12 Disinfection

Three basic strategies to keep microbiological contaminants out of drinking water:

1. Keeping microbe out of water source
2. Treating water to remove contaminants
3. Maintaining safe water distribution system

Disinfection has two components:

1. Primary disinfection - inactivation of microorganisms in the water
2. Secondary disinfection - maintaining disinfecting residual in distribution system

History

Source water protection and filtration used in second half of 1800s

1880: Koch showed chlorine could inactivate bacteria

1902: First used of chlorination for disinfecting water in Belgium

1908: First use in US at Jersey City, NJ with calcium hypochlorite

1913: First use of chlorine gas - Philadelphia

1941: 85% of public supplies chlorinated

Mid-1970s: Formation of THMs demonstrated

1980s: Giardia identified as important pathogen

Cryptosporidium identified more recently
Disinfection methods

1. Free chlorine – most common
2. Combined chlorine (chloramines)
3. Ozone – strongest oxidant
4. Chlorine dioxide
5. UV light

Chemical disinfection kinetics

**Chick's Law** – Harriet Chick, 1908

documented microorganism inactivation by phenol, mercuric chloride, silver nitrate

\[
\frac{dN}{dt} = -kN
\]

- \( N \) = number of organisms per volume \([L^3]\)
- \( k \) = Chick's Law constant \([T^{-1}]\)

Integrate to get:

\[
\ln\left(\frac{N}{N_0}\right) = -kt
\]

- \( N_0 \) = starting number of organisms
- \( N/N_0 \) = "survival ratio"

**Chick-Watson Model** – Herbert Watson, 1908

\( C^n t = K \) achieves particular level of disinfection (i.e. \( N/N_0 \))

- \( C \) = concentration of disinfectant
- \( n \) = empirical const called "coefficient of dilution"
- \( K \) = constant (function of microorganisms)
If \( n > 1 \), disinfectant efficiency decreases with dilution - concentration is more important than time.

\( n < 1 \), time is more important than conc.

\( n = 1 \), time and conc equally important.

\( n \) is slope of log C vs log t plot (see pg 4) by convention, 99.9% inactivation is plotted.

If \( n \neq 1 \), then Chick-Watson model is:

\[
\ln \left( \frac{N}{N_0} \right) = -\Lambda_{cw} Ct
\]

\( \Lambda_{cw} \) = Chick-Watson coefficient of specific lethality [L/mg-min]

Other models also exist - see MWH, 2005.

\( Ct \) is specified by USEPA rules for Giardia and Cryptosporidium for different disinfectants and pH. Unlike bacteria, no easy tests for Giardia and Crypto, so regulation focuses on technology (expressed as \( Ct \)) rather than monitoring.

Page 5 (from MWH, 2005, p. 1063) shows \( Ct \) to achieve 99.9% removal by various technologies.

Note: chlorine is relatively ineffective against Cryptosporidium (C. Parvum), UV is particularly effective against Giardia and Crypto.
Concentration versus contact time for 99% kill of E. coli by various forms of chlorine at 2°C to 6°C.

Figure by MIT OCW.

Concentration versus contact time for 99% kill of E. coli and three enteric viruses by HOCl at 0°C to 6°C.

Figure by MIT OCW.

Overview of disinfection requirements for 99 percent inactivation.

Chlorine disinfection

Most widely used - effective at low conc., inexpensive, forms residual. Drawback: forms THMs.

Applied as chlorine gas or hypochlorite.

Acts by oxidizing enzymes of cells, preventing essential metabolic processes.

Chlorine gas: \[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} \]

\[ \uparrow \text{hypochlorous acid} \]

\[ \text{HOCl} \rightleftharpoons \text{H}^+ + \text{OCl}^- \]

\[ \uparrow \text{hypochlorite ion} \]

Favored below pH 7.5 (favored above pH 7.5).

Hypochlorite: \[ \text{Ca(OCl)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OCl}^- \text{ (solid)} \]

\[ \text{NaOCl} \rightarrow \text{Na}^+ + \text{OCl}^- \text{ (liquid)} \]

Chlorox is 5.25% NaOCl equilibrates with HOCl.

\[ \text{HOCl} \text{ is more effective disinfectant than OCl}^- \]

...but both are excellent.
HOCl reacts with ammonia:

\[ \text{hypochlorous acid} \]

\[ \text{NH}_3 + \text{HOCl} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \]
monochloramine favored at \( \text{pH} \geq 6 \)

\[ \text{NH}_2\text{Cl} + 2\text{HOCl} \rightarrow \text{NHCl}_2 + 2\text{H}_2\text{O} \]
dichloramine favored at \( \text{pH} \leq 5 \)

\[ \text{NHCl}_2 + 3\text{HOCl} \rightarrow \text{NCl}_3 + 3\text{H}_2\text{O} \]
nitrogen trichloride (trichloramine)

Chloramines are effective against bacteria (e.g., pipe growth), much less effective against viruses.

Chloramine contributes to chlorine residual along with residual free chlorine (HOCl and OCl\(^{-}\)). Chloramines are longer lasting.

Chlorine also reacts with organics:

With phenol to form chlorophenols - strong taste and odor

With NOM (natural organic matter, e.g., humic acids) to form tri-halo methane (THMs)

\[ \text{CHCl}_3 \quad \text{chloroform} \]
\[ \text{CHCl}_2\text{Br} \quad \text{bromodichloromethane} \]
\[ \text{CHClBr}_2 \quad \text{dibromochloromethane} \]
\[ \text{CHBr}_3 \quad \text{bromoform} \]

Known as DBP - disinfection by-products. Problematic because THMs are suspected human carcinogens.
Chlorine dosage is determined so as to ensure adequate residual - known as breakpoint chlorination.

