



***Sterilization of Bulk Storage Vessels
with Chlorine Dioxide Gas***

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What is Chlorine Dioxide - ClO₂ ? Process Solutions

- Yellow to Greenish/Yellow Gas at Low Concentrations
- ClO₂ is a strong oxidizer (similar to liquid bleach, NaClO)
- Can be corrosive at high concentrations (but less than chlorine)
- Generated from Sodium Chlorite or Sodium Chlorate salt
- Dissolves quickly in water (Aqueous chlorine dioxide)
- Smells like chlorine (swimming pool)

➤ Major Industrial uses –

- Pulp and Paper Bleaching (by far largest user of ClO_2)
- Primary drinking water treatment (disinfection and odor control)
 - Control of iron, manganese, and phenolic compounds
 - More effective in presence of organic matter than chlorine
 - Reduces formation of THM by-products (carcinogens)
 - Maximum residual disinfection limit (MRDL)= 0.8 ppm
 - Rapidly breaks down to chlorite, chlorate, and chloride

Uses of Chlorine Dioxide - ClO_2

Process Solutions

- Sanitizers: Many EPA registered products
 - For hospital, food and non-food applications including: HVAC systems, animal containment areas
- Additives/deodorizers:
 - Low levels found in toothpastes, mouthwash, deodorizers, consumer cleaning solutions
- Enerfab and Purdue have been working on research with Gaseous chlorine dioxide since 1996 for food industry applications
 - Aseptic equipment sterilization
 - Direct sanitation of produce surfaces (reduce *E. coli*, *Salmonella*, *Listeria*)

GAS versus AQUEOUS FORMS

GAS

- Pure chlorine dioxide depending on generation method
- Most commonly stripped from aqueous solutions

Aqueous

- Gas dissolved in water
- Typically generated by mixing sodium chlorite with acid
- Not very stable, off-gasses ClO_2 when open to atmosphere
- Breaks down over time to chlorite and chloride

Stabilized Chlorine Dioxide

- Aqueous solution of sodium chlorite and high pH buffer
- (MUST BE ACTIVATED PRIOR TO USE)

Generation Methods

Process Solutions

Chlorine gas + sodium chlorite solution

Chlorine gas + technical grade sodium chlorite flakes

GAS

Hydrochloric acid + sodium chlorite solution

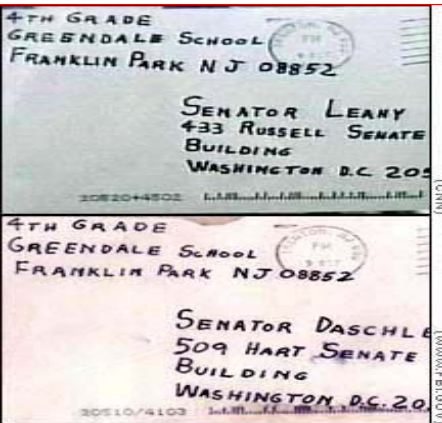
Hydrochloric acid + hypochlorite + sodium chlorite solution

Hydrogen peroxide + sulfuric acid + sodium chlorate solution

Electrolysis: Electricity + sodium chlorite solution

Aqueous

Chlorine Dioxide and Anthrax



2001



An EPA laboratory bus circles the Hart building to monitor the air for gas leaks

2002



Postal Office Decontamination in Hamilton Township, NJ

- Irritates eyes, nose, and respiratory system
 - (burning sensation)
- OSHA 8-hour Permissible Exposure Limit (PEL) 0.1 ppm
- Short-term exposure limit (STEL) 0.3 ppm (15 min)
- Safety Monitors Required around facility
- Gas must be generated on-site at time of use
- Gas can be explosive in air above 10% concentrations***
*** Enerfab generation method creates 4 % maximum concentration

EPA/FDA Registrations:

- First registered as aqueous disinfectant/sanitizer (1967)
- Many approved aqueous applications (food & non-food)
- Gas form registered as a sterilant (1988)
- Gaseous ClO_2 registered as a sterilant for manufacturing/processing equipment, surfaces, tools, and clean rooms

Chlorine Dioxide in the Food Industry Process Solutions

- The Code of Federal Regulations (21 CFR 173, FDA) currently allows the use of chlorine dioxide for numerous food processing applications at various concentrations.
 - ⇒ Up to 3 ppm chlorine dioxide in water may be used to wash fruits and vegetables followed by a potable water rinse, or further processing.
 - ⇒ Also approved for controlling microorganisms in process water contacting fresh poultry carcasses.
 - ⇒ Fogging potatoes in storage

