Disinfection through Chlorination

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Disinfection through Chlorination

WWW-6260

7 contact hours
9 CC10 hours

This class provides a comprehensive discussion of all aspects of disinfection with chlorine, the regulatory framework for using chlorine products, targeted pathogens and the generation of harmful disinfection by-products when chlorine reacts with natural organic materials (NOM) in the water. The disinfection action of chlorine in water and wastewater treatment, the hazards of chlorine and the formation of disinfection by-products is described along with the need for safe chemical handling and storage. This class is designed to help participants recognize how and when to use various forms of chlorine chemicals. Operators will benefit from this one-day course designed to review the benefits and drawbacks of switching from gas to liquid systems. Topics will include principles of feeding gas chlorine, pumping hypochlorite and chlorine dioxide solutions using metering pumps, e.g. diaphragm and peristaltic and preventative maintenance recommendations for both chlorine gas and liquid feed systems.

Objectives:

1. Discuss need for disinfection in water and wastewater systems
2. Identify the various chlorine disinfection methods such as gaseous chlorine, sodium and calcium hypochlorites, chlorine and ammonia, and chlorine dioxide.
3. Explain water and wastewater disinfection requirements:
   - Regulatory framework
   - Chlorine chemistry
   - Chlorination theory
   - Breakpoint chlorination
   - Pathogen inactivation and disinfection
   - Process application points
   - Formation and control of disinfection by-products (DBPs)
   - Dechlorination requirements (Wastewater)
   - “Inherently safer techniques” (ISTs), from gas to liquid chemicals
4. Discuss operational considerations, process control, and safety practices.
5. Idenfiy the chemical dosing math formula.

Class Outline:

A. Regulatory requirements **(30 minutes)**
   a. Filtration and disinfection – water treatment
   b. Effluent disinfection; Chlorination dechlorination – wastewater treatment

B. Integration of disinfection in water and wastewater treatment facilities **(15 minutes)**

C. Principles for the selection of an appropriate disinfection system **(15 minutes)**

D. Waterborne pathogens **(30 minutes)**

    a. Bacterial
    b. Viral
    c. Protozoan (parasites)

E. Disinfection performance indicators **(30 minutes)**
    a. Total Coliforms
    b. Fecal Coliforms
    c. E. Coliforms

F. Importance of water treatment prior to disinfection **(30 minutes)**

G. Chlorination **(30 minutes)**
    a. Properties and chemistry of Cl_2 gas systems
    b. Applications
    c. Disinfection performance
    d. By-products
    e. Operation and verification of performance
    f. Advantages and limitations Cl_2 gas systems

H. Hypochlorination **(60 minutes)**
    a. Properties and chemistry of hypochlorite solutions
        i. Sodium hypochlorite (NaOCl)
            1. Bleach
            2. 5 – 8% Cl solutions
            3. 12- 15% Cl solutions
        ii. Calcium hypochlorite ($Ca(OCl)_2$)
            1. 65-70% Cl solid tablets
    b. Applications
    c. Disinfection performance
    d. By-products
    e. Operation and verification of performance
    f. Advantages and limitations Cl_2 systems

I. Disinfectant by-product formation **(30 minutes)**
    a. Chlorine
    b. Natural Organic Material (NOM) in water
    c. Trihalomethanes (THMs)

J. By-product implications of disinfectants **(30 minutes)**

K. Chloramination - Chlorine and ammonia **(30 minutes)**
    a. Properties and chemistry of Cl_2 and NH_4 systems
    b. Generation of chloramines
    c. Disinfection performance
    d. By-products
    e. Operation and verification of performance Cl_2 and NH_4 systems
    f. Advantages and limitations

L. Chlorine dioxide **(30 minutes)**
    a. Properties and chemistry of ClO_2 systems
    b. Generation of chlorine dioxide
    c. Disinfection performance
    d. By-products
    e. Operation and verification of performance

f. Advantages and limitations ClO_2 systems

M. Summary of advantages and disadvantages of chlorine use **(90 minutes)**

a. **Advantages**

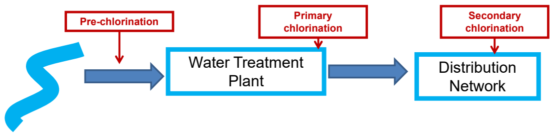
i. Is an effective biocide
ii. Provides a residual
iii. Oxidizes soluble iron, manganese, and sulfides
iv. Enhances color removal
v. Enhances taste and odor
vi. May enhance coagulation and filtration of particulate contaminants
vii. Is the easiest and least expensive disinfection method, regardless of system size
viii. Is the most widely used disinfection method, and therefore, the best known
ix. Is available as calcium and sodium hypochlorite
   1. Use of these solutions is more advantageous for smaller systems than chlorine gas because they are:
      a. easier to use
      b. safer
      c. need less equipment compared to chlorine gas

b. **Disadvantages**

i. May cause a deterioration in coagulation/filtration of dissolved organic substances
ii. Forms harmful disinfection byproducts
iii. Finished water could have taste and odor, problems, depending on the water quality and dosage
iv. Chlorine gas is a hazardous corrosive gas
v. Special leak containment and scrubber facilities could be required for chlorine gas
vi. Typically, sodium and calcium hypochlorite are more expensive than chlorine gas
vii. Sodium hypochlorite degrades over time, especially when exposure to light
viii. Sodium hypochlorite is a corrosive chemical
ix. Calcium hypochlorite must be stored in a cool, dry place because of its reaction with moisture and heat
x. A precipitate may form in a calcium hypochlorite solution because of impurities, therefore, an anti-scaling chemical may be needed
xi. Higher concentrations of hypochlorite solutions are unstable and will produce chlorate as a byproduct
xii. Is less effective at high pH
xiii. Forms oxygenated byproducts that are biodegradable, and which can enhance subsequent biological growth if a chlorine residual is not maintained
xiv. Could release of constituents bound in the distribution system (e.g., arsenic) by changing the redox state.

N. Final Exam **(30 minutes)**

Chlorination Technology



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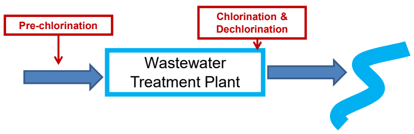

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Process Training Sessions

Before class starts, please:

- **Sign in** on Attendance Sheet

During classes, please:

- **Asks questions**
- Feel free to get up and leave the classroom at any time (i.e., rest rooms, phone calls, etc.)

After classes, please:

- **Answer questions** on post exam
- Fill out class evaluation

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Housekeeping

- Start class – 8:00 am
- Please mute/silence cell phones
- 10-minute Breaks – every hour
- Lunch – 11:30 am ~ 12:30 pm
- End class ~ 3:30 to 4:00 pm

3

Instructor Expectations

- Begin and end class on time
- Be interactive
- Share experiences and needs
- ***<u>Make this an enjoyable and informative experience!</u>***

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Groundrules

- Participate at your own comfort level
- Use terms understood by all
- Everyone is different, so please show respect for others
- Listen with an open mind
- Express thoughts and ideas

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Introduction

Focus, Objectives, and Agenda

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Class Focus and Agenda

- Introduction
  - Why use chlorine in treating:
    - Drinking water
    - Wastewater
- Chlorine Disinfection Processes:
  - With Cl_2
  - With hypochlorites, e.g., NaOCl and $Ca(OCl)_2$
  - With chloramines (Cl_2 + NH_4)

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Learning Objectives

- Objective 1
  - Discuss:
    - Why use chlorine?
    - Breakpoint chlorination theory
    - Basic processes
- Objective 2
  - Review treatment process concepts
    - Chlorination (Cl_2, NaOCl and $Ca(OCl)_2$
    - CL_2 + NH_3 = Monochloramines

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Learning Objectives

- Objective 3
  - Review process control concepts
    - Free chlorine residual
    - Total chlorine residual

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At the conclusion of the course, students should be able to Discuss:

- Basic theories of chlorine applications
- Equipment components
- Process O&M
- Normal and abnormal operations
- Control tests
- Process control calculations
- Solving operational problems
- Safety considerations

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Introduction

Chlorine Properties

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Properties of Chlorine

- Very reactive
- Characteristic odor
- Corrosive
- Establishes a chlorine residual after disinfection
- Escapes from water if exposed to air

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Properties of Chlorine

- Reacts with:
  - Iron, Manganese, hydrogen sulfide and nitrites
  - Ammonia to form chloramines:
    - Monochloramine
    - Dichloramine
    - Trichloramine
  - Natural organic materials (NOM) to form disinfectant by-products (DBPs)

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Properties of Chlorine

Chlorine may be found in three forms

Powder ***Liquid*** ***Gas***

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Properties of Chlorine

- Powder – Calcium hypochlorite, $Ca(OCl)_2$
  - First use in U.S.: 1908; Chicago, IL
  - "Chloride of lime"
- Liquid – Sodium hypochlorite, NaOCl
  - First use in U.S.: 1908; Jersey City, NJ
  - "Bleach"
- Gas – Gaseous Chlorine, Cl_2
  - First use in U.S.: 1910; Youngstown, Ohio
  - Most popular disinfectant after 1940
  - Use began to decline in the 1990's in favor of NaOCl

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History of Chlorine Disinfection

- 1847 - Chlorine was first used as a disinfectant in Vienna
- 1890's - The use of chlorine becomes commonplace in England
- 1908 - Initial U.S. applications of chlorination in Chicago and Jersey City water districts
- 1918 - Over one-thousand cities in USA use chlorination for drinking water supplies
- 1970 - Twenty-thousand chlorinated water municipalities exist in the United States

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History of Hypochlorite

- 1789 – France – bleaching in textile industry
- 1897 – England – disinfection of drinking water
- 1908 – First use of hypochlorite to treat drinking water
- 1930 – United States – Began using bleach in household laundry

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Early Chlorine Use and Bacterial Standard

- 1914 – U.S. Department of the Treasury
  - Enacted standards for a maximum bacterial concentration
  - 2 coliforms per 100 ml in drinking water
  - First requirement for drinking water disinfection
  - Led to a dramatic increase in chlorine use drinking water treatment plants
- 1920s – 1930s – Drinking water filtration and chlorination virtually eliminated epidemics of waterborne diseases in the U.S.

