Disinfection

- *Disinfection* is the selective destruction of disease causing organisms (viruses, bacteria, protozoans). It destroys most recognized pathogenic microorganisms, but not necessarily all microbial forms such as **bacterial spores**.

- *Sterilization* is the complete destruction of all organisms. Sterilization removes or destroys **all viable forms of microbial life**, including bacterial spores.
Chlorination

Death Rate for Typhoid Fever
United States, 1900-1960

Disinfection

- Disinfection is used to treat both domestic water and wastewater.

- Disinfection is used by industry also.
  - To control biological slime build-up in pipes
  - To control bacterial counts in food processing
Inactivation processes include denaturation of:
- proteins (structural proteins, enzymes, transport proteins)
- nucleic acids (genomic DNA or RNA, mRNA, tRNA, etc)
- lipids (lipid membranes, other lipids)
Definitions

- **Dose**: Concentration of disinfectant added, mass per liter of water.
- **Residual**: Concentration of disinfectant remaining and therefore available to combat existing or subsequent microbial contamination.
- **Demand**: Difference between dose and residual.
- **Instantaneous demand**: Concentration of disinfectant that is consumed as soon as it enters the water due to presence of reduced forms of inorganics such as Fe^{2+} or HS^{-} and easily oxidized organics.
Disinfection techniques can be
- physical (boiling, ultraviolet light) or
- chemical methods (chlorine, bromine, iodine, and ozone).
Common Disinfectants Used in Water Treatment

- Free Chlorine
- Monochloramine
- Ozone
- Chlorine Dioxide
- UV Light
- Boiling: At household level in many countries
## Oxidants Used in Drinking Water Treatment

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>MW</th>
<th>Reduced</th>
<th>$n_e^*$</th>
<th>Eq. wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$</td>
<td>71</td>
<td>2Cl$^-$</td>
<td>2</td>
<td>35.5</td>
</tr>
<tr>
<td>HOCl</td>
<td>52.5</td>
<td>Cl$^-$</td>
<td>2</td>
<td>26.25</td>
</tr>
<tr>
<td>OCl$^-$</td>
<td>51.5</td>
<td>Cl$^-$</td>
<td>2</td>
<td>25.75</td>
</tr>
<tr>
<td>NH$_2$Cl</td>
<td>51.5</td>
<td>Cl$^-$</td>
<td>2</td>
<td>25.75</td>
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<tr>
<td>NHCl$_2$</td>
<td>86</td>
<td>2Cl$^-$</td>
<td>4</td>
<td>21.5</td>
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<tr>
<td>O$_3$</td>
<td>48</td>
<td>3H$_2$O</td>
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<td>8</td>
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<tr>
<td>ClO$_2$</td>
<td>67.5</td>
<td>ClO$_2^-$</td>
<td>1</td>
<td>67.5</td>
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<tr>
<td>MnO$_4^-$</td>
<td>119</td>
<td>Mn$^{2+}$</td>
<td>5</td>
<td>23.8</td>
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<tr>
<td>H$_2$O$_2$</td>
<td>34</td>
<td>2H$_2$O</td>
<td>2</td>
<td>17</td>
</tr>
</tbody>
</table>

*$n_e = \text{moles of } e^- \text{ consumed per mole of oxidant reacting}$
Reduction Reactions of Chlorine species

\[ Cl_2(aq) + 2 \, e^- \leftrightarrow 2Cl^- \]
\[ HOCl + 2 \, e^- \leftrightarrow Cl^- \]
\[ OCl^- + 2 \, e^- \leftrightarrow Cl^- \]
\[ ClO_2 + e^- \leftrightarrow ClO_2^- \]
Chlorination

- Very widely used
  - Application of chlorine in various forms to water
    - Chlorine gas - Cl₂
    - Chlorine dioxide - ClO₂
    - Sodium hypochlorite - NaOCl
    - Calcium hypochlorite - Ca(OCl)₂
  - Chlorine gas (Cl₂) most commonly used in large systems
  - Relatively inexpensive
  - Safety concerns have prompted the use of other forms
    - Toxicity
    - Chlorination by-products (tri-halomethanes)
Chlorine disinfection:

