Water Treatment

- It is desired that drinking water be:
  - Safe
  - Clean
  - Clear
  - Free of disagreeable smells and odours
  - Free of pathogens (Over 7000 people a day die due to waterborne diseases that could be prevented with water treatment.)
  - Free of dissolved solids or minerals
  - Conveniently and inexpensively available.
- Sources of drinking water:
  - Ground water
  - Surface water
- The advantages of ground water include:
  - Fewer contaminants (usually)
  - Clarity
- Disadvantages of ground water include:
  - Radon
  - Hardness and alkalinity
  - Finite capacity of aquifers. If an aquifer is depleted, the ground above may subside and become vulnerable to flooding.
- The advantages of surface water include:
  - Availability
- Disadvantages of surface water include:
  - What is upstream?
  - Dissolved organic matter.
  - Biological and chemical oxygen demand.
- Since it was recognized that ground water was better than surface water, the first attempts at water treatment in the 19th century was to "make" ground water.
  - Surface water was trickled through sand.
  - Surface water was used to "reinject" underwater aquifers.
  - This does lead to a decline in the incidence of waterborne diseases such as cholera, typhoid, and amoebic dysentry.
- Modern water treatment consists (typically) of four stages:
  - Settling
  - Aeration
  - Coagulation

    - Disinfection
- Depending on the water supply, one or more of the first three steps may not be necessary.

Settling

- Water brought into a large holding pond an particulate is allowed to settle.
- If the pH is too low, it is adjusted to be greater than 6.5

Aeration

- Aeration has the objective of removing oxidizable substances.
    - These include be both chemical and biological species.
    - Fe^{2+} is removed at this stage to prevent rust stains ($Fe(OH)_3$).
    - Upon contact with air Fe^{2+} is quickly oxidized to Fe^{3+}.

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$$4\ H^+ + O_2 + 4\ e^- \rightarrow 2\ H_2O$$

$$\text{Net reaction: } 4\ Fe^2 + +4\ H^+ + O_2 \rightarrow 4\ Fe^3 + 2\ H_2O$$

    - If pH > 3,then:

$$Fe^{3+} + 3\ OH^- \rightarrow Fe(OH)_3$$

Coagulation (Secondary Settling)

- Coagulation has the objective of removing suspended solids such as:
    - Colloidal minerals
    - Bacteria
    - Pollen
    - Spores

  resulting in water that is clear.
- Since in the settling step, the pH of the water has been adjusted to pH > 6.5.
    - Minimum solubility of Al^3+ occures in the pH range 6.5 to 8.
    - Filter alum ($Al_2(SO_4)_3.18H_2O$) is used as a clarifying agent since it forms a gelatinous precipitate that settles slowly, carrying down the suspended solids.
    - Alternative settling agents are $Fe(OH)_3$ and activated silica, both of which form gelatinous precipitates.

Disinfection

- Disinfection of drinking water is essential
    - To kill any pathogens that persist through the earlier stages of treatment.
    - To prevent the growth of bacteria in the distribution system (in which water can spend up to a week).
    - To prevent recontamination of the water in the distribution system due to leaks.
- Disinfection agents include:
    - Chlorine
    - Chlorine Dioxide
    - Ozone

- Ultraviolet radiation

- Chlorine is the only one that leave a residual that can prevent recomtamination.
- Chlorine dissolved in water establishes the following equilibria:

$$\mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2(aq)}, \quad K_H = 8.0 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1}$$
$$\mathrm{Cl_2(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} + \mathrm{HOCl(aq)}$$
$$K_c = 4.5 \times 10^{-4} \text{ mol}^2 \text{ L}^{-2}$$
$$\mathrm{HOCl(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{OCl^-(aq)}$$
$$K_c = 3.0 \times 10^{-8} \text{ mol L}^{-1}$$

  - It is HOCl that is effective in killing microorganisms since it can penetrate the cell membrane.
  - Chlorine dose required depends on pH (need to keep pH below 2.5).
  - Desire chlorine residual of about 1 ppm.
- Disadvantages of chlorine include:
  - Taste and odour.
  - Chlorination of organic compounds.
  - Concerns about toxicity.
- Advantages of chlorine include:
  - Inexpensive
  - Residual

- Chlorine dioxide is often considered as an alternative to chlorine.
- Chlorine dioxide has the advantages:
  - Oxidizes organic compounds instead of chlorinating them.
  - Can use a physical plant very similar to that required for chlorine.
  - Possible to easily switch from chlorine temporarily if chlorine is causing problems.
- Disadvantages of chlorine dioxide include:
  - Must be manufactured on site from $NaClO_2$.