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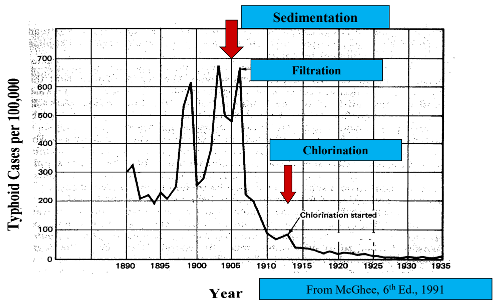
Waterborne Disease Control

Typhoid Cases 1890-1935 Philadelphia



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Disinfection

Waterborne Pathogens

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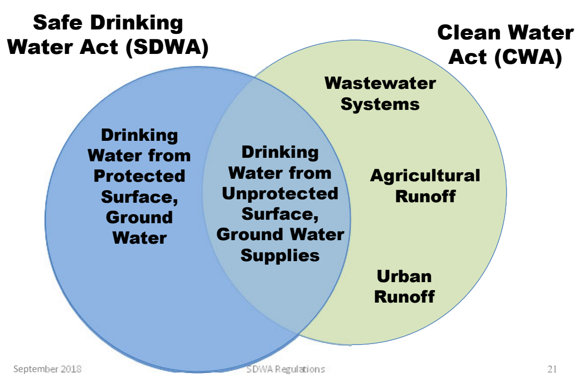
Regulations

Flagship U.S. Water Quality Regulations



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Federal Requirements

- 1972 Clean Water Act 1972 (WWTPs)
  - States can set disinfection criteria
  - Chlorine discharges from WWTPs ~ "zero" (Dechlorination)
- 1974 Safe Drinking Water Act (WTPs)
  - Surface Water Treatment Rule (SWTR - 1989)
    - Surface water sources must receive filtration and disinfection
    - Concentration and time (C x T) requirements for disinfection
  - Enhanced Surface Water Treatment Rules (ESWTR – 1998 - 2006)
    - Finished water turbidity standard of ≤ 0.3 NTU
    - **Profiling for Cryptosporidium** initiated

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Purpose of Disinfection

- Protect public health and the environment by preventing waterborne diseases
- Pathogens of greatest concern are enteric:
  - Bacteria
  - Viruses
  - Protozoan
- A ***pathogen*** is a bacteria, virus or protozoan capable of causing illness in humans

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Purpose of Disinfectant Addition

- Water
  - Disinfection
  - Iron and manganese oxidation
  - Taste and odor control
  - Zebra mussel control
  - Algae growth in plants
  - Improved particle removal
- Wastewater
  - Disinfection
  - Prevent slime growth
  - Foam control

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Disinfection

- Purpose: to destroy pathogenic organisms
- Disinfection is any process which prevents the growth of pathogens
- Disinfection processes inactivate microbes physically or chemically:
  - Inactivation is achieved by altering or destroying essential structures or functions of the microbe
  - Inactivation processes include denaturation of proteins, nucleic acids, and lipids

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Waterborne Illnesses

- Illnesses like cholera, typhoid and infectious hepatitis spread rapidly via contaminated water
- Two protozoans that are infectious and difficult to treat with chlorine compounds are:
  - *Giardia lamblia* (gastroenteritis)
  - *Cryptosporidium parvum* (cryptosporidiosis)

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Protozoa

Giardia

Cryptosporidium

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What is Disinfection?

- Destruction or inactivation of pathogenic microorganisms
- Prevents spread of waterborne diseases by protecting:
  - Drinking water consumers
  - Potable water supplies
  - Recreational users
  - Irrigation sources

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Disinfection Mechanisms

- Oxidation or rupture of cell wall
- Diffusion into cell and interference with cellular activity

Thus, the ability to oxidize biological molecules and the ability to diffuse through the cell walls are requirements of any effective disinfectant

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Disinfection Practices

- Most common include:
  - Gaseous chlorine (Cl_2)
  - Sodium hypochlorite (NaOCl)
  - Calcium hypochlorite ($Ca(ClO)_2$)
  - Ultraviolet (UV) irradiation
  - Ozone

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Methods of Disinfection

Chemical Oxidation	Physical Means
Chlorine	**Ultraviolet light**
Chloramines	Heat
Chlorine dioxide	Membranes

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Chlorination versus UV radiation

	Chlorine	UV
Disinfection by-products (DBPs)	Yes	No
Residual	Yes	No
Corrosive	Yes	No
Community safety risk	Yes	No
Effective against Crypto/ Giardia	No/Yes	Yes
Contact time	30 – 60 minutes	< 20 seconds
Lamp cleaning	N/A	Yes
Costs	Competitive when chlor/dechlor is required and fire codes must be met	

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Methods of Disinfection

- Disinfectants fall into two categories
  - Chemical
  - Physical
- Chemical disinfectants like chlorine are oxidants
- Physical means include ultraviolet light and heat
- Nearly all WTPs/WWTPs use chlorine and/or UV
- Few WTPs use ozone or chlorine dioxide
- Heat is used to reduce microbe concentrations in wastewater plant sludge, not usually plant effluent
- Membrane filtration shows promise for the future

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Properties of an Ideal Disinfectant

- Broad spectrum: active against all microbes
- Fast acting: produces rapid inactivation
- Effective in the presence of organic matter, suspended solids and other constituents
- Nontoxic; soluble; non-flammable; non-explosive
- Compatible with various materials/surfaces
- Stable or persistent for the intended exposure period
- Easy to generate and apply
- Economical

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Chlorine Disinfection

- Advantages:
  - Low cost
  - Easy to obtain
  - Effective at low doses
- Disadvantages:
  - Residual harmful to environment
  - Toxic and hazardous to handle

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Who Does What?

- In water treatment plants, nearly all use a chlorine product to maintain a chlorine residual
- In wastewater treatment:
  - Chlorine use has been decreasing as UV became viable in the 1980's/1990's in lieu of chlorination/dechlorination
  - Currently, approximately 75% of WWTPs use chlorine; most of the rest use UV
- In 2004, about half of chlorine users used gaseous chlorine and half used bulk liquid hypo; liquid is probably more prevalent than gas now

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Comparative Effectiveness of Disinfectants

	Crypto	Giardia	Viruses	Residual
Chlorine	**NE**	**G**	**E**	**G**
Chlorine dioxide	**P/F**	**G**	**G**	**F**
Ozone	**P/F/G**	**E**	**G/E**	**P**
Chloramines	**NE**	**P**	**P**	**G**
UV	**E**	**E**	**F**	**none**

NE – not effective
P – poor
F – fair
G – good
E - excellent

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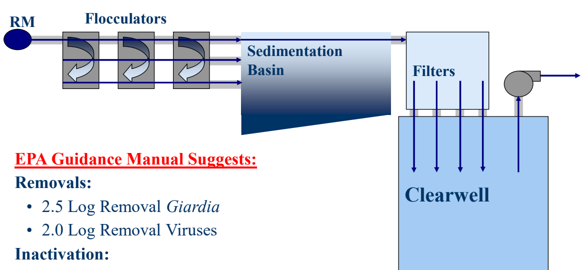
Filtration: Conventional



EPA Guidance Manual Suggests:

Removals:
- 2.5 Log Removal *Giardia*
- 2.0 Log Removal Viruses

Inactivation:
- 0.5 Log Inactivation *Giardia*
- 2.0 Log Inactivation Viruses

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Percentage vs. Log Reductions

Percentage Reductions	Log Reductions[1]
90	1-log
99	2-log
99.9	3-log
99.99	4-log

1. Negative base 10-log of the fraction remaining

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Percentage vs. Log Reductions

- 90% removal → 10% remaining
  - 10% → 0.1 → 1/10 → 10^{-1} = 1-log reduction
- 99% removal → 1% remaining
  - 1% → 0.01 → 1/100 → 10^{-2} = 2-log reduction
- 99.9% removal → 0.1% remaining
  - 0.1% → 0.001 → 1/1000 → 10^{-3} = 3-log reduction
- 99.99% removal → 0.01% remaining
  - 0.01% → 0.0001 → 1/10000 → 10^{-4} = 4-log reduction

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Pathogens and waterborne diseases

- Enter water sources via:
  - Inadequately disinfected wastewater
  - Animal waste feedlots
- Causes more human health problems than any other type of water pollution
- Coliform bacteria – indicators of fecal contamination of water
  - Water can hold other pathogens, such as giardiais, typhoid, hepatitis A

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Historical Notes on Pathogens/Indicators

- 1854 – John Snow documented cholera outbreak from sewage-contaminated well in London
- 1856 – William Budd made a similar demonstration for waterborne typhoid
- 1883 – Robert Koch microscopically identified bacteria causing cholera & typhoid
- 1891 – E. *coli* tube tests used to indicate fecal origin of typhoid bacteria in Hudson River, NY

From *Indicators for Waterborne Pathogens*, 2004, National Research Council of the National Academy of Sciences.

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Federal Requirements

- Federal Water Pollution Control Act 1972
- EPA recommended indicator organisms for WWTPs:
  - Fecal coliform, fresh & marine waters (1968)
  - E. coli for freshwaters (1972)
  - Enterococci for marine waters (1972)

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Indicator Organisms

Total coliform	Some from fecal sources
Fecal coliform	Subset of total coliform Human and non-human fecal sources
Escherichia coli (E. coli)	Subset of fecal coliform Likely human source in wastewater
Enterococci	Human-specific strains of fecal streptococci, survive in marine waters

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Testing

- Individual bacteria are too small to be seen with the naked eye.
- Testing methods increase the number of indicator organisms to make them easier to count and/or measure their activity.
- Rapid detection of fecal contamination

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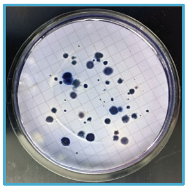
Fecal Coliform Colonies

- Indicator organisms grown on agar form colonies large enough to be seen without a microscope
- Counting the number of colonies can provide an estimate of the number of indicator organisms
- Colony forming units (#CFUs) per 100 ml



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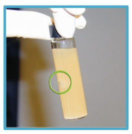
Most Probable Number (MPN)

- Bacteria grow suspended in media-filled test tubes
- Presence of indicator organisms determined by their reactions with certain substances
  - Lactose – total coliforms produce acid and gas
  - 4-methylumbelliferyl-beta-D-glucuronide (MUG) – *E. coli* produce byproducts that glow blue when exposed to a black light



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Most Probable Number (MPN)

- Record the number of test tubes or wells (in the Idexx Quanti-Tray™) that test positive.
- Statistical tables are used to determine the MPN of indicator organisms in the original sample.
- Laboratory results expressed as the MPN per 100 milliliters.

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Testing Methods for Different Indicator Organisms

Indicator Organism	Method Type	Method Sources
Total coliforms	MPN	U.S. EPA (1978c) page 114 Standard Methods 9221 B-2006
	Membrane Filter	U.S. EPA (1978c) page 108 Standard Methods 9222 D-2006
Fecal coliforms	MPN	U.S. EPA (1978c) page 132 U.S. EPA Method 1680 and 1681 Standard Methods 9221 C E-2006 Colilert-18 (Idexx Laboratories, Inc.)
	Membrane Filter	U.S. EPA (1978c) page 124 Standard Methods 9222 D-2006

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Testing Methods for Different Indicator Organisms

Indicator Organism	Method Type	Method Sources
E. coli	MPN	Standard Methods 9221 B.2-2006 / 9221 F-2006 Standard Methods 9223 B-2004 Colilert, Colilert-18 (Idexx Laboratories, Inc.)
	Membrane Filter	U.S. EPA Method 1603 mColiBlue-24 (Hach Company)

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Use of Geometric Means

- Arithmetic mean =
  - = (Sum of Values) / (Number of Values)
  - = (10 + 10 + 10 + 10 + 10,000) / 5 = 2008
- Average monthly MPN averages are calculated as a Geometric mean =
  - = (Product of Values) $^{(1 / \text{Number of Values})}$
  - = (A x B x C x D x E) $^{(1/5)}$
  - = (10 x 10 x 10 x 10 x 10,000) $^{(1/5)}$ = 40

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Waterborne Diseases

Bacteria	*Escherichia coli* (gastroenteritis) *Salmonella typhi* (typhoid fever) *Vibrio cholerae* (cholera) *Shigella* (dysentery)
Viruses	Norovirus (gastroenteritis) Rotavirus (gastroenteritis) Hepatitis A virus (infectious hepatitis) Adenovirus (respiratory, gastroenteritis)
Protozoa	*Giardia lamblia* (gastroenteritis) *Cryptosporidium parvum* (cryptosporidiosis)

