Chapter 4

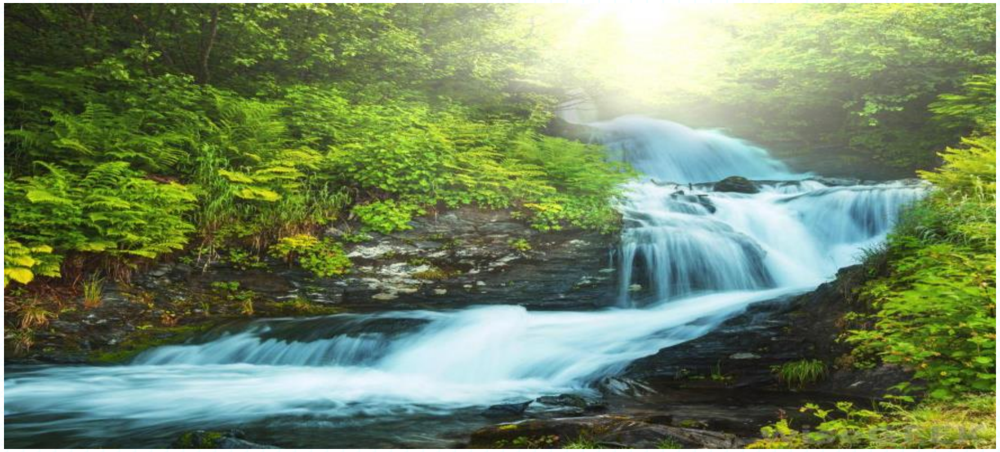
Drinking Water Quality & Treatment

SOURCES:

- Groundwater
  - Springs
  - Artesian wells

- Surface water
  - Rivers
  - Lakes
  - The sea
    (Desalination plants)

Ground- vs. Surface Water



Groundwater

- constant composition
- high mineral content
- low turbidity
- low color
- low or no D.O.
- high hardness
- high Fe, Mn

Surface water

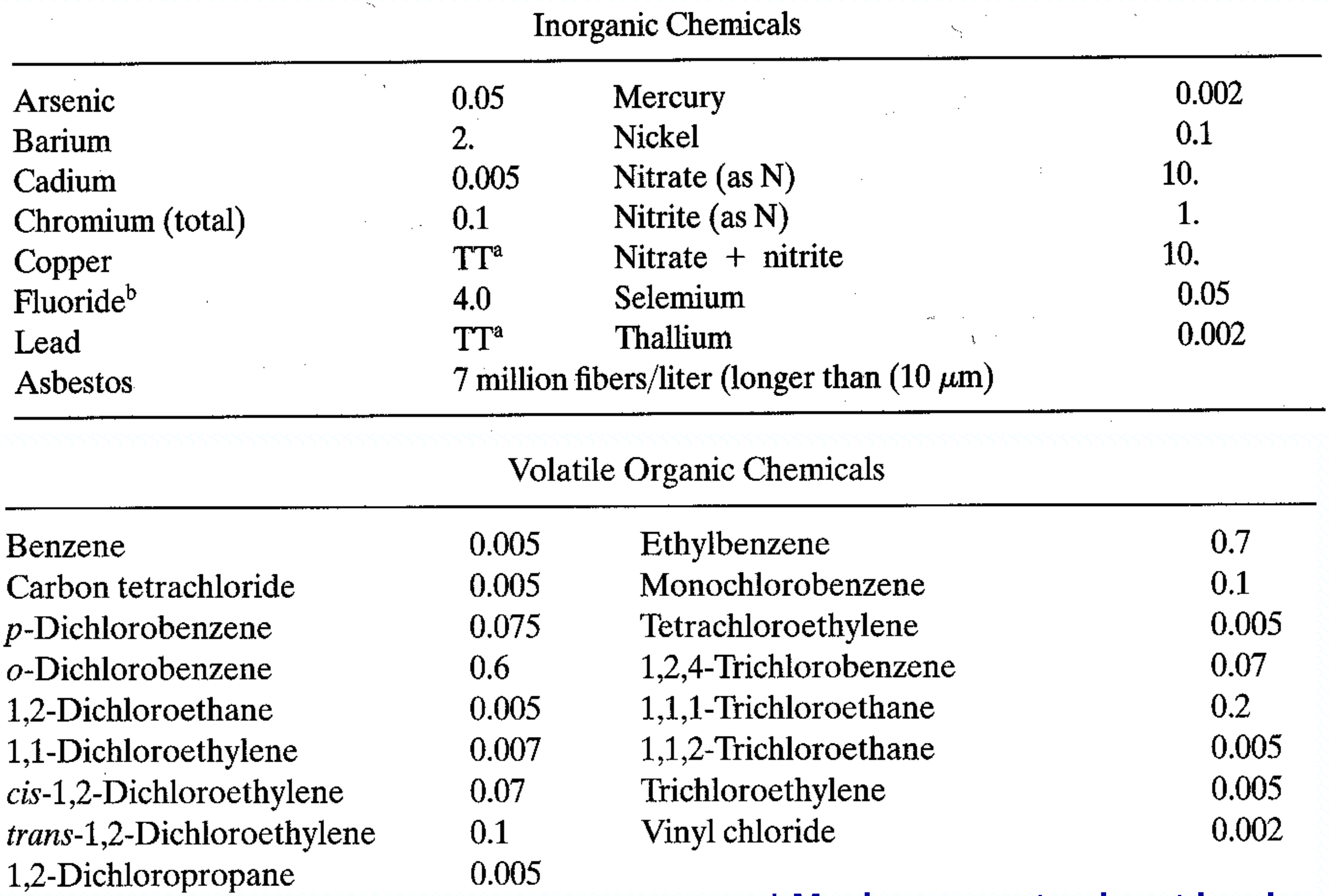
- variable composition
- low mineral content
- high turbidity
- colored
- D.O. present
- low hardness
- taste and odor

Objectives of Water Treatment

- The goal of municipal water treatment is **to provide water:**

1. With quality that meets regulatory criteria or standards to be both
    - ❖ potable
        - ○ Safe to drink – protective of human health
        - ○ Not necessarily esthetically pleasing, and
    - ❖ palatable
        - ○ esthetically pleasing
        - ○ presence of chemicals does not pose a threat to human health
        - ○ includes chloride, color, corrosivity, iron, manganese, taste and odor
2. In sufficient quantity that is continuous without interruption, and
3. At reasonable cost.

DW Standards: *Primary MCLs* (mg/L)*



Inorganic Chemicals

Arsenic	0.05	Mercury	0.002
Barium	2.	Nickel	0.1
Cadium	0.005	Nitrate (as N)	10.
Chromium (total)	0.1	Nitrite (as N)	1.
Copper	TT^a	Nitrate + nitrite	10.
Fluoride^b	4.0	Selemium	0.05
Lead	TT^a	Thallium	0.002
Asbestos	7 million fibers/liter (longer than (10 μm)		

Volatile Organic Chemicals

Benzene	0.005	Ethylbenzene	0.7
Carbon tetrachloride	0.005	Monochlorobenzene	0.1
p-Dichlorobenzene	0.075	Tetrachloroethylene	0.005
o-Dichlorobenzene	0.6	1,2,4-Trichlorobenzene	0.07
1,2-Dichloroethane	0.005	1,1,1-Trichloroethane	0.2
1,1-Dichloroethylene	0.007	1,1,2-Trichloroethane	0.005
cis-1,2-Dichloroethylene	0.07	Trichloroethylene	0.005
trans-1,2-Dichloroethylene	0.1	Vinyl chloride	0.002
1,2-Dichloropropane	0.005		

*** Maximum contaminant levels**

DW Standards: *Secondary MCLs* (mg/L)*

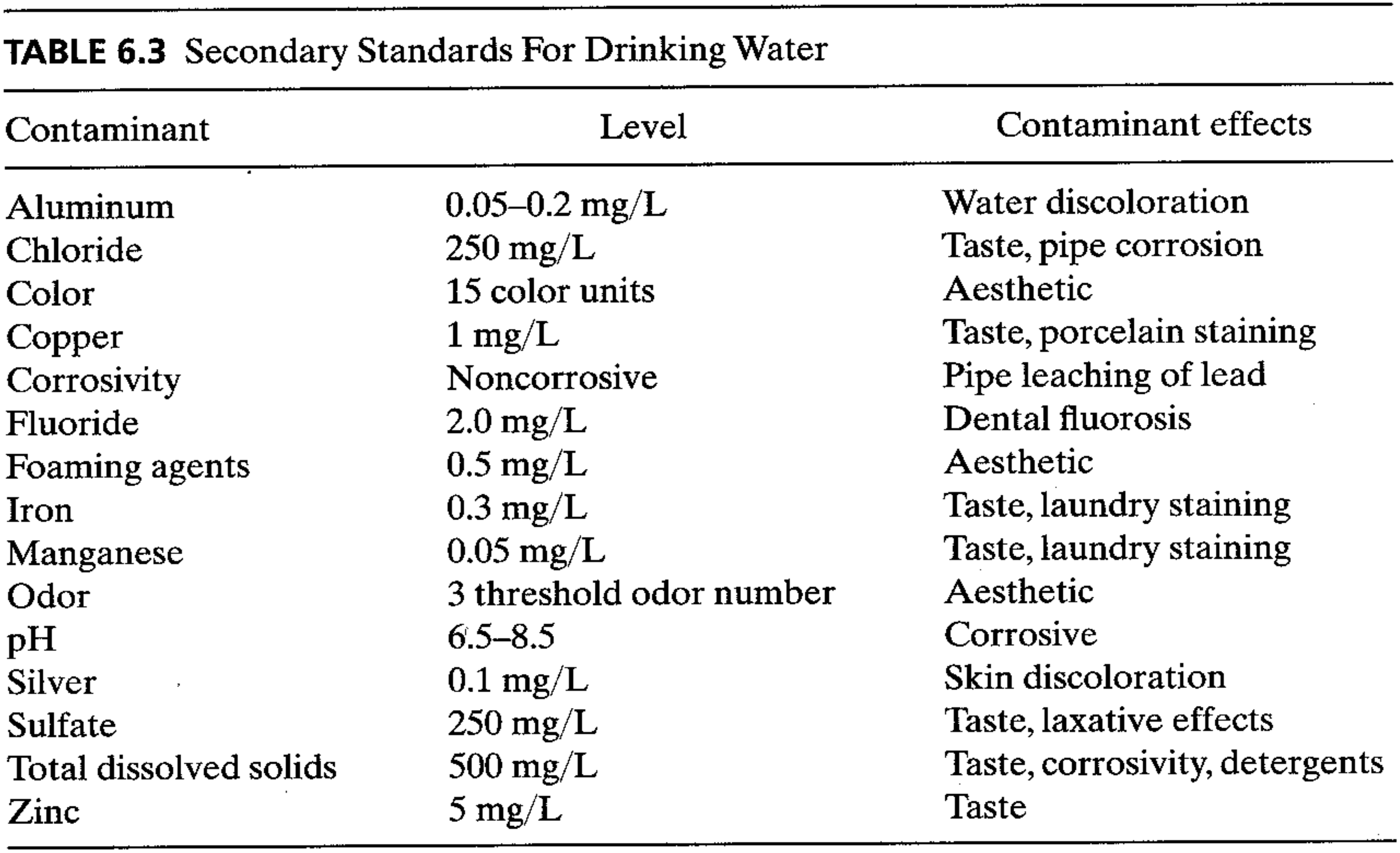


TABLE 6.3 Secondary Standards For Drinking Water

Contaminant	Level	Contaminant effects
Aluminum	0.05–0.2 mg/L	Water discoloration
Chloride	250 mg/L	Taste, pipe corrosion
Color	15 color units	Aesthetic
Copper	1 mg/L	Taste, porcelain staining
Corrosivity	Noncorrosive	Pipe leaching of lead
Fluoride	2.0 mg/L	Dental fluorosis
Foaming agents	0.5 mg/L	Aesthetic
Iron	0.3 mg/L	Taste, laundry staining
Manganese	0.05 mg/L	Taste, laundry staining
Odor	3 threshold odor number	Aesthetic
pH	6.5–8.5	Corrosive
Silver	0.1 mg/L	Skin discoloration
Sulfate	250 mg/L	Taste, laxative effects
Total dissolved solids	500 mg/L	Taste, corrosivity, detergents
Zinc	5 mg/L	Taste

*** Maximum contaminant levels**

Water Quality

- Defined in relation to intended use
  - Drinking water,
  - irrigation,
  - power generation, etc.

- Water Quality Parameters:
  - A. Physical (Aesthetic or Acceptability),
  - B. Chemical,
  - C. Radioactive,
  - D. Microbiological.

