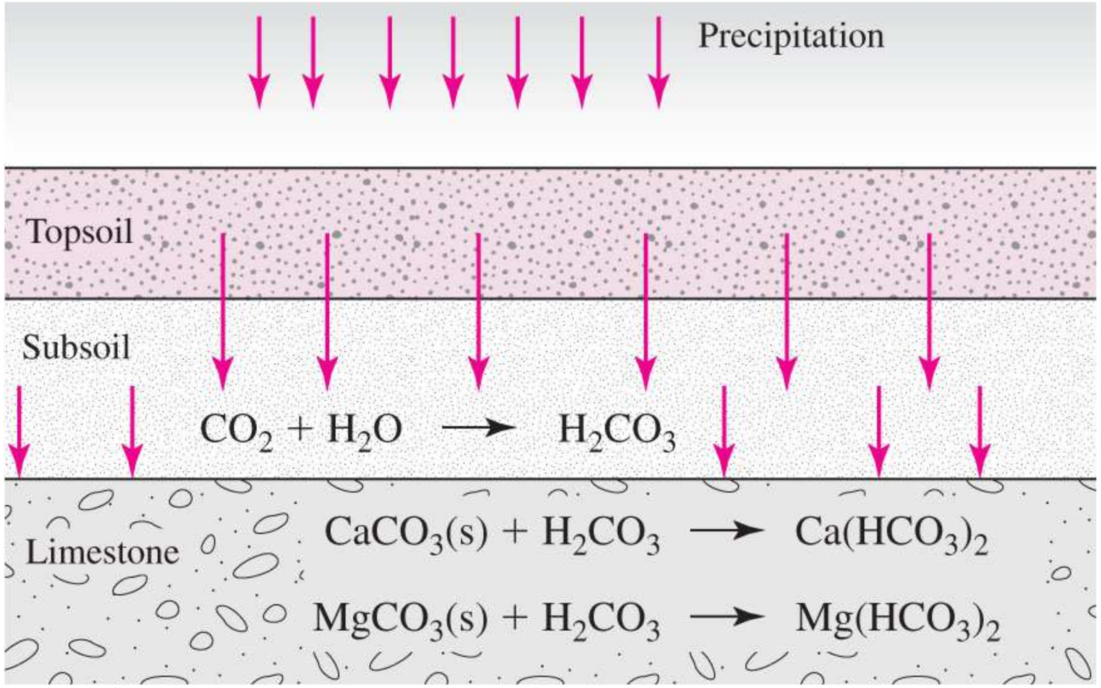
Softening

- Goal: to reduce hardness of water
- Hardness
  - The term used to characterize a water that does not lather well, causes a scum, and leaves scales
  - Caused by polyvalent cations (+2, +3, …)

http://www.watersoftenerbest.blogspot.com

http://www.proenv.com

Formation of hardness



- As rainwater infiltrates, the water gets CO_2 by the respiration of microorganisms
- Recall $CO_2 + H_2O \rightarrow H_2CO_3$
- Carbonic acid (H_2CO_3) dissolves limestone ($CaCO_3$, $MgCO_3$)
- Hardness is of concern in limestone areas