- Chlorination is a cheap, effective, relatively harmless (and therefore most popular) disinfection method.
- Chlorine is added as a gas or hypochlorite solution.
- Hypochlorous acid and hypochlorite ions form in solution, which are strong chemical oxidants, and kill microbes.
- Hypochlorous acid is a stronger chemical oxidant and therefore a better disinfectant than hypochlorite ions.
Chlorination Chemistry (Cl₂)

- Chlorine is a gas and dissolved chlorine has a tendency to escape to the atmosphere.
- The loss of chlorine by volatilization is minimal because chlorine rapidly hydrolyzes in water according to the following reactions.

**Hydrolysis reaction of chlorine** – formation of hypochlorous acid (HOCl)

When Cl₂ dissolves in water, one Cl atom oxidizes the other.

\[
Cl_2(g) + H_2O \leftrightarrow HOCl + H^+ + Cl^- \quad \text{(Reaction 1)}
\]
Chlorination Chemistry \((\text{Cl}_2)\)

**Ionization** – HOCl formed during the hydrolysis reaction ionizes to form the hypochlorite ion \((\text{OCl}^-)\).

\[
\text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^- \quad \text{(Reaction 2)}
\]

\[
K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]}
\]

\[
= 1.50 \times 10^{-8} \quad \text{(0°C)} \quad \text{pKa}=7.82
\]

\[
= 2.62 \times 10^{-8} \quad \text{(20°C)} \quad \text{pKa}=7.58
\]
Distribution of HOCl and OCl^−

\[ K_a = \frac{[H^+][OCl^-]}{[HOCl]} \]

- \( K_a = 1.50 \times 10^{-8} \) (0°C)
- \( K_a = 2.62 \times 10^{-8} \) (20°C)
This graph shows the ionization of hypochlorous acid (HOCl) at different pH values.

At a pH of 7.0, 76 percent of the chlorine is in its active, killing form (HOCl). The rest has ionized into the inactive form (OCl-).

At a pH of 7.8, only 33 percent of the chlorine is in HOCl form.
Dissociation of Hypochlorous Acid with pH and Temperature

<table>
<thead>
<tr>
<th>pH</th>
<th>% HOCl 0°C</th>
<th>% HOCl 20°C</th>
<th>pH</th>
<th>% HOCl 0°C</th>
<th>% HOCl 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>100</td>
<td>100</td>
<td>8</td>
<td>40.1</td>
<td>27.6</td>
</tr>
<tr>
<td>5</td>
<td>99.9</td>
<td>99.7</td>
<td>8.5</td>
<td>17.4</td>
<td>10.8</td>
</tr>
<tr>
<td>6</td>
<td>98.5</td>
<td>97.4</td>
<td>9</td>
<td>6.3</td>
<td>3.7</td>
</tr>
<tr>
<td>7</td>
<td>86.9</td>
<td>79.2</td>
<td>10</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>7.5</td>
<td>67.9</td>
<td>54.7</td>
<td>11</td>
<td>0.07</td>
<td>0.04</td>
</tr>
</tbody>
</table>
Free Residual Chlorine

Sum of hypochlorous acid and hypochlorite ion concentrations

$$[\text{HOCl}] + [\text{OCl}^-]$$

- The most stable oxidation state for Cl in water is −1 (Cl⁻).
- Therefore, both HOCl and OCl⁻ (which are in the +1 oxidation state) “want” to acquire electrons (i.e., to oxidize something) so that they can become more stable.
Redox Reactions of Chlorine in Drinking Water

- HOCl and OCl⁻ oxidize many organic compounds, including some that are part of microorganisms and essential for microbial life; hence they serve as disinfectants.