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Waterborne Disease Outbreaks Cause Irreparable Damage to Public and PWSs

Year	State/Territory	Cause of Disease	No. of People Affected
1985	Massachusetts	*Giardia lamblia* (protozoan)	703 illnesses
1987	Georgia	*Cryptosporidium parvum* (protozoan)	13,000 illnesses
1987	Puerto Rico	*Shigella sonnei* (bacterium)	1,800 illnesses
1989	Missouri	*E. coli* 0157 (bacterium)	243 illnesses / 4 deaths
1991	Puerto Rico	*Unknown*	9,847 illnesses
1993	Missouri	*Salmonella typhimurium* (bacterium)	650 illnesses / 7 deaths
1993	Wisconsin	*Cryptosporidium parvum* (protozoan)	400,000 illnesses 50+ deaths
1998	Texas	*Cryptosporidium parvum* (protozoan)	1,400 illnesses
1999	New York	*E. coli* 0157 (bacterium)	150 illnesses / 1 death
2000	Ontario	*E. coli* 0157 (bacterium)	1,000 illnesses / 7 deaths

Source: HDR's Handbook of Public Water Systems

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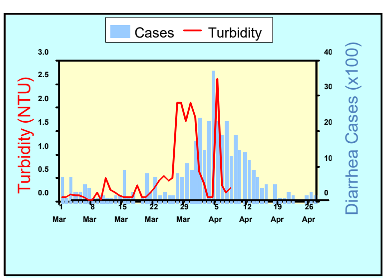
Milwaukee Disease Outbreak - 1993



403,000 illnesses (out of 1.6 million population)

Ineffective coagulation, flocculation, and filtration

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Chlorination

Theory of Operation

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Free Chlorine - Chemistry

- Three different chlorine chemicals
  - Cl_2 (gas)
  - NaOCl (liquid)
  - $Ca(OCl)_2$ (solid)
- Reactions form hypochlorous acid (HOCl):

  $Cl_2\ (g) + H_2O \Leftrightarrow HOCl + Cl^- + H^+$
- Hypochlorous acid (HOCl) in equilibrium with hypochlorite (OCl):

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

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Chlorination Chemicals

- Chlorine gas
  - 100% Cl_2
  - Ton containers, 150-lb cylinders or 90-ton railcars
- Sodium Hypochlorite
  - NaOCl or bleach – 12 - 15% Cl_2
  - Bulk or On-Site Generated
- Calcium Hypochlorite
  - $Ca(OCl)_2$, or HTH, - 65% Cl_2
  - Tablets or powder

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Chlorine Disinfection

- Chlorine - long established chemical disinfectant
- Excellent against bacteria and viruses; not so good against Giardia and Cryptosporidium
- CT = Concentration x Time
- Dose = Demand + Residual
- Residual, mg/l
  - Regulations/permit limits, pH, TSS
- Dechlorination

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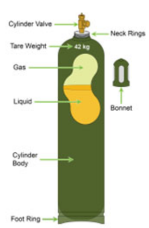
Gaseous Chlorine

- 100% pure chlorine
- First used in Philadelphia to treat drinking water in 1913
- By 1941, use of gaseous chlorine replaced most uses of hypochlorite compounds for water and wastewater disinfection



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Gaseous Chlorine

- A gas at normal room temperature and pressure
- The gas is compressed into a liquid and delivered in 90-ton railcars, 1-ton containers and 150-pound cylinders
- Liquid to Gas Volume Ratio: 1:456 at 32 °F and 1 atm.
- Highly toxic - a few breaths at 1,000 ppm will likely result in death

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Gaseous Chlorine

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Reaction: Cl_2(gas) in Water

Cl_2(gas) + H_2O ⇔ **HOCL** + HCl

Chlorine gas + Water ⇔ **Hypochlorous Acid** + Hydrochloric Acid

Hypochlorous Acid (HOCl) is the disinfectant

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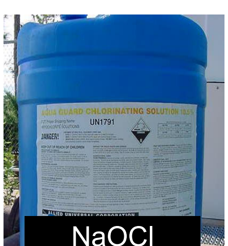
Hypochlorite Compounds



NaOCl
Bleach,
15% Cl_2

$Ca(OCl)_2$
HTH,
65% Cl_2

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Reaction: Bleach (NaOCl) in Water

$NaOCl + H_2O$ ⇔ **HOCL** + NaOH

Sodium Hypochlorite + Water ⇔
Hypochlorous Acid + Sodium Hydroxide

Hypochlorous Acid (HOCl) is the disinfectant

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Reaction: $Ca(OCl)_2$ in Water

$Ca(OCl)_2 + H_2O$ ⇔ **HOCL** + $Ca(OH)_2$

Calcium Hypochlorite + Water ⇔
Hypochlorous Acid + Calcium Hydroxide

Hypochlorous Acid (HOCl) is the disinfectant

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Hypochlorous Acid and Hypochlorite

- Gaseous chlorine and hypochlorite compounds form hypochlorous acid (HOCl):

  $Cl_2 + H_2O$ ⇔ HOCl + HCl

  $NaOCl + H_2O$ ⇔ HOCl + NaOH

  $Ca(OCl)_2 + H_2O$ ⇔ HOCl + $Ca(OH)_2$
- But, HOCl is in equilibrium with hypochlorite (OCl):

  HOCl ⇔ $H^+ + OCl^-$ (pH dependent)

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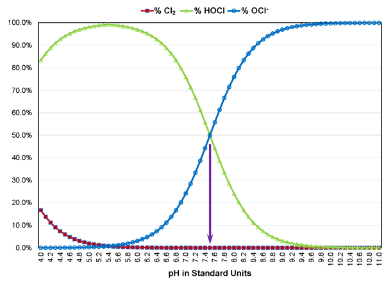
Hypochlorous Acid and Hypochlorite

- Equilibrium point at 20 °C is pH 7.58



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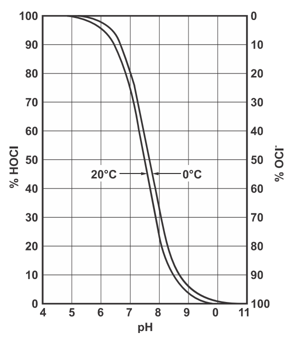
Hypochlorous Acid and Hypochlorite

- Note…
- More HOCl exists at pH's lower than 7.5
- At higher pH's, %HOCl is reduced, thus chlorine doses and/or contact times must be increased for disinfection



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Chlorination

Dose, Demand, Residual

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Chlorine Disinfection

- To be effective…
  - Chlorine concentration
  - Contact time
  - Proper mixing
  - Temperature
  - Number and type of organisms

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Chlorination Terms

Dose – Amount of chlorine added, mg/L

Demand – Amount of chlorine that reacts with inorganic and organic substances

Chlorine Residual = Dose - Demand = Chlorine remaining after contact time

Combined Chlorine Residual – Chlorine that has combined with ammonia to form chloramines

Free Chlorine Residual – Chlorine that exists as hypochlorous acid or hypochlorite

Total Chlorine Residual – Sum of combined and free chlorine residual

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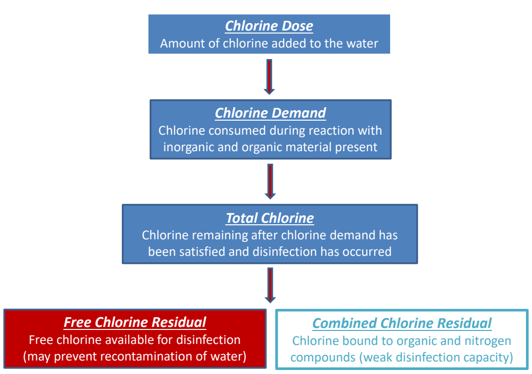
Chlorine Reactions in Water



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Cl_2 Dose, Demand, and Residual

DOSE = demand + residual

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Cl_2 Dose, Demand, and Residual

- **Dose:** **Total amount delivered**
- **Demand:** **What's consumed by constituents in the water**
- **Residual:** **What's left over**

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Disinfection Basics

- The chlorine dose required depends on two considerations:
  - Chlorine demand
  - Desired chlorine residual
  - Dose = Demand, mg/L + Residual, mg/L
- The chlorine demand is the amount used up reacting with:
  - Harmful organisms
  - Inorganic and organic substances
  - Best explained using the "Breakpoint Chlorination Curve"

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Breakpoint Chlorination

- Addition of chlorine to water until the chlorine demand (by inorganic and organic materials) has been satisfied
- Further addition of chlorine will result in formation of a free residual chlorine that is directly proportional to the amount of chlorine added beyond the breakpoint

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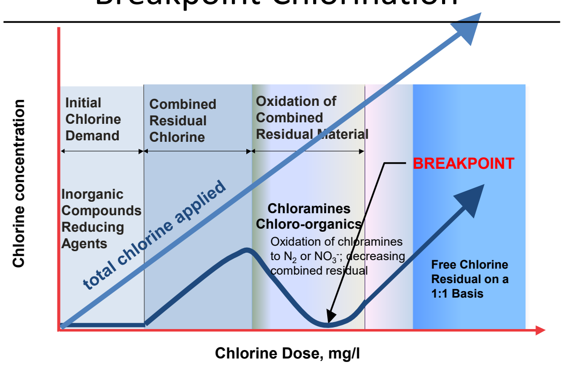
Breakpoint Chlorination



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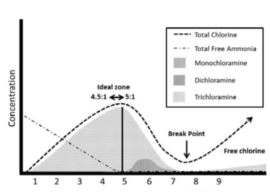
Breakpoint Chlorination Curve

- Understanding breakpoint chlorination and chlorine interactions with ammonia are critical for understanding chlorine demand:
  - Total Chlorine
  - Total Free Ammonia
  - Free Chlorine
  - Monochloramines
  - Dichloramines
  - Trichloramines



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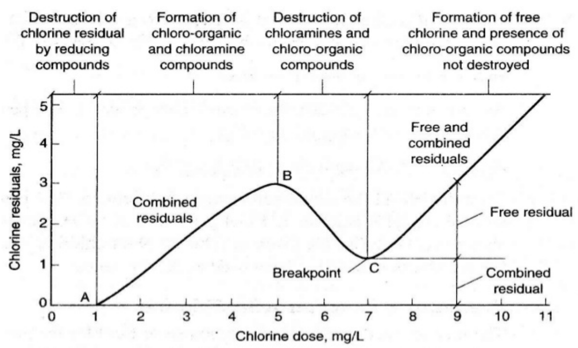
Breakpoint Chlorination Curve



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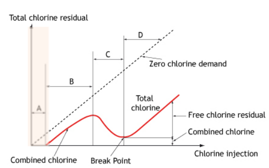
Breakpoint Chlorination Curve

- Zone A
- Chlorine demand from inorganic substances:
  - Hydrogen Sulfide - H_2S
  - Nitrite – NO_2^-
  - Manganese - Mn^{+2}
  - Iron - Fe^{+2}



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Chlorine Demand - Inorganic

- Chlorine oxidizes inorganic compounds before forming combined chlorine
- These initial reactions use up the oxidizing power of chlorine, converting Hypochlorus acid (HOCl) to chloride ion (Cl^-)
- Chloride ion (Cl^-) is not a disinfectant

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Oxidizing Equations

- Hydrogen Sulfide to Sulfuric Acid

  $4HOCl + H_2S \Rightarrow H_2SO_4 + 4H^+ + 4Cl^-$
- Nitrite to Nitrate:

  $HOCl + NO_2^- \Rightarrow NO_3^- + H^+ + Cl^-$
- Manganous ion to Manganic ion:

  $HOCl + Mn^{+2} + H^+ \Rightarrow Mn^{+4} + H_2O + Cl^-$
- Ferrous ion to Ferric ion

  $HOCl + 2Fe^{+2} + H^+ \Rightarrow 2Fe^{+3} + H_2O + Cl^-$

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Chlorine Demand - Inorganic

		Cl_2 Demand per part
Hydrogen Sulfide	H_2S	8.34 mg/L
Nitrite	NO_2^--N	5.1 mg/L
Manganese	Mn^{+2}	1.3 mg/L
Iron	Fe^{+2}	0.64 mg/L

Source: White's Handbook, 2010

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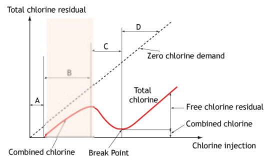
Breakpoint Chlorination Curve

- Zone B
- Formation of chloramines:
  - If ammonia present/added
  - $HOCl + NH_3 \Leftrightarrow NH_2Cl + H_2O$
    - HOCl: Hypochlorus acid
    - NH_3: Ammonia
    - NH_2Cl: Monochloramine
  - Weak disinfectant but free of DBPs!



