Hypochlorite Disinfection

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Hypochlorite Disinfection

7 contact hours
9 CC10 hours

This course focuses on the properties, use, and feed equipment when using hypochlorite for disinfection. Hypochlorites - sodium and calcium - are the most common form of disinfection used in water treatment. Students will be introduced to the uses and properties of hypochlorites, chemical handling including safety, regulatory requirements, and feed equipment. Various mathematics principles will be addressed throughout the workshop including changing % concentrations, dosage/feed rates, chlorine demand/dose, and CT calculations.

Learning Objectives:

1. Explain how hypochlorite is produced.
2. Perform mathematical calculations for changing % of concentrations of chemicals, dosage/feed rate/flow, chlorine demand or dose and CT.
3. Identify chemical feed equipment and explain important operation and maintenance considerations.
4. Use the MSDS sheet to identify the first aid measures to be taken in the event of a chemical burn.

8:15 - 8:30 Registration
8:30 - 9:30 Unit 1 (1 hr)
- Basic Hypochlorite Information
- Basic Hypochlorite Properties

9:30 - 10:15 Unit 2 (45 min)
- Storage and Handling
- Safety

10:15-10:30 Break
10:30-11:30 Unit 3 (1 hr)
- Math terms, principles, and rules for solving equations
- Unit Cancellation steps

11:30-12:30 Lunch
12:30 - 2:30 - Unit 3 (2 hr)
- Calculation changing % concentration of a chemical
- Dosage/Feed Rate/Flow
- Chlorine Demand or Dose

2:30 - 2:45 Break
2:45 - 3:30 Unit 3 (45 min)
- CT
- Review

3:30 - 4:15 Unit 4 (45 min)
- Regulatory Requirements
- Chlorination Mechanics and Terminology
- Feed Equipment

4:15 - 5:00 review questions (45 min)

Hypochlorite Disinfection

Presented by
Ed Jones

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College of Southern Maryland
La Plata, MD

1

Process Training Session

Before class starts, please:
- **Sign in** on the Attendance Sheet

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

At the end of class, please:
- **Answer questions** on post exam
- **Fill out** Class Evaluation

2

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
- Less lecture, more discussions
- Keep it simple
- ***Make this an enjoyable and informative experience!***

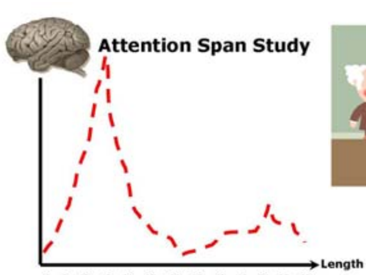
4

Discussions

- Student involvement will be encouraged in class discussions to:
  - Keep students attentive
  - More importantly, **help students retain and process information**

5

Attention Span - Lectures



Source: based on a study by Richard Mayer

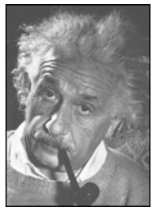
6

The Guiding Expectation

"Things should be made as simple as possible -- but no simpler."

Albert Einstein

www.physik.uni-frankfurt.de/~jr/physpiceinstein.html



7

Ground Rules

- Discussion is encouraged
- Participate at your own comfort level
- Use terms we all can understand
- Everyone is different, so please show respect for others in the room
- Listen with an open mind
- Express opinions - of things, not people
- Maintain confidences

8

Ice Breaker

- Before we start, let's introduce ourselves:
  - Name,
  - What do you do, and
  - What do you know/don't know about chlorination/dechlorination with…?
    1. Gases – Chlorine and Sulfur Dioxide (Cl_2 and SO_2)
    2. Liquids – Sodium Hypochlorite and Sodium Bisulfite ($NaOCl$ and $NaHSO_3$)
    3. Solids – Calcium Hypochlorite and Sodium Metabisulfite ($Ca(OCl)_2$ and $Na_2S_2O_5$)

9

Class Objectives

10

Learning Objectives

- To explain disinfection requirements:
  - Regulatory framework
    - Disinfection requirements
    - Disinfection By-products
  - Chlorination theory
    - Chemistry
    - Breakpoint chlorination
  - Dechlorination requirements
  - Switch to liquid chemicals

11

Learning Objectives

- To discuss O&M, process control, and safety practices
  - Chemical properties
  - Truck unloading
  - Storage
  - Conveyance:
    - Transfer pumps
    - Metering pumps
  - Dosing (Chlorination and Dechlorination)

12

Focus of Class

- Disinfection
- Breakpoint Chlorination
- Chlorine products:
  - Chlorine (Cl_2, gas)
  - Sodium Hypochlorite (NaOCl, solution) **(Emphasis)**
  - Calcium Hypochlorite ($Ca(OCl)_2$, solid/solution)
- Dechlorination products
  - Sulfur dioxide (SO_2, gas)
  - Sodium bisulfide ($NaHSO_3$, solution) **(Emphasis)**
- Summary and Conclusions

13

Presentation Goals

- Discuss chlorination:
  - Disinfection regulations
  - Theory and breakpoint chlorination
  - Dechlorination requirements
- Discuss types of sodium hypochlorite systems:
  - Chemical properties
  - Bulk storage
  - Conveyance
  - On-site generation

14

Presentation Goals

- Discuss sodium bisulfite systems
  - Chemical properties
  - Bulk storage
  - Conveyance
- Identify acceptable materials of construction for:
  - Bulk storage tanks
  - Piping and valves
  - Transfer pumps and metering pumps
  - Expected equipment service life

15

Class Agenda

- Introduction/Overview
- Chlorination Chemistry
- Breakpoint Chlorination
- Regulatory Framework
- Unit Treatment Processes:
  1. Chlorination/dechlorination
     - ✓ Chlorine gas/Sulfur dioxide
     - ✓ Sodium hypochlorite/Sodium Bisulfite **(Emphasis)**
  2. Equipment and Construction of Materials
  3. Chlorine Residual Monitoring
- Summary

16

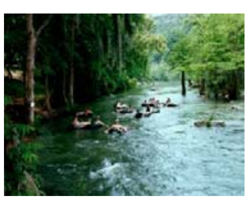
Need for Disinfection

Overview

17

What is Disinfection?

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



18

Chlorination

- Chlorine Gas (Cl_2)

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

- Sodium Hypochlorite (NaOCl)

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

- $HOCl \Leftrightarrow H^+ + OCl^-$ (in equilibrium)
  - HOCl – Hypochlorous acid
  - OCl^- – Hypochlorite ion

Chlorination

- Reduces pathogens in wastewater effluents
  - Chlorine use began more than 100 years ago
  - Good viral and bacterial reductions:
    - ✓Typically, 99.9+%
    - ✓Meets fecal coliform limits for WWTP discharges
- Toxicity of chlorine and its disinfection by-products (DBPs) on aquatic life is a major drawback
- Need dechlorination with or without (membrane) filtration to remove chlorine residual

History of Chlorine Gas Use

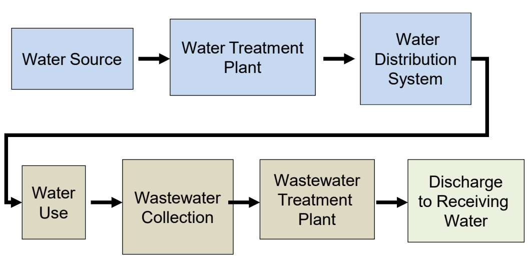
- 1847 - Chlorine was first used as a disinfectant in Vienna
- 1890's - The use of chlorine becomes commonplace in England
- 1908 - Initial U.S. applications of chlorination in Chicago and Jersey City water districts
- 1918 - Over one-thousand cities in USA use chlorination for drinking water supplies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

History of Hypochlorite Use

- 1789 – France – bleaching in textile industry
- 1897 – England – disinfection of drinking water
- 1930 – United States – Use in household laundry and drinking water disinfection
- 1970 – United States – Public water and wastewater treatment systems begin replacing chlorine gas with hypochlorites

22

Water Use Cycle



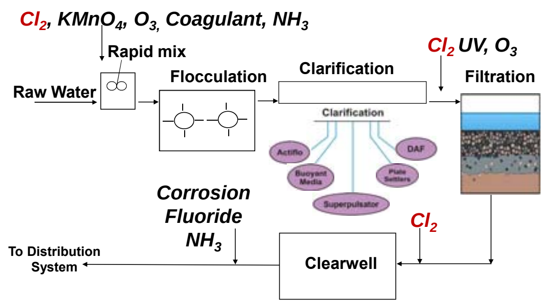
23

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

24

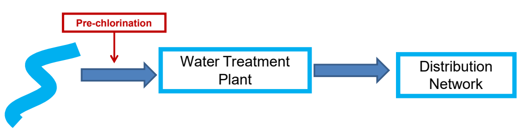
Typical Water Filtration Plant



25

Pre-Chlorination at WTPs

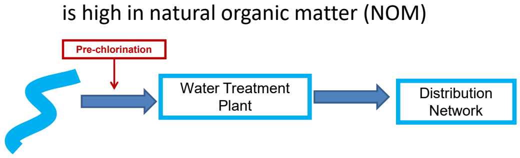
- Pre-chlorination is used to remove minerals (e.g. Iron, manganese)
  - Chlorine precipitates minerals as insoluble particulates
  - Precipitated minerals can be removed during water treatment (e.g., clarification, filtration)
- Pre-chlorination can also remove tastes/odors



26

Pre-Chlorination at WTPs

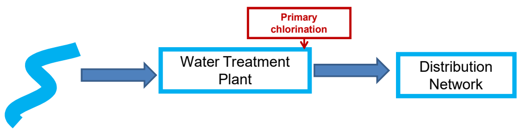
- Potential issues:
  - Raw water may have a high chlorine demand which requires high chlorine dose (high operational cost)
  - Disinfection by-products will form if water source is high in natural organic matter (NOM)



27

Primary Chlorination at WTPs

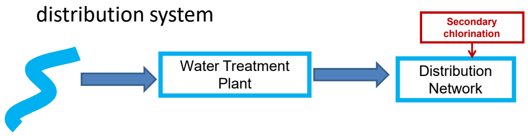
- Used for disinfection; most common & effective point of application; 100+ years of experience
- Most effective to add chlorine when turbidity is low; ideally <0.3 NTU (i.e., after clarification, filtration)
  - Use less chlorine
  - Less risk of disinfection by-product formation