- HOCl and OCl⁻ also oxidize some inorganic compounds, such as Fe^{2+}, Br⁻, Mn^{2+} (slowly at neutral pH, but rapidly at high pH), H₂S, and a few others.

\[
2\text{Fe}^{2+} + \text{HOCl} + 5\text{H}_2\text{O} \leftrightarrow 2\text{Fe(OH)}_3 (s) + \text{Cl}^- + 5\text{H}^+
\]

\[
\text{Br}^- + \text{HOCl} \leftrightarrow \text{HOBr} + \text{Cl}^-
\]

\[
\text{Mn}^{2+} + \text{HOCl} + \text{H}_2\text{O} \leftrightarrow \text{MnO}_2 (s) + \text{Cl}^- + 3\text{H}^+
\]

\[
\text{H}_2\text{S} + 4\text{HOCl} \leftrightarrow \text{SO}_4^{2-} + 4\text{Cl}^- + 6\text{H}^+
\]
Free Residual Chlorine (FRC)

- A measure of the residual free chlorine that is available for disinfection
- Used as a disinfection standard
- Specific levels of FRC must be maintained (0.5-1 mg/L) in the water supply to ensure effective disinfection treatment
Reactions of Chlorine with Reduced Inorganics

Iron Demand

\[ 2Fe(II) + HOCl + H^+ \leftrightarrow 2Fe(III) + Cl^- + H_2O \]

Manganese Demand

\[ Mn(II) + HOCl + H^+ \leftrightarrow Mn(IV) + Cl^- + H_2O \]

Sulfur Demand

\[ S^{2-} + 4HOCl + 4H^+ \leftrightarrow SO_4^{2-} + 4Cl^- + 4H_2O \]

Nitrite Demand

\[ NO_2^- + HOCl \leftrightarrow NO_3^- + Cl^- + H^+ \]
Reactions of Chlorine with Ammonia

- HOCl and OCl\(^-\) react with some compounds by exchanging Cl\(^+\) for an H\(^+\). For instance, at low OCl:N ratios, they react with ammonia (NH\(_3\)) as follows:

\[
\text{NH}_3 + \text{HOCl} \leftrightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}
\]

\[
\text{NH}_2\text{Cl} + \text{HOCl} \leftrightarrow \text{NHCl}_2 + \text{H}_2\text{O}
\]

\[
\text{NHCl}_2 + \text{HOCl} \leftrightarrow \text{NCl}_3 + \text{H}_2\text{O}
\]

- Simultaneously, some N gets oxidized, especially at higher OCl:N ratios, e.g.:

\[
2\text{NH}_2\text{Cl} + \text{HOCl} \leftrightarrow \text{N}_2 + \text{H}_2\text{O} + 3\text{H}^+ + 3\text{Cl}^-
\]

\[
\text{NHCl}_2 + 2\text{HOCl} + \text{H}_2\text{O} \leftrightarrow \text{NO}_3^- + 5\text{H}^+ + 4\text{Cl}^-
\]
Chloramine formation

- Chloramine formation depends upon pH, [HOCl], [NH$_3$], T and time.

- When pH>8 and [HOCl]/[NH$_3$] ≤ 1, NH$_2$Cl is the only chloramine.

- Reaction is fast (complete in less than 1 minute)

- Rate is fastest at pH 8.
Chlorine Demand

- The amount of Cl₂ necessary for disinfection is a function of the concentration of nitrogen compounds (organic N and ammonia).

- Cl₂ added reacts with these nitrogen compounds to form chloramines:

  \[ \text{HOCl} + \text{NH}_3 \leftrightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \quad \text{Monochloramine} \]
  \[ \text{HOCl} + \text{NH}_2\text{Cl} \leftrightarrow \text{NHCl}_2 + \text{H}_2\text{O} \quad \text{Dichloramine} \]
  \[ \text{HOCl} + \text{NHCl}_2 \leftrightarrow \text{NCl}_3 \quad \text{Trichloramine} \]

The chlorine present in the chloramines is termed *combined available chlorine*.

