected species, tested under specific operating conditions.

The relationship between the concentration C and the contact time t is expressed by the following empirical equation:
k = Cn • t

where :

"C" is the concentration of the disinfectant
"n" is the dilution coefficient
"t" is the contact time required for a set %of inactivation
"k" is a specific constant for each microbial population.

The logarithmic representation of this relationship provides the straight lines shown in Figure 17, in which "n" represents the slope.

When

n = 1, the product
C · t remains constant, and is characteristic of the disinfectant; an increase in the concentration implies a reduction in contact time.

If
n>1, the dominant factor for disinfection is the disinfectant concentration;

where as, if

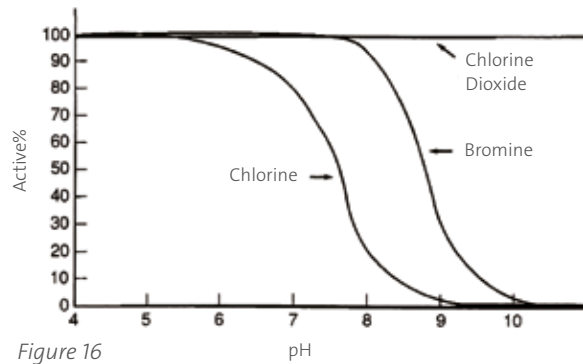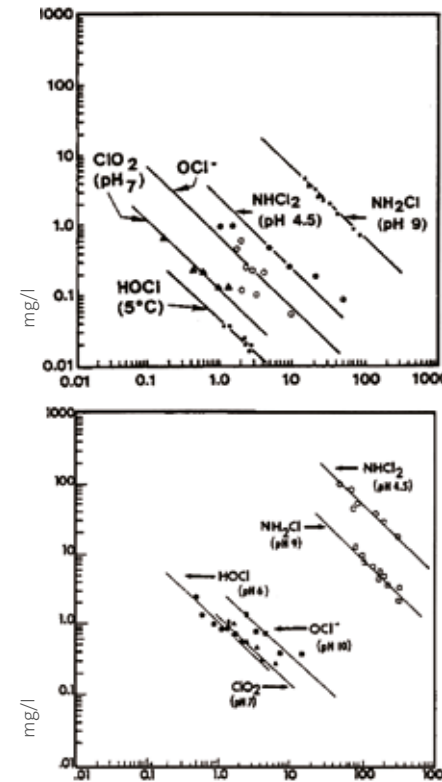n<1, the contact time is more important than the disinfectant concentration.

Figure 16

Figure 17: inactivation of 99% E. coli (a) ad Poliovirus 1 (b) using chlorine dioxide and other chlorine compounds.

On the basis of the concept C • t, working under certain conditions and on selected micro-organisms, it is possible to compare the efficiency of different disinfectants. In short, it appears that the lower the product Cn• t may be, the more active will be the disinfectant. The data make it clear that the disinfectant power of chlorine dioxide is inferior only to that of ozone, which shows the lowest values of C • t. It is, however, important to emphasise that the efficiency of a disinfectant must also be evaluated on the basis of other factors, such as its efficacy with variations in the pH and its persistence in treated water. In this report, the use of chlorine dioxide is particularly advantageous, as indicated below. The biocidal efficiency of chlorine decreases rapidly, passing from pH 7, in which the dominant form is hypochlorous acid (HClO) to pH 9 where the dominant form is the hypochlorite ion (ClO-). In this same pH interval, the biocidal efficiency of chlorine dioxide increases instead of diminishing, as shown in the chart in Figure 18, which illustrate the relationship between the ClO_2 concentration and the contact time needed to inactivate Poliovirus 1. The biocidal activity of ClO_2 occurs in environments with a pH value between 6 and 10; with a moderately alkaline pH (up to 10), the elevated biocidal efficiency is due either to the stability of the ClO_2, whose breakdown into ClO_2^- and ClO_3^- is significant only in conditions where pH > 11, or to the greater vulnerability of the micro-organisms. Thanks to its stability and persistence, chlorine dioxide is used with great advantage whenever a post-disinfection of treated waters is considered appropriate (for example in the distribution network of drinking water intended for human consumption after the disinfection treatment, that is, at the outlet of the waterworks).

Such a disinfection may be accomplished thanks to the sequential action of chlorine dioxide (an effective bactericide) and chlorite (bacteriostatic and slightly

biocidal). In Table 7, the biocidal efficiency, the stability, and the effects of pH on the efficiency of some disinfectants are reported.

The mechanism by which chlorine dioxide inactivates micro-organisms is not yet completely understood, but it has been, and still is the objective of two types of researches on one hand, the chemical reactions of ClO_2 with the molecular constituents of the micro-organism cells are being investigated and, on the other, the effects of the ClO_2 on their physiological functions are being explored. The first ones, conducted by Noss et al.and Olivieri et al., have demonstrated the fast reactivity of ClO_2 with certain amino acids (such as cysteine, tryptophan and tyrosine) but not with ribonucleic acid (RNA) in the viruses. The conclusion reached in these studies is that the inactivation of viruses by ClO_2 is due to the alteration of the proteins in the viral capsid.
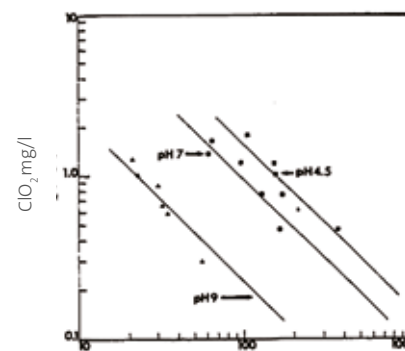

Figure 18: effect of pH on the efficiency of the Poliovirus 1 inactivation by chlorine dioxide.

Poliovirus RNA to such an extent as to damage the synthesis of the RNA itself. Other researcher have found that ClO_2 is reactive with fatty acids in the cytoplasmic membrane. The second type of studies have not yet clarified whether the primary action of ClO_2 takes place at the peripheral structure level (cellular membranes) or in the internal structures (nucleus, mitochondria). It is reasonable to think, however, that both activities contribute to the inactivation of the micro-organisms. In any case, action at the peripheral structures level (alteration of the proteins and lipids of the cellular membrane) would bring about an increase in the permeability of the membrane itself while action at the internal structures level would lead to an alteration of the protein synthesis and/or of the respiratory activity. In any case, the above mentioned actions ultimately cause the death of the cell.

5.9 Toxicity

Numerous studies have been conducted to evaluate the toxicity of chlorine dioxide and of its inorganic and organic by-products.

Health effects of chlorine dioxide, chlorites, and chlorates .
The oxidant action of chlorine dioxide, as was seen in the sections on the reactivity of ClO_2, ends with the formation of chlorites, chlorides and small quantities of chlorates. The formation of chlorites is equal to about 60-70 % of the consumed chlorine dioxide or, to say, to 0.6 - 0.7 mg of ClO_2^- per mg of ClO_2 used up.

Disinfectant	Biocidal efficiency *	Stability *	Effect of the PH efficiency (PH = 6-9)
Ozone	1	4	Little influence
Chlorine Dioxide	2	2	Efficiency slightly increases with the increase of the PH
Chlorine	3	3	Efficiency decreases considerably with the increase of the PH
Chloramines	4	1	Little influence

Table 7: characteristics of sone disinfectants.
* The indicated charateristics decreases from 1 to 4
(1 is the max, 4 is the min)

In the relevant applicative conditions of chlorine dioxide, in fact, the partial reduction of ClO_2 into chlorite, that is the intermediate step of the reduction of chlorine dioxide into chloride, represents the prevalent reaction. The chlorates can be formed by the oxidation of hypochlorous acid (HClO) on chlorite, resulting in turn from the reaction of ClO_2 with some organic substances, according to the following reaction:

$$HClO + ClO_2^- + OH^- \longrightarrow ClO_3^- + Cl^- + H_2O$$

Furthermore, small quantities of hypochlorous acid, as a result of organic substances naturally present in water (humic acids and the like), cause the formation of very limited quantities of Total Organic Halides (TOX). The formation of chlorites and chlorates can also take place through this breakdown of the ClO_2 in alkaline solutions.

The presence of chlorates is linked to the efficiency of chlorine dioxide production and the potential photolysis after exposure to sunlight. Toxicological studies available today indicate that, of the dosages of chlorine dioxide, chlorites (ClO_2^-) and chlorates (ClO_3^-) used in water treatment do not present any risks to health. The results of clinical and biochemical studies, carried out in the United States, on the effects of chlorine dioxide ingested by means of regular consumption to water, indicate that the chlorite concentrations threshold beyond which there could be a certain effect on health is equal to 24 ppm for healthy individuals and 5 ppm for individuals affected with a deficiency of the G6PD enzyme (Glucose -6- Phosphate Dehydrogenase). Toxicological studies made on animals have shown that the concentration of chlorite at which hemolytic stress begins to manifest itself is 250 ppm.

	Chlorine dioxide mg/l	Chlorite ClO_2^- mg/l	Chlorate ClO_3^- mg/l	Trihalomethanes THM mg/l	Bromate BrO_3^- mg/l
WHO 2004		0.7	0.7	See table below	0.01
EC DIRECTIVE 1998				0.1	0.01
USEPA 2002	0.8	1		0.08	0.01

TABLE 8: Acceptable limits for chlorine dioxide (ClO_2) and other compounds in drinking water

WHO 2004 regulation concerning THM	In mg/l
Bromoform	0.1
Chloroform	0.2
Dibromochloromethane	0.1
Dichlorobromomethane	0.06

The sum of the ratio of the concentration of each to its respective guideline value should not exceed 1.

The limits established for the residual concentrations of chlorine dioxide, chlorites, and chlorates and other compounds in drinking water are given in Table 8. To be noted is the formation of halogenated organic compounds as by-products of the oxidation of soluble organic fractions (NOM: Natural Organic Matter), which include (up to 75 %) humic and fulvic acids, present in the water. Since it is practically impossible to identify systematically and completely all of these halogenated compounds, methods and definitions have been adopted conventionally to determine their overall content. These are the so-called "aspecific" parameters usually indicated as OX (Organic Halides) which are capable of evaluating different fractions of organic chlorinated products, in accordance with analytical techniques and the adopted experimental conditions. Table 9 gives the acronyms most commonly used to identify the above mentioned fractions.

DENOMINATION	
POX	Purgable Organic Halides
AOX	Absorbable Organic Halides
TOX	Total Organic Halides
NPOX	Non Purgable Organic Halides
EOX	Extractable Organic Halides

Table 9: Aspecific parameters for the evaluation of halogenated organics.

where X = Cl, Br, I, F

In the present state of the art, trihalomethanes (THM) constitute an effective indicator of the total content of halogenated organic compounds and are commonly used in evaluating the disinfection process as regards to the formation of these kind of by-products. Evaluation of the THM, as well, is logically justified, because they represent the fraction which is potentially most toxic to humans health.

THM refers to the following four products:
• chloroform ($CHCl_3$);
• dichlorobromomethane ($CHCl_2Br$);
• dibromochloromethane ($CHBr_2Cl$);
• bromoform ($CHBr_3$).

Chemical	Formula	MW	BP(°C)	MP(°C)	Density (g/ml)
Chloroform	$CHCl_3$	119.4	61.7	-63.5	1,483
Dichloro-bromomethan	$CHCl_2Br$	163.8	90.1	-57.1	1,980
Dibromo-chloromethan	$CHBr_2Cl$	208.3	119		2,451
Bromoform	$CHBr_3$	252.7	149.5	8.3	2,889

Table 10: Characteristics of molecules identified as THM

MW= molecular weight
BP= boiling point
MP= melting point

CHLORINE DIOXIDE				CHLORINE			
$CHCl_3$ (µg/l)	$CHCl_2Br$ (µg/l)	$CHClBr_2$ (µg/l)	$CHBr_3$ (µg/l)	$CHCl_3$ (µg/l)	$CHCl_2Br$ (µg/l)	$CHClBr_2$ (µg/l)	$CHBr_3$ (µg/l)
0.46	0.23	0.36	0.62	8.01	8.44	8.75	3.18

Table 11: formation of THM during disinfection with chlorine dioxide and chlorine.

These chemicals have low boiling points, may already be present in water subject to the purifying process polluted by industrial activities. Except in cases of specific contamination, their concentration is normally very limited, at the level of the "detection limit" of survey methods presently available.

THM constitutes the "lightest" fraction of the family of chlorinated organics to which they belong. These molecules have been partially identified, but some are still unknown because of the analytical difficulty of their determination.

In recent years, with the refinement of various methods of specific analysis, it has been possible to assess quantitatively not only THM, but other subgroups of the same family, such as halogenacetic acids, halogenacetonitriles, trichlorophenol, and other aromatic and aliphatic hydrocarbons.
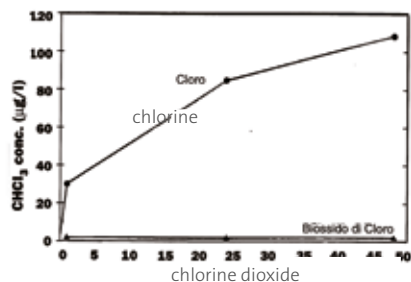

Figure 19: formation of chloroform in the treatment of water containing 5 mg/l of humic acid with chlorine and chlorine dioxide
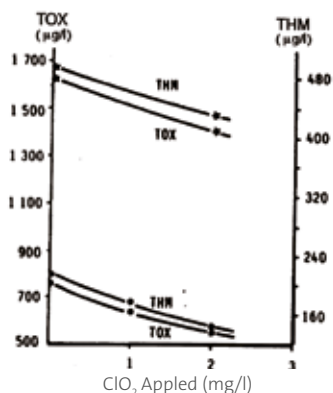

Figure 20: action of ClO$_2$ on fulvic acid, and potential formation of THM and TOX.
Treatment conditions:pre-oxidation with ClO$_2$ 2h TOC: 1.8 mg/l
post-disinfection with Cl$_2$: 20 mg/l TOC: 4.5 mg/l 7 days pH=7

Chlorine dioxide show a very slight chlorinating action, since its degradation contributes only minimally to the formation of hypochlorous acid which, in addition to oxidation also causes addition and substitution reactions (and therefore, chlorination reactions).

Furthermore, in comparison with chlorine, it can be said that chlorine dioxide does not produce THM, as may noted from the graph in Figure 19 which compares the formation of chloroform (CHCl$_3$) in the treatments of water containing 5 mg/l of humic acid with chlorine and chlorine dioxide. The comparison between the chlorinating action of chlorine and that of chlorine dioxide is also pointed out by the data in Table 11, taken from a study [31] which describes the formation of bromo-methanes, in addition to that of chloroform. The formation of bromo-methanes is linked to the oxidation of bromine into hypobromous acid, which react with the humic substances. Chlorine dioxide, which does not react with bromine, does not cause the formation of bromo-methanes, except after photolysis and, thus, after exposure to light. The quantities of TOX and AOX measured in water treated with chlorine dioxide are minimal, in percentages varying from 1 % to 25 % as compared to that produced by chlorine. It may be due in part to the presence of chlorine residue in the ClO$_2$ produced from chlorite and chlorine, and, in part, according to Rice, to the direct action of chlorine dioxide, with the formation at pH = 3 and 7.8 of 4 classes of oxidation by-products: benzenepolycarboxylic acid, dibasic aliphatic acids, carboxyphenylglucosilic acids and monobasic aliphatic acids. It must be pointed out that the by-products of chlorine dioxide oxidation possess neither any acute or chronic toxicity, nor any mutagenic or carcinogenic properties.

If utilised in pre-oxidation, chlorine dioxide considerably reduces the potential formation of THM and TOX. Studies addressing the reduction of potential formation of THM by means of ClO_2 have shown that it acts on the precursors making them not reactive or unavailable for the formation of halomethanes. The graph in Figure 20 demonstrates the formation of THM and TOX in the treatment of water containing two different quantities of fulvic acids (measured as TOC - Total Organic Carbon), with varying doses of ClO_2 used in pre-oxidation and with a dose 20 mg/l of Cl_2 in post-disinfection.

