Review for 1.85

Lecture 1 - students should skim lecture notes

Overview of water supply and wastewater generation
- 1 billion out of 6-billion world population do not have access to improved water supply
- 1854 - John Snow establishes link between water and disease
- Water use varies diurnally, from country to country, city to city, etc., with weather
- Average per capita use in U.S. ≅ 160 gpd/cap = 600 liters/day/capita
- Wastewater generation less than but closely related to water use
- Greatest sources of wastewater in households are toilets (40%) bathing (30%) laundry (15%)
- Wastewater contaminants include TSS, BOD, NH_4, N, P, oil & grease, pathogenic microorganisms

Lecture 2 - students should skim lecture notes

Water contaminants
- Bacteria
- Viruses
- Protozoa (especially Cryptosporidium parvum & Giardia lamblia)
- Helminth worms
- Organic chemicals
  - Pesticides and herbicides
  - Organic solvents
  - Fuel components
- Disinfection by-products (THMs and HAA5)
- Inorganic chemicals

Effects of contaminants vary widely - be generally familiar with these
Drinking water standards - MCLs published by EPA

Lectures 3 & 4 - Reactor vessels

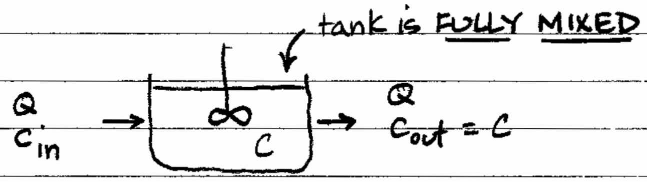
First-order kinetics assumed for most water and wastewater processes:

$$\frac{dC}{dt} = -kC$$

$$C(t) = C_o e^{-kt}$$

k = 1st order reaction rate constant $[1/T]$
C = concentration $[M/L^3]$
C_o = starting conc $[M/L^3]$

Fully-mixed tank (FMT) or continuous-flow stirred tank reactor (CFSTR)



t_R = hydraulic residence time = $\frac{\forall}{Q}$ $[T]$

$\forall$ = tank volume $[L^3]$

Outflow conc for "spike" injection of mass M

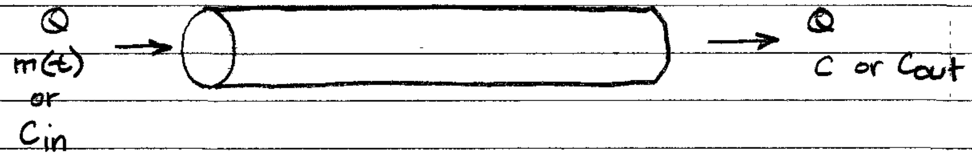
$$c(t) = C_o \exp -\left(kt + \frac{t}{t_R}\right)$$

$$C_o = \frac{M}{\forall}$$ for spike injection to FMT

Steady state outflow concentration for continuous inflow concentration C_{in}

$$C = \frac{C_{in}}{1 + kt_R}$$

Plug flow reactor (PFR)



Injected mass or conc. travels as plug through reactor with <u>NO MIXING</u>

For spike mass injection at time zero, outflow conc will be a spike at time $t = t_R = \frac{\forall}{Q}$

For continuous inflow Q at conc C_{in}, outflow conc, C, will be

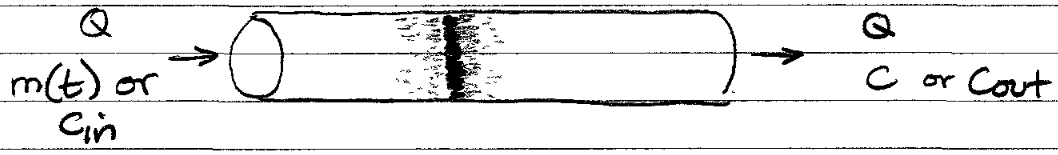
$$C = C_{in} e^{-kt_R}$$

PFR achieves greater treatment efficiency than FMT

$$\text{Efficiency} = \frac{C_{out}}{C_{in}} = \frac{C}{C_{in}}$$

$$\text{Removal} = \frac{C_{in} - C_{out}}{C_{in}} = 1 - \text{efficiency}$$

Dispersed flow reactor



similar to PFR but with some longitudinal mixing

Intermediate in spectrum between PFR (zero mixing) and FMT (infinite mixing)