Hardness

- Total hardness (TH)
  - Technically: the sum of all polyvalent cations

$$TH = (Ca^{2+}) + (Mg^{2+}) + (Fe^{3+}) + (Fe^{2+}) + (Ba^{2+}) + \cdots$$

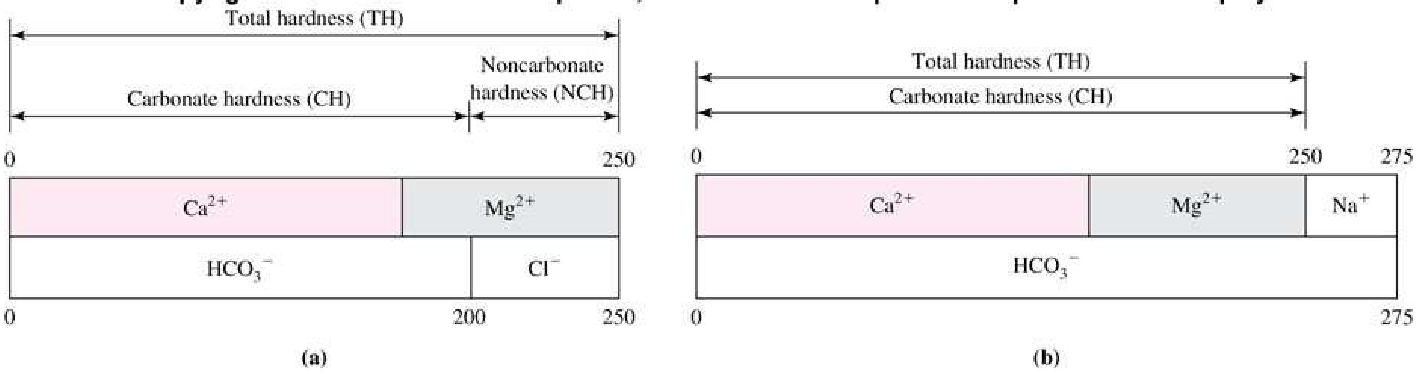
$$= \sum_{i=1}^{n} (X^{m+})_i$$

  - Practically (most of the time): the sum of Ca^{2+} and Mg^{2+}

$$TH \cong (Ca^{2+}) + (Mg^{2+})$$

Hardness

- Carbonate and noncarbonate hardness
  - Total hardness (TH) is divided into carbonate (CH) and noncarbonate (NCH) hardness (TH = CH + NCH)
  - Carbonate hardness: the maximum amount of hardness that can be associated with carbonates (HCO_3^- and CO_3^{2-})
    - When **TH > Alk** (≈ **[HCO_3^-]** + 2[CO_3^{2-}]), **CH = Alk**, NCH = TH - CH
    - When **TH ≤ Alk**, **CH = TH**, NCH = 0



Hardness

- Units
  - eq/L or meq/L
  - mg/L as $CaCO_3$ (recall alkalinity unit)
  - Unit conversion: (mg/L as $CaCO_3$) = 50 x (meq/L)

    (as $CaCO_3$ is 50 mg/meq)

Term	**Concentration range (mg/L as $CaCO_3$)**
Soft	<17.1
Slightly hard	17.1-60
Moderately hard	60-120
Hard	120-180
Very hard	>180

Hardness

Q: A sample of water having a pH of 7.0 has the following concentration of ions. Calculate the total hardness and the carbonate hardness of the water sample.

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

Lime-soda softening

- Addition of lime ($Ca(OH)_2$) and soda ash (Na_2CO_3)
- Precipitates Ca^{2+} and Mg^{2+} using following reactions:

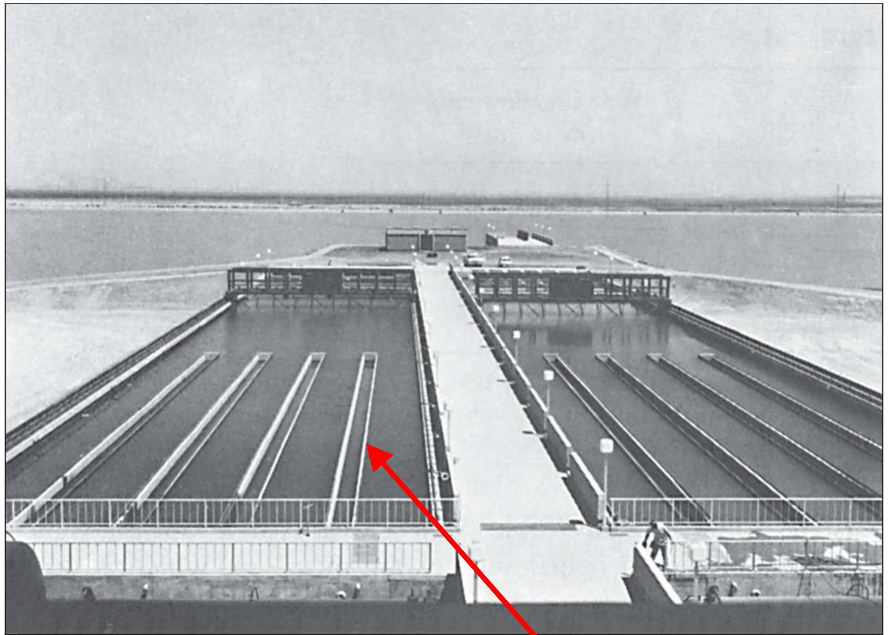
$$Ca^{2+} + CO_3{}^{2-} \rightleftharpoons CaCO_3\,(s)$$

