# 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 $Fe^{3+}$.

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

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

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:

$$Cl_2(g) \rightleftharpoons Cl_2(aq), \quad K_H = 8.0 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1}$$

$$Cl_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl(aq)$$

$$K_c = 4.5 \times 10^{-4} \text{ mol}^2 \text{ L}^{-2}$$

$$HOCl(aq) \rightleftharpoons H^+(aq) + OCl^-(aq)$$

$$K_c = 3.0 \times 10^{-8} \text{ mol L}^{-1}$$

  - 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 $NaClO_2$.

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

or

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

  - 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 ($\mu$m) 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, de-watered, 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.