Disinfection Practices for Water and Wastewater (Advanced)

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PMG Consulting, Inc.

OTCO Procrastinator's Workshop

December 15, 2020

Agenda

- General Relationships
  - Physical and chemical interactions
  - Demand-causing substances and byproduct formations
  - Residual development and maintenance
- Disinfection Methods
  - Chemistry for common disinfectants
- Pathogen Destruction Mechanisms
  - Disinfectant speciation
  - Biological destruction pathways

General Relationships

- Chemical and physical relationships govern all disinfection chemistry
  - Knowledge of these relationships increases operator skills and troubleshooting abilities
  - Allows operators to control conditions that optimize disinfection practices
- Treatment processes are managed to disinfect water for consumption and to meet regulatory objectives

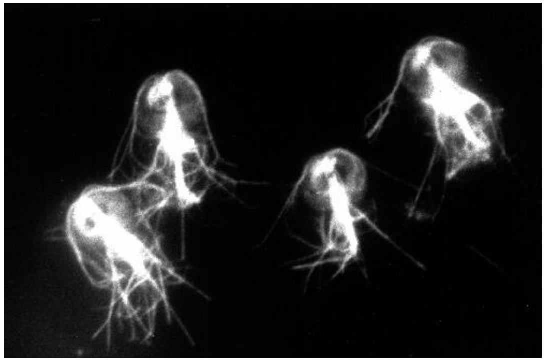
General Relationships

- Governing factors
  - Water pH
  - Mixing
  - Contact Time
  - Reaction Order
  - Residual concentration
  - Residual decay
  - Disinfecting power
  - Disinfection efficiency

General Relationships

Water pH

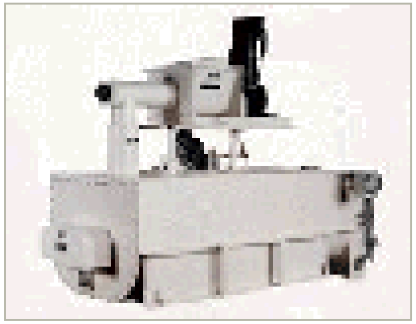
- High pH destroys microbial contaminants
- pH alters chemical species in water
- pH affects reaction rates and conversion rates



General Relationships

High pH

- Water-related microorganisms cannot tolerate pH values above about 7.8
- Lime/soda softening
  - 10.2 - 84% destruction
  - 10.6 - 92.4% destruction
  - 11.2 - 99.9% destruction
  - 11.5 - 99.99% destruction

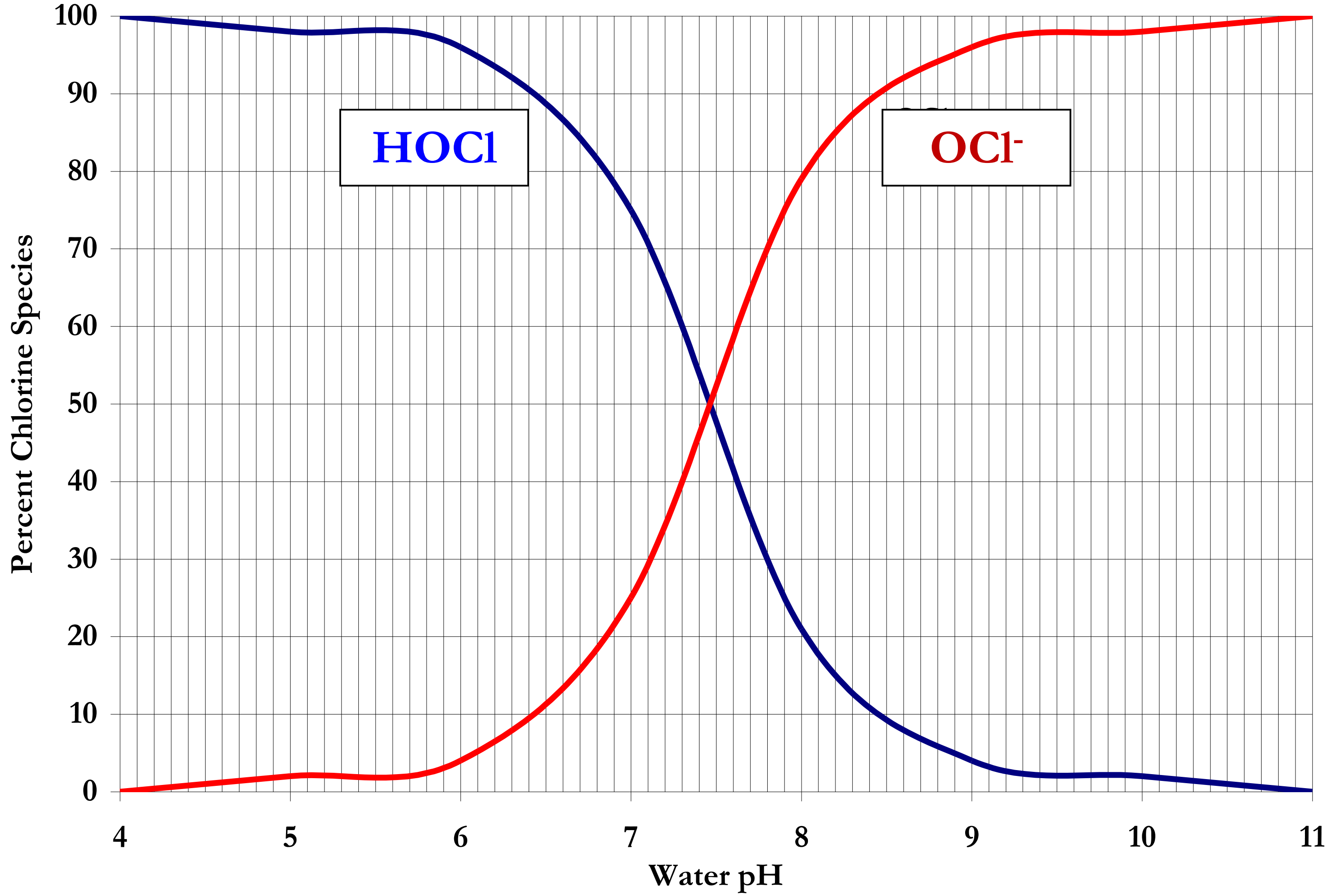


General Relationships

Water pH

- Chlorine more effective at low pH
  - Species at low pH predominantly hypochlorous acid (HOCl)
  - Species at high pH predominantly hypochlorite ion (OCl^{-})
- HOCl and OCl^{-} relationship based on pH and temperature
  - HOCl is 100 times more powerful than OCl^{-}

General Relationships



General Relationships

Water pH

- Affects conversion rates for free chlorine to monochloramine reactions
- Cl_2:N ratio 5, 25°C
  - pH 4 - 147 seconds
  - pH 7 - 0.2 seconds
  - pH 8.3 - 0.069 seconds
  - pH 12 - 33.2 seconds

General Relationships

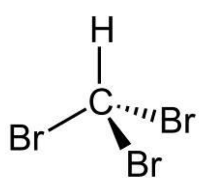
Mixing

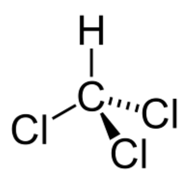
- Mixing research ongoing since 1936
- Water treatment often neglects mixing for disinfection
  - Injection into a pipe is most common
  - Some mixing occurs depending on pipe length and flow turbulence
- Wastewater applications historically used mixing to disperse disinfectant
  - Mechanical mixing prior to contact strongly recommended (Recommended Standards for Wastewater Works TSS)

General Relationships

Mixing

- Proper mixing increases disinfectant feed strength and reduces side reactions (White)
  - Chlorine/NH_4OH with mixing led to 85% monochloramine, 15% organo-chloramine formation
  - No mixing resulted in 45% monochloramine, 55% organo-chloramine formation
  - Other byproduct reactions also affected
    - DBP’s, free ammonia, free chlorine, monochloramine, etc.