Determined by lab experiments in which chlorine is added and residual is measured:

Chlorine demands:
1. At first, inorganic reducing chems. $\text{Cl}_2 \rightarrow 2\text{Cl}^-$
2. After satisfaction of initial demand, chloramines formed, creating combined residual
3. With increasing Cl dosage, formation favors dichloramine over monochloramine, then trichloramine over dichloramine. Trichloramine is unstable, breaks down to $\text{N}_2$ and reduces chlorine residual
4. Low point of chlorine residual is "breakpoint"
5. Further increase in Cl adds free residual

Desired dosage for water treatment is beyond the breakpoint.
Actual breakpoint concentration varies with the water quality of the raw water - typically 4-10 mg/L.
Desired residual = 0.2 mg/L at furthest point in distribution system.
(Note: 0.5 mg/L is generally objectionable to consumers.)
Dechlorination

Chlorination is also used as a final step in wastewater treatment, but here residual chlorine has adverse effects on aquatic life and is not desired.

Sulfur dioxide used to remove residual Cl:

\[
\begin{align*}
SO_2(g) + H_2O & \rightarrow H_2SO_3 \rightarrow H^+ + HSO_3^- \\
& \rightarrow 2H^+ + SO_3^{2-}
\end{align*}
\]

\[
SO_3^{2-} + HOCI \rightarrow SO_4^{2-} + Cl^- + H^+
\]

\[
SO_3^{2+} + NH_2Cl + H_2O, \rightarrow SO_4^{2-} + Cl^- + NH_4^+
\]

Chlorination

Cl₂ added with proprietary chlorinators (see Fig 11.17 in VH text)

Desired Ct is best achieved in plug flow (or nearly plug flow) reactors

Typical chlorine contact chamber is serpentine chamber with baffles - see pg 10 - Figure from Droste, 1997, p. 522
Typical contact chamber for chlorination. Baffles are provided to promote plug flow. When chlorine has been applied at elevated concentrations, sulfite is added to reduce chlorine to levels that will not cause consumer reaction to chlorine taste and odor.

Figure by MIT OCW.

Ozonation

Ozone \((O_3)\) is more powerful oxidant than \(HOCl\)

Ozone inactivates microorganisms by:
1. Direct oxidation
2. Decomposition into hydroxyl radicals \(HO^*\) which are also strong reactants

Widely used in Europe, increasingly used in US

Advantages: excellent disinfectant (including for Giardia and Cryptosporidium) does not form THMs, chlorophenols effective against taste and odor requires short contact time

Disadvantages: short contact-time reactors prone to short-circuiting more costly than \(Cl_2\) does not create disinfecting residual may produce harmful by-products ozone gas is potentially explosive

Ozone treatment design based on \(Ct\), with consideration of ozone decay over time

Ozone is sparingly soluble — usually introduced as gas by fine-bubble porous diffusers in deep basins

Ozone consumption by specific water to be treated measured in \(Ct\) (analogous to determining chlorine demand) \(C_{residual} = C_{dose} - C_{demand}\)

Decay of \(C_{residual}\) over time measured in \(Ct\) reactors pulsed with ozone \(\rightarrow C_t vs. t\)

Integrate \(C_t vs. t\) to get \(Ct\)
Ozone contactors usually introduce O₃ and get water contact in same tank (pg 13 from MWH pg 1121)

Ozone bubbled into chamber creates fully-mixed conditions.

But desire plug flow to ensure Cₜ is achieved

Solution is to create tanks-in-series to approximate PFR

Some designs seek counter-current flow to achieve better O₂ transfer (bubble rise is slowed by counterflow of water)

Ozone is generated on-site in a corona discharge - electric arc generated by high voltage between two plates separated by air gap

\[ O₂ \rightarrow O₃ \]

\[ O⁺ + O₂ \rightarrow O₃ \]

(same effect as lightning storm)

Chlorine Dioxide ClO₂

stronger oxidant than Cl₂

creates long-lasting residual

effective against taste and odor

produces few by-products, however chlorate and chlorite ions are produced but limited by regulations to non-toxic conc.

widely used in Europe, less common in U.S.

more expensive than Cl₂
Schematics cross-sectional views of two alternate designs for five-chamber, over-under ozone contact chamber: (a) with chimneys and (b) without chimneys.

Figure by MIT OCW.

UV radiation

Disinfects by:
- damaging nucleic acids — DNA, RNA
- forms hydroxyl radicals — strong oxidant

200-300 nm wavelength is absorbed by DNA. $\rightarrow$ disinfecting range for UV. (also range likely to cause skin cancer)

Very effective against cryptosporidium

Radiation produced by lamps
- Low-pressure UV lamp — 254 nm only
- Medium-pressure UV lamp — 210-300 nm range

Medium-pressure disinfects more but takes more power.

Interferences due to
- Absorption by dissolved substances in water
- Shading of organisms by particulates

UV contactors have very short residence times — seconds to minutes.

Short-circuiting is a potential problem.

Somewhat more expensive than chlorination

Treatment equipment consists of array of electricity-powered lamps suspended in water flow — see picture pg. 16.

Or, pipe with long lamp down the middle — pg. 17

SODIS — solar disinfection — is low-tech solution that uses sunlight to disinfect water
Ultraviolet sources and germicidal range: 1) Ultraviolet portion of electromagnetic spectrum, 2) Output from low-pressure UV lamp, and 3) Output from medium-pressure UV lamp.
ULTRAVIOLET LIGHT UNIT

Figure by MIT OCW. Adapted from: Mancl, Karen M. "Bacteria in Drinking Water." The Ohio State University Extension Bulletin. Bulletin 795 (1989).