

Crystallization

- ▷ Homogeneous crystallization
 - spontaneous crystal formation via thermodynamic
- ▷ Heterogeneous crystallization
 - crystals form at a nucleation site

1-6-1

Mechanical Separation

Need 2 things

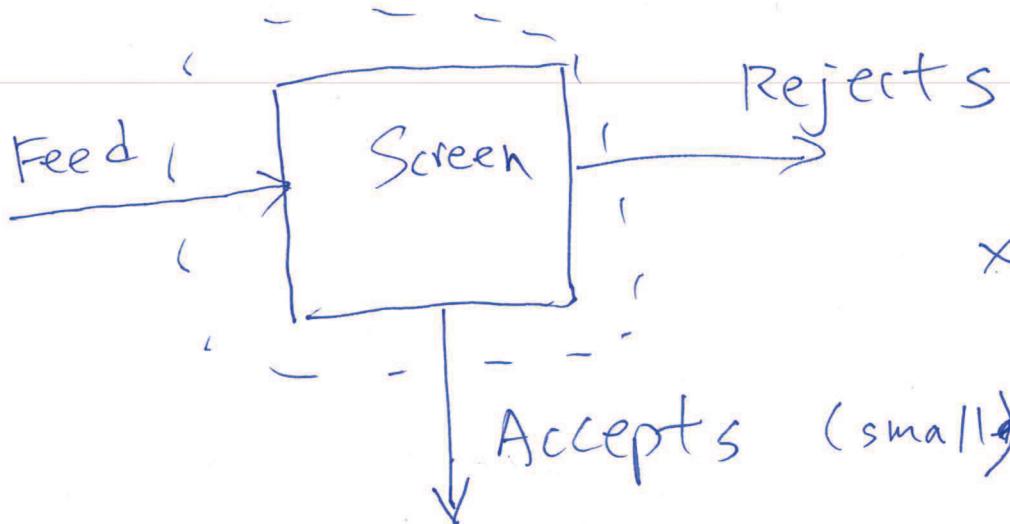
- At least 2 things that are different in a way we care about
- Process where the physical property causes them to ~~be~~ behave differently

Physical Properties

- ▷ Size □ Miscibility □ Density □ Hardness
- ▷ Magnetic □ Solubility □ Shape (Morphology)
- ▷ Wettability □ Electrical conductivity
- Chemical structure/affinity
- Motility

2-1-1
~~REVIEW~~

Screening Effectiveness



~~x_i~~ = mass fraction
of the stuff
we want in
stream i.

$$F = R + A; x_f F = x_R R + x_A A$$

Accepting Effectiveness

$$\epsilon_A = \frac{\text{mass of what we want in } A}{\text{mass of " in } F}$$

$$= \frac{x_A A}{x_f F} = \frac{x_A}{x_f} \cdot \frac{(x_F - x_R)}{(x_A - x_R)}$$

Rejecting Effectiveness

$$\epsilon_R = \frac{(1-x_R) R}{(1-x_f) F} = \frac{(1-x_R)}{(1-x_f)} \cdot \frac{(x_A - x_f)}{(x_A - x_R)}$$

Overall Effectiveness

$$\epsilon = \epsilon_A \epsilon_R = \frac{x_A}{x_f} \cdot \frac{(x_F - x_R)}{(x_A - x_R)} \cdot \frac{(x_A - x_f)}{(x_A - x_R)} \cdot \frac{(1-x_R)}{(1-x_f)}$$

$$x_f F = x_R (F - A) + x_A A$$

$$F(x_f - x_R) = A(x_A - x_R)$$

$$\frac{A}{F} = \frac{(x_f - x_R)}{(x_A - x_R)} ; \quad ; \quad \frac{R}{F} = \frac{(x_A - x_f)}{(x_A - x_R)}$$

\equiv When the screen is undamaged:

$$x_A = 1 ; \quad (1 - x_R)(x_A - x_f) = (1 - x_f)(x_A - x_R)$$

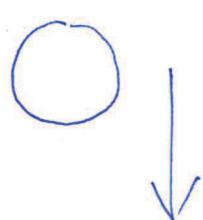
$$\hookrightarrow \frac{(1 - x_R)}{(1 - x_f)} = \frac{(x_A - x_R)}{(x_A - x_f)} = \frac{(1 - x_R)}{(1 - x_f)}$$

Then :

$$\epsilon = \frac{1}{x_f} \cdot \frac{(x_f - x_R)}{(1 - x_R)} \cdot \frac{\cancel{(1 - x_f)}}{\cancel{(1 - x_R)}} \cdot \frac{\cancel{(1 - x_R)}}{\cancel{(1 - x_f)}}$$

$$\epsilon = \frac{(x_f - x_R)}{x_f(1 - x_R)}$$

Sedimentation



Force Balance

$$ma = \sum_i F_i = m \frac{du}{dt} = m \frac{d^2x}{dt^2}$$

$$\sum_i F_i = F_b + F_d + F_g$$

$$= m_p g - \frac{m_p}{\rho_p} \ell g - C_D \frac{\rho u_p^2 A_p}{2}$$

$$C_D = f(u_p)$$

$$A + \text{small } Re: \quad \frac{24}{Re} = \frac{24 \mu}{\rho u_c l_c}$$

2-2-3

Force Balance on a Particle

$$m \frac{d^2x}{dt^2} = m \frac{du}{dt} = mg(1 - \frac{\rho}{\rho_p}) - C_D \frac{\rho u^2 A_p}{2}$$

Designing a Sedimentation Unit

- How fast will the particle settle?
- How long until terminal velocity is reached?