28

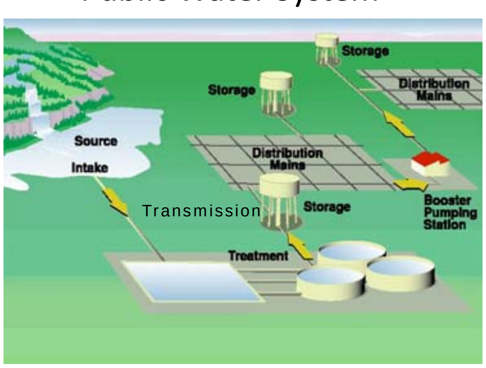
Secondary Chlorination in Distribution System

- 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



29

Public Water System



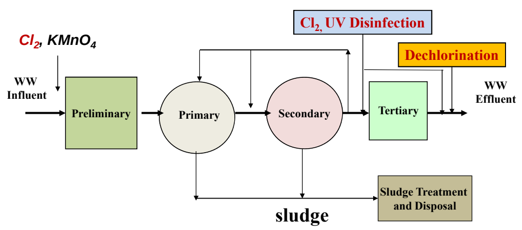
30

Chlorine Addition

- At WWTPs:
  - Pre-chlorination
  - Effluent disinfection
    - ✓Minimum 0.5 mg/L chlorine concentration before dechlorination
  - Need for dechlorination
    - ✓Maximum 0.05 mg/L chlorine concentration after dechlorination

31

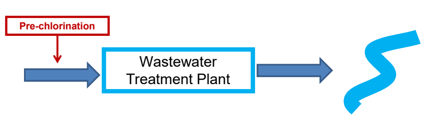
Conventional WWTP Process



32

Pre-Chlorination at WWTPs

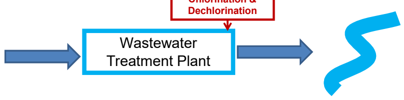
- Objectives of pre-chlorination are:
  - Odor control
  - Protection of plant structures from H_2S
  - Aid in sedimentation
  - Reduction or delay of biochemical oxygen demand (BOD).



33

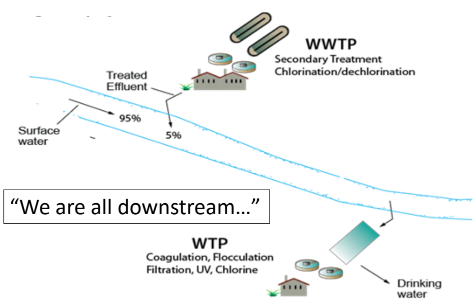
Chlorination at WWTP Effluents

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



34

De facto Reuse of Wastewater



35

Wastewater Treatment

- Sewage is an environmental health hazard (wastewater effluent)
- Purpose of municipal wastewater treatment is to limit pollution in the receiving waterway
- Receiving waterways are usually sources of drinking water

36

Wastewater Impacts to Natural Receiving Waters

- Treated wastewater is often discharged to nearby natural waters
  - Biological oxygen demand (BOD)
  - Chemicals (nitrogen, phosphorus)
  - Synthetic Chemicals
  - Antibiotics
  - **Microbial Pathogens**
  - **Total Residual Chlorine**
  - Metals

37

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

38

Mechanisms of Disinfection

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

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

What does chlorine do to cells?

- HOCl enters cell wall efficiently, permeating and poking holes in cell walls of exposed bacteria
- Enzyme systems of microbes are affected, deactivating organisms and their ability to reproduce
- In most bacteria, HOCl causes adverse reactions of respiratory, transport, and nucleic acid-DNA systems

40

Comparative Effectiveness of Disinfectants

Treatment Process	**Microorganisms**		
	Viruses	**Bacteria**	**Protozoans**
Free chlorine	Very effective	Very effective	Less effective
Chlorine dioxide	Effective	Very effective	Effective
Iodine	Effective	Effective	Not effective
UV light	Effective	Very effective	Very effective
Natural sunlight	Effective	Effective	Less effective
Boiling (heat)	Very effective	Very effective	Very effective
Membrane Filtration	Variably effective	Very effective	Very effective

41

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

42

Who Does What?

	WWTPs > 1 mgd In USA, 2008
Chlorine (gas or liquid)	**75.3 %**
UV	**20.6 %**
Ozone	**0.2 %**
None	**3.9 %**

Source: Disinfection of Wastewater Effluent – Comparison of Alternative Technologies, WERF, 2008.

43

Potential Health Issues

- Microbial Health Concerns
  - Cryptosporidiosis and Giardiasis
    - ✓ Vomiting and diarrhea, potentially life threatening for immune compromised, elderly and young
- 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 even worse???

44

When is Wastewater Disinfection Required?

- Discharge to surface waters:
  - Near water supply intakes
  - Used for primary contact recreation
  - Used for shellfish harvesting
  - Used for irrigation of crops
  - Other direct and indirect reuse and reclamation purposes
- Discharge to groundwaters:
  - Used as a water supply source
  - Used for irrigation of crops and greenspace
  - Other direct and indirect reuse and reclamation purposes

45

Waterborne Diseases

- Many human diseases are caused by infectious microorganisms in drinking water
- Most of the bacteria, viruses, and protozoa that cause waterborne diseases affect the digestive system and thus propagate themselves via sewage
- Wastewater disinfection provides part of a multi-barrier to prevent disease spread in drinking water
- Wastewater disinfection is the only barrier to disease spread from direct contact activities like swimming

46

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)

47

Bacteria

- Single celled organisms that can self replicate
- 0.5 – 5 um (500 – 5000 nm) in size
- Feces of a healthy person contains 10^6 to 10^9 of each of the following bacteria groups per gram of feces:
  - Enterobacteria, enterococci, lactobacilli, clostridia, bacteroides, bifidobacteria, and eubacteria
  - *Escherichia coli* (common fecal coliform) is in the enterobacteria group
- Diarrhea is the major symptom for many bacterial infections
- The most serious waterborne diseases are typhoid fever, paratyphoid fever, dysentery, and cholera

48

Viruses

- Intracellular parasites that replicate only in living hosts' cells
- Lack the metabolic systems required for self replication
- 20 – 100 nm in size (about 1/50 that of bacteria cell)
- Human feces contain over 100 serotypes of enteric viruses

49

Protozoans

- Intestinal parasites that replicate in the host and exist in two forms
  - Attached to the intestinal wall where they actively feed and reproduce
  - Floating through the intestine while transforming into a **Cyst**
- Cysts
  - Infectious to others
  - 10 – 15 um in length
  - Commonly cause diarrhea or dysentery

50

Common Waterborne Diseases

Disease	Organism	Organism Source	Symptom
Gastroenteritis	Salmonella (bacteria)	Animal/human Feces	Acute diarrhea and vomiting
Typhoid	Salmonella typhosa (bacteria)	Human Feces	Inflamed intestine, high temperature – **fatal**
Dysentery	Shigella (bacteria)	Human Feces	Diarrhea
Cholera	Vibrio comma (bacteria)	Human Feces	Severe diarrhea and vomiting – **fatal**
Infectious hepatitis	Virus	Human Feces	Yellowed skin, enlarged liver
Amoebic dysentery	Entamoeba histolytica (protozoa)	Human Feces	Diarrhea
Giardiasis	Giardia lamblia (protozoan)	Animal/human Feces	Diarrhea
Cryptosporidiosis	Cryptosporidium (protozoa)	Animal/human Feces	Acute diarrhea and vomiting

Water Quality Regulations

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

52

Coliform Bacteria

- MPN of coliform bacteria are estimated to indicate the presence of bacteria originating from the intestines of warm-blooded animals
- Coliform bacteria are generally considered harmless
  - But their presence may indicate the presence of pathogenic organisms

53

Coliform Bacteria

- Comprises all the aerobic and facultative anaerobic gram negative, nonspore-forming, rod-shaped bacteria that ferment lactose within 48 hours at 35 °C
- Coliform bacteria can be split into fecal and nonfecal groups
- The fecal group can grow at higher temperatures (44.5 °C) than the non-fecal coliforms

54

Fecal Coliform

- Indicator microorganism
  - Cultured in standard tests to indicate contamination (laboratory)
  - Membrane filter technique
    - Direct count of colonies trapped and cultured
  - Multiple tube fermentation method
    - Provides an estimate of the MPN per 100 mL
  - Measured as colonies/100 mL

55

Coliform 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

56

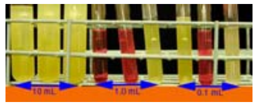
Coliform Bacteria – Approved Methods

- Number per 100 mL
- Coliform (fecal)
  - Membrane filtration
- E. coli
  - Multiple tube (Colilert®)
  - Membrane filtration
    - ✓m-ColiBlue24®
    - ✓Modified mTEC agar

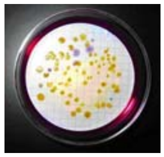
57

Enumerating Indicator Bacteria

- Multiple Tube Fermentation
  - Statistical estimate
  - MPN /100 mL
  - MPN - Most Probable Number



- Membrane Filtration
  - Direct count
  - CFU /100 mL
  - CFU - Colony Forming Units



58

Water Quality Regulations

- 1972 Clean Water Act required secondary treatment
- Setting allowable disinfection criteria was delegated to the states
- EPA originally recommended using fecal coliform as the indicator organism for wastewater disinfection, based on Public Health Service studies in the 1960's
- Later EPA recommended E coli and Enterococci as indicator organisms - better correlated to actual gastroenteritis in humans after swimming in affected waters
- Many states still use fecal coliform…!

59

Water Quality Regulations

- Disinfection fecal coliform/E coli limits are usually expressed as geometric means, instead of arithmetic means
- Why? Microbes grow exponentially…high values not uncommon in disinfection
- Using geometric means reduces the impact on the mean of a single high value per week, or a few high values per month

60

Water Quality Regulations

- Arithmetic mean = Average of 'n' numbers
  - = (Sum of Values) / (Number of Values)
  - = (10 + 10 + 10 + 10 + 10,000) / 5 = **2008**
- Geometric mean = the 'n'th root product of 'n' numbers
  - = (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**

61

Geometric Mean Calculation

- A small wastewater plant collected 7 samples during the month for determining a geometric mean of E. Coli CFUs. The 9 individual results were 4, 10, 7, 2, 5, 3, and 9 CFUs/100 ml. Determine the geometric mean of the results.