General Relationships

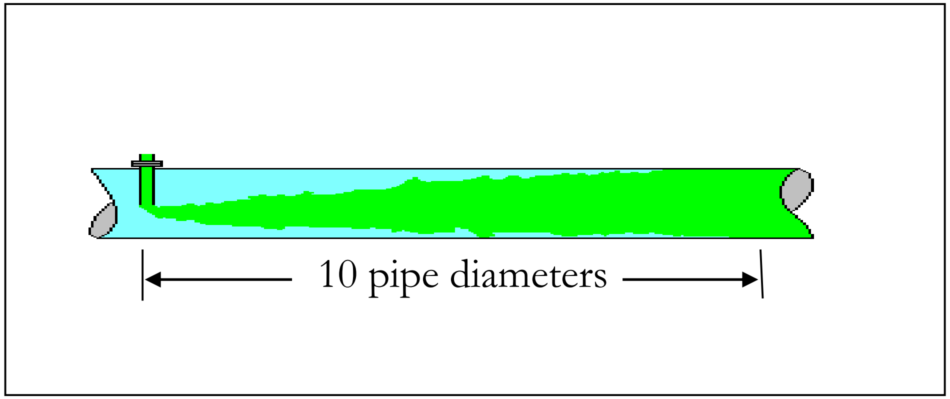
Mixing

- Researchers suggest minimum 500 sec^{-1} G value for disinfectant mixing
- Variations among researchers range from 500 sec^{-1} to 1,000 sec^{-1}
  - Turbulence needed for chemical dispersion
  - Effective mixing known to reduce byproduct concentrations from side reactions

General Relationships

Mixing

- Pipe mixing George White and others
  - Introduce chemical into middle of pipe flow
  - Turbulent flow conditions (Reynolds numbers greater than 100,000)
  - At least 10 pipe diameters travel length
  - Produce G values of at least 500 sec^{-1}



General Relationships

Mixing

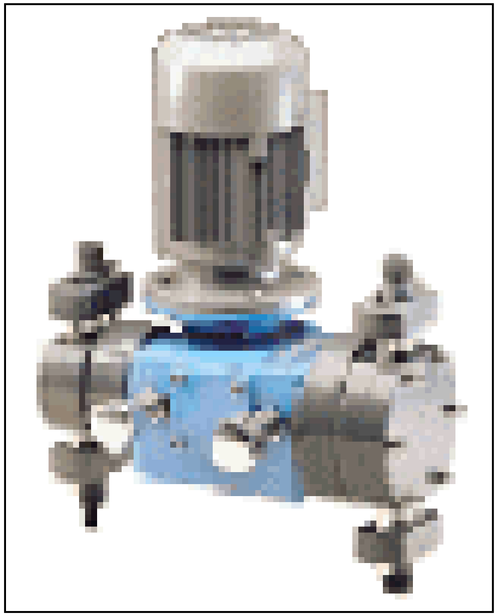
- G value equation Camp & Stein (1953)
  - Well understood relationships between mixing energy and water temperature
  - Colder water provides more efficient mixing
  - Warmer water needs more energy for the same G values

$$G = \sqrt{\frac{P}{\mu V}}$$

General Relationships

Contact Time

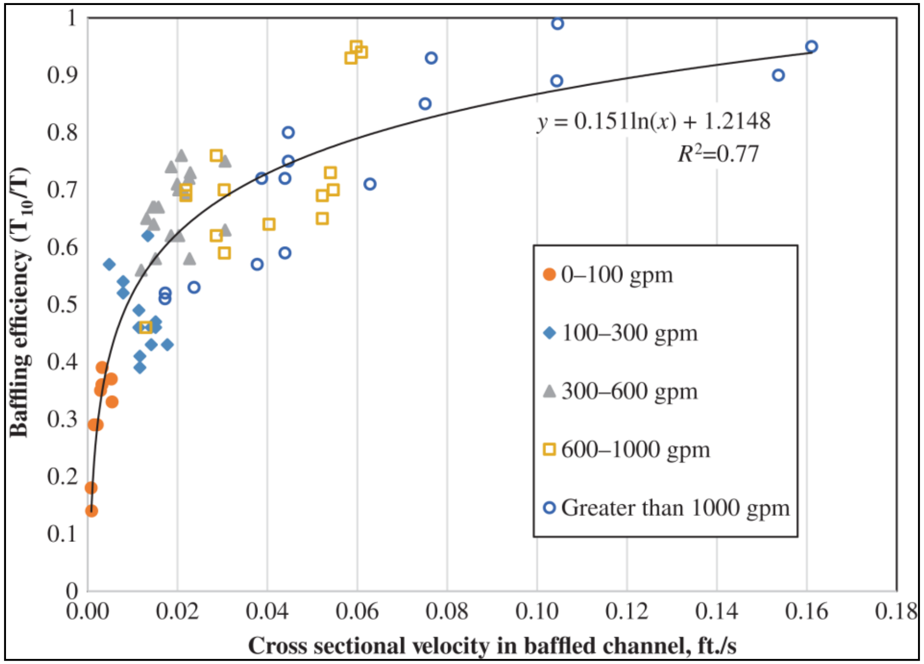
- Important for disinfection and microbial destruction
- Critical factors
  - Contact chamber design
  - Short-circuiting affects
  - Reaction rates
  - Competing reactions



General Relationships

Contact Time

- Other important factors
  - Water temperature
  - Water pH
  - Disinfectant residual
  - Type of disinfectant



General Relationships

Contact Time

- Disinfectant application does little for disinfection
  - Demand reactions compete for disinfectant
  - Mixing must disperse disinfectant quickly
- Persistent residuals needed for microbial destruction
  - Residuals function of pH, demand, contact time, water temperature
  - Residuals responsible for pathogen destruction

General Relationships

Reaction Order

- Disinfectants work in specific order of reaction
- Inorganics react first and consume oxidation potential
  - Iron, manganese, NH_3, IA & IIA periodic table elements
- Organics react next and consume oxidation potential and disinfectant
  - Humic and fulvic acids, tastes and odors, hydrocarbons, cyanotoxins, proteins, carbohydrates, biopolymers, organic acids
- Microbials react last and consume disinfectant
  - Destruction mechanisms presented later

General Relationships

Disinfecting Power

- Type of disinfectant impacts residual development and disinfection process
  - Free chlorine - 0.2 mg/L 10 minutes contact
  - Combined chlorine -1.0 mg/L 60 minutes contact
  - Chlorine dioxide - 0.04 mg/L 15 minutes contact

(Based on reactions with E. Coli for 99.9% inactivation)

General Relationships

Disinfecting Power

OH radical (•OH-)	24,400,000
Ozone	18,000,000
Bicarbonate radical (•HCO_3^-)	351,000
Hydrogen peroxide	347,000
Chlorine dioxide	263,000
Hypochlorous acid	10,000
Hypochlorite ion	100
Monochloramine	1.0
Fluorine	0.90
Bromine	0.63
Iodine	0.56