Peclet Number, $\mathbb{P}$, represents degree of mixing

$$\mathbb{P} = \frac{UL}{D} \qquad \text{(also called } Pe\text{)}$$

U = advective velocity [L/T]
L = length of reactor [L]
D = dispersion coeff [L^2/T]

Longitudinal dispersion coeff for open-channel flow

$$D = 0.03 \frac{UW^2}{R_H}$$

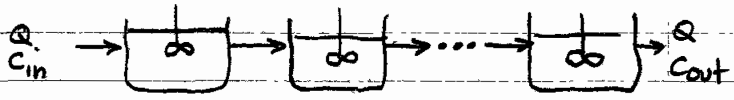
W = channel width [L]
R_H = channel hydraulic radius [L]

Steady-state outflow conc from dispersed flow reactor is given by Wehner-Wilhelm equation

$$\frac{C_{out}}{C_{in}} = \frac{4a \exp(\mathbb{P}/2)}{(1+a)^2 \exp(a\mathbb{P}/2) - (1-a)^2 \exp(-a\mathbb{P}/2)}$$

$$a = \left(1 + \frac{4kt_R}{\mathbb{P}}\right)^{1/2}$$

Tanks-in-series reactor



1 tank = FMT $\qquad$ ∞ tanks = PFR
some tanks $\simeq$ Dispersed flow reactor

Outflow from n equal tanks for spike mass inflow

$$\frac{C_{out}}{C_0} = \frac{n^n}{(n-1)!} \left(\frac{t}{nt'_R}\right)^{n-1} \exp\left(-\frac{t}{t'_R} + kt\right)$$

t'_R = residence time for single tank

$$C_0 = \frac{M}{n\forall}$$

$\forall$ = volume of single tank

Outflow from n^{th} tank for steady-state inflow C_{in} to first tank:

$$\frac{C_{out}}{C_{in}} = \frac{1}{(1 + k t'_R)^n}$$

Reactor hydraulics are evaluated with tracer tests: spike input of tracer in inflow, conc measured in outflow

PFR not achieved perfectly in practice due to short-circuiting, incomplete initial mixing zone, density currents, mixing/dispersion in reactor

Hydraulics indicated by residence time dist$^{\underline{n}}$, RTD

$$RTD(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt}$$

Lectures 5 & 6 - Sedimentation and Flocculation

Particle settling depends on force balance between gravity, buoyancy, and drag

Drag is a function of Reynolds No.

$$Re = \frac{V_s d}{\nu}$$

V_s = settling velocity

d = particle diameter

ν = kinematic viscosity of water

For $Re < 1$, settling is given by Stoke's Law for creeping flow

$$V_s = \frac{g d^2 (\rho_p - \rho_w)}{18 \eta}$$

ρ_p = particle density

ρ_w = water density

g = gravitational accel.

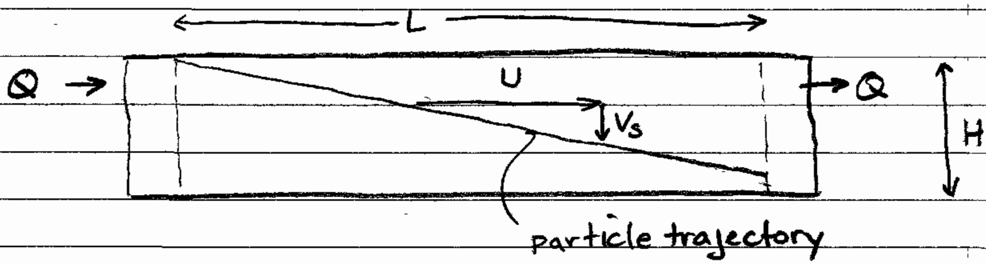
η = dynamic viscosity of water
$= \nu \rho_w$

For $1 < Re < 10^4$ → transition flow

V_s requires iterative solution

Discrete (Type I) settling in sedimentation tank

Particle falls at constant settling velocity



$U = \frac{Q}{HW}$ = flow velocity in tank

H, W = tank height and width

Overflow rate $V_o = \frac{Q}{LW} = \frac{Q}{A_p}$

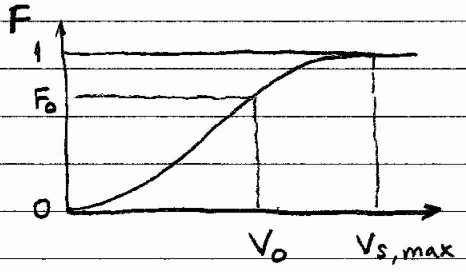
A_p = plan area of tank

Removal ratio (fraction of incoming sediment that is removed)