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Chloramination

Chlorine reactions with ammonia:

1. $HOCl + NH_3 \Leftrightarrow NH_2Cl + H_2O$
2. $HOCl + NH_2Cl \Leftrightarrow NHCl_2 + H_2O$
3. $HOCl + NHCl_2 \Leftrightarrow NCl_3 + H_2O$

If more chlorine is added:

4. $HOCl + NCl_3 \Leftrightarrow HOCl + (N_2, Cl^-, H_2O, H^+, NO_3$ and other species)

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Chloramination

- Reaction of chlorine with ammonia forms
  - "Combined chlorine"
- Offers limited disinfection
  - Effective against bacteria but not viruses
- Add chlorine and ammonia compounds separately
- Apply ammonia first; prevents formation of trichloramines and DBPs

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Forms of Ammonia

- Ammonia can be added in one of three forms to form chloramines:
  - Anhydrous Ammonia (Gas) – Most popular
  - Aqueous Ammonia (Liquid) – Safest
  - Ammonium Sulfate (Solid) – Must be kept dry

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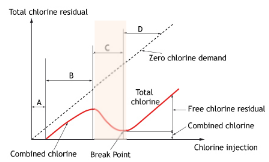
Breakpoint Chlorination Curve

- Zone C
- Destruction of:
  - Monochloramines
- Then formation of:
  - Dichloramines
  - $HOCl + NH_2Cl \Leftrightarrow NHCl_2 + H_2O$
- Then conversion of dichloramines to trichloramines
  - $HOCl + NHCl_2 \Leftrightarrow NCl_3 + H_2O$



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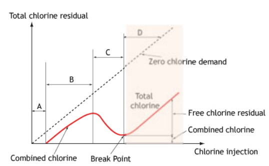
Breakpoint Chlorination Curve

- Zone D
- Free Chlorine Residual
- Formation of:
  - Trichloramines: NCl_3
  - Disinfection By-Products (DBPs) if NOM is present



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Chloramination

- Adding ammonia may compromise water quality at the tap
- Residual chloramines can pass through RO membranes on dialysis machines
- Chloramines toxic to fish (in aquariums)
- Complex process, requires careful control and continual monitoring
- Taste and odor issues

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Taste and Odor Thresholds

- Free chlorine (HOCl) 20 mg/L
- Monochloramine (NH_2Cl) 5.0 mg/L
- Dichloramine ($NHCl_2$) 0.8 mg/L
- Trichloramine (NCl_3) 0.02 mg/L

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Chlorination

Applications

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Chlorine Addition

- In Public Water Systems:
  - Pre-chlorination at WTP
  - Primary disinfection at WTP
  - Secondary "booster" disinfection in distribution system
  - SDWA Regulation, chlorine residual:
    - Minimum: 0.2 mg/L
    - Maximum: 4.0 mg/L

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Chlorine Addition

- At WWTPs:
  - Pre-chlorination
  - Effluent disinfection
    - Minimum 0.5 mg/L chlorine concentration before dechlorination
  - Need for dechlorination
    - Maximum 0.1 mg/L chlorine concentration after dechlorination

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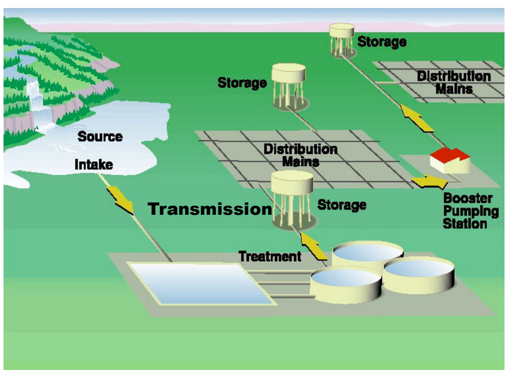
Public Water System



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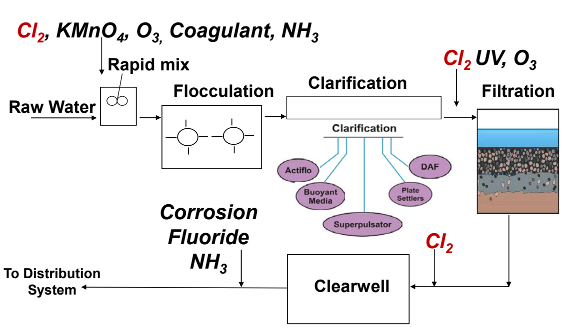
Typical Water Filtration Plant



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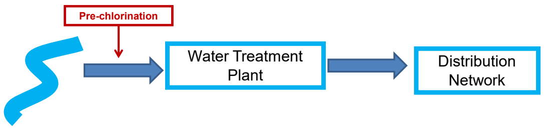
Pre-Chlorination at WTPs

- Pre-chlorination is used to remove minerals (e.g. Iron, manganese)
  - Chlorine precipitates minerals as insoluble particulates
  - Precipitated minerals can be removed during water treatment (e.g., clarification, filtration)
- Pre-chlorination can also remove tastes/odors



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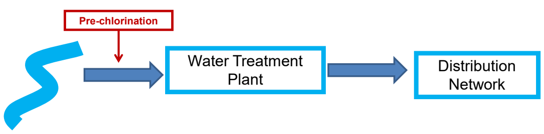
Pre-Chlorination at WTPs

- Potential issues:
  - Raw water may have a high chlorine demand which requires high chlorine dose (high operational cost)
  - Disinfection by-products will form if water source is high in natural organic matter (NOM)



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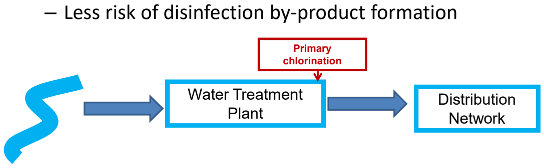
Primary Chlorination at WTPs

- Used for disinfection; most common & effective point of application; 100+ years of experience
- Most effective to add chlorine when turbidity is low; ideally <0.3 NTU (i.e., after clarification, filtration)
  - Use less chlorine
  - Less risk of disinfection by-product formation



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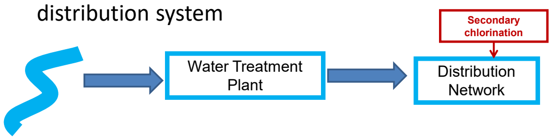
Secondary Chlorination in Distribution System

- Used to maintain chlorine concentration during distribution **(i.e. ≥0.2 mg/L)**
- 'Booster station' adds more chlorine to the water at strategic points during distribution if chlorine concentration is too low
- Helps keep the water safe throughout the distribution system



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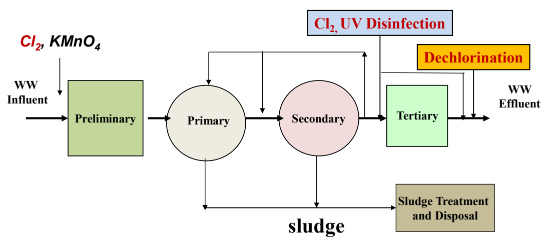
Conventional WWTP Process



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Pre-Chlorination at WWTPs

- Pre-chlorination is used to:
  - Temporarily prevent further wastewater decomposition and reduce associated problems
- Objectives of pre-chlorination are:
  - Odor control
  - Protection of plant structures from H_2S
  - Aid in sedimentation
  - Reduction or delay of biochemical oxygen demand (BOD).

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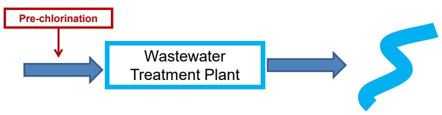
Pre-Chlorination at WWTPs

- Objectives of pre-chlorination are:
  - Odor control
  - Protection of plant structures from H_2S
  - Aid in sedimentation
  - Reduction or delay of biochemical oxygen demand (BOD).



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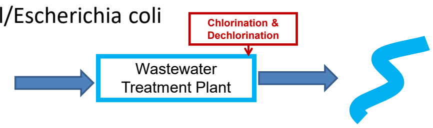
Chlorination at WWTP Effluents

- Chlorination
  - 100 years of experience
  - Gas versus liquid;
  - Dechlorination required
- Eliminates harmful organisms
  - Coliform bacteria
  - Fecal/Escherichia coli



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Chlorination

Concentration x Time

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Factors Affecting Chlorination

- Concentration of disinfectant, C, mg/L
- Contact time, t, minutes
- **Concentration x time = Ct**
  - Effects of Temperature
  - Effects of pH
- Disinfectant species
- Type and concentration of target organism
- Chlorine demand

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Factors Affecting Chlorination

- ***For effective disinfection, at least 30 minutes of contact time is recommended, where the residual chlorine concentration is ≥0.5 mg/L and the pH of the water is <pH 8.***

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"CT" Values

- Disinfection proportional to "C x T"
  - **C = concentration of disinfectant, mg/l**
  - **T = contact time, minutes**
- CT = Chlorine, mg/l x time, minutes
- CT values specific to:
  - Disinfectant
  - Target organism
  - Reduction requirements

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"CT" Values

- In water supply systems, the "Ct" is calculated from when chlorine is added in the clearwell to when drinking water reaches the system's first customer
- In wastewater treatment, the "Ct" is calculated based on the detention time in the effluent chlorine contact tank

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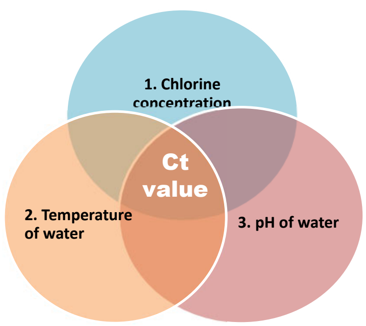
Factors Affecting Ct Value



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Factors Affecting Ct, Chlorine Dose

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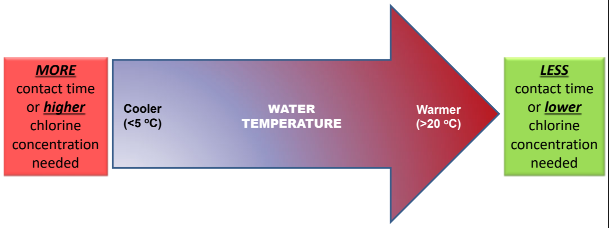
Factors Affecting Ct, Temperature



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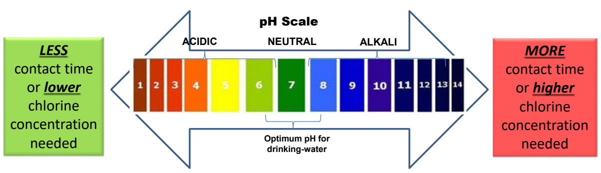
Factors Affecting Ct, pH

- pH measures acid or alkaline (or basic**)** conditions in water
  - pH 7 considered neutral, pH <7 considered acidic and pH >7 considered alkali



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Factors Affecting Ct, pH

- **For effective chlorination, the pH of the water should be < pH 8.0**
- To balance water quality considerations, including chlorination, the optimum pH of drinking-water is generally between pH 6.5 and pH 8.5
- Where water is >pH 8.0, higher chlorine concentrations or more contact time will be required!