General Relationships

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Iodine	0.56

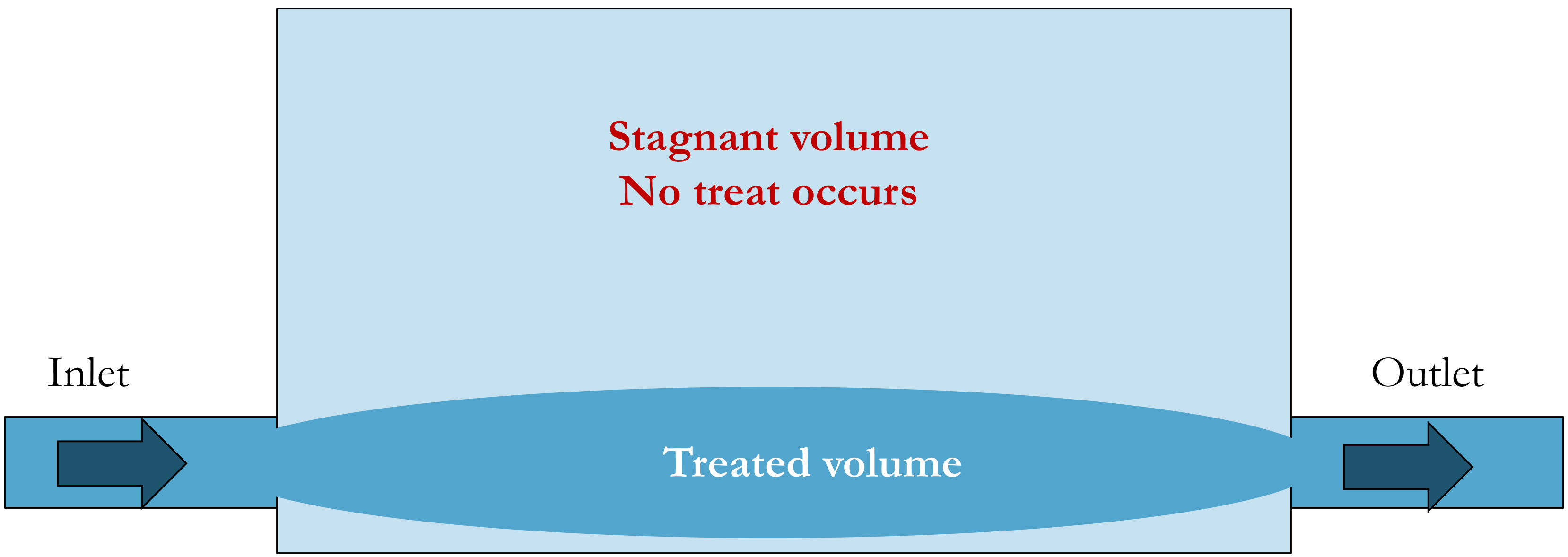
General Relationships

Short-circuiting

- Single most detrimental affect
  - Describes general flow path in basin
  - Defines stagnant areas where no disinfection occurs
  - Increases volume needed to demonstrate effective disinfection
  - Reduces process efficiency

General Relationships

Short-circuiting



General Relationships

Disinfection Byproducts

- Side reactions during disinfection
- Byproducts have no disinfecting power
  - Organo-chloramines
  - Hydrochloric acid (HCl)
  - Iron and manganese precipitates
  - Trihalomethanes (THMs)
  - Haloacetic acids (HAA5s)
  - Other DBPs
    - USEPA estimates more than 800 DBP's exist

General Relationships

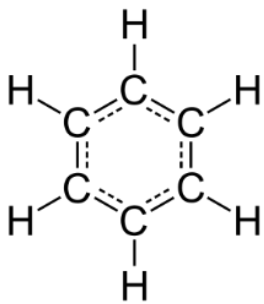
Disinfectant Demand

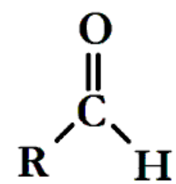
- Demand = Dosage - Residual
  - Dissolved gases
  - Chemical substances (ammonia, others)
  - Inorganic matter
    - Iron, manganese, NH_3, IA & IIA periodic chart elements
  - Organic matter
  - Biological organisms

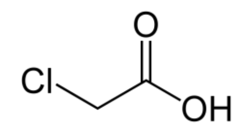
General Relationships

Disinfectant Demand

- Organic matter reacts to create DBPs
  - Humic acids
  - Fulvic acids
  - Transphilic acids
  - Hydrophilics
  - TOC, BOD, CBOD, and AOC
  - Aromatic hydrocarbons
  - Aldehydes, ketones, carbohydrates
  - Proteins, fats







General Relationships

Disinfectant Demand

- Ammonia and nitrogen compounds
  - Direct reaction with many chlorine forms
- Pathogenic microorganisms
  - Most removed by coagulation and filtration processes, or by secondary wastewater treatment processes
  - Some destroyed by chemical softening and high pH
  - Small remaining populations inactivated by disinfection

General Relationships

Residual Maintenance

- Essential for effective disinfection
- Residuals have specific reactive life
- Residual decay
  - Time (water age in system)
  - Temperature (especially storage tanks)
  - Introduction of demand causing substances
  - Competing reactions
  - Aeration (very high air to water ratios)

General Relationships

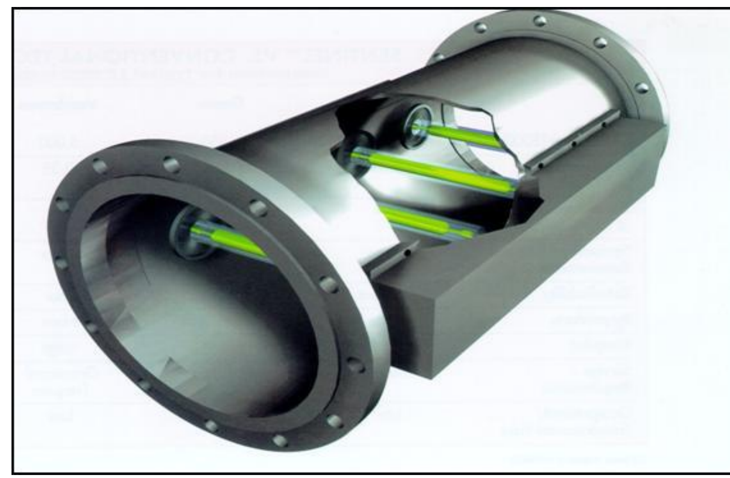
Residual Maintenance

- Residual half-lifes
  - Ozone $t_{1/2}$= 20 minutes in water
  - Free chlorine $t_{1/2}$= 140 minutes in water
  - Monochloramine $t_{1/2}$= 1,680 minutes in water
  - Chlorine dioxide $t_{1/2}$= 93 minutes in water
- Begin decay after residual achieved
  - Decay dependent on water quality and temperature

General Relationships

Residual Maintenance

- Residuals regulated in drinking water
  - 0.2 mg/L free Cl_2
  - 1.0 mg/L combined Cl_2
  - 0.04 mg/L chlorine dioxide
  - 4.0 mg/L as Cl_2 MRDL
- UV produces no residual
  - Required secondary disinfectant