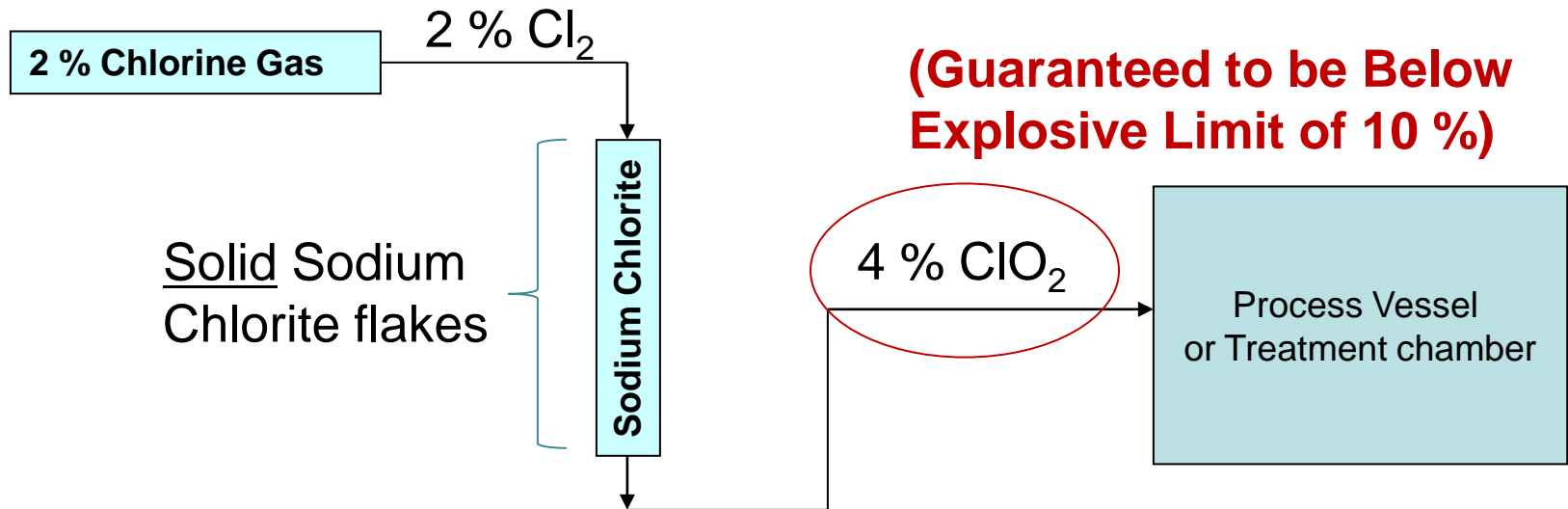
- The Code of Federal Regulations (40 CFR 180.940) also allows the use of chlorine dioxide as a terminal food equipment sanitizing solution at levels of 100 – 200 ppm in water. (also found in 21 CFR 178.1010)

Chlorine Dioxide Gas Generation Process Solutions

Enerfab Generation Process: ClO_2 Generated by Flowing Chlorine Gas Through Sodium Chlorite Canisters



2% Chlorine Gas Generates 4% Chlorine Dioxide



MOLDS: Aspergillus niger, Penicillium citrium,

BACTERIA: Leuconostoc mesenteroides, and Lactobacillus buchneri

Both commonly found in citrus juices

Time to kill 90 % of organisms on stainless steel surfaces (below)

Log Reduction Time \pm standard deviation (minutes)				
ClO ₂ (mg/L)	MOLDS		BACTERIA	
	P. citrium	A. niger	L.buchneri	L. mesenteroides
0.3	13.2 \pm 2.7	12.6 \pm 2.6	7.2 \pm 1.2	10.8 \pm 1.8
0.5	12.1 \pm 2.0	12.3 \pm 1.5	5.1 \pm 0.4	8.6 \pm 0.6
1	11.6 \pm 1.5	11.0 \pm 1.3	2.4 \pm 0.2	6.2 \pm 1.0
2	10.2 \pm 1.1	9.2 \pm 1.3	0.8 \pm 0.1	3.3 \pm 0.6
z-value	18.6	12.6	1.7	3.4

Important Factors for Disinfection

- Concentration (mg/l)
- Contact time
- Purity
- Relative humidity (higher is better)
- Surface: stainless, paper, Munkadur (epoxy)
- Crevices
- Presence of liquid water (acts as a sink)

- Gas sterilization of pilot-scale aseptic processing line and surge tank
- Evaluated using *Lactobacillus buchneri* (10^6), in orange juice
- Gas concentration 1 mg/liter; relative humidity 85 %
- Gas circulated through 1 ½” stainless tubing around stainless tank

Results

- *L. buchneri* grown in orange juice required 2 hrs to obtain sterility.
- Demonstrated that chlorine dioxide is effective against microorganisms in a high acid environment.