Application

In every application of chlorine dioxide, as well as in treatments with chlorine or hypochlorite, it is important to determine the "disinfectant demand" before starting the feeding. The "chlorine dioxide demand", described in the Appendix, represents the quantity of chlorine dioxide that reacts with water under test within a set time (from 5 to 60 minutes, depending on plant contact time). This amount is a reference for chlorine dioxide applications, since it can always be considered an useful indication about the water quality. The effective dosage of ClO_2 used in the application can be, according to each case: a) inferior to, b) equal to, c) slightly higher than the demand itself. Respectively, these situations correspond to:

a) wastewater (where 20-30% of the demand is normally sufficient to reach the required bacteriological levels);
b) drinking water (in pre-oxidation);
c) drinking water (in post-disinfection).

It must be kept in mind that the demand refers to the total requirement of ClO_2 for the water to be treated and, therefore, includes, but does not differentiate, the quantity of ClO_2 consumed reacting with present microorganisms and that consumed reacting with present chemicals. For the same reason, in order to achieve a correct application of ClO_2 and reach the target, it is necessary to perform other complementary analyses (for example, some microbiological analyses).

6.1 Drinking water disinfection

In Italy, water destined for human consumption must comply with the quality requirements of the governmental regulation D.P.R.236/88.

In particular, with respect to microbiological limits (absence of faecal coliforms and faecal streptococci, and a limit of 5 total coliforms per 100 ml in not more than 5 % of tested samples within one year and for no more that 2 consecutive samples drawn at the same point) approximately 95 % of the Italian water works provide a pre/post-disinfection phase. In terms of volumes of drinking water supply (in Italy, approximately 6 billion m^3/year), it is believed that at least half the quantity is treated by chlorine dioxide in one of the production phases. Chlorine dioxide may be used in the treatment of drinking water either as a disinfectant or as an oxidant. As a disinfectant, it can be used in the pre-oxidation phase as well as in the post-disinfection phase. In the purification treatment of surface water, pre-oxidation is used to control the growth of bacteria and algae during the subsequent phases of the treatment.

The use of chlorine dioxide in this phase, in place of chlorine/hypochlorite, has the advantage of considerably reducing the formation of halogenated organics (usually called Adsorbable Organic Halides or AOX), which, for water in distribution, must not exceed 30 mg/l as indicated in D.P.R. 236/88 and, in particular, of not producing trihalomethanes (THM). The formation of THM may occur more easily after treatment of surface waters containing high levels of organic precursors (with TOC - Total Organic Carbon – greater than 1 mg/l) but even with ground waters which are generally characterised by low TOC values (lower than 1 mg/l). Furthermore, in the pre-oxidation phase chlorine dioxide oxidises colloidal substances improving the coagulation process and, therefore, turbidity removal. In the post-disinfection phase, chlorine dioxide develops a dual action, bactericidal and virucidal in the form of ClO_2, and bacteriostatic and weakly bactericidal in the form of chlorite (ClO_2^-). As a bactericidal agent it can remain active in water for at least 48hours and its effectiveness is guaranteed for longer periods than that of chlorine.

Thus, the use of chlorine dioxide in this phase can guarantee the inhibition of "bacterial regrowth" in the distribution network. Furthermore, in the presence of viral contamination, the virucidal and sporicidal powers of ClO_2 are better than those of Cl_2. As an oxidant, chlorine dioxide is used for:

1) The removal of iron and manganese:
Iron and manganese, that are present in reduced form or in complexes with organic substances, humic and fulvic acids in particular, are oxidised into hydroxides which precipitate since they have little solubility. Chlorine dioxide is more effective than chlorine, above all, in manganese removal because the reaction rate of chlorine dioxide is faster at pH > 7.

Furthermore, in contrast with chlorine, the oxidation reaction does not involve significant reduction of alkalinity and the consequent alteration of the calcium-carbonate balance in the treated water. The chemical reactions of chlorine dioxide with iron and manganese have been described in the chapter "Reactivity with Inorganics".

2) The reduction of turbidity and colour:
The turbidity of the water is related to the presence of colloidal particles in suspension, whose elimination requires coagulants feeding to aggregate particles into separable flocs. The action of chlorine dioxide in this phase of the treatment is helpful, as it assists the formation of flocs, through its oxidant action on the substances which coat colloids keeping them in suspension.

3) The removal of odours and flavours:
The presence of odours and flavours in water is due to numerous compounds, both from natural origin and resulting from pollution phenomena, namely:
- metabolites of organisms (algae, actinomycetes, and the like) present in surface waters;

- phenolics, originating from industrial pollution, or the decay of algae, or, together with chloramines, formed in cases where the water has been pre-oxidised with chlorine;
- chlorides and bromides present in ground waters affected by sea water contamination;
- hydrocarbons, derived from pollution. The oxidising, bactericidal, fungicidal, and algaecidal actions of ClO_2 makes it used to improve the organoleptic characteristics of the water with the advantage of avoiding the formation of chlorophenols and chloramines. However, its non-reactivity with some hydrocarbons may render it ineffectual for the removal of odours related to them.

4) The control of algae growth:

The presence of algae gives to water an unpleasant odour, flavour and colour, obstructs the removal of turbidity, and may block or foul the distribution system or sand filters. Chlorine dioxide is even effective as an algaecide because of its ability to attack the pyrrolic chain ring of chlorophyll. Therefore, the control of algae growth is carried out by means of a dose of chlorine dioxide of about 0.5 - 1 mg/l; this is added to the water collection basin, preferably during night hours, to avoid its degradation following exposure to light.

5) The removal of some pesticides:

The pesticides which can be removed by means of ClO_2 are DMDT (dimethoxydichlorine) and aldrin [42]. Herbicides, such as paraquat and diquat, are eliminated in a few minutes at pH above 8. For the pre-oxidation and reduction of organic pollutants, required dosages are between 0.5 and 2 mg/l, with contact times usually as low as 15 to 30 minutes, depending on the water characteristics; in the case of postdisinfection, 0.2 - 0.4 mg/l of ClO_2 are generally used.

At these dosages, the potential chlorite residual is such that it does not constitute any health hazard. Such values are strictly linked to the conditions and structure of the distribution network of drinking water which, in some cases, can even

require further ClO_2 feeding along the line to maintain a minimum residual concentration of disinfectant. The action of chlorine dioxide in pre-oxidation is related, above all, to the organic matter, present both in a dissolved form (DOC – Dissolved Organic Carbon) and in colloidal form. The pH and temperature, which can strongly influence other pre-oxidation treatments (a classic case is hypochlorite), are irrelevant in the case of chlorine dioxide. The eventual chlorite residual can be easily removed through successive passage via Granular Activated Carbon (GAC) filters, usually installed in a drinking water plant to improve the both chemical and microbiological quality of the treated water. As examples of ClO_2 applications for the treatment of water intended for human consumption, some of our own experiments are reported below.

Chlorine dioxide in the disinfection treatment of a reservoir

The research purpose was to find the ClO_2 dosage and to confront some chemical (AOX, Tottal THM) and microbiological (total coliforms, faecal coliforms and faecal streptcocci) parameters linked to disinfection treatment, using chlorine dioxide and chlorine (in the liquid form of sodium hypochlorite). Three different dosages of chlorine dioxide were after a contact time of 15 minutes: result were compared with those obtained using 1 mg/l of active chlorine.

The relevant data are reported in table A.

It is remarkable that AOX value rose considerably (at 55% increase) after treatment by chlorine while, in the chlorine dioxide test, the AOX content increased only 10%. Similar trends were also observed for the TTHM parameter.

Bacteria killing was satisfactory and at 0.42 mg/l dosage there was compliance with local regulations; the same results have not been achieved by hypochlorite.

PARAMETER	Water	ClO_2 0.57 mg/l (100% demand)	ClO_2 0.42 mg/l (75% demand)	ClO_2 0.28 mg/l (50% demand)	Cl_2 1 mg/l
PH	8.8	-	-	-	-
TOC (mg/l)	1.6	1.5	1.5	1.6	1.6
Sulfate (mg/l)	118	116	118	116	116
Chlorides (mg/l)	33	33	33	33	36
Nitrates (mg/l)	9.3	9.1	9.2	9.1	9.1
AOX (µg/l)	68	75	72	70	105
Free Chlorine residual (mg/l)*	-	0.27	0.18	0.12	0.76
Chlorate (mg/l)	-	0.05	0.04	0.03	0.07
TTMH (µg/l)	26	21	21	16	42
Total coliforms (CFU/100ml)	3000	2	5	20	105
Faecal coliforms (CFU/100ml)	25	absent	absent	3	5
Faecal streptococci (CFU/100ml)	5	absent	absent	absent	1

TABLE A: chemical and microbiological characteristics of water before and after disinfection treatment.
*DPD method

PARAMETER	Water data
PH	7.9
TOC (mg/l)	3.5
Turbidity (NTU)	7
Ammonia NH_4^+ (mg/l)	0.5
ClO_2 demand in 1 hour (mg/l)	2.05
AOX (µg/l)	12
Total THM (µg/l)	absent
Trichloroethane 1.1.1. CH_3CCl_3 (µg/l)	0.1
Tetrachloromethane CCl_4 (µg/l)	absent
Trichloroetylhene $CHCl=CCl_2$ (µg/l)	0.5
Tetrachloroetylhene $CCl_2=CCl_2$ (µg/l)	absent
Total coliforms (CFU/100ml)	400
Faecal coliforms (CFU/100ml)	100
Faecal streptococci (CFU/100ml)	20

TABLE B:
chemical and microbiological characteristics of water at plant inlet.

PARAMETER	Water data before the GAC filter	Water at the outlet (distribution network)
Free chlorine residual (mg/l) *	0.06	0.57
Total chlorine residual (mg/l) *	0.09	0.67
AOX (µg/l)	99	101
Total TMH (µg/l)	21.3	25.4
Trichloroethane 1.1.1. CH_3CCl_3 (µg/l)	absent	0.75
Tetrachloromethane CCl_4 (µg/l)	1.4	absent
Trichloroetylhene $CHCl=CCl2$ (µg/l)	22.4	29.1
Tetrachloroetylhene $CCl_2=CCl_2$ (µg/l)	4.5	3.5
Total coliforms (CFU/100ml)	22	absent
Faecal coliforms (CFU/100ml)	3	absent
Faecal streptococci (CFU/100ml)	20	3

TABLE C:
chemical and microbiological characteristics of water treated by sodium hypochlorite (3 mg Cl_2/l in pre-oxidation and 1.2 mg Cl_2/l in post-disinfection)

Chlorine dioxide in river water disinfection treatment

In a drinking water plant which utilises water from a mountain river tests were performed to evaluate the substitution of present disinfection treatment by sodium hypochlorite, both in pre-oxidation and in post-disinfection, with chlorine dioxide.

The problems arising from the hypochlorite treatment were primarily due to an excessive formation of chlorinated organics that exceeds the limits, allowed by exception, of 50 µg AOX/l, due in part to the pre-oxidation treatment (by 3 mg/l chlorine active as hypochlorite) and, in part, to post-disinfection phase (using 1.2 mg/l chlorine active).

Figure A shows a plant flow sheet, with sampling points:
• Raw water at inlet;
• Treated water, drawn before carbon filters (GAC);
• Treated water at outlet (at distributing network).

Table B: shows the chemical and microbiological characteristics of the water at the inlet, and Table C, some characteristic data on water treated by hypochlorite, before carbon filters and after post- disinfection.
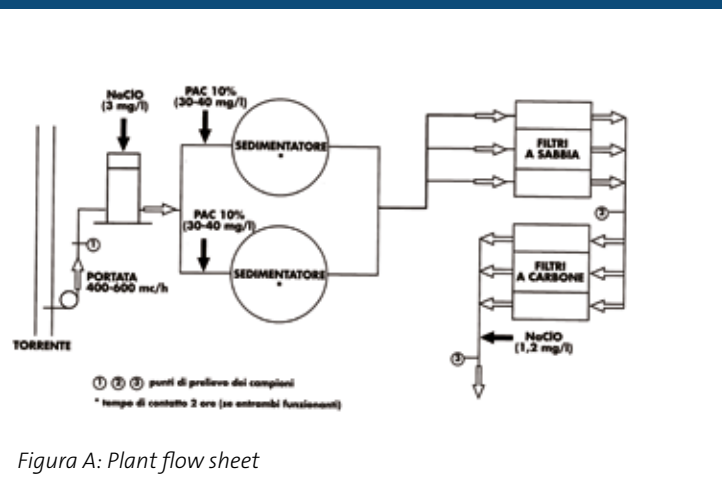

Figura A: Plant flow sheet

The chlorine dioxide treatment was carried out on inlet water with an hour contact time and at dosages, respectively of 2.05, 1.74, 1.43 and 1.02 mg/l equivalent to 100, 85, 70 and 50% of the ClO_2 demand. Results are shown in Table D.

PARAMETER	ClO_2 2.05 mg/l	ClO_2 1.74 mg/l	ClO_2 1.43 mg/l	ClO_2 1.02 mg/l
Free chlorine residual (mg/l) *	0.38	0.31	0.24	0.21
Total chlorine residual (mg/l) *	0.46	0.4	0.32	0.25
AOX (µg/l)	26	25	23	20
Total THM (µg/l)	6	4	4	3.5
Trichloroethane 1.1.1. CH_3CCl_3 (µg/l)	0.5	0.3	0.3	0.2
Tetrachloromethane CCl_4 (µg/l)	absent	absent	absent	absent
Trichloroetylhene $CHCl=CCl_2$ (µg/l)	absent	absent	absent	absent
Tetrachloroetylhene $CCl_2=CCl_2$ (µg/l)	4	3	3	2
Total coliforms (CFU/100ml)	absent	absent	absent	6
Faecal coliforms (CFU/100ml)	absent	absent	absent	absent
Faecal streptococci (CFU/100ml)	absent	absent	2	absent

TABLE D: chemical and microbiological characteristics of water sampled at plant inlet and treated by different quantities of ClO_2 in laboratory.

When comparing the results obtained with sodium hypochlorite (table C) and chlorine dioxide (table D) treatments, the following remarks may be made:

• Following disinfection by hypochlorite, there is an elevated AOX formation, with values well above those permitted by Italian law;

• Treatment by chlorine dioxide can replace sodium hypochlorite since it is more effective in the lowering of microbiological parameters and, at the same time, allows a negligible formation of disinfection by-products (DBP).

Chlorine dioxide dosage to be applied in the plant should be planned at around 1.5 mg/l in pre-oxidation and 0.4 mg/l in post-disinfection.

6.2 Desalinated water

Chlorine dioxide disinfection technology to avoid bromate formation in desalinated seawater in potable waterworks.

Throughout the world is expanding the consumers demand of a higher level of water quality and quantity. The source of water greatly varies from country to country and in some areas desalination of sea water is the dominant process for potable water. Desalination is a process that removes dissolved minerals (including but not limited to salt) from seawater, brackish water, or treated wastewater. A number of technologies have been developed for desalination but, at the end, pure desalinated water is acidic and is thus corrosive to pipes, so it has to be mixed with other sources of water that are piped onsite or else adjusted for pH, hardness, alkalinity and disinfectant residual before being piped offsite to comply with potable water regulation.

Recently bromate ion was found in potable water produced from salty sources(1).

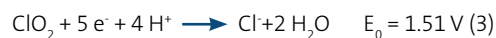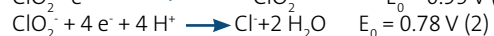Recently bromate ion was found in potable water produced from salty sources(1).
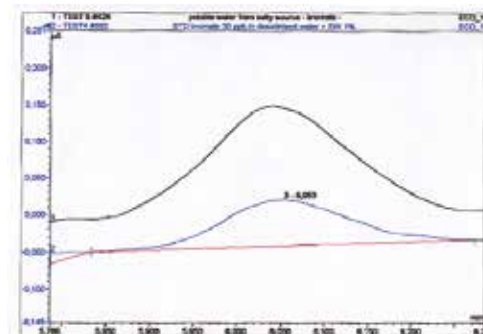
The two major sources of bromates in drinking water are using in the disinfection process:

a) ozonation when bromide ion is present in the raw water (2) (3)

b) and sodium hypochlorite solutions especially when produced by electrolyzing sea water (4). Bromate has been classified in Group 2B (possibly carcinogenic to humans), is mutagenic both in vitro and in vivo. Provisional guideline is 0.01 mg/l. The guideline value is provisional because of limitations in available analytical and treatment methods and uncertainties in the toxicological data. (5). There is therefore a need for alternative disinfectants for such a kind of water able to maintain the same level of microbiological protection and to minimise the presence of by-products. In this context is very promising chlorine dioxide, a powerful disinfectant and oxidant very well known and utilised worldwide since 1960.