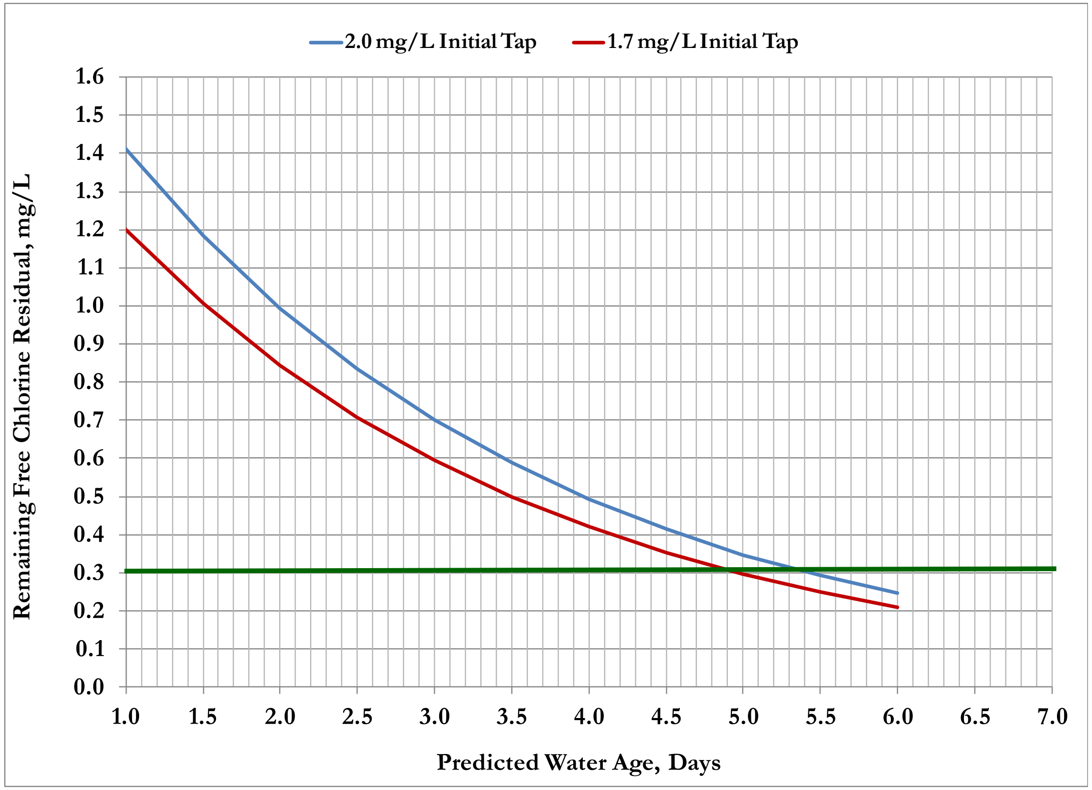


General Relationships

Residual Maintenance

- Decay modeling can be helpful

$$C_t = C_o e^{-kt}$$



Chlorine

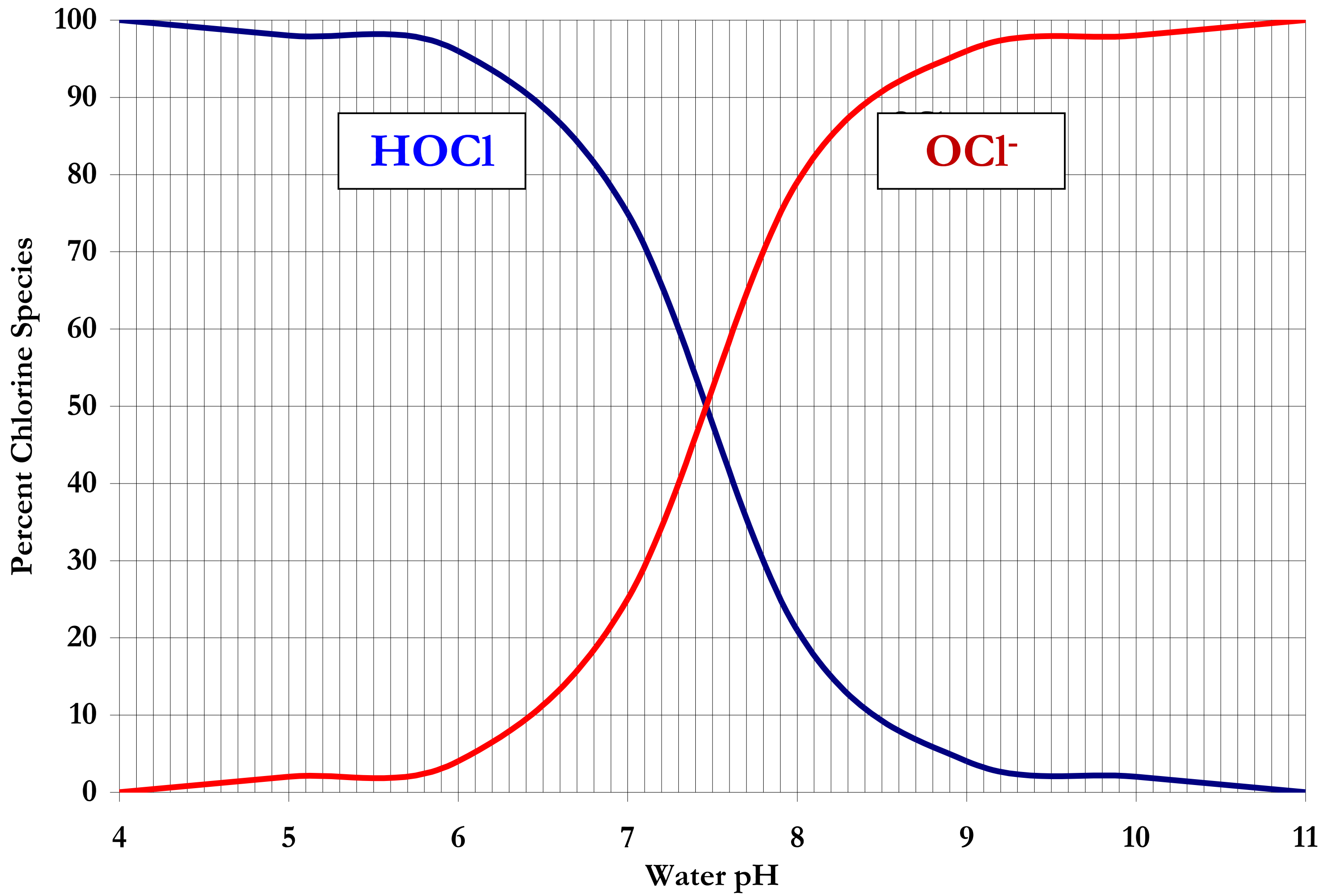
Chlorine

$$Cl_2 + H_2O \Rightarrow HOCl + HCl$$

$$HOCl \Leftrightarrow OCl^- + H^+$$

pH and temperature dependent

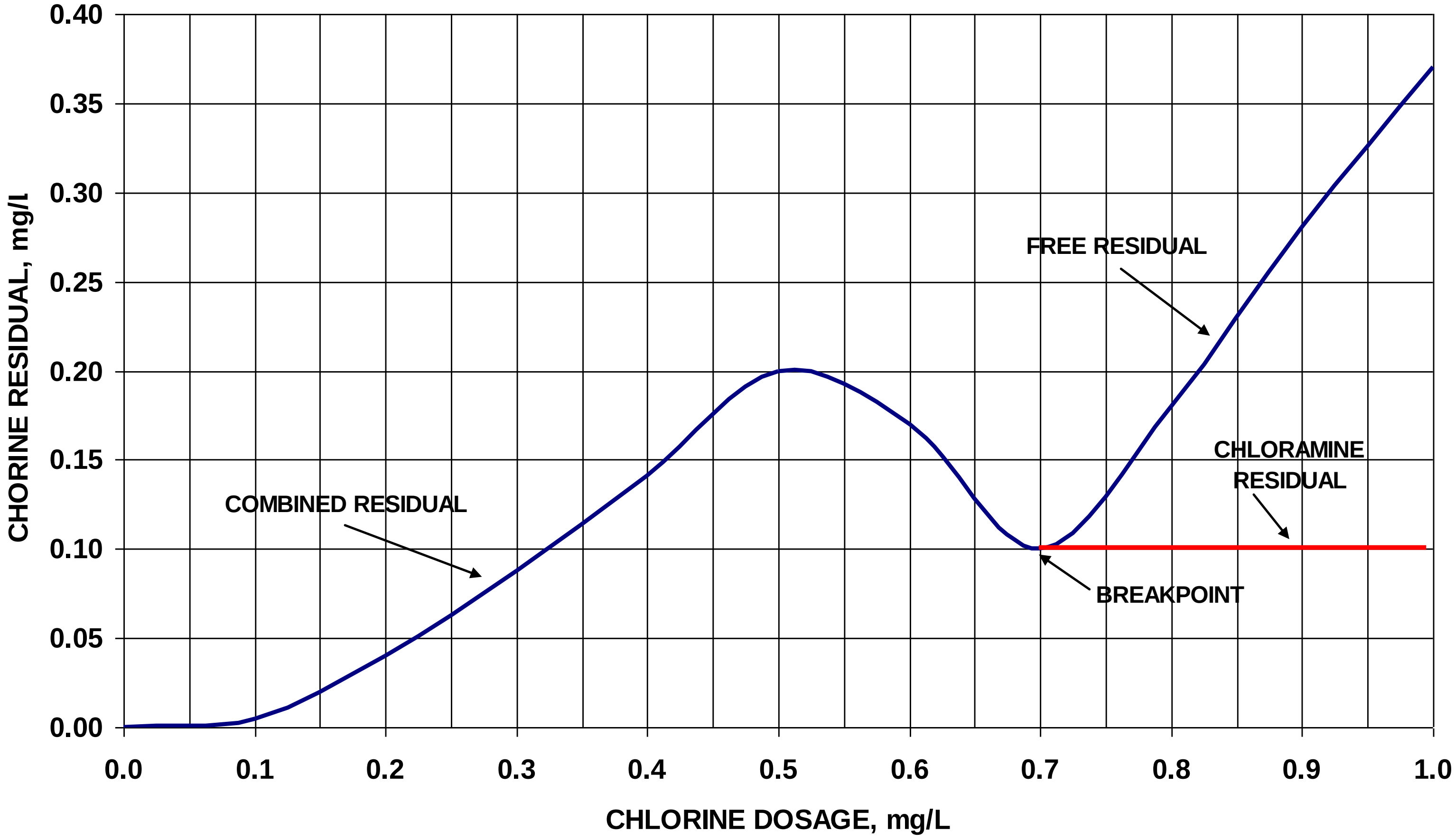
Chlorine


HOCl
OCl-
Percent Chlorine Species
Water pH
100
90
80
70
60
50
40
30
20
10
0
4
5
6
7
8
9
10
11