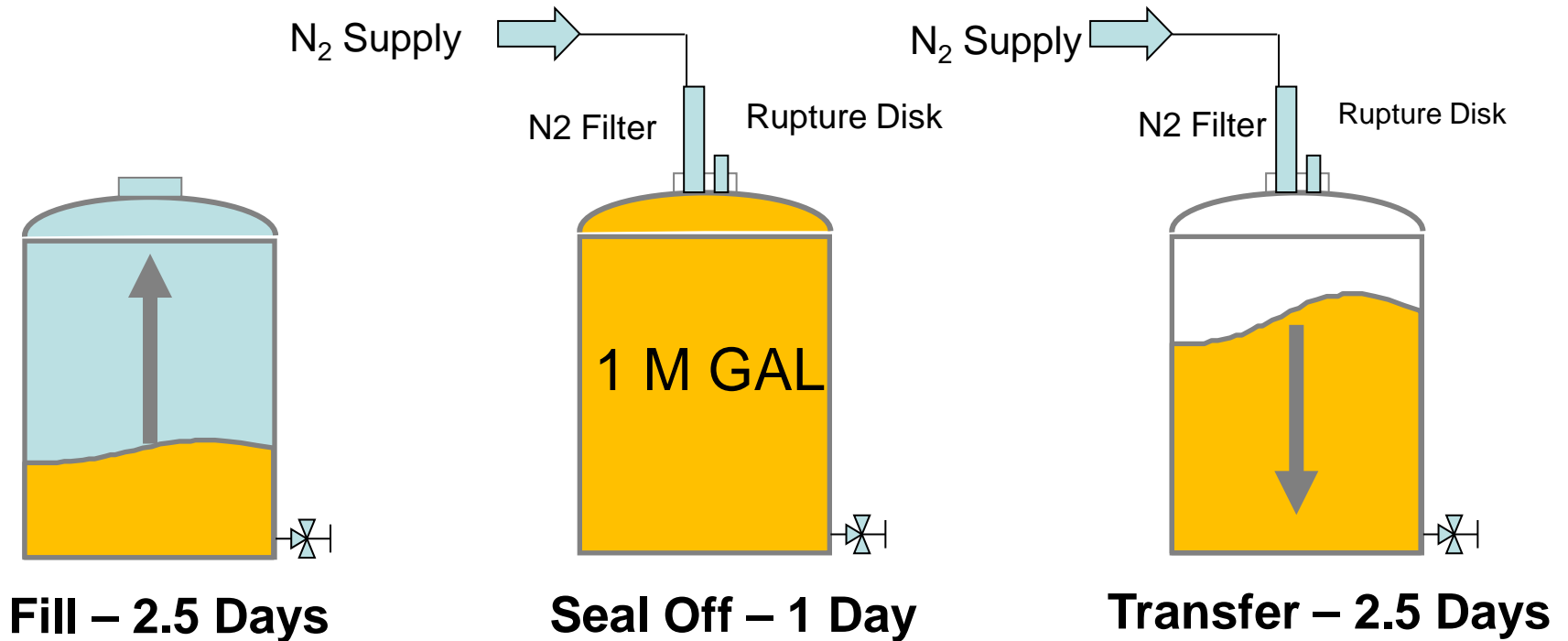


Why Chlorine Dioxide?

- ClO₂ is a broad-spectrum biocide (kills bacteria, yeast, molds, and inactivates viruses)
- Bulk Aseptic Storage Requires a Commercially Sterile Container
- Storage Tanks have been Historically Sterilized with Iodophor, an effective but timely process
- Three Main Drivers Behind Use of Chlorine Dioxide
 - ⇒ Reduction in Sterilization Time
 - ⇒ Reduction in Sterilization Cost
 - ⇒ Reduction in Water Usage