Steady state:

$$mg(1 - \frac{\rho}{\rho_p}) = C_D \frac{\rho u^2 A_p}{2}$$

$$u^2 = \frac{2mg}{\rho \rho_p A_p} \frac{1}{C_D} (1 - \frac{\rho}{\rho_p})$$

$$\left\{ \begin{array}{l} C_D = \frac{24}{Re} \quad \text{for } Re < 0.1 \\ = \frac{24}{Re} \left(1 + 0.14 Re^{0.70} \right) \quad \text{for } 0.1 \leq Re < 10^3 \\ = 0.445 \quad \text{for } \cancel{Re > 10^5} \\ \quad \quad \quad 10^3 \leq Re < 2 \times 10^5 \end{array} \right.$$

$$z = \frac{x}{l_c} ; v = \frac{u}{u_c} ; \tau = \frac{t}{t_c}$$

$$\frac{m l_c}{t_c^2} \frac{d^2 z}{d\tau^2} = \frac{m u_c}{t_c} \frac{dv}{d\tau} = mg(1 - \frac{v}{e_p}) - C_D \frac{\rho u_c^2 A_p}{2} v^2$$

$$\frac{l_c}{u_c t_c} \frac{d^2 z}{d\tau^2} = \frac{dy}{d\tau} = \frac{g t_c}{u_c} (1 - \frac{v}{e_p}) - C_D \frac{\rho u_c t_c A_p}{2 m} v^2$$

choose $t_c = \frac{u_c (1 - e/e_p)}{g (1 - e/e_p)}$; $l_c = u_c t_c$

$$\frac{d^2 z}{d\tau^2} = \frac{dv}{d\tau} = 1 - C_D \frac{\rho u_c^2 (1 - e/e_p) A_p}{2 m g (1 - e/e_p)} v^2$$

choose $u_c = \sqrt{\frac{2 m g (1 - e/e_p)}{\rho (1 - e/e_p) A_p}}$ [$\cancel{\text{kg}} \cdot \frac{m}{s^2} \cdot \frac{m^3}{\cancel{\text{kg}}} \cdot \frac{1}{m^2} = \frac{m^2}{s^2}$]

$$\frac{d^2 z}{d\tau^2} = \frac{dv}{d\tau} = 1 - C_D v^2 ; C_D(u)$$

$$\frac{dz}{d\tau} = v$$

2-3-2

Non-spherical Particles

- Effective diameter
 - Shape parameter
 - Sphericity ≤ 1
 - Volume shape factor: $k = \frac{V_p}{d_i^3}$
 - circularity:
- Enough for Engineering calculations

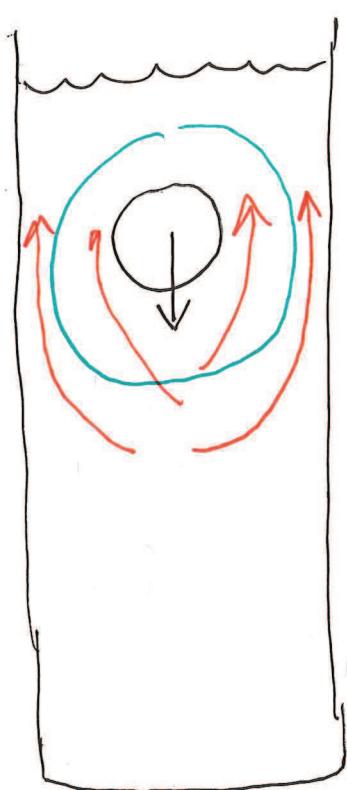
2-4-1

circularity: Perimeter of the projected area of eq. sphere

Actual Perimeter

$$\cancel{\pi D} = \cancel{\pi (6V/\pi)^{1/3}} \\ = \underline{\pi (6V/\pi)^{1/3}}$$

P_p



Particle near walls settle
slower

Hindered Settling

uniformly-sized spheres

$$U_t = U_{t,0} (1 - \phi)^n \quad - \text{Eqn A}$$

U_t = terminal velocity

$U_{t,0}$ = terminal velocity of single particle

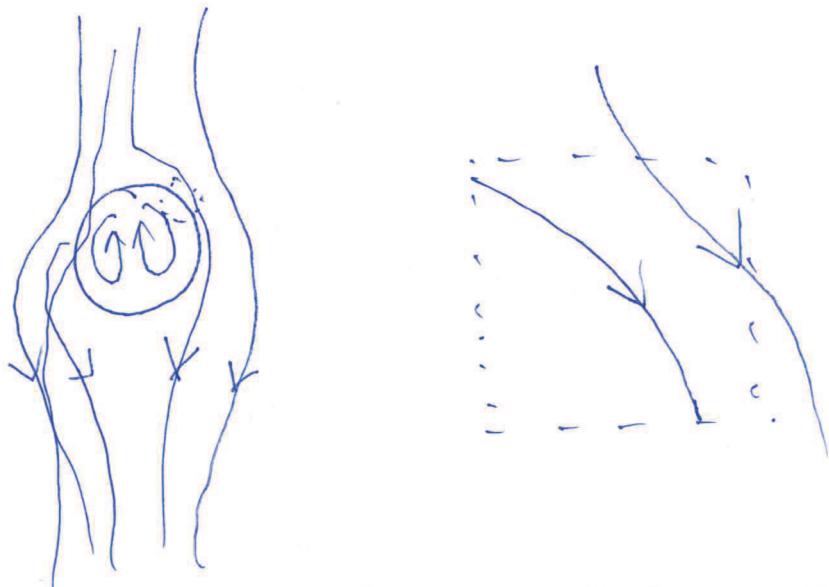
ϕ = volume fraction of particles

n = exponent (function of Reynolds #)

For eqn \star :

- Also for distributions of sphere sizes, but ϕ from all particles

Bubbles



For pure or "clean" bubble the boundary or interface can freely move. So there is less resistance to motion.

For a "dirty" interface. The boundary behaves like a solid boundary.

$$\text{Bond } \# = \frac{\text{gravitational force}}{\text{surface tension}}$$

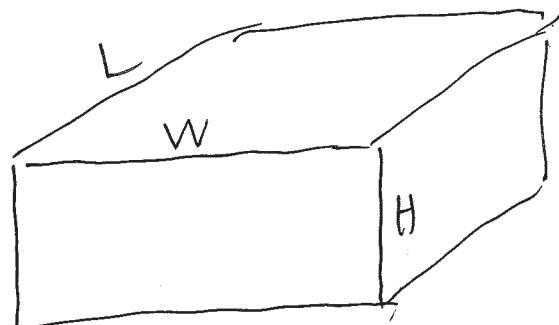
or Eötvös #

Ideal continuous sedimentation

Residence Time: Average time fluid spends in the unit.

