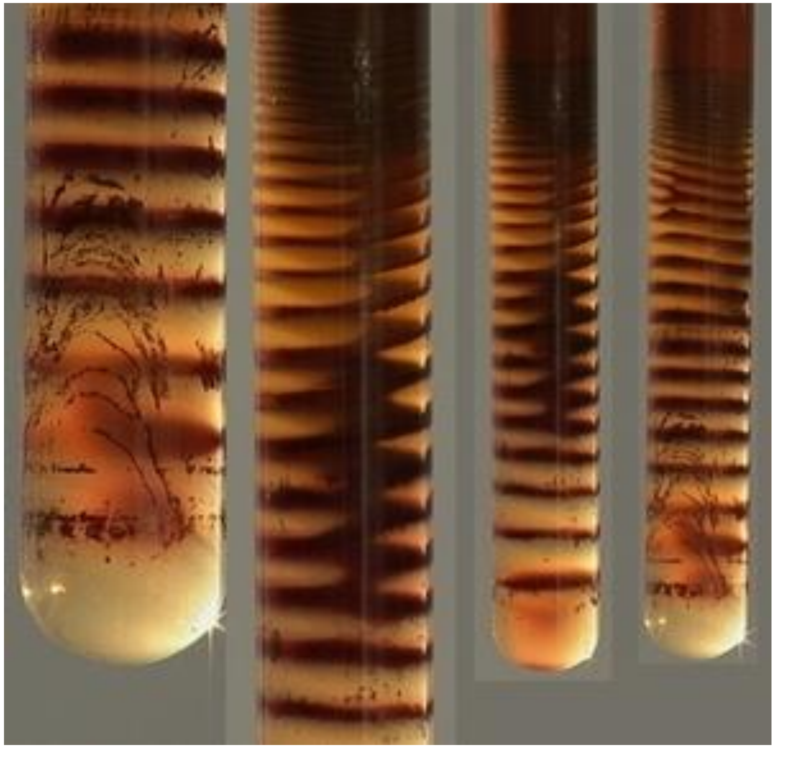
- Project
- Describing Methods

Reactive Transport

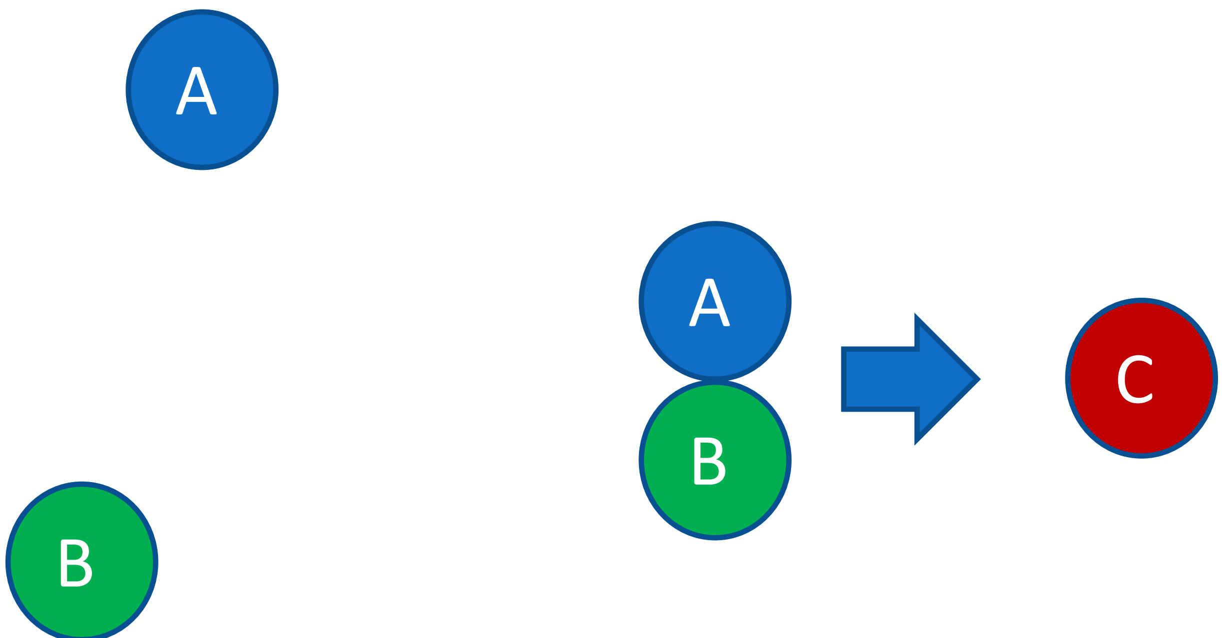


Silver dichromate forming Leisegang rings in a test tube experiment

Reactive Transport

Conceptual

A+B→C



Reactions require transport

Conceptual Model

A+B←→C

Reaction Rate

- Intrinsic rate
- Transport-- combine reactants, remove products

Processes

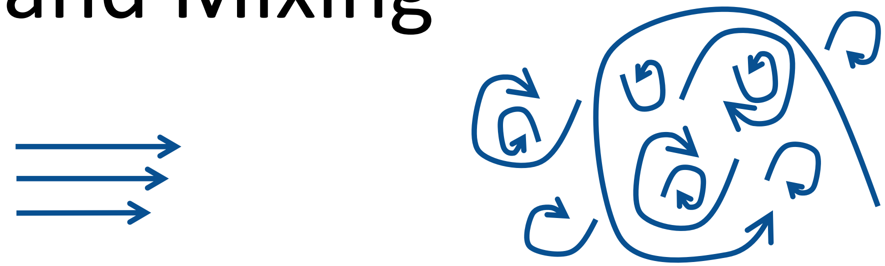
- Advection
- Dispersion
- Diffusion

Scale

Time scale for reaction, t_r
Time scale for transport, t_t

Damkohler Numbers: t_t/t_r
Da_I: t_{advect}/t_{react}
Da_{II}: $t_{disperse}/t_{react}$

Reaction Locations and Mixing



Bulk Material

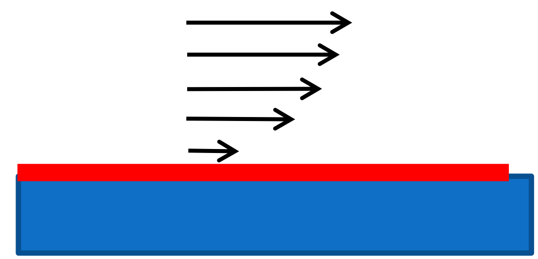
Fluid— Multi-scale mixing, dispersion, length scale

Solid– Diffusion dominant

Interfaces

Fluid-Solid

Liquid-Gas



No flow at interface→diffusion

Mass transfer over stagnant layer

Important Scales

Time scales

advection: $t_{cf} = \dfrac{L}{v}$

dispersion: $t_{cd} = \dfrac{L^2}{D}$

reaction: $t_{cr} = \dfrac{C_o}{R}$

Peclet number, *Pe* (advection/diffusion rate): $\dfrac{t_{cd}}{t_{ca}} = \dfrac{L^2}{D}\dfrac{v}{L} = \dfrac{vL}{D}$