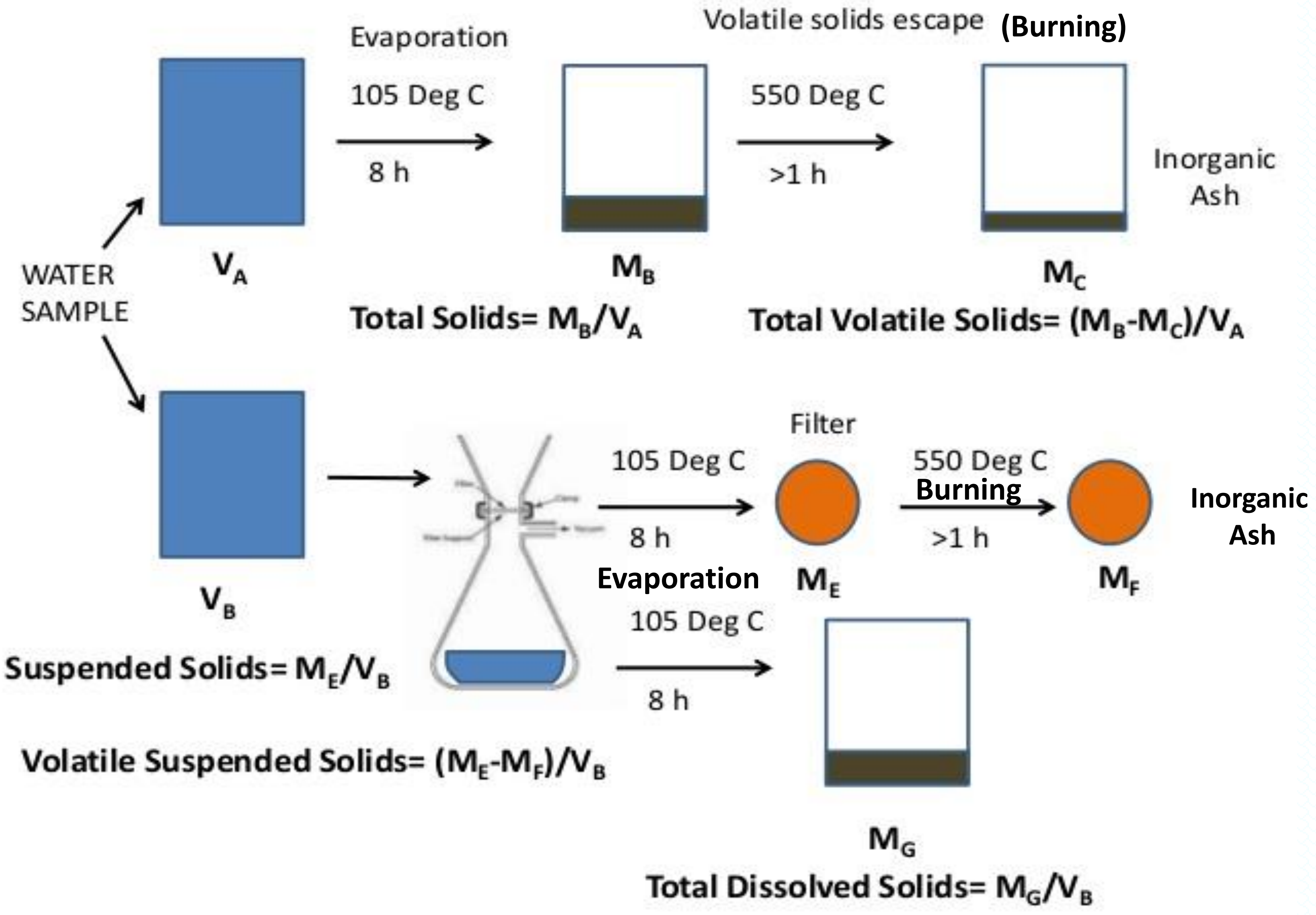
A. Physical Parameters

1. Suspended solids (big particles)
2. Turbidity (tiny particles)
3. Odor and Taste
4. Color
5. Temperature.

1. Suspended solids (big particles)

- Organic and inorganic particles in water are generally termed *suspended solids (TSS).*
- Imhoff cones are used to measure for settleable solids, which are larger than TSS.
- TSS are measured by filtering a water sample, drying and weighing the filter paper.

TS, TVS, TSS, VSS, TDS



WATER SAMPLE

V_A

Evaporation

105 Deg C

8 h

M_B

Total Solids= M_B/V_A

Volatile solids escape **(Burning)**

550 Deg C

>1 h

M_C

Inorganic Ash

Total Volatile Solids= $(M_B-M_C)/V_A$

V_B

Suspended Solids= M_E/V_B

Filter

105 Deg C

8 h

M_E

550 Deg C

Burning

>1 h

M_F

Inorganic Ash

Volatile Suspended Solids= $(M_E-M_F)/V_B$

Evaporation

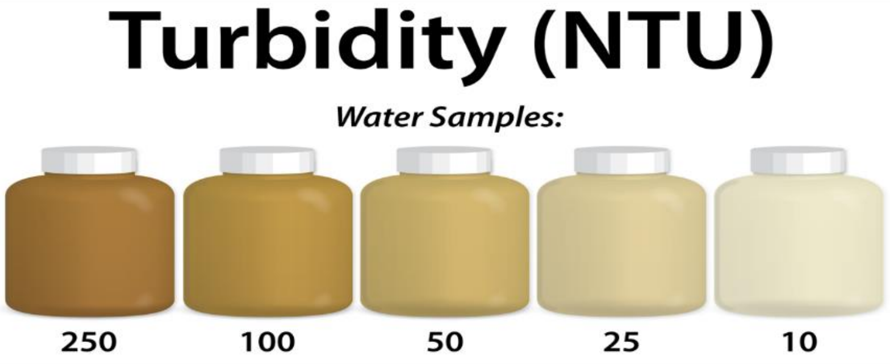
105 Deg C

8 h

M_G

Total Dissolved Solids= M_G/V_B

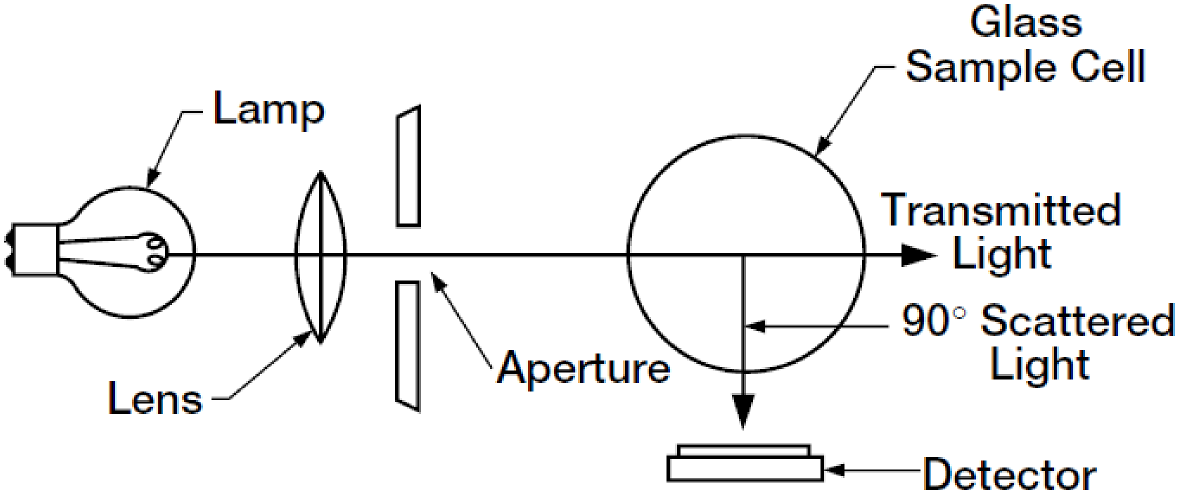
2. Turbidity



1. Used to assess the clarity of water
2. Due to *colloids* : particles that do not settle readily
3. When colloidal matter accumulates, light is scattered and the water appeared *turbid.*
4. Substances that cause turbidity include:
   - clay, silt,
   - tiny fragments of organic matter, and
   - microscopic organisms (e.g. bacteria, algae)

Turbidity measurement:

- ❑ measured in units that relate the clarity of the water sample to that of standardized suspension of silica (SiO2).
- ❑ The interference in the passage of light caused by a suspension of 1 mg/l of silica is equivalent to one **turbidity units** (TU).
- ❑ Measurement: Nephelometers (NTU).



3. Odor

1. A physical characteristics of drinking water that is important for *aesthetic reasons.*
2. It may be caused by dissolved or suspended colloidal particles of *organic nature.*
3. It is measured by human panel or electronic nose (olfactory device) expressed in terms of a threshold odor number (TON).

TON: It is the ratio by which the sample has to be diluted for the odor to become virtually unnoticeable.

Example: 50 ml is diluted to vol. of 200 ml.

The dilution # equals 200/50 = 4 = TON

3. Taste

1. Taste is an aesthetic water quality parameter.
2. Caused by presence of organic and / or inorganic substances:

- Organics cause both odor & Taste problems.
- Inorganics (e.g. soil components) are usually odorless and *may* be responsible for taste.

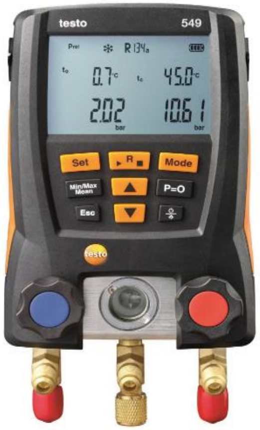
Odor & Taste :

most commonly caused by:

algae, decomposed organic matter, and dissolved gases.

4. Color

- is a physical characteristics of drinking water that are important for esthetic reasons.
- It may be caused by dissolved or suspended colloidal particles.
- One color unit is equivalent to the color produced by a 1 mg/L solution of platinum (Pt).



5. Temperature

- **Warm water tastes flat. Cooling suppresses odors and tastes and makes water more palatable.**
- **Temperature also effects the chlorination and purification of water.**
- **Disinfection takes longer when water is colder**
- **At lower T, purification capacity is reduced with reverse osmosis treatment equipment.**
- **Water having physical characteristics exceeding the limits or making it less palatable should not, as a general rule, be used for drinking.**

B. Chemical Parameters

Total dissolved solids:

- Alkalinity
- Hardness
- Fluoride
- Metal ions
- Organics
- Nutrients

ANALYSIS:

- *Gross: alkalinity, hardness.*
- *Specific ions:* Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, $NO3^{-}$, *pH* (H^{+} *or* OH^{-})

Dissolved CO_2, pH, alkalinity, hardness

- All four parameters are interrelated
- Air is source of CO_2 (180-300 ppm by volume before industrial revolution; 380 ppm at present)
- Aerobic plant and animal respiration also produces CO_2
- CO_2 is more soluble in water than O_2. In seawater, dissolved CO_2 levels range from 67 to 111 mg/L
- CO_2 influences the carbonate system in water as follows:

<u>Carbon dioxide dissolves in water and produces carbonic acid</u>

$CO_2 + H_2O = H_2CO_3$

<u>Carbonic acid dissociates producing H^+</u>

$H_2CO_3 = HCO_3^- + H^+$

$HCO_3^- = CO_3^{2-} + H^+$

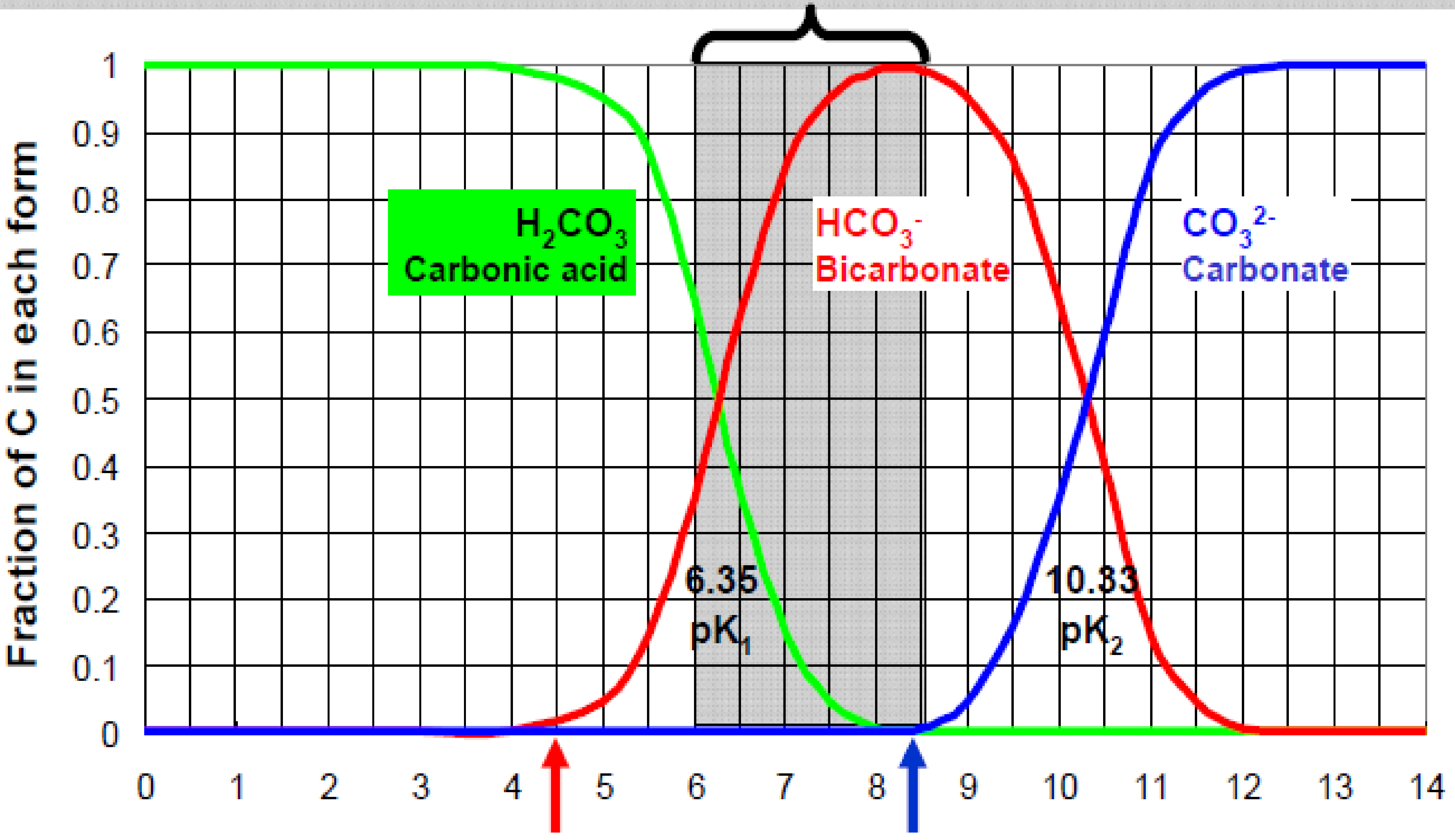
- Increased H^+ can lower the pH of water (normally 7.5-8.4 in seawater and 6.0-8.5 in freshwater)
- The ability of water to absorb H^+ ions (anions) without a change in pH is known as its alkalinity.
- In freshwater, **alkalinity** typically is due to the presence of excess **carbonate anion** (from the weathering of silicate or carbonate rocks) that when hydrolyzed produces OH^- (and neutralizes H^+) as follows:

<u>Hydrolysis of carbonate and carbonate produces OH^-</u>

$CO_3^{2-} + H_2O = HCO_3^- + OH^-$

$HCO_3^- + H_2O = H_2CO_3 + OH^-$

Common range pH in natural waters

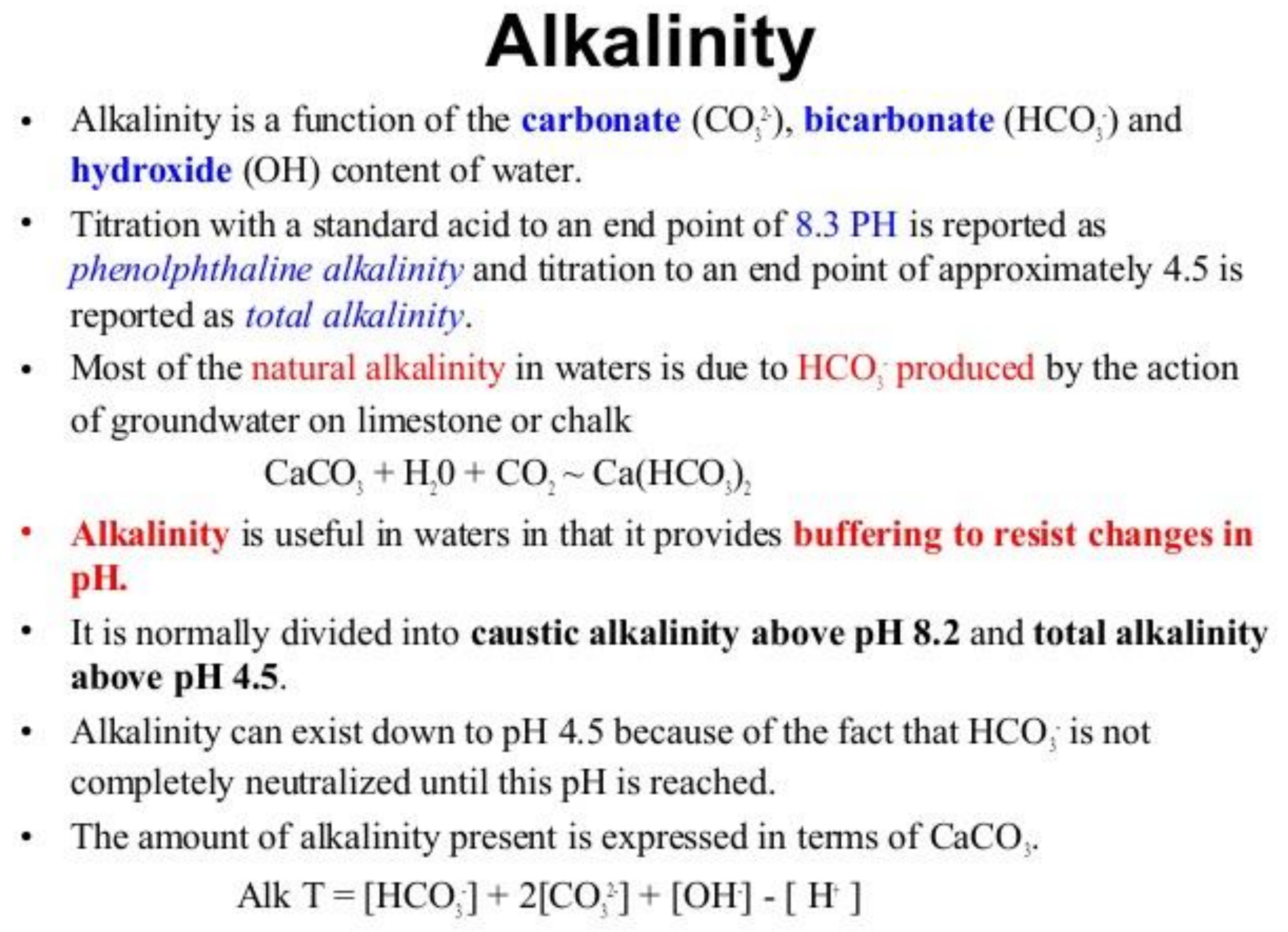


$pH < \sim 4.5$ all HCO_3^- is gone

$pH < \sim 8.3$ all CO_3^{2-} is gone

In most natural waters, bicarbonate is the dominant carbonate species

Chemical Parameters



Alkalinity

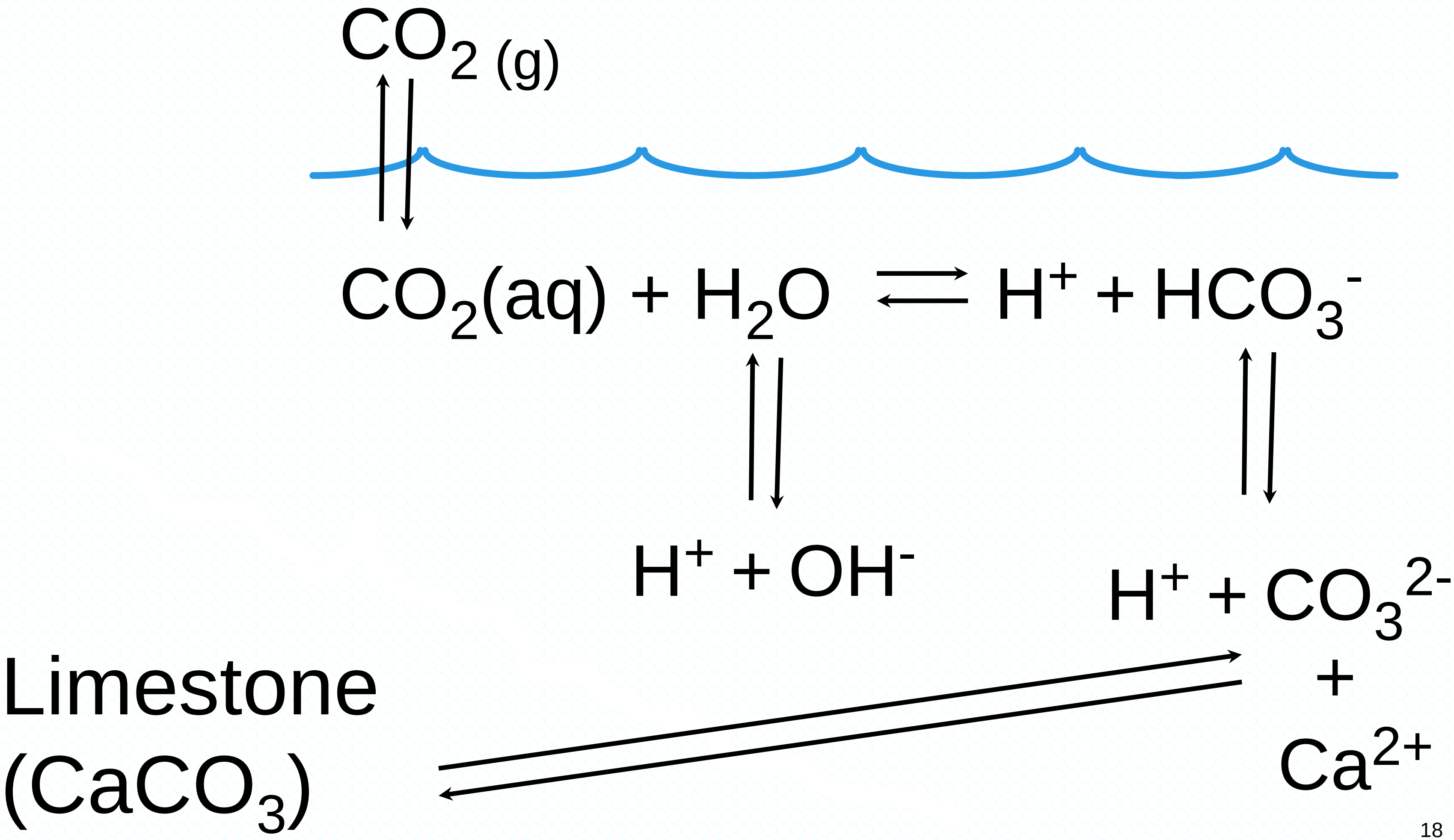
- Alkalinity is a function of the **carbonate** (CO_3^{2-}), **bicarbonate** (HCO_3^-) and **hydroxide** (OH) content of water.
- Titration with a standard acid to an end point of 8.3 PH is reported as *phenolphthaline alkalinity* and titration to an end point of approximately 4.5 is reported as *total alkalinity*.
- Most of the natural alkalinity in waters is due to HCO_3^- produced by the action of groundwater on limestone or chalk

$$CaCO_3 + H_20 + CO_2 \sim Ca(HCO_3)_2$$

- **Alkalinity** is useful in waters in that it provides **buffering to resist changes in pH.**
- It is normally divided into **caustic alkalinity above pH 8.2** and **total alkalinity above pH 4.5**.
- Alkalinity can exist down to pH 4.5 because of the fact that HCO_3^- is not completely neutralized until this pH is reached.
- The amount of alkalinity present is expressed in terms of $CaCO_3$.

$$Alk\ T = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [\ H^+\ ]$$

Alkalinity: CO_3^{2-} ,HCO_3^- , OH^-



$CO_{2\,(g)}$

$CO_2(aq) + H_2O \rightleftharpoons H^+ + HCO_3^-$

$H^+ + OH^-$

$H^+ + CO_3^{2-}$

$+$

Ca^{2+}

Limestone

($CaCO_3$)

Hardness

- Multivalent cations, particularly magnesium and calcium, causes the hardness.
- These ions are easily precipitated and form scales especially in heat transfer equipment and a problem arise up.
- Correlated with TDS (as part of it), they represent total concentration of Ca and Mg, and is reported in equivalent CaCO3 (mg/L)
- Other ions (Fe2+, Al3+) may also contribute to hardness.

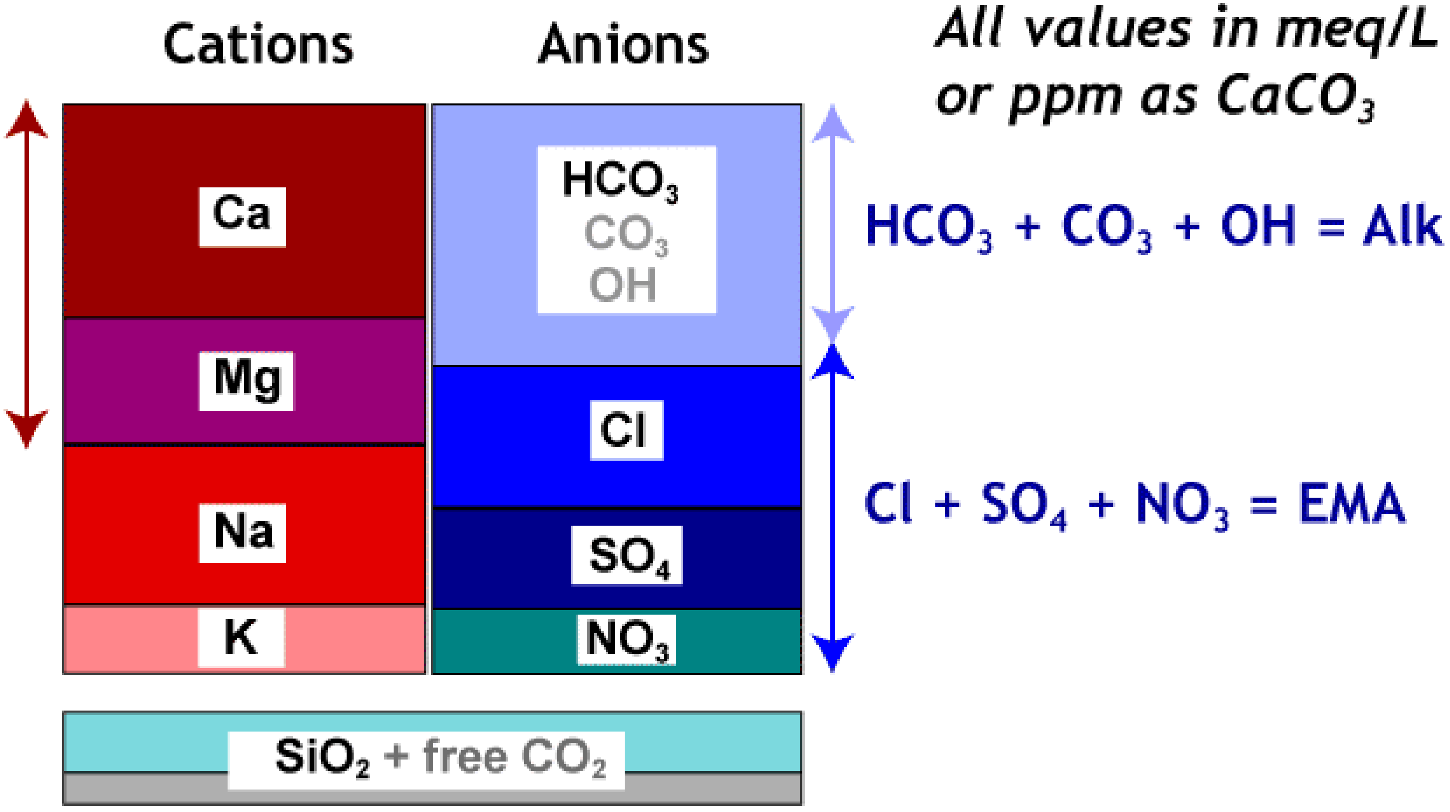
Hard water problems:

- leaves solid deposits in boilers, hot water pipes, heaters, …) and
- They also react with soap and detergents requiring more soap or detergent and form a difficult–to-remove scum
  - Advantage: hard water is less corrosive than soft water.