\bar{u} = average velocity of the flow

$$Q = \bar{u} WH \rightarrow \bar{u} = \frac{Q}{WH}$$



Assume terminal velocity at all times.

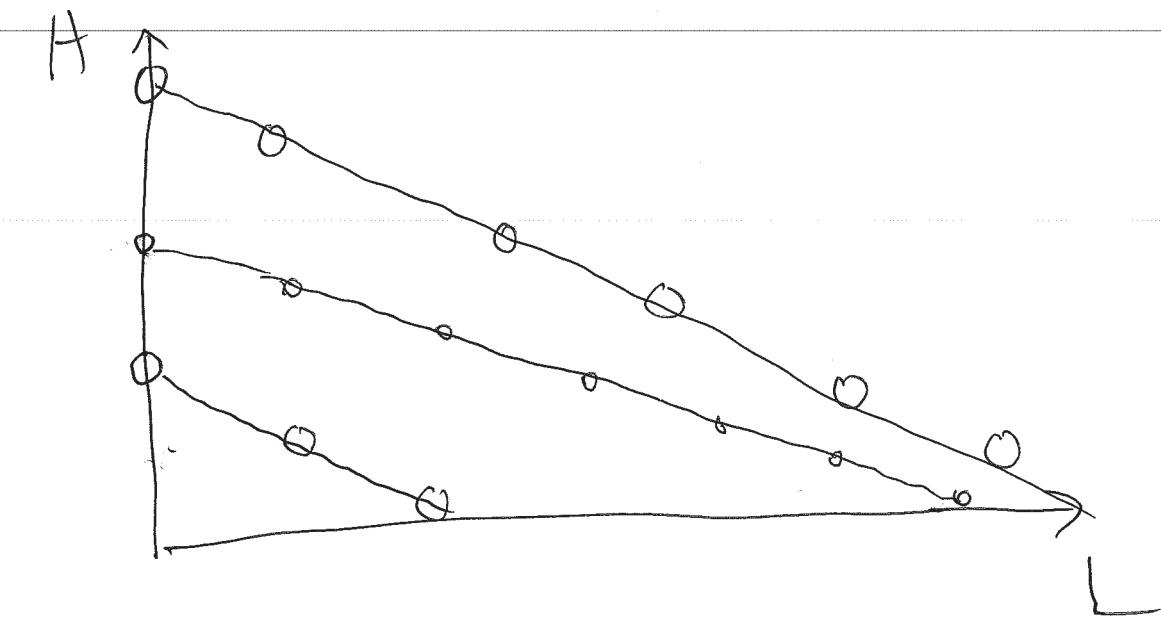
$$t_r = \frac{L}{\bar{u}} ; \quad u_t - \text{terminal velocity}$$

$$t_s = \frac{H}{u_t} ; \quad t_s \leq t_r \text{ for } \cancel{\text{successful}} \text{ separation}$$

$$t_r = \frac{LWH}{Q} = \frac{AH}{Q}$$

$$\frac{H}{u_t} \leq \frac{AH}{Q} \rightarrow u_t \geq \frac{Q}{A}$$

$$\therefore u_{t,\min} = \frac{Q}{A}$$



For a give particle size:
the height distribution is uniform

Fraction of particles that will
be removed:

$$X = \frac{U_t}{U_{t,\min}}$$

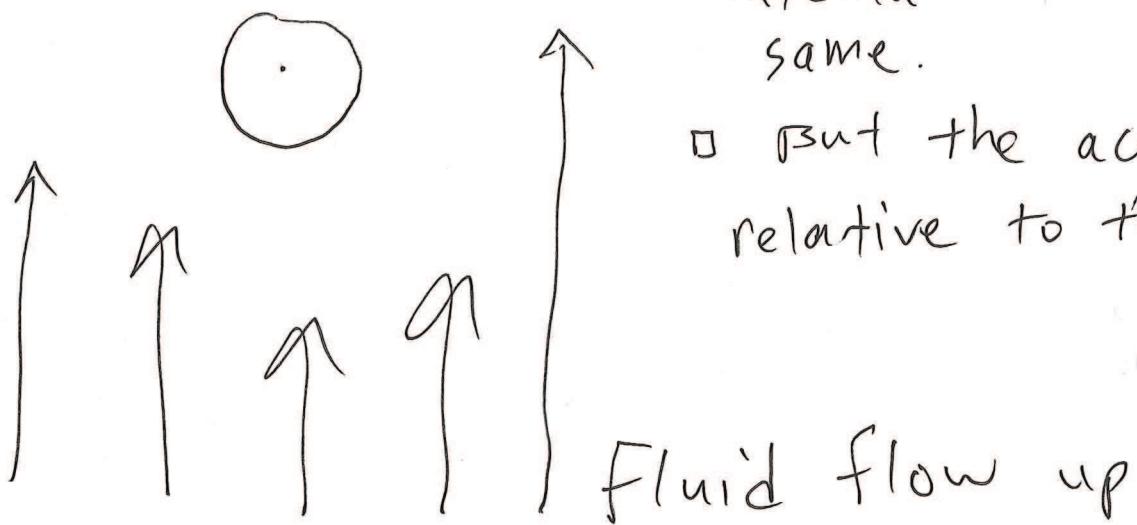
Design Considerations

- Scour velocity
- Compaction time
- Mechanical constraints
- Fudge factors

Elutriation

☐ terminal velocity calculations are the same.