Damkohler I, Da_I (reaction/advection rate): $\dfrac{t_{ca}}{t_{cr}} = \dfrac{\frac{L}{v}}{\frac{C_o}{R}} = \dfrac{RL}{vC_o}$; 1st order, $k_1 = R / C_o$

Damkohler II, Da_{II} (reaction/diffusion rate): $\dfrac{t_{cd}}{t_{cr}} = \dfrac{\frac{L^2}{D}}{\frac{C_o}{R}} = \dfrac{RL^2}{DC_o}$

Coupled effects

Reaction ←→Transport

- Reaction changes K , porous media flow

  karst, diagenesis

- Reaction changes *D*, subsequent reaction rate

  Biofouling, reactor performance

- Heat affects reaction rate

  Geothermal, remediation

- Other chemicals, competing/synergistic reaction

  Bioprocesses, waste water treatment

- Precipitates affect density, flow

  Flocculation, mixtures

- Stress affects reaction, reduces K, flow

  Diagenesis, sintering

Cave in Bali

Biofouling in pipe

Geyser in Yellowstone

Styolites in limestone

Coupled effects

Reaction changes K

A+B→C

Precipitation-Dissolution-change porosity

Couple through porosity, ϕ

Kozeny-Carmen equation $$k = k_o \left(\frac{\phi}{\phi_o}\right)^3 \left(\frac{1-\phi_o}{1-\phi}\right)^2$$

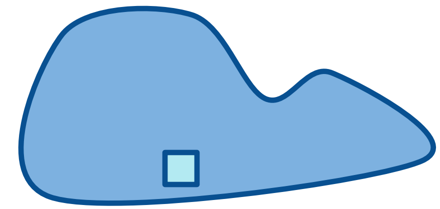
Verma Pruess (1988) $$k = k_o \left(\frac{\phi - \phi_c}{\phi_o - \phi_c}\right)^n$$