Chlorine

- Free chlorine
  - HOCl
  - OCl^-
- Combined chlorine
  - Monochloramine
  - Other chloramine species
- Total chlorine
  - Free chlorine
  - Chloramine species

Breakpoint Chlorination



Chloramines

Chloramines

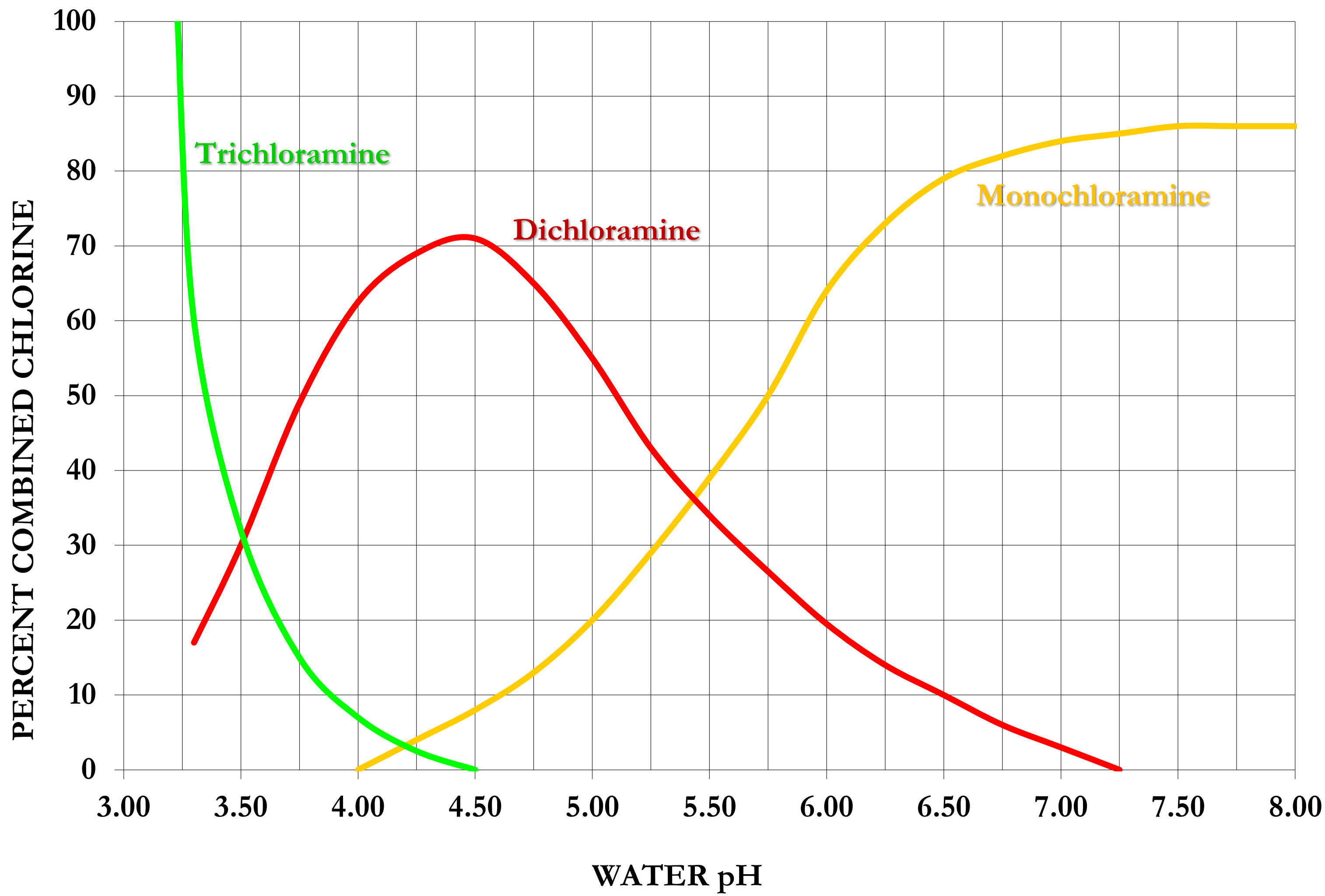
-

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

$$HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O$$

pH and temperature dependent
Chlorine/nitrogen ratio dependent

Chloramines



Chloramines

- Three forms
  - Monochloramine
  - Dichloramine
  - Trichloramine
- Cl_2:N ratio dependency
  - Monochloramine 4.5:1
  - Dichloramine 7.6:1
  - Trichloramine 15:1

Chloramines

- Equilibrium reverse reaction can lead to nitrification

$$NH_2Cl + H_2O \Leftrightarrow HOCl + NH_3$$

- Conversion to hydroxylamines - high pH conditions

$$NH_2Cl + OH^- \Rightarrow NH_2OH + Cl^-$$

Chlorine Dioxide

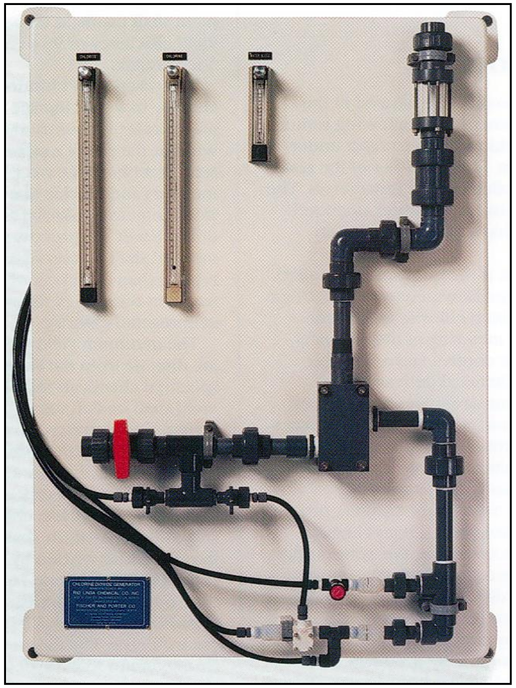
Chlorine Dioxide

- Chlorine gas and liquid sodium chlorite in special generator
- ClO_2 concentrations 200 mg/L to 5,000 mg/L
- 95% or greater conversion common
- Sight glass confirms ClO_2 generation **neon green color**

$$2NaClO_2 + Cl_2 \Rightarrow 2ClO_2 + 2NaCl$$

Chlorine Dioxide

- 1 lb. Cl_2 gas plus 1.68 lbs $NaOCl_2$ makes 1 lb. ClO_2
- Byproducts from generation
  - Chlorite ClO_2^-
  - Chlorate ClO_3^-
  - Chloride Cl^-
  - NaCl (can clog generator column)



Chlorine Dioxide

- Two chemical system
  - $NaOCl_2$
  - Cl_2

Chlorine Dioxide

- Chlorite regulated in drinking water - 1.0 mg/L
- ClO_2 and OH^- decomposes to byproducts

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

Chlorine Dioxide

- Chlorite regulated in drinking water - 1.0 mg/L
- ClO_2 and OH^- decomposes to byproducts