$$\boxed{Hardness, eq/m^3 = (Ca^{+2}) + (Mg^{+2})}$$

Chemical Parameters

Hardness



All values in meq/L or ppm as $CaCO_3$

$HCO_3 + CO_3 + OH = Alk$

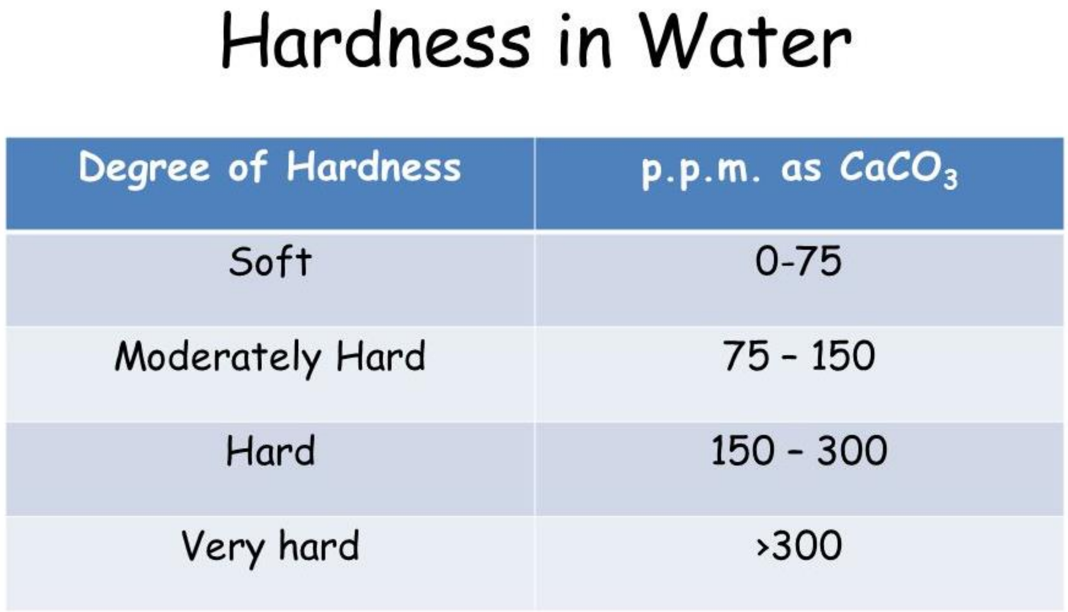
$Cl + SO_4 + NO_3 = EMA$

$\sum$cations = $\sum$anions

The analysis must be BALANCED

EMA: Equivalent Mineral Acidity

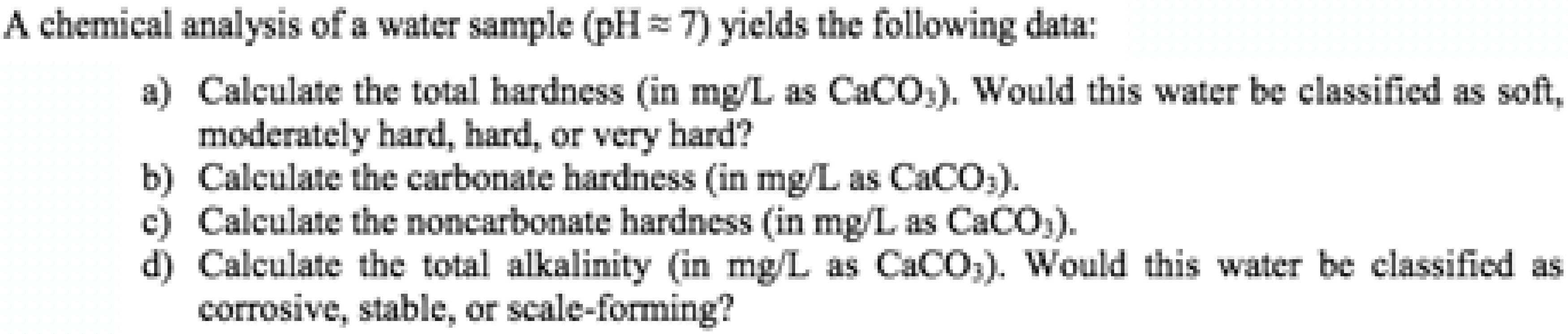
Chemical Parameters



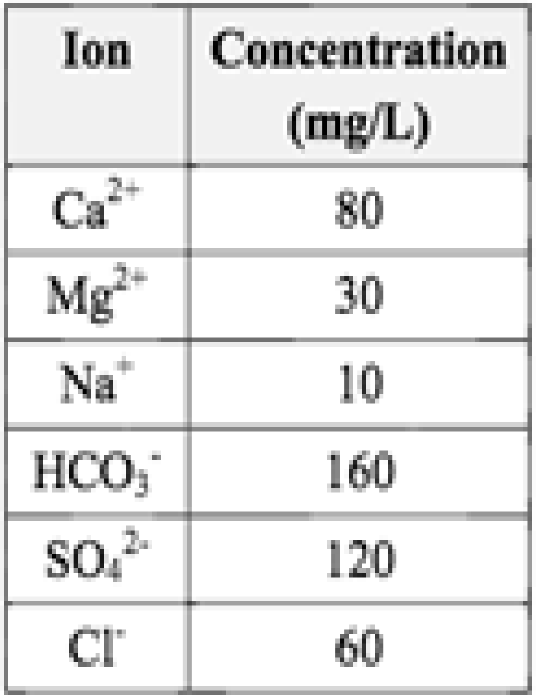
Hardness in Water

Degree of Hardness	p.p.m. as $CaCO_3$
Soft	0-75
Moderately Hard	75 - 150
Hard	150 - 300
Very hard	>300

Exercise



A chemical analysis of a water sample (pH ≈ 7) yields the following data:

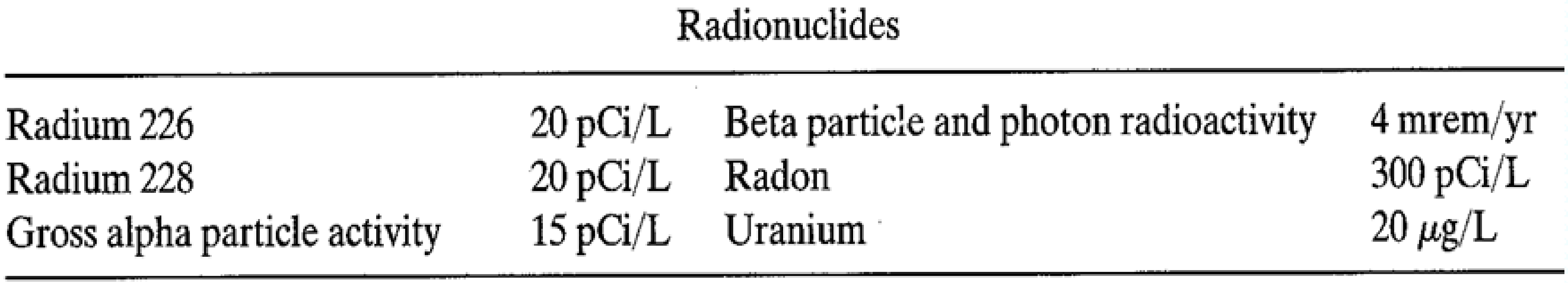


Ion	Concentration (mg/L)
Ca^{2+}	80
Mg^{2+}	30
Na^{+}	10
HCO_3^{-}	160
SO_4^{2-}	120
Cl^{-}	60

a) Calculate the total hardness (in mg/L as $CaCO_3$). Would this water be classified as soft, moderately hard, hard, or very hard?
b) Calculate the carbonate hardness (in mg/L as $CaCO_3$).
c) Calculate the noncarbonate hardness (in mg/L as $CaCO_3$).
d) Calculate the total alkalinity (in mg/L as $CaCO_3$). Would this water be classified as corrosive, stable, or scale-forming?

C. Radioactive Parameters

(Primary MCLs)



Radionuclides

Radium 226	20 pCi/L	Beta particle and photon radioactivity	4 mrem/yr
Radium 228	20 pCi/L	Radon	300 pCi/L
Gross alpha particle activity	15 pCi/L	Uranium	20 μg/L

1 Ci = decay rate of 1 g Radium-226
(decay of 3.7x10 10 atoms/s)

D. Microbiological Parameters

Figure 22-3a Environment, 5/e

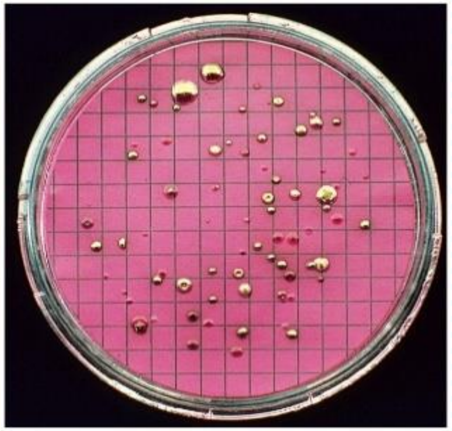


Figure 22-3b Environment, 5/e

Microorganisms:

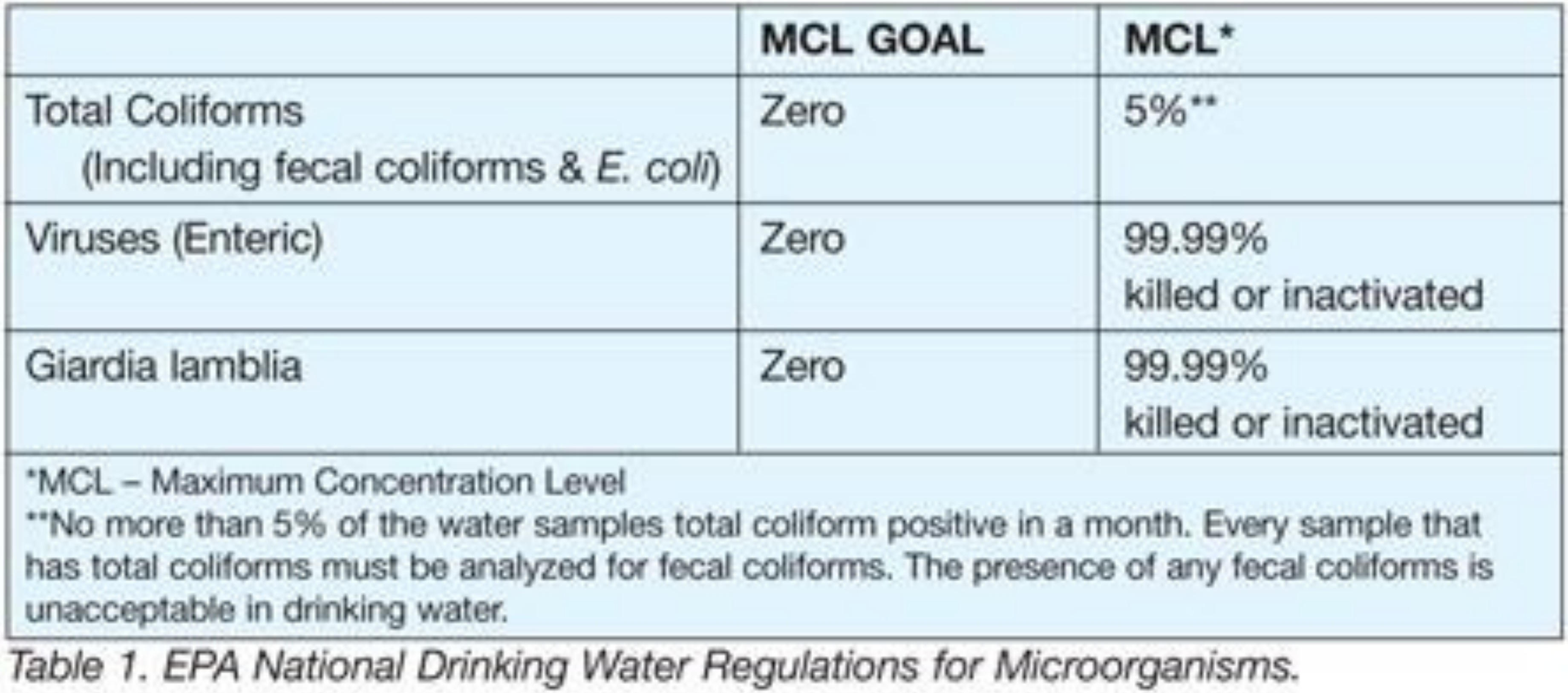
1. Bacteria
2. Protozoa
3. Parasitic Worms
4. Viruses
5. Algae
6. Fungi
7. Pollution indicators: Coliform bacteria

- *E. coli* used as an indicator of water quality: normal inhabitant of intestines of humans and many animals.
  - Fecal Indicator Bacteria (FIB)
  - Indicator of presence of fecal matter
  - Total coliforms are typically reported

A ***fecal coliform bacteria*** test is used to indicate the likely presence of disease-causing bacteria in water.Results reported as Most Probable Number (MPN) per 100 mL

- Incubation at moderate temperature (35^{o}C) for 48 hr

Microbiological Parameters



	MCL GOAL	**MCL***
Total Coliforms (Including fecal coliforms & *E. coli*)	Zero	5%**
Viruses (Enteric)	Zero	99.99% killed or inactivated
Giardia lamblia	Zero	99.99% killed or inactivated

*MCL – Maximum Concentration Level

**No more than 5% of the water samples total coliform positive in a month. Every sample that has total coliforms must be analyzed for fecal coliforms. The presence of any fecal coliforms is unacceptable in drinking water.

Table 1. EPA National Drinking Water Regulations for Microorganisms.