Combined available chlorine can disinfect but is not as effective as free residual chlorine.
Reactions of Chlorine with Ammonia

• Chlorinated ammonia species are referred to as mono-, di-, and tri chloramine. Chloramines are referred to collectively as *combined chlorine*, as opposed to HOCl and OCl− (and Cl2), which are called *free chlorine*.

• Chlorine is in the +1 oxidation state in chloramines, so it is still unstable (and an oxidant), but less so than in free chlorine. Chloramines are therefore disinfectants, but are weaker than free chlorine.

• The short-hand for all forms of chlorine in the +1 oxidation state is “Cl2” so free and combined chlorine are written as “free Cl2” and “combined Cl2” respectively (not “free Cl” and “combined Cl”)
Chlorine Demand

- Organic N and ammonia exert a chlorine demand
  - Wastewater (40-60 mg/L)
  - Potable water (2-5 mg/L)

- Once demand is met additional Cl$_2$ added reacts to form free residual chlorine which is more effective for disinfection

- Cl$_2$ forms useful for disinfection exists as
  - Combined available chlorine- chloramaines (chlorine demand)
  - Free residual chlorine – hypochlorite and chlorite ions
  - Both forms can disinfect but free chlorine is more effective
Breakpoint Chlorination

- Chlorination to satisfy all the chlorine demand in order to obtain free chlorine.
  - Inorganic chlorine demand
  - Organic chlorine demand
  - Ammonia reaction to form chloramines (combined chlorine)
  - Oxidation of chloramines to N$_2$, NO, NO$_3^-$.
Breakpoint Chlorination

■ Chloramine formation reactions

\[ HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O \] (1)
\[ HOCl + NH_2Cl \leftrightarrow NHCl_2 + H_2O \] (2)
\[ HOCl + NHCl_2 \leftrightarrow NCl_3 \] (3)

■ Oxidation of Chloramines

1) If reaction product is \( N_2 \)

\[ 2NH_2Cl \leftrightarrow N_2 + 4H^+ + 2Cl^- + 2e^- \]
\[ HOCl + H^+ + 2e^- \leftrightarrow Cl^- + H_2O \]

\[ 2NH_2Cl + HOCl \leftrightarrow N_2 + 3Cl^- + 4H^+ + H_2O \] (4)
Breakpoint Chlorination

Add reactions 1 and 4

\[ 2\text{NH}_2\text{Cl} + \text{HOCl} \leftrightarrow \text{N}_2 + 3\text{Cl}^- + 3\text{H}^+ + \text{H}_2\text{O} \quad (4) \]
\[ 2\text{NH}_3 + 2\text{HOCl} \leftrightarrow 2\text{NH}_2\text{Cl} + 2\text{H}_2\text{O} \quad (1) \]

\[ 2\text{NH}_3 + 3\text{HOCl} \leftrightarrow \text{N}_2 + 3\text{H}^+ + 3\text{Cl}^- + \text{H}_2\text{O} \quad (5) \]

\[ \frac{\text{Cl}_2}{N} = 1.5 \quad \text{molar ratio} \]

*If N\(_2\) is the reaction product. (same ratio for other chloramines)*
2) If reaction product is NO

\[
\begin{align*}
2 & \quad \text{NH}_2\text{Cl} + H_2O & \leftrightarrow & \quad NO + 4H^+ + Cl^- + 3e^- & \quad (6) \\
3 & \quad \text{HOCl} + H^+ + 2e^- & \leftrightarrow & \quad Cl^- + H_2O & \quad (1) \\
\hline
2\text{NH}_2\text{Cl} + 3\text{HOCl} & \leftrightarrow & 2\text{NO} + 5\text{Cl}^- + 5H^+ + H_2O & \quad (7)
\end{align*}
\]
2) If reaction product is NO