Answer: Geo. Mean = (Product of Values) $^{(1 / \# \text{ values})}$

Geo. Mean = (4 x 10 x 7 x 2 x 5 x 3 x 9)$^{1/7}$

Geo. Mean = (75,600)$^{1/7}$ = 5

62

Removal Efficiency is Dependent on Microbial Type

- *Giardia* and *Cryptosporidium*
  - Filtration is best
    - ✓Large size
    - ✓Resistant cyst and oocyst
- Bacteria and Enteric Viruses
  - Disinfection is ultimate barrier
  - Filtration and coagulation also help via adsorption to particles
    - ✓Dependent on surface charge of virus

63

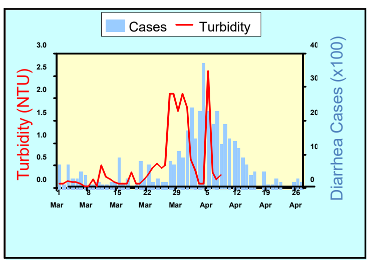
Waterborne Disease Outbreaks Cause Irreparable Damage to Public and PWSs

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

64

Milwaukee Disease Outbreak - 1993



403,000 illnesses (out of 1.6 million population)

Ineffective coagulation, flocculation, and filtration

Chlorination/Dechlorination

Overview

66

Chlorination

- Process of adding a chlorine product to water or wastewater for disinfection, e.g., inactivation of pathogens
- Chlorine chemicals (i.e., oxidizing agents):
  - Compressed elemental (Cl_2) gas
  - Hypochlorites:
    - **Aqueous sodium hypochlorite solution (Bleach): NaOCl**
    - Anhydrous (solid) calcium hypochlorite: $Ca(OCl)_2$

67

Properties of Chlorine

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

68

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)

69

Properties of Chlorine

Chlorine may be found in three forms

Powder

Liquid

Gas

70

Chlorination/Dechlorination Chemicals

- Chemicals used for chlorination and dechlorination are a function of:
  - Availability
  - Cost perspective: Economies of scale
  - Operator training and expertise: chemical storage and handling
  - Operator and community safety concerns
  - Contaminant concerns:
    - D/DBPs
    - Perchlorate (New…!)

71

Chlorination/Dechlorination Chemicals

- When using chlorine gas:
  - Low concentration of dissolved chlorine
  - D/DPBs can form
  - Perchlorate, chlorate and chlorite are not expected to form

72

Chlorination/Dechlorination

- Sodium hypochlorite is an "aqueous solution" of NaOCL in which water (H_2O) is the solvent

73

Sodium hypochlorite, NaOCl

- Manufactured by the reaction of chlorine with sodium hydroxide and water
- To minimize decomposition, excess sodium hydroxide is required to maintain a pH between 11 and 13
- Household bleaches: 3% to 8% NaOCl
- Water/wastewater disinfection applications: typically 10% – 15% active NaOCl

74

Hypochlorite Solutions

- Sodium hypochlorite solutions are clear, greenish to yellow liquids with a chlorine odor
- Calcium hypochlorite is a white solid that readily decomposes in water releasing chlorine
- Sodium and calcium hypochlorites are used primarily as bleaching agents or disinfectants

75

Calcium Hypochlorite Solutions

- Calcium hypochlorite:
  - White solid that readily decomposes in water releasing chlorine
  - Tablets or granules
  - 65 to 70% chlorine

76

Chlorination

- **<u>Chlorination w/Sodium Hypochlorite (NaOCL)</u>**
  1. **NaOCL** + $H_2O \rightarrow$ **HOCl** + NaOH
  - **HOCl - Hypochlorous acid**
  - NaOH - Sodium hydroxide
  2. **HOCl** $\Leftrightarrow$ H^+ + OCl^- (in equilibrium)
  - **HOCl** – most effective form of dissolved chlorine
  - H^+ - Hydrogen ion
  - OCl^- - hypochlorite ion (less active form of dissolved chlorine)

77

Dechlorination

- WWTPs have been chlorinating effluent discharges for more than 100 years
- Residual chlorine can have a negative impact on aquatic life in receiving waters
- Chlorine hazardous to both plant life and fish
- Need dechlorination

78

Dechlorination

- Process of removing chlorine from water (e.g., disinfected wastewater) before discharging it into the environment
- Dechlorination chemicals (i.e., reducing agents):
  - Compressed sulfur dioxide (SO_2) gas
  - Sulfites, metabisulfites and thiosulfates:
    - **Aqueous bisulfite solutions:**
      - ✓ **Sodium bisulfite: $NaHSO_3$**
    - Anhydrous (solid) forms:
      - ✓ Sodium sulfite: Na_2SO_3
      - ✓ Sodium metabisulfite: $Na_2S_2O_5$
      - ✓ Calcium thiosulfate: CaS_2O_3

79

Chlorination/Dechlorination

- Sodium bisulfite is an "aqueous solution" of $NaHSO_3$
- Sodium bisulfite is a yellowish-white solution with a strong pungent SO_2
- Sodium bisulfite is added following chlorine disinfection prior to discharging chlorinated effluent to receiving water

80

Dechlorination

- **Dechlorination w/Sodium Bisulfite ($NaHSO_3$):**
  1. $NaHSO_3 + H_2O \rightarrow H_2SO_3 + NaOH$
  - H_2SO_3 – Sulfurous acid
  - NaOH – Sodium hydroxide
  2. $H_2SO_3 + \mathbf{HOCl} \rightarrow 3H^+ + Cl^- + SO_4^{-2} \rightarrow HCl + H_2SO_4$
  - **HOCl - Hypochlorous acid**
  - H: Hydrogen ion; Cl: Chloride ion; SO_4^{-2} sulfate ion
  - H_2SO_4 – Sulfuric acid
  - HCl - Hydrochloric acid

81

Chlorination/Dechlorination

- All sulfur chemicals are explosive if mixed with acids or oxidizers like bleach
- Refer to chemical Safety Data Sheets (SDS) when handling bleach and bisulfites
- PPE for handling bleach and bisulfites include:
  - Respirators
  - Face shields
  - Goggles
  - Chemical gloves
  - Aprons

82

Chlorination/Dechlorination

History and Evolution

83

Prior to 1900

- 1846 – Vienna, Austria: Hospital began chlorinated water to reduce patient infections
- 1854 – London, England: Dr. John Snow used chlorine to disinfect the Broad Street Pump water supply (i.e., cause of a cholera outbreak due to sewage contamination)

84

1850s – Cholera Epidemic in London

- British epidemiologist, Dr. John Snow, proved that cholera was a waterborne disease by linking the illness to sewage contamination of a public well
- Dr. Snow applied chlorine to purify the water, which paved the way for water disinfection
- This led to first government regulation of public water

Water Pump Monument to John Snow in London, England
http://en.wikipedia.org/wiki/John_Snow_(physician)

85

Prior to 1900

- 1879 – England: Chlorinated lime (i.e., Calcium hypochlorite) used to treat typhoid patient wastes before disposal into the sewer
- 1893 – Hamburg, Germany: chlorine used on a plant scale basis for disinfecting drinking water
- 1897 – Kent, England: potable water distribution mains disinfected using bleach

86

After 1900

- 1903 – Middlekerke, Belgium: The first use of chlorine gas for disinfection of drinking water
  - Previous chlorination was with chlorinated lime (Calcium hypochlorite)
- 1908 – Jersey City, NJ water utility became the first in the U.S. to use full scale drinking water chlorination, using sodium hypochlorite

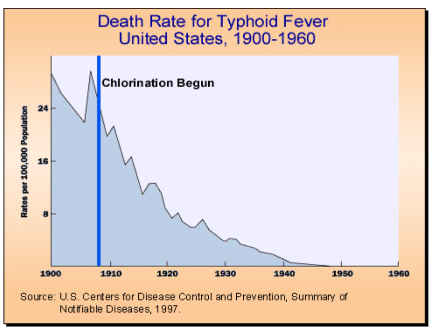
87

After 1900

- 1908 – Chicago, IL: the Bubbly Creek Filter Plant began chlorination using chlorinated lime
- 1910 – Youngstown, Ohio: First to use compressed chlorine gas from a steel cylinders for water chlorination

88

Drop of Typhoid Fever Death Rates



89

After 1900

- 1914 – The U.S. Department of the Treasury enacted standards calling for a maximum bacterial concentration of 2 coliforms per 100 ml in drinking water:
  - Required drinking water disinfection
  - Chlorination was only option at the time
  - Lead to a dramatic:
    - Increase use of chlorination at water treatment plants
    - Decrease in infectious diseases

90

After 1900

- 1920s – 1930s – Drinking water filtration and chlorination had virtually eliminated epidemics of waterborne diseases in the U.S.
- 1940s – 1990s – Disinfection with chlorine gas was the method of choice for most facilities
  - Cheap
  - Readily available

91

After 1900

- 1970s – Awareness of disinfection byproducts (DBPs) formed by reaction of chlorine with natural organic compounds in water
  - Possible health effects of DBPs were investigated
- 1979 – Initial DBP rule
- 1998: Stage 1 Disinfectants and Disinfection Byproducts (D/DBP) Rule issued
- 2006: Stage 2 D/DBP Rule issued

92

Disinfectant By-Products (DBPs)

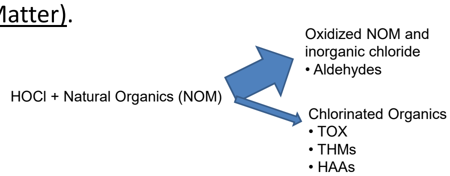
- By-products of reactions between disinfectant (chlorine, ozone, etc.) and precursors like suspended solids, natural organic matter (NOM), and/or bromide present in source water

Waste Water Treatment Plant

93

Disinfection By-products (DBPs) Formation

- Disinfection by-products arise in water treatment through the reaction of a Disinfectant and background water constituents (most often Natural Organic Matter).



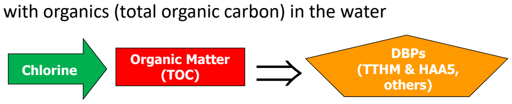
All chemical disinfectants form DBPs

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

95

The Flip Side:
Disinfection Byproduct (DBP) Formation

- DBPs are formed when chlorine (or other disinfectant) reacts with organics (total organic carbon) in the water



- Formation is impacted by:
  - Reactions within the bulk water (due to increased chlorine, temperature, organics, etc.)
  - Reactions within the distribution system infrastructure (e.g., biofilm, etc.)
  - Water age (time)

96

Disinfectant By-Products (DBPs)

Disinfectant + Bacteria → Dead Bacteria
Disinfectant + Virus → Dead Virus
Disinfectant + Giardia cyst → Dead Giardia cyst

Disinfectant + Precursor → DBPs

All disinfectants form disinfection by-products!!!

