

# Ozone Disinfection and Oxidation

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a place of mind

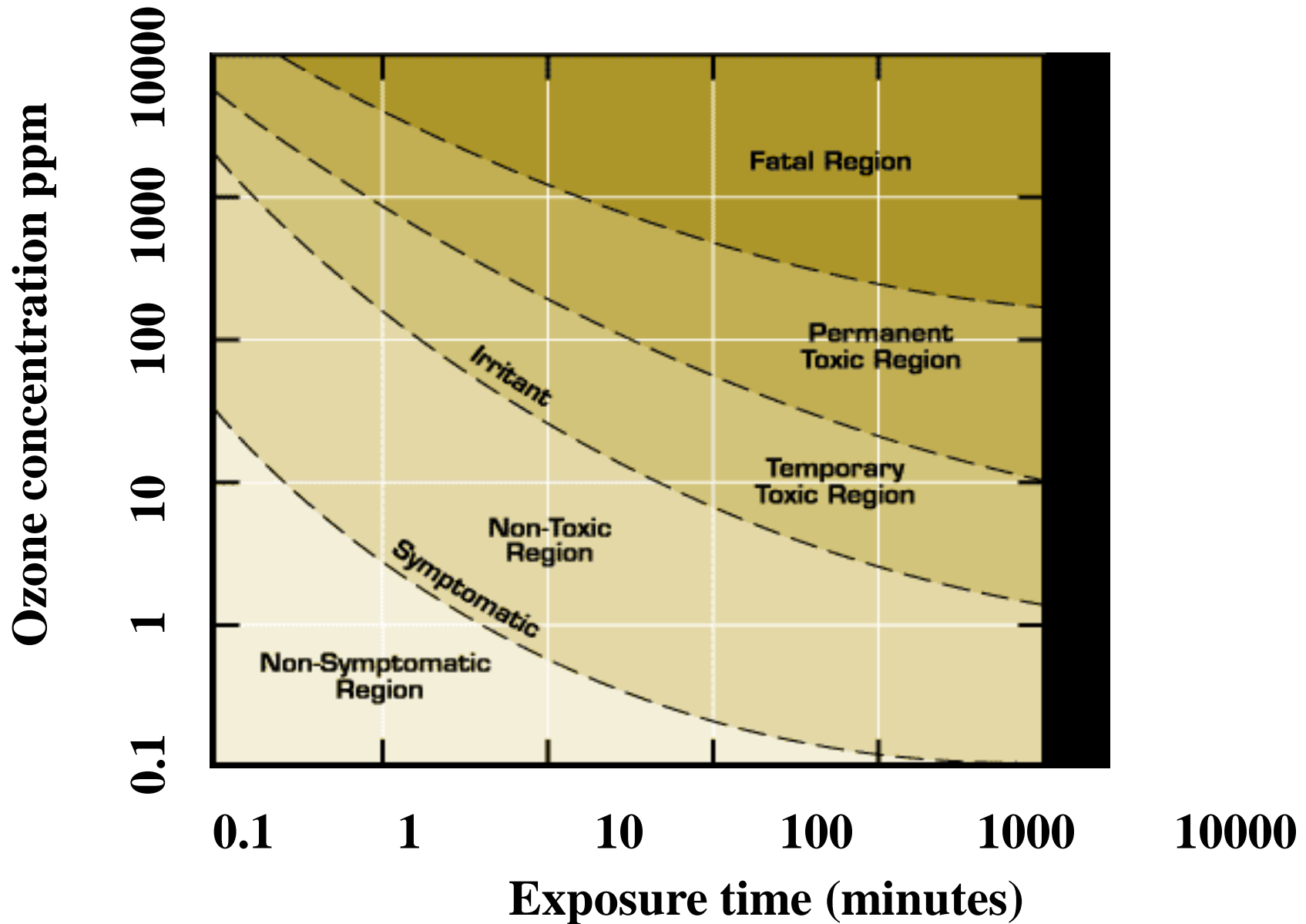
THE UNIVERSITY OF BRITISH COLUMBIA

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# What is Ozone?

- Unstable form of oxygen
- Produced on-site (electricity and oxygen)
- Reversible reaction ( $2\text{O}_3 \rightleftharpoons 3\text{O}_2$ ) - *reacts with itself and with OH<sup>-</sup> in water; less stable at higher pH*
- It has a pungent characteristic odour
- The odour is generally detectable by the human nose at concentrations between 0.02 and 0.05 ppm or approx. 1/100th of the recommended 15 minute exposure level.

# Toxicity of Ozone to Human



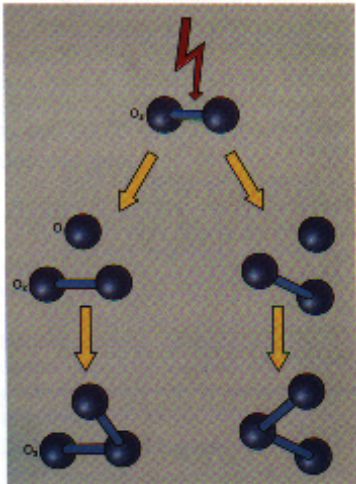
# History of Ozone

- 1783 - first discovered by Van Marum
- 1857 - the first electric discharge ozone generation device was constructed by Siemens
- 1893 - the first commercial application for potable water disinfection in Oudshoorn, the Netherlands
- 1906, an ozone installation for water treatment process in Nice, France (*this plant represents the oldest ozonation installation in continuous operation*)
- 1906 - First US ozone installation at New York City's Jerome Park Reservoir for taste and odour removal

# Ozone for Water Treatment

- Increased interest as an alternative to free chlorine (strong oxidant; strong microbiocidal activity; perhaps less toxic DBPs)
- Very powerful oxidant (more than hypochlorous acid)
- In aqueous solution is relatively unstable, having a half time of 20 to 30 min in distilled water at 20 °C
- Ozone cannot be stored, and must be prepared on-site
- Formed by passing dry air (or oxygen) through high voltage electrodes to produce gaseous ozone that is bubbled into the water to be treated