Add reactions 1 and 7

\[
2\text{NH}_2\text{Cl} + 3\text{HOCl} \leftrightarrow 2\text{NO} + 5\text{Cl}^- + 5\text{H}^+ + \text{H}_2\text{O} \quad (7)
\]

\[
2\text{NH}_3 + 2\text{HOCl} \leftrightarrow 2\text{NH}_2\text{Cl} + 2\text{H}_2\text{O} \quad (1)
\]

\[
2\text{NH}_3 + 5\text{HOCl} \leftrightarrow 2\text{NO} + 5\text{H}^+ + 5\text{Cl}^- + 3\text{H}_2\text{O} \quad (8)
\]

\[
\frac{\text{Cl}_2}{\text{N}} = 2.5 \quad \text{molar ratio}
\]

If NO is the reaction product. (same ratio for other chloramines)

\[
\text{Practical Ratio} \sim = 2 \quad \text{(molar ratio)}
\]
\[
\frac{Cl_2}{N} = 1.0 \quad \text{molar ratio}
\]

Chloramine formation reactions are dominant.

\[
\frac{1.0 \times 71}{14} = 5 \quad \text{mass ratio}
\]

\[
\frac{Cl_2}{N} = 1.5 \quad \text{molar ratio}
\]

\[
\frac{1.5 \times 71}{14} = 7.6 \quad \text{mass ratio}
\]

Chloramine oxidation reactions are dominant.

\[
\frac{Cl_2}{N} = 2.5 \quad \text{molar ratio}
\]

\[
\frac{2.5 \times 71}{14} = 12.7 \quad \text{mass ratio}
\]
The "Breakpoint Chlorination" Curve:
Reaction of HOCl with Pure H₂O + NH₃

Regions 1 and 2: Formation of combined Cl₂ dominates over oxidation of N; Conc’n of residual Cl₂ increases with increasing Cl₂:N ratio

Region 3: Oxidation of N dominates over formation of combined Cl₂; when Cl₂:N ratio increases, more combined Cl₂ is oxidized than is formed

Region 4: All N oxidized; increase in Cl₂:N ratio leads to increase in free Cl₂ residual
Reactions of Chlorine with Organics (NOM)

One Person’s Idea of an NOM Molecule

Free $\text{Cl}_2$ reacts with NOM molecules in two ways: (1) oxidation, generating $\text{Cl}^-$, and (2) substitution to form chlorinated organics.
Consumption of Free Cl$_2$ by Reaction with NOM and Inorganics

Region 1: Almost all Cl$_2$ added reacts with NOM or inorganics; negligible residual

Region 2: For each increment of Cl$_2$ added, some reacts with NOM or inorganics, but some remains as free Cl$_2$ residual

Region 3: Essentially all of the incremental Cl$_2$ remains in solution as free Cl$_2$ residual
Breakpoint Curve for Chlorination of Water Containing NH₃, NOM and Inorganics

*Regions described on following slide*
Breakpoint Curve for Chlorination of Water Containing NH₃, NOM and Inorganics

Region 1: Almost all Cl₂ added reacts with NOM or inorganics; negligible residual

Region 2: For each increment of Cl₂ added, some reacts with NOM or inorganics, but most reacts with NH₃ to form combined residual

Region 3: Most Cl₂ added oxidizes chloramines, so total Cl₂ residual declines; residual essentially all combined

Region 4: Most Cl₂ added remains as free residual, but some reacts with NOM or inorganics that were unreactive with combined Cl₂

Region 5: Essentially all of the incremental Cl₂ remains in solution as free Cl₂ residual
Reactions of Chlorine with NOM

The total conc’n of Cl and Br that gets incorporated into organics is referred to as the total organic halogen concentration, TOX. Identifiable molecules account for about one-half of the TOX.
Schematic Summary: Reactions of Chlorine with NOM

\[ + \text{Cl}_2 + \text{Br}^- \rightarrow \text{THMs} \]

THMs: Trihalomethanes
Cl\(^-\): Chloride
Br\(^-\): Bromide
HAAs: Haloacetic Acids
Disinfection Kinetics

Chick’s Law (1908)- most widely used

Like most biological processes, disinfection follows a first-order reaction with respect to the number of microbes of a certain species surviving as a function of time at a constant level of a disinfectant.

