Water Treatment – Preparation of water for drinking and municipal distribution
(Nazaroff & Alvarez-Cohen, pages 302 and following; Mihelcic & Zimmerman, Chapter 10)

Consumers in industrialized countries expect safe drinking water, that is:
- Clear
- Colorless
- Odorless
- Free of harmful chemicals
- Free of pathogens.

Natural water, however, rarely exhibits these properties.

<table>
<thead>
<tr>
<th>Type of impurity</th>
<th>Specific constituents</th>
<th>Typical concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major inorganic constituents</td>
<td>Usually in ionic form: calcium, chloride, fluoride, iron, manganese, nitrate (NO₃⁻), sodium, sulfur</td>
<td>1 – 1000 mg/L</td>
</tr>
<tr>
<td>Minor inorganic constituents</td>
<td>Arsenic, cadmium, copper, lead, mercury, nickel, zinc, etc.</td>
<td>0.1 – 10 μg/L</td>
</tr>
<tr>
<td>Natural organic compounds</td>
<td>Biological detritus (Total Organic carbon = TOC)</td>
<td>0.1 – 20 mg/L</td>
</tr>
<tr>
<td>Anthropogenic organic compounds</td>
<td>Synthetic organic chemicals, agricultural, industrial &amp; household chemicals (benzene, vinyl chloride, PCBs, PCE, TCE)</td>
<td>from 1 μg/L to tens of mg/L</td>
</tr>
<tr>
<td>Living organisms</td>
<td>Bacteria, algae, viruses</td>
<td>millions</td>
</tr>
</tbody>
</table>

(Mihelcic & Zimmerman, Table 10.1)

Arsenic

Naturally occurring arsenic is widespread, and in many places of the world, arsenic is present in the groundwater. The World health Organization (WHO) has set a drinking-water guideline for arsenic of 10 μg/L (= 10 ppbm).

Long-term exposure to arsenic via drinking-water causes cancer of the skin, lungs, urinary bladder, and kidney, as well as other skin changes such as pigmentation changes and thickening (hyperkeratosis).

Increased risks of lung and bladder cancer and of arsenic-associated skin lesions have been observed at drinking-water arsenic concentrations of less than 0.05 mg/L.

Simple technology to remove arsenic from groundwater, which can be implemented in under-developed countries.
Schematic of a typical municipal drinking-water treatment system  
(Mihelcic & Zimmerman, Figure 10.3a)

Coagulation & Flocculation  
(Nazaroff & Alvarez-Cohen, Section 6.D.2)  
(Mihelcic & Zimmerman, Section 10.5)

This is generally a middle step in water preparation for municipal distribution, after basic screening for the removal of debris and pH adjustment.

The objective is to remove particles that would otherwise take too long to settle. It also offers the advantage of being able to remove some of the dissolved organic matter.

Coagulation is a charge neutralization step that is achieved by the addition of a chemical such as
- alumina $\text{Al}_2(\text{SO}_4)_3$,
- sodium aluminate $\text{Na}_2\text{Al}_2\text{O}_4$,
- aluminum chloride $\text{AlCl}_3$,
- ferric sulfate $\text{Fe}_2(\text{SO}_4)_3$,
- ferric chloride $\text{FeCl}_3$.

(Mihelcic & Zimmerman, Figure 10.6)
The water is then gently stirred to promote aggregation of particles in bigger clouds of particles, called flocs. This step is flocculation.

The end step is the settling of the larger, aggregate particles in a settling tank.

**Water Softening = Hardness Removal**
(Nazaroff & Alvarez-Cohen, Section 6.D.4)
(Mihelcic & Zimmerman, Section 10.6)

Hardness of water is caused by 2+ ions, primarily Ca++ and Mg++, usually associated with the carbonate ions (HCO₃⁻ and CO₃²⁻) or sulfate ions (SO₄²⁻). It is a common occurrence with groundwater.