$$10\ \mathrm{NaClO_2} + 5\ \mathrm{H_2SO_4} \rightarrow$$
$$8\ \mathrm{ClO_2} + 5\ \mathrm{Na_2SO_4} + 2\ \mathrm{HCl} + 4\ \mathrm{H_2O}$$

or

$$2\ \mathrm{NaClO_2} + \mathrm{Cl_2} \rightarrow 2\ \mathrm{ClO_2} + 2\ \mathrm{NaCl}$$
$$(\text{Must keep pH} < 3.5)$$

  - The first reaction is preferred because it is chlorine free.
  - There is no residual disinfection, therefore the water must be "finished" with chlorine before distribution.
- There is some concerned about toxicity of ClO_2.
  - At levels of 50 ppm $NaClO_2$, hemolysis can occur.
  - Finished water has less than 1 ppm ClO_2, which is shortlived.

- Ozone requires a completely different physical infrastructure than chlorine or chlorine dioxide.
  - Usually implemented in new facilities.
  - Economic only on a larger scale.

- Generated by running a high voltage electrical discharge through air giving about 1
- Ozone absorbed by water ($K_H = 1.3 \times 10^{-2}$ mol L^{-1} atm^{-1}.)

- Advantages of ozone include:
  - Oxidizes organics
  - Air is the main raw material required.
- Disadvantages include:
  - pH control is necessary.
  - Finishing with chlorine is necessary.

- Ultraviolet radiation with $\lambda < 300$ nm damages pyridine base pairs in DNA sequences.
  - Causes cell death and thus death of microbes.
- Can be generated by mercury arc lamps ($\lambda = 254$ nm) with about 40% efficiency.
- Advantages of UV water treatment include:
  - Contact time is short (< 10 s).
  - No large reservoir required.
  - Low installation cost.
  - Do not need to control or monitor pH or temperature.
  - No toxic residues.
  - Cost competitive with chlorine treatment.
  - Possible to implement on a small or portable scale as an emergency or remote, stand alone system.
- Disadvantages of UV treatment include:
  - Water source must be clear of suspended matter and organic molecules that could absorb the UV.
  - If suspended matter or organic molecules are present, then pretreatment with activated charcoal may be required.
  - No residual disinfection. The water must be used immediately or be finished with chlorine.

Quality Control in Water Treatment and Distribution

- Before water treatment:
  - What are the potential contaminants in the watershed or aquifer?
  - What dissolved inorganic species are present?
  - What organic chemical species are present, especially those that can survive the treatment process and lead to unacceptable taste or smell?
  - For treatment with chlorine, chlorine dioxide, or ozone: what is the demand of the raw water for the disinfecting agent.
  - For treatment with UV, is the clarity acceptable.
  - Is the quality of the incoming water consistent with the capacity of the treatment facility.
- During water treatment:

    - Are the pH and temperature in the appropriate range for the treatment process?
- After water treatment:
    - Is there an appropriate level of residual chlorine?
    - Are any pathogens present?
    - Are there any undesirable chemicals present that formed during the treatment process or survived the treatment process?
    - Is further treatement (softening, deionization, filtering) required.
    - Are the taste, smell, and appearance acceptable.

Sewage Treatment

- Sewage treatment parallels water treatment.
    - Primary treatment consists of settling and skimming
    - Seconday treatment consists of reducing the biological oxygen demand.
    - Tertiary treatment reduces the concentration of particular contaminants, such as phosphorous.
    - Finishing consists of disinfection.
- Primary sewage treatment
    - Physical separation of solids and immiscibles.
    - Raw sewage enters a lagoon through one or more coarse screens that remove large objects.
    - A grit tank allows for the deposition of grit, sand, etc.
    - The sewage then moves slowly through the clarifier slowly enough for solids to settle.
    - At the same time, greasy material is skimmed off.
    - The result of primary treatment is clear effluent with a very high biological oxygen demand.
    - Solids removed are landfilled.
    - Some facilities use coagulating agents such as alum to aid the settling in the lagoon. This can reduce the BOD to the point that secondary treatment may not be necessary.
- Secondary treatment
    - Reduction of biological oxygen demand by at least 90%.
    - Usually done with either a trickling filter or an activated sludge reactor.
    - A trickling filter is a bed of sand of graduated particle size, ranging from coarse gravel on top to very fine sand on the bottom.
    - The trickling filter is colonized with microbes which reduce the BOD by utilizing the carbon compounds found in the sewage.
    - The activated sludge reactor is more compact and can be enclosed in climates too cold for optimum biological activity.
    - The reactor is a large tank in which the waste water is aerated to provide sufficient oxygen for the biological removal of BOD.
    - Microbial sludge leaving the reactor is reinjected to maintain colonization of microbes.
    - Many issues involved in the disposal of sewage sludge.
- Tertiary treatment is usually focused on the removal of phosphorous.