\[
\frac{dN}{dt} = -k \cdot N
\]

where,

N: Number of organisms
k: Susceptibility coefficient
Disinfection Kinetics

**disinfection**

\[
\frac{dN}{dt} = -k \cdot N
\]

\[
\ln \frac{N}{N_0} = -kt
\]

**first-order chemical reaction**

\[
\frac{d[A]}{dt} = -k \cdot [A]
\]

\[
\ln \frac{[A]_t}{[A]_0} = -kt
\]

The graph shows a linear relationship between \(\ln \frac{N}{N_0}\) and time, with a slope of \(-k\).
Disinfection Kinetics

Chick’s Law holds for ideal conditions:

- All cells of a single species are equally susceptible to the disinfectants.

- Cells and the disinfectant are uniformly dispersed in water.

- Concentration of disinfectant and the water matrix remains constant through the contact period.
Log reduction

Log-reduction terminology was developed as a way to express levels of decreased biological contamination in water by factors of 10 that could be easily converted to percent reduction.

- **1 log reduction** is equivalent to a 90 % reduction. $N/N_0 = 0.1$
- **2 log reduction** is 99 % reduction. $N/N_0 = 0.01$
- **3 log reduction** is 99.9 % reduction. $N/N_0 = 0.001$
- **4 log reduction** is 99.99 % reduction in biological contaminants (such as viruses). $N/N_0 = 0.0001$
**C\(t\) concept**

In disinfection, the ability to inactivate microorganisms is a function of both disinfectant concentration and time.

*for a specified percent kill*

\[ C^n \cdot t = K \]

**C:** Concentration of disinfectant.
**t:** contact time
**n:** a constant (coefficient of dilution)

- \(n=1\) , C and t are equally effective
- \(n>1\) , C is more effective
- \(n<1\) , t is more effective
\textit{C. t} concept

\((C \cdot t)\) is a relatively new concept in regulations.

It is the multiplication of required concentration of disinfectant raised to a power by the required contact time.
Under the same conditions

K=0.24 , for e-coli with chlorine
K=1.20 , for poliovirus with chlorine

It is more difficult to kill poliovirus with chlorine than to kill e-coli.
<table>
<thead>
<tr>
<th>Disinfectant</th>
<th>pH</th>
<th>Concentration (mg/L)</th>
<th>Virus state</th>
<th>T-99.99 (min.)</th>
<th>CT</th>
</tr>
</thead>
<tbody>
<tr>
<td>free chlorine</td>
<td>8</td>
<td>0.4</td>
<td>dispersed</td>
<td>5.5</td>
<td>2.0</td>
</tr>
<tr>
<td>free chlorine</td>
<td>8</td>
<td>0.4</td>
<td>cell-associated</td>
<td>70.0</td>
<td>27.0</td>
</tr>
<tr>
<td>free chlorine</td>
<td>10</td>
<td>0.4</td>
<td>dispersed</td>
<td>50.0</td>
<td>19.3</td>
</tr>
<tr>
<td>free chlorine</td>
<td>10</td>
<td>0.4</td>
<td>cell-associated</td>
<td>253.0</td>
<td>104.0</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>6</td>
<td>0.5</td>
<td>dispersed</td>
<td>40.0</td>
<td>14.0</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>6</td>
<td>0.5</td>
<td>cell-associated</td>
<td>55.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>9</td>
<td>0.5</td>
<td>dispersed</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>9</td>
<td>0.5</td>
<td>cell-associated</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Ozone</td>
<td>8</td>
<td>0.3</td>
<td>dispersed</td>
<td>&lt;0.1</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Monochloramine</td>
<td>8</td>
<td>10.0</td>
<td>dispersed</td>
<td>116.0</td>
<td>1,225.0*</td>
</tr>
<tr>
<td>Monochloramine</td>
<td>8</td>
<td>10.0</td>
<td>cell-associated</td>
<td>170</td>
<td>1,740.0*</td>
</tr>
</tbody>
</table>

* by extrapolation from experiments with 60-minute contact times

Disinfection by J(Hans) van Leeuwen
Disinfection: Characteristics and Regulations