# Ozone Generation Principles



Feed gas with Oxygen

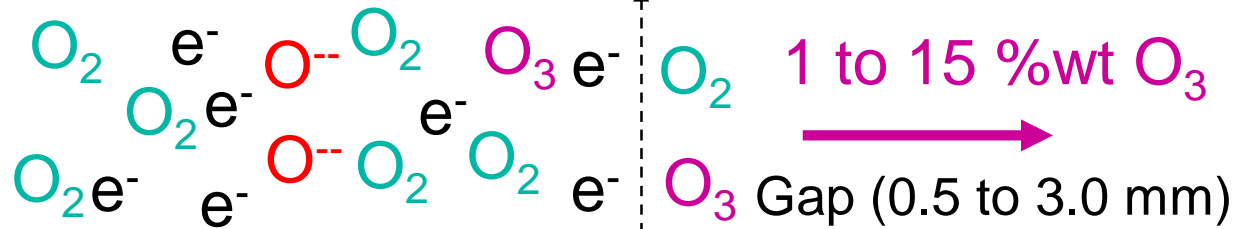
23 to 99 %wt  $O_2$

High Voltage

Power Supply

Metallic Coating

Glass/Ceramic Dielectric



Stainless Steel

Cooling Water

Ground Electrode

# Ozone Production Efficiency

## 1. UV Lamp

- Ave. ozone
- production/ UV lamp - 0.1 wt%

## 2. Corona Discharge

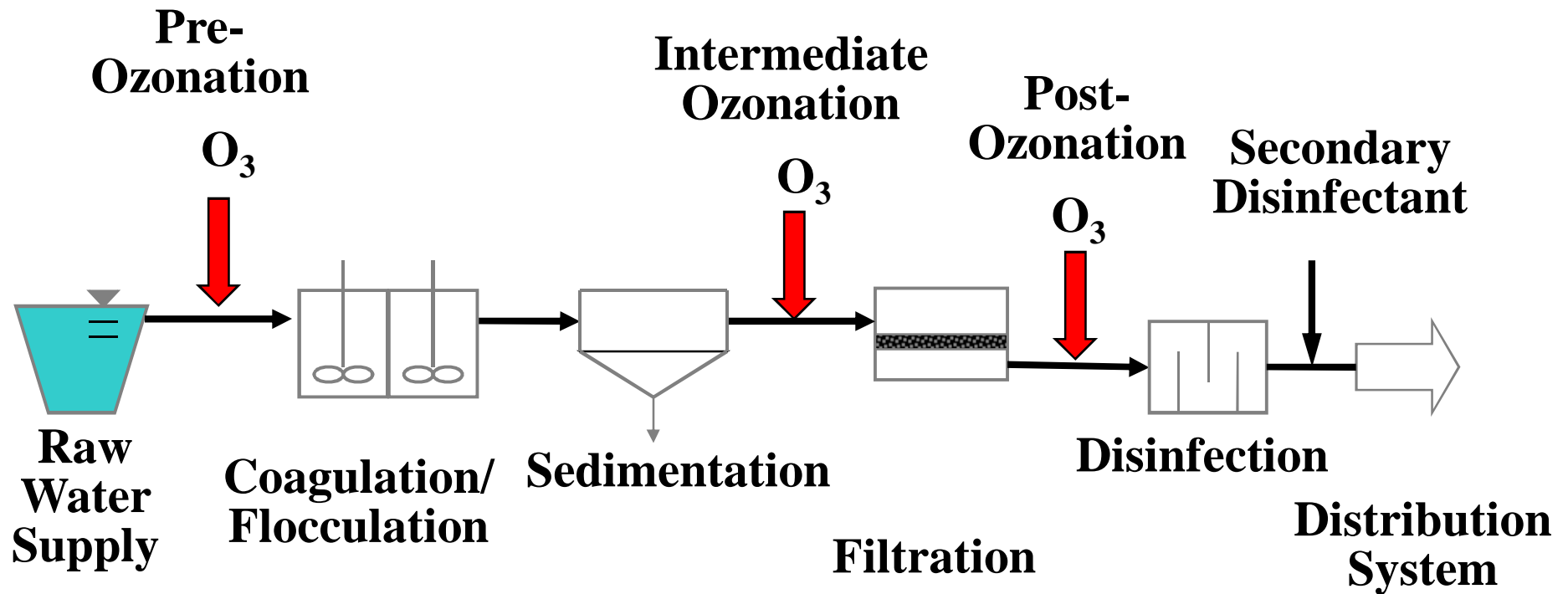
- Ave. Ozone production
- 0 - 10 wt%

## Energy Consumption

- 20 kWh/kg O<sub>3</sub> with air
- 10 kWh/kg O<sub>3</sub> with O<sub>2</sub>

# Ozone Application Points

*(within water treatment train)*





# What is it Used For?

- **Chemical oxidation** (*one of strongest oxidants*)
  - DBP Control
  - Organics Oxidation
- **Disinfection**
- Micro-flocculation
- Taste and Odor Control
- Iron and Manganese Oxidation
- Hydrogen Sulfide Oxidation
- Colour removal

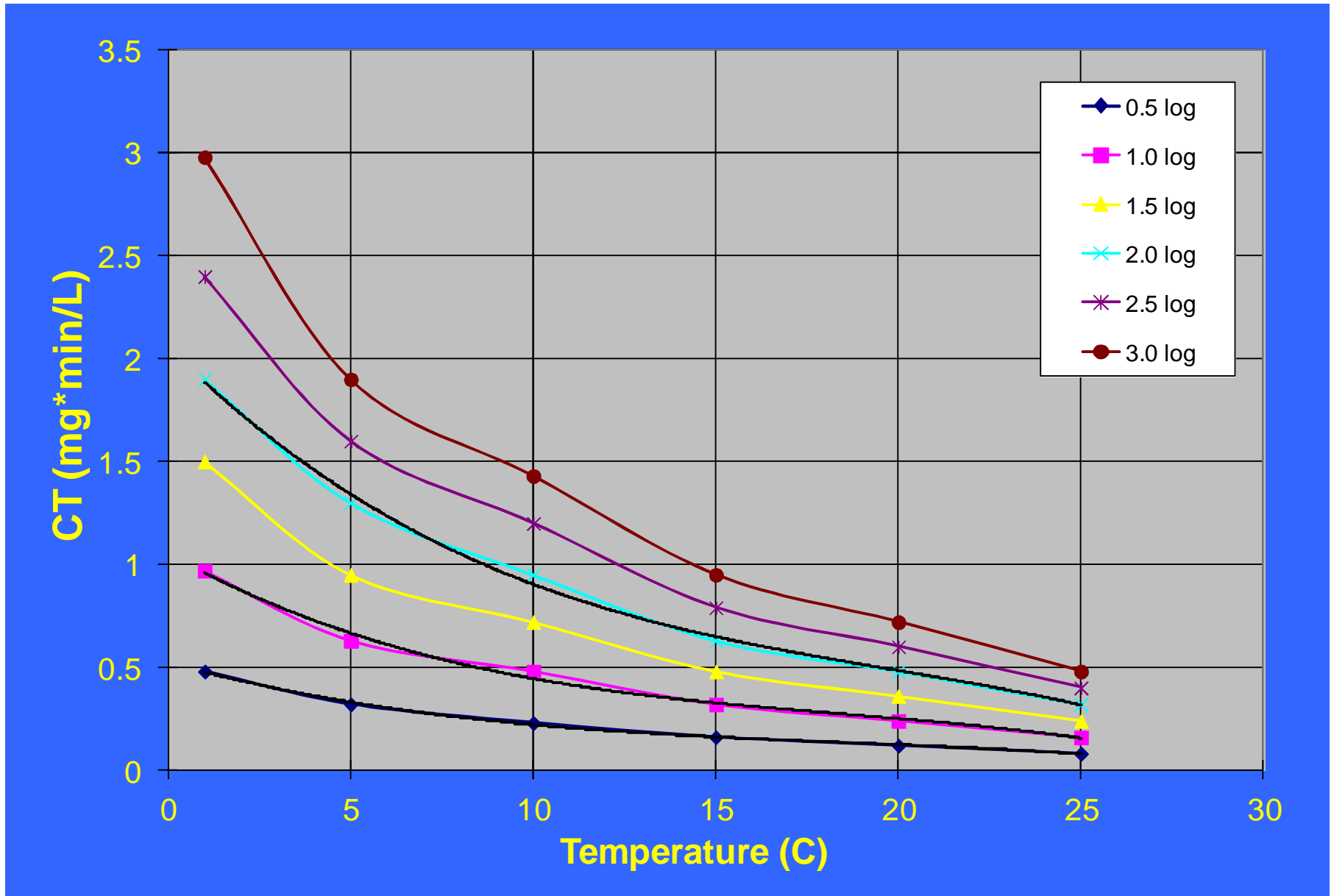
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# Disinfection Activity and the CT Concept

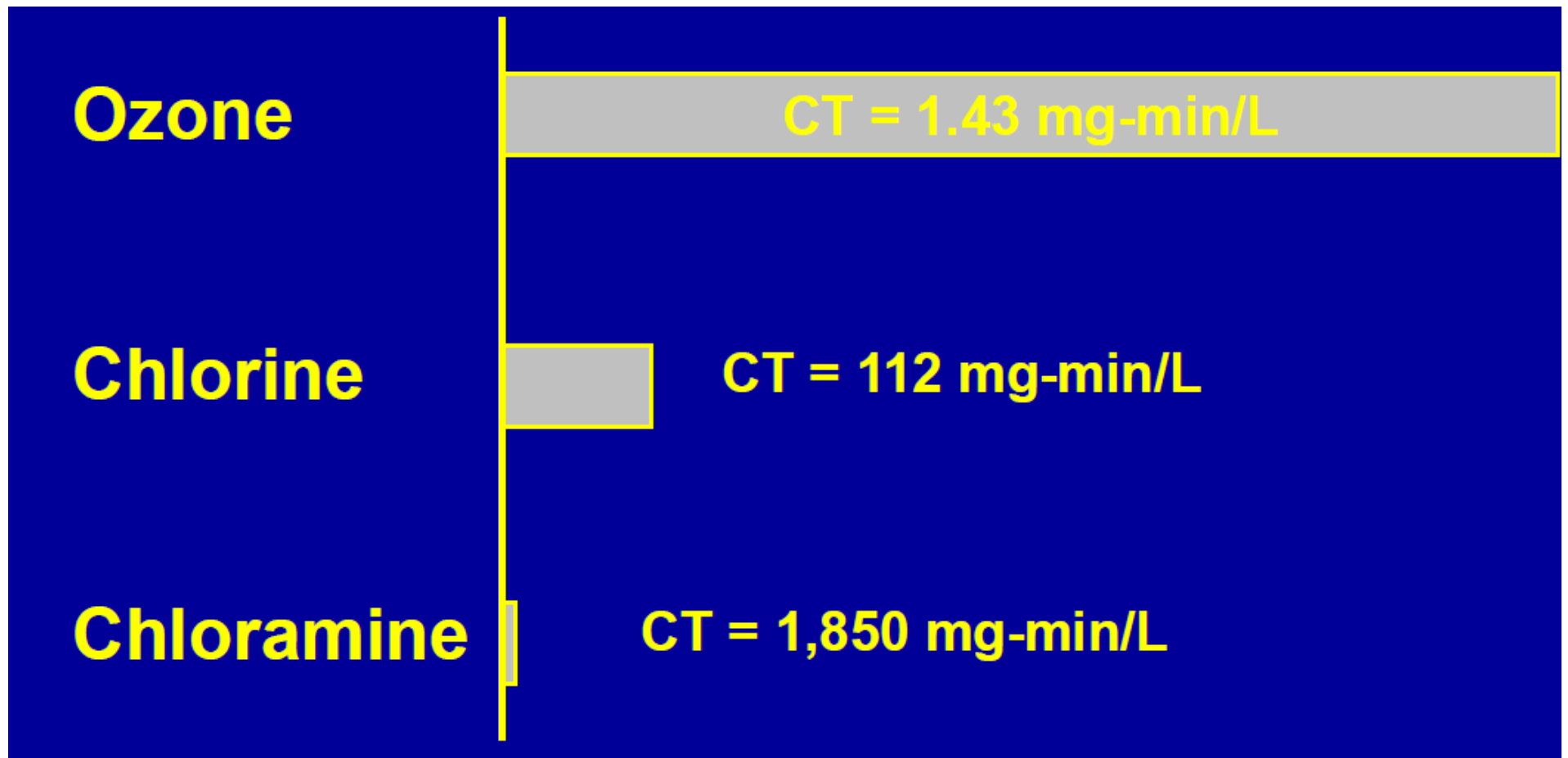
- Disinfection activity can be expressed as the product of disinfectant concentration ( $C$ ) and contact time ( $t$ )
  - Assumes first order kinetics (Chick's Law) such that disinfectant concentration and contact time have the same “weight” or contribution in disinfection activity and in contributing to  $CT$
- Example: If  $C.t = 100$  mg/l-minutes, then
  - If  $C = 10$  mg/l,  $T$  must = 10 min. in order to get  $C.t = 100$  mg/l-min.
  - If  $C = 1$  mg/l, then  $T$  must = 100 min. to get  $C.t = 100$  mg/l-min.
  - So, any combination of  $C$  and  $t$  giving a product of 100 is acceptable because  $C$  and  $t$  are interchangeable
- The  $C.t$  concept fails if disinfection kinetics do not follow Chick's Law (are not first-order or exponential)