Chorine dioxide chemistry

Chlorine dioxide is an oxidant that can be reduced in a variety of ways, depending on the system conditions and the nature of the reducing agent. (6) (7) (8)

In aqueous solutions, the following reactions may occur with the respective E0 calculated at 25 °C:

$$ClO_2 + e^- \longrightarrow ClO_2^- \qquad E_0 = 0.95\ V\ (1)$$
$$ClO_2^- + 4\ e^- + 4\ H^+ \longrightarrow Cl^- + 2\ H_2O \qquad E_0 = 0.78\ V\ (2)$$

$$ClO_2 + 5\ e^- + 4\ H^+ \longrightarrow Cl^- + 2\ H_2O \qquad E_0 = 1.51\ V\ (3)$$

Both reactions depend on the pH values and (1) is usually the main one in the case of drinking water. It should be noted that with protonisation of the chlorite ion, chlorous acid is formed:

$$ClO_2^- + H^+ \longrightarrow HClO_2\ (4)$$

which, in view of its oxidation potential, is considered to be a strong oxidant:

$$HClO_2 + 3\ H^+ + 4\ e^- \longrightarrow Cl^- + 2\ H_2O \qquad E_0 = 1.57\ V\ (5)$$
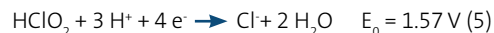
In Table 1 the redox potential values (E_0) are shown for some types of oxidising chemicals normally involved in disinfection processes.
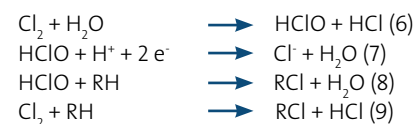
Reactions
Redox Potential (Volt)

Reaction	Redox Potential (Volt)
$HClO_2 + 3\ H^+ + 4\ e^- = Cl^- + 2\ H_2O$	1.57
$ClO_2 + 4\ H^+ + 5\ e^- = Cl^- + 2\ H_2O$	1.51
$HClO + H^+ + 2\ e^- = Cl^- + H_2O$	1.49
$Cl_2 + 2\ e^- = 2\ Cl^-$	1.36
$HBrO + H^+ + 2\ e^- = Br^- + H_2O$	1.33
$O_3 + H_2O + 2\ e^- = O_2 + OH^-$	1.24
$Br_2 + 2\ e^- = 2\ Br^-$	1.07
$HIO + H^+ + 2\ e^- = I^- + H_2O$	0.99
$ClO_2(aq) + e^- = ClO_2^-$	0.95
$ClO^- + 2\ H_2O + 2\ e^- = Cl^- + 2\ OH^-$	0.90
$ClO_2^- + 2\ H_2O + 4\ e^- = Cl^- + 4\ OH^-$	0.78
$NH_2Cl + H_2O + 2\ e^- = NH_3 + Cl^- + OH^-$	0.75
$I_2 + 2\ e^- = 2\ I^-$	0.54

As can be seen from this listed series of redox potentials, chlorine dioxide does not react with bromides to form bromine, unlike ozone, chlorine, and hypochlorite. Thanks to its radical structure ClO_2 functions first as an electron receiver and thus as an oxidant, unlike chlorine and hypochlorous acid which not only act as oxidants, but also stimulate addition and substitution reactions (and, therefore, chlorination reactions). For chlorine dioxide, the reactions are mainly numbers (1), (2) and (3), while, for chlorine gas and hypochlorite they are:

$$Cl_2 + H_2O \longrightarrow HClO + HCl\ (6)$$
$$HClO + H^+ + 2\ e^- \longrightarrow Cl^- + H_2O\ (7)$$
$$HClO + RH \longrightarrow RCl + H_2O\ (8)$$
$$Cl_2 + RH \longrightarrow RCl + HCl\ (9)$$

Ozonation of waters containing bromide ions (Br-) results in Br- oxidation by ozone and its decomposition by-product (e.g.,hydroxyl radical (OH-) to form different intermediate brominated species (e.g., hypobromous acid (HOBr), hypobromite ions (OBr-), bromite (BrO_2^-), bromide radicals (Br+), and hypobromite radicals (BrO^+) and eventually to form bromate (BrO_3^-), a suspected carcinogen.

Materials and methods

Bromate was determined by ion chromatography according to EPA Method 300.1 with these experimental conditions:
ION chromatograph: DIONEX IC 25
Columns: Dionex AG 9 HC, AS) –HC
Suppressor: external source electrolytic mode, 100 mA current
Eluent: 9.0 mM Na_2CO_3
Sample loop: 200 µL
Eluent flow: 1.0 mL/min.

The calibration curve for bromate is between 10 and 100 µg/L. In these conditions the retention time for bromate ion is around 6.05 minute. The other anions, (chlorite, chlorate and bromide ions), were determined with the same equipment in the same conditions but a sample loop of 100 µL.

Pure Chlorine dioxide was prepared according to method 4500- ClO_2 B (Standard Methods for examination of water and wastewater, AWWA, 1995). Chlorine Dioxide residual was determined by CPR (chlorine phenol red) according to Italian method UNICHIM 77. Conductivity, pH, residual free chlorine were determined following Italian IRSA-CNR Methods (2003). (9)

Result and discussion

In the industrial practice, some seawater is added to distilled water from desalination plant for giving a certain degree of salinity, besides some other adjustments on other chemical physical parameters.

Two samples of raw seawater and distillated water from a waterworks located in the Gulf area were characterised with the following results.

SEAWATER		DISTILLED WATER	
pH	7.9	pH	7.4
conductivity mS/cm	60.8	conductivity µS/cm	50
residual free chlorine	absent	chloride mg/L	14.2
		chlorate mg/L	n.d
		nitrate mg/L	n.d
		bromide mg/L	0.06
		sulphate mg/L	2.0

nd= not detectable

Different mixture of the two sample were prepared to evaluate the presence of bromate ion:

| Mixture	Bromate ion µg/L	Bromide ion mg/L
Distillate water + 0.3% Seawater	n.r.	0.33
Distillate water + 0.5% Seawater	n.r.	0.47
Distillate water + 1.0% Seawater	n.r.	0.86
Distillate water + 5.0% Seawater	n.r.	4.28

In order to evaluate if chlorine dioxide leads to formation of bromate ion, samples with 0.3% of seawater and samples with 1.0% of seawater, in amber glasswares completely filled and kept closed at a temperature of 40 °C, were treated with two different dosages of chlorine dioxide (0.5 and 1.0 mg/L).After one hour of contact time the residual concentration of chlorine dioxide was monitored by CPR (chlorine phenol red) method and bromate formation was controlled after sparging with nitrogen for at least 15 minutes.

Mixture	Residual ClO_2 mg/L	Chlorite µg/L	Chlorate mg/L	Bromate µg/L	Bromide mg/L
Distillate water + 0.3% Seawater + 0.5 mg/l ClO_2	0.48	nd	nd	nd	0.33
Distillate water + 1.0% Seawater + 0.5 mg/l ClO_2	0.51	nd	nd	nd	0.87
Distillate water + 0.3% Seawater + 1.0 mg/l ClO_2	0.97	nd	nd	nd	0.33
Distillate water + 1.0% Seawater + 1.0 mg/l ClO_2	1.0	nd	nd	nd	0.87

The data demonstrate that in such conditions chlorine dioxide is stable and does not lead to the formation of bromate ion. One sample (Distillate water + 1.0% Seawater + 1.0 mg/l ClO_2) was also kept always at 40 °C for a longer period of time (till 5 days) confirming the previous data.

Mixture	Contact time hour	Residual ClO_2 mg/L	Chlorite mg/L	Chlorate mg/L	Bromate µg/L	Bromide mg/L
Distillate water + 1.0% Seawater + 1.0 mg/l ClO_2	1	1.0	nd	nd	nd	0.87
Distillate water + 1.0% Seawater + 1.0 mg/l ClO_2	24	0.86	0.08	nd	nd	0.88
Distillate water + 1.0% Seawater + 1.0 mg/l ClO_2	48	0.78	0.11	nd	nd	0.86
Distillate water + 1.0% Seawater + 1.0 mg/l ClO_2	120	0.42	0.26	0.05	nd	0.88
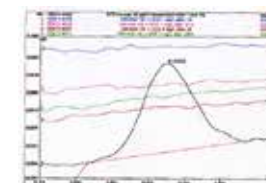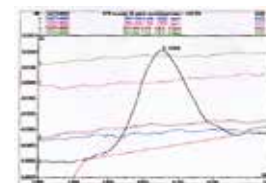
During the time some loss of chlorine dioxide was detected due to possible reaction with the aqueous matrix but also during the sampling procedure for analysis. Even after a long stretch of time no bromate formation was observed and the concentration of bromide remains practically constant. Due to the purity of chlorine dioxide utilised, the formation of chlorate has been extremely low or even undetectable also because the water pH does not induce any disproportionation phenomena

$(2ClO_2 + 2OH^- \longrightarrow ClO_3^- + ClO_2^- + H_2O)$.

The chlorine Dioxide conversion during the time to chlorite decreases and this fact seems to confirm that some chlorine dioxide was lost during sampling procedure.

time	ClO₂ dosed	ClO₂ residual	ClO₂ consumed	Chlorite formed	conversion ClO₂ to Chlorite
h	mg/L	mg/L	mg/L	mg/L	%
1	1.00	1.00	0.00	0.00	0
24	1.00	0.86	0.14	0.08	57
48	1.00	0.78	0.22	0.10	45
120	1.00	0.42	0.58	0.22	38

These lab data demonstrate that at 40 °C, under dark, with extremely long contact time, chlorine dioxide is not able to oxidise bromide even in such condition where the water require only a small consumption of disinfectant and where there is always a simultaneous presence of chlorine dioxide and the potentially oxidisable bromide in accordance with the electrochemical values of the Redox potentials.

These lab data have been confirmed also in the practice with a 1 year disinfection treatment in a waterworks in the Gulf region where chlorine dioxide ha been produced on site with a new Grundfos generating system concept, which allows to generate as average 98% pure chlorine dioxide. Purity, in particular for potable water purposes, is of paramount importance because it is well known that, in some cases, just during the generation process some by-products (chlorate for example) can be formed and then directly inserted into the water to be treated.

Conclusion

Bromate is an increasing public health problem in some parts of the world where potable water is produced from salty sources. The use of chlorine dioxide is very promising to solve this problem and to increase the quality of the distributed water. It has been confirmed, both in Lab and in industrial practice, that this powerful disinfectant/oxidant is very stable during the time in the pipes and, consequently, the formation of chlorite is very low and well under the WHO guideline value. Chlorate can be minimised adopting new production technology able to form highly pure chlorine dioxide solutions. Chlorine dioxide, in the conditions usually encountered in potable water production from salty source, does not oxidise bromide and, consequently, no formation of bromate can be detected with this chemical. Besides is well known that chlorine dioxide does not produce TTHMs and, in comparison with chlorine or hypochlorite solutions, decrease dramatically the AOX content.

Bibliography

1) Khaleej Times on Line- 31 Dec.2005 – UAE working to rid drinking water of chemical linked to cancer
2) R.Minear, G.Amy – Disinfection by-products in water treatment – The chemistry of their formation and control – 1996
3) Croué J.P., Koudjonou B.K., Legube B. (1996) Parameters Affecting the Formation of Bromate Ion during Ozonation. Ozone Science & Engineering. 18, 1-18.
4) HS Weinberg, CA. Delcomyn, V. Unnam- Bromate in chlorinated drinking waters: occurrence and implications for future regulation – Environ.Sci.Tech, 2003, Jul 15; 37(14):3104-10
5) WHO – Guidelines for Drinking-water quality- Third Edition – 2004
6) Chlorine Dioxide – Caffaro Monography, 2002
7) W.Massechelein –Chlorine Dioxide- Ann arbor Science 1979
8) D.Gates- The Chlorine Dioxide Handbook – AWWA 1997
9) AWWA – Standard Methods for the examination of water and wastewater- 19th Ed-1995
10) IRSA-CNR – Metodi Analitici per le acque – 2003
11) Fletcher I, Hemmings P- Determination of Chlorine Dioxide in potable water using chlorophenol red- Analyst 110,695,1985

6.3 Wastewater disinfection

Main applications of chlorine dioxide in this field are:
• waste water disinfection before effluent discharge or for water recycling,
• removal of odours formed in anaerobic conditions,
• improvement of sludge sedimentation rate in activated sludge processes,
• removal of pollutants, such as tetraethyl lead, cyanides, nitrites, sulfides, aromatic hydrocarbons, phenols, and the like.

Wastewater disinfection is a stage of the purification process, which will assume an ever increasing importance, especially in relation to the final destination of the treated water. In fact, traditional processes of sewage treatment do not provide a complete elimination of the infectious risk of waters that leave the treatment plants, while legislation, still lacking, prescribes as microbiologic parameters, more and more restrictive limits in relation to the final receptor. The Italian law of reference for wastewater effluents (Law No. 319, dated 05/10/76 or "Merli Law") does not prescribe specific obligations for disinfection and leaves to local competent Authorities the control of the applications of limits relative to microbiological parameters (see Table 12), when asked by actual uses of the effluent waters (for example for drinking, bathing, irrigation).

total coliform	20,000 mpn/100 ml
faecal coliforms	12,000 mpn/100 ml
faecal streptococci	2,000 mpn/100 ml

Table 12: legal limits according to law n 319/76 standard A rearding microbiotical parameters

In the case of discharge to waters used for bathing, the European Community regulation (EC Directive No. 76/169) for bacteria prescribes a maximum value of 2,000 Total Coliforms/100 ml and of 100 Faecals Coliforms/100 ml, while Italian Regulations (Law No. 319/76) establish a limit between 2 and 20 Total Coliforms/100 ml, for water to be used for irrigation, depending on the type of crop concerned (Appendix 5, CITAI Deliberation of 02/04/77). In the disinfection of waste waters, chlorine dioxide has many advantages over chlorine. In the case of chlorine, in fact, the presence of considerable quantities of ammonia and organic substances in waste waters induces a consumption of disinfectant with formation of chloramines which have a bactericidal effect up to 80 times lower than that of free chlorine [43]. Furthermore, when reacting with organic substances, chlorine produces halogenated organics (AOX), which may accumulate in the environment and pollute the waters with very important consequences in cases when the treated water will be reused for irrigation purposes. Chlorine dioxide, instead, does not react with ammonia, creates limited quantities of halogenated organics in presence of organic substances, oxidises phenols, is active over a wide pH range, forms a measurable residue which can be used for automatic dosage, and lastly, does not usually require a subsequent phase of dechlorination (with sodium bisulfite, for instance).

Bactericidal effects of chlorine and clorine dioxide:

Test conducted by the US Enviromental Production Agency (US-EPA) on secondary effluents, fitered and not filtered, show that, for a 60 minutes contact time, the residual necessary to reach the same killing of total coliforms in between 2 and 70 times lower for chlorine dioxide than for chlorine (44), as may be seen in figures A and B.
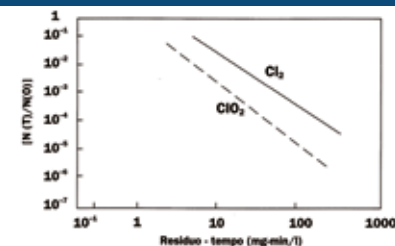

Figure A: inactivation of coliforms by means of chlorine and chlorine dioxide in non-filtered effluents of municipal wastewater.
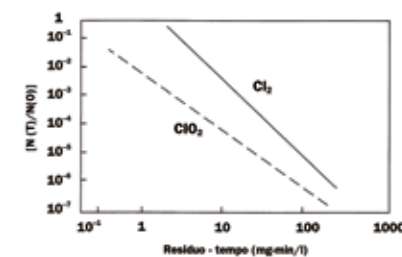

FigureB: inactivation of coliforms by means if chlorine and chlorine dioxide in filtered effluents of municipal wastewater.