97

Disinfection By-products (DBPs)

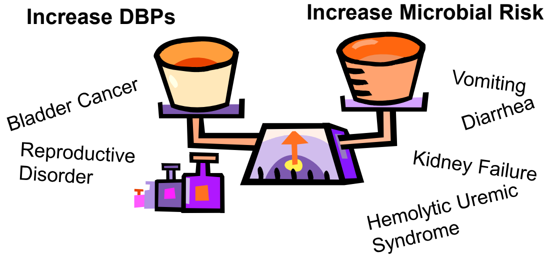
- The World Health Organization has stated that:
  - "…the risks to health from disinfection by-products are extremely small in comparison with the risks associated with inadequate disinfection."

98

Risks Must be Balanced

Increase Chlorine = Increase DBPs

Decrease Chlorine = Increase Microbial Risk



99

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

100

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			

101

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		-			

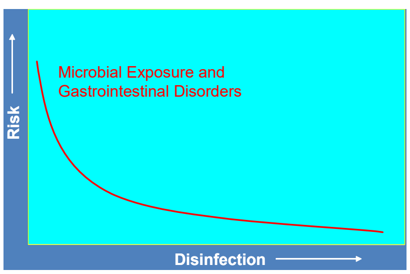
102

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)					

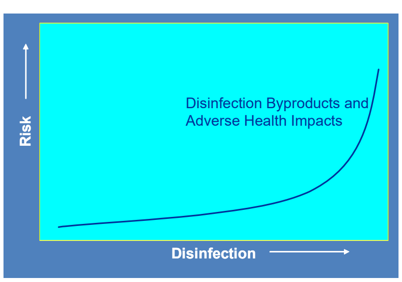
103

Microbial Risks



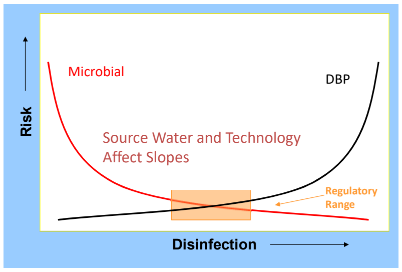
104

Disinfection Byproduct Risks



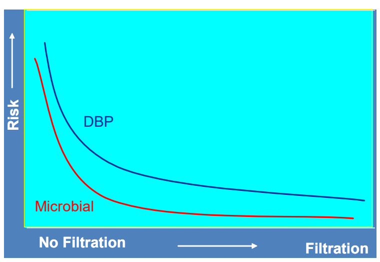
105

Microbial versus DBP Risk Trade-Offs



106

Filtration Reduces both Microbial and DBP Risks



107

After 1900

- OSHA, EPA, Fire Code, and Homeland Security regulations are making chlorine gas an increasingly expensive and undesirable disinfection alternative
- Vulnerability Assessments and Emergency Response Plans required

108

Safety and Security Regulations

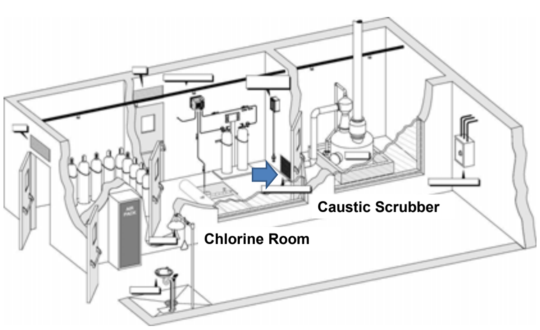
- Regulations:
  - Clean Air Act Amendment of 1990
  - OSHA's/USEPA's 1993 Risk Management Program (RMP)
    - ✓Develop a **community** Risk Management Plan
    - ✓ Prevent/minimize consequences of accidental releases of toxic and flammable chemicals
    - ✓Public must be notified of any release of toxic of flammable substances
    - ✓ Compliance required by 1996

109

Safety and Security Regulations

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

110



Chlorine room designed to meet OSHA and Fire Code requirements

111

Self-Contained Breathing Apparatus (SCBA)

112

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

113

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

114

After 2000

- Sodium hypochlorite (bleach) becomes the second most common disinfection method
- Recent trends and concerns:
  - Bleach degrades over time, losing strength
  - More difficult for operators to control residuals
  - New drinking water regulations associated with potential contaminants such as
    - Perchlorate
    - Chlorate
    - Bromate

115

Chlorination/Dechlorination

Chemicals

Chlorination/Dechlorination Chemicals

- Chlorine/Sulfur Dioxide:
  - Gases
  - Cl_2/SO_2
- **Sodium Hypochlorite/Sodium Bisulfite:**
  - Liquids
  - $NaOCl/NaHSO_3$
- Calcium Hypochlorite/Calcium Thiosulfate
  - Solids/liquids
  - $Ca(OCl)_2/CaS_2O_3$

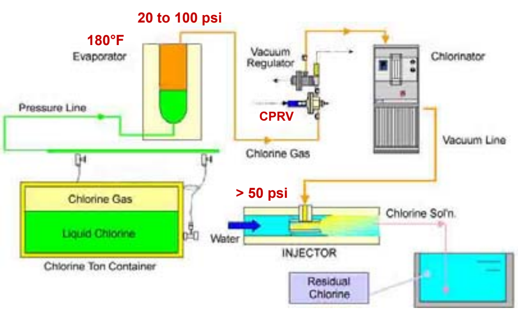
Who Does What?

- Chlorine chemical use has been decreasing in the US since UV became an option in the 1980's
- The current number of chlorine users is likely less than 75%, with a corresponding increase in UV use.
- In 2004, about half of chlorine users used gaseous chlorine and half used bulk liquid hypo. Liquid hypo is probably more prevalent now than gas
- Most hypochlorite users buy liquid hypo in bulk; a few users generate hypo on-site

Chlorination/Dechlorination - Cl_2/SO_2

- For larger plants, with more trained staff and resources:
  - Chlorine gas (Cl_2) for chlorination and sulfur dioxide gas (SO_2) for dechlorination have been popular
  - Lower bulk chemical costs and faster reaction rates
  - Concerns over possible release of gases into the atmosphere have cause concerns by residents in nearby communities

Liquid Chlorine Feed System



Chlorination/Dechlorination Chemicals

- Chlorine gas for disinfection and sulfur dioxide for dechlorination have been the chemicals of choice for medium to larger capacity wastewater treatment plants

- Solutions of sodium hypochlorite for disinfection and sulfate/sulfite compounds for dechlorination tend to be used at smaller plants

Chlorine/Sulfur Dioxide Treatment-Equipment

7

Chlorination/Dechlorination - $NaOCl/NaHSO_3$

- Safety concerns surrounding the storage and handling of pressurized gas have forced some large treatment plants away from gas to use liquid hypochlorite/bisulfite systems
- The complexity of gas storage and automated dosing systems also requires more experienced and highly trained operators
- Liquid chemical feed systems may be less complex

8

Chlorination Chemicals

- Chlorine gas
  - 100% Cl_2
  - Pressurized containers
- Sodium Hypochlorite Solution
  - NaOCl or bleach – 15% Cl_2
  - Bulk or On-Site Generated
- Calcium Hypochlorite
  - $Ca(OCl)_2$, or HTH®, - 65% Cl_2
  - Tablets, granules or powder

9

Chlorination

- Chlorine gas
- Hypochlorite

Sodium hypochlorite tanks

1-ton chlorine cylinders

10

Chlorine Disinfection

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

11

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

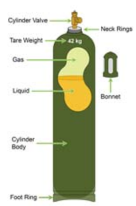
12

Gaseous Chlorine

13

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



14

150 lb Tanks

1

Ton Cylinders

2

Chlorine Products
<u>LESS THAN</u> 100% pure

Bleach,
12.5% Cl_2

HTH,
65% Cl_2

3

Water Quality Issues with Hypo

- pH Boost - Typically 0.3 to 0.4 Units
- THM's – Typically slight reduction (from Chlorine Gas)
- Chlorates – May Be Regulated in the Future; Ensure Quality Supplier
- Chlorides/Sodium – Ensure Quality Supplier
- Chloramine Formation – May be slightly more effective than Chlorine Gas because of pH shift

4

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.

5

Sodium Hypochlorite Degradation

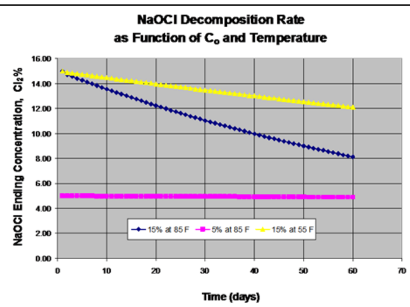
- Hypochlorite has a relatively short shelf life
- The concentration of the hypochlorite will degrade over time
  - Degradation results in chlorate ion formation and out-gassing of oxygen
- The rate of degradation is a function of impurities, heat, UV (i.e., sunlight) and hypochlorite concentration

6

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

NaOCL Degradation/Decomposition



Sodium Hypochlorite Degradation

- Dilute stored hypochlorite solutions upon delivery
- Store hypochlorite solutions at lower temperatures
- Control the pH of stored hypochlorite solutions at a pH of 11 to 13, even after dilution

Sodium Hypochlorite Degradation

- Control the removal of transition metal ions by:
  - Purchasing filtered hypochlorite solutions
  - Using low-metal ion concentration feedwater for on-site generation systems
- Use fresh hypochlorite solutions when possible
- For utilities using on-site generation hypochlorite, use low-bromide salt to minimize the amount of bromide present in the brine

10

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)

11

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

12

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.