$$Mg^{2+} + 2OH^{-} \rightleftharpoons Mg(OH)_2(s)$$

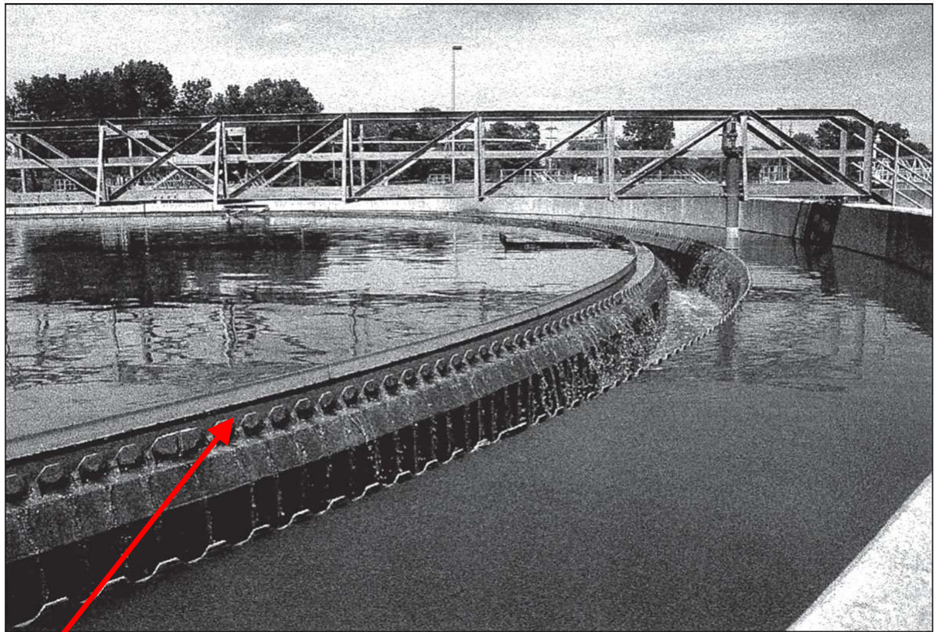
- Target on Ca^{2+} and carbonate hardness first, leaving as much Mg^{2+} and noncarbonate hardness as possible
  - pH of water should be ~10.3 for Ca^{2+} precipitation and ~11 for Mg^{2+} precipitation
  - Have to provide $CO_3{}^{2-}$ for noncarbonate hardness

Sedimentation

- Sedimentation basins: (a) rectangular (b) circular



(a)



(b)

Weir

Sedimentation

- Design parameters
  - Retention time, t_0: 2-4 hr

$$t_o = \frac{V}{Q}$$

V = volume of the sedimentation basin (m^3)

Q = water flow rate (m^3/s)

  - Overflow rate, v_0: directly related to the removal efficiency

$$v_o = \frac{Q}{A_c}$$

A_c = surface area of the sedimentation basin (m^2)

= W (width) x L (length)