# CT for Giardia Inactivation Credit



# Ozone Disinfection Power

CT for 3-log *Giardia* cyst inactivation @ 10°C and pH 7



# Ozone Disinfection

## (advantages and disadvantages)

### Advantages

- Adequate disinfection
- Reduction of chlorine or chloramine dosage
- Reduction of some DBPs: THMs, HAAs, and HANs
- Very small THM formation when applied with chloramine

### Disadvantages

- Reduction with bromide ion resulting in brominated DBPs
- Increase in biodegradable organic matter
- No residual disinfectant

# Ozone vs. UV and Membrane

- Membrane integrity and cleaning is an important factor, depending on raw water quality
- Taste and odour problems can not be resolved with UV or membrane applications
- Micropollutants cannot be removed by UV or membranes. *data indicates that ozone has an improved capability to remove these compounds*
- Algae toxins are not affected by membrane or UV applications
- Ozone is known for its ability to remove algae toxins

# What is it Used For?

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  - DBP Control
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- **Disinfection**
- Micro-flocculation
- Taste and Odor Control
- Iron and Manganese Oxidation
- Hydrogen Sulfide Oxidation



# Ozonation of water

- Ozone reacts with substances in two different ways
  - direct
  - indirect
- These different reaction pathways lead to different oxidation products and are controlled by different types of kinetics

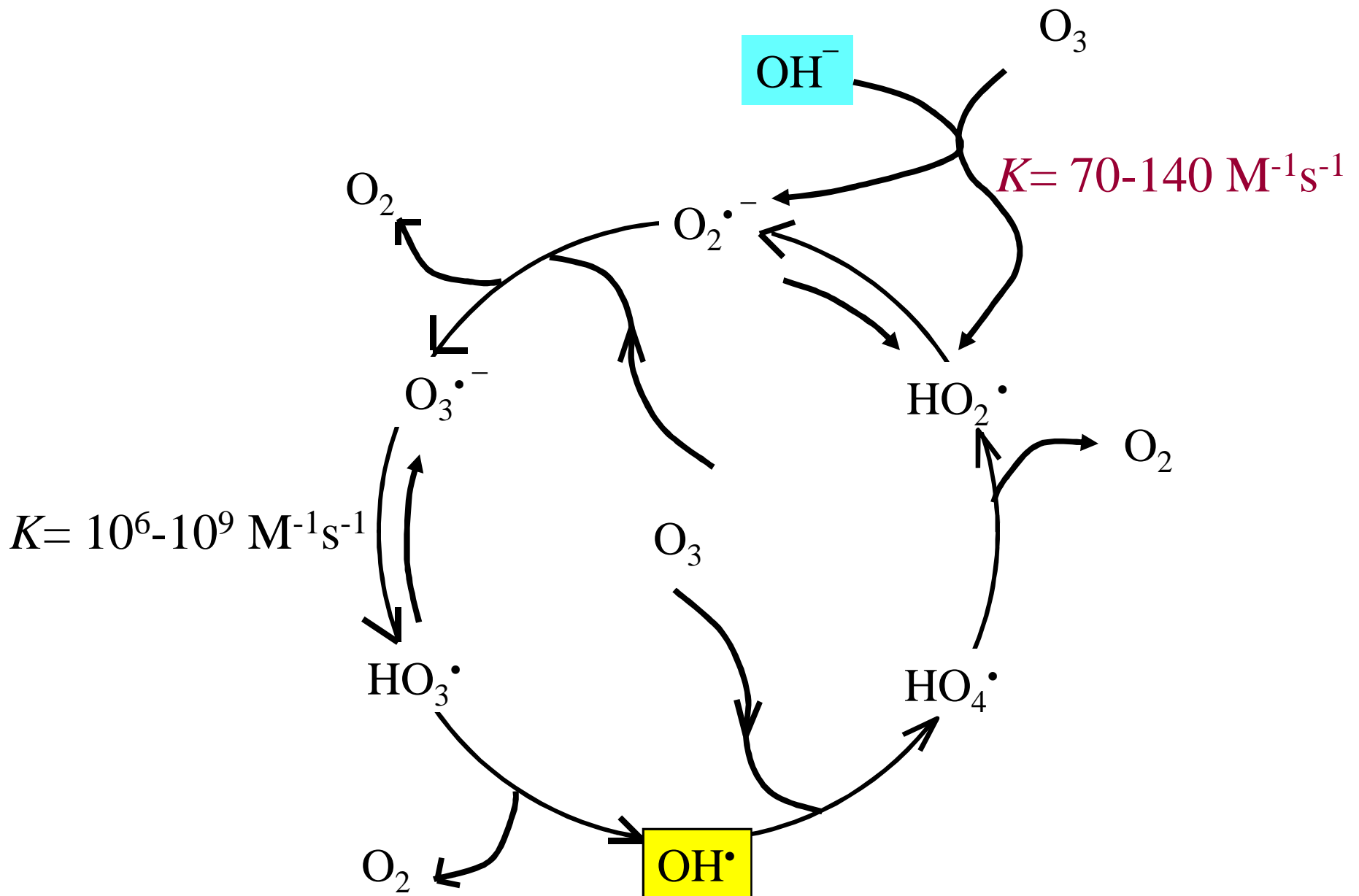
## **Direct reaction:**

- This is a selective reaction with relatively slow reaction rate constant (e.g.  $k=1.0 \cdot 10^3 \text{ M}^{-1}\text{s}^{-1}$ )
- The ozone molecule reacts with the unsaturated bond due to its dipolar structure and leads to a splitting of the bond

# Degree of removal of trace organics (full scale water treatment)

<u>substance</u>	<u>Removal (%)</u>
Taste & odor	20-90
Alkanes	<10
Aromatics & chloroaromatics	30-100
Aldehydes, alcohols	Low
Pesticides	0-80

# Indirect Reaction Pathway



# Factors Affecting Ozonation Reactor

## ■ Ozone concentration

- The equilibrium  $O_3$  conc. in water, all other things being equal, will vary with the ozone conc. in the feed gas

## ■ Bubble size

- Smaller bubbles have a larger surface area per unit volume

## ■ Pressure

- The gas transfer rate is dependent on pressure

## ■ The ozone demand of water

- Presence of reduced Fe and Mn speeds up the removal of ozone

## ■ pH

- At elevated pH values ozone decays rapidly

# How Much Ozone is Needed?

- Based on:
  - Pilot Plant Studies
  - Previous Experience
  - Extrapolated Models
- Typical Dosages:
  - Disinfection 1-3 mg/L
  - Chemical Oxidation
    - 4-6 mg O<sub>3</sub>/mg S
    - 1.0 mg O<sub>3</sub>/mg NO<sub>2</sub>
    - 0.9 mg O<sub>3</sub>/mg Mn
    - 0.4 mg O<sub>3</sub>/mg Fe



# How Long Does it React?

- Reactors (Contactors) are multi-celled chambers or pipelines
- Range from 4 minutes up to 40 minutes
- Longer contact times for cold water disinfection



# Design Considerations

1. Selection of a feed gas system
2. Preparation of the feed gas system
3. Selection of the ozone generator
4. Design of the ozone contact basin
5. Destruction of off-gas ozone.