13

Perchlorate
(EPA Notice - January 2012)

- EPA proposed to Regulate Perchlorate
  - EPA considering a Maximum Contaminant Level Goal
  - 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!!!**

14

Perchlorate

- May 2019 - EPA published proposed perchlorate drinking water regulations
  - EPA requested comments on a proposal to establish a Maximum Contaminant Level (MCL) and a health-based Maximum Contaminant Level Goal (MCLG) at 56 micrograms per liter
  - Three alternative regulatory options:
    - o 18 micrograms per liter.
    - o 90 micrograms per liter.
    - o Withdrawal of perchlorate regulations

15

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	

16

Chlorine Content of Chemical Disinfectants		
Chemical	% Cl	Amount of Chemical to yield 1 lb pure Cl
Chlorine gas or liquid (Cl_2)	100	1.0 lb
Liquid Sodium hypochlorite (NaOCl)	15	0.8 gallons
"	12.5	1.0 gallons
"	5	2.4 gallons
"	1	12.0 gallons
Solid calcium hypochlorite [$Ca(OCl)_2$]	65	1.54 lb

17

Calcium Hypochlorite

- Is typically 1.5 to 2 times the cost of liquid sodium hypochlorite
- May be preferred by smaller users because of newer "puck-type" calcium hypochlorite systems

18

Chlorination/Dechlorination

Process Control

19

Process Control Concepts

- Manual
- Feedback
- Feedforward
- Feedback/Feedforward
- Advanced Control

20

Manual Control

- Operator observes problems and takes corrective action
- Sometimes, nothing more than a guess
- "Open loop" control
  - No direct connection between desired output (setpoint) and process variable
  - Operator may have to constantly observe and change manipulated variable to ultimately correct problem

21

Automation Control Loops

- **Feedback Control**: uses direct measurements of the controlled process variables (PV) to adjust the values of the manipulated variables
- **Feedforward Control**: uses direct measurement of the disturbances to adjust the values of the manipulated variables
- **Combined Control**: different combinations of the first two types
- Control objective - to keep control variables at desired levels, e.g., set points (SP)

22

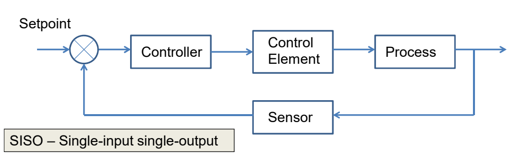
Feedback Control Loop

- Feedback control is a common control strategy; its simplicity accounts for its popularity
- The feedback controller works with minimum knowledge of the process; it needs only to know which direction to move
- How much to move is usually adjusted by trial and error

23

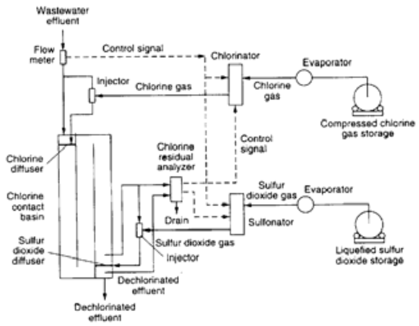
Feedback Control Loop

- Output information is used to adjust process controls
- Feedback controller receives sensor output on process variable and compares it to setpoint



24

Chlorine Dose Control – TRC Residual



25

Residual Chlorine Analyzers

- "Chemist in a Box"
- Measures either free **or** combined chlorine
- Uses colorimetric measurement process
- Replace reagents monthly
- Latest amperometric devices use no reagents, but have limitations

26

Total Residual Monitoring

- The US EPA Standard Method 4500-Cl outlines different methods to detect residual chlorine, including:
  - Iodometric Method
  - Amperometric Titration Method
  - Low-Level Amperometric Titration Method
  - DPD Colorimetric Method
  - Syringaldazine (FACTS) Method
  - Iodometric Electrode Technique
- Detection limits are as low as 0.010 mg/L (or 10 g/L (ppb), depending on the sophistication of the equipment.

27

Total Chlorine Monitoring

- The most accurate chlorine residual measurement method is amperometric titration
- Since this method requires considerable operator training and skill to be accurate, other methods, particularly the DPD colorimetric method, have been widely used

28

Total Chlorine Monitoring

- Detection limit of the DPD method is not sensitive enough to confirm that the chlorine residual is meeting the target level
- Operators typically overdose with dechlorination chemicals, e.g., sodium Bisulfite to total chlorine residual should be 1.5:1
- Dechlorination chemical residual is not as harmful as a chlorine residual

29

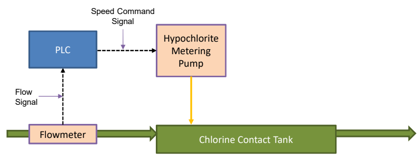
Total Chlorine Monitoring

- Use of on-line chlorine residual monitoring devices work reliably at plants with tertiary treatment effluent
- Chemical feeds use a combination of flow and chlorine residual feedback
- Common to set the dechlorination equipment to pace the chlorination equipment so that a slight excess of dechlorination chemical is always added

30

Feedforward Control Loop

- Measurement comes before the mechanical action (e.g., pump speed change)
- Example: Flow-paced chemical feed



31

Feedforward Control Loop

- Feedforward control avoids delays of feedback control
- Input disturbances are measured and accounted for before they have time to affect the system
- Difficulty with feedforward control:
  - Effects of disturbances on process must be anticipated
  - No surprises

32

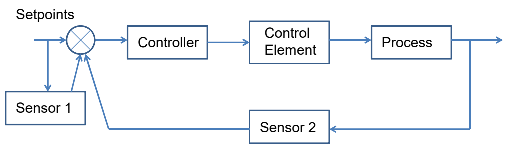
Feedforward Control Loop

- Complete compensation for disturbances is difficult due to variations, imperfections in mathematical models, and imperfections in the control actions
  - Usually combined with feedback control
- **Feedback and feedforward controls are common in water and wastewater utility processes**

33

Feedback/Feedforward Control Loop

- Feedback and feedforward (e.g., compound) information is used to adjust process controls
- Controller receives sensor outputs on process input and output variables and compares it to setpoints



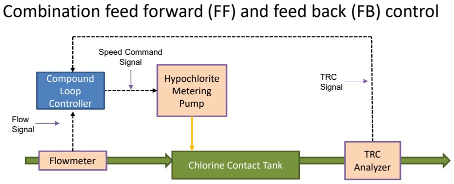
Feedback/Feedforward Control Loop

- Benefits of feedback control:
  - Controlling unknown disturbances
  - Not having to know exactly how a system will respond
- Benefits of feedforward control:
  - Responding to disturbances before they can affect process

Cascade control – Feedback as primary control loop with a feedforward secondary loop

Feedback/Feedforward Control Loop

- Measurement is made before mechanical action but adjusted based upon measurement downstream of the mechanical action
- Combination feed forward (FF) and feed back (FB) control



Chlorine Residual Monitoring

37

Chlorine Dose Control

- Chlorine residual analyzers can be used to monitor chlorine feed
- ORP analyzers can be used to monitor both chlorination and dechlorination operations

38

Do you have a free Cl_2 residual?

39

Chlorine Dose Control - ORP

- The ORP system monitors both the oxidant and reductant demand in the water and automatically modulates the amount of sodium hypochlorite and sodium bisulfite required to meet chlorine residual and fecal coliform limits in the plant effluent
- The controller compensates for changes in lag time between the chemical injection point and the sensor location
- In water disinfection applications, the ORP value of the solution is more meaningful than mg/L measurements of free residual or total chlorine

40

pH/ORP Analyzers

- pH = negative log of H^+ concentration (acid/base)
- ORP = oxidation-reduction potential
- Two methods – differential and combination
- We specify differential electrodes
  - Longer lasting
  - Replaceable parts
  - Resists poisoning

41

pH/ORP Analyzer Uses

- Each process has its own favorable range
- Wastewater process contains many oxidation-reduction reactions
- BNR process changes pH and ORP

42

ORP Ranges for Processes

Biochemical Reaction	ORP, mV
Nitrification	+100 to +350
cBOD degradation with air (O_2)	+50 to +250
Denitrification	+50 to -50
Acid formation (fermentation)	-100 to -225
Methane production	-175 to -400

43

Chlorination/Dechlorination

Dechlorination Theory

44

Dechlorination

- Chlorine and chlorination by-products are toxic to aquatic life in receiving streams
- Discharge requirement: neutralization of chlorine:
  - "Zero"
  - < 0.05 mg/L
  - Beginning in the 1970's

45

Dechlorination Chemicals



- Sulfur dioxide gas
  - 100% SO_2
  - 90-ton railcars, ton containers or 150-lb cylinders
- Sodium Bisulfite Solutions
  - $NaHSO_3$
  - 25% and 38%
- Calcium Thiosulfate
  - CaS_2O_3
  - Granules
  - Solutions - No-Chlor™

46

Dechlorination

- Typically, dechlorination is accomplished by adding sulfur dioxide (SO_2) or aqueous solutions of sulfite salts:
  - Sodium sulfite (Na_2SO_3)
  - Sodium bisulfite ($NaHSO_3$)
  - Sodium metabisulfite ($Na_2S_2O_5$)
  - Sodium thiosulfate ($Na_2S_2O_3$)

47

Dechlorination Basics

- Converts chlorine in free and combined forms to chloride (Cl^-)
- Reaction is quick; < 15 seconds with SO_2 and Sodium Bisulfite ($NaHSO_3$)
- Protects aquatic life from Total Residual Chlorine (TRC)

48

Dechlorination Basics

- SO_2 and $NaHSO_3$ dissolve rapidly in water, forming sulfurous acid (H_2SO_3)
- H_2SO_3 in water reacts with free chlorine (HOCl) as well as chloramines (NH_2Cl) to form hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and ammonium bisulfate (NH_4HSO_4)

$$H_2SO_3 + HOCl \rightarrow 3H^+ + Cl^- + SO_4^{-2} \rightarrow HCl + H_2SO_4$$

$$H_2SO_3 + NH_2Cl + H_2O \rightarrow 2H^+ + NH_4^+ + Cl^- + SO_4^{-2} \rightarrow HCl + NH_4HSO_4$$

49

Sodium Bisulfite Concentration

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

50

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_3	0.53 mg/L

Source: WERF Disinfection Alternatives 2008

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

- SO_2, $NaHSO_3$ react in ~15 seconds
- CaS_2O_3 reacts in ~ 5 minutes

51

Chlorination

Chemistry

52

Hypochlorous Acid and Hypochlorite

- All chlorine chemicals produce **hypochlorous acid (HOCl)** when added to water
- **Hypochlorous acid (HOCl)** is the disinfectant
- Chlorine and hypochlorite compounds form **hypochlorous acid (HOCl)** as follows:

$$Cl_2 + H_2O \Leftrightarrow \mathbf{HOCl} + HCl$$

$$NaOCl + H_2O \Leftrightarrow \mathbf{HOCl} + NaOH$$

$$Ca(OCl)_2 + H_2O \Leftrightarrow \mathbf{HOCl} + Ca(OH)_2$$

53

Hypochlorous Acid and Hypochlorite

- Hypochlorous acid (**HOCl**) breaks down further to form hydrogen ions (H^+) and hypochlorite ions (OCl^-) in equilibrium:

$$\mathbf{HOCl} \Leftrightarrow H^+ + OCl^-$$

- The percentages of **HOCl** and (OCL^-) vary with both pH and temperature
- Hypochlorite ions (OCl^-) are weaker biocidal agents than Hypochlorous acid (**HOCl**)

