CHLORINE DIOXIDE

IN

WATER TREATMENT

ION EXCHANGE (INDIA) LTD

ClO_2 – Introduction

Chlorine is able to form the following compounds with oxygen, having oxidation states in the positive

Oxidation State	Formula	Name
+1	Cl_2O	Chlorine monoxide or anhydride of HOCl
+2	ClO	Never isolated, it has a half life of 0.01 seconds
+3	Cl_2O_3	Dichlorine trioxide or chlorous acid anhydride
+4	ClO_2	Chlorine Dioxide
+5	Cl_2O_5	Dichlorine pentoxide or chloric acid anhydride
+7	Cl_2O_7	Dichlorine heptoxide or perchloric acid anhydride

Compounds with an odd number of chlorine atoms, plus an unpaired electron, are unstable, and are called radicals. This includes chlorine dioxide.

ClO_2 : Properties

Physical properties

CAS Number	**[10049-04-4]**
Odour	**Mixture of chlorine and ozone.**
Freezing point	**-59°C**
Boiling point	**11°C**
Colour	**Yellow (gas), red (liquid)**
Solubility in water	**Freely soluble. 8g/L (30°C)**

ClO_2 : Properties

Chemical properties

Ammonia with chlorine and chlorine dioxide

$H_3N^{\delta-} + ClO_2^{\delta-} \rightarrow$ No reaction

Water with chlorine and chlorine dioxide

$H_2O + ClO_2 \rightarrow$ No reaction

ClO_2 : Properties

Electrochemical reaction

Chlorite ions (ClO_2^-) is an oxidizing agents.

$ClO_2^- + 4H^+ + 4e^- \rightarrow Cl^- + 2H_2O$; $E_{pH=7}$=0.37 V).

(slow reaction)

The E^o indicates that ClO_2^- ion is a weak oxidizer than ClO_2 molecule

ClO_2 : Properties

$Cl0_2$ reacts with

Cyanides

Nitrites

Sulfides

Fe^{2+} etc

Phenols and other easily oxidizable organic moieties.

ClO_2 : Properties

Microbial control

Chlorine dioxide is used to control microbiological growth in many industries.

Dairy industry, Beverage industry, Pulp and paper industries, Fruit and Vegetable processing industries, Poultry industry, Food processing applications.

ClO_2 : Properties

Microbial Control

Biocide for Microbial control

Bacterial Recovery

Bio dispersant

ClO_2 : Properties

$Cl0_2$ kills the following:

- viruses
- bacteria
- giardia
- cryptosporidium
- botulism
- e. coli
- cholera

ClO_2 : Properties

Biocide	Microbial activity
ClO2	Broad spectrum being effective against all bacteria, viruses and spore formers such as Giardia and Crvotosooridium
O_3	Broad spectrum, effective against all types of micro organisms
OCl^-	Relatively ineffective against most viruses, moulds, fungi and spore formers
H2O2	Unless used at high concentration, relatively ineffective
Quat	Relatively ineffective against certain bacteria and spore formers
Phenol	Effective against most micro- organisms, except certain spore formers such as Glardia

ClO_2 : Properties

Bacterial recovery

The rate of re-establishment of bacterial population by itself after sterilization is called bacterial recovery.

Such rapid re-growth of bacteria is much lower in ClO_2 treated water than after high chlorination.

G. Norrman, W. G. Characklis, and J. D. Bryers, Dev. Ind. Microbiol., 18, 581(1977).
L. Novak, J. Heat Transfer, 104, 663(1982).
R. O. Lewis, Materials Performance, 21, 31(1982).
P. V. Roberts, E. M. Aieta, J. D. Berg, and B. M. Chow, "Chlorine Dioxide for Wastewater Disinfection: A Feasibility Evaluation", EPA-600/2-81-June 1981.

ClO_2 : Properties

Bio-dispersant

Molecule which have the ability to penetrate through the bio-film are called bio-dispersants.

ClO_2 : Properties

Bio-dispersant properties

Traditional oxidizing biocides (like NaOCl) do not penetrate the biofilm. They only impinge on the surface layers killing them but leaving the underlying bacteria unaffected.

But,

ClO2 can penetrate the slime layer as it is a true gas.

ClO_2 : Properties

Bio-dispersant

Due to the biodispersant action, the microbes, inorganic particles, inert dirt, algal mass etc are surfaced out of the bio-film.