Removal ratio $= \frac{V_s}{V_o}$

(For Type I settling of uniform-size particle)

For distribution of particles with variable V_s:



Fraction of particles removed out of settling velocity $dist^{\underline{n}}$ F:

$$\text{Fraction removed} = (1-F_o) + \int_0^{F_o} \frac{v}{V_o}\, dF$$

where $F_o = F(V_o)$

Flocculated (Type II) settling

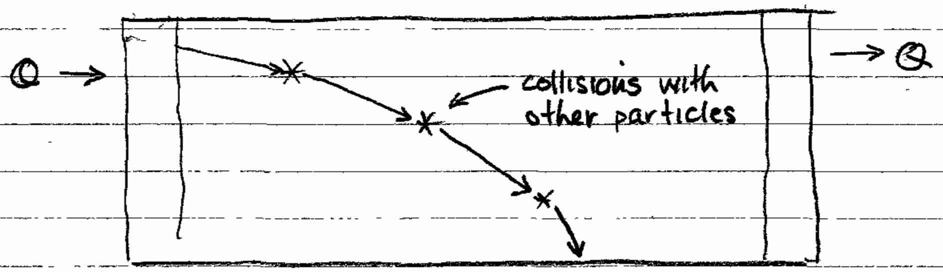
Coagulation – chemical destabilization (elimination of negative electrical charge on particles) and initial coalescing of particles

Flocculation – formation of larger particles (flocs) from destabilized particles

Coagulation caused by
1. Double-layer compression
2. Charge neutralization
3. Entrapment in precipitates
4. Particle bridging

Flocculation caused by
1. Brownian motion
2. Stirring
3. Differential settlement

Particle trajectories are not straight lines in sedimentation tanks



Design for Type II sedimentation requires lab tests to:

1. Determine preferred coagulants (metal salts and/or polymers)
2. Define settling behavior
   Plotted as removal percentage isolines on depth vs. time plots

Type III settling - Zone or hindered settling

Type IV Settling - Compression settling

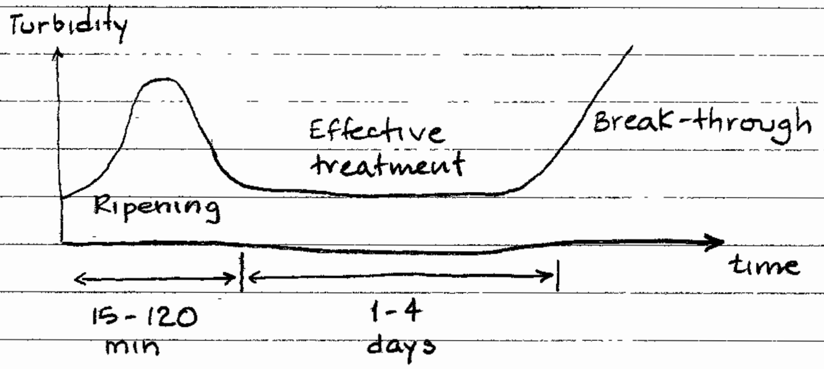
Sedimentation tanks come in both rectangular and circular designs
- Rectangular tanks are theoretically more efficient but sludge removal is easier in circular tanks
- Shallow tanks are theoretically superior but a depth of ~3 m is needed to minimize resuspension of settled solids

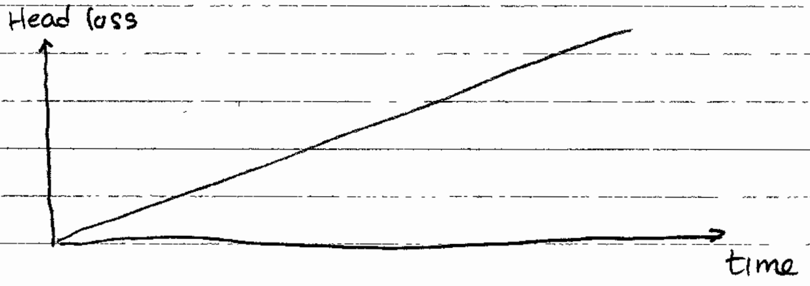
Lecture 7 - Filtration

Slow sand filtration
- Fine sand loaded at low rates, 0.05-0.2 $\frac{m}{hr}$
- Treatment by straining and biological degradation in schmutzdecke on sand surface
- Does not require chemical treatment prior to filtration
- Not commonly used for municipal water treatment