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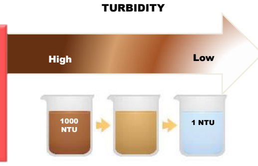
Factors Affecting Ct, Turbidity

- Chlorine reactive substances may consume chlorine and increase chorine demand
- May also ‘shield’ microorganisms from inactivating chlorine effects

MORE contact time or ***higher*** chlorine concentration needed



LESS contact time or ***lower*** chlorine concentration needed

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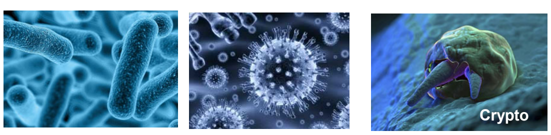
Factors Affecting Ct, Microorganism



BACTERIA VIRUSES PROTOZOA

LESS contact time or ***lower*** chlorine concentration needed

MOST EFFECTIVE → LEAST EFFECTIVE

MORE contact time or ***higher*** chlorine concentration needed

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Chlorination

Chlorine Decay

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Chlorine Decay

- Chlorine decay is the decrease in chlorine concentration in drinking water as it passes from:
  - The water treatment plant
  - Through the distribution system
  - To the consumer

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Chlorine Decay

- Due to chlorine decay:
  - The concentration of chlorine at the end of the distribution system will be less then the concentration at the water treatment plant

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Chlorine Decay

- Rate and extent of chlorine decay influenced by:
  - Level of chlorine reactive substances in treated water as well as in distribution tanks and pipes (i.e., organic and inorganic material)
  - Type of material used in the distribution tanks, pipes and fittings
  - How long the water remains in the distribution system

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Optimizing Chlorine Dose

- *Priority:* always add enough chlorine at the WTP so that:
  - The *minimum required contact time* for effective disinfection *is achieved*
  - The *residual chlorine concentration* at all points in distribution system is *≥0.2 mg/L*
- To balance effective disinfection against consumer acceptability considerations:
  - Target a *residual chlorine concentration of ~ 0.5 mg/L* in the distribution system

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Optimizing Chlorine Dose

- May need to maintain a higher residual chlorine concentration in some parts of the distribution system to ensure *a minimum residual chlorine concentration of 0.2 mg/L* throughout the entire system:
  - Have a higher residual chlorine early in the system
  - To maintain an adequate residual chlorine concentration at the end of the distribution system

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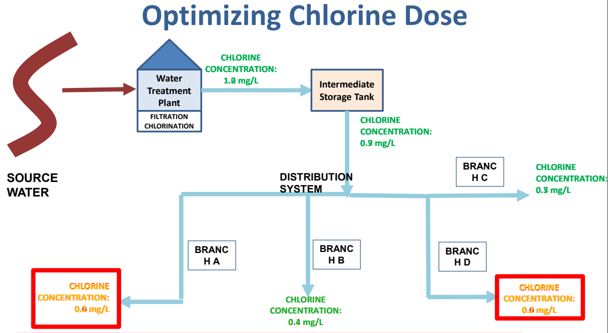
Optimizing Chlorine Dose



Increased chlorine dose at the water treatment plant ensures >0.2 mg/L is maintained at all points in the distribution system

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Chlorine Demand and Decay

- Understanding the *chlorine demand* and *chlorine decay* of water in the treatment and supply system is important:
  - To determine the correct chlorine dose at the water treatment plant
  - *Dose enough chlorine at the water treatment plant to ensure* ≥ 0.2 mg/L *at the point of consumer delivery*

Chlorination

Disinfection By-Products

1

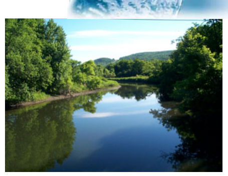
Chlorination

- Priority 1 – Protect against acute microbial contamination
- Priority 2 – Control/minimize formation of disinfection by-products (DBPs)

2

Disinfection By-Products (DBPs)

- Disinfection by-products are formed when chlorine reacts with natural organic matter (NOM) present in source water



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Disinfection By-products (DBPs)

- The World Health Organization has stated that:
  - "…the risks to health from disinfection by-products are extremely small in comparison with the risks associated with inadequate disinfection."

4

DBP Formation

NOM = natural organic matter

NOM + Cl_2 --------> THMs, HAAs, other chlorinated DBPs

NOM + Cl_2 + Br^- --------> brominated THMs, HAAs, other DBPs

{Depends on chlorine dose, NOM concentration (and type), temperature, pH, time}

5

All Disinfectants form DBPs

- Chlorine – TTHMs, HAAs, other chlorinated DBPs (haloacetonitriles, haloketones, etc)
- Chloramines – N-nitrosodimethylamine (NDMA), other nitrogenous DBPs
- Chlorine dioxide – chlorite, chlorate
- Ozone – bromate, aldehydes, keytones, etc.

6

Disinfection By-products (DBPs)

- The most common DBPs are trihalomethanes (THMs) and haloacetic acids (HAAs)
- Trihalomethanes are the main health hazard created from chlorination; two different types:
  - Bromoform
  - Dibromochloromethane

7

Natural Organic Matter (NOM)

- Present in all surface water sources
- Surface waters consist of:
  - Living organisms: Algae, protozoa, bacteria, viruses
  - Non-living material: Decayed vegetation, humic substances
- Usually measured as TOC
- Largest fraction of TOC is usually humic

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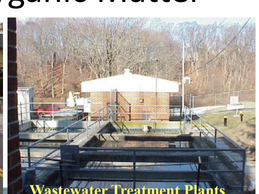
Sources of Organic Matter



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NOM Removal

Why Do We Care?

- Exerts a disinfectant demand
- **Precursor to THMs and HAAs and other DBPs**
- Source of color, tastes and odors
- Coagulant demand – NOM controls the optimum coagulant dose for most waters, *not turbidity*
- Fouling of membrane filters
- Carbon source for biofilm growth

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Potential Health Issues?

- Disinfection By-Product Health Concerns
  - Cancer
    - Bladder, colon and rectal
  - Reproductive
    - Neural tube defects and miscarriages
  - Brominated compounds are thought to pose a greater health risk than chlorinated compounds
  - Nitrogenated compounds may be worse???

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Disinfectants and Disinfection Byproducts (DBPs)

- Chlorine Disinfectants
  - Chlorine
  - Chloramines
  - Chlorine Dioxide
- Maximum Residual Disinfectant Level (MRDL)
  - Level of a disinfectant added for water treatment that may not be exceeded at the consumer's tap without an unacceptable possibility of adverse health effects

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Disinfectants and Disinfection Byproducts (DBPs)

- Due to the potential carcinogenicity of these compounds:
  - Drinking water regulations require regular monitoring of the concentration of these compounds in the distribution systems of municipal water systems

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Disinfectants and Disinfection Byproducts (DBPs)

Regulated DBP Contaminants	MCL (mg/L)	MCLG (mg/L)	Regulated Disinfectants	MRDL* (mg/L)	MRDLG* (mg/L)
Total Trihalomethanes (TTHMs)	0.080		Chlorine	4.0 as Cl_2	4
Chloroform		-			
Bromodichloromethane		Zero			
Dibromochloromethane		0.06			
Bromoform		zero			

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Disinfectants and Disinfection Byproducts (DBPs)

Regulated DBP Contaminants	MCL (mg/L)	MCLG (mg/L)	Regulated Disinfectants	MRDL* (mg/L)	MRDLG* (mg/L)
Five Haloacetic Acids (HAA5)	0.060		Chloramines	4.0 as Cl_2	4
Monochloroacetic acid		-	Chlorine dioxide	0.8	0.8
Dichloroacetic acid		Zero			
Trichloroacetic acid		0.3			
Bromoacetic acid		-			
Dibromoacetic acid		-			

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Disinfectants and Disinfection Byproducts (DBPs)

Regulated DBP Contaminants	MCL (mg/L)	MCLG (mg/L)		MRDL* (mg/L)	MRDLG* (mg/L)
Bromate (plants using ozone)	0.010	Zero	*Stage 1 DBPR includes maximum residual disinfectant levels (MRDLs) and goals (MRDLGs) which are similar to MCLs and MCLGs but for disinfectants		
Chlorite (plants using chlorine dioxide)	1.0	0.8			
Treatment Technique					
Enhanced coagulation/enhanced softening to improve removal of DBP precursors (See Step 1 TOC Table for systems using conventional filtration treatment)					

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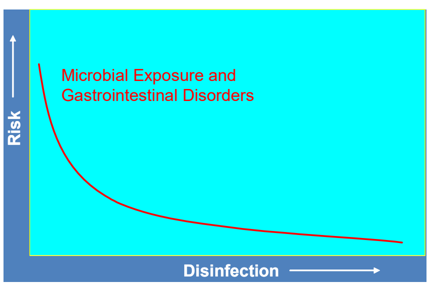
Microbial Risks



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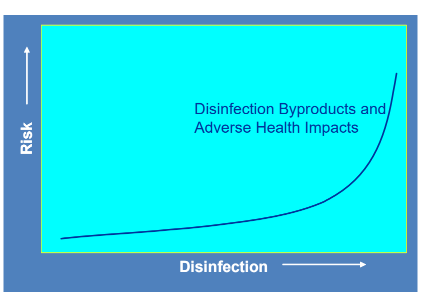
Disinfection Byproduct Risks



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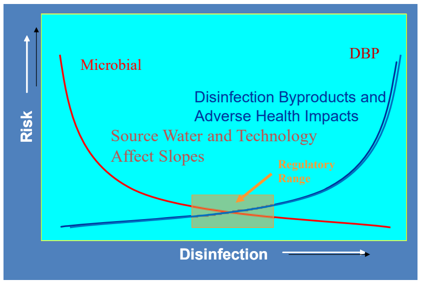
Microbial vs. DBP Risk Trade-Offs