# Feed Gas Selection

- Ozone may be generated from air, oxygen- enriched air, or oxygen.
- Concentration of ozone:
  - Air: 1.5~5% by weight
  - High-purity oxygen: 8~14% by the same generator
- Both air and pure oxygen must be treated prior to being fed to the ozone generator to maximize the ozone production and to minimize maintenance work on the ozonator.
- Oxygen: stored as a liquid (LOX) or generated on-site through either a cryogenic process with vacuum swing adsorption (VSA) or with pressure swing adsorption (PSA).



# Air vs. High Purity Gas Oxygen Feed

<b>Source</b>	<b>Advantages</b>	<b>Disadvantages</b>
<b>Air</b>	Commonly used equipment Proven technology Suitable for small and large systems	More energy consumed per ozone volume produced Extensive gas handling equipment required Max. ozone conc. of 3~5%
<b>Oxygen (general)</b>	Higher ozone conc. (8~14%) Approximately doubles ozone conc. for same generator Suitable for small and large systems	Safety concerns Oxygen resistant materials required
<b>LOX</b>	Less equipment required Simple to operate and maintain Suitable for small and intermediate systems Can store excess oxygen to meet peak demands	Variable LOX costs Storage of oxygen on site (fire codes, i.e., safety concerns) Loss of LOX in storage when not in use
<b>Cryogenic</b>	Equipment similar to air preparation systems Feasible for large systems Can store excess oxygen to meet peak demands	More complex than LOX Extensive gas handling equipment required Capital intensive Complex systems to operate and maintain

# Feed Gas Treatment

- Dust- reduces the efficiency of ozone production
- Oil - fouls the dielectric
- Nitrogen gas - produces nitric acid
- Moisture - reduces the life span of the dielectric of the ozone generator and increases the power requirement

*Generally composed of a precompressor with a 5  $\mu\text{m}$  paper filter, main compressor, after cooler, oil coalescer, refrigerant dryer (optional), heat reactivated desiccant dryer with activated alumina and molecular sieves or silica gel, 1  $\mu\text{m}$  filter, hygrometer, gas flow meter, and pressure- regulating valve.*

# Ozone Generation

Generated by passing a high voltage alternating current (6 ~ 20 kV) across a dielectric discharge gap through which oxygen-bearing gas is injected.

1. Low-frequency (50 ~ 60 Hz) units with variable voltage (10 ~ 20 kV) (single phase power);
2. Medium-frequency (200 ~ 1000 Hz) units with constant voltage, variable voltage, or frequency control (8 ~ 10 kV) (three phase power);
3. High-frequency (600 ~ 2000 Hz) units (8 ~ 10 kV) (three phase power).

# Ozone Generation

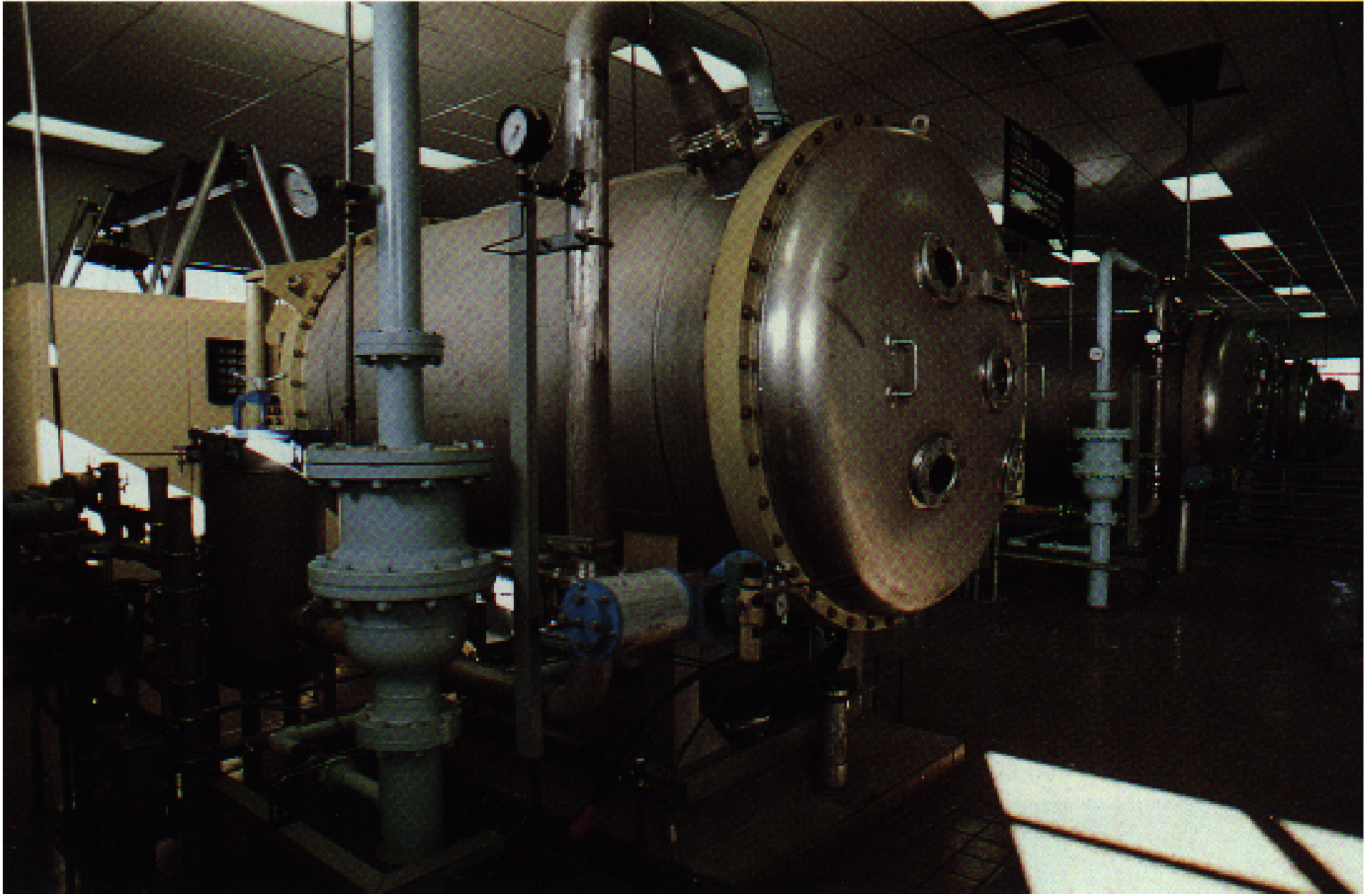
<b>Characteristic</b>	<b>Low (50 ~ 60 Hz)</b>	<b>Medium (up to 1,000 Hz)</b>	<b>High (&gt; 1,000 Hz)</b>
Degree of electronics sophistication	Low	High	High
Peak voltages	19.5	11.5	10
Turndown ratio	5:1	10:1	10:1
Cooling water required (gal/lb of ozone produced)	0.5 ~ 1.0	0.5 ~ 1.5	0.25 ~ 1
Typical application range	< 500 lb/day	to 2,000 lb/day	to 2,000 lb/day
Operating concentrations <ul style="list-style-type: none"> <li>• wt - % in air</li> <li>• wt - % in oxygen</li> </ul>	0.5 ~ 1.5% 2.0 ~ 5.0%	1.0 ~ 2.5% <sup>+</sup> 2 ~ 12%	1.0 ~ 2.5% <sup>+</sup> 2 ~ 12%
Optimum ozone production (as a proportion of total generator capacity)	60 ~ 75%	90 ~ 95%	90 ~ 95%
Optimum cooling water differential	8° ~ 10°F	5° ~ 8°F	5° ~ 8°F
Power required (kW-h/lb O <sub>3</sub> )	Air feed: 8 ~ 12 O <sub>2</sub> feed: 4 ~ 6	Air feed: 8 ~ 12 O <sub>2</sub> feed: 4 ~ 6	Air feed: 8 ~ 12 O <sub>2</sub> feed: 4 ~ 6
Air feed system power requirements (kW-h/lb O <sub>3</sub> )	5 ~ 7	5 ~ 7	5 ~ 7