Drinking Water Treatment

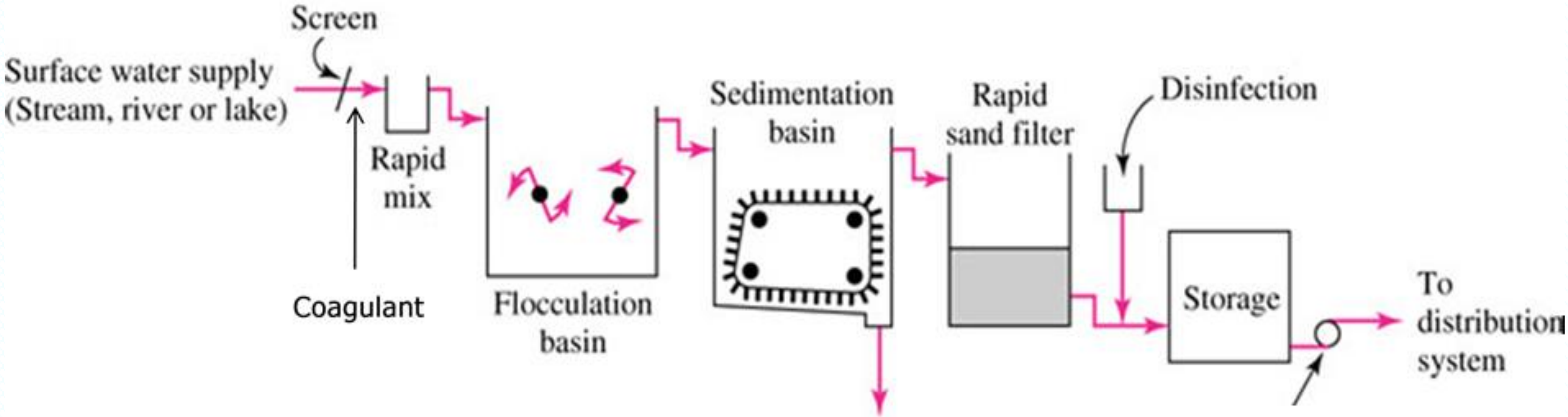
I. Surface Water Treatment

- Primary objectives are to
  1) Remove suspended material (turbidity) and color
  2) Eliminate pathogenic organisms
- Treatment technologies largely based on <u>coagulation and flocculation</u>

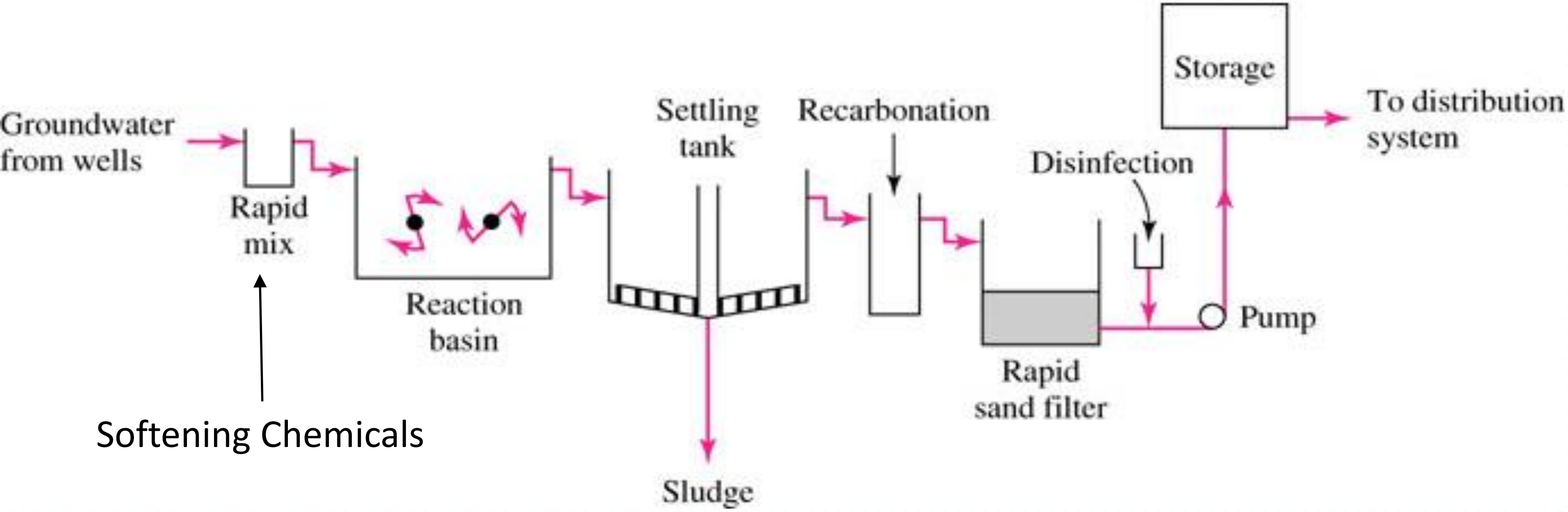
II. Groundwater Treatment

- Primary objectives are to
  1) Remove hardness and other minerals
  2) Eliminate pathogenic organisms
- Treatment technologies largely based on <u>chemical precipitation</u>

Surface Water Treatment



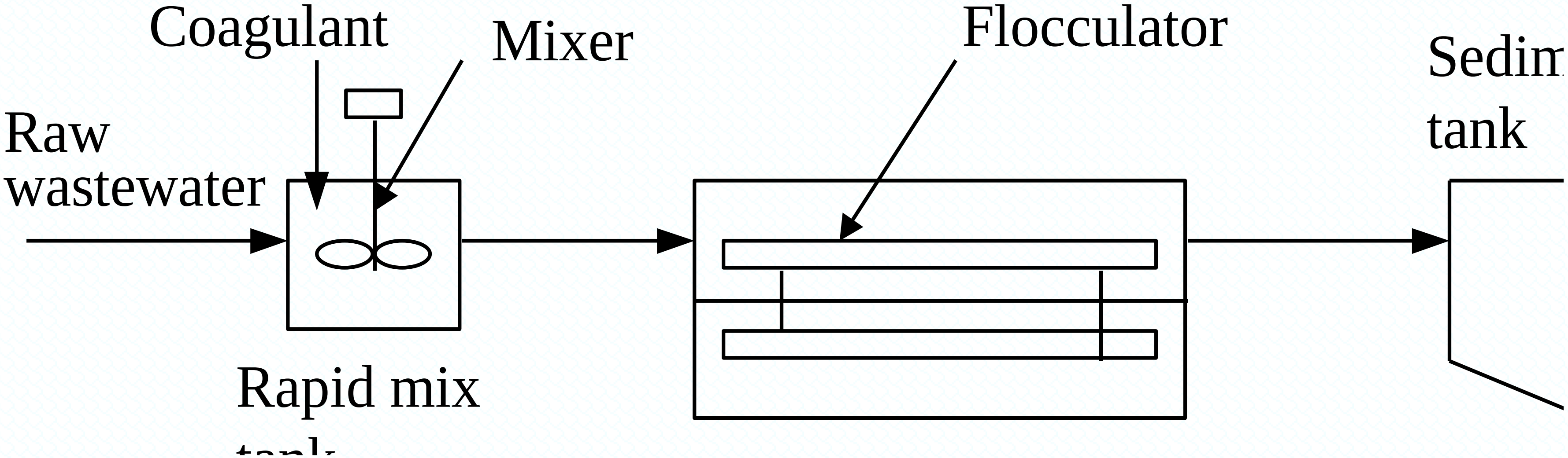
Groundwater Water Treatment



Surface Water Treatment

Removal of turbidity:

1. rapid mix tank
2. flocculation tanks
3. settling (sedimentation) tanks



Coagulant

Mixer

Flocculator

Raw wastewater

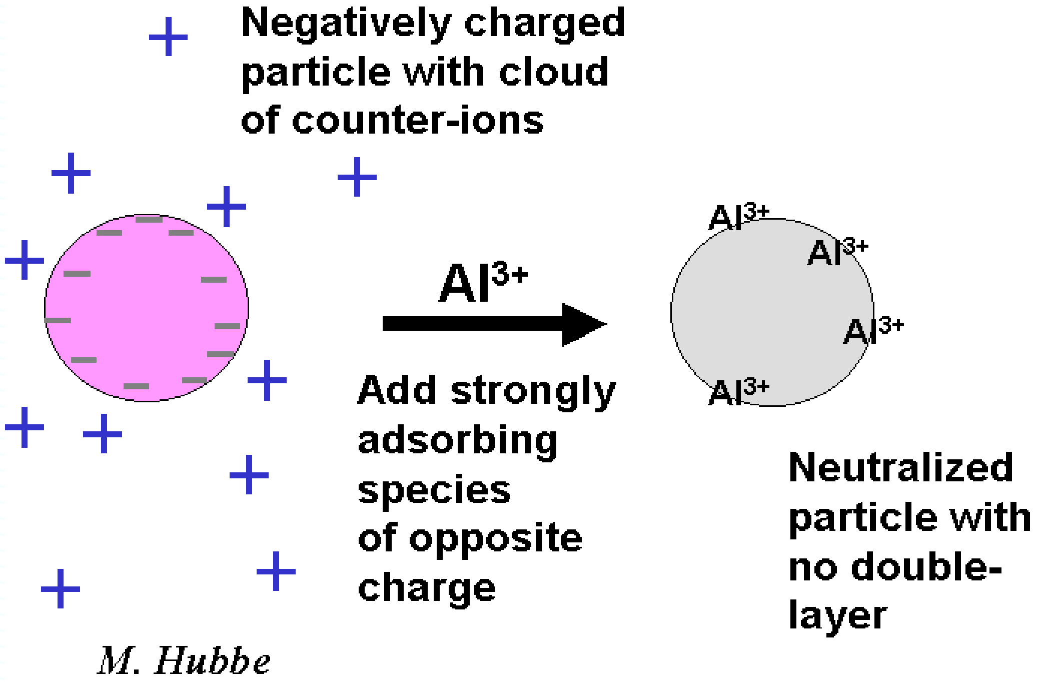
Sedim tank

Rapid mix tank

Coagulation

Addition and rapid mixing of a coagulant with the water to:

1. neutralize surface charges
2. collapse the surface layer around the particles
3. allow the particles to come together and agglomerate
4. allow formation of floc that can readily settle



Common Coagulants

- **Alum**
  - Hydrated aluminum sulfate [$Al_2(SO_4)_3 \cdot 14H_2O$]
  - Alum, when added to water, will be hydrolyzed to form gelatinous hydroxide [$Al(OH)_3$] precipitate.
    - This will carry suspended solids as it settles by gravity.
- **Anhydrous Fe^{3+} (as $FeCl_3$)**
  - Forms $Fe(OH)_3(s)$ in a wide range of pH 4-11
- **Anhydrous Fe^{2+} ($FeSO_4 \cdot 7H_2O$)**
  - Must be oxidized to Fe^{3+} first at pH higher than 8.5

Good Coagulants

1. Non-toxic and relatively inexpensive
2. Insoluble in neutral pH range
3. Do not need high concentrations of metals left in treated water
4. Trivalent cations are most effective

Aluminum Chemistry

- With alum addition, what happens to water pH?

$$\mathbf{Al_2(SO4)_3.14\ H_2O \Leftrightarrow 2Al(OH)_3\downarrow + 8H_2O + 3H_2SO_4}$$

- 1 mole of alum consumes 6 moles of bicarbonate (HCO_3^-)

$$\mathbf{Al_2(SO4)_3.14\ H_2O + 6HCO_3^- \Leftrightarrow 2Al(OH)_3\downarrow + 6CO_2 + 14H_2O + 3SO_4^{-2}}$$

- If alkalinity is not enough, pH will be reduced greatly

$$\mathbf{Al_2(SO_4)_3.14H_2O \leftrightarrow 2Al(OH)_3\downarrow\ + 3H_2SO_4\ ^- + 14H_2O}$$

- Lime or sodium carbonate may be needed to neutralize the acid.

(Optimum pH: 5.5 – 6.5)

Iron Chemistry

$$FeCl_3 + 3HCO_3^- \Leftrightarrow Fe(OH)_3\downarrow + 3CO_2 + 3Cl^-$$

- With iron salt addition, what happens to water pH:
  (Wider pH range of: 4 – 9; Best pH range of 4.5 – 5.5)
- 1 mole of $FeCl_3$ consumes 3 moles of bicarbonate (HCO_3^-)
- If alkalinity is not enough, pH will reduce greatly due to hydrochloric acid formation.
- Lime or sodium carbonate may be needed to neutralize the acid. Lime is the cheapest.

Flocculation is

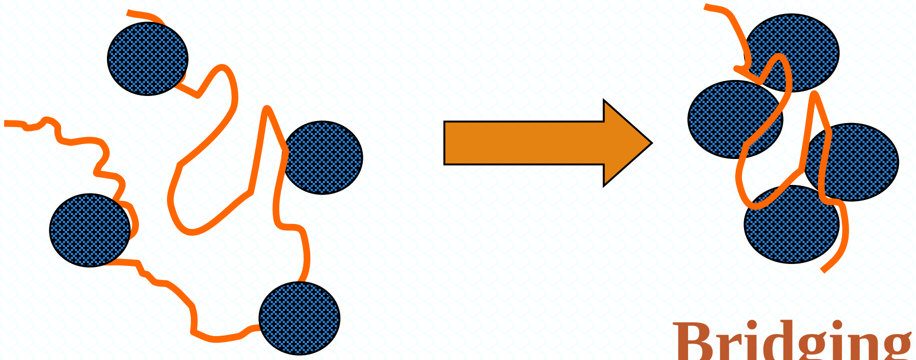
- The process that leads to the formation of large voluminous flocs, which are loosely held aggregates of coagulated particles and solids.

- The slow mixing is one of the fundamentals necessary to promote collisions between particles to form flocs.

Flocculation Chemical (Coagulant-Aids):

1. inorganic: polyaluminum chloride
2. Synthetic Polymers (Polyelectrolytes): polyacrylic acid, polyacrylamide derivatives
3. naturally occurring flocculants: Starch, cellulose derivatives, proteinaceous materials, and gums composed of polysaccharides chitosan, sodium alginate