Idealized disinfection curves

- Same disinfection efficiency (99% here) achieved by any combination of $C$ and $t$ that gives same $C^{0.86t}$ value.
- $C^{0.86t}$ required for given disinfection varies widely for different organisms.
Disinfection Kinetics

In Chick’s Law

\[ \ln \frac{N}{N_0} = -k \cdot t \]

In Chick-Watson Law

\[ \ln \frac{N}{N_0} = -k_o C^n \cdot t \]

If \( n = 1 \)

\[ k_o = \frac{-\ln\left(\frac{N}{N_0}\right)}{C \cdot t} \]

Extent of disinfection of microorganisms per unit conc. of the disinfectant per unit time
**C. t concept**

- If $k_o$ is high, then disinfection is effective.
- If $k_o$ is low, then disinfection does not provide the desired percent kill.
For 99% kill at 5°C, the following $k_o$ values, (L/mg.min), were reported:

<table>
<thead>
<tr>
<th>Disinfectant</th>
<th>E-Coli</th>
<th>Viruses</th>
<th>Spores</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$</td>
<td>500</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>HOCl</td>
<td>20</td>
<td>1.0 and up</td>
<td>0.05</td>
</tr>
<tr>
<td>OCl$^-$</td>
<td>0.2</td>
<td>&lt;0.02</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>NH$_2$Cl</td>
<td>0.1</td>
<td>0.005</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Environmental Variables

- The key environmental variables that can affect disinfection are temperature and pH.

\[
\ln \frac{k_1}{k_2} = \frac{E_a (T_2 - T_1)}{RT_1 T_2}
\]

where:
- \(k_1, k_2\) = rate konstants at temp. \(T_1\) and \(T_2\)
- \(E_a\) = activation energy, (J mol\(^{-1}\)) (varies with pH)
- \(T_1, T_2\) = temperature, (°K)
- \(R\) = gas constant, 8.314 J mol·K\(^{-1}\)
Environmental Variables

Disinfection rate doubles for every 10°C increase in temperature.

\[ \frac{k_{T+10^0C}}{k_T} = Q \approx 2 \]
13.41 The rate constants of some reactions double with every 10-degree rise in temperature. Assume that a reaction takes place at 295 K and 305 K. What must the activation energy be for the rate constant to double as described?
Bacteria have surface charges similar to inorganic colloids due to hydrolysis of aminoacids.

Therefore, $OCl^-$ is less effective than $HOCl$, i.e., low pH is better.

For $O_3$ also low pH is better. Because at high pH, $O_3$ is converted into $OH^*$ (free hydroxyl radical).

For $ClO_2$, high pH is more effective.
### CT values for Giardia and Virus Inactivation Using Chloramines

<table>
<thead>
<tr>
<th>Log Inactivation</th>
<th>Temperature (°C)</th>
<th>Required CT (mg-min/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>15</td>
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<tr>
<td><strong>Giardia</strong></td>
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<tr>
<td>1</td>
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<td>500</td>
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<td>1000</td>
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<tr>
<td>3</td>
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<td>1500</td>
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## CT values for Inactivation Using Chlorine Dioxide

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<tr>
<td>1</td>
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Concentration – Contact Time

**FIGURE 24.1** Concentration versus Contact Time for 99% Kill of E. coli by Various Forms of Chlorine at 2°C to 6°C

**FIGURE 24.2** Concentration versus Contact Time for 99% Kill of E. coli and Three Enteric Viruses by HOCI at 0°C to 6°C

Adapted from "Water Treatment Technology."
Factors Affecting Chlorine Disinfection

- Method of Initial Contact
- Contact Time
- Concentration of Disinfectant
- Concentration of Organisms
- Environmental Variables
Initial Contact Methods

- The method of introducing the chlorine into the water stream can have a significant impact on its ability to disinfect.
Contact Time

Contact time for effective disinfection is a function of:

- Free residual chlorine concentration
- Temperature
- Presence of interfering materials
- Organism’s resistance to chlorine disinfection
  - Bacteria are easier to kill than viruses
  - Encysted bacteria are resistant
  - Many Protozoa can encyst too and are resistant (Giardia, Cryptosporidium)
Dechlorination

- Dechlorination may be necessary for treated wastewater being released back to environmental waters
  - May adversely affect fish and other aquatic life
  - Sodium dioxide, sodium sulfite, sodium metabisulfite, and activated carbon are used to remove excess $\text{Cl}_2$
Disinfection and Disinfection By-Products (DBPs)

- Free Cl is an excellent disinfectant for most pathogens; some spore-forming organisms (Giardia and Cryptosporidium) are exceptions. Free Cl also tends to generate chlorinated DBPs

- Combined Cl is a weaker disinfectant than free Cl, but it forms almost no chlorinated DBPs
Regulations for Chlorinated Organics

Maximum Contaminant Levels (MCLs) exist for:

- Total TriHaloMethanes (TTHMs), 80 μg/L
- The sum of five HaloAcetic Acids (HAA$_5^*$), 60 μg/L

Maximum Contaminant Levels Goals (MCLGs) (the “no adverse health effect level”):

- Zero for CHCl$_3$, CHCl$_2$Br, CHBr$_3$, DCAA
- 0.06 mg/L for CHClBr$_2$, 0.3 for TCAA

All chlorinated and brominated organics are referred to as *(halogenated) disinfection byproducts, DBPs.*

*MCAA, DCAA, TCAA, DBAA, TBAA*
Approaches for Reducing DBP Concentrations in Finished Water

• Use a disinfectant that is less likely to form DBPs or forms less problematic ones
• Remove or alter the NOM so that it doesn’t react with the free Cl₂
• Remove DBPs after they form

The first two of the above options are employed fairly commonly. Approaches to implement the third option have largely been abandoned.
Alternative Disinfectants

- Chloramines (NH$_2$Cl and NHCl$_2$)
  - Weaker oxidant than free chlorine; acceptable disinfectant, but higher doses required than for free Cl$_2$
  - Stable; provides a long-term residual for downstream protection
  - Forms virtually no halogenated DBPs
  - Subject to some biodegradation in presence of O$_2$, especially in warm water
  - Recent evidence suggests it might allow release of very high concentrations of Pb, if the distribution system has historically been exposed to free Cl$_2$

Conclusion: Not highly attractive as primary disinfectant, but good for generating long-lasting residual with low DBP formation after an initial dose of some other, stronger disinfectant; concerns about interactions with pipes not yet resolved
Alternative Disinfectants

- Ozone ($O_3$)
  - Very strong oxidant; excellent disinfectant
  - Unstable; $O_3$ gas must be generated on-site and used immediately; leaves no stable residual for downstream protection
  - Forms no halogenated DBPs, but reacts with $Br^-$ to form bromate ($BrO_4^-$), with MCL of 0.01 mg/L, and MCLG of zero
  - Breaks down NOM into more degradable segments (with both good and bad consequences)

Conclusion: Excellent primary disinfectant for many waters; not satisfactory as a sole disinfectant
Alternative Disinfectants

- Chlorine Dioxide (ClO₂)
  - Strong oxidant; better oxidant of Fe²⁺ and Mn²⁺ than free Cl₂. Comparable to free Cl₂ as disinfectant, better for Giardia and Cryptosporidium; insensitive to pH
  - Can transfer from water to gas phase, where it is explosive if highly concentrated or compressed; therefore, ClO₂ generally produced onsite as a concentrated (1-2%) solution
  - Low concentrations of ClO₂ gas can react with household materials to produce offensive odors
  - Seems to form halogenated NOM, but not THMs or HAAs; does form chlorite (ClO₂⁻) with MCL of 1.0 mg/L, and MCLG of 0.8 mg/L

Conclusion: Good primary disinfectant to avoid DBP formation, but problematic because of ClO₂⁻ formation; useful in special circumstances (e.g., for Mn²⁺ oxidation)