Rapid sand filtration
- Coarse, uniform filter media
- Treatment by particle capture, not by straining
- Requires pre-treatment with coagulants
- Depth filtration - entire depth of bed contributes to removal

Changes in effluent and head loss over time:





When head loss or turbidity exceed limits, filter is backwashed

Filters may use single, dual or multi-media

Uniformity coeff of media $= UC = \frac{d_{60}}{d_{10}}$

d_{10} = effective size = grain size at which 10% by weight of media has $d < d_{10}$

Flow through rapid filters is Forcheimer flow - between laminar and turbulent

$$1 \leq Re \leq 100$$

$$Re = \frac{\rho_w V_f d}{\mu_w}$$

ρ_w μ_w = density, dynamic viscosity of water
V_f = filtration rate = Q/A_p
d = grain size (use d_{10})

Forcheimer flow gives head loss as

$$\frac{h_L}{L} = K_1 V_f + K_2 V_f^2$$

Note = not Darcy's Law, which applies when $Re < 1$

L = depth of media

Rapid filtration mechanisms

Straining not important

Particle removal predicted by $\frac{\partial C}{\partial z} = -\lambda C$

C = particle conc $[M/L^3]$ or $[number/L^3]$
z = depth into filter $[L]$
λ = filtration coeff $[L^{-1}]$

Media particles act as collectors for smaller particles in water by:

1. Interception
2. Sedimentation (gravity)
3. Brownian transport (diffusive transport)

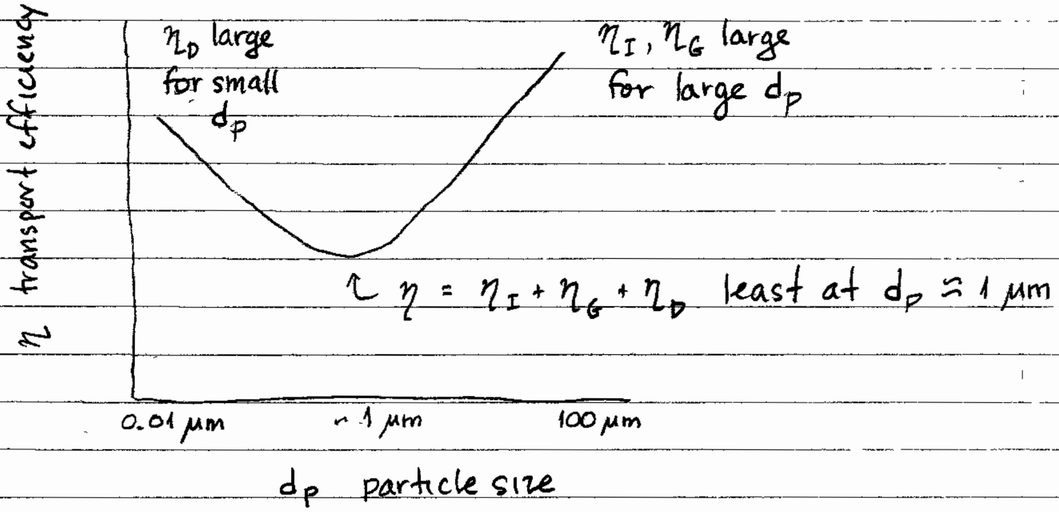
η = transport efficiency = $\eta_I + \eta_G + \eta_D$

α = attachment efficiency = function of chemical pre-treatment with coagulant

$$\frac{C_{out}}{C_{in}} = \exp\left(\frac{-3(1-n)\eta\alpha}{2d_c} L\right)$$

d_c = collector (media) particle diameter
n = porosity of filter media
L = depth of filter media

η is function of filtered particle size, d_p



Filter design requires filter bed, support for filter bed, nozzles for backwash flow, troughs to capture backwash flow, outflow for normal filtrate flow