$$ClO_2 + 2OH^- \Rightarrow ClO_3^- + \boxed{ClO_2^-} + H_2O$$

Sodium Hypochlorite

Sodium Hypochlorite

- 1 pound Cl_2 plus 1.13 pounds NaOH makes 1.05 pounds NaOCl

$$Cl_2 + 2NaOH \Rightarrow NaOCl + NaCl + H_2O + heat$$

$$NaOCl + H_2O \Rightarrow HOCl + OH^- + Na^+$$

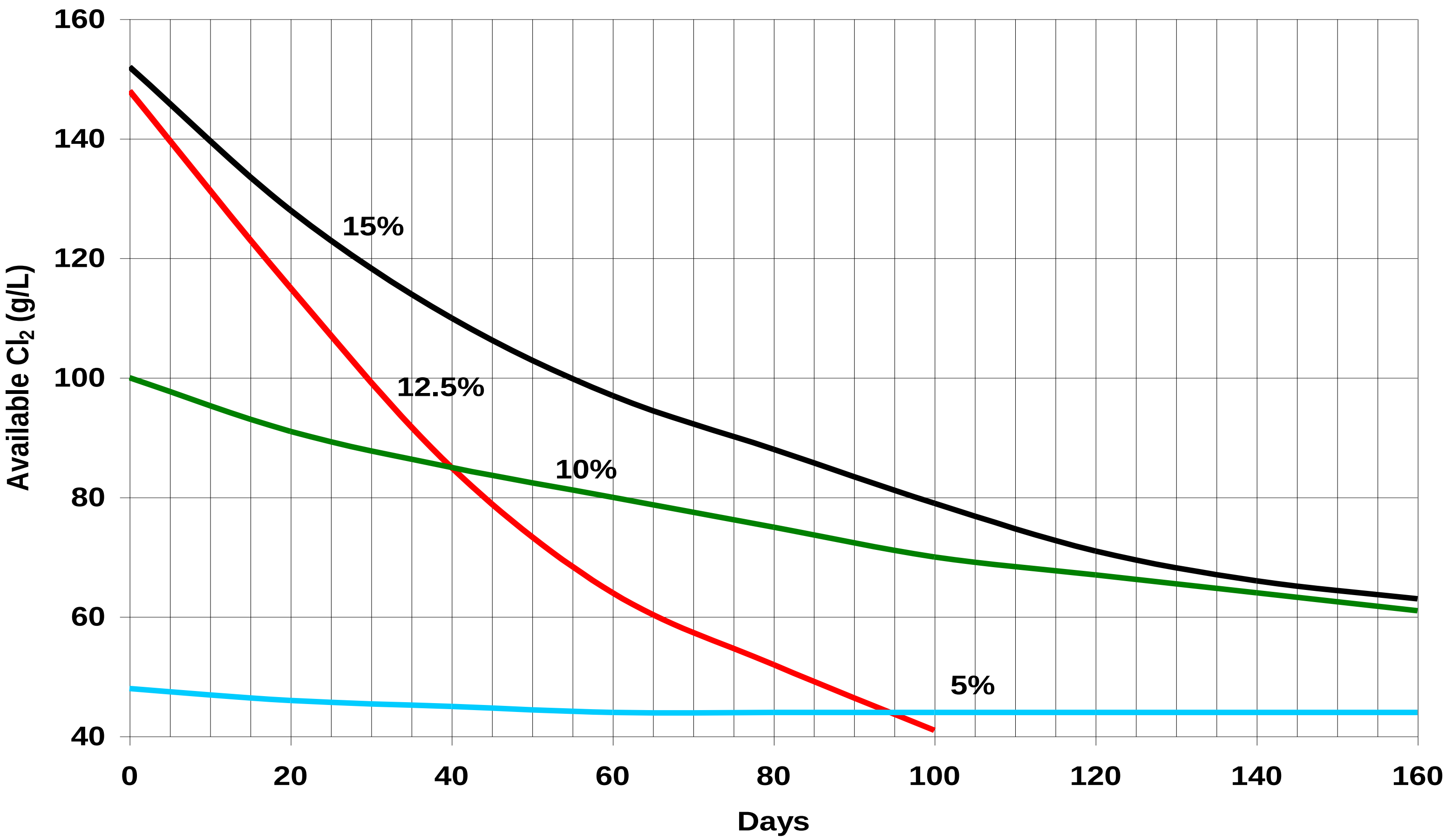
$$HOCl \Leftrightarrow OCl^- + H^+$$

- NaOH added to maintain pH>12, reduce off gassing
- Onsite generation also available
  - 0.8 % and 12.5% strength

Sodium Hypochlorite

- Decay influenced by
  - Chemical concentration
  - Heat
  - UV light
  - pH (<11 rapid)
  - Heavy metal cations

Sodium Hypochlorite



Sodium Hypochlorite

- Na^+ does not disinfect
- OCl^- is the disinfectant
- 12.5% NaOCl
  - About 8.6% OCl^-
  - About 1.04 lbs/gal

- Check strength and adjust feed rate as solution decays
  - Procedures in Sodium Hypochlorite Handbook (OxiChem)

Sodium Hypochlorite

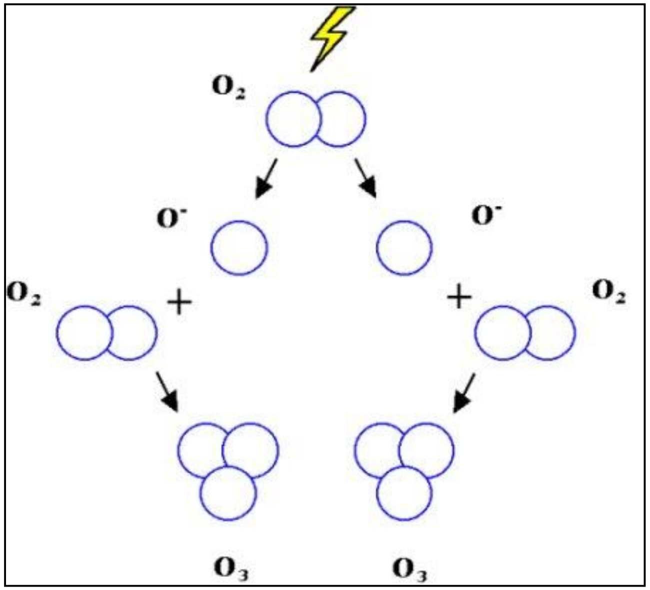
- Decomposition produces oxygen off gas and increased chlorite ion (ClO_2^-)
- Off gas creates operating problems
  - Pumps
  - Valves