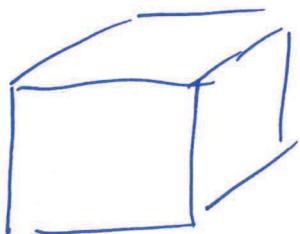
☐ but the actual ^{velocity} is relative to the flow ~~absolute~~ _{velocity}



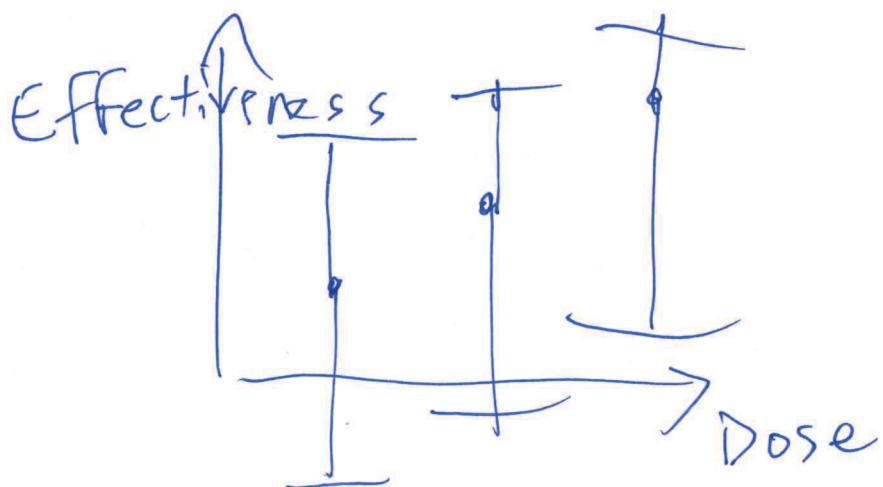
Fluid flow up

2-6-1

Sig Fig Example



$$D = 1.3753'' \rightarrow \pm 0.001''$$



2-7-1

Filtration

- Basis of separation = size or chemical affinity
- Need a pressure drop across the filter.
 - High pressure upstream
 - Vacuum downstream
- Filter aid: to prevent clogging
 - usually disposed of w/ cake

Filtrate: solution to be filtered

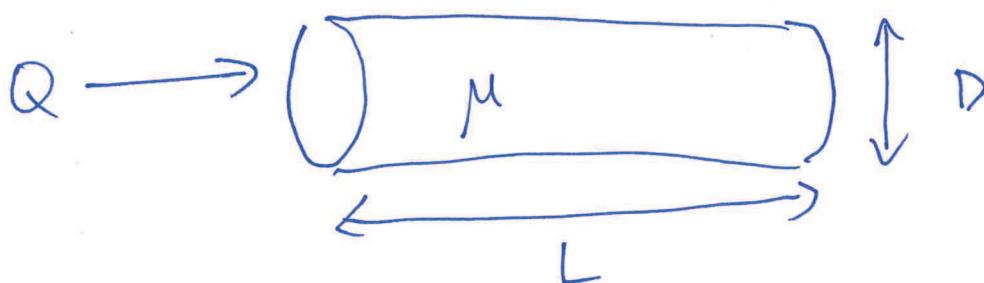
Permeate: solution that passes through filter

Retentate: solution that does not pass through

Precipitate: solids captured on filter

Flow through Porous Media

Hagen-Poiseuille Flow (Laminar Flow)



$$\bar{u} = \frac{Q}{A}$$

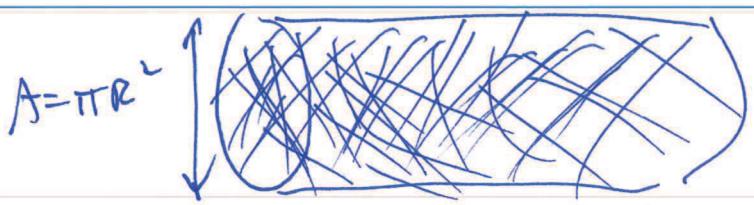
$$\Delta P = \frac{8\mu L \bar{u}}{R^2} = \frac{8}{R^2} \frac{\mu L Q}{A}$$

Darcy's Law

$$\Delta P = \frac{1}{K} \frac{\mu L Q}{A}$$

$$K = \text{permeability [E] } m^2$$

$$K \sim (\text{pore diameter})^2$$



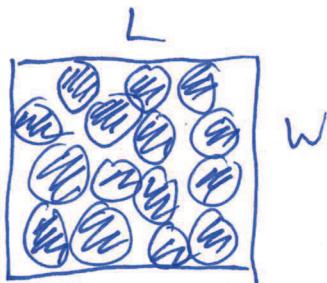
$$A = \pi R^2$$

For Darcy's Law
we use A of the
empty region:

$$A_{\text{actual}} = \epsilon A ; \quad \epsilon = \text{porosity} [-]$$

specific example

$$\epsilon = \frac{\text{empty area}}{\text{total area}}$$



$$A = L \cdot W$$

$$A_{\text{actual}} = \epsilon A$$

~~$\epsilon = \text{Area of}$~~

$$\text{Ans} \quad \bar{u}_{\text{superficial}} = \frac{Q}{A}$$

$$\bar{u}_{\text{actual}} = \frac{Q}{A_{\text{actual}}} = \frac{Q}{\epsilon A} = \frac{\bar{u}_{\text{superficial}}}{\epsilon}$$

When the porous media is made up of
~~granular~~ granular material:

$$\frac{1}{K} = \frac{150(1-\epsilon)^2}{\psi^2 D_p^2 \epsilon^3} ; \quad Re_{\text{superficial}} < 0.1$$

$$Re_s = \frac{\rho D_p Q}{\mu A} ; \quad \psi = \text{sphericity}$$

D_p = particle diameter
(of granular material)

Darcy's Law: $\Delta P = \frac{1}{K} \frac{\mu L Q}{A}$

Kozeny-Carman Equation:

$$\Delta P = \frac{150 (1-\epsilon)^2}{\psi^2 D_p^2 \epsilon^3} + \frac{\mu L Q}{A} \quad Re_s < 0.1$$

$$Re_s = \frac{\rho Q D_p}{\mu A} > 1000 :$$

$$\frac{1}{K} = \frac{1.75 \rho Q (1-\epsilon)}{A \psi D_p \mu \epsilon^3} = \frac{1.75 (1-\epsilon)}{\psi D_p^2 \epsilon^3} Re$$

D_p = Sauter-mean diameter

For All $Re < 2 \times 10^5$: Ergun Eqn.

$$\frac{1}{K_E} = \frac{150 (1-\epsilon)^2}{\psi^2 D_p^2 \epsilon^3} + \frac{1.75 (1-\epsilon)}{\psi D_p^2 \epsilon^3} Re$$

$$= \frac{(1-\epsilon)}{\epsilon^3 \psi D_p^2} \left(\frac{150 (1-\epsilon)}{\psi} + 1.75 Re \right)$$

$$\hookrightarrow \Delta P = \frac{1}{K_E} \frac{\mu L Q}{A} \leftarrow \text{valid for } 0.3 < \epsilon < 0.7$$