Lecture 8 - Lime-Soda Ash softening

Hardness = conc of divalent metal ions, Ca^{++}, Mg^{++}, Sr^{++}, Fe^{++}, Mn^{++}

Ca and Mg are by far the most common and highest concentrations

Hard water causes scale, interferes with soap

Degrees of hardness:

Soft	0-55 mg/L as $CaCO_3$
Moderate	55-120
Hard	120-250
Very hard	> 250

$$\text{Definition of hardness} = \Sigma [M^{++}] \times \frac{50}{\text{equiv. wt. of } M^{++}}$$

M^{++} refers to metal ions

Equivalent weight is MW / valence

e.g.

	MW	valence	eq. wt.
Ca^{2+}	40	2	20
Mg^{2+}	24.4	2	12.2

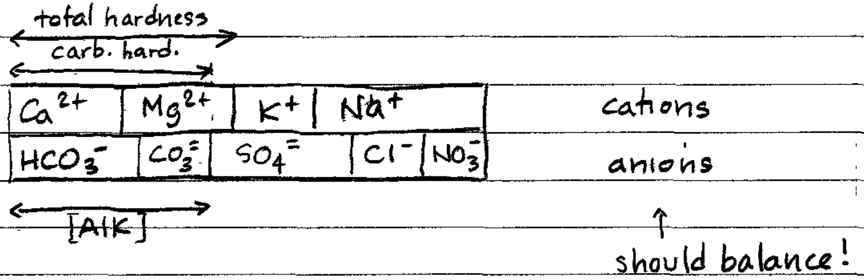
Water with $[Ca^{2+}] = 70$ mg/L, $[Mg^{2+}] = 9.7$ mg/L

$$\text{Hardness} = \frac{70}{20} \cdot 50 + \frac{9.7}{12.2} \cdot 50$$

$$= 214.8 \text{ mg/L as } CaCO_3$$

Carbonate hardness = part of total hardness equivalent to carbonate + bicarbonate alkalinity

Bar chart plots concentrations in equivalents:



If [Alk] < total hardness, carb. hardness = [Alk]

If [Alk] > total hardness, carb. hardness = total hardness

Hardness is removed by addition of lime (CaO or $Ca(OH)_2$) and soda ash (Na_2CO_3)

Lime reacts first with CO_2: $CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$

Then with carb. hardness: $Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$

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

Then with Mg non-carb. hardness:

$$Mg^{2+} + SO_4^{2-} + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{2+} + SO_4^{2-}$$

Soda ash can then be added to remove remaining hardness if necessary:

$$Ca^{2+} + SO_4^{2-} + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2Na^+ + SO_4^{2-}$$
$$Ca^{2+} + 2Cl^- + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2Na^+ + 2Cl^-$$

Water is then recarbonated by adding CO_2:

$$Ca^{2+} + 2(OH^-) + CO_2 \rightarrow CaCO_3 + H_2O$$
$$Ca^{2+} + CO_3^{2-} + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

Recarbonation stabilizes agressive water

$$\text{Stability index} = I = pH_{actual} - pH_{equil}$$

$$pH_{equil} = pH \text{ at } CaCO_3 \text{ equilibrium}$$
$$= pCa + p[Alk] + \log(K_s/K_2)$$

K_s = equil constant for $CaCO_3 \rightleftarrows Ca^{2+} + CO_3^{2-}$
K_2 = equil constant for $HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$

Compute lime and soda ash doses by stoichiometric requirements - easiest procedure is to tabulate ionic makeup of water in equivalents

Not all hardness can be removed - residual hardness is dictated by solubility of $CaCO_3$ and $Mg(OH)_2$
30 mg/L Ca , 10 mg/L Mg

To account for residual hardness and incomplete reactions, excess lime is added beyond amount computed by stoichiometry -
Excess lime is usually 30 to 35 mg/L of CaO

Lime is added as either dry lime CaO or slaked (hydrated) lime $Ca(OH)_2$

Lecture 9 - Adsorption and Ion Exchange

Adsorption by activated carbon to treat
- taste and odor
- synthetic organic chemicals
- color

Adsorption process represented by empirically derived isotherms

Linear isotherm $q_A = K_d C_A$

q_A = solid phase conc [M/M]