This causes turbidity in the system. The turbidity is directly proportional to the biodispersant activity.

Chlorine dioxide in Water Treatment Applications

- Drinking water treatment
- Cooling water treatment
- Waste water treatment

ClO_2 : Drinking water

- ClO_2 is approved worldwide at 0.5ppm to 1.5ppm residual in water.
- Reduction of taste and odour problems from algal blooms.
- Precipitation of iron or manganese in water at any pH
- 0.25ppm residual chlorine dioxide at a 20 second contact line will give a 99.99% kill of pathogenic bacteria.
- Long life residual for post disinfectant
- Bio-film removal

ClO_2 : Drinking water

Odour control

In 1944, ClO_2 was used to control taste and odor problems (due to phenolics) at a potable water facility at Niagara Falls, N.Y.

Ridenour, *et al, Water and Sewage Works*, 96(8)1949

ClO_2 was then used in municipal potable water treatment facilities which had similar problems.

I. F. Synan, J. D. MacMahon, and G. P. Vincent, J. Amer. Water Works Assoc., 37, 869(1945).

G. P. Vincent, J. D. MacMahon, and J. F. Synan, Am. J. Pub. Health, 1045 (Sept 1946).

ClO_2 : Drinking water

- *As regulated by EPA (as of January 1, 2002), the maximum residual disinfectant levels in drinking water for chlorine dioxide and chlorite ion are 0.8 and 1.0 mg/L, respectively (EPA 2002e, 2002g).*

- *The maximum contaminant level (MCL) for its oxidation product, chlorite ion, in drinking water is 1.0 mg/L (EPA 2002e).*

ClO_2 : Drinking water

- Chlorite, the predominant oxidation by-product of chlorine dioxide, has been shown to produce signs of hemolytic stress when fed to animals, at levels 50 ppm.

- The concern over individuals susceptible to oxidative stress has led to the limit for total chlorine dioxide, chlorite, and chlorate in drinking water being set at 1.0 ppm.

ClO_2 : Drinking water

However, in several studies performed on human subjects, no effect was observed.

J. R. Lubbers, S. Chauhan, J. K. Miller, and J. R. Bianchine, "The Effects of Chronic Administration of Chlorite to Glucose-6-Phosphate Dehydrogenase Deficient Healthy Adult Male Volunteers", JEPTO 5-4/5:239, 1984.

J. R. Lubbers, S. Chauhan, J. K. Miller, and J. R. Bianchine, "The Effects of Chronic Administration of Chlorine Dioxide, Chlorite and Chlorate to Normal Healthy Adult Male Volunteers", JEPTO 54/5:229, 1984.

J. R. Lubbers, S. Chauhan, and J. R. Bianchine, "Controlled Clinical Evaluations of Chlorine Dioxide, Chlorite, and Chlorate in Man", Environ. Health Perspect., 46, 57(1982).

J. R. Lubbers, and J. R. Bianchine, "Effects of the Acute Rising Dose Administration of Chlorine Dioxide, Chlorate and Chlorite to Normal healthy Adult Male Volunteers", JEPTO 54/5:215, 1984.

ClO_2 : Cl_2

Chlorine	Chlorine dioxide
Highly corrosive	Much less corrosive.
Hydrolysis & form HOCl	Does not hydrolyze
pH Dependent Ineffective above pH 7	Not pH dependent «pH 11
Does not remove bio-film	Removes bio-film
Forms chlorinated by products	Does not form chlorinated by-products
Can not be stripped off from aqueous solution	Can be stripped off from aqueous solution using a stream of air.
Reacts with ammonia and amines	Reacts little with secondary amine and not at all with ammonia

ClO_2 : O_3

	OZONE	ClO2
Microbial range	Broad spectrum, effective against all types of micro organisms	Broad spectrum being effective against all bacteria, viruses and spore formers
Contact time	Seconds to minutes	Few seconds to minutes
Con.	0.1 ppm to 10 ppm	0.1 ppm to 100 ppm
Usage	Drinking & waste water disinfection, with some chemical oxidation applications	Drinking and waste water disinfection and deodorization and chemical oxidation

ClO_2 : O_3

	OZONE	ClO2
Reaction with ammonia	Reacts with ammonia	No reaction with ammonia
pH range	Not suitable above 8.5	Works even at pH 11
Half life	Short in contaminated system	Long half life.
Bacterial recovery	Rapid regrowth of bacteria is expected	Regrowth is very low.
Biodispersant	The efficiency of ozone on bio-film is controversial.	Proven for biofilm removal.