Flocculation



Bridging effect

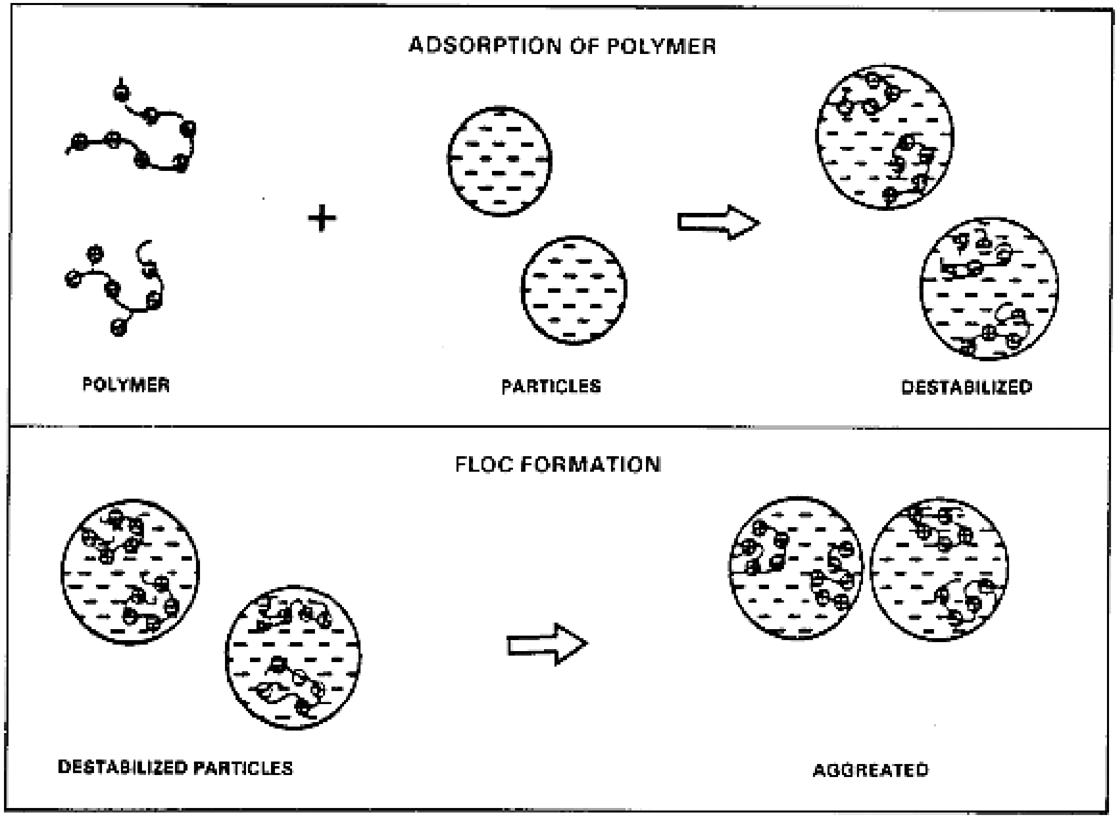
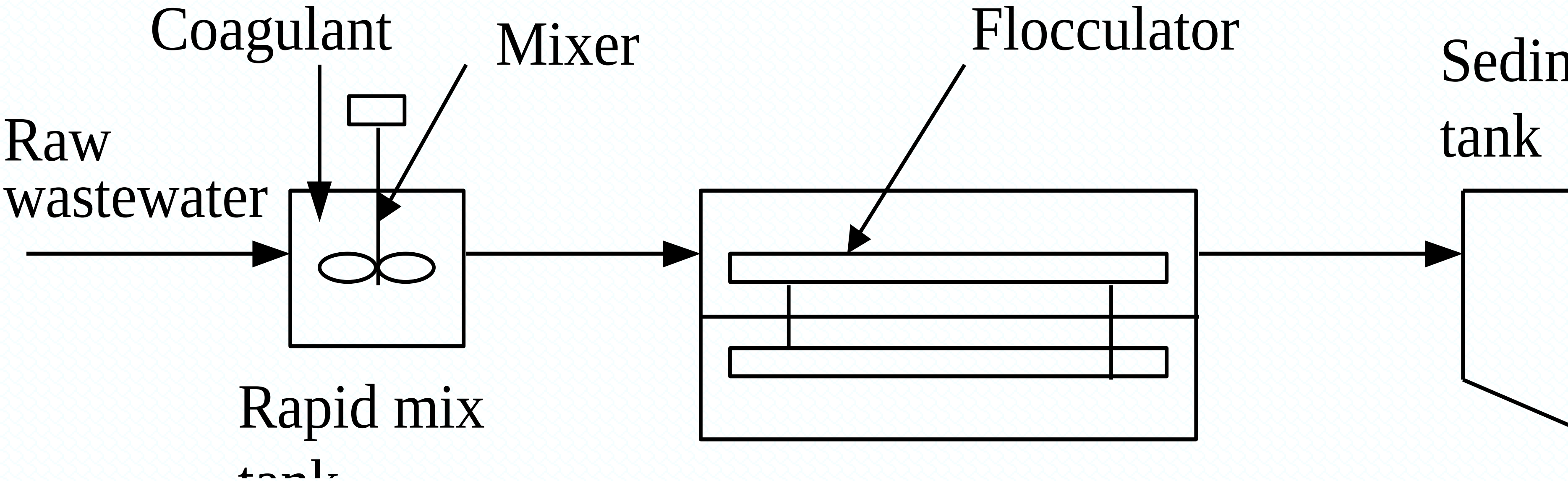


Figure 1-2. Floc formation process

The recoil of the macromolecules helps to draw several particles together.

Mixing & Flocculation Units


Coagulant

Mixer

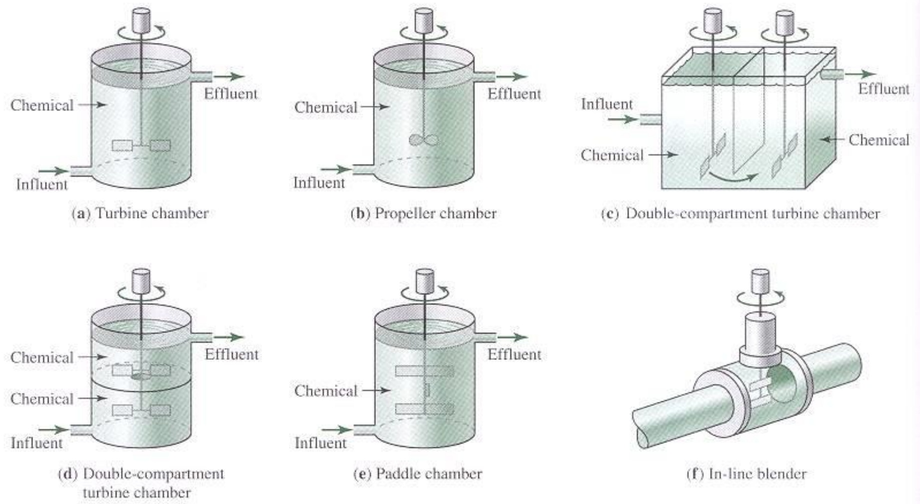
Flocculator

Sedin

tank

Raw wastewater

Rapid mix tank



(a) Turbine chamber

(b) Propeller chamber

(c) Double-compartment turbine chamber

(d) Double-compartment turbine chamber

(e) Paddle chamber

(f) In-line blender

FIGURE 9–7

Paddle flocculator.

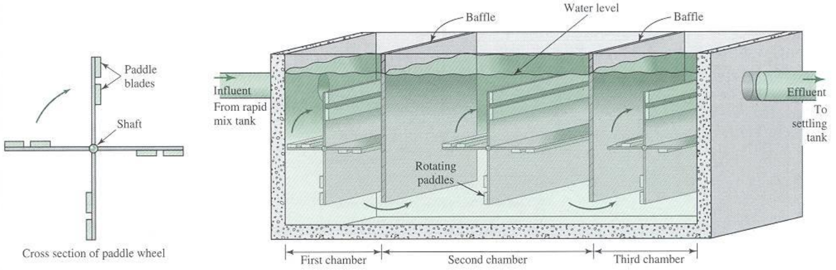
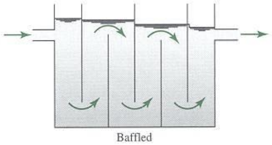


FIGURE 9–8

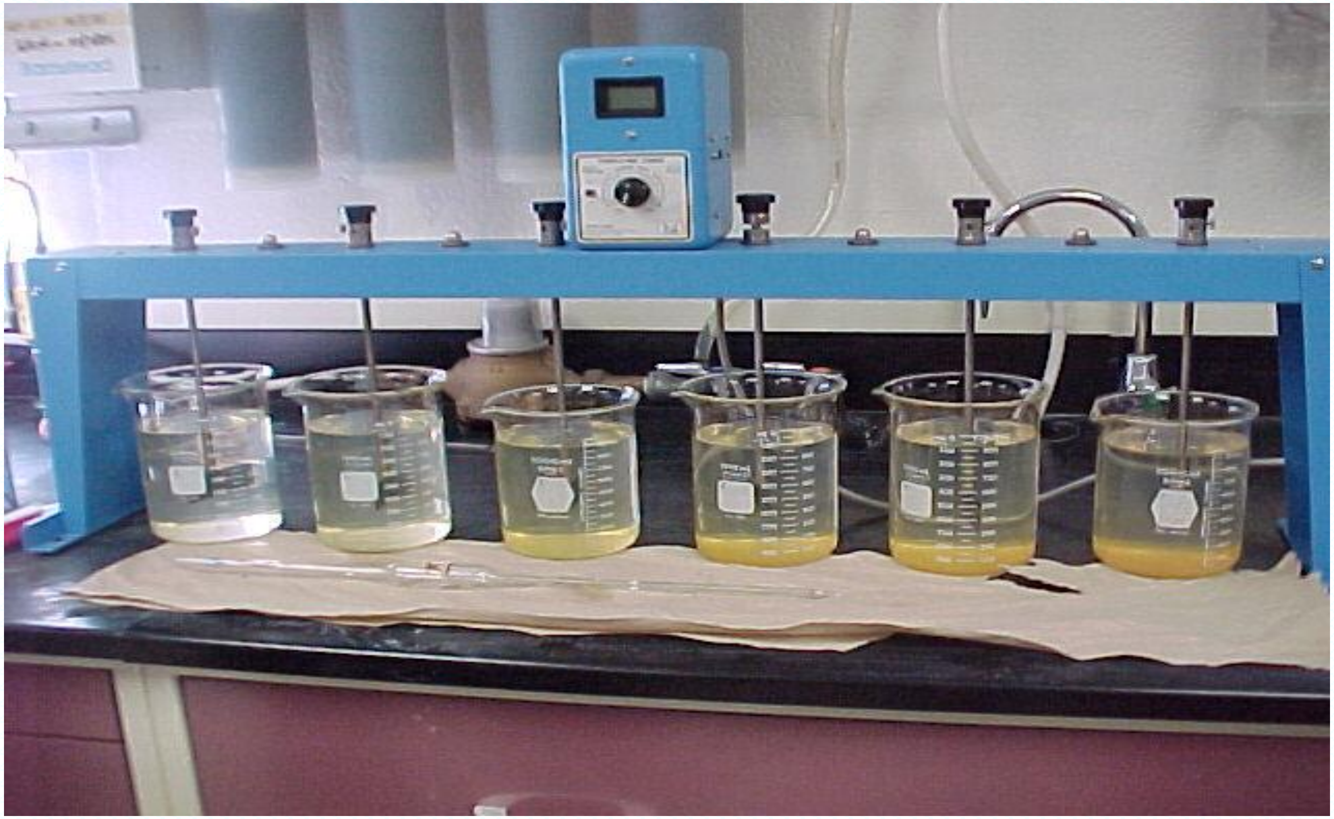
Baffled chamber flocculator.



Jar Test

Determining Coagulant Dose & Optimum pH

- ❑ The jar test – a laboratory procedure to determine the optimum p
and the optimum coagulant dose
- ❑ A jar test simulates the coagulation and flocculation processes



Jar Test set-up

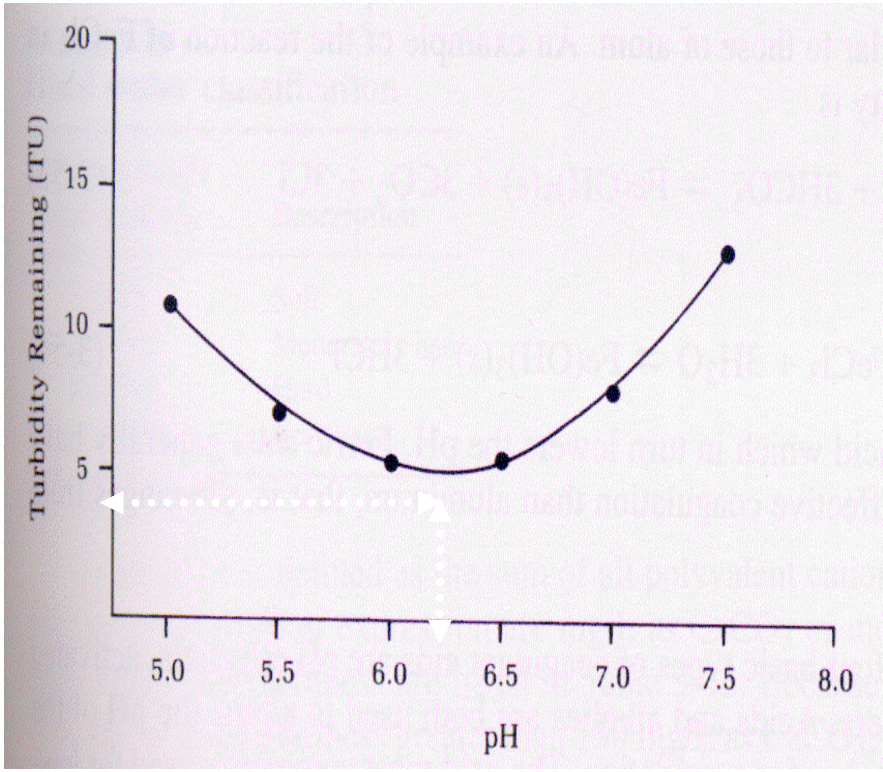
determining optimum pH

- Fill the jars with raw water sample – usually 6 jars
- Adjust pH while mixing using H_2SO_4 or NaOH (pH: 5.0; 5.5; 6.0; 6.5; 7.0; 7.5)
- Add same dose of selected coagulant to each jar (Coagulant dose: 5 or 10 mg/L)
- **Rapid mix** each jar at 100 to 150 rpm for 1 minute.
- **Reduce the stirring speed** to 25 to 30 rpm and continue mixing for 15 to 20 min.
- Turn off mixers and allow flocs to **settle** for 30 to 45 mins
- Measure the final residual turbidity in each jar
- Plot residual turbidity against pH.

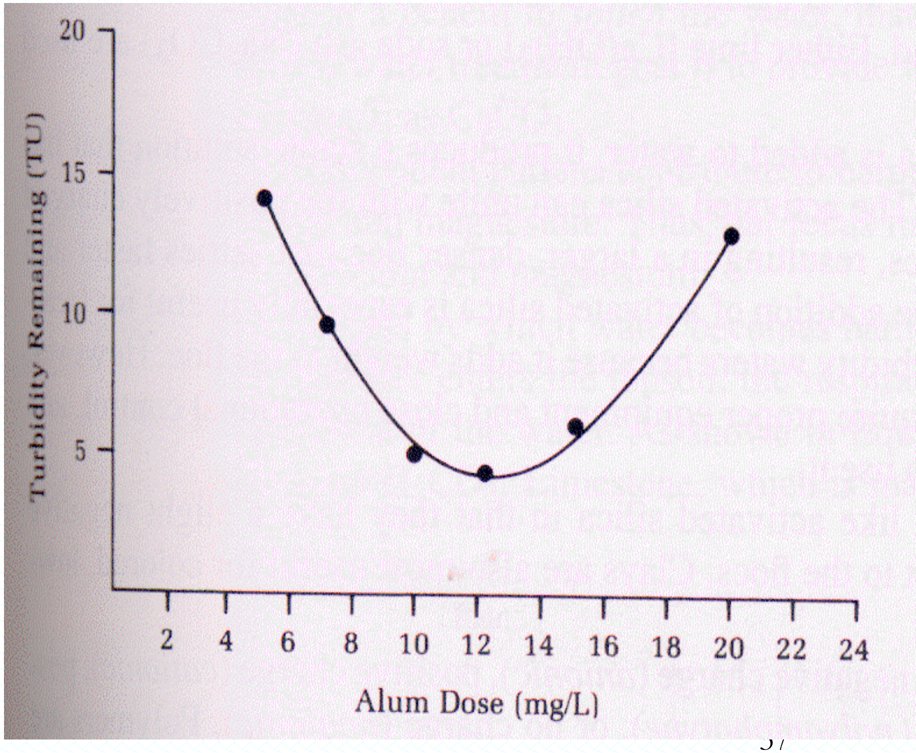
Optimum coagulant dose

- Repeat all the previous steps
- This time adjust pH of all jars at optimum found from first test while mixing using H_2SO_4 or NaOH
- Add different doses of the selected coagulant (alum or iron) to each jar (Coagulant dose: 5; 7; 10; 12; 15; 20 mg/L)
- Rapid mix each jar at 100 to 150 rpm for 1 minute.
- **Reduce the stirring speed** to 25 to 30 rpm for 15 to 20 mins
- Turn off the mixers and allow flocs to **settle** for 30 to 45 mins
- Measure the final residual turbidity in each jar
- Plot residual turbidity against coagulant dose.