Bactericidal effect of chlorine dioxide

At Peschiera (VR) "Garda Uno" wastewater treatment plant, in collaboration with the Health and Environmental Health Department of Brescia University, a research was performed on chlorine dioxide application to a waste water disinfection treatment. Approximately 90,000 m^3/day are treated for a total of 500,000 equivalent inhabitants in a tourism area; therefore wastewater has significant swings, either in the organic pollutants, nutrients and bacteria content.

The ClO$_2$ dosage was modified during the experiment in order to succeed in satisfying the requirements of bacterial reduction and keep chlorine residual lower than 0.2 mg/l.

In Table A, results are reported [46], from which it appears that average percentage of bacteria killing were always above 90% (total coliforms 93.8%, faecal 95.2% and faecal streptococci 91.2%).

PARAMETER	April-May 1993 2 mg/l ClO$_2$		June-July 1993 3 mg/l ClO$_2$		January-March 1994 1.5 mg/l ClO$_2$	
	INLET	EXIT	INLET	EXIT	INLET	EXIT
Total Coliforms (CFU/100 ml)	3.1*10^5	7.6*10^3	4.8*10^5	1.1*10^4	8.4*10^4	2.7*10^3
Faecal Coliforms (CFU/100ml)	2.1*10^4	2.3*10^2	7.9*10^4	1.6*10^3	1.6*10^3	1.6*10^2
Faecal Streptoc. (CFU/100ml)	8.7*10^4	4.7*10^3	2.1*10^5	2.9*10^3	1.5*10^4	1.3*10^3
Residual Chlorine (mg/l)*	-	0.16	-	1.19	-	0.16
AOX (µg/l)	33.3	50.2	42.3	57.7	31	37.5
THM (µg/l)	2.80	3.02	1.18	2.58	0.50	0.84
Total Chlorinat. Solvents (µg/l)	5.80	6.65	5.54	8.08	1.10	2.16

Table A: Bacteriological and chemical average data on waste water samples
*DPD method

The bactericidal and virucidal effectiveness of ClO$_2$ allows it to be used even in the treatment of hospital wastewater for which, given their great health hazard, the "Water Environmental Protection Governmental Committee" of February 4, 1977 states a mandatory disinfection.

Chlorine dioxide in the disinfection of hospital wastewater

Laboratory tests on waste water samples coming from the Infective Diseases Section of Sacco Hospital in Milan, confirm the bactericidal and virucidal effectiveness of chlorine dioxide, in concurrence with very modest formations of halogenated organic by-products (AOX), even on wastewater potentially dangerous from a hygienic-sanitary standpoint [48].
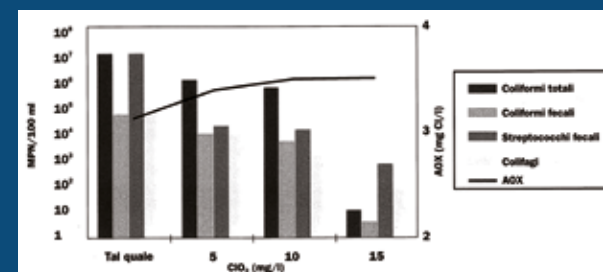

Figure A: Killing of microbiological relevant indexes and absorbable organic halides (AOX) formation in relation to disinfectant dosage

The virucidal activity was evaluated by contaminating the untreated sewage with Poliovirus type 1 vaccine (viral load 200,000 TClD50) and treating it with increasing doses of chlorine dioxide (5, 10 and 15 mg/l) for 30 minutes, as may be seen in the graph of Figure A. high killing percentages were reported with 5 mg ClO_2/l and total killing with 10 mg ClO_2/l treatment.

Given the wide chemical and biological variability of waste waters and the different possibilities of purifying treatments to which they may be subjected, the dosage of chlorine dioxide may vary considerably depending on the following parameters: suspended solids, bacterial content, organic carbon content (TOC), temperature and pH. In waters that have undergone a tertiary treatment and have a content of dissolved organic carbons (DOC) and suspended solids of less than 10 mg/l, in the presence of an adequate mixing phase, approximately 1.5 - 2 mg/l of ClO_2 are generally necessary with a contact time of even less than 15 minutes, so that the microbiological limits of Italian Law may be complied with. Under these conditions, the dosage represents approximately 20 - 30 % of the ClO_2 demand. In the case of hospital waste waters that may contain a large number of microorganisms responsible for serious infections, the dosage can reach 10 mg/l.

6.4 Slime treatment and pulp bleaching

In the context of the paper-making industry, chlorine dioxide is used for water treatment at paper mills and for pulp bleaching. Water has an essential role in the paper manufacturing process: it permits the fibers to be transported from the apparatus which defiber the woodpulp down to the manufacturing wire of the sheet of paper. These waters (called white waters) which, as a result of technological innovations, are subject to always more advanced recycling, constitute an ideal environment for the development of biomasses, in particular bacteria and fungi, due to the presence of organic substrates, favourable temperatures and neutral or slightly alkaline pH. The development of bacteria, fungi, yeasts and algae in the pipes and tanks give rise to a viscous deposit, commonly called "slime", which causes many problems of soiling and breakage of the continuous sheet of paper. Its uncontrolled presence generally limits the efficiency of the production cycle, and in some cases, with frequent stops of production, causes consequent relevant economical losses. Slime control by biocides addition is now a common production practice. Thanks to its bactericidal, algaecidal and fungicidal properties, chlorine dioxide may be used effectively for this purpose in paper mill waters, by virtue also even being able to act in a wide pH range. The use of ClO_2, in place of organic biocides and chlorine allows to keep the plant clean effectively at low dosages (60 – 120 g/ton of paper), to reduce production downtimes, without affecting the AOX content in the paper and in the waste waters. ClO_2 is added to both the raw water and the wet end and can be used in the disinfection of clarified waste waters. In this respect it can be considered the ideal agent for an integrated treatment of all the water in paper mills.

Experimentation on paper mill sludge has also shown the effectiveness of chlorine dioxide and sodium chlorite in scavenging unpleasant odours due to anaerobic fermentation.

6.5 Anti-slime treatment with chlorine dioxide In paper mills

Case A

In a Italian paper mill producing 500 tons/days of coated and uncoated printing and writing papers, a preliminary trial was performed to evaluate the effectiveness of chlorine dioxide as an anti-slime agent in wet end of the paper machine. Samples of process water were subject to microbiological tests, the obtained results are reported in the graphs of Figure A and B. They show a high biocidal effect of chlorine on all the microorganisms under examination [53].
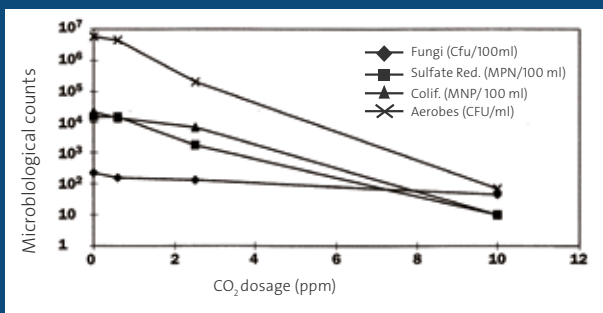

Figure A: Microbiological killing by ClO_2 on a "Raw Water" sample
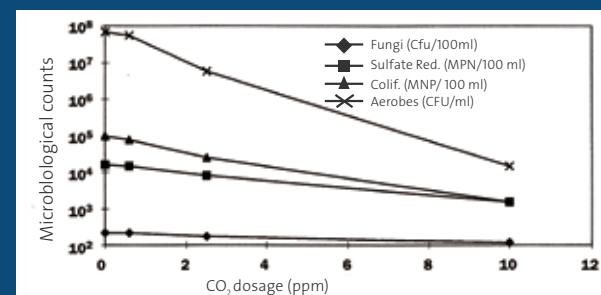

Figure B: Microbiological killing by ClO_2 on a "Broke Chest" sample

Following the positive results obtained during the experimental test, the paper mill completely replaced the conventional biocides with chlorine dioxide, developing an integrated treatment for all production waste.

In Figure C, the process flow-sheet is shown, with feeding points of chlorine dioxide.
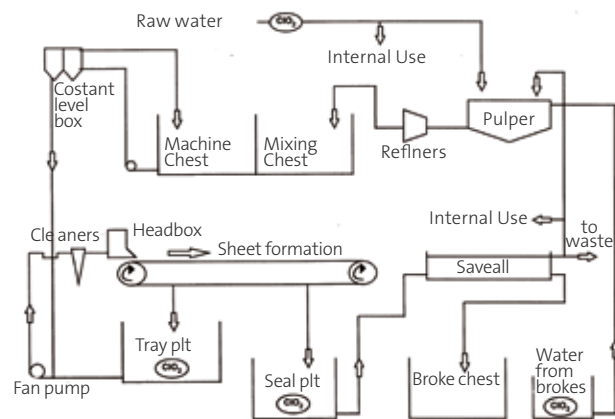
Figure C: Machine flow sheet with ClO$_2$ feeding points

The raw water (lake water) treatment was effected directly at the suction of the pumps at a dosage of approximately 0.4 - 0.5 mg/l of ClO$_2$ (depending of the season) on a flow of approximately 1,000 m³/h, in such a way as to obtain a 0.1 - 0.3 mg/l residual ClO$_2$.

The anti-slime treatment on the machine wet end was achieved by adding chlorine dioxide at the following points:

• Tray pit, used to directly dilute the furnish coming from the "machine chest" and sent to the "headbox", where every type of deposit, due smile, can jeopardise the formation of the sheet on the wire;

• Seal pit (secondary white waters), where ClO$_2$ has a double disinfectant effect, both on the recovered furnish which returns directly into the "broke chest" and on the clarified phase, which can be reused in the "pulper" dilution;

• Chest where waters from the "broke thickener" are collected, which, then, feed the "pulper".

Total ClO$_2$ dosage in the wet end is actually approximately 170 g/t of paper, in order to maintain total bacterial counts below 107 CFU/ml, that have been identified as a critical value.

Chlorine dioxide is used also for the treatment of primary sludge of the setting wastewater treatment plant of the paper mill.

The actual 10 mg/l dosage of ClO$_2$ insures on one hand a higher degree of brightness to sludge which, because it still contains valuable fibers, is recycled in the machine and, on the other hand, a more effective control of sulfate reducing bacteria (SRB) which could otherwise cause unpleasant odours in the sludge.

Case B

Tests of anti-slime treatment performed at a paper mill of Northern Italy, have confirmed the effectiveness of chlorine dioxide as a disinfectant for process water. In comparison with the use of chlorine, 60 ppm of ClO_2 have shown a better deposit control in the machine wet end and reduction of AOX content. Table A shows the percentages of bacteria reduction obtained by 60 ppm chlorine dioxide (typical of this treatment). 12 hours since the starting of the trial [54].

Sample	Total aerobic count (%)	Total anaerobic count (%)	Total Coliforms count (%)
Broke Chest	99.80	99.93	99.99
Headbox	99.90	99.92	99.99
White Water	99.90	99.96	99.99

TABLE A: Percentages of bacteria reduction at three points in a uncoated paper machine

In the treatment of pulp, chlorine dioxide acts as a bleaching agent without altering its mechanical properties. ClO_2, in fact, acts on the lignin, and to a lesser degree on the hemicelluloses, with the formation of ligninic and cholorligninic acids, in a selective way without degrading the cellulose polymer. At the same time, chlorine dioxide maintains high viscosity values, which is an important parameter in the production of regenerated cellulose (rayon yarn and viscose staple), and of tear index and breaking length, which are relevant parameters in the paper-making process. Pulp bleaching has several phases and is a function of the cooking process: historically the first process was acid by means of sulfite.

It has now been replaced by alkaline cooking with sodium sulfate called the "kraft" process. This choice was prompted by two reasons : first, to facilitate the recovery of cooking salts and the subsequent reduction of the environmental problem of the exhausted liquor, and second, because of better mechanical properties of the resulting fiber. However, an alkaline cooking has a negative effect on the optical characteristics of the unbleached pulp and needs a stronger bleaching. Initially, this was an alternating sequence of acid chlorinations (indicated as C) and of alkaline extractions (indicated as E), followed by a final treatment with hypochlorite (H); the entire phase sequence was generally represented as C/E/C/E/H. Once the superior capacity of chlorine dioxide (D) was recognised, sequences of C/E/D/E/D type were adopted. Therefore environmental motivations have successfully forced pulp producers to replace chlorine gas with chlorine dioxide, obtaining celluloses known as ECF (Elemental Chlorine Free) with better mechanical and optical characteristics. On an emotional drive to eliminate completely all chemical molecules containing chlorine atoms in any form, consumers were informed of the necessity to use cellulose bleached without chlorine- and chlorine derivatives (TCF or Totally Chlorine Free). This decision, has brought forth pulps with lower mechanical and optical characteristics, produced with much lower yields of wood and use of more costly reagents, such as hydrogen peroxide or ozone.

6.6 Cooling water treatment

Introduction

Bio-fouling refers to the undesirable accumulation of a biotic deposit on a surface. This consists of an organic film composed by micro-organisms embedded in a polymeric matrix of their own making. Complex fouling deposits, like those found in industrial environments, often consist of bio-films in intimate association with inorganic particles, corrosion products and macro-fouling organisms.

Complex fouling deposits, are a significant concern regarding the efficiency of cooling water systems, heat exchanger and pipes in general. The first stage of fouling formation is uncontrolled growth of microorganisms on surfaces, with a preliminary formation of biofilm, which gives slime, which is the product of living cells and their metabolic residues. The mechanism of biofilm (film of biological origin) formation can be summarised as follows:

- preliminary coverage of the surface by primary colonising bacteria and other organisms from water;
- transition stage with multi-layers of cells which become embedded in their own polymer material;
- final development of mature bio-film in which the population density is high. At the base of these mature bio-films conditions are completely anaerobic and favour the activity of fermentative and sulphate reducing bacteria (SRBs). The activity of SRBs in bio-films on metallic surfaces are responsible for the corrosion phenomena.

Bio-film is the substrate where other biological and inorganic materials can settle and adhere, increasing the thickness of material attached to the inside walls of the pipes and therefore changing the ideal operating conditions of the system.

However, the term "fouling" is used to refer to the final mixture of biofilm (microbial masses and their extra-cellular polymeric substances, EPS), suspended solids, corrosion products and macrorganisms subsequently adhering and growing on surfaces. The fouling reaches maximum development after the adhesion of marine (or marine originated) animals. In general, "macro-fouling" refers to the growth of crustacea (barnacles), mollusks (mussels and clams) and Coelenterates (hydroids), whereas "micro-fouling" is referred to algae and bacteria. The most important crostaceous fouling species is balanus, that has a planctonic larva that can produce at the surface a strong extracellular material called cement, and adheres strongly to many materials. Mussels are considered the most characteristic macro-fouling species. They are a bivalva species, have two shells and form big colonies on a great number of materials and are the main responsible of clogging in industrial pipes. It is very difficult to destroy and detach mussel shells from pipe walls due to their strong adhesion.

The presence of fouling causes:
- higher operational costs, because lower heat transfer causes production losses and increase in flow resistance demands more pumping energy;
- higher maintenance costs, for cleaning operations or replacement of pipes broken by under deposit corrosion or by over- heating;
- decreasing of plant factor, i.e. less operational time because more shutdowns are necessary to clean or repair the equipment.