ClO_2 : Industrial Cooling water treatment

It is being used as oxidizing biocide in cooling water treatment.

Unlike other oxidizing biocides, it is possesses additional advantageous !!!

ClO_2 : Industrial Cooling water treatment

As an oxidizing biocide

Do not react with contaminants like ammonia

Stable in water for a long period

Able to kill microorganism effectively

Should behave as an efficient biodispersant

Less corrosive

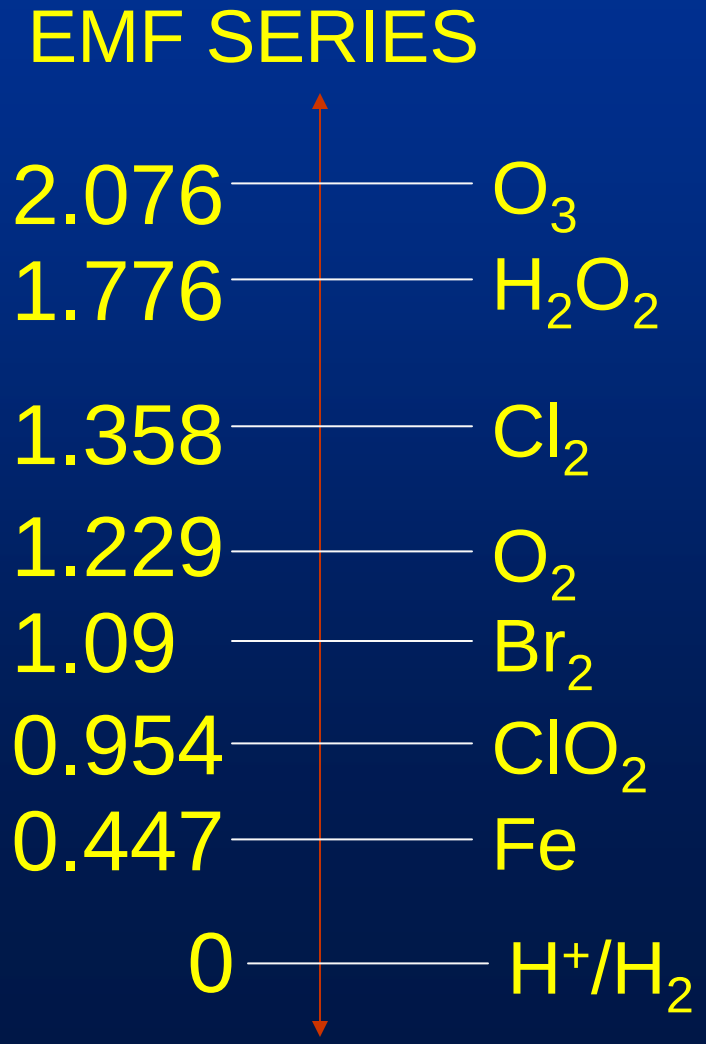
Do not affect the cooling tower wood

ClO_2 : Industrial Cooling water treatment

Less corrosive

Do not affect the cooling tower wood

ClO_2 : Industrial Cooling water treatment



Less corrosive than all other oxidizing biocides.