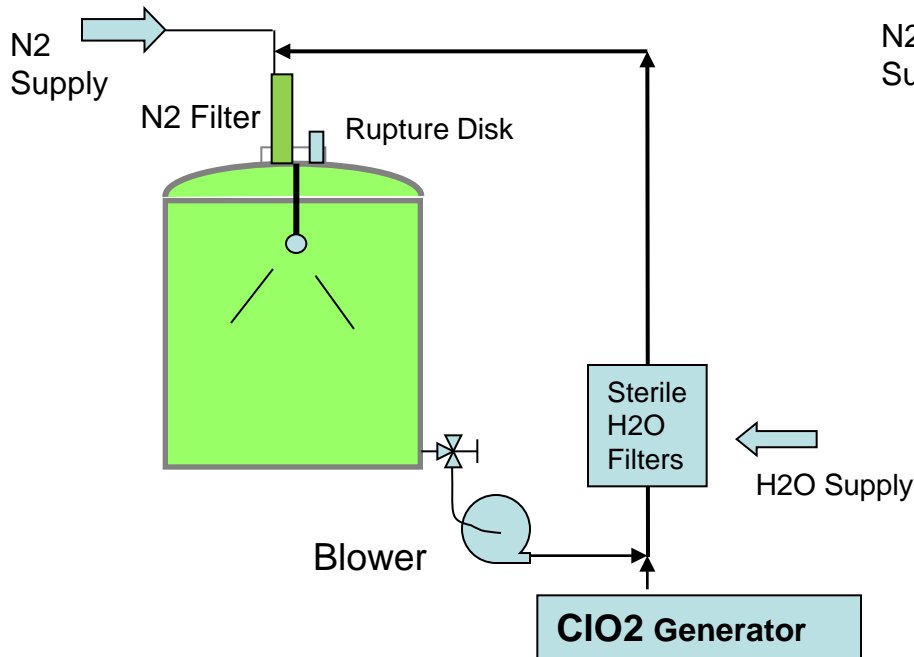
Current Sterilization Technology Process Solutions

- Million Gallon Bulk Storage Tanks (high acid products)
- Flooded with 1 Million gallons of Iodophor at 25 ppm
- Steam sterilize Nitrogen Filter
- Requires 6 days for entire sterilization process.

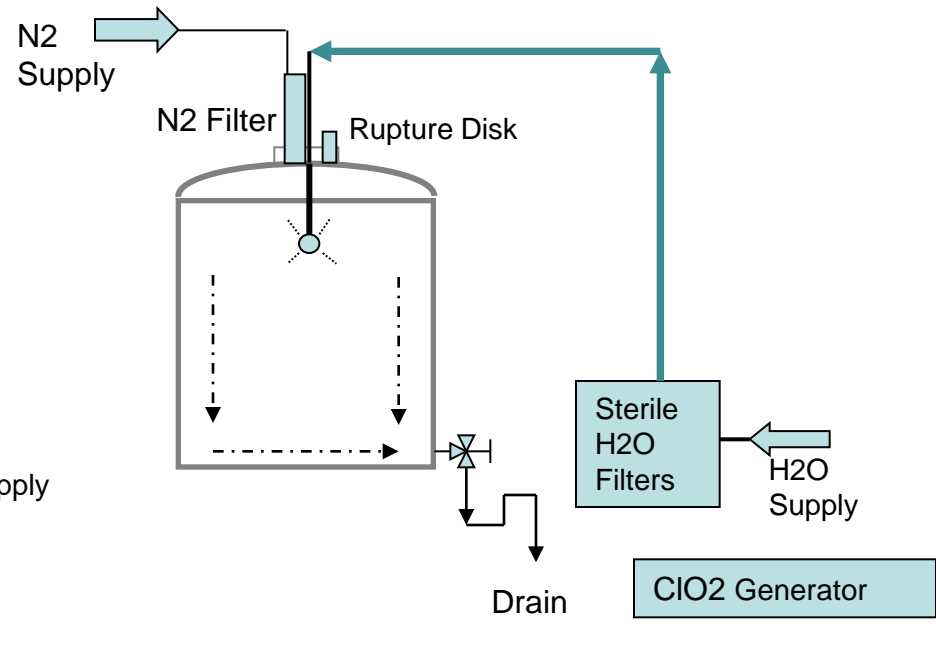


Chlorine Dioxide Tank Sterilization

- Performed at Ambient Temp
- Gas sterilization of N₂ Filter
- Sterilization Time < 1 Day
- Reduction in Utility Costs
- Reduction in Waste Water



Injection & Recirculation



Sterile Rinse

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Equipment for Bulk Storage Facilities

- A Bulk Aseptic Storage Facility with 1,000,000 Gallon Tanks Sterilized with Chlorine Dioxide Gas