*Source: Adapted from Rice (1996) with modifications.*

# Ozone Generator & Contactors



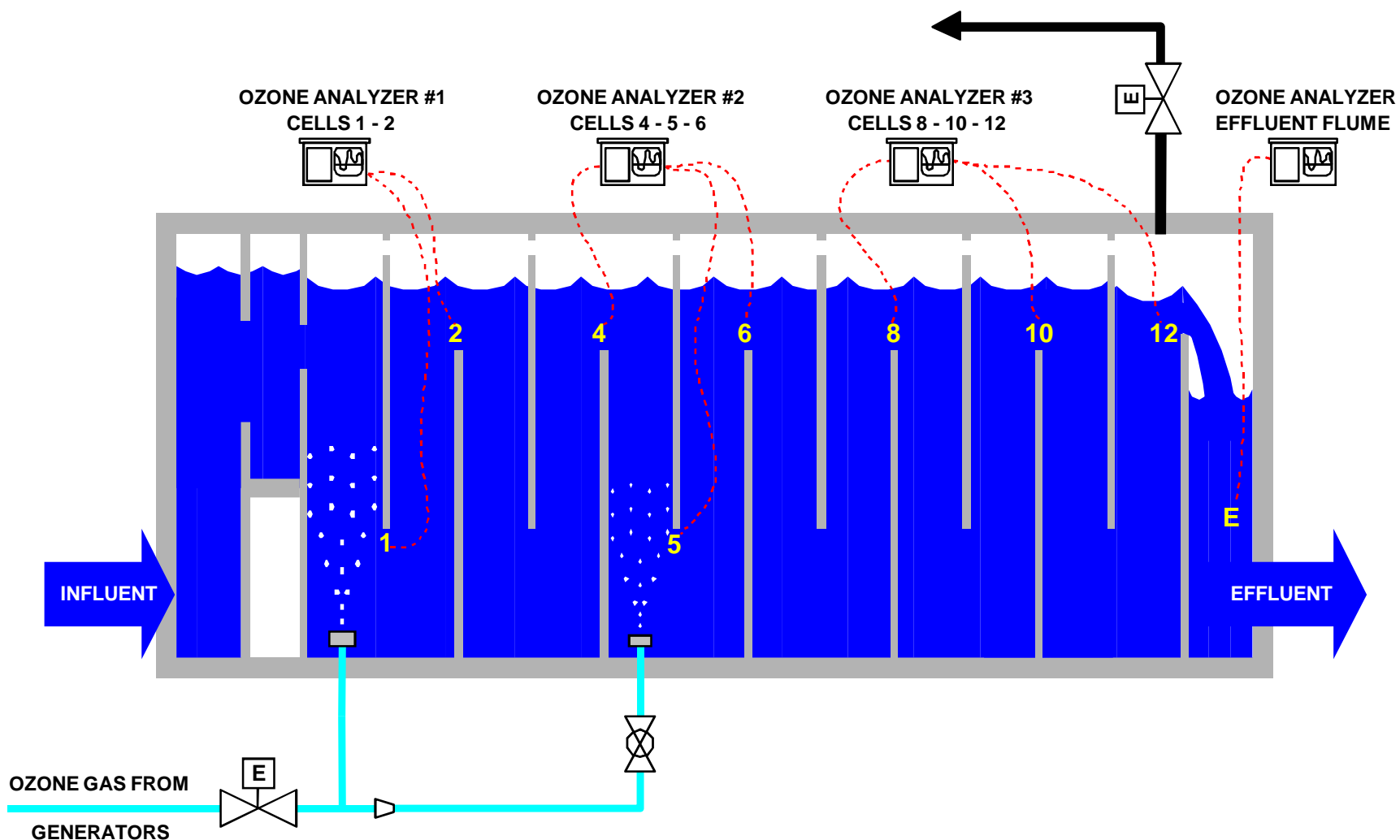
# Ozone Generators



# Ozone Contact Tank

- Ozone solubility: low  
20°C: 6.43 and 12.86 mg/L for ozone conc. of 18.11 and 36.21 mg/L. *Thus, effective mixing is critical.*
- Diffused bubbles (con- and counter-current);
- Positive pressure injection (U-tube);
- Negative pressure (Venturi tube);
- Turbine mixer tank;
- Packed tower; and
- In-line
- Completely closed; composed of concrete, located outside, two cells in each tank, capable of handling 50% of the max. daily flow.