When Filtering:

$$L = \frac{V_{cake}}{A} \rightarrow V_{particles} = (1-\epsilon) V_{cake}$$

$$L = \frac{V_{\text{particles}}(t)}{(1-\epsilon) A} ; \quad \frac{c_s V_{\text{flow}}(t)}{\rho_p} = V_{\text{particles}}(t)$$

$$L(t) = \frac{c_s V(t)}{\rho_p A (1-\epsilon)} ; \quad Q = \frac{dV}{dt}$$

$$\Delta P = \frac{1}{K_E} \frac{\mu c_s V}{\rho_p A^2 (1-\epsilon)} \frac{dV}{dt}$$

$V(t)$ = total volume of fluid through cake

$$\Delta P = \underbrace{\frac{1}{K_E \rho_p (1-\epsilon)}}_{\alpha} \frac{\mu c_s V}{A^2} \frac{dV}{dt}$$

α = specific cake resistance

c_s = concentration of particles $\frac{\text{kg}}{\text{m}^3}$

In compressible cakes

$\alpha = \text{constant}$

Compressible cakes

$$\alpha = \alpha_0 (\Delta P)^s \quad \text{or} \quad \alpha = \alpha_0 (1 + \beta (\Delta P))^s$$

α_0 = specific cake resistance @ $\Delta P = 0$

β, s = empirical fitting parameter

Filtration Process

- Constant Flow Rate
- Constant Pressure

Constant Flow Rate Process

$$\Delta P = \alpha \frac{\mu C_s V}{A^2} \frac{dV}{dt} \quad V = \text{Volume}$$

$$\frac{dV}{dt} = Q ; \quad V(t) = Qt + V_0$$

For a clean filter : $V_0 = 0$

$$\Delta P(t) = \alpha \frac{\mu C_s Q^2}{A^2} t ; \quad \text{compressible cake} \quad \hookrightarrow \alpha = \alpha_0 (1 + \beta(\Delta P)^s)$$

$$\Delta P(t) = \alpha_0 (1 + \beta(\Delta P)^s) \frac{\mu C_s Q^2}{A^2} t$$

$$\Delta P_{\text{total}} = \Delta P_{\text{cake}} + \Delta P_{\text{filter}}$$

$$\Delta P(t)_{\text{total}} = \alpha_0 (1 + \beta(\Delta P)^s) \frac{\mu C_s Q^2}{A^2} t + \frac{1}{K} \frac{m L Q}{A}$$

ΔP_{cake}

Rearrange :

$$\Delta P - \frac{1}{K} \frac{\mu L Q}{A} = \alpha \frac{\mu C_s Q^2}{A^2} + t$$

$$t = \frac{\Delta P - \frac{1}{K} \frac{\mu L Q}{A}}{\alpha \frac{\mu C_s Q^2}{A^2}}$$

2-9-2

Constant Pressure Filtration

$$\Delta P_{\text{cake}} = \alpha \frac{\mu C_s V}{A^2} \frac{dV}{dt}$$

$$\Delta P_{\text{total}} = \Delta P_{\text{cake}} + \Delta P_{\text{filter}}$$

$$\Delta P_{\text{total}} = \alpha \frac{\mu C_s V}{A^2} \frac{dV}{dt} + \cancel{\frac{1}{K} \frac{\mu \epsilon L}{A} \frac{dV}{dt}} + \frac{1}{K} \frac{\mu \epsilon L}{A} \frac{dV}{dt}$$

$$\Delta P = \frac{dV}{dt} \left(\alpha \frac{\mu C_s V}{A^2} + \frac{1}{K} \frac{\mu L}{A} \right)$$

$$\frac{dt}{dV} = \frac{1}{\Delta P} \left(\alpha \frac{\mu C_s V}{A^2} + \frac{1}{K} \frac{\mu L}{A} \right)$$

$$\int_{t_0}^t dt = \int_{V_0}^V \frac{1}{\Delta P} \left(\alpha \frac{\mu C_s V}{A^2} + \frac{1}{K} \frac{\mu L}{A} \right) dV$$

$$t - t_0 = \left[\frac{\alpha \mu C_s V^2}{2 \Delta P A^2} + \frac{\mu L}{K A \Delta P} V \right]_{V_0}^V$$

2-10-1

For a clean filter initially : (No flow yet)

$$t_0 = 0 ; V_0 = 0$$

$$t = \frac{\alpha \mu C_s V^2}{2 \Delta P A^2} + \frac{\mu L}{K A \Delta P} V$$

For industry

$$\frac{t}{V} = \frac{\alpha \mu C_s}{2 \Delta P A^2} V + \frac{\mu L}{K A \Delta P}$$

$$K_c = \frac{\alpha \mu C_s}{A^2 \Delta P} ; \quad \frac{1}{Q_0} = \frac{\mu L}{K A \Delta P}$$

$$\frac{t}{V} = \frac{1}{2} K_c V + \frac{1}{Q_0}$$

$$\hookrightarrow t = \alpha_0 \left(1 + \beta (\Delta P_{cake})^s \right) \frac{K_c}{2\alpha} V^2 + \frac{\mu L}{K A \Delta P} V$$

$$\Delta P_{cake} = \Delta P - \Delta P_{filter} = \Delta P - \frac{\mu L}{K A} \frac{dV}{dt}$$

Assume : $\Delta P_{filter} \ll \Delta P_{cake}$ for calculating α .

$$\frac{dV}{dt} = \Delta P \left[\alpha \frac{\mu C_s V}{A^2} + \frac{\mu L}{K A} \right]^{-1} = \left[\frac{K_c}{\cancel{\alpha}} V + \frac{1}{Q_0} \right]^{-1}$$

Multistep Filtration Process

- Two steps : 1. Constant Flow Rate
2. Constant Pressure

$$1. \Delta P_1 = \alpha(\Delta P_{cake}) \frac{\mu c_s Q^2}{A^2} t + \frac{1}{K} \frac{\mu L Q}{A}$$

or

$$t = \frac{\Delta P_1 - \frac{1}{K} \frac{\mu L Q}{A}}{\alpha(\Delta P_{cake}) \frac{\mu c_s Q^2}{A^2}}$$