* Large, dense particles → greater settling velocity

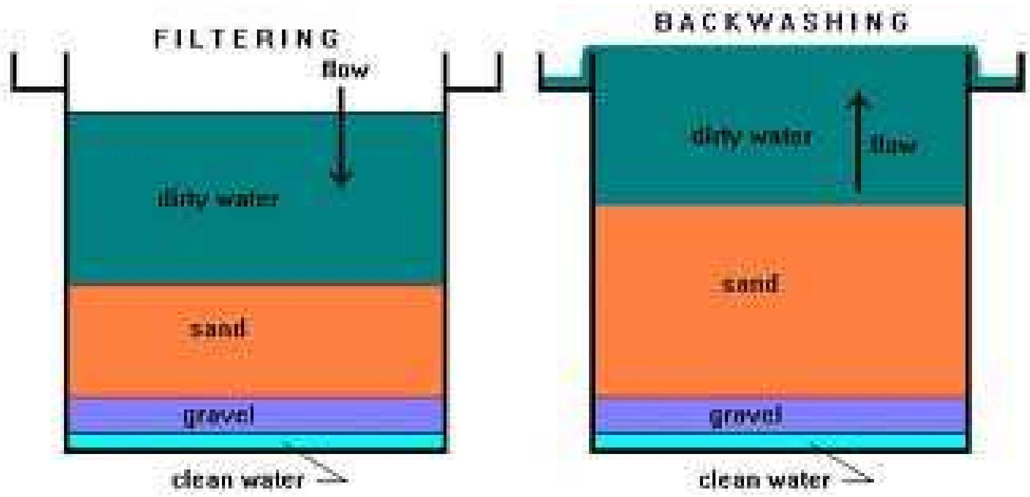
→ greater v_0 allowed

Filtration

- The effluent of the sedimentation basin still contains particles that are too small to settle
- Filtration is the final step of particle removal from water
- Goal: additional turbidity and pathogen removal
  - Pathogens are small particles (virus: 5-50 nm, bacteria: 0.5-10 µm, protozoa oocysts: 2-20 µm)
- Water flows downward through a bed of granular media, and particles in water are trapped by the media

Filtration

- As particles are removed, filter becomes clogged → "head loss" increases → water becomes harder to pass the filter & effluent turbidity increases
- "Backwash" of filter needed (takes about 10-15 min, about once per day)



http://www.rpi.edu

- Backwash
  - Water flow upward at a high speed to expand the media
  - Particles are washed out and collected

Filtration

- Filter media
  - Single media: sand only
  - Dual media: anthracite coal and sand (most common)
  - Multimedia: anthracite coal, sand, and garnet
- Large, lighter particles on the top and small, heavier particles on the bottom → can use full depth of the filter bed & maintain the layers after backwashing

Material	Grain density (g/cm^3)	Effective size (mm)
Anthracite coal	1.6-1.7	1.5-2.5
Sand	2.4-2.6	0.6-0.95
Garnet	4.5	0.4-0.5

Reading assignment

Textbook Ch 10 p. 470-488

Disinfection

- Goal: to inactivate (kill) pathogens
- Disinfection kinetics
  - Chick's law:

$$\frac{dN}{dt} = -kN \longrightarrow ln\left(\frac{N}{N_0}\right) = -kt$$

N = number of organisms

k = first-order reaction constant

  - Chick-Watson law: consider the concentration of the disinfectant as a variable

$$ln\left(\frac{N}{N_0}\right) = -k'C^n t$$

$k = k'C^n$

C = disinfectant concentration, mg/L

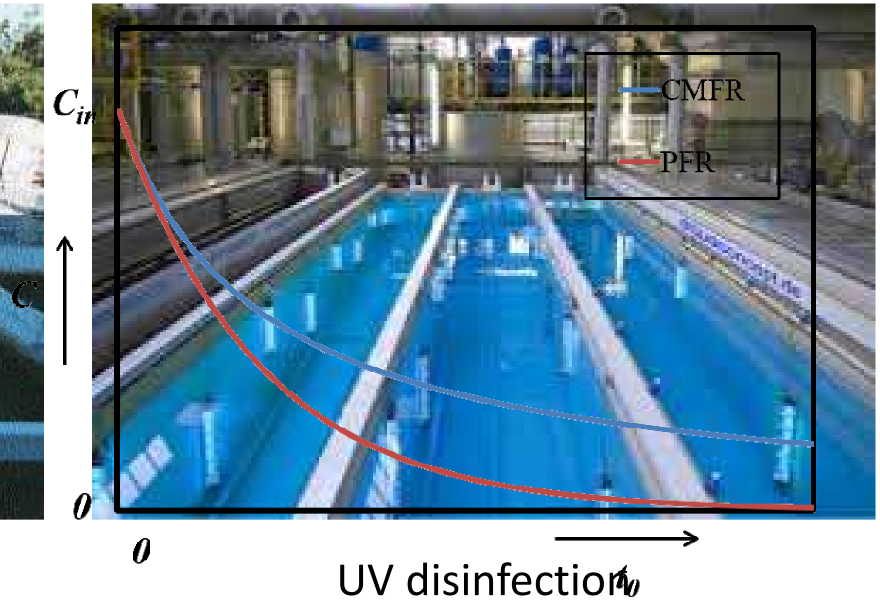
n = coefficient

→ The efficiency of disinfection depends on disinfectant concentration (*C*) and contact time (*t*)

Disinfection

- Goal: to inactivate (kill) pathogens by 99-99.9% (2-3 log removal)
- What is the appropriate reactor design?