So-called complexation agents can be added to prevent the 2+ ions from precipitating. Better, hardness can be removed, which softens the water.

*Example of process*: The lime-soda ash softening process

\[
\text{Ca(HCO}_3\text{)}_2 + \text{Ca(OH)}_2 \rightarrow 2 \text{ CaCO}_3(\text{solid}) + 2 \text{ H}_2\text{O}
\]

\[
\text{Mg(HCO}_3\text{)}_2 + 2 \text{ Ca(OH)}_2 \rightarrow 2 \text{ CaCO}_3(\text{solid}) + \text{ Mg(OH)}_2(\text{solid}) + 2 \text{ H}_2\text{O}
\]
Disinfection
(Nazaroff & Alvarez-Cohen, Section 6.D.1)
(Mihelcic & Zimmerman, Section 10.9)

**Purpose:**
To reduce risk of disease transmission associated with either drinking or waste water.

**Objective:**
To kill or inactivate microorganisms.

**Methods:**

<table>
<thead>
<tr>
<th>Method</th>
<th>Effectiveness</th>
<th>Cost/Convenience</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling of water</td>
<td>Very effective</td>
<td>Very energy intensive</td>
</tr>
<tr>
<td>Irradiation with UV light</td>
<td>Limited efficacy</td>
<td>Cheap and convenient\ Requires clear water</td>
</tr>
<tr>
<td>Chemical disinfection by chlorine or chlorinated compound</td>
<td>Very effective\ Leaves lasting residuals</td>
<td>Cheap to expensive\ May create harmful by-products</td>
</tr>
<tr>
<td>Chemical disinfection by ozone</td>
<td>Very effective</td>
<td>Quite expensive\ No residual left</td>
</tr>
</tbody>
</table>
Disinfection by chlorine

The active ingredient that kills microorganisms is hypochlorous acid, HOCl.

HOCl must be made in the water from a chlorinated precursor. The most common method is the injection of pure chlorine gas, Cl₂.

More expensive but safer than handling chlorine gas is the use of sodium hypochlorite (NaOCl – commonly called bleach) or calcium hypochlorite (Ca(OCl)₂), a solid.

U.S. standards for drinking water:
- minimum contact of 45 minutes
- minimum residual chlorine concentration of 1.1 mg/L
  (from initial dose of 2 to 5 mg/L)

U.S. practice for end of wastewater treatment:
- injection of 40 to 60 mg/L.

Chlorine chemistry in pure water

Let us consider the use of chlorine gas as the disinfection method.

First, Cl₂ in gas (from compressed bottle, handled with care!) penetrates the water, following Henry's Law:

\[ \text{Cl}_2(g) \leftrightarrow \text{Cl}_2(aq) \quad \text{with} \quad K_H = 0.062 \text{ M/atm at 25°C} \]

Aqueous Cl₂ reacts rapidly with water to form hypochlorous acid:

\[ \text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \]

with constant

\[ K = \frac{[\text{HOCl}][\text{H}^+][\text{Cl}^-]}{[\text{Cl}_2]} \approx 5 \times 10^{-4} \text{ M}^2 \]

The preceding two reactions are highly tilted to the right, meaning that chlorine gas most easily goes into hypochlorous acid in the water.
However, hypochlorous acid HOCl is not just consumed in killing microorganisms; it also decays spontaneously into:

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

with constant

\[
K_2 = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} = 2.6 \times 10^{-8} \text{ M}
\]

The hypochlorite ion OCl\(^-\) is much less potent as a disinfectant than HOCl.

To keep the previous reaction tilted to the left (in favor of HOCl and against OCl\(^-\)), the pH must be controlled.

\[\text{Figure 6.D.1. The fraction of hypochlorous species (HOCl + OCl\(^-\)) that is present as undissociated hypochlorous acid (HOCl), versus pH. (From Nazaroff & Alvarez-Cohen, 2001)}\]