2. From prior notes:

$$\int_{t_0}^t dt = \int_{V_0}^V \frac{1}{\Delta P_2} \left(\alpha \frac{\mu c_s V}{A^2} + \frac{1}{K} \frac{\mu L}{A} \right) dV$$

$$t - t_0 = \left[\alpha \frac{\mu c_s V^2}{2 \Delta P_2 A^2} + \frac{\mu L}{\Delta P_2 K A} V \right]_{V_0}^V$$

t_0 = time when the first step ends
or in other words when $\Delta P_1 = \Delta P_2$

$$V_0 = Q t_0$$

$$t = t_0 + \alpha \frac{\mu c_s}{2 \Delta P_2 A^2} [V^2 - V_0^2] + \frac{\mu L}{\Delta P_2 K A} (V - V_0)$$

$$\frac{\alpha M C_s}{A^2 \Delta P_2} = K_c ; \quad \frac{1}{Q_0} = \frac{\mu L}{K A \Delta P_2}$$

$$t = t_0 + \frac{K_c}{2} V^2 - \frac{K_c}{2} V_0^2 + \frac{1}{Q_0} V - \frac{1}{Q_0} V_0$$

$$\frac{K_c}{2} V^2 + \frac{1}{Q_0} V + \left(t_0 - t - \frac{K_c}{2} V_0^2 - \frac{1}{Q_0} V_0 \right) = 0$$

$$V = \frac{-\frac{1}{Q_0} \pm \sqrt{\left(\frac{1}{Q_0}\right)^2 - 4 \frac{K_c}{2} F}}{K_c}$$

Positive Root:

$$V = \frac{-\frac{1}{Q_0} + \sqrt{\frac{1}{Q_0^2} - 2 K_c F}}{K_c}$$

$$\text{when } V_0 = t_0 = 0 \rightarrow F = -t$$

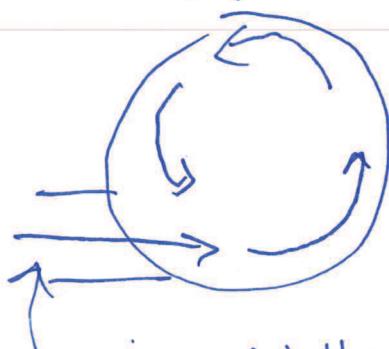
Centrifugal Separations

2 ways to create centrifugal force

- Rotate fluid
- Rotate vessel

Cyclone

Top View



Hydrocyclone - liquid carrier fluid

Tangentially introduced flow

Force Balance on a Particle w/ Centrifugal Force

$$m_p \frac{d^2 \vec{x}}{dt^2} = \sum_i \vec{F}_i = \vec{F}_{\text{centrifugal}} + \vec{F}_g - \vec{F}_{\text{drag}} - \vec{F}_{\text{buoyancy}}$$

in a centrifuge

$$m_p \frac{d^2 \vec{x}}{dt^2} = m_p g \hat{\mathbf{e}}_z + \underbrace{m_p \omega^2 r \hat{\mathbf{e}}_r}_{\text{centrifugal force}} - \vec{F}_{\text{drag}} - \vec{F}_{\text{buoyancy}}$$

$\hat{\mathbf{e}}_i$ = unit vector in the direction i

ω = rotation rate [=] $\frac{\text{rad}}{\text{s}}$

Assume : $F_{\text{centrifugal}} \gg F_g$

$$m_p \frac{d^2 r}{dt^2} = m_p \omega^2 r - C_D \frac{\rho u_p^2 A_p}{2} - \frac{m_p(\rho) \omega^2 r}{\rho_p}$$

Terminal Velocity (steady-state)

$$m_p \omega^2 r \left(1 - \frac{\rho}{\rho_p}\right) = C_D \frac{\rho u_p^2 A_p}{2}$$

Because centrifugation is often slow:

we assume low Reynolds #.

$$C_D = \frac{24}{Re} \quad \therefore Re = \frac{\rho u_p D_p}{\mu} \quad M$$

$$m_p \omega^2 r (1 - \frac{e}{e_p}) = \frac{24 \mu}{\rho \omega R D_p} \frac{\rho u_p^2 A_p}{2} = \frac{12 \mu u_p A_p}{D_p}$$

$$u_p = \frac{m_p \omega^2 r (1 - e/e_p) D_p}{12 \mu A_p} \neq \text{constant}$$

Centrifugal force:

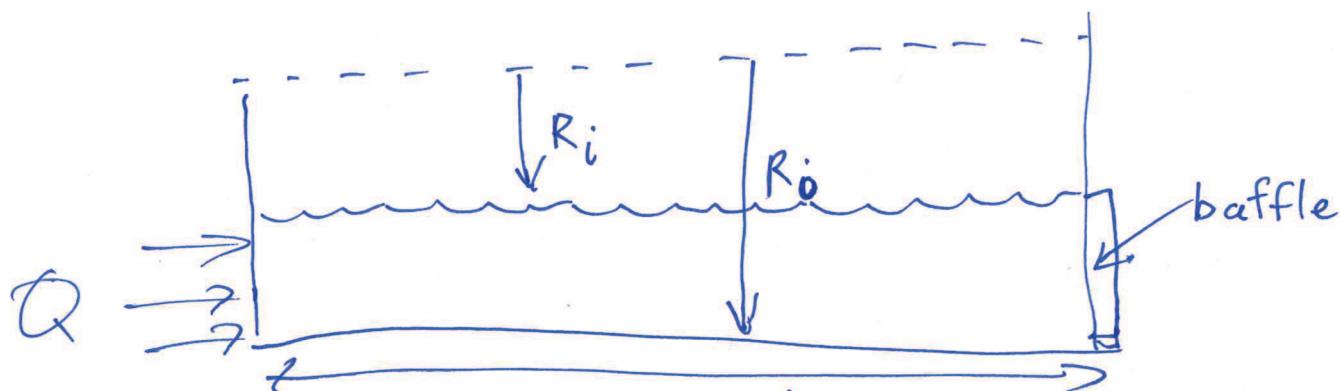
$$\text{Centrifuge: } m_p \omega^2 r$$

$$\text{Cyclone: } m_p \frac{u_{tan}^2}{r}$$

Pay attention to
radial dependence

~~Centrifug~~

Ideal Continuous Centrifuge



$$Q = \text{flow rate } \left[\frac{m^3}{s} \right] L$$

Residence Time

$$t_R = \frac{V}{Q} = \frac{\pi (R_o^2 - R_i^2) L}{Q}$$

terminal velocity of a particle:

$$u_p = \frac{m_p \omega^2 r (1 - e/e_p) D_p}{12 \mu A_p} = \frac{dr}{dt}$$

$$\int_{r_i}^{r_o} \frac{dr}{r} = \int_0^t \frac{m_p \omega^2 (1 - e/e_p) D_p}{12 \mu A_p} dt$$

$$\ln(r) \Big|_{r_i}^{r_o} = \frac{m_p \omega^2 (1 - e/e_p) D_p}{12 \mu A_p} t$$

$$\ln\left(\frac{r_o}{r_i}\right) = \frac{m_p \omega^2 (1 - e/e_p) D_p}{12 \mu A_p} t$$

$$t_s = \frac{12 \mu A_p \ln(r_o/r_i)}{m_p \omega^2 (1 - e/e_p) D_p}$$

$$1000 \text{ RPM} \cdot \frac{\text{min}}{60 \text{ s}} \cdot \frac{2\pi}{\text{rev}}$$

Because this is non-linear we instead define a "cut point" for the separator

→ Flow rate at which particles of the

"cut diameter" will just settle from

$$r_c = \frac{R_o + R_i}{2} \text{ to the edge } \approx r_o = R_o. \quad 2-13-1$$

$$t_s = \frac{12\mu A_{p,c} \ln(R_o/(R_o + R_i)/2)}{m_{p,c} \omega^2 (1 - e/e_p) P_{p,c}} = \frac{V}{Q_c}$$

$$Q_c = \frac{\pi (R_o^2 - R_i^2) L m_{p,c} \omega^2 (1 - e/e_p) P_{p,c}}{12\mu A_{p,c} \ln(\frac{2R_o}{R_o + R_i})}$$

Capacity of a centrifuge to operate
at with a particular cut diameter.

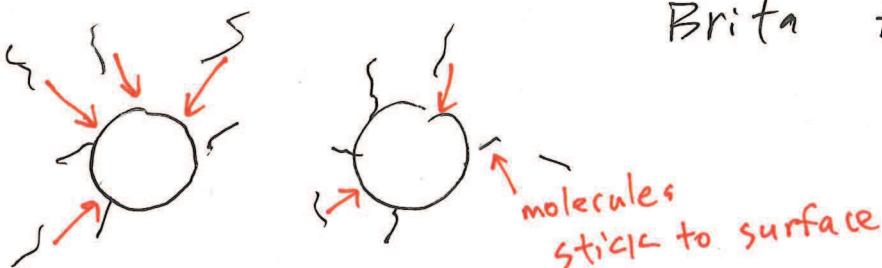
2-13-2

Sorption

Adsorption - stick to surface of material

Absorption - penetrates into material

Brita filter = adsorption



Chromatography

Mobile phase = gas or liquid

Stationary phase = liquid or solid

2-13-2 + 2-14-1

Why use chromatography?

Pros:

- very high selectivity
- Relatively short columns
- Very high purity (pharmaceuticals)
- No heating required
- Low energy consumption

Cons:

- Relatively expensive (packing cost)
- Relatively low throughput

Retention Time

t_m - elution time for mobile phase

t_r - retention time (total time in the column)

$$\frac{t_m}{t_r} = \frac{n_m}{n_m + n_s} = \frac{1}{1 + \frac{n_s}{n_m}} = \frac{1}{1 + K'}$$

$$\frac{n_s}{n_m} = \frac{q V_s}{c V_m} = \frac{q (1-\epsilon) X}{c \epsilon X} = \frac{1-\epsilon}{\epsilon} K$$

$$t_r = t_m (1 + K') = t_m \left(1 + \frac{1-\epsilon}{\epsilon} K\right)$$

n_m = number of moles in the mobile phase

n_s = number of moles in the stationary phase

k' = molar partition coefficient

q = concentration in stationary phase [=] $\frac{\text{mol}}{\text{m}^3}$ or $\frac{\text{kg}}{\text{m}^3}$

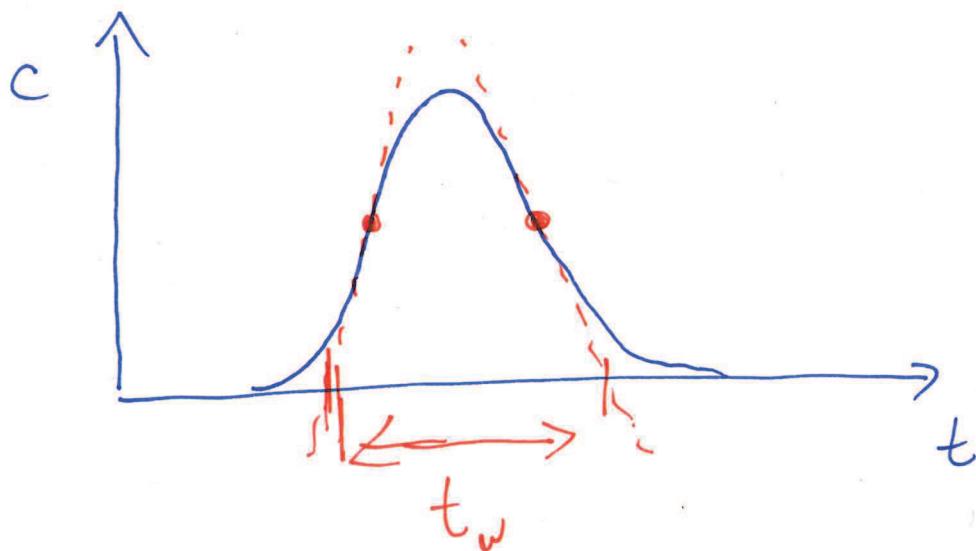
C = concentration in mobile phase [=] $\frac{\text{mol}}{\text{m}^3}$ or $\frac{\text{kg}}{\text{m}^3}$

ϵ = porosity in the column (including intra-particle porosity)

K = partition coefficient based on concentrations

2-14-3

Peak Broadening



Broadening occurs: due to

- Axial diffusion
- Departure from plug flow
- Mass transfer resistances in equilibration

2-15-1

Dispersion in peak broadening is a function of the mobile phase velocity.