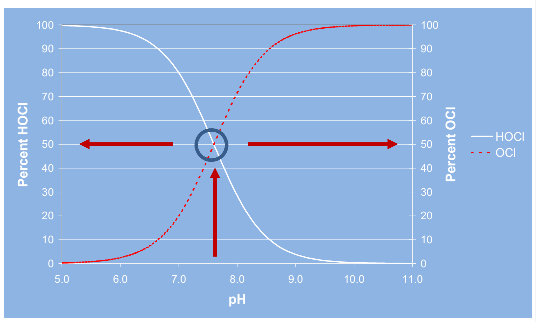
54

Chlorine in Water

- $Cl_2 + H_2O \Rightarrow$ **HOCl** + HCl (< pH 6)
- HOCl (**Hypochlorous Acid**) - 'Biocidal' agent
- **HOCl** $\Leftrightarrow$ H + OCl^- (> pH 9 complete)
- OCl^- (**Hypochlorite Ion**) - 'Oxidizing' agent
- **(%HOCl = %OCl^-) @pH 7.6 / 20C**

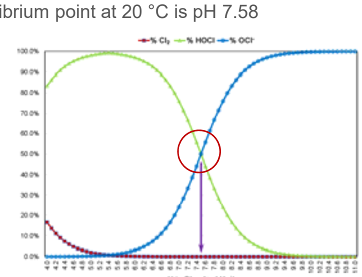
55

Hypochlorous Acid and Hypochlorite



Hypochlorous Acid and Hypochlorite

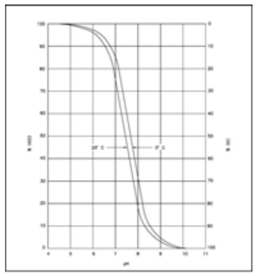
- Equilibrium point at 20 °C is pH 7.58



57

Chlorination

- HOCl is the most potent form of chlorine for disinfection – the bacterial "biocide"
- As pH increases, the amount of HOCl decreases
- Consequently, disinfection efficiency decreases as wastewater pH increases



58

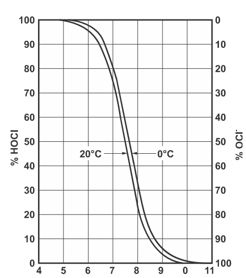
Hypochlorous Acid and Hypochlorite

- Hypochlorous acid (**HOCl**) is more effective at low pH's, so disinfection takes less time at lower pH
- Equilibrium between hypochlorous acid (**HOCl**) and hypochlorite ion (OCl^-):
  - Near pH 7.6, percentages are equal
  - Above pH 8.5, **HOCl** is less than 10% of the total
  - Below pH 6.5, **HOCl** is more than 90% of the total

59

Hypochlorous Acid and Hypochlorite

- More HOCl at pH below 7.6
- HOCl disinfects best
- At higher pH's, chlorine doses **and** contact times must increase



60

Chlorination

Dose, Demand, Residual

61

What determines the performance of chlorine disinfection?

- The effectiveness of chlorination depends on
  - pH of wastewater
  - Dose (C), mg/L
  - Contact time (T) – Amount of time wastewater is in contact with the chlorine
  - "CT" = Dose x Contact time
  - Chlorine demand of the wastewater
  - Chlorine residual
  - Fecal coliform count in wastewater
  - Other wastewater characteristics.

62

Chlorine Disinfection

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

63

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

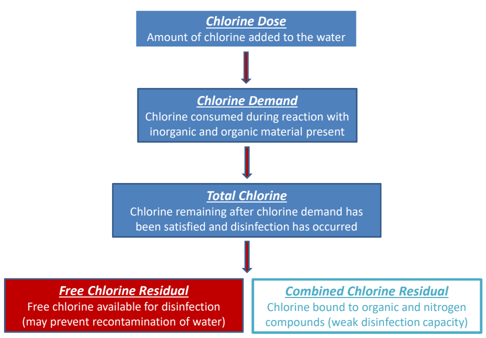
Combined Chlorine Residual – Chlorine that has combined with ammonia to form chloramines

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

Total Chlorine Residual – Sum of combined and free chlorine residual

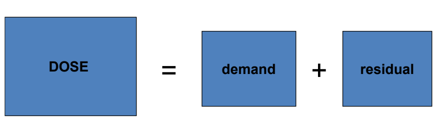
64

Chlorine Reactions in Water



65

Cl_2 Dose, Demand, and Residual



66

Cl_2 Dose, Demand, and Residual

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

67

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"

68

Chlorine Dose

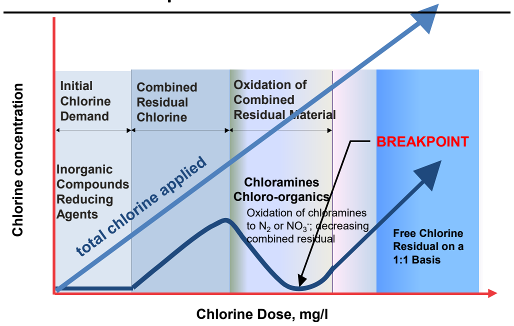
- Dose is a function of water quality
- Dose must be controlled to respond to fluctuating water quality conditions
  - Cl_2 + microorganisms → dead microorganisms
  - Cl_2 + Fe(II) → Fe(III)
  - Cl_2 + NOM → THMs and other DBPs

69

Breakpoint Chlorination

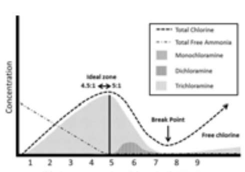
- Addition of chlorine to water until the chlorine demand (by inorganic and organic materials) has been satisfied
- Further addition of chlorine will result in formation of a free residual chlorine that is directly proportional to the amount of chlorine added beyond the breakpoint

Breakpoint Chlorination

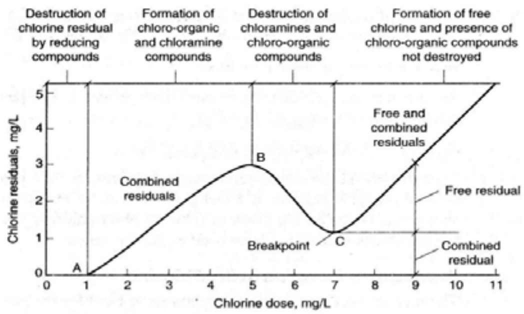


Breakpoint Chlorination Curve

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



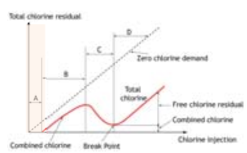
Breakpoint Chlorination Curve



73

Breakpoint Chlorination Curve

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



74

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

75

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

76

Chlorine Demand - Inorganic

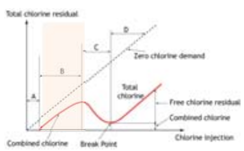
		Cl_2 Demand per part
Hydrogen Sulfide	H_2S	8.34 mg/L
Nitrite	NO_2^--N	5.1 mg/L
Manganese	Mn^{+2}	1.3 mg/L
Iron	Fe^{+2}	0.64 mg/L

Source: White's Handbook, 2010

77

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!



78

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)

79

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

80

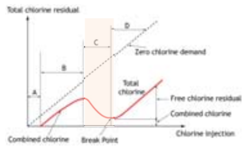
Forms of Ammonia

- 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

81

Breakpoint Chlorination Curve

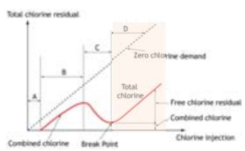
- Zone C
- Destruction of:
  - Monochloramines
- Then formation of:
  - Dichloramines
  - $HOCl + NH_2Cl \Leftrightarrow NHCl_2 + H_2O$
- Then conversion of dichloramines to trichloramines
  - $HOCl + NHCl_2 \Leftrightarrow NCl_3 + H_2O$



82

Breakpoint Chlorination Curve

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



83

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

84

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

85

Chlorination Disinfection

Concentration x Time

1

Disinfection

- Effectiveness is based on "Dosage":

Dosage = "Dose" X "Time"

Where: **Dosage = <u>rate of application of a dose</u>**

Dose = Quantity:

Chlorine residual concentration

Time = Detention, contact, or exposure

2

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

3

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.***

4

"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

5

"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

6

“CT” Values

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

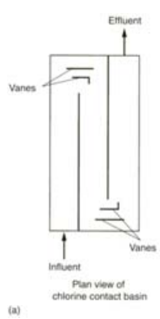
7

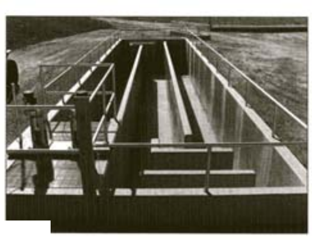
Chlorination Basics

- Minimum chlorine residual $\geq$ 0.5 mg/L
- Detention time $\geq$ 30 minutes
- Chlorine (mg/L) x Time (minutes) $\geq$ 20

8

Chlorine Contact Tanks





9

Chlorine Design Basics - Mixing

- Good mixing essential
  - Maintains proper ratio of chlorine to ammonia to form chloramines
  - Keeps dechlorination dose near theoretical
- Flash mixer for chlorine
- Mixer or hydraulic energy for dechlor
  - Contact tank weir
  - Parshall flume

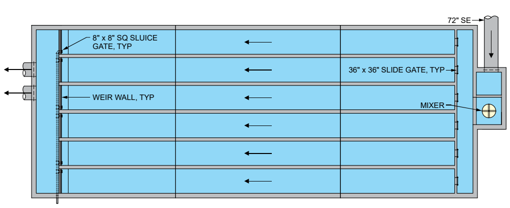
10

Chlorine Design Basics Contact Time

- Volume based on contact time
  - 15 min at peak flow (Ten States Standards)
  - 20 min at peak flow (Virginia SCAT)
- Path length-to-width (L:W) ratio
  - 40:1 recommended, maximum
  - 30:1 recommended in Tennessee
  - No guidance in Ten States Standards
- Use client experience

11

Chlorine Contact Tanks – Single Pass



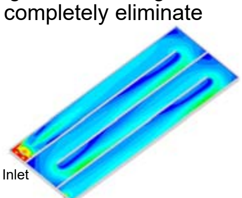
- Parallel single pass tanks reduce dead spots
- Rapid mixer at head of tank where chlorine is added
- Full-width weirs at the tank effluent to promote even flow in the tanks