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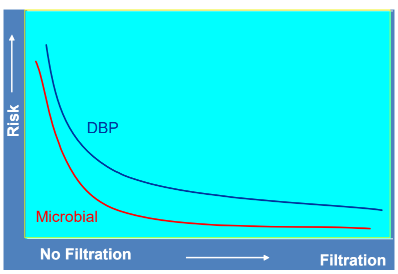
Filtration Reduces both Microbial and DBP Risks



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Disinfection By-Products

Regulations

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Disinfectants and Disinfection Byproducts (D/DBP) Rules

- Applies to any Public Water System that adds a disinfectant (SW – Surface Water; GW – Ground Water)
- Effective dates:
  - Stage 1 D/DBP Rule - January 2002 (>10,000 SW)
  - Stage 1 D/DBP Rule - January 2004 (SW<10,000 and GW)
  - Stage 2 D/DBP Rule – January 2006 – October 2013 (all populations; SW and GW)
- Balance benefits of acute microbial protection against risks of chronic exposure to disinfection by-products

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Monitoring Requirements

Monitoring Frequency and Number of Sites

Stage 1 DBPR:
•Plant-based
•Dependent on number of treatment plants or wells

Stage 2 DBPR:
•Population-based
•Dependent on population served

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SDWA Individual Rules

- Stage 1 Disinfectants/Disinfection Byproducts Rule (DBP)
  - Increases requirements for some regulated DBPs
  - Sets new requirements for haloacetic acids, chlorite, and bromate

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Specific Requirements MCLs and MRDLs

Compound(s)	Stage 1 & 2 (mg/L)
TTHMs	0.080
HAA5	0.060
Bromate	0.010
Chlorite	1.0
Chlorine	4.0
Chloramines	4.0
Chlorine Dioxide	0.8

Stage 1: System-wide Running Annual Avg. (RAA)

Stage 2: Locational Running Annual Avg. (LRAA)

MRDLs for Chlorine and Chloramines may be exceeded in response to public health problems

Stage 1 Sampling Frequency

Surface	Sampling Frequency	Ground
≥10,000	4/plant/quarter (1 max, 3 rep. RT)	
500 - <10,000	1/plant/quarter (max RT)	≥10,000
< 500	1/plant/year (warmest month)	< 10,000

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Stage 1 D/DBP Monitoring Requirements

- Chlorine dioxide
  - Chlorine dioxide plants
  - Daily at entrance to distribution system
  - Compliance - Daily/follow up monitoring
- Chlorine/Chloramines
  - All systems
  - Same location and frequency as Total Coliform Rule monitoring
  - Compliance - Running annual average

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Stage 1 D/DBP Monitoring Requirements

- **TTHM/HAA5 - Routine Monitoring**
  - Surface Water Systems >10,000 = 4/plant/Q
  - Surface Water Systems 500 – 9,999 = 1/plant/Q
  - Surface Water Systems <500 = 1/plant/Y* (warmest)
  - Ground Water Systems >10,000 = 1/plant/Q
  - Ground Water Systems <10,000 = 1/plant/Y* (warmest)
- Single sample represents the maximum residence time
- Multiple samples - 25% samples represent the maximum residence time
- Compliance - Running Annual Average
- *Increase to 1/Q if MCL is exceeded

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Stage 2 D/DBP Rule

- Provides greater public health and protection through:
  - Identifying locations with highest Disinfection Byproducts (DBPs)
  - Basing Compliance on Locational Running Annual Average (LRAA)
  - Requiring tests for connected and consecutive water systems
- Population Based Monitoring for all systems with disinfection

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Stage 2 DBPR Requirements

- Purpose: to ensure that all locations in the distribution system comply with the MCLs – "environmental justice"
- Phase 2A
  - LRAA of 120/100 μg/L at Stage 1 locations
  - Continue to meet system-wide RAA of 80/60
- Phase 2B
  - LRAA of 80/60 at new "representative" high locations
- Initial Distribution System Evaluation (IDSE)
- Significant Excursions

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D/DBP Rule: Stage 2

- Compliance Monitoring
  - Locational Running Annual Average (LRAA)
    - MCLs: 80/60
  - Monitoring for Large SW systems (> 10,000)
    - Quarterly sampling
    - At least one quarterly sample at peak month
    - 4-20 DS locations determined by IDSE *and* stage 1 locations
      - 2-8 at high THM sites, and 1-7 at high HAA sites
  - Monitoring for small SW systems (< 10,000)
    - 2 locations as determined by IDSE

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Disinfection

Equipment

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Chlorine Gas Containers

- Three size containers for chlorine gas and sulfur dioxide gas:
  - 150-lb cylinders
  - 1-ton containers
  - 90-ton rail cars
- Weights are for the chemical and do not include the container weight.

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150-lb Cylinders

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150-lb Cylinders

- Seamless steel containers with a valve at the top
- A bonnet covers and protects the valve when not in use.
- Filled to 80% capacity to allow for liquid expansion
- Moved, stored and used in the upright position

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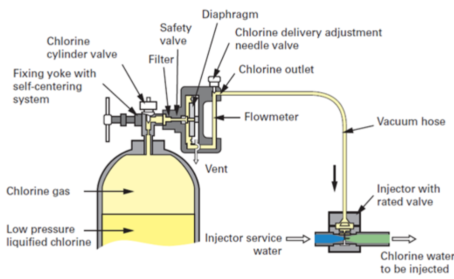
150-lb Cylinders



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150-lb Cylinders: Fusible Plug

- Normally, most chlorine in the cylinder is liquid
- Liquid chlorine converts to gas as temperature increases
- Gas exerts more pressure on the cylinder
- Fusible plug on the cylinder melts at 70 and 74 °C (158 and 165 °F) to relieve pressure and prevent the cylinder from exploding

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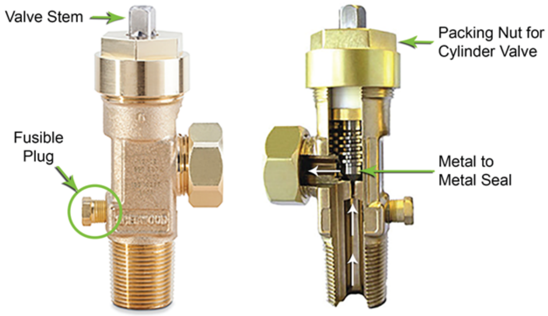
150-lb Cylinders: Fusible Plug



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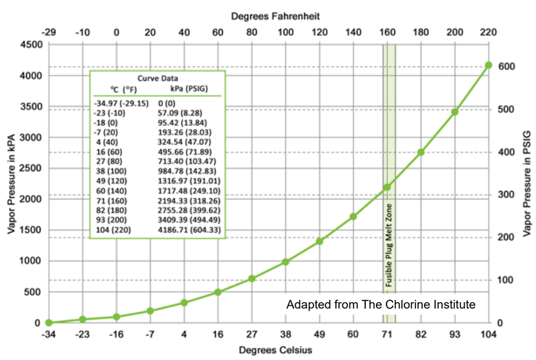
Fusible Plug Melt Zone



°C (°F)	kPa (PSIG)
-34.97 (-29.15)	0 (0)
-23 (-10)	57.09 (8.28)
-18 (0)	95.42 (13.84)
-7 (20)	193.26 (28.03)
4 (40)	324.54 (47.07)
16 (60)	495.66 (71.89)
27 (80)	713.40 (103.47)
38 (100)	984.78 (142.83)
49 (120)	1316.97 (191.01)
60 (140)	1717.48 (249.10)
71 (160)	2194.33 (318.26)
82 (180)	2755.28 (399.62)
93 (200)	3409.39 (494.49)
104 (220)	4186.71 (604.33)

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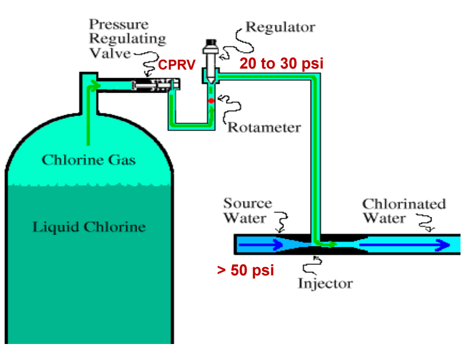
Chlorine Gas Feed System



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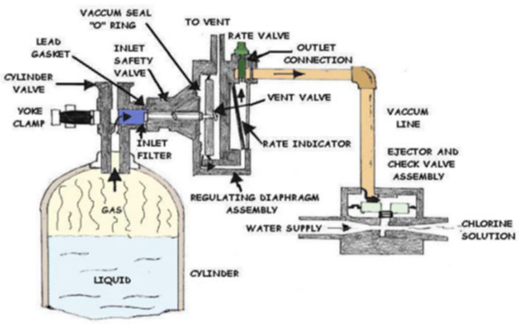
Chlorine Gas Feed System



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Ton Containers

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Ton Containers

- Fusible plugs (Total 6; 3 on each end) and protective cap on ton container

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Ton Containers

- Moved, stored, and used in a horizontal position
- Valves are protected by domed covers when not in use
- Cradles hold the containers in place
- Trunnions allow the container to be rotated in the cradle

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Ton Containers

Chemical Scales

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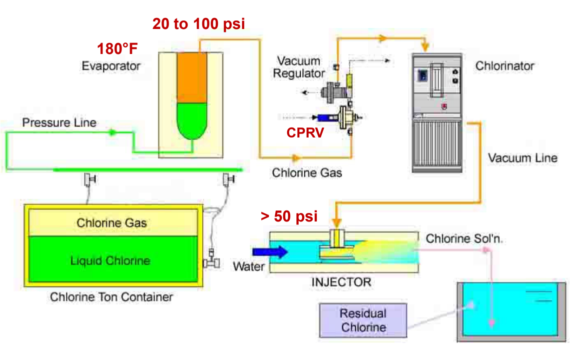
Liquid Chlorine Feed System



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Ton Containers

- Provide either liquid or gaseous chlorine through eduction pipes
  - Align valves vertically.
  - Upper valve supplies chlorine gas.
  - Lower valve supplies chlorine liquid.
  - An eduction tube is connected to each valve.
- Each container has six fusible plugs to relieve pressure.

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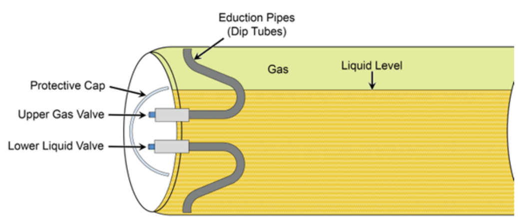
Ton Container – Induction Tube



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Railcars

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Railcar

- 90-ton storage in railcar
- Can feed liquid directly to the process or on-site storage tanks
- Equipped with two liquid valves and a safety valve that provides overpressure protection
- Two gas valves are for adding air to increase car pressure.