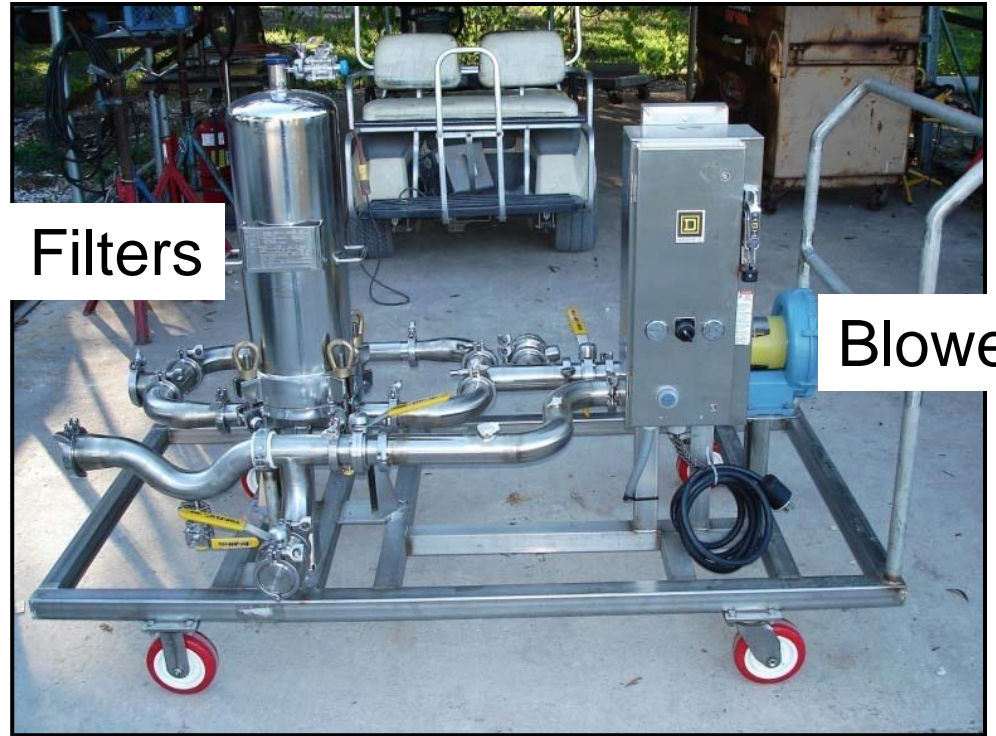
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Chlorine Dioxide Generator



Chlorine Dioxide Equipment



Portable For Small Tank Sterilization

1. 98 % Reduction in Water Use

- 1,000,000 Gallons of Iodophor vs 18,000 Gallons of Sterile Rinse Water

2. 90 % reduction in sterilization time

- 134 Hours for Iodophor Flood Sterilization vs 12 hrs for Chlorine Dioxide Gas

3. 63 % reduction in sterilization cost**

- vs. Cost of 1,000,000 Gallons of Iodophor

** Does not include capital equipment costs

Chlorine Dioxide in the Citrus Industry

- 39 Aseptic Intermodal Containers Currently in Service
 - ⇒ Sterilized with Chlorine Dioxide Gas
 - ⇒ Nearly 20,000,000 Gallons of Aseptic Product Transferred to Date
- Chlorine Dioxide has been Used to Sterilize Aseptic Transfer Lines for Loading and Unloading of Aseptic Intermodal Containers
- Recently Commissioned Bulk Aseptic Storage Facilities with Tanks as large as 1.5 million gallon capacity Sterilized with Chlorine Dioxide Gas

Potential Uses for Chlorine Dioxide

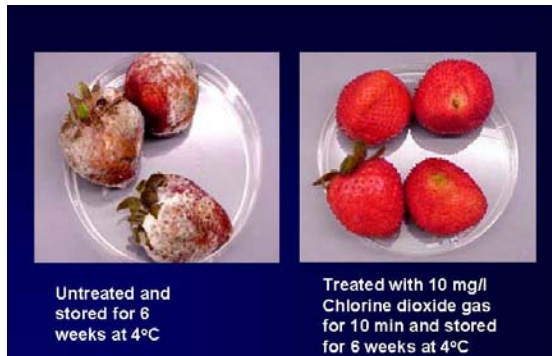
Bulk Tank Sterilization

Process Line Sterilization

Aseptic Transport Container Sterilization

Microbial Control on Produce Surfaces

Building Fumigation



Summary

Advantages

- Chlorine dioxide is effective for sterilization of bulk tanks
- Easy to generate at inherently safe levels due to generation method
- Under proper generation conditions (i.e., no excess chlorine)
- Biocidal properties are less influenced by pH than chlorine*
- ClO_2 gas is more convenient (especially for large vessels) than liquid sanitizers
- ClO_2 gas sterilization results in considerable savings in operational cost, maintenance costs, and time

QUESTIONS?