12

Chlorine Contact Tanks

Serpentine tanks have high ratios of length to width, but this does not completely eliminate dead spots

- Every serpentine turn creates dead spots at the corners of the turn and along the inside wall downstream of the turn
- Dark blue represents zero velocity; red/orange/yellow are faster velocities



13

Typical Range of CT Values

Bacteria	CT, Free Chlorine mg-min/L
2-Log (99%)	0.4-0.8
3-Log (99.9%)	1.5-3
4-Log(99.99%)	10-12

Source: Tchobanoglous in WERF Alternative Disinfectants, 2008

- Absolute CT value required will depend on water quality, pH, and temperature

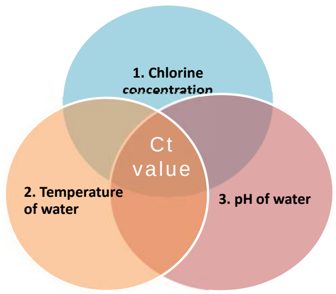
14

Chlorine Dosages

	Min. Cl Dosage Mg/L-min	Min. Contact Time, minutes	Min. Cl Residual mg/L	Max. Cl Residual mg/L
Typical	> 20	> 30	> 0.2	< 4.0
Virus inactivation	> 4	3-log reduction		
Giardia inactivation	> 100			

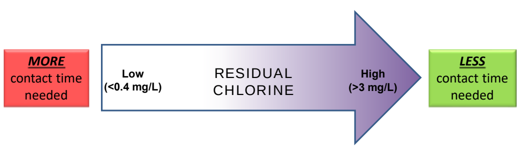
15

Factors Affecting Ct Value



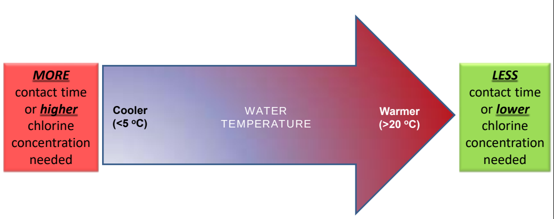
16

Factors Affecting Ct, Chlorine Dose



17

Factors Affecting Ct, Temperature

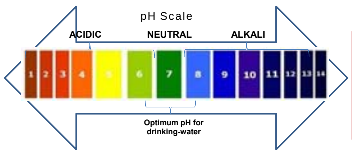


18

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

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



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

19

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!

20

Factors Affecting Ct, Turbidity

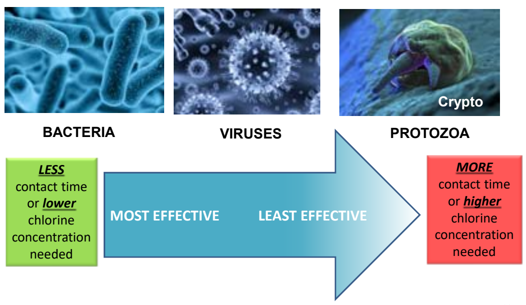
- Chlorine reactive substances may consume chlorine and increase chorine demand
- May also 'shield' microorganisms from inactivating chlorine effects

MORE
contact time or
higher chlorine
concentration
needed

LESS
contact time or
lower chlorine
concentration
needed

21

Factors Affecting Ct, Microorganism



22

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

23

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)

24

Chemicals

Bulk Storage and Conveyance

25

Properties of Sodium Hypochlorite

- Sodium Hypochlorite used in water and wastewater treatment is typically delivered in 12.0% trade concentrations
- Similar to common household bleach which has a concentration of about 5 to 8% trade
- 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

26

Sodium Hypochlorite Degradation

- Primary
  - $3NaOCl = 2NaCl + NaClO_3$ (Sodium Chlorate)
- Secondary
  - $2NaOCl = 2NaCl + O_2$ (Gassing)
- Factors:
  - Heat
  - UV (e.g., Sunlight)
  - Impurities (Primarily Heavy Metals)

27

Hypochlorite Degradation Reduction Strategies

- If possible store indoors
- If possible air condition the storage room to maintain temperature at 65° Fahrenheit
- Reduce storage volume so that the average retention period is about 15 days

28

Delivery to End-User

- Bulk Delivery in 5,000-gallon tanker truck
- “Poured” from Small Delivery 26’ Flat-Bed Truck w/installed HDLPE totes or tanks
- 300-gallon totes (forklift)
- 55 gallon drums
- 15, 30 gallon totes
- 2.5 gallon “jugs”

29

Chemical Information – Health Effects

- Inhalation:
  Respiratory irritant
- Skin Contact:
  Can cause burns to skin and eyes
- Eye Contact:
  Permanent loss of sight
- Ingestion:
  Convulsions and coma if ingested

30

Chemical System Design

- Delivery
- Bulk Storage
- Chemical Feed Equipment
- Piping

31

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

32

Chemical System Design

- Engineering Design Essentials:
  - Eliminate Problems from Any Bleach Gassing
  - Eliminate Calcium Carbonate Buildup
  - Minimize Product Degradation
  - Improve Life of Equipment
  - Minimize Maintenance
  - Ensure No Startup Problems
  - Eliminate Problems from Using a Corrosive Material

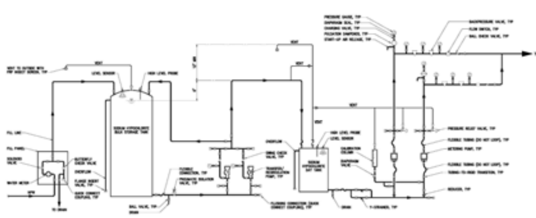
33

Chemical System Design

- **Bulk storage tank**
  - Generally sized for 30-day storage at maximum month flow and average dose
- **Transfer/recirculation pumps**
  - Used to transfer chemical from bulk storage to day tank
  - Also used for recirculation of diluted chemical in bulk tank
- **Day tanks**
  - If used, generally sized for 24-hour storage at maximum month flow and maximum dose
- **Metering pumps**
  - Sized to feed the range of maximum flow and dose down to minimum flow and dose

34

Bulk Hypochlorite Schematic



35

Bulk Hypochlorite System Design

- Bulk Storage Tanks
  - 30-day maximum supply
  - Contain 4,000- to 4,500-gallon tanker truck load of 15% NaOCl plus dilution water
- Day Tank (if used)
  - Contain one day or one shift supply of chemical

36

Bulk Delivery Site Should Have . . .

- 2” Supported Male Connection w/Cap
- Bag Filter – 1 micron
- Safety Shower/Eye Wash/Running Water
- Security/Lights
- Hook Up Protection / Labeled Lines
- Proper Venting for Blow Off
- “Catch Bucket”
- Accessible Roadway and Turn Around

37

Bulk Hypochlorite System Design

- Sodium hypochlorite is delivered in 4,000-gallon tanker truck loads
- Bulk storage tanks should be sized to hold a full load of chemical plus dilution water required to dilute chemical to the desired concentration
- Because of the rapid degradation of sodium hypochlorite, tanks should be sized to hold no more than 15 to 20 days supply of chemical

38

Bulk Hypochlorite System Design

- More than one bulk storage tank should be used for hypochlorite storage
  - Tanks can be rinsed and completely emptied between loads
  - Prevent any impurities in an old batch of hypochlorite from accelerating degradation of a fresh batch of chemical

39

Bulk Hypochlorite System Design

- Sodium hypochlorite solution is usually delivered at 12 to15% trade
  - If 10% sodium hypochlorite is desired, 2,000 gallons of water should be added to the 4,000 gallons of 15% hypo.
  - If 5% sodium hypochlorite is desired, 8,000 gallons of water should be added to the 4,000 gallons of 15% hypo.

40

Bulk Hypochlorite System Design

- Day tanks should be sized according to the owner's preference.
  - Tanks sized to hold a day's supply of 5% sodium hypochlorite can be fairly large.
  - If a smaller day tank is desired, it can be sized to be refilled once per shift.

41

Bulk Delivery by Tanker Truck

- 2" to 3" supported male connection w/cap
- Bag filter – 1 micron
- Safety shower/eye wash/running water
- Security/Lights
- Hook up protection /labeled lines
- Proper venting for blow off
- "Catch bucket"
- Accessible roadway and turn around

42

Bulk Delivery by Tanker Truck

43

Fill Station Design

- Design the fill lines to make it nearly impossible for someone to accidentally fill the sodium hypochlorite tank with sodium bisulfite and kill themselves

44

Fill Line

- Air Pressure – 15 to 25 psi
- Trucks Carry Up to 60’ Hose
- Long Length – Consider Upsizing to 3”
- Length Proportional to Offload Time
- Maximum Length – 200’
- Proper supports – 45 Degree Down
- Keep Line Vented

45

Bulk Hypochlorite System Design

- Recirculation and Transfer Pumps
  - Recirculate contents of bulk tank and transfer to day tank in reasonable amount of time
- Air Mixing System
  - Designed based on capacity of bulk tank
- Metering Pumps
  - Cover full range of required NaOCl feed rates

46

Materials of Construction

- Suitable Storage Tank Materials
  - High Density Polyethylene (HDPE)
    - ✓Typical Service Life (outdoors): 4-6 years
    - ✓Typical Service Life (indoor): 6-9 years
  - Fiberglass Reinforced Plastic (FRP)
    - ✓Typical Service Life: 10-20 years
  - Concrete Tank Lined with PVC
  - Rubber Lined Steel

47

Materials of Construction

- High Density Polyethylene (HDPE)
  - <u>Maximum Size?:</u>
    12,500 gallons might be the maximum practical HDPE tank size based on reports by a prominent Southeast hypochlorite supplier of failures of larger tanks
  - <u>Material Specification:</u>
    Cross linked polyethylene exterior shell with an interior linear polyethylene liner
  - <u>Design Specific Gravity/Max. Temp.:</u>
    1.9 / 140 degree F
-

48

Bulk Hypochlorite Equipment - Tanks

Polyethylene

- Used for bulk storage and day tanks
- Capacity limited to 10,000 – 12,000 gallons
- High-density crosslinked polyethylene with linear polyethylene liner
- Linear polyethylene
- Can be black to prevent UV exposure

49

Tanks - Simplified Layout

50

Flexible Connections

- Flexible connections are required, in the lower 1/3 of the HDPE tank wall, to increase tank longevity
- **The tank warranty is VOID if flexible connections are not used**