Therefore a given column there will be optimal flow velocity.

Resolution for two peaks :

$$R = \frac{t_{R,2} - t_{R,1}}{0.5(t_{w,2} + t_{w,1})}$$

$$R = 1 \text{ when } \frac{t_{w,2} + t_{w,1}}{2} = t_{R,2} - t_{R,1}$$

$R < 1$ - poor separation

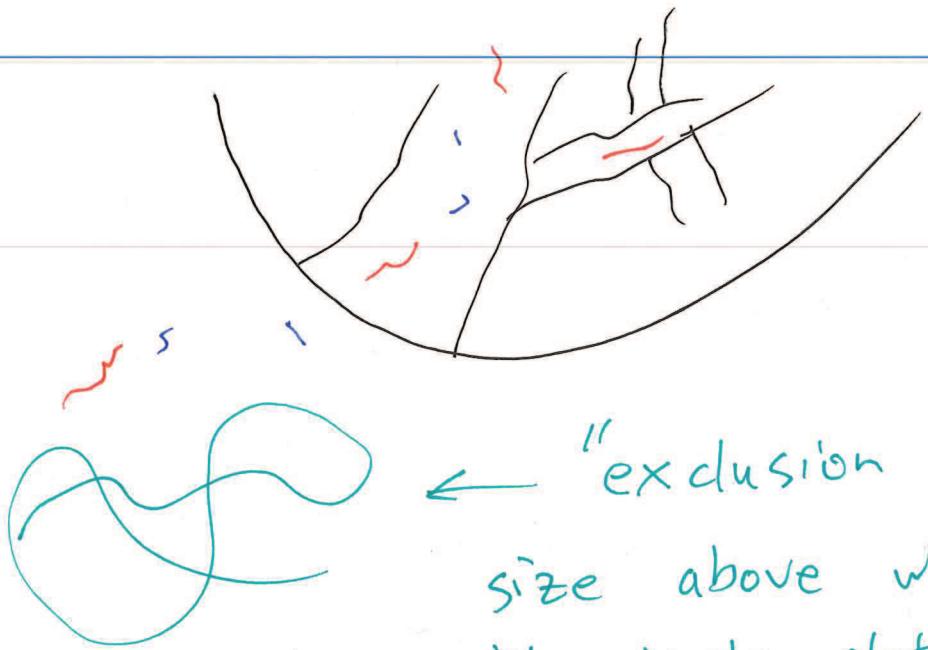
$R > 1$ - better separation

Two Types of Chromatography

口 Size Exclusion Chromatography

stationary phase =





"exclusion limit"
size above which the solute
will simply elute with the
mobile phase.

Ion Exchange chromatography



For deionized water



R = stationary phase

X = solute

In a column: Adsorption

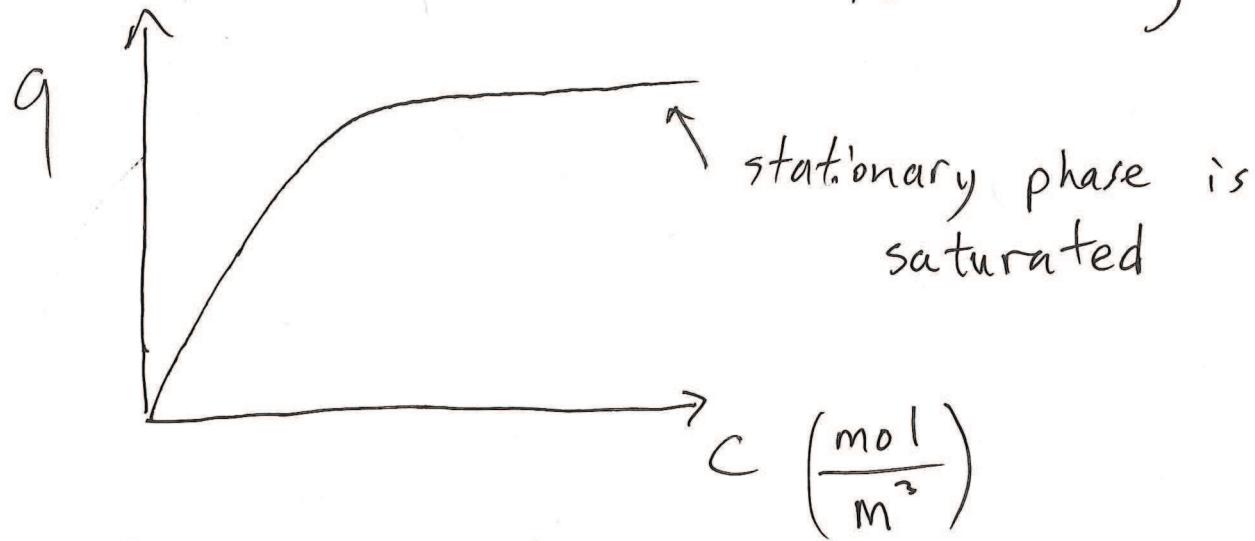
C = concentration of solute in mobile phase

$$C + S \rightleftharpoons q$$

S = empty area on/in stationary phase

q = concentration of solute in stationary phase

For monolayer adsorption



Property $q \in] \frac{\text{mol}}{\text{m}^2} \rightarrow \text{but often } q \in] \frac{\text{mol}}{\text{m}^3}$

the volume of the stationary phase is used in place of the surface area.

Volume of column $\textcolor{red}{A} = V_{\text{mobile}} + V_{\text{stationary}}$

Models for Adsorption = Isotherms

simplest model: $q = K$ ← not very useful

Linear model: $q = KC$

- Good when q is small

Freundlich: $q = m C^{\frac{1}{n}}$

Langmuir Model: $q = \frac{q_{\infty} C}{K_{eq} + C}$

q_{∞} = maximum adsorbed concentration

↑ These models are for single components

- Multiple components require multiple component isotherm model
- These data can be used to measure surface area of packing.