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Safety and Security Regulations

- Regulations:
  - Uniform Fire Code (UFC)
    - 1992 revisions of the UFC requires complete containment and neutralization of a catastrophic leak of chlorine gas.
    - A chlorine gas scrubber would be needed to contain and neutralize such a leak.
    - At least 27 states have adopted the UFC revisions

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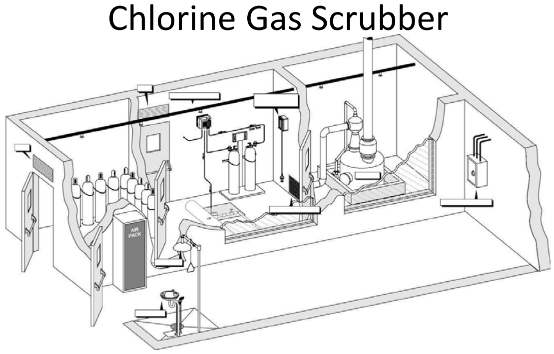
Chlorine Gas Scrubber



Chlorine room designed to meet OSHA and Article 80 requirements

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SCBA

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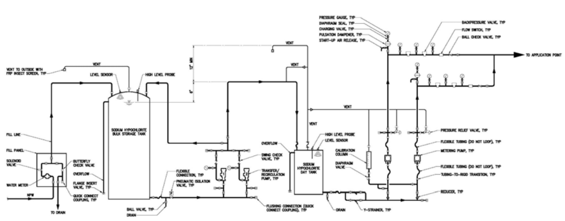
Production of Sodium Hypochlorite

- Bulk Hypochlorite Production
  - Chlorine and Caustic
    $$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O + Heat$$
  - Electrolytic Formation
    $$NaCl + H_2O + 2e^- \rightarrow NaOCl + H_2$$
- Onsite Hypochlorite Generation
  $$NaCl + H_2O + 2e^- \rightarrow NaOCl + H_2$$

1

Bulk Hypochlorite Schematic



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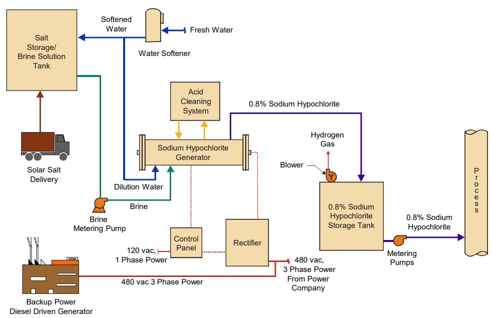
On-Site Hypochlorite Generation

- Growing interest in generating sodium hypochlorite on site
  - Produces a dilute solution (0.8%) that isn't prone to degradation, so loss of concentration and off-gassing aren't an issue
  - Produced on site from salt solution, so fluctuations in hypochlorite pricing are less of an issue
  - Equipment is more complex to operate and maintain than bulk hypo equipment

3

On-Site Hypochlorite Generation



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On-Site Generation- Disadvantages

- By-product of process is hydrogen gas
- Salt used needs to be solar or food-grade- potential source of bromate
- High Capital Costs
- Energy usage
- Instrumentation

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Properties of Sodium Hypochlorite

- Mildly Corrosive
- Has Free Sodium Hydroxide (Caustic Soda)
- pH=12.5 to 13
- Pale Yellow Solution, 12.5% to 15% By Volume
- Non-Flammable
- Incompatible with many other chemicals
- **Relatively Short Shelf Life** - Concentration, heat, and sunlight (UV) cause decomposition

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Safety and Building Code Compliance

- Corrosive chemical at >12%, irritant at 5%
- Sprinkler system for indoor storage area for corrosive chemicals
- Secondary containment
  - Largest container plus sprinkler water for a period of 20 minutes
- Positive mechanical ventilation
- Tank overfill protection
- Check local building codes

7

Sodium Hypochlorite Concentration

Trade %	Freezing Point, ºF	pH
0.8	32	Maintain between 12 and 13 w/ excess caustic
5	22	
10	7	
15	-8	

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Sodium Hypochlorite Concentration

Trade % (available chlorine)	Specific Gravity (@ 10 gpl excess NaOH)	Weight % (available chlorine)	Available Chlorine, lb/gal
0.8	1.017	0.79	0.067
5	1.076	4.65	0.417
10	1.146	8.76	0.834
15	1.205	12.44	1.25

To find available chlorine in lb/gal, multiply trade % by 0.08345.

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Sodium Hypochlorite Concentration

$$\frac{grams}{Liter} = \frac{weight\ of\ available\ chlorine, g}{volume\ of\ NaOCl\ solution, L}$$

$$Trade\ Percent = \frac{gpl}{10} = \%\ by\ volume$$

$$Weight\ Percent = \frac{trade\ percent}{specific\ gravity\ of\ solution}$$

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Properties of Sodium Hypochlorite

- Sodium Hypochlorite used in water and wastewater treatment is typically delivered in 12.0% trade concentrations
- Common household bleach concentration is typically about 5.25% trade; NGT 8%
- Out-gassing occurs with sodium hypochlorite due to decomposition of the chemical
  - Chlorine and oxygen are the most prevalent gases to consider when designing piping
  - Hypochlorite trapped between two closed valves can build pressure until the pipe fails

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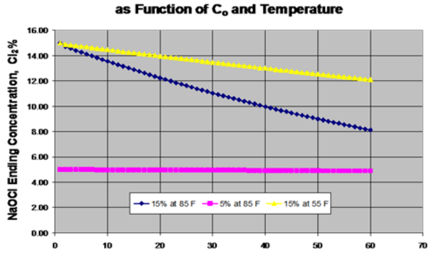
Chlorine Design Basics
Storage of Bulk Hypochlorite

NaOCl Decomposition Rate as Function of C_o and Temperature



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NaOCL Degradation/Decomposition

- Time of Manufacture - 12.5 Trade Percent
- Average Manufacturer <u>@ 80 Degrees</u>
  - 2 Days Later – 12.34 Trade Percent
  - 7 Days Later – 11.96 Trade Percent
  - 14 Days Later – 11.47 Trade Percent
  - 21 Days Later – 11.01 Trade Percent
  - 28 Days Later – 10.59 Trade Percent
  - 35 Days Later – 10.21 Trade Percent

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NaOCL Degradation/Decomposition

- Hypochlorite decomposes to:
  - Salt (NaCl), Chlorates (ClO_3^-), and Oxygen (O_2)
  - $3NaOCl \rightarrow 2NaCl + NaClO_3$ (Sodium Chlorate)
  - $2NaOCl \rightarrow 2NaCl + O_2$ (Gassing)
- Factors:
  - Temperature (Heat)
  - UV (e.g., Sunlight)
  - Impurities (Primarily Heavy Metals)
  - Concentration (Strength of solution)

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Stability of Sodium Hypochlorite

Decomposition of Hypochlorite

- Loss of Product Concentration
  - Wasted money
  - Feed equipment no longer sized correctly
- Production of chlorate and perchlorate
  - SDWA regulated disinfection by-product

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Perchlorate

Common name	Stock name	Oxidation state	Formula
Hypochlorite	Chlorate(I)	**+1**	**ClO^-**
Chlorite	Chlorate(III)	+3	**ClO_2^-**
Chlorate	Chlorate(V)	**+5**	**ClO_3^-**
Perchlorate	**Chlorate(VII)**	+7	**ClO_4^-**

Perchlorate adversely affects human health by interfering with iodine uptake into the thyroid gland.

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Perchlorate
(EPA Notice - January 2012)

- EPA Will Regulate Perchlorate
  - EPA has 24 months to propose an MCL
  - ~ 24 additional months for promulgation
  - CA MCL = 6 μg/L; MA MCL = 2 μg/L; NV Action Level = 18 μg/L
  - EPA's Federal Register notification from 2010: MCL as low as 1 μg/L
- Sources of Perchlorate
  - Munitions
  - Rocket fuel
  - Industrial sites
  - Fireworks, flares
  - **Hypochlorite (Bleach) - Drinking water and wastewater treatment!!!**

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Chemical System Design

- Equipment
  - Bulk storage tanks – dilution, mixing and storage
  - Recirculation/transfer pumps – mixing and transfer to day tanks
  - Air mixing system
  - Day tanks – short-term storage
  - Metering pumps – transfer to application point
  - Instruments – tank level, pump flow measurement

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Bulk Hypochlorite Equipment - Tanks

Polyethylene

- Limited Volumes
- Special Fittings (IMFO)- Allow for the tank to drain completely
- When laying these tanks out, note that the connections are fixed. Unlike FRP tanks, the manufacturer will NOT rearrange tank fittings based on design layout

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Tanks - Simplified Layout

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Bulk Hypochlorite Equipment Air Mixing System

- Air Mixing System
  - Pulses of air are released beneath a round accumulator plate fastened to bottom of tank
  - Bubbles rise toward surface of tank, creating mixing action
  - No moving parts

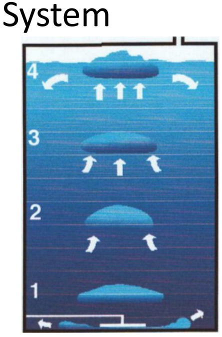

Photo courtesy of Pulsair.com

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Bulk Hypochlorite Equipment - Pumps

- Recirculation and Transfer Pumps
  - Magnetic drive centrifugal pumps
    - Plastic construction
    - Titanium construction
    - Teflon-lined
  - Centrifugal pumps with seal water
    - Fiberglass pump body with titanium shaft and hardware
  - Viton o-rings and gaskets

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Bulk Hypochlorite Equipment Metering Pumps

- **Mechanically-actuated diaphragm**
  - Elastomer-faced diaphragm
  - Common pump head materials – PVC, Kynar, stainless steel
- **Hydraulically-actuated diaphragm**
  - Flat and tube diaphragms available
  - Common pump head materials – PVC, Kynar, stainless steel, cast iron (for tube diaphragms)
- **Peristaltic**
  - Tube must be compatible with pumped chemical
- **Accessories include:**
  - Pressure relief valves, pulsation dampeners, backpressure valves

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Bulk Hypochlorite Equipment Metering Pumps

- Diaphragm Pumps
  - Mechanical or hydraulic diaphragm pumps
  - Solenoid pumps for low feed rates
  - Good range of capacities
  - Good turndown – stroke length and frequency can be adjusted
  - Heads can be equipped with degassing valves

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Bulk Hypochlorite Equipment Metering Pumps

- Diaphragm Pumps
  - Flat Diaphragm – Kynar or PVC pump head
  - Suction and Discharge Valve Assemblies – PVC, Kynar or Teflon
  - O-rings and gaskets – Viton
  - Exterior – Plastic or painted with protective epoxy coating

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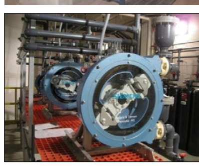
Bulk Hypochlorite Equipment Metering Pumps

- Peristaltic Pumps
  - Great range of feed rates
  - Pump heads don't air-lock from off-gassing
  - Turndown not as good as diaphragm pumps because only motor speed can be adjusted
  - Tube - Hypalon
  - Exterior – Plastic or painted with protective epoxy coating



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Bulk Hypochlorite Equipment Metering Pump Accessories

- Calibration chamber
- Pulsation dampener
- Pressure relief valve
- Backpressure valves
- Pressure gauges

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Daily Chemical Usage Calculations

- $w = 8.34 \times Q \times C = lbs/day$
  - w = dry weight of the chemical, Lb/day
  - Q = Plant flow rate, MGD
  - C = Chemical dose concentration, mg/L or ppm
- $q = \dfrac{w}{8.34 \times sg \times S/100} = \dfrac{8.34 \times Q \times C}{8.34 \times sg \times S/100}$
  - q= chemical feed rate, gpd
  - w = dry weight of chemical, Lb/day
  - sg = specific gravity
  - S = % of chemical solution, %