51

Materials of Construction

- Fiberglass Reinforced Plastic (FRP)
  - Material Specification:
    Derakane 411 premium grade vinyl ester resins with corrosion cured using BPO-DMA catalyst cure system
  - Design Specific Gravity/Max. Temp.:
    1.3 s.g./140 degree F
  - Assuring receipt of a high quality FRP storage tank is challenging due to a few poor suppliers in the market

52

Bulk Hypochlorite Equipment - Tanks

Fiberglass Reinforced Plastic (FRP)

- Custom made, so available in large capacities
- Used mostly for bulk storage
- Heat trace and insulate if outside
- Resins
  - Ashland Hetron 922 or Derakane 411
  - Hetron FR992 or Derakane 510A for fire resistance
  - BPO-DMA cure and dry heat post cure

53

Bulk Hypochlorite Equipment - Tanks

Polyethylene

- Limited Volumes
- Special Fittings - 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

54

Chemical Feed Equipment

- Eductors vs. Positive Displacement Pumps
- PD Pumps – Peristaltic vs. Diaphragm
- Pump Skids vs. Wall /Floor Mounting
- Height of Equipment – Suction Lift Issues
- Degasification Valves – When To Use
- Vapor Lock Issues – Bleed Valve or Vent
- Control Issues – Flow Meters / 4-20 ma
- 99% of Most Operational Problems Come from Over-sizing Pumps

55

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

56

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

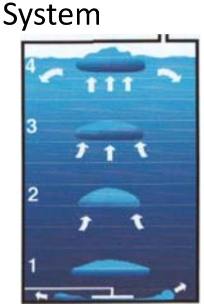


Photo courtesy of Pulsair.com

57

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

58

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

59

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

60

Bulk Hypochlorite Equipment Metering Pumps

- Peristaltic Pumps
  - Great range of feed rates
  - Pump heads don't get air-locked 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

61

Bulk Hypochlorite Equipment Metering Pump Accessories

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

62

Daily Chemical Usage Calculations

- *w = 8.34 x Q x C = lbs/day*
  - *w = dry weight of the chemical, Lb/day*
  - *Q = Plant flow rate, MGD*
  - *C = Chemical dose concentration, mg/L or ppm*

- $q = \frac{w}{8.34 \times sg \times S/100} = \frac{8.34 \times Q \times C}{8.34 \times sg \times S/100}$
  - *q= chemical feed rate, gpd*
  - *w = dry weight of chemical, Lb/day*
  - *sg = specific gravity*
  - *S = % of chemical solution, %*

63

Bulk Hypochlorite Equipment Valves

- Diaphragm valves
  - Throttling – calibration column
  - Suitable for chemicals that crystallize or off-gas (sodium hypochlorite)
- Vented ball valves
  - Isolation
  - Vented ball valves suitable for chemicals that off-gas (sodium hypochlorite)

64

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1

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  - Isolation
  - Vented ball valves suitable for chemicals that off-gas (sodium hypochlorite)

2

Materials of Construction

- Suitable Valves
  - Valves in hypochlorite service will eventually leak
  - PVC/CPVC Vented Ball Valves
  - PVC/CPVC Diaphragm Valves

3

Materials of Construction

- Ball Valves
  - Service Life: 3 to 6 years
  - Ball valves have wetted stems that are sealed with o-rings
    - ✓It's likely that ball valves may begin to leak

4

Materials of Construction

- Diaphragm Valves
  - Service Life: 3 to 6 years
  - The diaphragm seals the valve's bonnet compartment
    - ✓The stem of a diaphragm valve is neverexposed to the chemical

5

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

6

Piping to Chemical Feed Equipment

- Purpose – Minimize Off-Gassing
- Pipe Sizing – Optimize velocity
- Minimize Length – Maximum 50’
- Stack Vents/Sightglasses – Carry Off Gases
- Minimize Bends – Keep Gases in Solution
- Use of Flexible Piping/Tubing
- Eliminate “High Spots” – Piping Pitch
- Use of Strainers – “Catch” PVC shavings

7

Materials of Construction

- Pipe and valves – PVC or CPVC with solvent welding (solvent specifically for hypo)
- Handrails and grating – fiberglass with vinyl ester resin
- Metal fasteners and hardware – Hastelloy
- Piping support – FRP or PVC

8

Materials of Construction

- Plastics
  - PVC
  - CPVC
  - PTFE (Teflon®)
  - PVDF (Kynar®)
  - HDPE

9

Materials of Construction

- Elastomers
  - FKM (Viton ®)
    - ✓Suitable for valve seats, o-rings and diaphragms
    - ✓Viton is trade marked by DuPont
    - ✓There are different grades of Viton
  - Teflon (PTFE) backed with EPDM rubber is also suitable

10

Materials of Construction

- Metals
  - Steel lined with Teflon and possibly Kynar
  - Titanium
  - Tantalum (electrodes in magnetic flow meters and pressure gauge diaphragm seals)
  - Silver
  - Gold
  - Platinum
  - Hastelloy C (for storage tank anchor bolts)

11

Materials of Construction

- Unsuitable Materials – Metals
  - Stainless Steel
  - Carbon Steel
  - Monel
  - Brass
  - Copper

12

Materials of Construction

- Unsuitable Materials – Elastomers & Plastics
  - Plasticized PVC (e.g., clear PVC tubing)
  - Buna-N
  - Nitrile
  - Many resins used in FRP construction
  - Hypalon
  - Silicone
  - Ethylene Propylene Diene Monomer (EPDM)
  - Polypropylene

13

Piping

14

Materials of Construction

- Suitable Hypochlorite Piping Materials
  - Titanium **(not recommended)**
  - Steel lined with Teflon **(not recommended)**
  - Steel lined with Kynar **(not recommended)**
  - Polyethylene **(not recommended)**
  - Schedule 80 PVC **(recommended)**
  - Schedule 80 CPVC **(recommended)**

15

Materials of Construction

- Piping - Titanium and Lined Steel **(not recommended)**
  - Very expensive
  - Titanium is only considered in high temperature reaction vessel type applications
  - Most utility staff are not capable of maintaining this type of piping system

16

Materials of Construction

- Piping - Polyethylene **(not recommended)**
  - Most utility staff are not capable of maintaining this type of piping system
  - Difficult to obtain an acceptable installation given the quality of workmanship provided through municipal contracting

17

Materials of Construction

- Piping - PVC and CPVC **(recommended)**
  - The vast majority of 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)

18

Materials of Construction

- Piping - PVC and CPVC **(recommended)**
  - PVC and CPVC has a tendency to become more brittle over time due to chemical attack (PVC & CPVC Service Life: 15+/- years)
  - CPVC can shatter like glass after it becomes brittle
  - Many chemical piping systems above ground are exposed to the sun (high temperatures). As temperature goes up the pressure capacity of the pipe decreases
  - **CPVC is generally recommended over PVC**

19

Materials of Construction

- PVC and CPVC pipe joints
  - Solvent welded:
    - ✓Solvent welded (i.e., glued) pipe, fittings and valves are preferred
  - Threaded:
    - ✓Do not use threaded joints for sodium hypochlorite connections unless it can not be avoided
    - ✓Threaded connections tend to leak. Some threaded joints are unavoidable (e.g., backpressure valves)
  - Flanged:
    - ✓Glued joints are preferable to flanged joints
    - ✓Minimize the use of flanged joints

20

Materials of Construction

- Solvent welded joints
  - Recommended Primer: IPS Weld-On P-70
  - Recommended Glue: IPS Weld-On CPVC 724
  - Reference: ASTM D 2855 Standard Practice for Making Solvent-Cemented Joints with Poly(Vinyl Chloride) (PVC) Pipe and Fittings
  - Reference: ASTM F402-93 - Standard Practice for Safe Handling of Solvent Cements, Primers, and Cleaners Used for Joining Thermoplastic Pipe and Fittings

21

Materials of Construction

- Threaded Joints
  - If threaded connections must be used, threads must be new, sharp, and secured with a caustic resistant Teflon tape or paste. Odyssey Manufacturing recommends specifying Teflon tape meeting the requirements of A-A-58092 or MIL-T-27730A. Note that MIL-T-27730A is a defunct standard that is still used by industry and can be used to specify the quality of the tape. Only 1-2 wraps should be made on the threads. If more wraps are made, this causes the fittings to crack over time.

22

Materials of Construction

- Pipe Joints- they will leak- keep them accessible

23

Materials of Construction

- Valve – End Styles
  - Flanged: Available in 1/2 to 4 inches size range
  - Threaded Union: Available in 1/2 to 2 inches size range **Threaded joints should not be used**
  - Solvent Welded Union: Available in 1/2 to 2 inches size range
  - Union Joint Valves: This type of joint provides a leak path past the o-ring seal.

24

Materials of Construction

- Secondary containment
  - The necessity of secondary containment for piping and storage tanks is driven by regulations, client preferences, and engineering judgment
    - ✓ Example 1:
      Some states require secondary containment; engineers provide secondary containment in locations where a leak could cause harm to plant staff
    - ✓ Example 2:
      Some municipalities want their hypochlorite pipes in secondary containment

25

Summary

- Chlorination/dechlorination of wastewater effluent will continue for some time in the future
- Trend in chlorination/dechlorination will be towards safer to handle and easier to use chemicals, despite increases in costs
- Operators tend to slightly overdose dechlorination chemicals to ensure that the chlorine residual is "zero"

26

Summary

- Trend in wastewater chlorination/dechlorination is towards liquid chemicals and UV light
  - "Inherently Safer Technologies" (ISTs)
    - ✓ Safer for the WWTP operator and surrounding community
    - ✓ Without pressurized gas systems, WWTP is less likely a terrorist target
  - Sodium hypochlorite and sodium bisulfite are liquid chemicals of choice
  - WWTP operators need training on chemical handling, safety precautions, and health effects of chemicals

27

Summary

- Sodium hypochlorite chemical feed systems will need special considerations to minimize chemical degradation and leaks in the chemical feed system
- Sodium hypochlorite can be delivered in bulk or generated on site
- Sodium bisulfate can be delivered in bulk, but chemical feed systems will need special considerations to prevent freezing
- WWTP operators need to be aware of chemical properties and compatible materials of construction in chemical feed system components

28

Conclusion

- Chlorine and hypochlorites are both viable disinfectants
- Each has its own set of advantages and disadvantages
- Each chemical disinfectant produces undesirable byproducts

- *Trend today is toward hypochlorites*

29

Questions

30

Thank You

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College of Southern Maryland
La Plata, MD

31