The following parameters concerning water quality also play a role in the development of fouling:
- temperature - the rate of microbial growth depends on seasonal temperature fluctuation;
- dissolved gas - the content of oxygen affects the growth of several aquatic species;
- the availability of nutrients (Phosphorus and Nitrogen)

these are the basic elements required for biosynthesis:
• pH and suspended solids
• Dissolved solids and turbidity
• pH and alkalinity

Biofouling growth may be prevented in part during the design phase, by using suitable materials (i.e. copper, AISI 316 stainless steel or treatment of the surfaces with special polymers) and by dimensioning the pipes in such a way as to obtain a flow rate (> 1 m/s) which will hinder adhesion of the organisms. There are moreover, physical and chemical preventive methods for controlling fouling in cooling water systems. Physical treatments are used mainly during shutdowns. Chemical treatments are based on non-oxidising biocides or, more commonly, on oxidising biocides, like chlorine gas. Compliance with regulations on water discharges and the necessity of safe biocides to handle have led to the choice of chlorine dioxide as biocide for cooling systems of large plants. While sodium hypochlorite or chlorine are effective in controlling fouling, used in waters with high organic substances, they lead to the formation of halogenated organics (in particular, trihalomethanes) which are released in the environment. Sometimes the amount of chlorine, or hypochlorite, required to keep the system clean is so high to require the use of a reducing chemical in order to lower the residual chlorine at the discharge and complying with the limits imposed by legislation (for instance Italian Law N°. 319 of 05/10/1976 prescribes for a maximum content of residual free chlorine of 0.2 ppm for discharges and Qatar Supreme Council for the Environment & Natural Reserves Regulation, fixes the limit to discharge in seawater at 0.05ppm). Furthermore, the storage and transportation of chlorine gas present considerable environmental and safety risks. In the course of a trial conducted by Department of Biology at the University of Triest, a laboratory simulation was created to evaluate and compare the effectiveness of chlorine dioxide and sodium hypochlorite in controlling fouling.

The plant where the experimentation was conducted was composed of four feed basins with a controlled flow of sea water and a pump system for the dosage of the biocide under examination. Control panels were immersed inside the basins to evaluate the formation of fouling in time. Graphs of Figure A, B, C and D show the results obtained respectively with:

A: no treatment (*reference);
B: sea water with 0.2 ppm of NaClO active chlorine;
C: sea water with 0.1 ppm of residual chlorine dioxide;
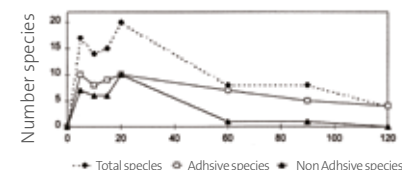D: sea water with 0.2 ppm of residual chlorine dioxide.

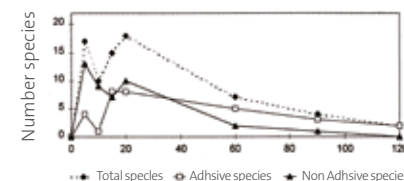*Figure A: State of diverse organism species in the absence treatment*

Figure B: State diverse organism species in the presence of 0.2 ppm of active chlorine

It can be seen that the so-called "adhesive" species, distinguishable by their capacity of adhering very strongly to the substrate, were relatively more represented and abundant on the panels immersed in the sea water (refer to blank – Figure A). Their presence was less, instead, on the panels immersed in the basin treated with 0.2 ppm of active chlorine.

(Figure B) where, however, the species were in fair number. On the contrary, they were scarce and practically absent in the case of treatment with chlorine dioxide (Figure C and D): this is a demonstration of the greater selectivity of

ClO_2 than that of $NaClO$ as regards to the adhesive species which are condidered responsible for formation of first stage of fouling (primary slime).
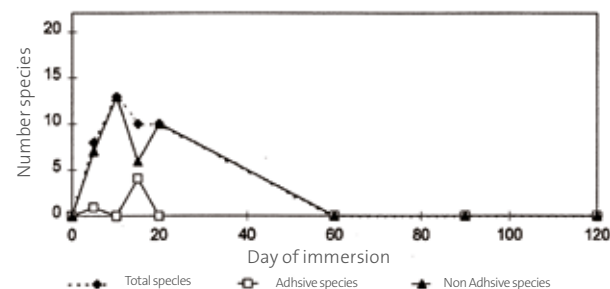

Figure A: Different organisms behavior in the presence of 0.1 ppm of residual ClO_2
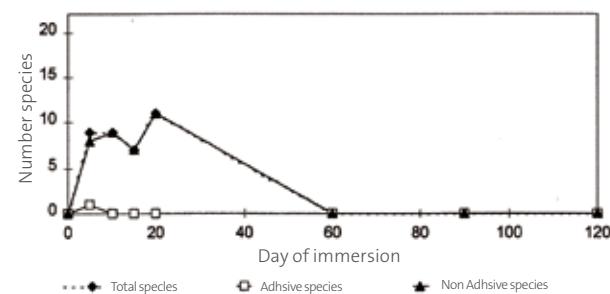

Figure B: Different organisms behavior in the presence of 0.2 ppm of residual ClO_2

As relevant case, we focuses on the possibility to minimise the problems related to micro and macro-fouling in once-through cooling systems and desalination plant by shot or continuous injection of chlorine dioxide into the seawater at the intake. A special on line monitoring instrument, installed after chlorine dioxide injection point, permits to check the fouling growth due to marine micro-organism and, in the meantime, the residual of chlorine dioxide.

Chlorine dioxide has proved to be an efficient antifouling agent used 1h/day maintaining residual of ClO_2 in the range of 0.05 to 0.1 mg/L during the dosing shots or 10-12 h/day without any residual at several power station and petrochemical plant in Mediterranean sea and Persian Gulf, which use seawater both in condenser and evaporators to produce demineralised water. In order to illustrate chlorine dioxide behaviour, we report 4 power station dosage programmes (one using also river water cooling tower during the summer) and 1 petrochemical plant application. Three different technologies for on site generation of chlorine dioxide have been reported. A full case history selected among the 4 power station is also reported.

The cooling systems usually have the following three basic designs: once-through, open recirculating and closed recirculating.

In once-through systems the cooling water, taken from a reservoir, passes through heat exchangers absorbing heat only once and then it is discharged back into the original water source. This process creates a high water withdrawal rate and it is usual where large and cheap volumes of water are available, as near sea coast, great lakes or big rivers. In Mediterranean and Gulf area, these systems are found in refineries, petrochemical or steel plants as in power stations.

As written above, the efficiency of the cooling water systems is usually affected by three main factors: corrosion, scale and fouling or any combination of them. Here we focus on the aspects connected with fouling.

If research tests allow better control of the physical, chemical and biological factors and provide a framework for evaluating the fouling phenomena, measurements at the process site are necessary to evaluate the potential for fouling as well as the effectiveness of antifouling treatment programs. Direct and indirect measurements of deposit quantity and composition can be carried out in order to monitor the progress of the fouling.

Direct measurements (deposit mass, thickness and composition, chemical and biological characteristics of the supplied water) are usually carried out. Indirect measurements (fluid frictional resistance, heat transfer resistance) can complete the possible available information. Also visual inspection of surfaces (especially, pitting; valves, fittings) can give immediately some indications for deposit nature and structure.

On-line and side-stream fouling monitors, visual inspection, samples for destructive analyses and monitoring microbial quality of the feed-water can help in the identification of fouling and in finding the best way to control it.

Chlorine dioxide as antifouling agent

It has been demonstrated (Bartole and Bressan, 1993; Bartole et al, 1996) that Chlorine Dioxide has a strong antivegetative effect being able to lessen the development of the primary slime, to reduce the biomass weakening the polymeric matrix and the number and type of "pioneer" species (Diatoms, Cyanophyceae, Silicoflagellatae) which have a marked tendency to colonise the surfaces promoting bio-fouling.

According to seasonal and/or daily parameters (temperature, organisms population, light), to operational parameters (water velocity, water source position etc.), ClO_2 can be dosed in a continuous or in an intermittent way providing always a good mix with the feed water.

To maintain the best control of bio-fouling process and to reduce after growth phenomena, shock dosages (higher dosages for shorter time at fixed intervals of time) or a continuous/intermittent treatment programme can be carried out. Shock dosages can be extremely effective and provide a high inactivation rate of the organisms.

In the "shock programme" the ClO_2 dose must satisfy the "ClO_2 feed water demand" at the forecast contact time and a ClO_2 residual of about 0.1 mg/L should be present. This is the usual treatment procedure in special cases where bio-fouling has already reached the maximum development and it is necessary a strong cleaning action often in conjunction with physical methods.

In the continuous or intermittent procedure, ClO_2 dosage is basically determined on the basis of the "ClO_2 feed water demand" taking into account the transportation of the disinfectant to the interface, the contact time, the structure and type of surfaces.

The dose, that varies according to conditions of the water source, is a fraction of the ClO_2 demand (usually between 5.25%) and therefore, generally speaking, is between 0.05 ¸ 0.25 mg/L on average. In reality, ClO_2 is generally added in higher concentration (i.e. 0.4 ¸ 0.5 mg/L) but only for some hours a day (intermittent treatment).
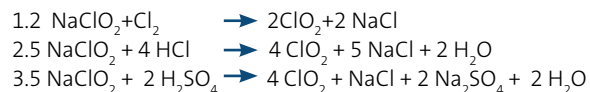
ClO_2 reacts quickly with feed water and bio-film biological and chemical components exploiting its oxidising power. No residual ClO_2 is found at the outfall.

In a field test carried out in a nuclear power station in Spain it was found, matching the results obtained treating the sea feed water with 0.2 mg/L of ClO_2 and 1.1 mg/L of active chlorine from a hypochlorite solution, that lower doses of ClO_2 and shorter contact times were necessary to obtain a 100% mortality of mussels of different size (Bielza et al. 1991).

Chlorine dioxide application

In the present article five dosage programmes have been reported. Three method of chlorine dioxide generation have been applied in power stations and petrochemical plant, which use Mediterranean seawater to feed their once through cooling systems. In all the cases on line monitoring system for micro-fouling and probe for macro-fouling have been installed.

Generation of chlorine dioxide:

1.2 $NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2\ NaCl$
2.5 $NaClO_2 + 4\ HCl \rightarrow 4\ ClO_2 + 5\ NaCl + 2\ H_2O$
3.5 $NaClO_2 + 2\ H_2SO_4 \rightarrow 4\ ClO_2 + NaCl + 2\ Na_2SO_4 + 2\ H_2O$

The first reaction has been used in an American power station located Alexandria (Egypt), the second in two power stations and a petrochemical plant located near Venice (Italy) and the third one in a power station located in Malta. A complete technology of generation has been developed in order to produce chlorine dioxide in any situation present in a power station: chlorine gas, chlorinator, electrochlorinator hydrochloric acid and sulphuric acid.

Types of chlorine dioxide generators

The types of generators used work either under vacuum or by pumps. In the first case, chlorine dioxide is generated by injection of sodium chlorite into the chlorinated water (0.5% Cl_2) coming from the existing chlorinator. In the second case typical under vacuum generators are used and, in the third case the the special Grundfos generator, which works under water (submerged) installed at the seawater intake is used. This kind of equipment is very safe because the reaction takes place some meters under the sea and the reaction chamber is very small, therefore in case of any kind of inconvenient eventual trace of chlorine dioxide that could escape the generator is dissolved in the seawater without any problem. In a different version, submerged generator can be installed inside the main water line or in a by-pass.

Treatment programmes

All the programmes have been studied according to seawater quality, temperature, cooling system and residence time of the plant and adjusted after on line fouling control: the monitoring equipment is really the driver of the treatment, in fact it allows to know whether fouling is growing inside the condenser and, consequently drive the dosage modality.

1. In the first case (power station in Egypt), using 98,000 m^3/h of seawater, after one year treatment, the programme is the following: ½ hour shot injection in the morning and ½ hour in the evening during the winter time (total 60 minutes/day); 3 similar shot during the summer time (total 90 minutes/day) the residual of chlorine dioxide at the discharge point is max. 0.1 ppm.

2. In public power station near Venice, using 100,000 m^3/h of seawater, after 3 year treatment the programme is the following: Only during summer (from March to October) 1 shot per day at concentration of 1 ppm as long as 1:30 hour. There is no residual of chlorine dioxide at the discharge point.

3. In a private power station near Venice, using 48,000 m^3/h of seawater after 3 year treatment the programme is the following: From April to October 0.2 ppm continuously + 1 shot per day at concentration of 1 ppm as long as 1 hour, From November to March, 2 shot per day at concentration of 1 ppm as long as 2 hour. There is no residual of chlorine dioxide at the discharge point.

4. In the petrochemical plant near Venice, using 50,000 m^3/h of seawater after 5 year treatment the programme is the following: in winter time continuous dosage at concentration of 0.1 ppm, in Summer time 0.5 ppm. There is no residual of chlorine dioxide at the discharge point.

5. In public power station in Malta, using 48,000 m^3/h of seawater, after 5 months treatment the programme is:½ hour shot injection in the morning and ½ hour in the evening during the winter time (total 60 minutes/day); 3 similar shot during the summer time (total 90 minutes/day) the residual of chlorine dioxide at the discharge point is max. 0.1 ppm.

6. In SABIC petrochemical complex at Al Jubail (Al Kajan), sea water cooling towers with open recyrculating system, for 150,000m^3/h the programme is: 2 ½ hours shot injection in the morning and 2 ½ hours in the evening during the summer time (total 5 hours/day), dosage 0.3ppm; 1 hour shot injection in the morning and 1 hour in the evening during the summer time (total 5 hours/day) , dosage: 0.3ppm;

7. In QAPCO petrochemical complex (Qatar), using 33,000 m^3/h of seawater (once-through system), the programme is: 5 hours shot injection during the summer time (dosage: 0.3ppm).

A case history

We report a full case history related to a power plant located in Sidi Krir (Egypt) where chlorine dioxide was applied. A special monitoring system named EASYAREADOX was also installed to control the performance of the treatment.

Description of the Facility and Cooling Water: Sidi Krir 3 and 4 is the first privately owned power plant in Egypt. It is owned 61% by Intergen, a company based in the US, and 39% by Edison, a company based in Italy. The plant is often referred to as Egypt BOOT #1. The plant owners have built the plant, they own it and they operate it—in 20 years they will transfer the ownership of the plant over to the Egyptian Electric Authority. The plant went into commercial operating service in January 2002.

The power plant is a conventional gas fired steam generating electric station located on the north coast of Egypt about 30 km west of Alexandria, Egypt.

The generating units are rated at 2 x 340 MW (net electrical). The typical high load plant net heat rate is about 8900 BTU/kWhr. The majority of the plant's rejected heat is discharged to the Mediterranean Sea.

The plant cooling system consists of two identical systems (one for each unit) that pump about 98,000 metric tons of seawater per hour. At full load this water undergoes a temperature rise of about 9 degrees C between the seawater inlet and discharge. The seawater inlet temperature varies from a low of about 16°C in the winter to a high of about 31°C in the summer—the time weighted average temperature is about 25°C. Seawater is drawn in via an intake structure intended to result in low water velocities located about 350 meters off the shoreline of the power plant in about 8 meters of water. The discharge is via a discharge cap located at a similar distance from shore and depth as the intake structure.

All of the cooling water pipes are cement or cement lined, the condenser water box is rubber lined and the condenser tubes and tube sheets are titanium.

Original biocide concepts

The designer's original concept to control biological growth was chlorination via a chlorinator fed from one-ton liquid chlorine cylinders. No studies were conducted of the biological activity in the local waters and no serious consideration was given to the ability of the chlorinated water to be adequately toxic for the organisms present and simultaneously comply with the environmental limits established for the cooling water discharge.

Simple studies by the owner of the effectiveness of chlorine to kill organisms as found near the power plant indicated that high dosages of chlorine would be required and the residual chlorine value in the water discharge would exceed the environmental permit level. The results of these simple tests are shown in the following graph:
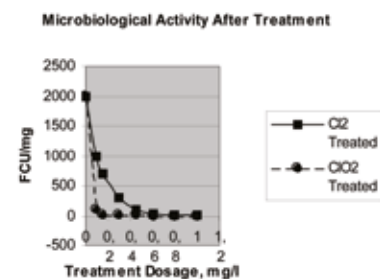
A small dosage of chlorine dioxide was much more effective than chlorine to reduce the number of living organisms.

Other tests showed that the chlorine demand of the water a short time after shocking with chlorine significantly increased while the demand for chlorine dioxide remained constant for the same period. That is to say much of the chlorine injected into the water simply reacted with the water and thus became unavailable to affect the organisms.