- Usually achieved by preciptation with lime (a source of Ca^{2+}) or Al^{3+} or Fe^{3+}. The latter two form gelatinous precipitates which can further remove any microorganisms left from secondary treatment.

- Finishing usually involves a heavy dose of chlorine to kill remaining pathogens.
  - There is concern about chlorination of organics.

Sewage Sludge

- By-product of sewage treatment
  - High water content ($\sim$ 95%)
  - Difficult to handle
  - Needs to be digested to facilitate coagulation and dewatering.
  - Digestion of sludge produces methane, which can be used for co-generation of electricity or heat.
  - Dewatered sludge must be disposed of.
- Disposal of sludge may be by:
  - Landfilling
  - Incineration
  - Ocean dumping
  - Using as fertilizer.
- In using sewage sludge as fertilizer, there are a number of considerations.
  - High organic content with nitrogen and phosphorous can restore nutrients to soil in disturbed sites.
  - Allows soils to retain water.
  - Inexpensive alternative to other methods of disposal.
  - Sludge is low in nutrients compared to conventional fertilizers, so cost of handling and shipping must be kept low. In practice, this means that only local use in practical.
- Sludge may contain toxic substances.
  - Both organic and inorganic toxins can survive sewage treatment.
  - Oxidation resistant organics such as organochlorine compounds.
  - Inorganics such as As, Cd, Pb, Hg, and Zn, which usually have industrial sources.
  - Pathogens
  - Toxins may be taken up by vegetation, therefore most jurisdictions have strict limits on the use of sludge on agricultural lands.
  - Transfer of pathogens avoided by waiting periods between application of sludge and harvest.
  - Some metals are not harmful to human health, but can harm ruminants. (Cu is toxic to sheep.
- Fate of metal from sludge depends on properties of the soil.
  - Porous, gravelly soils allow transport of dissolved metals to watershed.
  - High organic muck soils facilitate biological uptake.
  - Clay soils have ion exchange properties and bind metal ions tightly, greatly reducing their mobility.
  - pH affects speciation, solubility, biological uptake, and binding to clay.

Tertiary Sewage Treatment

- Focused on one or more specific elements in the sewage, including P.
  - P is usually the limiting element in biological systems.
- P in sewage.
  - P can usually give rise to eutrophication.
  - Anthropogenic sources include fertilizer and detergent.
  - Phosphates removed by precipitation with Ca^{2+}, Al^{3+}, and Fe^{3+}.
- Tertiary treatment can also be used to further reduce BOD
  - Secondary treatment leaves a BOD of about 50 ppm O_2.
  - This is usually in the form of suspended organic matter.
  - May be removed by microstraining or coagulation.
  - Very fine (μm) stainless steel screens are used for microstraining.
  - Filter alum is used for coagulation and has the advantage of simultaneously reducing phosphate.
  - Tertiary BOD reduction is desirable so that high doses of chlorine are not required for disinfection.
- Tertiary treatment may include disinfection with chlorine
  - High doses of chlorined can lead to undesirable reactions between NH_3 and Cl_2 and between organic compounds and chlorine.
  - Production of chlorinated organics also an issue.

Other Aqueous Wastes

- The nature of the waste depends on the nature of the source.
  - Food processing
  - Pulp and paper
  - Metal finishing
  - Chemical manufacturing
  - Petroleum refining
  - Mining
  - Agriculture
  - Landfills

High Strength Aqueous Waste

- Very high BOD
- Come primarily from food processing and pulp and paper
- Contain naturally occurring orgranic compounds.
- If discharged into sewage system, can overwhelm the capacity of the sewage treatment facility.
  - Treatment required before discharge.
  - If municipalities allow discharge into sewage system, a commensurate levy is charged.

- Pulp and paper waste is primarily lignin.
    - Treated by biological degradation in vigourously aereated lagoons.
    - Alternative treatment involveds closed bioreactors (which is less vulnerable to weather variation).
    - Resulting sludge needs to be digested, dewatered, and landfilled.

Low Strength Aqueous Waste

- Oily wastes generated by petroleum refining.
    - Interfere with oxygen transport across surface of water.
    - Broken down by long treatment in aeration lagoons or bioreactors.
    - Mechanical separation is difficult, especially if emulsifiers are present.
    - Water may be removed by evaporation.
    - Oily component may be combusted or ozonized.
- Landfarming is also used.
    - Oily waste is spread out on soil and microbes are allowed to degrade it.
    - Persistent organic compounds accumulate.
    - Volatile organics evaporate.
    - Environmental impact and land costs are issues.
- Treatment with activated charcoal may be considered.