$= \dfrac{\text{mass of absorbate}}{\text{mass of absorbent}}$

C_A = water phase conc $[M/L^3]$

K_d = partition coeff. $[L^3/M]$

Langmuir isotherm

$$q_A = \frac{Q_M K_{ad} C_A}{1 + K_{ad} C_A}$$

Q_M = max solid phase conc [M/M]

K_{ad} = Langmuir adsorption coeff $[L^3/M]$

C_A/q_A plots as straight line vs C_A

BET isotherm

$$\frac{q_A}{Q_M} = \frac{B_A C_A}{(C_{S,A} - C_A)[1 + (B_A - 1)(C_A/C_{SA})]}$$

B_A = constant

$C_{s,A}$ = saturation conc in water

Freundlich isotherm (most common for act. carbon)

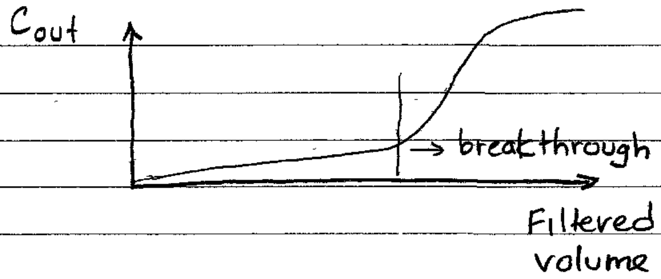
$$q_e = K_F C_A^{1/n}$$

K_F, n = empical coeffs

log q_e plots as straight line against C_A

PAC - powder activated carbon - applied in suspension
GAC - granular activated carbon - appled in beds

GAC is used until breakthrough, then replaced by fresh carbon



Ion exchange

Similar to adsorption in principle and application, but depends on different chemical mechanism

Used to remove hardness, other cations or anions

Reaction

$$Ca^{+2} + \underset{\substack{\uparrow \\ \text{exchange} \\ \text{resin}}}{2Na\cdot Ex} \rightleftharpoons Ca\cdot Ex_2 + 2Na^+$$

Exchanger is regenerated by passing through strong brine that causes reverse reaction

Preference series shows which ions exchange

$Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > NH_4^+ > Na^+ > H^+$

$SO_4^{2-} > I^- > NO_3^- > Br^- > Cl^- > OH^-$

Iron and manganese removal

Water low in oxygen may contain reduced Fe^{2+}, Mn^{2+}

Once oxidized Fe^{3+} Mn^{3+} Mn^{4+} precipitate and cause staining of laundry and fixtures

Treated:
1. In-situ in aquifer
2. Sequestration
3. Ion exchange with Greensand
4. Oxidation
   Aeration treats Fe but not Mn
   Strong oxidizers treat Fe and Mn – chlorine or permanganate $KMnO_4$
5. Lime - soda ash softening

Lecture 10 – Air stripping

Removes volatile organic compounds (VOCs)
ammonia
H_2S

Governing principle is Henry's Law $\frac{C_G}{C_W} = H'$

C_G C_W = mole conc in gas, water (moles/m³)
H' = dimensionless Henry's Law const

Exchange across air-water interface is limited by diffusion through air and/or water thin films

Usually water film controls:

Rate of mass transfer across air-water interface

$$\frac{dm}{dt} = -D_W A \left[\frac{C_G/H' - C_W}{\delta_W} \right]$$

m = mass
D_W = diffusion coeff in water
δ_W = thickness of water-side thin film
A = interface surface area

Counter-current air stripper increases A, decreases δ_W and C_A to increase dm/dt

Air stripper parameters:

Stripping factor, $S \equiv \frac{Q_a}{Q_W} H'$

$H' = \left(\frac{Q_a}{Q_W}\right)_{min}$ = minimum air to water ratio assuming perfect efficiency of stripping tower (i.e. tower achieves Henry's Law equilibrium)

S = multiple of $(Q_a/Q_W)_{min}$ is actual tower (usually ~3.5)

Q_a, Q_W = flow rates of air, water through tower

Required stripping tower height, L

$$L = \frac{Q_W}{A_T K_L a} \left(\frac{S}{S-1} \right) \ln \left[\frac{1 + (C_{in}/C_{out})(S-1)}{S} \right]$$