# Conventional Contactor Design

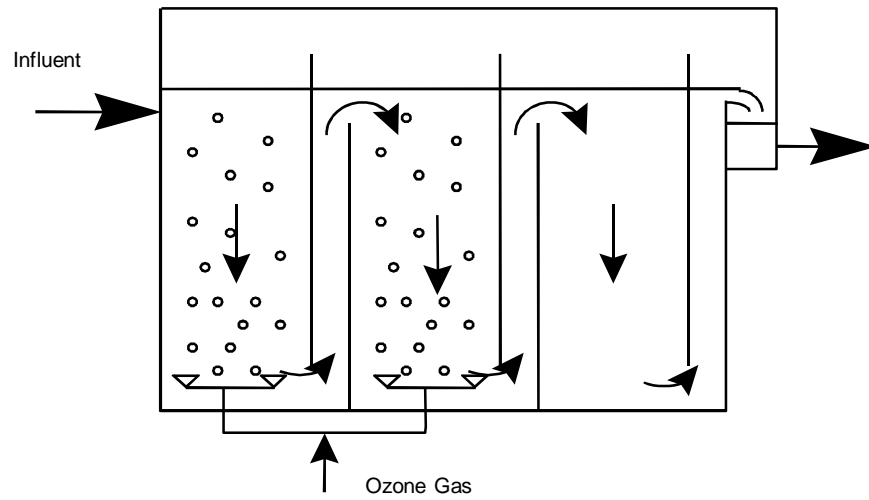


*Measure "Conc." at several points in the contactor*

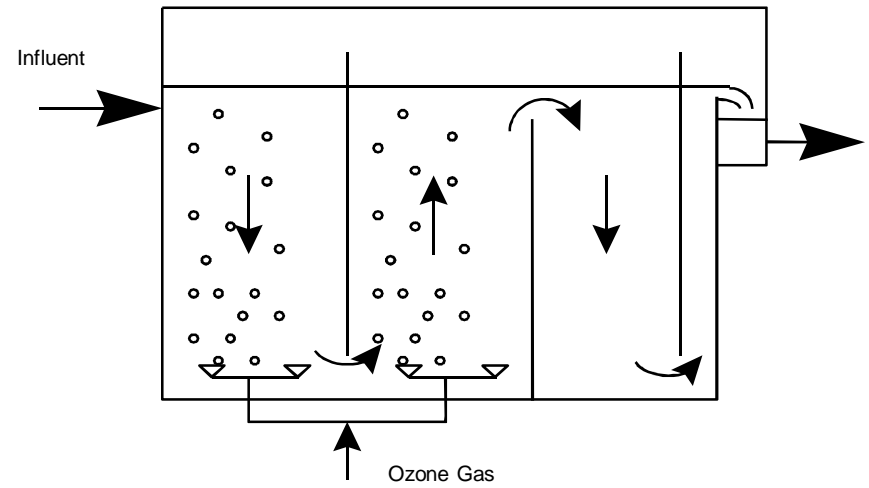


# Ozone Bubble Contactor

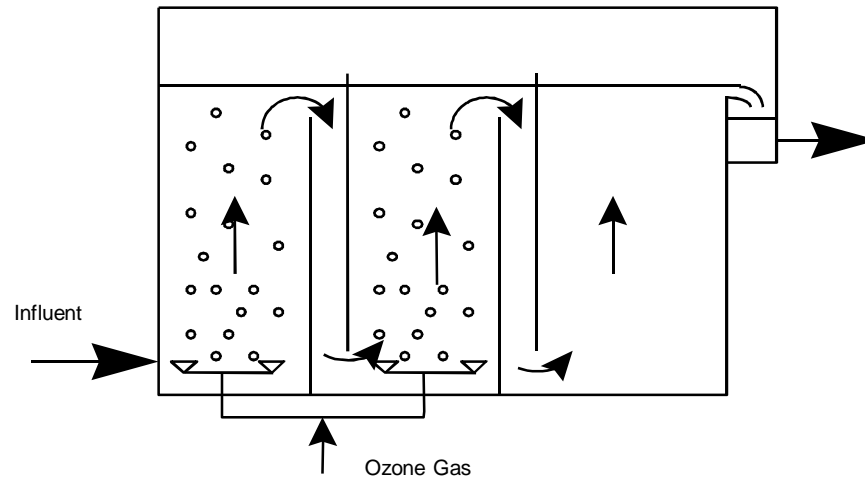
Counter Current Contactor



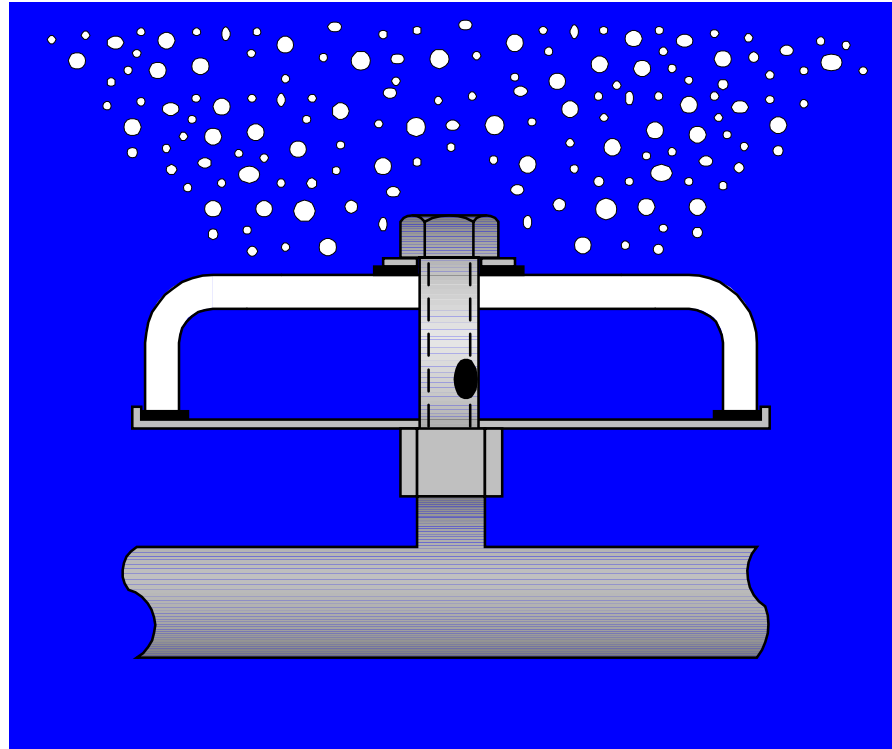
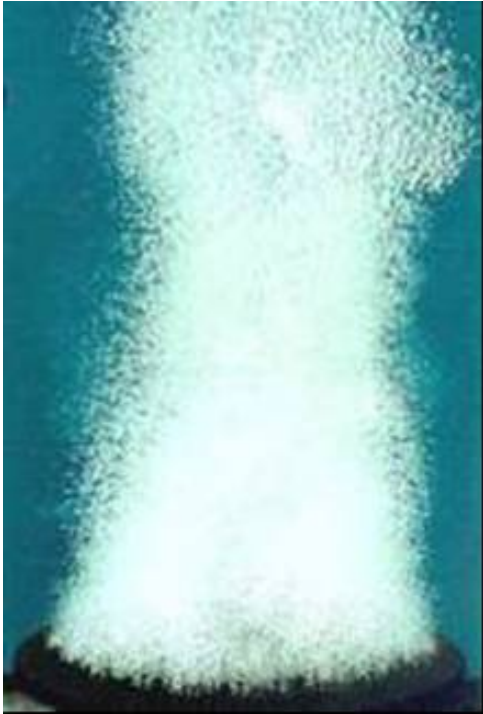
Counter and Cocurrent Contactor



Cocurrent Contactor



# Ozone Diffuser



7" Ceramic Dome  
Diffusers

# Ozone Contactor Diffusers



# Ozone Contactor Diffusers



# Bubble Diffuser Contactor

(advantages & disadvantages)

## Advantages

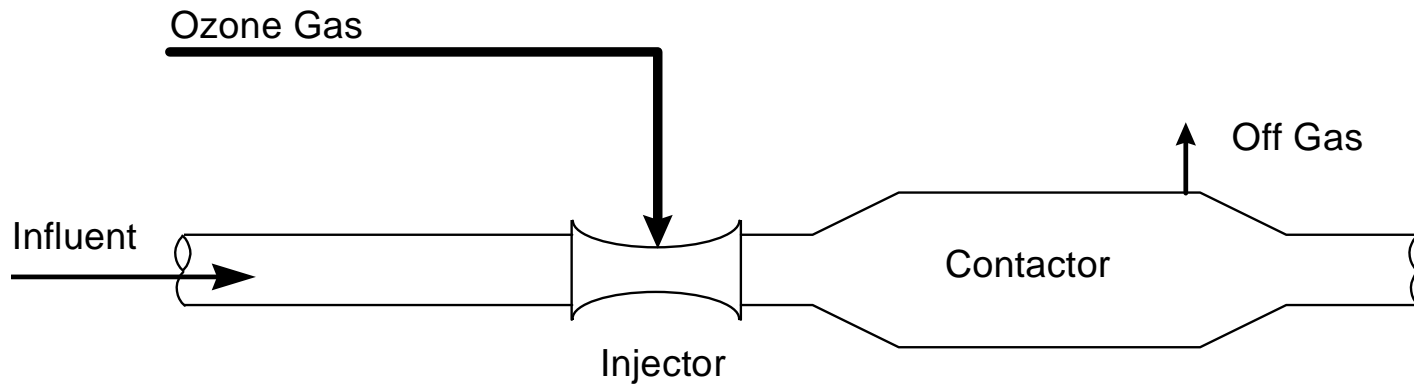
- No moving parts
- Effective ozone transfer
- Low hydraulic headloss
- Operational simplicity

## Disadvantages

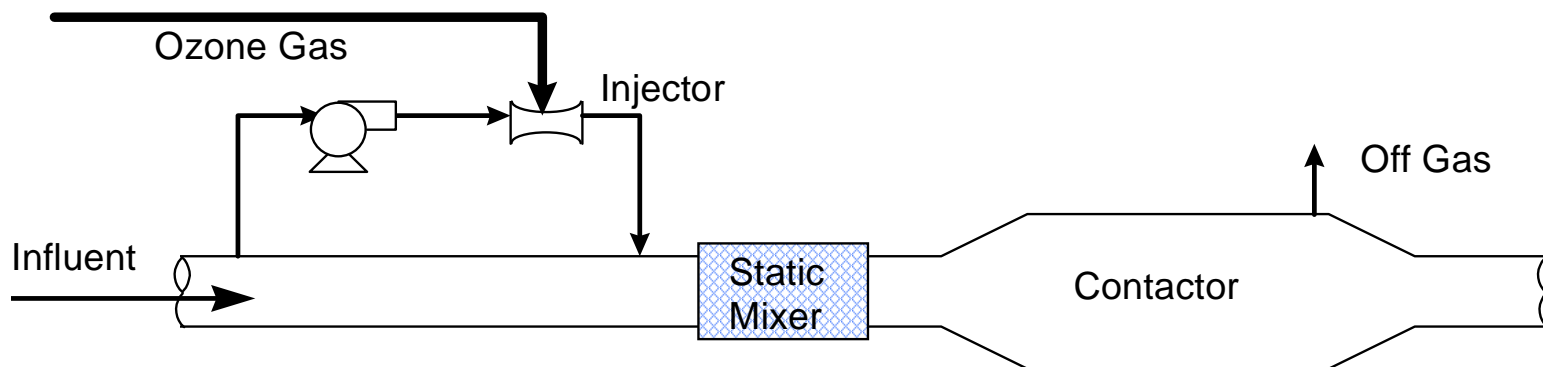
- Deep contact basins
- Vertical channeling of bubbles
- Maintenance of gaskets and piping