Ozone

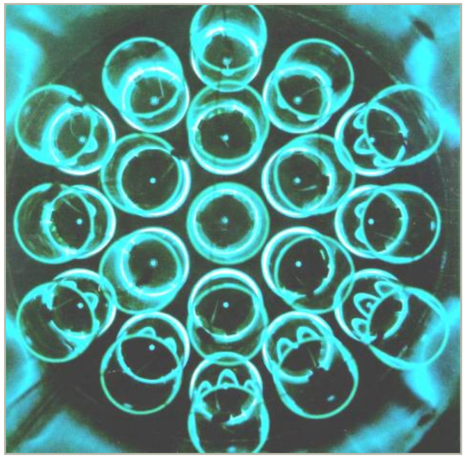
Ozone

$$O_2 + \hbar \nu \Rightarrow O^{-} + O^{-}$$

$$O^{-} + O_2 \Rightarrow O_3$$

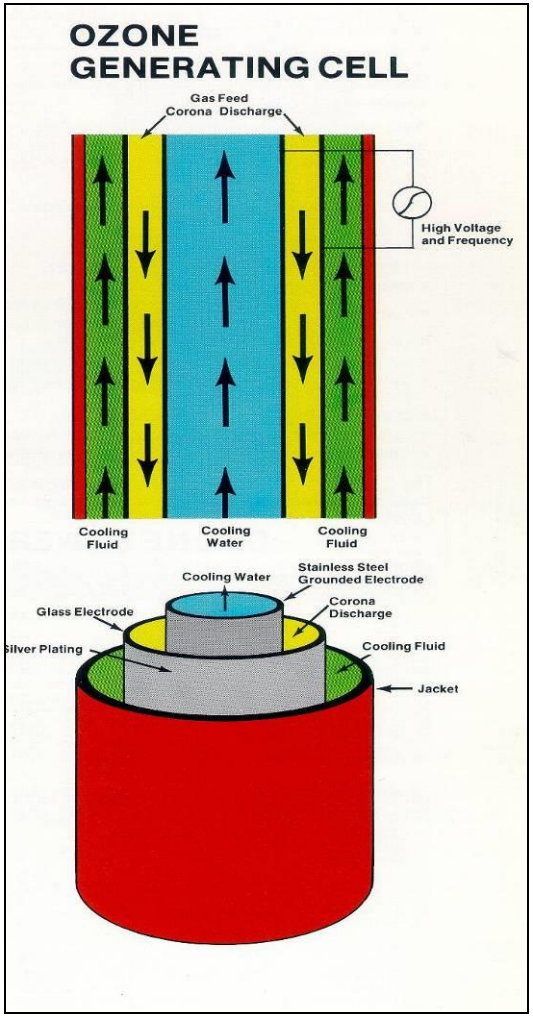


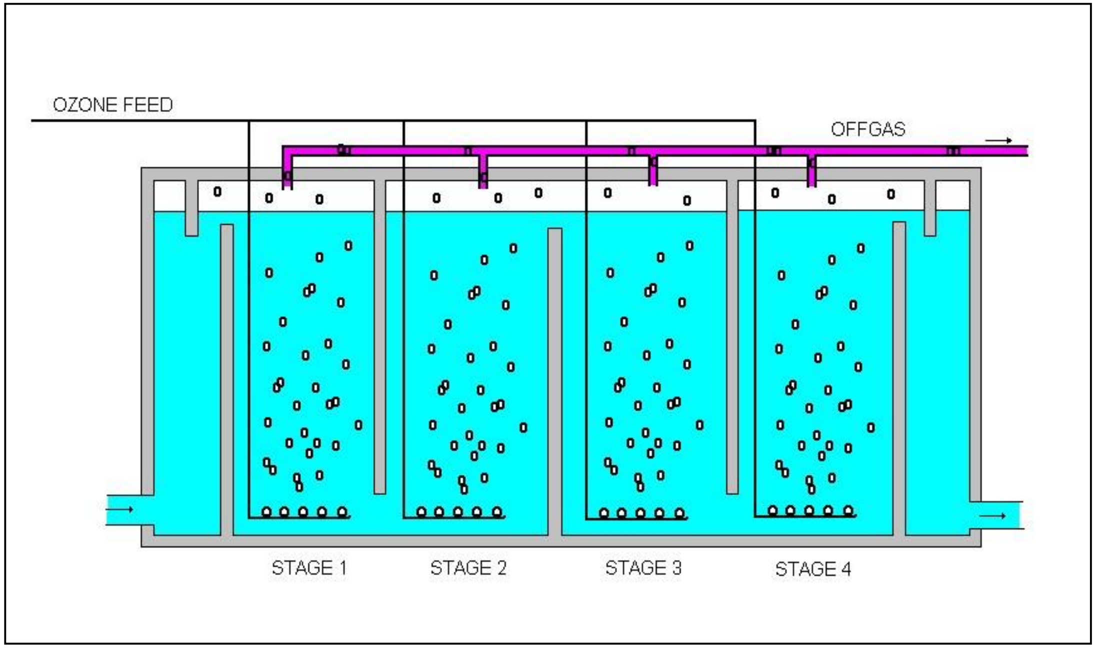
Ozone



- Corona discharge operation
- Feed gas moisture free (-50°C)
- Dew point monitors and shutdown
- Ozone concentrations 1.5% to 10%
- 600 times to 3,000 times more effective than chlorine

Ozone


OZONE
GENERATING CELL
Gas Feed
Corona Discharge
High Voltage
and Frequency
Cooling
Fluid
Cooling
Water
Cooling
Fluid
Cooling Water
Stainless Steel
Grounded Electrode
Corona
Discharge
Glass Electrode
Silver Plating
Cooling Fluid
Jacket


OZONE FEED
OFFGAS
STAGE 1
STAGE 2
STAGE 3
STAGE 4

Ozone

- Gas not transferred into water becomes off gas
- Off gas destruction / reuse
  - Catalytic
  - Thermal
  - Reused into first stage contactor (Monroe, Michigan)

Mixed Oxidants

Mixed Oxidants

- Solution strength typically 0.8 percent (8,000 mg/L)
- Dilute solutions reduce off gassing and increase stability
- Eliminates safety concerns with chlorine
- Mixed oxidants more effective than single disinfectant
  - NaOCl and HOCl

Mixed Oxidants

$$2NaCl + 2H_2O + \hbar\nu \Rightarrow 2NaOH + Cl_2 + \boxed{H_2}$$

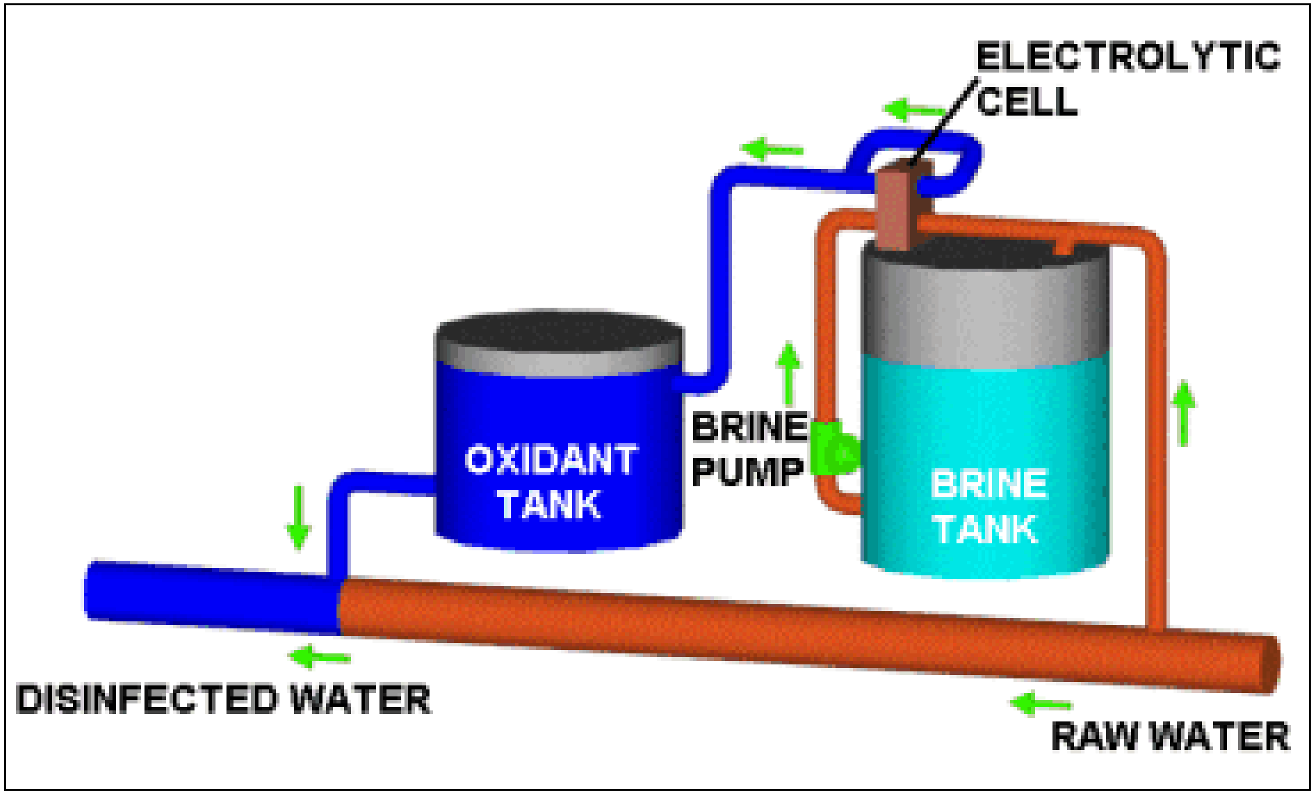
$$Cl_2 + OH^- \Leftrightarrow HOCl + Cl^-$$

$$HOCl \Leftrightarrow H^+ + OCl^-$$

$$Na^+ + OCl^- \Leftrightarrow NaOCl$$

Mixed Oxidants

MIOX Generating System



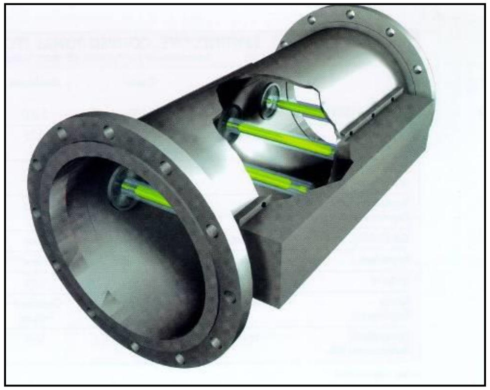
Mixed Oxidants

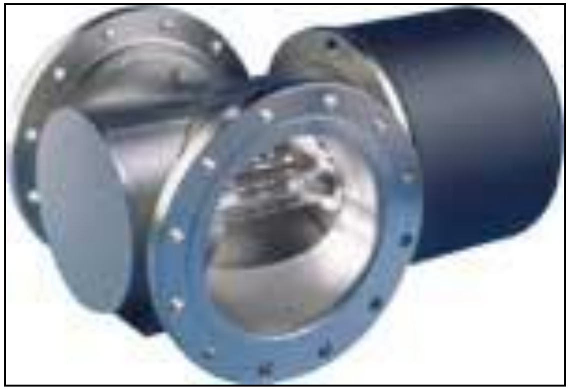
- Four (4) pounds salt and four (4) kW current make one pound mixed oxidant
- Capacities up to 1,000 lbs/day
- Softened water important brine preparation
  - Total hardness less than 20 mg/L
- Water temperature important
  - Must be greater than 40°F