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Materials of Construction

- Piping - PVC and CPVC **(recommended)**
  - Most hypochlorite piping systems are constructed of PVC and/or CPVC
  - PVC and CPVC are easy to install and cost effective
  - A CPVC pipe system (including fittings) will cost roughly about 2 times the cost of a PVC pipe system
  - CPVC has a higher temperature rating than PVC (180 degrees versus 130 degrees)

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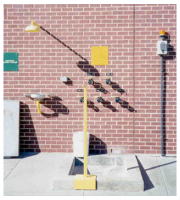
Bulk Hypochlorite Equipment

- Safety Equipment
  - Local alarm horn and lights to signal high tank level, high level in containment area
  - Emergency shower and eyewash stations
  - Fire extinguishers
  - Hazard identification signs
  - Person protective equipment (PPE)
    - goggles, aprons, gloves



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Disinfection

Chlorine Contact Tanks

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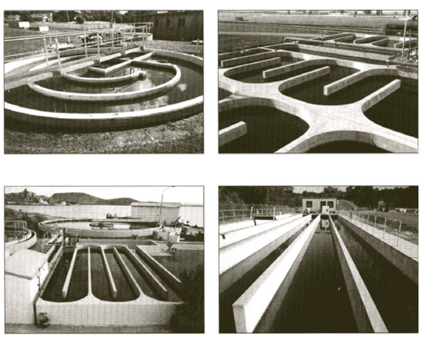
Chlorine Applications - Contact Tanks



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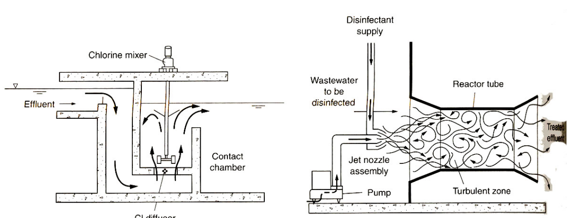
Chlorine Application - Mixing



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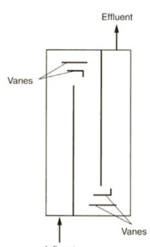
Chlorine Applications - Contact Tanks

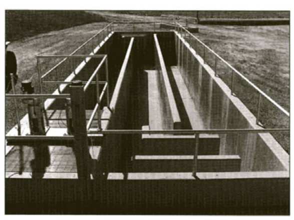
- Volume based on contact time
  - 15 min at peak flow (Ten States Standards)
  - 20 min at peak flow (Virginia Sewage Collection and Treatment (SCAT) regulations
  - 30 min at average flows
- Path length-to-width (L:W) ratio
  - 40:1 recommended in NEIWPCC TR-16
  - 30:1 recommended in Tennessee
  - No guidance in Ten States Standards

34

Chlorine Applications - Contact Tanks



Plan view of chlorine contact basin



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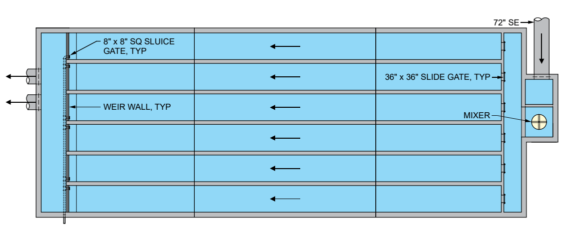
Chlorine Applications - Contact Tanks

Parallel single pass tanks reduce dead spots



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Disinfection

Dechlorination

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Dechlorination

- Chlorine and chlorination by-products are toxic to aquatic life in receiving streams
- Neutralization of chlorine:
  - < 0.05 mg/L (1970's)
  - Sulfur dioxide (gas)
  - Sodium bisulfite (liquid)

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Dechlorination Basics

- Reaction is quick; less than 15 seconds with SO_2 and Sodium Bisulfite ($NaHSO_3$)
- Both chemicals form sulfurous acid (H_2SO_3) in water which reacts with free chlorine (HOCl) as well as chloramines (NH_2Cl):

$$H_2SO_3 + HOCl \rightarrow 3H^+ + Cl^- + SO_4^{-2}$$

$$H_2SO_3 + NH_2Cl + H_2O \rightarrow 2H^+ + NH_4^+ + Cl^- + SO_4^{-2}$$

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Dechlorination Chemicals

		Theoretical Dose per mg/L TRC
Sulfur dioxide gas	SO_2	0.9 mg/L
Sodium bisulfite	$NaHSO_3$	1.5 mg/L
Calcium thiosulfate	CaS_2O_5	0.53 mg/L

Source: WERF Disinfection Alternatives 2008

- Excess dechlorinatioin chemicals are typically added to assure removal of total residual chlorine

- SO_2, $NaHSO_3$ reacts in ~15 seconds
- CaS_2O_5 reacts in ~ 5 minutes

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Chlorine/Sulfur Dioxide Treatment

- Chlorination for disinfection
- Chlorine residual: less than 0.05 mg/L in wastewater effluent (after dechlorination)
- Wastewater plants use sulfur dioxide for removal of free chlorine (Dechlorination)
- 1-ton chlorine and sulfur dioxide tanks

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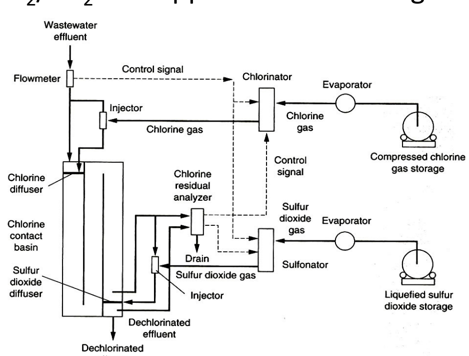
Cl_2/SO_2 Gas Application Flow Diagram



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Chlorine/Sulfur Dioxide Treatment- Equipment

Load Cells

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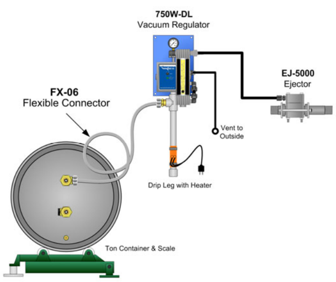
Chlorine/Sulfur Dioxide Treatment- Equipment



Whip connected to Valve

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SO_2 Railcar

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Chlorination/Sulfur Dioxide Equipment-Normal Operations

- Valve manifold is open
- In-service cylinder valves are open
- Verify that flow meter readings are in pounds per day (ppd)
- Verify that flow meter is reading within expected range for your plant

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Chlorination/Sulfurdioxide Equipment-Abnormal Operations

- Gas leaks: low and high alarms go off
- Gas flow is below expected range
- Cylinder weight is less than expected

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Chlorination/Sulfurdioxide PM

- PAPR (Powered Air-Purifying Respirator) with gas cartridge
- Personal gas monitor
- Safety goggles
- Work gloves
- Latex gloves
- Normal work attire (hard hat, long-sleeves/pants, safety shoes)

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Oxidation Reduction Potential (ORP)

- Chlorination/dechlorination can be controlled and monitored by ORP
- ORP measures transfer of electrons:
  - Chlorine forms that are toxic to microorganisms are missing one or more electrons and satisfy their need for electrons by stealing them from organics or other donors through an electrical attraction.
- Electrical potential can be monitored by ORP and is measurable in millivolts (mV)
- Higher mV = greater disinfecting capability

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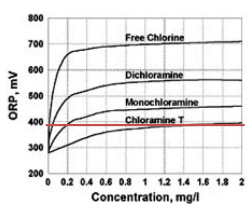
Chlorination Set Point

- Select a set point that gives the desired fecal kill
- The set point is dependant on the chlorine residual species



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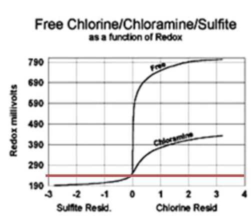
Dechlorination Set point

- Start with a low set point to assure compliance
- Gradually increase set point if chemical savings is desired



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Dechlorination Application - Mixing

- Good mixing essential
  - Maintains proper ratio of Sodium Bisulfite to Sodium Hypochlorite
  - Keeps dechlorination dose near theoretical
- Mixer or hydraulic energy for dechlor
  - Cascade
  - Effluent channel
  - Effluent Parshall flume

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Sodium Bisulfite Concentration

Trade %	Specific Gravity	Freezing Point, ºF
25	1.21	20
38	1.33	43

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Chlorination/Dechlorination

- **Chlorination with Sodium Hypochlorite**
  - NaOCL + H_2O → **HOCl** + NaOH
- **Declorination with Sodium Bisulfite:**
  - $NaHSO_3$ + **HOCl** → $NaHSO_4$ + HCl

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Dechlorination Basics

- **Declorination with Sodium Bisulfite:**
  - $NaHSO_3$ + **HOCl** → $NaHSO_4$ + HCl
  - Removing chlorine protects aquatic life from TRC
  - Converts chlorine in free and combined forms to chlorides (Cl^-)
  - Dechlorination of combined chlorine forms may produce ammonia
  - Most plants will have their TRC limits removed from the NPDES permits if they switch from chlorine disinfection to UV

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Chemical Usage

Safety and Security Regulations

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Safety and Security Regulations

- Regulations:
  - Homeland Security Act of 2002 (P.L. 107-296) created Department of Homeland Security (DHS)
    - Responsibility for assessing and protecting the nation's critical infrastructures
    - High-risk chemical facilities
    - Apply consistent **"Inherently Safer Technologies" (IST)** approaches for all high-risk chemical facilities
    - Excludes water and wastewater systems

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Safety and Security Regulations

- Regulations:
  - The Public Health Security and Bioterrorism Preparedness and Response Act of 2002 (P.L. 107-188) amended the Safe Drinking Water Act
    - Required some 8,400 community water systems to assess vulnerabilities and prepare emergency response plans.
    - Directed EPA to review methods to prevent, detect, and respond to threats to water safety and infrastructure security.

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Safety and Security Regulations

- Regulations:
  - Homeland Security Presidential Directive (HSPD-7) of 2003 affirmed EPA's lead role in protecting the water and wastewater infrastructure.
    - Under this directive, EPA has responsibility for developing and providing tools and training on improving security to roughly:
      - 52,000 community water systems
      - 16,000 municipal wastewater treatment facilities.

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Safety and Security Regulations

- Regulations:
  - OSHA's/USEPA's 1993 Risk Management Program (RMP)
    - Develop a **community** Risk Management Plan
    - Prevent/minimize consequences of accidental releases of toxic and flammable chemicals
    - Public must be notified of any release of toxic of flammable substances
    - Compliance required by 1996

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Summary

- Chlorination will continue for some time at WTPs and WWTPs
- Trend in chlorine disinfection is towards liquid chemicals
  - "Inherently Safer Technologies" (ISTs)\
  - Safer for WTP and WWTP operators and surrounding community
  - Without pressurized gas systems, WTPs and WWTPs are less likely terrorist targets

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Summary

- Sodium hypochlorite and sodium bisulfite are liquid chemicals of choice for WWTP chlorination/dechlorination
- Operators tend to slightly overdose dechlorination chemicals to ensure that the chlorine residual is "zero"

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Conclusion

- Chlorine, hypochlorite and UV are all viable disinfectants
- Each has its own set of advantages and disadvantages
- Each chemical disinfectant produces undesirable byproducts
- *Trend today is towards hypochlorite and UV*

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Questions

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Thank You

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