Installation of the chlorine dioxide system

Inadequate consideration was also given to minimizing the risks associated with handling as many as 40 one-ton liquid chlorine cylinders on the site. No consideration was given to the potential dangers of shipping in excess of 400 tons of liquid chlorine on the highways of Egypt. The concept of "safe driving practices" has a unique meaning in Egypt. Accidents and inadequate insurance coverage are all too commonplace there.

Due to the concerns of the owners with respect to on-site and off-site safety relative to chlorine and evidence at other power plants in the region that biological growth could not be prevented or controlled while maintaining the level of residual chlorine in the discharge water below 0.2 ppm the owners decided to consider technologies other than chlorination for biocide treatment of the water.

Because of the investment structure of the project and various uncertainties as the first private power developer in Egypt capital intensive alternatives were not considered favorably. The owners purchased a very inexpensive sodium chlorite injection system that would allow the owners to fully utilise the already existing chlorination system. In fact, the cost of the sodium chlorite injection system was almost significantly offset by the decision to purchase only 10 one ton chlorine cylinders instead of the originally planned 40 cylinders.

## Operating experience with chlorine dioxide

Because Sid Krir 3 and 4 is a new power plant we cannot provide comparisons of biocide results using just chlorine versus using sodium chlorite. Chlorination was utilised for about 4 months of cooling water system service before there was a significant heat load on the condenser. There was no evidence biological fouling during the time period in late 2001.

Full Utilisation of the chlorine dioxide technology began in November 2001 and is ongoing. The power plant has run well through the end of June—available at about 90% since commercial operation began in January 2002.

Based on 6 months of commercial operation we can compare chlorine dioxide system performance to our expectations.

As winter turned to spring we tried to economise too much as the water and air became warmer and we did experience the growth of some mussels in April. At the same time the EASYAREDOX unit was clearly telling us that there was an environment existing to allow such growth to happen. The graph below shows the relevant time period and the clear increase in background conductivity. With only 2 or 3 one-hour shock treatments of chlorine dioxide the mussels were killed and, since then, there has been no evidence of any additional bio-growth.
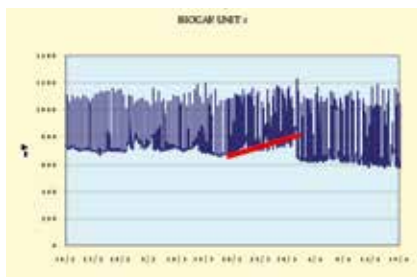
The use of the EASYAREADOX monitor is a major improvement over the use of chlorine monitors to detect residual chlorine.

The EASYAREADOX unit allows the plant to optimise and minimise their dosing program based on real and immediately available results.

Condenser performance

As mentioned previously there is no comparison available for condenser performance before starting the use of chlorine dioxide. We can only compare actual condenser performance to expected performance.

In making this comparison we must make some assumptions regarding cooling water flow—it presents the greatest source of inaccuracy in the results. With the assumption that the cooling water flow is in accordance with the pump test curve we are able to show that actual condenser performance is better than expected as displayed on the data curve below. The expected performance is based upon a 90% cleanliness factor so we can conclude that the actual condenser cleanliness is better than 90%.

Results

For the waters being used by Sidi Krir power plant to cool their condensers there is no way that chlorination, only, of the water could have been effective to prevent biological growth and allowed the plant to operate within its environmental permit conditions.
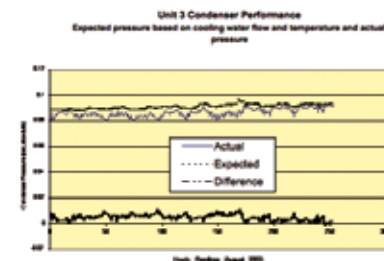
The use of chlorine dioxide has allowed the plant to very effectively prevent growth and the plant is in compliance with all permits. Additional benefit has been realised in annual cost and safety.

Conclusions

We underline the following advantages:
1. Chlorine dioxide has allowed to minimise the growing of both micro and macro-fouling inside cooling systems of power stations and petrochemical plant at very low dosage rate,
2. Monitoring system has demonstrated to be the "Brain" of the treatment programme. It has permitted to inject chlorine dioxide in a proper quantity and in the right moment, saving material and protecting the environment.

6.7 Disinfection in the food industry

Chlorine dioxide is used successfully in numerous applications for the food industry and, in particular, for the following activities and operations:

1. washing and transporting of fruit and vegetables and processing of fish and meat
2. disinfection of cooling waters
3. washing of containers for foods and beverages
4. production of frozen foods
5. production of beer

1. Washing and transporting of fruit and vegetables and processing of fish and meat
In the canning and other food industries (including sugar works), the products are transported from the unloading point to the inside the processing plant by means of water fluitation. Chlorine dioxide is dosed into the water for washing and transporting in order to control the micro-organisms which are present on the surface of the products, to reduce contamination in the plant and, thereby, time and costs involved in cleaning the channels. Treatment with chlorine dioxide instead of chlorine, has the advantage of not forming chloramines or other undesirable by-products which may be dangerous to human health. Formation of chloramines must be avoided because it may cause organoleptic changes in the product (unpleasant tastes and odours). For this application, the ClO_2 dosage strongly depends on the type of food and related microbiological level of contamination and ranges from 2 ppm (to leave a residual chlorine dioxide of about 0.5 ppm) to 5 ppm for shrimp and prawn processing to 9 ppm (EPA authorizated) for chicken processing. With a definitely higher dosage, chlorine dioxide may be used also for the treatment of water used for washing, transporting, processing and grading of fresh products prior to selling (100 - 150 mg/l) [59] and for pre-refrigeration (200 - 250 mg/l) which is intended to slow down the processes of ripening/overripening and the development of pathogens (especially fungi) [60].

for the treatment of water used for washing, transporting, processing and grading of fresh products prior to selling (100 - 150 mg/l) [59] and for pre-refrigeration (200 - 250 mg/l) which is intended to slow down the processes of ripening/overripening and the development of pathogens (especially fungi) [60].

2. Disinfection of cooling waters
Satisfactory results have been obtained by using chlorine dioxide for the disinfection of cooling waters for food containers. It is important that the water used is free of bacteria to avoid the consequent deterioration of the product and microbial poisoning and/or infections. Furthermore, it is useful to have available cooling water free of microorganisms because cans can break in the system and create an optimal substrate for the growth of bacterial colonies. For this application the dosage of 1.2 - 1.5 ppm of chlorine dioxide is recommended or one that will leave in any case a residue between 0.2 and 0.5 ppm.

3. Washing of containers for foods and beverages
The quality of a food good (liquid or solid) can be affected by poor washing and disinfection of its containers. Washing of the containers is particularly important in cases where they are intended to contain substrates which are easily biodegradable (such as milk, beer, fruit juices and soft drinks). In particular, in the wash process of glass bottles, a second rinse is provided which takes place under conditions ideal for bacterial growth (temperature around 30 - 40 °C, high humidity, pH around 9). For this reason, microbiological control, hence, disinfection must be provided. Disinfection by chlorine dioxide is better than by hypochlorite, because the former is still active at high pH and it does not form chlorophenols and halogenated organics. The containers are disinfected by 0.5 to 2 ppm chlorine dioxide, depending on the characteristics of the water but, in any case, such as to have about 0.2 ppm as residue. A very short contact time is sufficient (even less than one minute).

4. Production of frozen foods

In addition to the treatment of the water used for transportation and washing, as already stated, chlorine dioxide may be used in the production process for frozen foods to disinfect the water used to for transportation and freezing, a step which is taken after processing (washing, slicing, chopping and the like). In fact, if the refrigerator circuit is not treated with a disinfectant, a microbial contamination may occur, most usually by bacteria of the Listeria type, since they survive even at low temperatures. To avoid this problem, the water in the freezer is treated with chlorine dioxide in such a way as to leave a 0.2 - 0.5 ppm as residue.

5. Production of beer.

Beer brewing needs 6 - 10 liters of water per liter of produced beer. The water which enters in the composition of the final product must obviously be micro-organisms free, and must not give any odours or flavours to the beer altering its taste. Treatment based on chlorine dioxide has several advantages since, because it produces no chlorophenols and only a negligible amount of chlorinated organics, it does not affect the taste of the beer and guarantees the elimination of micro-organisms even over a large (6 - 9) pH range. For this application, the dosage may vary between 0.05 and 0.5 ppm. In the food industry, the integrated use of chlorine dioxide is possible as well as convenient, as reported in Table 13, in all the operations where water is utilised.

Table 13: Integrated used of chlorine dioxide in the food industry

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Chlorine dioxide may be used for the treatment of:

A. Feedwater (primary water) and/or intended for human consumption
(in cases where it is taken from a well and not distributed by a water system).

B. Water for general washing purposes
(waters for washing or transporting)

C. Cooling water
• In the tomato preserving industry (evaporator towers)
• In breweries
• In cheese factories
• In cooked meat processing industries
• In canneries where food is canned after sterilisation by heat

D. Waster used in processing
(for example in breweries, shrimp and chicken processing)

E. Wastewater
(for disinfection prior to discharge in the environment)

From a chemical point of wiev, bleaching agents are divided into oxidising or reducing chemicals. Among the principal oxidants, by far the most commonly used, are hypochlorite, hydrogen peroxide, chlorite, peracetic acid, and per-salts like perborate and percarbonate, while among the principal reducents are sulfur dioxide, sulfites, bisulfites and hydrosulfites.

Table 14 shows the applicability of the different bleaching agents, in relation to natural, artificial or synthetic fibers. Bleaching with chlorite is per formed at acid pH, between 3 and 5, which is a compromise between the reaction rate and the risk of damaging the fibers. Under these conditions, chlorine dioxide is the active agent. The operative pH has made difficult chlorite use: plants, that have materials originally designed for hypochlorite, may easily adopt hydrogen peroxide high pH, not chlorite low pH bleaching. Chlorite, however, is preferred in polyester-cotton blends bleaching for its good results without fibers damage or effluent pollution. A peculiar characteristic of chlorite, still linked to its use in acid environments, is the reduced extraction of greasy substances and waxes which are naturally present in cotton for instance and which give to the fiber a characteristic "hand", without synthetic softeners.

FIBER	Hypochlorite	Chlorite	Peroxide	Reducing Agents
Cotton, Rayon	++	++	++	++
Wool, Silk	-	-	++	++
Polyamidic	-	++	(+)	++
Polyester	+	++	+	+
Acrylic	+	++	(+)	+

++ = Very suitable
+ = suitable without damage to the fiber, but does not bleach
(+)= suitable, but only with special precautions
- = Not suitable

6.8 Scavenging of noxious gases

Chlorine dioxide reacts with hydrogen sulfide, that is oxidised, either in oil or natural gas production or in scrubbers of noxious gas or in other plants, such as NOx reduction in incinerators. In the scrubbers, chlorine dioxide is generally added such as to have a greater than 5 ppm residue. Thanks to its bacteriostatic rather than its biocidal activity, chlorite is used to prevent the formation of bad smells, for example in biological or chemical sludge tanks, when there are anaerobic conditions.

Analytical methods

In order to utilise chlorine dioxide correctly, it is necessary to effect, more or less frequently, analytical controls to determine the quantity of chlorine dioxide effectively added to water to treat, the yield of a generator, the quantity of residual ClO_2 in treated water, and the like. In some cases, in addition to chlorine dioxide, it is necessary to determine other types of chemicals which are eventually present in the dioxide solutions caused by sidereactions, or are formed by reaction with substances contained in the water to be treated. In fact, the evaluation of the purity of chlorine dioxide produced, and, thus, that of the generator efficiency, require in addition to the determination of ClO_2 concentration, those of residual chlorite, the chlorine and the chlorates which are eventually formed. In particular, in water intended for human consumption the following determinations must be made: measurement of the amount of ClO_2 after treatment, in order to evaluate its effectiveness and to verify that the residual concentration is not such as to alter the organoleptic properties of the water; measure of types of chemicals formed by the reaction between chlorine dioxide with substances present in the water to be treated, chlorites, chlorates, and chlorine in the form of hypochlorite or chloramines. In waste waters and in those for industrial use (for example, cooling water) it may be sufficient to determine the amount of added ClO_2 and the residue remaining and, thus, that discharged. The analytical techniques used for the determination of ClO_2 vary according to whether the solution being analysed is concentrated or diluted. A list of the methods of analysis which may be used is reported in Table 15.

	ClO_2	ClO_2^-	ClO_3^-	Cl_2	Principal Applications	Notes and References
CONTROL OF GENERATOR EFFICIENCY (CONCENTRADED SOLUTIONS)						
Iodometric Measurement	Yes >200 mg/l	Yes	Yes	Yes	All	The most commonly used method [62]
Absorption at 445 nm	Yes 200-700 mg/l	No	No	No	All	Selective method [2]
CONTROL OF RESIDUAL OXIDANTS (DILUTED SOLUTIONS)						
Colorimetry with red Chlorophenol (CPR)	Yes 0.02-0.7 mg/l	No	No	No	Drinking water, waste water, once-through cooling water	No interference at the usual concentrations [2]
Colorimetric measurement with chrome violent K acid (ACVK)	Yes 0.1-1.5 mg/l	No	No	No	Drinking water, waste water, once-through cooling water	No interference at the usual concen-trations [2]
Colorimetric measurement with DPD	Yes 0.1-1 mg/l	Yes	No	Yes	Waste water, drinking water	[63]
Colorimetric measurement at pH = 7	Yes 0.05-1 mg/l	No	No	Yes	Drinking water	Cl_2 + ClO_2 [64]
Ionic Chromatography	No	>0.01 mg/l	>0.03 mg/l	-	Drinking water, waste water	The most reli-able method after degassing ClO_2 [66]

Table 15: List of analytical methods.

## 7.1 Analysis of concentrated solutions of ClO_2

Iodometric Titration
The iodometric titration method is applicable for concentrations of ClO_2 > 200 mg/l. It is used to evaluate the efficiency of generators which produce chlorine dioxide in concentrated solution (20 - 30 g/l).
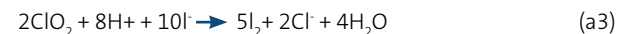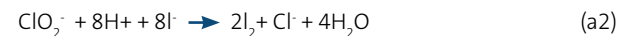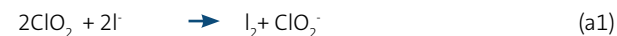
Principle:

The iodometric method consists in the titration of the elementary iodine released by the action of the oxidized compounds of the chlorine on potassium iodide (KI), added to the sample on which the determinations are being made. It is based on the following fundamental reactions:

Oxidation of the iodide by ClO_2 and by ClO_2^-

$2ClO_2$ + 2I⁻ $\longrightarrow$ I2 + ClO_2^- (a1)

ClO_2^- + 4H⁺ + 4I⁻ $\longrightarrow$ 2I2 + Cl⁻ + $2H_2O$ (a2)
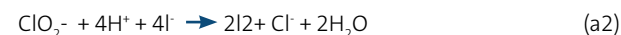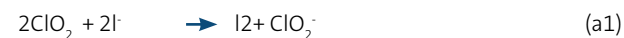
The oxidation of the iodide by ClO_2 takes place at neutral pH (pH=7) and leads to the release of one mole of iodine (I2) for every two moles of ClO_2. Chlorites, on the contrary, do not react with iodide in neutral environments; such reactions occur only in acid environment (pH 2). In this case they are:

$2ClO_2$ + 2I⁻ $\longrightarrow$ I_2 + ClO_2^- (a1)

ClO_2^- + 8H+ + 8I⁻ $\longrightarrow$ $2I_2$ + Cl⁻ + $4H_2O$ (a2)

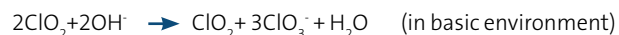$2ClO_2$ + 8H+ + 10I⁻ $\longrightarrow$ $5I_2$ + 2Cl⁻ + $4H_2O$ (a3)

The iodine which is formed in neutral solutions (ClO_2 + e⁻ = ClO_2^-) is in a ratio of 1/5 compared with that formed in acid environment (ClO_2 + 5 e⁻ = Cl⁻). Oxidation of iodide by Cl_2 (neutral or acid environment).