# Side Stream Ozone Injection System

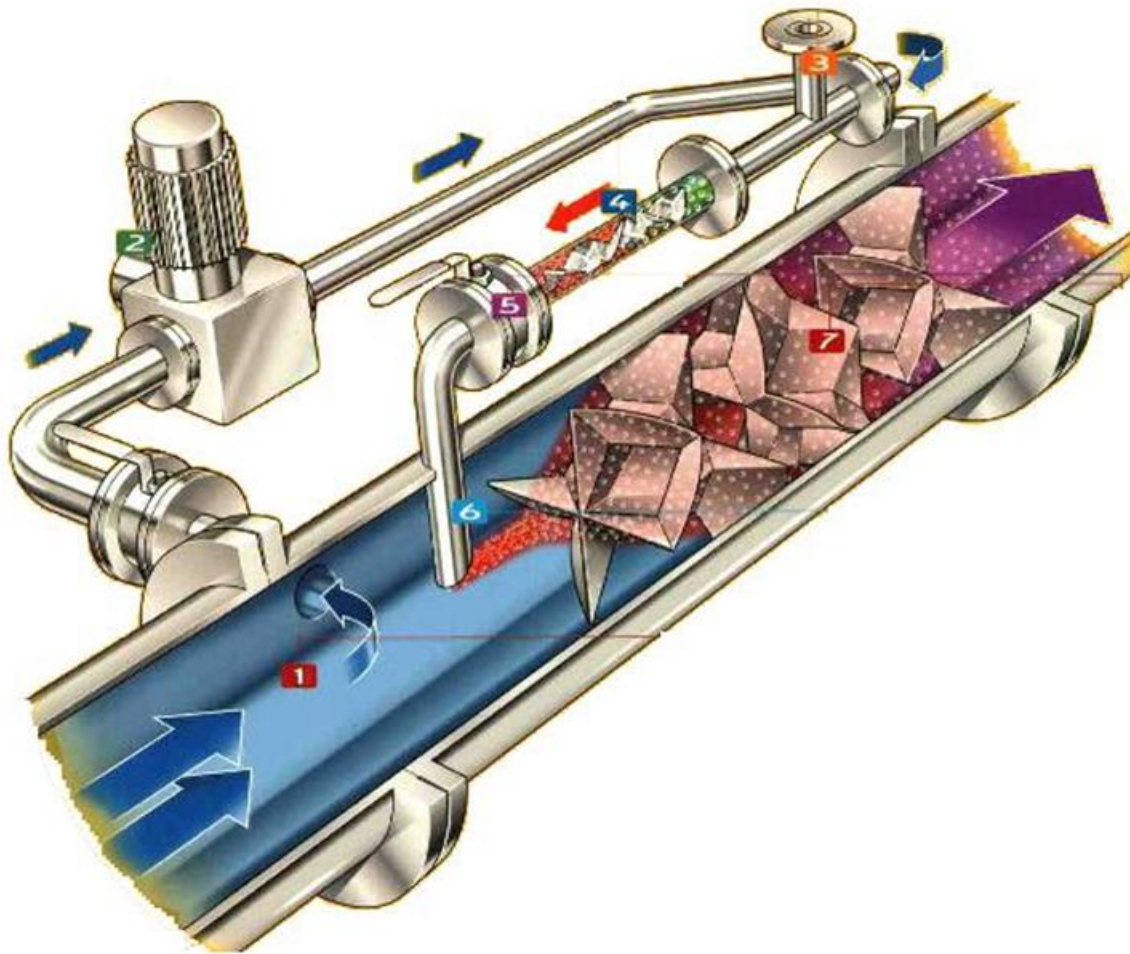
## A. In-line Injector System



## B. Sidestream Injector System



# Side Stream Ozone Injection



## Advantages

- Efficient gas dispersion
- High mass transfer efficiency
- No moving parts
- Compact design
- Low capital cost
- No contacting tanks

# **Injection Contacting**

## **(advantages and disadvantages)**

### **Advantages**

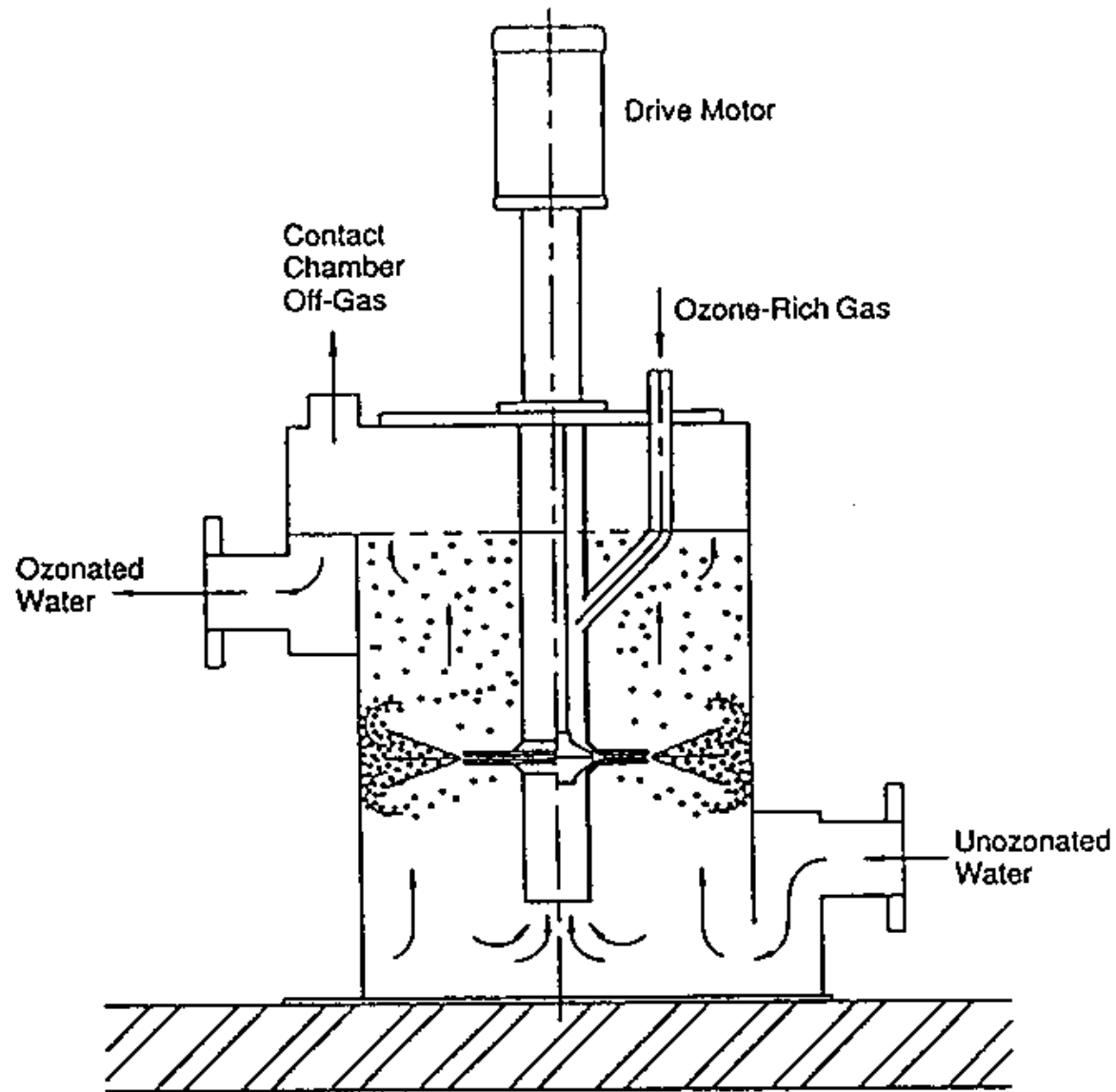
- Injection and static mixing have no moving parts
- Very effective ozone transfer
- Contactor depth less than bubble diffusion

### **Disadvantages**

- Additional headloss (energy usage) due to static mixers which may require pumping
- Turndown capability limited by injection system
- More complex operation and high cost



# Turbine Mixer Ozone Contactor



# **Turbine Mixer Ozone Contactor**

## **(advantages and disadvantages)**

### **Advantages**

- Ozone transfer is enhanced by high turbulence resulting in small bubble size
- Contactor depth less than bubble diffusion
- Aspirating turbines can draw off-gas from other chambers for reuse
- Eliminates diffuser clogging concerns

### **Disadvantages**

- Require energy input
- Constant gas flow rate should be maintained, reducing ozone transfer efficiency
- Maintenance requirements for turbine and motor

# Off-Gas Destruction

- Ozone transfer efficiency: 90 ~ 95%.
  - Hence, 5 ~ 10% goes to off-gas (500 ppm by volume).
  - Must be reduced to levels below the OSHA (< 0.0002 g/m for 8 hr working day) and local Air Quality Management District (AQMD) standards.
- 1. Thermal destruction (570 ~ 660°F) for the air feed gas system
- 2. Thermal destruction with catalyst (85 ~ 120°F) for the oxygen feed gas system
- 3. Catalytic destruction: metal (platinum or palladium), metal oxides (aluminum oxide or manganese oxide), or hydroxides and peroxides. *Lower operating cost*

# Other Design Criteria

- **Ozone dosage** 1.5~3 mg/L (normal)
- **# of ozone generator** Min. two, preferably three, one always as standby

## Ozone generator

- Min. production 10~20% of rated capacity
- Max. production 75% of rated capacity
- Cooling water temp. < 24°C at the inlet
- Vessel construction Pressure vessel (15 psig) constructed with 304 SS or 316 SS with Teflon gaskets