C_{in} = conc in inflow water
C_{out} = conc in effluent water

K_L = liquid phase mass transfer coeff
= D_W / δ_W

A_T = cross-section area of tower

a = interface area per unit volume of tower

Q_W = water flow rate through tower

L = NTU · HTU

NTU = number of transfer units

HTU = height of transfer unit

$$= \frac{Q_W}{A_T K_L a}$$

Design charts give $(1 - C_{in}/C_{out})$ vs. NTU and S

Lecture 11 – Trip to Cambridge Water Treatment Plant

Plant uses dissolved air flotation (DAF) to remove sediment by floating particles upwards with air bubbles

Lecture 12 Disinfection

Two modes: Primary disinfection to inactivate pathogens
Secondary disinfection to maintain disinfection in water distⁿ system

Disinfection methods
1. Free chlorine
2. Combined chlorine (chloramine)
3. Ozone
4. Chlorine dioxide
5. UV light

Disinfection kinetics by Chick-Watson model

$C^n t = K$ to achieve N/N_0

C = chemical disinfectant conc.
t = time of exposure to disinfectant
n, K = constants
N = ending pathogen conc
N_0 = starting pathogen conc

If $n \approx 1$

$$\ln\left(\frac{N}{N_0}\right) = -\Lambda_{CW}\, Ct$$

Λ_{CW} = Chick-Watson coeff of specific lethality

Minimum values of Ct are specified by EPA to achieve Giadia and Cryptosporidium inactivation

Chlorine disinfection

Cl gas: $Cl_2 + H_2O \rightarrow HOCl + HCl$

$$HOCl \underset{pH<7.5}{\overset{pH>7.5}{\rightleftharpoons}} H^+ + OCl^-$$

Hypochlorite: $Ca(OCl)_2 \rightarrow Ca^{2+} + 2OCl^-$

$$NaOCl \rightarrow Na^+ + 2OCl^-$$

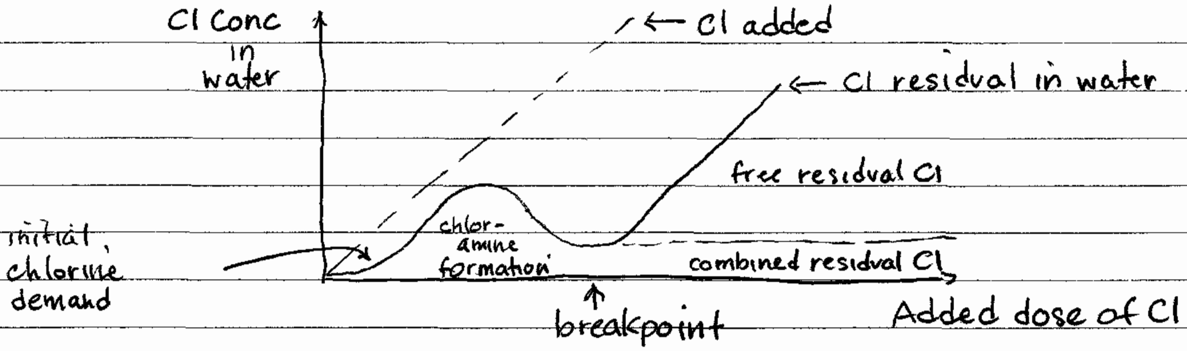
$HOCl$ and OCl^- are effective disinfectants
$HOCl$ is better than OCl^-

Chloramines NH_2Cl $NHCl_2$ NCl_3

Act as disinfectants and form long-lasting residuals

Chlorine creates Disinfection By-Products (DBP)
Trihalomethanes = $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$
THMs

Breakpoint chlorination determines Cl dose to create residual:



Chlorine demand is (Cl added) - (Cl residual in water)

Chlorine dose needs to be greater than breakpoint

Dechlorination of chlorine treated wastewater

Residual Cl is harmful to aquatic life

Sulfur dioxide removes residual Cl

Chlorination treatment in chlorine contact chambers

Plug flow desired to ensure Ct requirement is met

Serpentine contact chamber design

Ozonation

More powerful oxidant than HOCl - very good disinfectant, removes taste and odor, does not create THMs, but does not create disinfecting residual

Ozone gas bubbled through water to achieve required Ct

UV

Inactivates by UV damage to DNA and RNA and by creating OH radicals (strong oxidizers)
Very effective against crypto

Treatment by short time exposure to light from UV lamps