Chlorine disinfection



UV disinfection

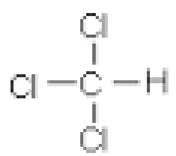
Types of disinfectants

Disinfectant	Advantage	Disadvantage
Chlorine (Cl_2)	• Effective for most microorganisms • leaves residual	• Forms disinfection byproducts • Not effective to some protozoa • Taste and odor problem
Chloramine	• More stable residual than chlorine • Less disinfection byproduct than chlorine	• Less effective than chlorine
Ozone	• Very powerful • Effective for most microorganisms, including protozoa	• Must be produced on-site • Forms disinfection byproducts • No residual
UV	• Effective for bacteria & protozoa • No disinfection byproducts	• Less effective for some viruses • No residual • Effectiveness affected by turbidity

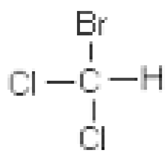
Disinfection byproducts

- Disinfectants may react with Br^- or naturally occurring organic matter to make disinfection byproducts (DBPs)
- Some DBPs are known or possible human carcinogens
- Major DBPs
  - Chlorine disinfection: trihalomethanes (THMs), haloacetic acids (HAAs)

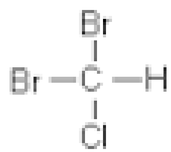
tri halo methanes (THMs)



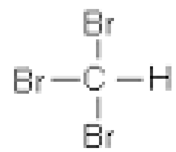
chloroform



bromodichloro methane



chlorodibromo methane

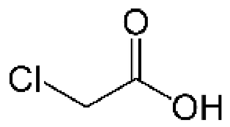


bromoform

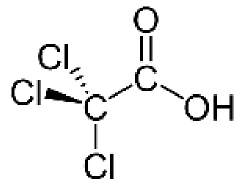
Disinfection byproducts

– Chlorine disinfection: trihalomethanes (THMs), haloacetic acids (HAAs)

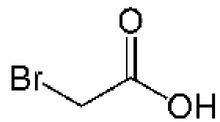
halo acetic acids (HAAs)



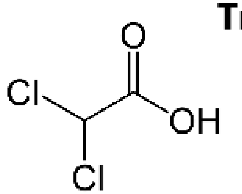
Chloroacetic Acid



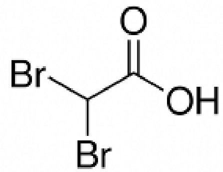
Trichloroacetic Acid



Bromoacetic Acid



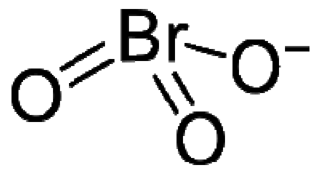
Dichloroacetic Acid



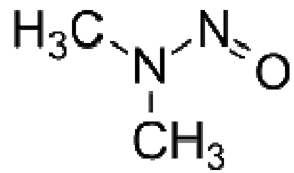
Dibromoacetic Acid

Disinfection byproducts

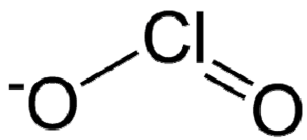
– Ozone disinfection: bromate (BrO_3^-)



– Chloramine (or chlorine) disinfection:
N-nitrosodimethylamine (NDMA)



– Chlorine dioxide disinfection: chlorite (ClO_2^-)



- Balance needed for disinfectant dose!
  – Disinfectant dose ↑, then pathogen kill ↑, but disinfection byproduct ↑

Disinfection byproducts

Does swimming do good or bad for your health??

Chlorine disinfection chemistry

- Chlorine may be added to water as Cl_2, NaOCl, or $Ca(OCl)_2$
- Large plants mostly use Cl_2
- Cl_2 rapidly reacts with water to form HOCl:

$$Cl_2\,(g) + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

- HOCl is a weak acid that dissociates to form OCl^- with a pK_a of 7.54 at 25°C:

$$HOCl \rightleftharpoons H^+ + OCl^-$$

- Both HOCl and OCl^- can kill pathogens, but HOCl is much stronger

Chlorine disinfection chemistry

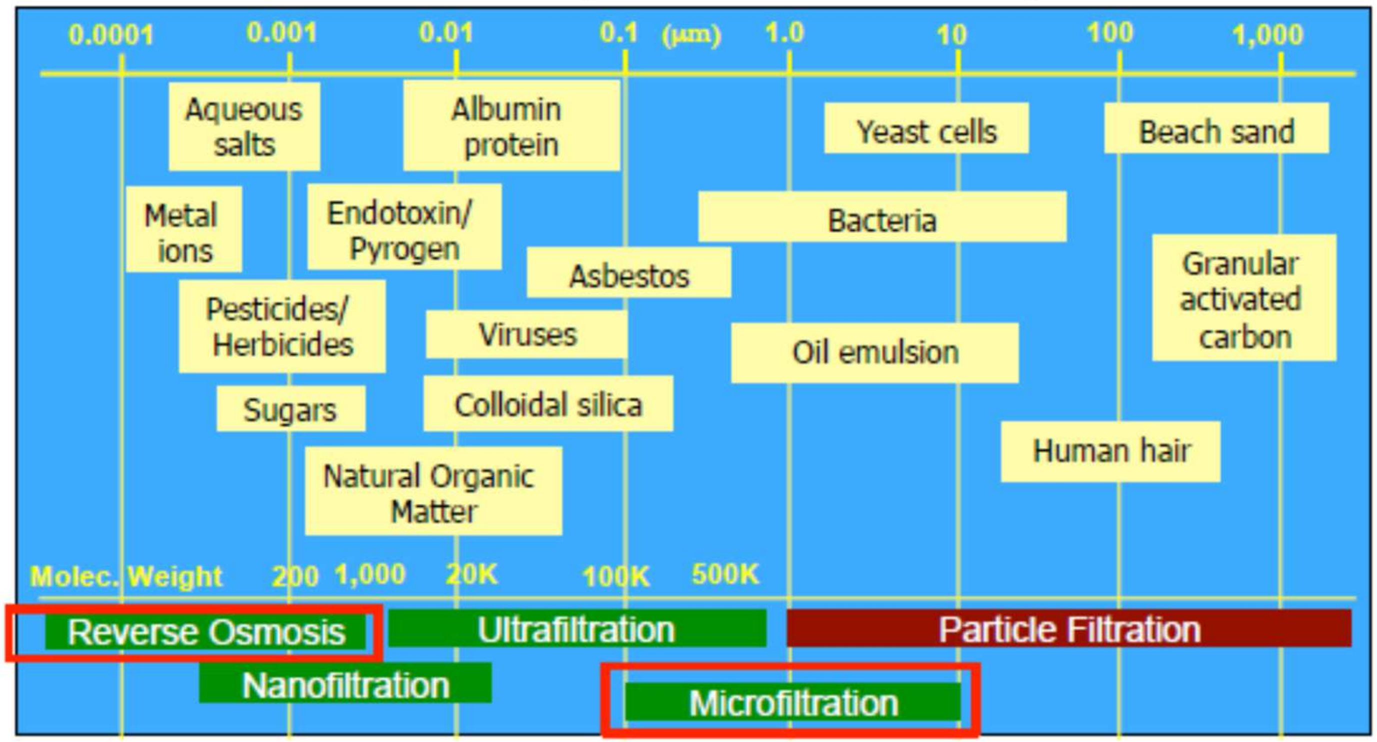
Q: So, for chlorine disinfection, would you prefer high pH (pH>7.54) or low pH (pH<7.54)?

Chlorine disinfection

- Factors affecting chlorine disinfection
  - Dosage
  - Contact time
  - Turbidity: the presence of particles (turbidity) hides the pathogen from disinfectant – this is one of the reason why we remove particles!
  - Other reactive species: some substances in water can consume chlorine (ex: ammonia)
  - pH: effective at $pH<7.5$
  - Water temperature: temperature ↑, then pathogen kill rate ↑, but chlorine stability ↓

Membrane processes

- Getting more and more popular
- Opening size: microfiltration > ultrafiltration > nanofiltration > reverse osmosis



Sludge treatment & disposal

- Large amount of sludge (=mass of settled solids) is produced during the water treatment because of the addition of coagulants or lime
- Major goal of sludge treatment: removing as much water as possible
- When appropriate sludge treatment is accomplished, the sludge is disposed in the landfill

Sludge in the sedimentation basin

http://www.norfolk.gov

Reading assignment

Textbook Ch 10 p. 488-507