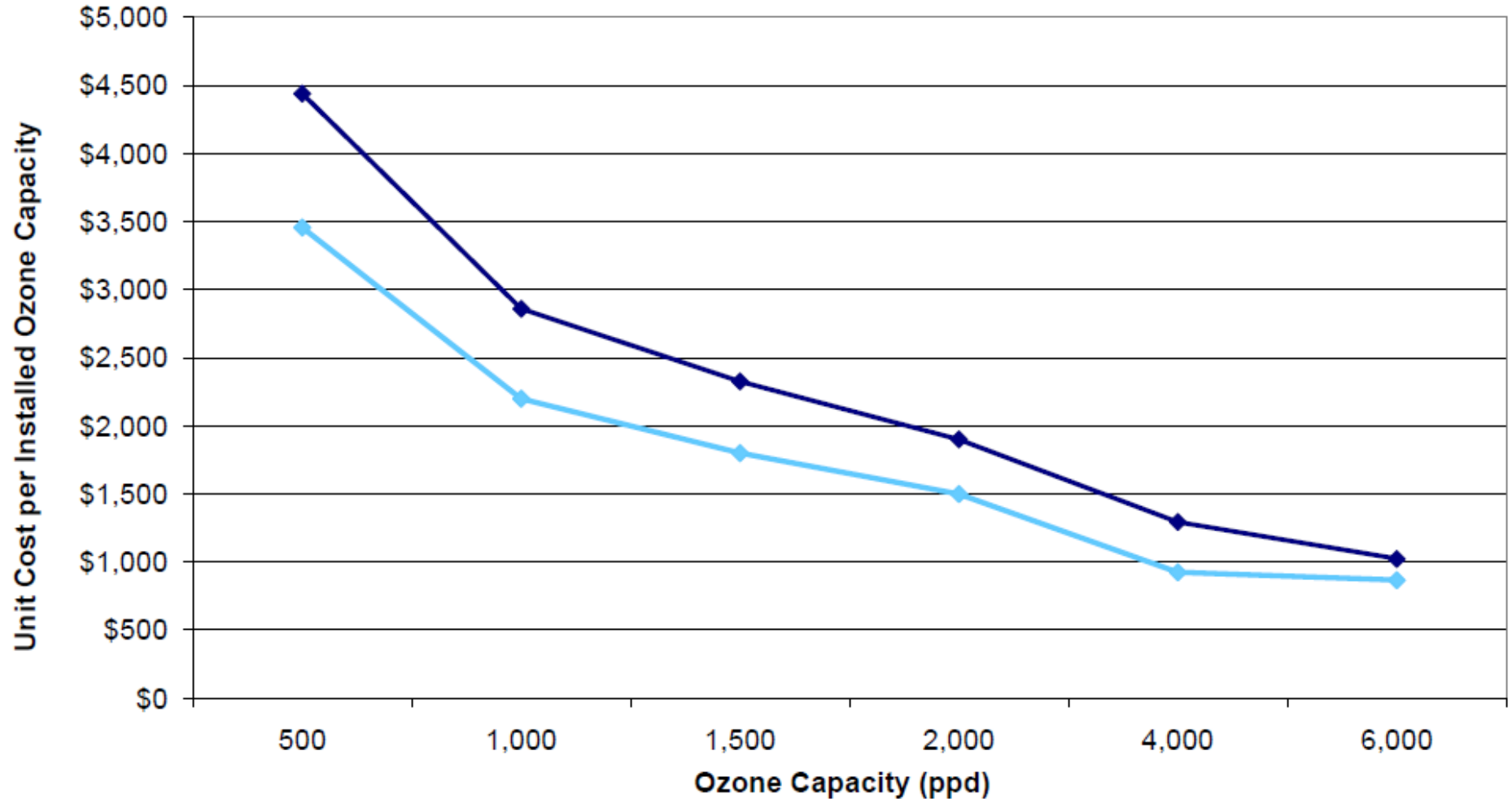
## Ozone contact tanks

- Number of tanks Min. two
- Transfer efficiency Min. 95% if possible (90~95%)
- Retention time 5~15 min. (usually < 8 min)
- Water depth 18~20 ft
- Diffuser depth 16~18 ft

# Representative WTP Ozone System Costs

<b>APPLICATION</b>						
Facility Name	Danville, IN	Lawton, OK	Lake City, FL	Wichita, KS T/O Control, Micro-flocculation	Albuquerque, NM	Dekalb Cty, GA
Role of Ozone	Fe & Mn Removal	Disinfection	H2S Removal		Disinfection, T&O	Disinfection
Facility Capacity	1.4 MGD	5 MGD	9 MGD	80 mgd	92 MGD	150 MGD
Installed Capacity Ozone Generation - lbs/day	80 ppd	440 ppd	900 ppd	3,340 lb/d	2,400 ppd	6,000 ppd
Feed gas	LOX	LOX	LOX	LOX	LOX	LOX
<b>CAPITAL COSTS</b>						
Generators	\$175,000	\$540,000	\$705,000	\$1,866,510	\$825,000	\$1,175,000
Feed Gas (1)	\$50,000	\$95,000	\$60,000	\$464,955	\$55,000	\$170,000
Contacting (2)	\$165,000	\$230,000	\$465,000	\$359,030	\$860,000	\$950,000
Instrumentation and Control	\$90,000	\$135,000	\$120,000	\$21,185	\$190,000	\$210,000
Safety	\$35,000	\$30,000	\$40,000	\$44,600	\$40,000	\$85,000
Other * (3)	\$85,000	\$270,000	\$210,000	\$110,051	\$230,000	\$310,000
Subtotal	\$600,000	\$1,300,000	\$1,600,000	\$2,821,731	\$2,200,000	\$2,900,000

# Representative WTP Ozone System Costs



# Cost Factors

## Factors influencing Capital Cost

- Process (dose, contacting)
- Feed Gas
- Injection/Contacting

## Factors influencing O&M Costs

- Local power and LOX costs
- Process Control

# Ozone Applications in other industries

- **Hospitality**
  - Gaming halls, casinos, bowling venues
- **Food processing and storage**
  - Fruits and vegetables cleanings and storage
  - Fresh meat, fish and poultry washing
- **Farming applications**
  - Fish and poultry farms
- **Horticulture**
  - Nurseries, cut flower storage, mushroom growing
- **Retail and workplace**
  - Office space, business centres, restaurants



# Ozone Applications *in Hospitality Industry*

- Ozone has been applied in large scale in HVAC systems of many hospitality businesses and public areas
  - Increased IAQ problems due to sealed buildings and less makeup (outside) air metered into HVAC systems.
  - Increased public intolerance for smoking and the realization that many common chemicals contribute to poor IAQ.
  - Attractive payback economics due to savings in energy and in replenishments for carbon filters (which are otherwise used)
  - New ozone generator and ozone monitor designs.

# Ozone Applications *in Hospitality Industry*

- Case of Bingo Hall in Washington State
  - ~ 2000 m<sup>2</sup> total area (with ~800 m<sup>2</sup> smoking area)
  - complaints from players and employees in the smoking section about strong odors and physical discomfort associated with exposure to excessive levels of tobacco smoke, VOCs – burning and itchy eyes, dry throat, headaches, nausea
  - Two 3,500 cfm exhaust fans were added to the smoking section to evacuate the smoke
  - The energy cost of exhausting 7,000 cfm of conditioned air ran in excess of \$350 per month and caused the internal temperature to fluctuate beyond acceptable norms during extremes of temperature.

# Ozone Applications *in Hospitality Industry*

- Case of Bingo Hall in Washington State

**Two options of Activated Carbon and Ozone were considered**

- Activated Carbon was estimated to cost about **\$25,000 per year** (cost of replenishment of expended carbon)
- With **four 10 grams per hour ozone generators**, the installed price of ozone was around **\$22,000** plus small O&M expenses for quarterly cleanings and annual monitor calibration.

In addition, energy savings of **more than \$250 per month** due to reduced demand for outside air and reduced operation of the 7,000 cfm exhaust system.

# Challenges with the Use of Ozone in public areas

- Ozone concentration in public areas must be kept below harmful levels
- Safe concentrations generally are considered in the range 0.05-0.10 ppm
  - Most HVAC systems are programmed not to exceed 0.03-0.05 ppm
- O<sub>3</sub> concentrations are higher in the supply ducts, where the ozone generators feed in (typically 0.3-0.5 ppm).
- Bacteria, mold, mildew, and VOCs are greatly reduced in those ducts, and thus eventually in the entire HVAC system (O<sub>3</sub> drops in concentration by a factor of 10 or so due to these reactions as well as due to normal "half life" reversion back to oxygen

# Ozone Applications *in Food Processing*

- Case of fruit and vegetable cleaning and washing
  - Ozone dissolved in water for washing and disinfecting can dramatically reduce losses from spoiled produce
  - When compared to the traditional use of chlorine it offers distinct advantages.
    - The level of ozone in the rinse water can be conveniently and accurately controlled.
    - Ozone is not pH dependant.
    - Ozone does not cause the weight loss in fruit that chlorine does.
    - Ozone leaves no residue to taint the product.
    - It is produced as required and therefore needs no storage.

# **Ozone Applications** *in Fresh Meat, Fish & Poultry*

- Ozone dissolved in water as a wash or spray can be used in food processing as a potent disinfectant (to kill bacteria, viruses, parasites and fungi).
  - In 1997 ozone gained the FDA approval of GRAS (Generally Recognised As Safe) and later in 2001 was allowed as a direct food additive in contact with food including meat and poultry
- Gaseous ozone in storage or even processing environments can provide an effective treatment against airborne and surface contamination.

# What Have I told You?

- **Applications of ozone in disinfection and oxidation**
  - **Water treatment**
  - **Taste and odour control**
  - **Air treatment**
  - **Food processing**

# What to Watch For?

## The Design and Implementation of OZONE requires technical knowledge

- Design phase is very important and proper design is essential
- Control approaches vary for different applications
- Optimized dosage and tracking of systems performance should be considered
- Be aware of safety issues
- **Good Design + Trained and Aware Staff = Safe, efficient and sometimes low cost ozone system**



# Thank You !



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**a place of mind**

THE UNIVERSITY OF BRITISH COLUMBIA