The severity is less on iron surface

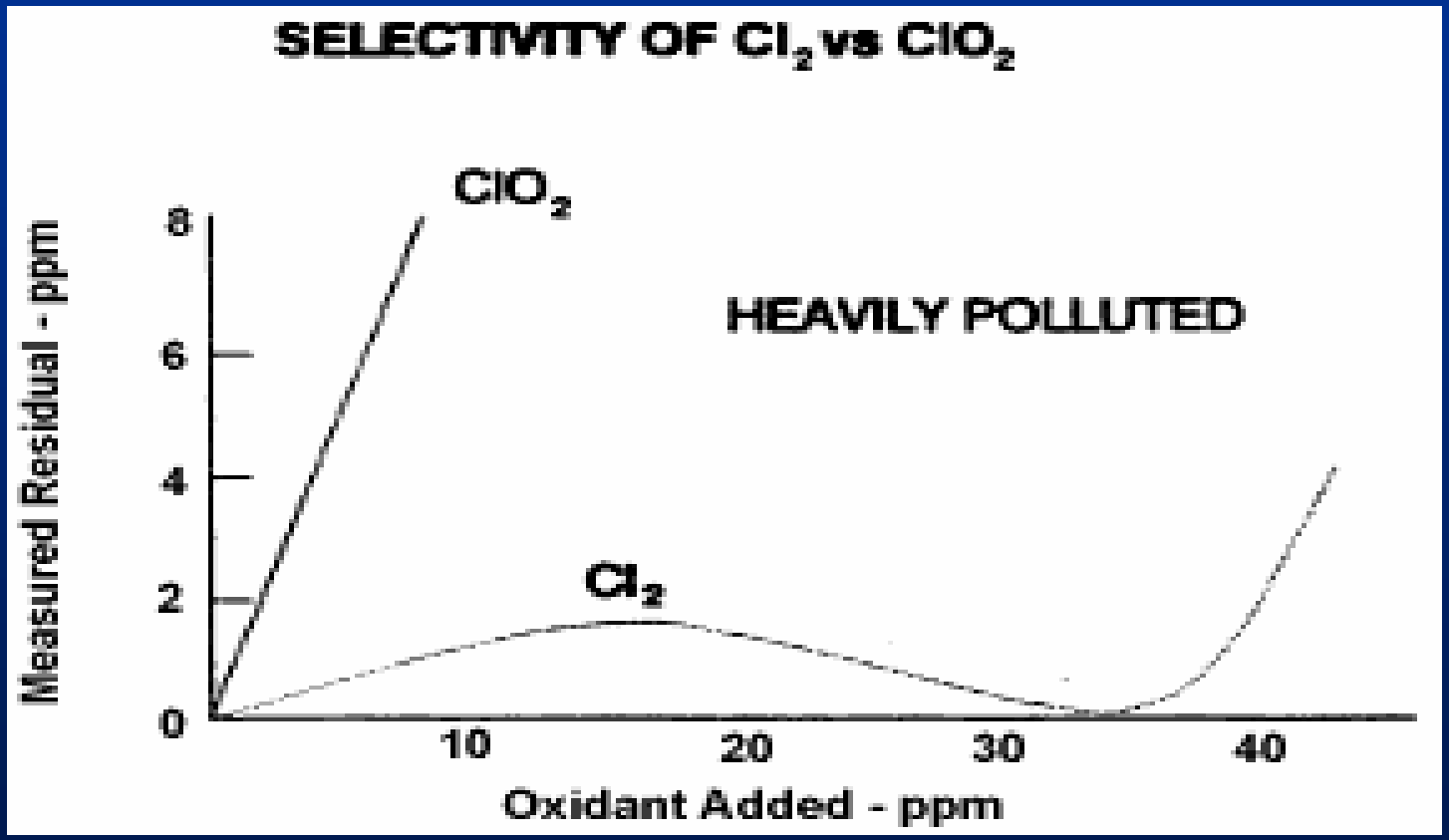
ClO_2 : Waste water treatment

Selective towards specific environmentally objectionable waste materials, including phenols, sulfides, cyanides, thiosulfates, and mercaptans.

W. C. Lauer, S. R. Lohman, and S. E. Rogers, "Experience With Chlorine Dioxide at Denver's Reuse Plant," J. Amer. Water Works Assoc., 78:6:79 June 1986.
J. S. Rauh, "Disinfection and Oxidation of Wastes by Chlorine Dioxide," J. Environ. Sci., 22(2), 42 (1979).
J. E. Wajon, D. J. Rosenblatt, and E. P. Burrows, "Oxidation of Phenol and Hydroquinone by Chlorine Dioxide," Environ. Sci. Technol., 16(7), 396 (1982).

ClO_2 : Waste water treatment

Demand for chlorine dioxide and chlorine.



R. S. Ingols, and G. M. Ridenour, "Chemical Properties of Chlorine Dioxide," J. Amer. Water Works Assoc., 40, 1207 (1948).

C. Rav-Acha, "The Reactions of Chlorine Dioxide with Aquatic Organic Materials and Their Health Effects", Water Res., 18:11:84(1984).