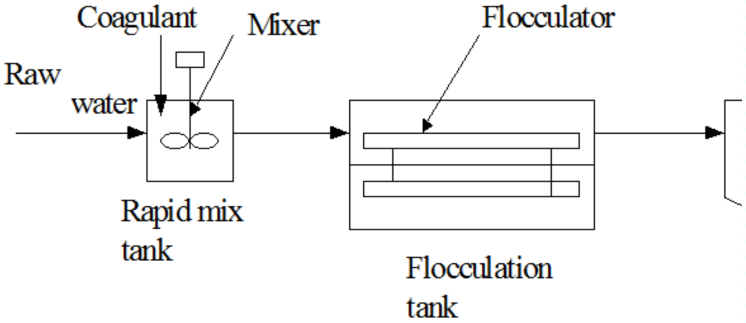
Jar Tests – optimum pH



Jar Tests – optimum dose



Coagulation / Flocculation Calculations



Measuring the degree of mixing

Velocity gradient: $\boxed{G = \sqrt{P/(\mu V)}}$

P = power input (W)
V = volume of basin(cu. m)
μ = fluid viscosity (Pa.s)

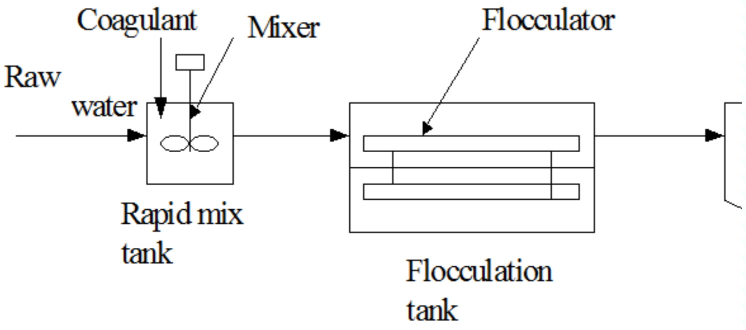
G values for rapid mixing

Detention time, t_0 (s)	G (s^{-1})
0.5	3500
10 – 20	1000
20 – 30	900
30 – 40	800
Longer	700

Gt_0 values for flocculation

Type	G (s^{-1})	Gt_0
Low turbidity, color removal coagulation	20 – 70	60,000 – 200,000
High turbidity, solids removal coagulation	50 - 150	90,000 – 180,000
Softening, 10% solids	130 - 200	200,000 – 250,000
Softening, 39% solids	150 - 300	390,000 – 400,000

Coagulation / Flocculation Calculations



Designing a flocculator

Power input:

$$\boxed{P = \frac{K_T (n)^3 (D_i)^5 \rho}{g}}$$

K_T = impeller constant
n = rotational speed (rpm)
Di = impeller dia (m)

Values of impeller constant K_T

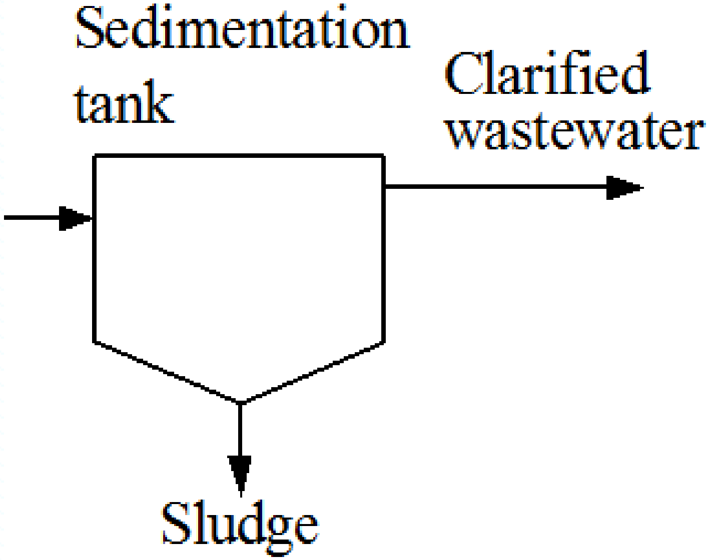
Type of impeller	K_T
Propeller, pitch of 1, 3 blades	0.32
Propeller, pitch of 2, 3 blades	1.00
Turbine, 6 flat blades, vaned disc	6.30
Turbine, 6 curved blades	4.80
Fan turbine, 6 blades at 45°	1.65
Shrouded turbine, 6 curved blades	1.08
Shrouded turbine, with stator, no baffles	1.12

Power and rotational speed of some standard mixers

Model	n (rpm)	P (kW)
JTQ50	30, 45	0.37
JTQ75	45, 70	0.56
JTQ100	45, 110	0.75
JTQ150	45, 110	1.12
JTQ200	70, 110	1.50
JTQ300	110, 175	2.24
JTQ500	175	3.74

JWI, Inc. of Holland

2. Sedimentation:



- ☐ Flocs settle out and is scraped and vacuumed off the bed of large sedimentation tanks.
- ☐ Clarified water drains out of the top of these tanks in a giant decanting process.
- ☐ For settling tank design and details, refer to Pre-requisite course notes (particulate separation).

3. Filtration

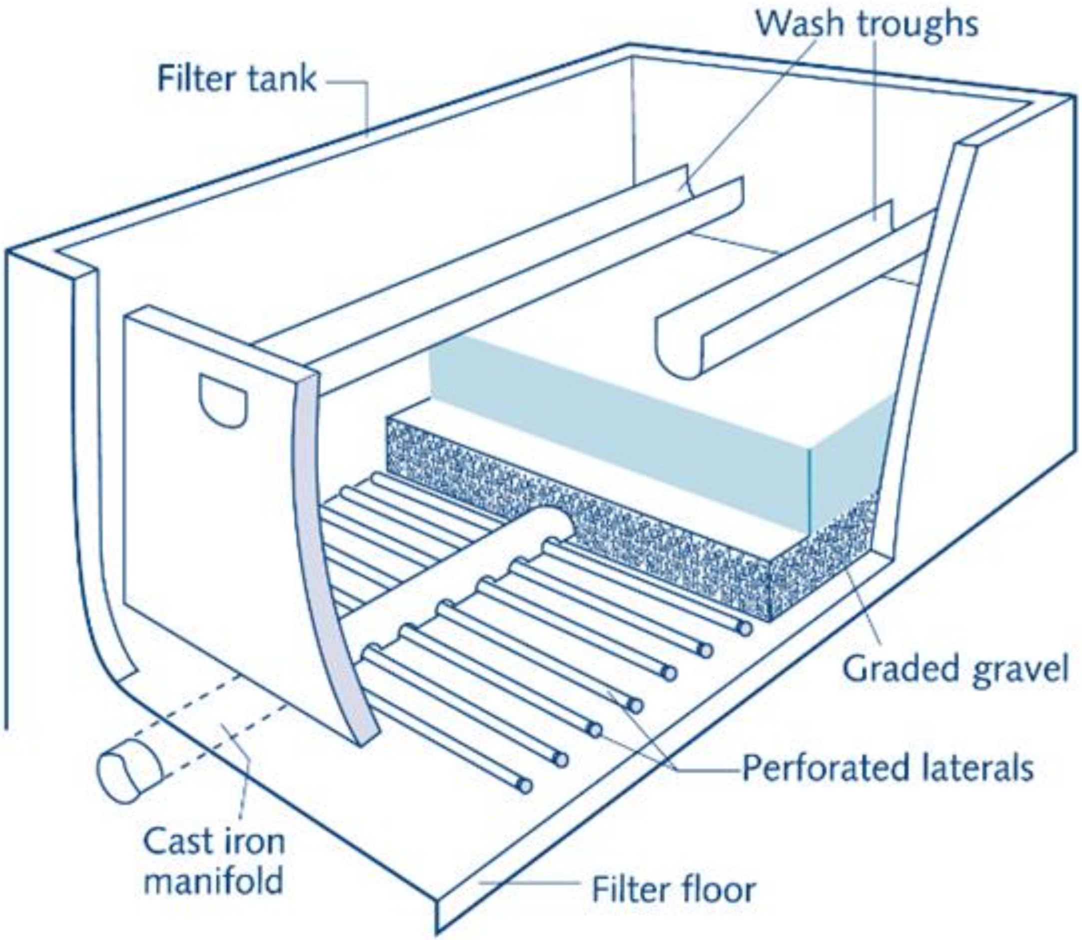
- ☐ Removal of those particles that are too small to be effectively removed during sedimentation
- ☐ Sedimentation effluent: 1 - 10 JTU &Desired effluent level: <0.3 JTU

Slow sand filters AND Rapid sand filters

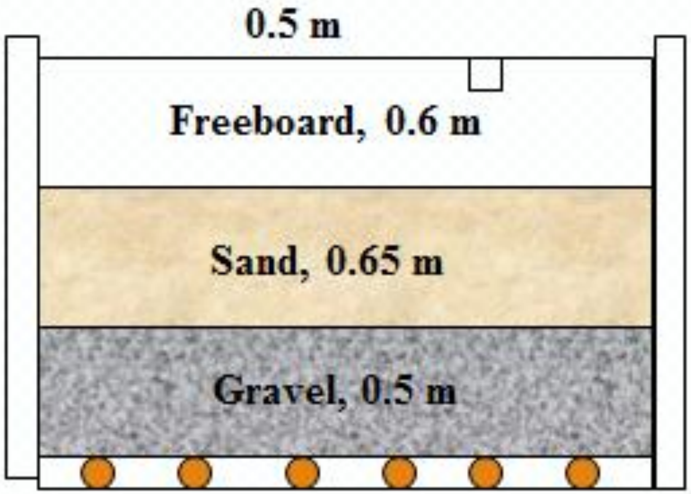
Either slow or rapid filtration (depends on size of plant / volume of water considerations).

- **Rapid-sand filters**
  - force water through a 0.45-1 m layer of sand (d_p=0.4-1.2mm) and work faster, needing a smaller area. But they need frequent back-washing
- **Slow-sand filters**
  - (d_p=0.15-0.35mm) require a much larger area but reduce bacteriological and viral levels to a greater degree. The top 1 inch must be periodically scraped off and the filter occasionally back-washed

3. Filtration



Typical Gravity Filter

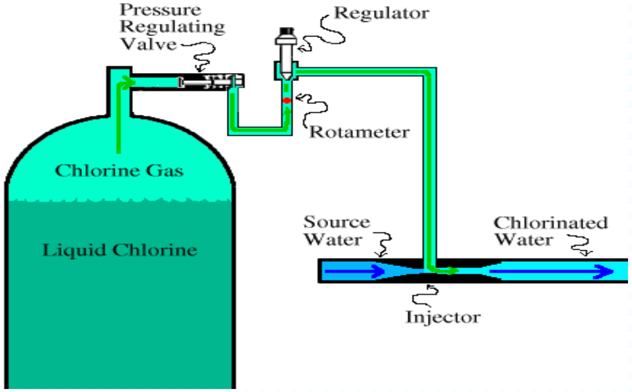


Underdrain System

4. Disinfection:

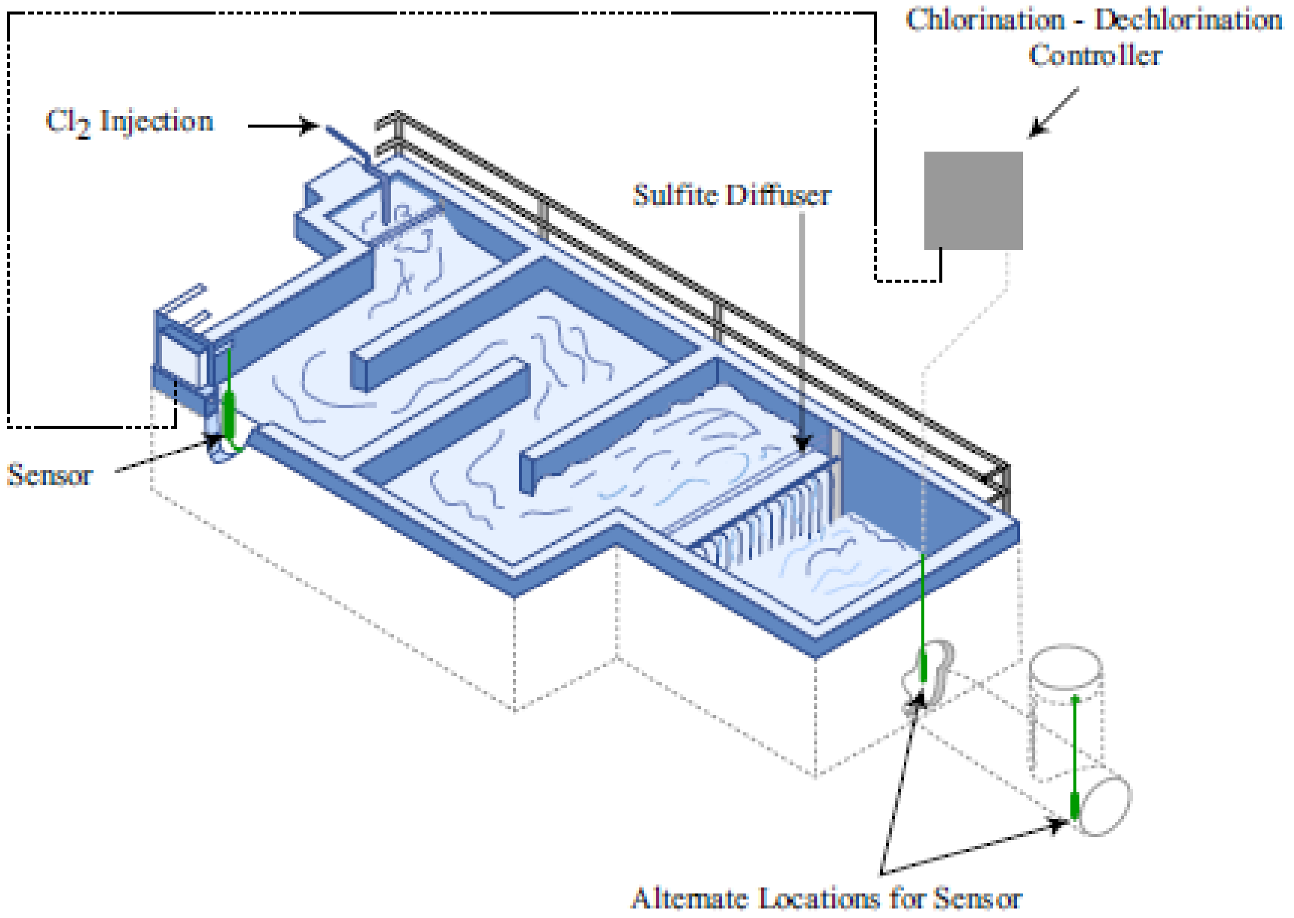
1) Disinfection is typically the last step in a water (*and waste-water*) treatment system
2) Residual disinfectant is needed in distribution system after water (*or wastewater*) treatment
3) Water completely *free of suspended sediment* is treated with a powerful oxidizing agent usually chlorine gas.
4) A residual of chlorine disinfectant is left in the water to prevent reinfection. Chlorine can form *harmful byproducts* and has suspected links to stomach cancer and miscarriages. Many agencies now residually disinfect with Chloramine.
5) In addition to disinfection, chlorine also has the following functions:
    1) taste and odor control as an oxidizing agent
    2) oxidation of Fe^{2+} and Mn^{2+} in groundwater
    3) ammonium removal in domestic waste treatment
    4) slime, biofouling control