Cl_2 + 2I- $\longrightarrow$ I2 + 2Cl⁻ (b)

Oxidation of iodide by ClO_3^- :

Chlorates do not interfere with the oxidation of iodides, because the reaction is very slow and may occur only in strongly acid environment and in the presence of potassium bromide (KBr) as a catalyst, that is:

$$2ClO_2 + 2OH^- \longrightarrow ClO_2 + 3ClO_3^- + H_2O \quad \text{(in basic environment)}$$

$$ClO_3^- + 6kBr + 6HCl \longrightarrow 3Br_2 + 6kCl + Cl^- + 3H_2O$$

$$3Br_2 + 6kC \longrightarrow 3I_2 + 6kBl$$

Sampling:

Particular attention must be paid during the collection and titration of the chlorine dioxide solutions, because it is a matter of relatively unstable solutions of a gas in water. At all the concentrations in which it is produced, the elevated pressure of the ClO_2 vapour may favour degassing; therefore, it is not advantageous to sample the concentrated solution directly. Some generators are provided with a dilution circuit which brings the concentration to approximately 1 - 2 g/l; in such case it is suitable to sample the diluted solution. In cases where it is necessary to draw the concentrated solution, it is advisable to use a sampling pipette with two taps, with which to dilute directly the solution with distilled water up to 0.2 - 0.5 g/l. The samples to be analysed are then taken from this diluted solution, taking the dilution factor into account.The sampling glassware must be made of neutral glass.

Reagents:

1) Potassium iodide (KI)
2) Sodium thiosulfate ($Na_2S_2O_3$), 0.1 N solution
3) Starch, 0.5 % solution 5 g of soluble starch are dissolved in 1 liter of boiling distilled water. The solution remains turbid and can be kept for approximately 3 weeks.
4) Buffer solution 33 g of $NaH_2PO_4 \cdot H_2O$ 132 g of $Na_2HPO_4 \cdot 12H_2O$ are dissolved in approximately 800 ml of distilled water. The solution is then adjusted to pH 7.05 with NaOH 2N and brought up to 1 liter.
5) Sulfuric acid (H_2SO_4), 10 % solution 57 ml of concentrated sulfuric acid (95-97 % concentration of sulfuric acid) are added to 900 ml of distilled water.
6) Sulfuric acid (H_2SO_4), 15 % solution 91 ml of concentrated sulfuric acid are added to 900 ml of distilled water.
7) Caustic soda (NaOH), 30 % solution 300 g of sodium hydroxide (NaOH) are dissolved in 700 ml of distilled water. Since there is a considerable development of heat, it is best to let the solution to cool overnight before using it.
8) Potassium bromide (KBr), 10 % solution. Dissolve 10 g of KBr in 90 ml of distilled water.
9) Hydrochloric acid (HCl), 37 % solution.

Procedure:

For the quantitative determination of chlorine dioxide, chlorine, sodium chlorite and sodium chlorate, four multiple titrations must be performed, for precision, in neutral and acid environment (Titrations A, B, and D), as well as in alkaline environment (Titration C). The elementary iodine which is formed and which can, depending on its concentration, endow the solution with a coloration from yellow to brown, is reduced again with a solution of sodium thiosulfate ($Na_2S_2O_3$) 0.1 N which transforms into sodium tetrathionate ($Na2S4O_6$):

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

The point of equivalence of the titration is highlighted by means of starch as an indicator. In the presence of elementary iodine, the starch forms a dark blue iodine-starch complex and this coloration disappears at the point of equivalence.

Titration A (pH = 7.2):

30 ml of distilled water + 40 ml of buffer solution + 1 g of potassium iodide are first placed into a 300 ml Erlenmeyer flask. Then, 20 ml of the ClO_2 solution under examination are added and the flask is left in the dark for 5 minutes. It is then titrated with $Na_2S_2O_3$ 0.1 N with the addition of 2 - 3 ml of starch as an indicator (ml used = A). The titration is as follows: chlorine + 1/5 chlorine dioxide

Titration B (acid environment):

20 ml of 10 % sulfuric acid are added to the same sample, prepared according to A, which is, then, stirred and placed in the dark for 5 minutes. It is, then, titrated with $Na_2S_2O_3$ 0.1 N (ml used = B). The titration is as follows: sodium chlorite + 4/5 chlorine dioxide.

$$KClO_2 + 4KI + 2H_2SO_4 \longrightarrow 2I_2 + KCl + 2K_2SO_4 + 2H_2O$$

$$NaClO_2 + 4KI + 2H_2SO_4 \longrightarrow 2I_2 + NaKCl + 2K_2SO_4 + 2H_2O$$

Titration C (basic environment):

30 ml of 30 % caustic soda solution + 20 ml of ClO_2 solution under examination are placed into a 50 ml Erlenmeyer flask. The closed flask is, then, left exposed to light for 30 minutes. During this period, the flask is
repeatedly agitated until the yellow colour of ClO_2 and any white fumes disappear. After this preliminary operation, the contents of the flask (after rinsing down its walls with distilled water) are transferred into another 500 ml flask and 1 g of KI is added.

At this point they are acidified with 120 ml of 15 % H_2SO_4 and the solution is placed in the dark for 5 minutes. It is, then, titrated with $Na_2S_2O_3$ 0.1 N, with the addition of 2 - 3 ml of starch as an indicator (ml used = C). Titration is as follows: chlorine + 2/5 chlorine dioxide + sodium chlorite

$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$$

$$NaClO_2 + 4KI + 2H_2SO_4 \longrightarrow 2I_2 + NaKCl + 2K_2SO_4 + 2H_2O$$

$$Cl_2 + 2KI \longrightarrow I_2 + KCl$$

Titration D (acid environment):

5 ml of 10 % potassium bromide KBr solution and 25 ml of concentrated hydrochloric acid are placed into a 50 ml Erlenmeyer flask. 20 ml of ClO_2 solution under examination are added and the flask is closed. The flask is exposed to light for 20 minutes. After this operation, 1 g of KI is added and the flask is placed in the dark for 5 minutes. The solution is transferred into a 500 ml Erlenmeyer flask containing 30 ml of 30 % caustic soda solution and 100 ml of distilled water. It is, then, titrated with $Na_2S_2O_3$ 0.1 N, with the addition of 2 - 3 ml of starch as an indicator (ml used = D1). The same procedure is followed with 20 ml of distilled water instead of the sample, as a blank test (ml used = D2).

D = D1 - D2.
The titration is as follows:
chlorine + chlorine dioxide + sodium chlorite
+ sodium chlorate

$$2ClO_2 + 10kBr + 8HCl \longrightarrow 5Br_2 + 10kCl + 4H_2O$$

$$Cl_2 + 2KBr \longrightarrow Br_2 + 2KCl$$

$$NaClO_2 + 4KBr + 2HCl \longrightarrow 2Br_2 + 4KCl + NaCl -+ 2H_2O$$

$$NaClO_3 + 6KBr + 6HCl \longrightarrow 3Br_2 + 6KCl + NaCl -+ 3H_2O$$

$$Br_2 + 2KI \longrightarrow I_2 + 2KBr$$

Results

The following system of equations is obtained from the 4 titrations:

$A = Cl_2 + 1/5\ ClO_2$
$B = ClO_2^- + 4/5\ ClO_2$
$C = Cl_2 + 2/5\ ClO_2 + ClO_2^-$
$D = Cl_2 + ClO_2 + ClO_2^- + ClO_3^-$

in which A, B, C , and D represent the millimeters of $Na_2S_2O_3$ 0.1 N that are used to titrate a 20 ml sample.

From the solution of the system, the unknowns values of Cl_2, ClO_2, ClO_3^- and ClO_2^-, are obtained, which, multiplied by the normality of the titrating solution (0.1 N), and for 50 (in reference to 1 liter) represent the concentrations of the species in meq/l.

ClO_2 (meq/l) = [5 (A + B - C) /3] • 5 (1)
Cl_2 (meq/l) = [(2A - B + C) /3] • 5 (2)
$NaClO_2$ (meq/l) = [(4C - 4A - B) /3] • 5 (3)
$NaClO_3$ (meq/l) = [D - (A + B)] . 5 (4)

Table 16 reports the equivalent weights of Cl_2 , ClO_2, ClO_3^- and ClO_2^-, taken into account that each species, by oxidising the iodide, is reduced to chloride in appropriate pH conditions.

		Molecular weight	Equivalent N°/mole	Weight equivalent
ClO_2	pH 7	67.5	1	67.5
ClO_2	pH 2	67.5	5	13.5
Cl_2	pH 2 and 7	71.0	2	35.5
$NaClO_2$	pH 2	90.4	4	22.6
$NaClO_3$	pH 2	106.30	6	17.7

Table 16: Equivalent weights of Cl_2, ClO_2, ClO_3^-, ClO_2^- in the reduction reaction to chloride.

By multiplying the concentrations expressed in meq/l by the respective weight equivalents, the following are obtained in mg/l :

ClO_2 (mg/l) = 13.5 • [5 (A + B - C) /3] • 5
Cl_2 (mg/l) = 35.5 • [(2A - B + C) /3] • 5
$NaClO_2$ (mg/l) = 22.6 • [(4C - 4A - B) /3] • 5
$NaClO_3$ (mg/l) = 17.7 • [D - (A + B)] • 5

7.2 Analysis of residual chlorine dioxide in water

Chlorophenol Red Method (CPR)
(Unichim Method 77)
The oxidant action of chlorine dioxide on substances present in the water to be treated, as already seen in the previous paragraphs, may lead to the formation of chlorites, chlorates and chlorine in the form of hypochlorite. The chlorophenol red method (CPR) method makes it possible to analyse the quantity of residual chlorine dioxide present after treatment, in the presence of chlorites, chlorates and hypochlorite. The method is utilised for natural and drinking water, but only in a limited way to waste waters. The method is applicable for concentrations of ClO_2 starting from 0.05 mg/l with the limits of the Lambert-Beer Law; for higher concentrations, the sample has to be diluted. The analysis must be conducted immediately after sampling, in order to avoid that the concentration of ClO_2 might decrease over time in the presence of oxidisable substances and under the action of light.

Principle:

This method is based on the oxidising reaction of ClO_2 on chlorophenol red (CPR) with splitting of the aromatic compound which leads to a change in colour. One mole of CPR reacts with two moles of ClO_2 with consequent decolourisation of the CPR.

Equipment:

• Normal laborator and equipment treated with active chlorine solution and subsequently rinsed until there is a total absence of oxidants.
• 50 and 100 ml pipettes, fitted with a pump system for filling
• Prism (or grid) spectrometer, or alternatively a colorimeter with filters suitable for measuring absorption at 575 nm with various measuring cells
• Glass photometric cells with optical range from 1 to 5 cm membranes.

Reagents:

1) Distilled water, free from oxidising or reducing substances capable of interfering with the applied reaction under examination.
2) Buffer solution at pH 7: dissolve in distilled water, in the following order, 1.76 g of KH_2PO_4 and 3.64 g of $Na_2HPO_4 \cdot 2H_2O$; bring up to 100 ml and stir.
3) Reactive to chlorophenol red $0.333 \cdot 10^{-3}$ M: dissolve 0.141 g of chlorophenol red (dichlorophenolsulfophthalein MW 423.3) in 100 ml of NaOH 0.01 M and bring up to 1,000 ml with water. The solution, left to settle overnight, is filtered through 0.45 μ m membranes.
4) Sodium hypochlorite, 0.1g/l solution, which is obtained by diluting a commercial solution of hypochlorite.
5) Chlorine dioxide, in 0.5g/l mother solution for titration: obtained by reaction of 1.0 g of 100 % sodium chlorite dissolved in 900 ml of distilled water containing 3.5g of acetic anhydride (analytical grade). The solution is brought to volume (1,000 ml). The reagents are added slowly, at low temperature to avoid the loss of ClO_2 in the gas phase. The solution must be prepared at least once a week and conserved in dark glass bottles at a temperature of 1 - 4 °C. Once ready, the titre of the solution must be tested with the colorimetric method described earlier.

Procedure:

Preparation of the calibrating solutions Starting from a mother solution of ClO_2 prepare for a series of solutions containing respectively 0.05 - 0.1 - 0.2 - 0.25 mg/l of ClO_2 dilution with distilled water. These solutions are not preservable and therefore, must be prepared immediately prior proceeding with the calibration curve.

Calibration Curve:

In a series of 250 ml flasks place 2 ml of CPR solution, 1 ml of buffer solution at pH 7, and a 50 ml portion of the above mentioned calibration solutions. After a few minutes read off the absorption on the 575 nm spectrophotometer in cells of 1 cm.

The initial absorption, corresponding to white, must have a value of no less than 0.65 - 0.7 A.U. Trace the absorption-concentration diagram of ClO_2, and verify to see whether or not, within the range of the tested values, it conforms to the Lambert-Beer Law.

ClO_2 Determination:

Draw samples of 50 ml from the water to be analysed and proceed as outlined above. Extract the concentration of ClO_2 in mg/l from the calibration curve. Readings must be done in comparison to a blank test consisting of a solution of reagents in distilled water, excluding CPR. Measurements must be made twice and compared with the values obtained by iodometric measurement of the active chlorine.

Results:

The chlorine dioxide contained in the water sample, expressed in mg/l, is calculated in the following manner:

$C = C_2 - C_1$

where:

C = concentration of ClO_2 in mg/l
C1 = concentration of ClO_2 in mg/l in the blank test (calculated from the calibration curve)
C2 = concentration of ClO_2 in mg/l in the sample (calculated from the calibration curve)

Interference:

The following compounds may interfere with the measurement of ClO_2:

• halogenated oxidant products, such as chlorates, bromates, chlorites and chloramines in high concentrations (between 100 and 10,000 ppm);
• free chlorine at pH 7 and hypochlorite at pH 9 which react with the CPR, giving rise to a blue coloration. However, the reaction velocity is low (5 - 10 times slower than that of the ClO_2)
• nitrites, nitrates and other strong anions in concentrations above 1 g/l.

Precision and accuracy:

The CPR method has not be subject to inter-laboratory tests to verify its reliability, especially in the presence of other sources of active chlorine. Tests performed in the presence of hypochlorite, in equimolar ratio with ClO_2, immediately following the addition of this oxidant to avoid secondary reactions, indicate that this compound has only a marginal effect.

Principle:

This method is an extension of the DPD method used to determine free chlorine and chloramines in water (IRSA-CNR method n° 4060 [63]). With the above mentioned method, 1/5 of chlorine dioxide is also measured out. If the sample is acidified a head of time, in the presence of iodine, the chlorite ion also reacts. After neutralisation, through the addition of sodium bicarbonate, the colour which develops corresponds to the totality of chlorine, including that of chlorites. Free chlorine must be eliminated by adding glycine prior to the reaction with the DPD reagent on dioxide. The differentiation between free chlorine and dioxide is based on the fact that glycine converts the free chlorine very quickly into chloraminoacetic acid without having any effect on chlorine dioxide. The method can be used for total chlorine content less than 5 mg/l. For higher quantities it is necessar y to dilute the sample appropriately.

Interference:

Manganese in the oxidised state interferes, but its interferences can be corrected by taking a preliminary measurement in the presence of sodium arsenite. The interference of iron (III) and copper (II) to the extent of 10 - 20 mg/l may be masked by adding sequestrants of EDTA type to the buffer solution or to that of the DPD reagent. This eliminates errors caused by the presence of dissolved oxygen and prevents the potential catalytic reactions favoured by trace metal.

Reagents:

1) Solution of 24 g of anhydrous Na_2HPO_4 and 46 g of anhydrous KH_2PO_4 in 500 ml of distilled water. Add 100 ml of distilled water containing 800 mg of disodium EDTA salt. Bring up to 1 liter.
2) Solution of N,N-diethyl-p-phenylenediamine (DPD). Dissolve 1.5 g of pentahydrated DPD sulfate or 1.1 g of anhydrous DPD sulphate in distilled water. Add 8 ml of 40% sulfuric acid and bring volume up to 1 liter with distilled water. Keep the solution in dark glass bottles and in the dark.
3) Solution of ferrous-ammonium sulphate (FAS). Dissolve 1.106 g of $Fe(NH_4)2(SO_4)2.6H_2O$ in distilled water containing 1 ml of 40 % sulfuric acid. Bring up to volume (1 liter). This standard solution may be used for a month and its titre must be tested by cross-titration with potassium dichromate.
4) Potassium iodide KI in crystals.
5) Solution of potassium iodide. Dissolve 500 mg of solid KI in 100 ml of distilled water. Conserve in dark bottles, preferably in a refrigerator.
6) Glycine solution. Dissolve 10 g of glycine (amino-acetic acid) in 100 ml of distilled water. Conserve in a refrigerator, and prepare fresh solution if it becomes turbid;
7) Solution of sulfuric acid. Dilute 5 ml of concentrated sulfuric acid to 100 ml.
8) Solution of sodium bicarbonate. Dissolve 27.5 g $NaHCO_3$ in 500 ml of distilled water.
9) Dehydrated sodium salt of Ethylenediaminotetraacetic acid (EDTA).