ClO_2 : GENERATION

GENERATION

Sodium chlorite - $NaClO_2$

Sodium chlorate - $NaClO_3$

ClO_2 : GENERATION

Sodium chlorite methods

$$2\ NaClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ NaCl \quad (1)$$

$$2\ NaClO_2 + 2\ HCl + NaOCl \rightarrow 2\ ClO_2 + 3\ NaCl + H_2O \quad (2)$$

$$5\ NaClO_2 + 4\ HCl \rightarrow 5\ NaCl + 4\ ClO_2 \quad (3)$$

$$NaClO_2 + H_2O \rightarrow ClO_2 + NaOH + 1/2\ H_2 \quad (4)$$

ClO_2 : GENERATION

Sodium chlorite methods

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ClO_2 : GENERATION

ClO2 formation is an electron transfer reaction

$NaClO_2 + H_2O \rightarrow ClO_2^- + Na^+$

$ClO_2^- \rightarrow ClO_2 + e^-$

Electron removal by chemical or electrochemical methods

ClO_2 : GENERATION

ClO2 generation with acid

$5NaClO_2 + 5HCl \rightarrow 5\ HClO_2 + 5NaCl$

$5HClO_2 \rightarrow 4ClO_2 + 2\ H_2O + HCl$

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

ClO_2 : GENERATION

Methodologies and Challenges

Features	Cl_2 water	Hypo+acid	Acid
Easy generation	Yes	Yes	No
Towards complete conversion	Yes	Yes	No
Excess chlorine in product	Very high	Low	Nil
Reactor Safety	Safe	Moderate	Moderate
Product output	1 Kg/hr	0.4 Kg/hr	10-20 g/hr

INDION CHLOGEN D1

Photo 1

INDION CHLOGEN D1

Features

1. HAZOP study conducted.
2. Based on gas chlorination.
3. High ClO2 generation efficiency
4. Use of only one pump.
5. Auto/manual mode operation.
6. Manual operation timer based.
7. Designed production : 1 Kg/hr.

INDION CHLOGEN D2

Photo 2

INDION
CHLOGEN D2

Features

1. Novel design.
2. HAZOP study conducted.
3. Use of 3 Pumps.
4. High ClO_2 generation efficiency.
5. Less low chlorine residuals.
6. Auto/Manual mode operation.
7. Timer based manual mode operation.
8. Designed production 0.4 Kg/hr (max).

ClO_2 generation - Reagents

Chemicals (Purity)	Model D1	Model D2
Raw Water	1 M^3/hr	
Indion 1496 (25%)	2.2 L/hr	
Indion 1496 (8%)		7.0 L/hr
Cl_2 flow rate (gas)	0.5 Kg	
Indion 9059 (10%)	-	5.5 L/h
Con. HCl (33%)	-	6.3 L/hr
Final Water quantity at the point of dose of 1496		
pH of Cl_2 water	2.0±0.5	
FRC minimum	250 ppm	

ClO_2 generation - Analysis

DPD method

Able to distinguish between chlorine and chlorine dioxide

ORP method

Can not be distinguished between oxidants. Based on Nearnst Eqn.

Ampirometry method

Able to distinguish chlorine, bromine and chlorine dioxide

Advantageous of chlorine dioxide

- Chlorine dioxide is easy to generate.
- Control of taste and odour problems from algae and decaying plant material can be achieved.
- Oxidizes Iron, Manganese and Sulfides.
- Can enhance clarification process
- Biocidal effectiveness is not effected by pH.

Advantageous of chlorine dioxide

- Chlorine dioxide is more effective than Cl_2 viruses and protozoan.
- Chlorine dioxide provides residual disinfections.
- Halogenated byproducts - THM formation is prevented as long as the generation system does not allow for the release of free chlorine.

Disadvantageous of chlorine dioxide

- **Sodium chlorite costs are high.**
- **Chlorine dioxide decomposes in sunlight.**
- **Extended storage of chlorine dioxide solution can contribute to byproduct formation.**
- **Chlorine dioxide can product noxious odours in some systems.**
- **Chlorine dioxide forms DBPs of chlorite and chlorate.**

Conclusion

Efficient microbial control

Approved for drinking water treatment

Long shelf life in water

Less corrosive

No chemical reaction with ammonia

Efficient biodispersant

Overall cost benefit !