Disinfectants



1. Gaseous Cl_2
   - Most commonly used
   - Advantage: provide residual chlorine for the protection from bacterial growth in distribution system
   - Disadvantage: The formation of disinfection by-products (trihalomethanes) presents a health risk
2. Chlorine dioxide (ClO_2):
   - No disinfection by-products such as trihalomethanes
3. $Ca(ClO)_2$: Safer than Cl_2
4. Ozone: generated on site
5. UV lamps

Chlorination System



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.

Adapted from: Binnie, C., M. Kimber, and G. Smethurst. *Basic Water Treatment*. 3rd ed. Cambridge, UK: Royal Society of Chemistry, 2002.

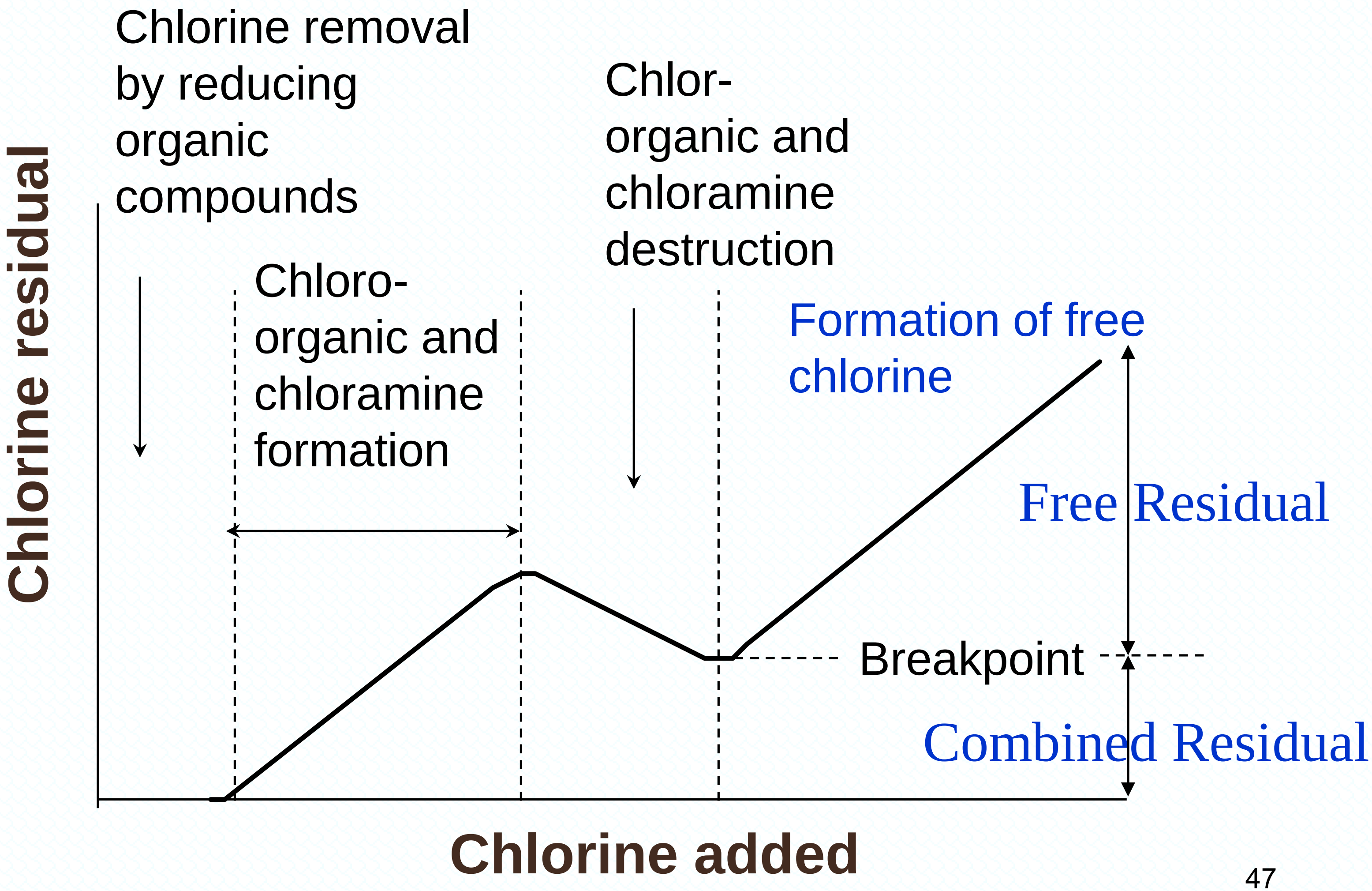
Chemistry of Chlorine in Water

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl$$

1. HOCl is a weak acid ($HOCl = H^+ + OCl^-$) with Ka = 4.5×10^{-4}
2. $HOCl$ and OCl^- are <u>free available chlorine</u> which are very effective in killing bacteria
3. Small amount of ammonium (NH_4^+) in water is *desired to form* Chloramines: NH_2Cl, $NHCl_2$, NCl_3
   - ➢ Chloramines (<u>combined available chlorine</u>) are weaker disinfectants than free available chlorine but are desired <u>residual chlorine</u> to be retained in water distribution system
4. Excessive amount of ammonium (NH_4^+) in water is <u>undesirable</u> because it consume excess demand of Cl_2

Chlorine Demand or Breakpoint Chlorination

Equil. Among species
Solution chemistry & Conditions



Chlorine removal by reducing organic compounds

Chloro-organic and chloramine formation

Chlor-organic and chloramine destruction

Formation of free chlorine

Free Residual

Breakpoint

Combined Residual

Disinfection CT* Concept

CT = 0.9847 C **0.1758 pH2.7519 temp**- 0.1467**

Inactivation is a function of Contact time, Concentration, pH, and Temperature.

To get credit for 99.9% inactivation of *Gardia microorganism*:

Contact Time (min)

chlorine (mg/L)	pH 6.5		pH 7.5	
	2°C	**10°C**	**2°C**	**10°C**
0.5	300	178	430	254
1.0	159	94	228	134

***CT: Concentration** (mg/L) **x Contact Time** (minutes)

Groundwater Softening

- Hardness is an important water quality parameter in determining the suitability of water for domestic and industrial uses
  1. Hard waters require considerable amounts of soap to produce foam
  2. Hard waters produce scale in hot-water pipes, heaters and boilers;

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3\,(s) + CO_2\,(g) + H_2O$$

- Principal cations causing hardness and the major anions associated with them (in decreasing order of abundance in natural waters) are:
  - Cations: Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+}, Mn^{2+}
  - Anions: HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, SiO_3^{2-}

Carbonate and Noncarbonate Hardness

- **Total hardness =**

  Carbonate hardness + Non-carbonate hardness

A) Carbonate hardness = temporary hardness; eliminated at elevated temperatures in boilers

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$
$$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

B) Non-carbonate hardness = permanent hardness;

can not be removed or precipitated by boiling.

Non-carbonate hardness cations are associated with **SO_4^{2-}, Cl^- and NO_3^-.**

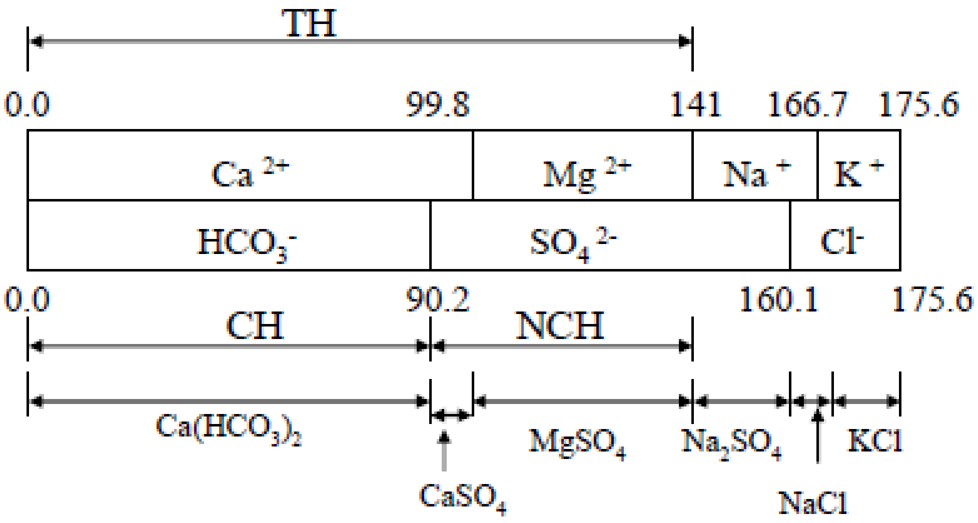
Examples

Ion	Conc. mg/L	M.W. mg/mmol	|n|	Eq. Wt. mg/meq	Conc. meq/L	Conc. mg/L as $CaCO_3$
Ca^{2+}	40.0	40.1	2	20.05	1.995	99.8
Mg^{2+}	10.0	24.3	2	12.15	.823	41.2
Na^+	11.8	23.0	1	23.0	.51	25.7
K^+	7.0	39.1	1	39.1	.179	8.95
HCO_3^-	110.0	61.0	1	61.0	1.80	90.2
SO_4^{2-}	67.2	96.1	2	48.05	1.40	69.9
Cl^-	11.0	35.5	1	35.5	.031	15.5

- A sample of water having a pH of 7.2 has the following concentrations of ions

Ca^{2+}	40 mg/L
Mg^{2+}	10 mg/L
Na^+	11.8 mg/L
K^+	7.0 mg/L
HCO_3^-	110 mg/L
SO_4^{2-}	67.2 mg/L
Cl^-	11 mg/L

- Construct a bar chart of the ions in term of mg/L $CaCO_3$
- Calculate the TH, CH, NCH, Alkalinity



Exercise:*

- Find carbonate and non-carbonate hardness as well as total hardness (in mg/L as $CaCO_3$) of water containing:

Ca^{2+} = 80 mg/L, Mg^{2+} = 30 mg/L,

Pb^{2+} = 160 mg/L, Fe^{3+} = 50 mg/L

Na^{+} = 72 mg/L, K^{+} = 6 mg/L

Cl^{-} = 100 mg/L, SO_4^{2-} = 201 mg/L,

HCO_3^{-} = 165 mg/L

pH = 7.5

**For more examples, see textbook and other Environ. Eng. References*

Water Softening Methods

1) Ion exchange 2) Reverse osmosis 3) Chemical precipitation

Chemical Softening: Ca^{2+}, $Mg^{2+} \rightarrow CaCO_3\,(s)$, $Mg(OH)_2\,(s)$

A. lime-only process: when Ca^{2+} is present primarily as "bicarbonate hardness". Mg will precipitate as $Mg(OH)_2$

B. lime-soda [$Ca(OH)_2$-Na_2CO_3] process: when bicarbonate is not present at substantial level.

Lime [$Ca(OH)_2$] Process

- Lime to remove Ca^{2+} in the form of carbonate:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$$

- Lime to remove Mg^{2+} in the form of carbonate:

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3\downarrow + 2H_2O$$

- Additional lime must be added to remove $MgCO_3$

$$MgCO_3 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + Mg(OH)_2\downarrow$$

Lime-Soda [$Ca(OH)_2$-Na_2CO_3] Process

- Mg^{2+} hardness in the form of a sulfate (or chloride) requires both lime and soda ash:

$$MgSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Mg(OH)_2\downarrow$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$$

- CO_2 in the water will also consume lime:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$$

Recarbonation

- Because of the lime that was added, the water has a pH over 11.
- Compressed carbon dioxide gas is bubbled through the water to lower pH and stop the chemical reactions of softening.
- The high pH also creates a bitter taste in the water.
- Recarbonation removes this bitterness. (Many places use liquid CO2)

$$CO_2 + H_2O \leftrightarrow H_2CO_3 + CO_3^{2-} \rightarrow 2HCO_3^-$$

REFERENCES

1. Davis, M.L. and Cornwell, D.A. Introduction to Environmental Engineering, McGraw-Hill, 5th Edition, 2013.
2. Parsons, S. and Jefferson, B. Introduction to Potable Water Treatment Processes, Wiley-Blackwell, 2006.
3. Spellman, F.R. and Drinan, J.E. The Drinking Water Handbook, 2nd Edition, CRC Press, 2012.