UV Disinfection

UV Disinfection

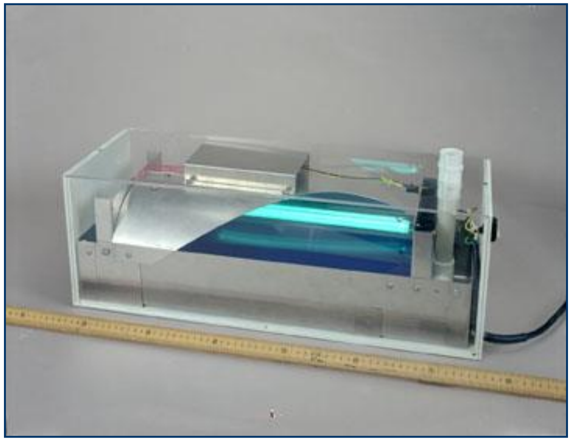
- More common in wastewater
  - Fecal coliform reductions
  - No residual destruction
- Cryptosporidium inactivation requirements show need for UV in drinking water
  - Crypto cannot be inactivated by free chlorine





UV Disinfection

- UV-C light 100 nm to 280 nm likely has germicidal properties
- Transmittance dependent on
  - Turbidity
  - Suspended solids
  - Iron, manganese
  - Hardness
  - Hydrogen sulfide (H_2S)



$$UVA = \log \frac{1}{UVT}$$

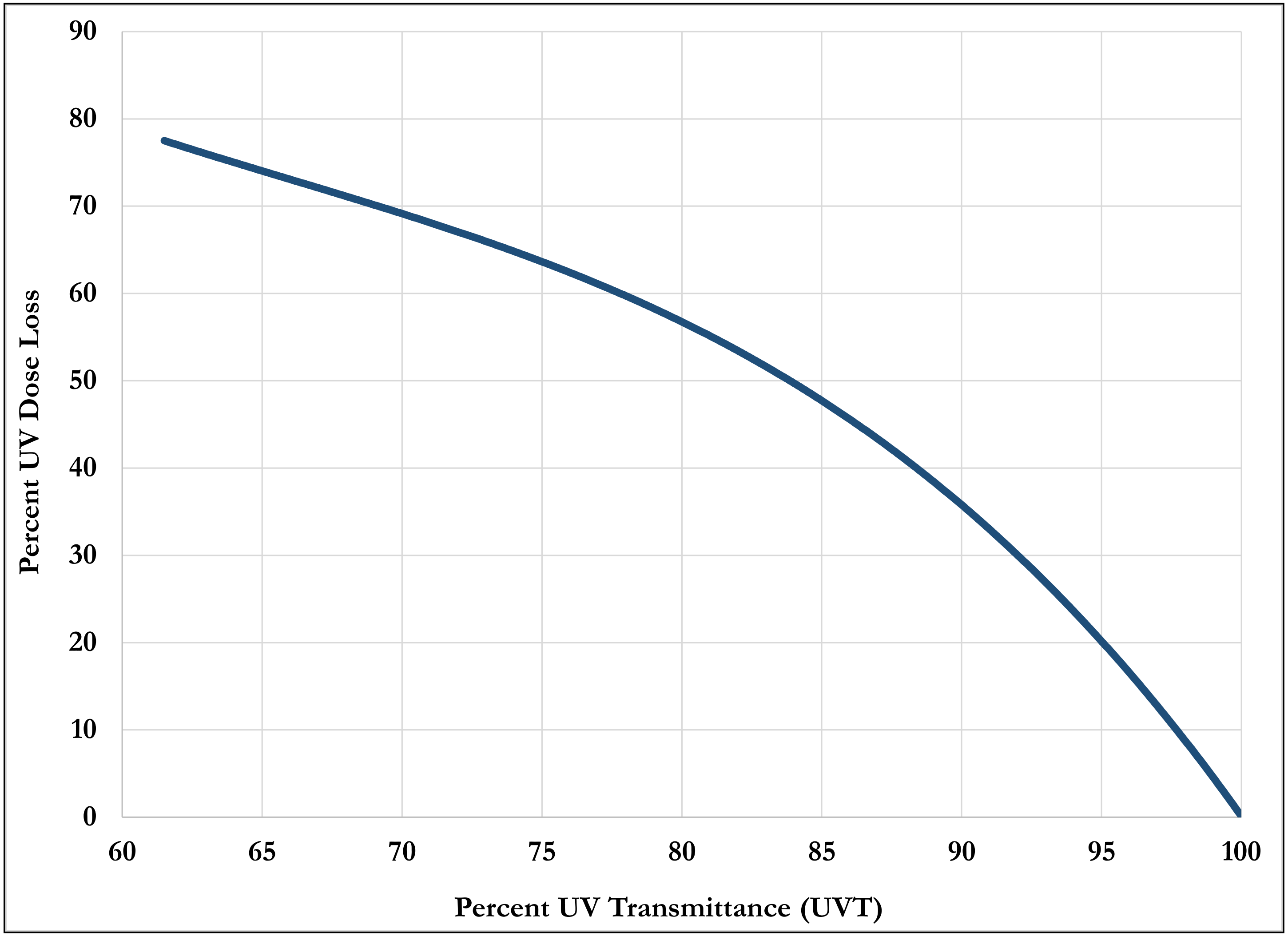
UV Disinfection

	LP	LPHO	MP
Spectra	monochromatic	monochromatic	polychromatic
Power (W)	70-90	200-250	1,300-5,000
Temp, ^{o}C	40-60	100-200	600-900
Life, hours	8K-10K	8K-10K	3K-5K
No. lamps	10-15	4-8	1-6

UV Disinfection

- UV dose related to contact time and UV intensity
- Dosing is complex
  - Water quality
  - Lamp type
  - UV intensity
  - Reactor design
  - Hydraulic flow
  - Sensor performance

UV Disinfection



UV Disinfection

- No residual concentration
- Post disinfectant needed for residual maintenance in water
- Critical UV design parameters
  - Field validation of reactor dosing
  - Sleeve degradation due to fouling
  - Gradual decline of lamp output with age
  - 8% reduction in output decreases UV dose 38%

UV Disinfection

E. Coli	9.6 mJ/cm^2
Hepatitis A	10.2 mJ/cm^2
Salmonella typhi	8.2 mJ/cm^2
Poliovirus	30 mJ/cm^2
Rotavirus	36 mJ/cm^2
Cryptosporidium parvum	10 mJ/cm^2
Giardia lamblia	10 mJ/cm^2

Reactor dosing 3.5 to 4.5 times higher

Destruction Mechanisms

Chlorine

- Destruction mechanisms (free chlorine)
  - HOCl penetrates cell wall
  - HOCl reacts with enzymes used for glucose production
  - Reacts with nucleic acid effects respiration in viruses
  - OCl^- will not penetrate cell wall (negative charges repel)

Chloramines

- Destruction mechanisms
  - Electrochemical reaction with enzymes within microbial cell
  - Disruption of enzyme system fails to repair/grow cells
  - HOCl presence in NH_2Cl may increase disinfection capability

Chlorine Dioxide

- Destruction mechanisms
  - Disruption of protein synthesis
  - Breakdown ability to maintain/repair cells
  - pH 6.5, ClO_2 kills 99% E. coli in 60 minutes
  - pH 8.5, ClO_2 kill 99% E. coli in 15 minutes
  - Virus kill like E. coli

Ozone

- Destruction mechanisms
  - Physiological damage to DNA inactivating replication
  - Virus inactivation by nucleic acid damage
  - Ozone may diffuse through cell wall rather than by chemical reaction
- Residual ozone inactivates, not gas bubbles

UV Disinfection

- Destruction mechanisms
  - Alteration of DNA
  - Organism cannot reproduce, cannot infect

Questions

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