Chlorine dioxidemongraph:
Procedure:

The DPD method can be carried out in two different ways:
1. by means of titration with ferrousammonium sulfate (FAS);
2. by means of colorimetric reading at 515 nm.

1. Titration Method:

a) Determination of Chlorine Dioxide:

Add 2 ml of glycine solution to 100 ml of chlorine dioxide. In a second beaker, place 5 ml of buffer solution and 5 ml of DPD solution: add 200 mg of EDTA and mix. Add the sample to which glycine was added. Mix and titrate rapidly with ferrous ammoniacal sulphate solution until the red colouring disappears (titration G, where G represents the volume of iron-ammoniacal sulfate);

b) Determination of free chlorine, monochloramines and di-chloramines:

Into a flask place 5 ml of buffer solution and 5 ml of DPD solution, and add about 1 g of potassium iodide crystals. Add 100 ml of sample, mix and let it rest for two minutes. Titrate with solution of ferrous ammoniacalsulfate until the red coloration disappears (titration C, where C represents the used volume);

c) Determination of total chlorine (including chlorites):

To the already titrated sample, add 2 ml of sulfuric acid. After 2 minutes, add 5 ml of sodium bicarbonate solution. Continue to titrate with ferrous ammoniacal sulfate solution until the disappearance of the red coloration (titration D, where D represents the used volume).

Results:

The contents of the various types of samples being tested (100 ml) are calculated in the following manner, bearing in mind that 1 ml of ferrous ammoniacal sulfate corresponds to 0.1 mg of chlorine:
• the contents of chlorine dioxide, ClO_2 is equal to 5G
• the contents of chlorite, ClO_2
• is equal to D - (C + 4G)
• the contents of free chlorine and chloramines is equal to C - G
• the contents of total chlorine is equal to D.

2. Colorimetric Method:

It is possible to use a colorimetric methods which provides for readings at a wavelength of 515 nm with a spectrophotometer equipped with a cell of 1 cm. In this case, it is necessary to calibrate the instrument with solutions of known titres of chlorine in the 0.05 - 4 mg/l range starting with a solution containing 100 mg/l of chlorine.

Procedure (valid for samples with total content of chlorine not above 5 mg/l)

a) Determination of chlorine dioxide:

add 2 ml of the glycine solution to a 100 ml of sample. In a beaker, pour 5 ml each of phosphate buffer and of DPD solution, and add 200 mg of EDTA; mix. Pour the sample pre-treated with the glycine solution into the beaker. Titrate rapidly with FAS until the red colouring disappears(reading G)MONOGRCHLORINE DIOXIDE

b) Determination of free chlorine and chloramines:

in a beaker, pour 5 ml each of buffer solution and of DPD solution, and about 1 g of KI in crystals. Add 100 ml of the sample and let it rest for two minutes. Titrate with FAS until the red coloration disappears (reading C);

c) Determination of total chlorine (including the chlorites): to the already titrated:

sample (see b), add 1 ml of sulfuric acid solution. Wait 2 minutes, then add 5 ml of bicarbonate solution. Continue the titration with FAS until the coloration disappears (reading D).

Calculations:

For each 100 ml of sample, each 1 ml of used ferrous-ammonium sulfate (FAS) solution corresponds to 1 mg/l of chlorine. All the species are expressed as chlorine.
chlorine dioxide = 5 G
chlorite   = D - (C + 4 G)
free chlorine+chloramines =C-G
total available chlorine = D

Please note: Instead of titrating with the standard FAS solution, it is possible to adopt a colorimetric procedure which provides for readings for each of the passages described previously at a wavelength of 515 nm with a spectrophotometer equipped with a cell of 1 cm. In this case, it is necessary to calibrate the instrument in advance with solutions of known titres of chlorine in the 0.05 (0.5 – 4 mg/l) range starting with a more concentrated solution with 100 mg/l of chlorine.

References

[1] W.J. Masschelein, "Chlorine Dioxide. Chemistry and Environmental impact of Oxichlorine Compounds", Ann Arbor Science Pubblishers, Ann Arbor, Michigan (1979)

[2] J. Kepinski, J. Trzeszczynski, Roczniki Chem. 38-201 (1964); Chemical Abstract 61-3751 (1964)

[3] M. Doré, "Chimie des oxidant", Technique et Documentation - Lavoisier, Paris (1989)

[4] D.E. Emerich "Reactions of Oxychlorine Species in Acqueous Solution" Doctorat dissertation, Miami Univ., Oxoford, Ohio (1981)

[5] E.M. Aieta, P.V. Roberts, M. Hernandez, " Determination of Chlorine Dioxide, Chlorine, Chlorite and Chlorate in Water" Jour. AWWA, 64-74, (1984)

[6] E.M. Aieta, J.D. Berg " A Review of Chlorine Dioxide in Drinking Water Treatment", Jour. AWWA, 62-72, (1986)

[7] W.J. Masschelein, "Chlorine Dioxide" Eckenfelder, 170-193

[8] vedi voce (4) Eckenfelder

[9] Office International de l'eau " Le Dioxide de Chlore. Production, Utilisation - Controle." (1993)

[10] G. Holst, Ind. Eng. Chem., 42, 2359, (1950)

[11] J. Hoigné, H. Bader, " Kinetik typischer Reaktionen von Chlordioxid mit Wasserhinalstaffen", Vom Wasser, 59, 253, (1982)

[12] C. Schirle, Bulletin Institut Textile de France, 41, 21, (1953)

[13] CH.I. Noss, F. S. Hauchman, V.P. Olivieri, Water Research, 20 (3), 351, (1986)

[14] H. Ben Amor, J. De Laat, M. Doré, Environmental Technologies Letters, 6, 489, (1985)

[15] J.E. Wajon, D.H. Rosenblatt, E.P. Burrows, Environmental Science Technologies, 16, 396, (1982)

[16] J.C. Hoff, E.E. Geldreich, "Comparison of the biocidal efficiency of alternative disinfectants" in Proceedings AWWA Seminar, Atalanta Georgia, 15 June 1980 (1980)

[17] J.C. Hoff, "Inactivation of microbial agents by chemical disinfectants", US EPA 600/286/067 (1986)

[18] C.I. Noss et al., "Reactivity of chlorine dioxide with nucleic acids and proteins", Water Chlorination: Environmental Impact Health Effects, Vol.4 Ann Arbor, Mich. (1983)

[19]   V.P. Olivieri et al., "Mode of action of chlorine dioxide on selected viruses", Water Chlorination: Environmental Impact Health Effects, Vol.5 Ann Arbor, Mich. (1985)

[20]   M.E. Alvarez, R.T. O'Brien , "Mechanism of inactivation of Poliovirus by chlorine dioxide and iodine", Appl. Envir. Microbiol., 44, 1064 (1982)

[21]   E.H. Ghandbari et al., "Reaction of chlorine and chlorine dioxide with free fatty acids, fatty acids esters and triglycerides", Water Chlorination: environmental impact and health effects., Vol 4, Ann Arbor Sci. Publ., Ann Arbor, Mich. (1983)

[22]   J.D. Berg et al., "Effect of chlorine dioxide on selected membrane functions in E. coli", Journal Appl. Bacteriology (1986)

[23]   M.A. Bernarde et al., "Kinetics and mechanism of bacterial disinfection by chlorine dioxide", Appl. Microbiol., 15, 257 (1967)

[24]   H. Ben Amor, J. De Laat, M. Doré, Proc.of the 5th European symposium on Organic Micropollulants in the Aquatic Environment, Rome, Italy (1987)

[25]   C. Gomella, P. Musquere, "La désinfection des eaux par le chlore, l'ozone et le dioxyde de chlore", XIII Congrès de l'A.I.D.E., Paris (1980)

[26]   Orme Zavaletta (US EPA), " Chlorine Dioxide Risk Assessment for drinking Water". second Int. Symposium - Chlorine Dioxide: Drinking Water Issues May 1992 Houston (1992)

[27]   J.R. Lubbers, R.G. Bianchine, "Effects of Acute Dose Administration of Chlorine Dioxide, Chlorate and Chlorite to Normal Healthy Male Volunteers", J. Environ. Pathol. Toxicol. and Oncology, 5:215-218, (1984) a

[28]   J.R. Lubbers, S. Chauhan, J.K. Miller, R.G. Bianchine, "The Effects of Chronic Dose Administration of Chlorine Dioxide, Chlorate and Chlorite to Normal Healthy Adult Male Volunteers", J.Environ. Pathol. Toxicol. and Oncology, 5:229-238, (1984) b

[29]   J.R. Lubbers, S. Chauhan, J.K. Miller, R.G.Biachine, "Ef fects of Chronic Administration of Chlorine Dioxide, Chlorate and Chlorite to G-6-PD Deficient Healthy Adult Male Volunteers", J. Environ. Pathol. Toxicol. and Oncology, 5: 239-242, (1984) c

[30]   J.M. Symons et al. "Treatment Techniques for Controlling Trihalomethanes in Drinking Water". EPA-600/2-81-156 Cincinnati, Ohio (1981)

[31]   "Etude du dioxide de chlore comme post-désinfectant en reseau de distribution". Etude NANCIEAU Mars – Aout 1992

[32]   R.G. Zika et al., "Sunlight-Induced Pothodecomposition of Chlorine Dioxide", Water Chlorination: Environmental Impact Health Effects, Vol.5 Ann Arbor, Mich. (1985)

[33]   S.J. Fleischacker, S.J. Randtke, "Formation of Organic Chlorine in Public Water Supplies", Journal AWWA, 75:3:132 (1983)

[34]   B.M. Chow, P.V. Roberts, "Halogenated Byproduct Formation by Chlorine Dioxide and Chlorine", Jour. Environmental Engrg. Div.-ASCE, 107: EE4 (1981)

[35]   R.G. Rice, M. Gomez-Taylor, "Occurrence of by products of strong oxidants reacting with drinking water contaminantsscope of the problem." Environmental Health Perspectives 69, 31-44 (1986)

[36]   B.W. Lykins, J.A. Goodrich, J.C. Hoff, "Concerns with using chlorine-dioxide disinfection in the USA", Aqua, vol. 39, 6, 376-386 (1990)

[37]   First Int. Symposium on Health Effects of Drinking Water Disinfectants and Disinfectant By-Products. Proc. In Environmental Health prspectives, Vol. 46 (1982)

[38]   H.J. Brauch, G. Baldauf, H. Sontheimer, "Untersuchungen zur Bildung chlororganischer Verbindungen bei der Chlordioxidbehandlung huminsäurehaltiger Wässer"Vom Wasser, 56, 25 (1981)

[39]   R.N. Aston, G.P. Vincent, Proc. 9th Ann. Course Water Plant Operators 10:54 (1947)

[40]   J. Flores, J.F. Ruana, "Eau de Tarragone: problèmes de goût e d'odeur", T.S.M. L'Eau, settembre, 469- 475, (1988)

[41]   G.S. Walker, F.P. Lee, E.M. Aieta, Chlorine Dioxide for Taste and Odor Control", AWWA Journal 3, 84- (1986)

[42]   Lur'e, YuYu et al. Vodosnabzh. Sanit. Tekn 4:7 (1973); Chem. Abstr.79:23266 (1973)

[43] N. Narkis, Y. Kott, "Comparison between chlorine dioxide and chlorine for use as a disinfectant of wastewater effluents", Water Science and Technology vol.26 n°7-8, 1483-1492, (1992)

[44] P.V. Roberts, E.M. Aieta, J.D. Berg, B.M. Chow: "Chlorine dioxide for wastewater disinfection: a feasibility evaluation", Doc. EPA 600/2-81-902, (1981)

[45] S. Monarca, G. Nardi, D. Feretti, F. Dorè, A. Francesconi, M. Grottolo: "Uso del biossido di cloro nella disinfezione delle acque reflue di depuratori civili: recenti esperienze", Inquinamento n. 5, 110-116, (1992)

[46] S. Monarca, G. Nardi, A. Zanardini, R. Taliento, M. Belluati, D. Feretti "Esperienza di disinfezione di acque provenienti da trattamenti di depurazione", Inquinamento n. 6, 83-88 (1996)

[47] H. Leclerc, C. Ogher, "Les eaux usée des hôpitaux et leur importance épidemiologique", Rev. Epidém. Med. Soc. Santé Publ. 22, 185-189, (1974)

[48] S. Monarca, G. Nardi, D. Feretti, F. Dorè, A. Francesconi, M. Grottolo, U. Bracchi, M. Tanzi, G. Bragonzi, M. Perna: "Acque reflue ospedaliere: valutazione di un trattamento di disinfezione con biossido di cloro", Inquinamento n. 7, 77-83 (1995)

[49] J.P. Gautier, M. Pouillot, "Un bactéricide efficace pour le traitement des slimes en papeterie: le bioxyde de chlore", L'Eau, L'Industrie, Les Nuissances, n°127, 45-48 Aprile (1989)

[50] R. Giatti, "Utilizzo del biossido di cloro come antilimo nel processo produttivo della cartiera di Valchiampo", Industria della Carta, 31, n° 3 (1993)

[51] Caffaro, "Il biossido di cloro: il trattamento integrato per le acque di cartiera"

[52] Caffaro, "Stabilizzazione dei fanghi di cartiera con biossido di cloro e clorito di sodio"

[53] M. Firpi, F. Dorè, J.P. Guatier, "Chlorine dioxide in paper production: recent technological developments based on on-line experiments", Symposium Internacional EUCEPA, Barcellona (1990)

[54] ISIA, "Trattamento antilimo con ClO2 - Esperienza presso una cartiera".

[55] E. Heuser, O. Merlan, Cellusosechemie 4:101 (1923)

[56] T.R. Bott, "Biofilm formation and control in flowing acqueous systems", C413/003 IMechE 213-221 (1991)

[57] C. Sebastio, "Ricerca sull'impiego del ClO_2 nel trattamento antifouling delle acque marine d'esercizio dei grandi sistemi industriali", Il Notiziario dell'Ecologia, III n°7 28-30 (1985)

[58] S. Geraci, R. Ambrogi, V. Festa, S. Piraino: "Field and laboratory efficay of chlorine dioxide as antifouling in cooling systems of power plants", OEBALIA, Vol. XIX, Suppl. 383-393 (1993)

[59] A. Sozzi, F.L. Gorini, "Il biossido di cloro per prevenire i marciumi delle pesche", Annali I.V.T.P.A., vol. XIII (1992)

[60] A. Testoni, "La prerefrigerazione: tecnologie e riflessi sulla qualità della frutta", Frutticoltura, n° 5, 23-31 (1991)

[61] F. Corbani, "Nobilitazione dei tessili" Centro tessile cotoniero e abbigliamento S.p.A., seconda ristampa, Vol. 1, 337-364 (1994)

[62] Metodo Industrie Chimiche ISIA.

[63] IRSA-CNR, "Metodi analitici per le acque", 186-189 Istituto Poligrafico e Zecca dello Stato (1994)

[64] American Public Health Association, "Standard Methods for Examination of Water and Wastewater" 18th edition Washington (1992)

[65] American Public Health Association, "Standard Methods for Examination of Water and Wastewater" 19th edition Washington (1995)

[66] ISO 10304-4 (draft). "Water Quality dissolved chloride and chlorite by liquid chromatography of ion". Part 4: Method for Water of low contamination.

The information about the properties of sodium chlorite and chlorite dioxide included in this handbook are derived from the laboratory and the field, or cited from qualified literature.

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