Permeable reactors

Karst

Governing Equation

Advection-Dispersion-Reaction



$$c = \frac{M_s}{L_c^{\,3}}$$

$$\nabla \cdot \Gamma + \frac{\partial c}{\partial t} = \mathcal{S}$$

$$\Gamma = \mathcal{D} + \mathcal{A}$$

Storage $\quad c = C \quad \frac{\partial c}{\partial t} = \frac{\partial C}{\partial t}$

Advective Flux $\quad \mathcal{A} = \mathbf{q}C$

Diffusive Flux (Fick's Law) $\quad \mathcal{D} = -D^{*}\nabla C$

Dispersive Flux $\quad \mathcal{D}_h = -D_h \nabla C$

Source $\quad \mathcal{S}$=R

Governing $\quad \nabla \cdot (-\left(D^{*} + D_h\right)\nabla C) + \nabla \cdot \mathbf{q}C + \frac{\partial C}{\partial t} = R$

$$\frac{\partial C}{\partial t} = \nabla \cdot (D\nabla C) - \nabla \cdot \left(\mathbf{q}C\right) + R$$

homogeneous, flux divergence free

$$\frac{\partial C}{\partial t} = D\nabla^2 C - \mathbf{q} \cdot \nabla C + R$$

Simulation of Advection-Dispersion-Reaction

$$\frac{\partial C}{\partial t} = D\nabla^2 C - \mathbf{q} \cdot \nabla C + R$$

Governing

$$C = N_1$$
$$\mathbf{n} \cdot J = 0$$
$$\mathbf{n} \cdot J = N_2$$
$$\mathbf{n} \cdot qC = 0$$
$$\mathbf{n} \cdot qC = N_3$$
$$\mathbf{n} \cdot J = -k(C - N_4)$$

Boundary

Dirichlet, Specify Conc

Neuman, Specify diffusive flux

Specify advective flux

Cauchy, flux proportional to gradient

Initial Conditions

$C(x,y,z,0) = C_i$

Parameters

D: hydrodynamic dispersion

R: reaction rate→kinetics

μ, ρ: fluid properties

k: permeability

q, *P* Flow, pressure

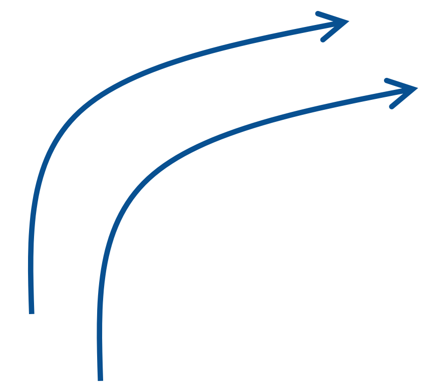
T Temperature

σ Stress

C_i other conc

Idealized Conceptual Models

Case 1. 1-D flow, Steady



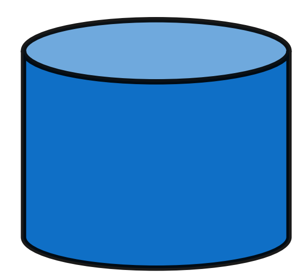
Steady state, *C* changes with *x*, not *t*

Plug flow reactor

Along streamtube/flowpath

Reactive wall

Case 2. Thoroughly mixed, transient

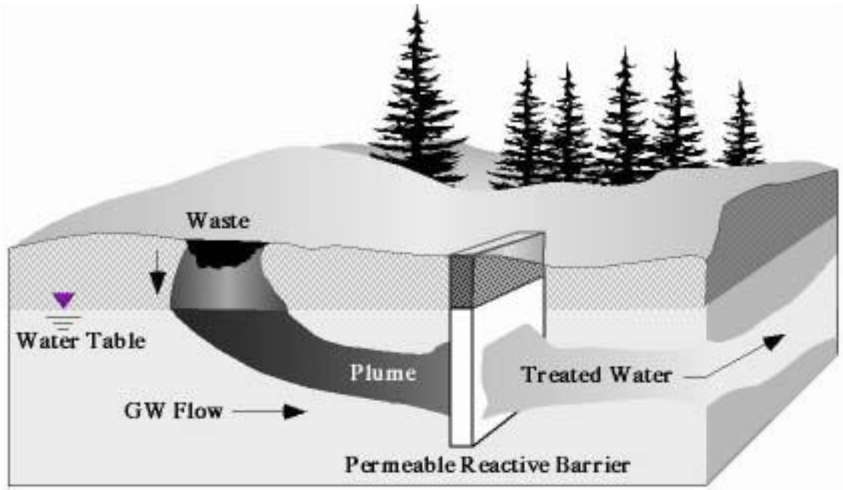


Transient, *C* changes with t, not x

Tank reactor, CSTR

Pore, Pond, Lake, Atmosphere

Permeable reactive barrier

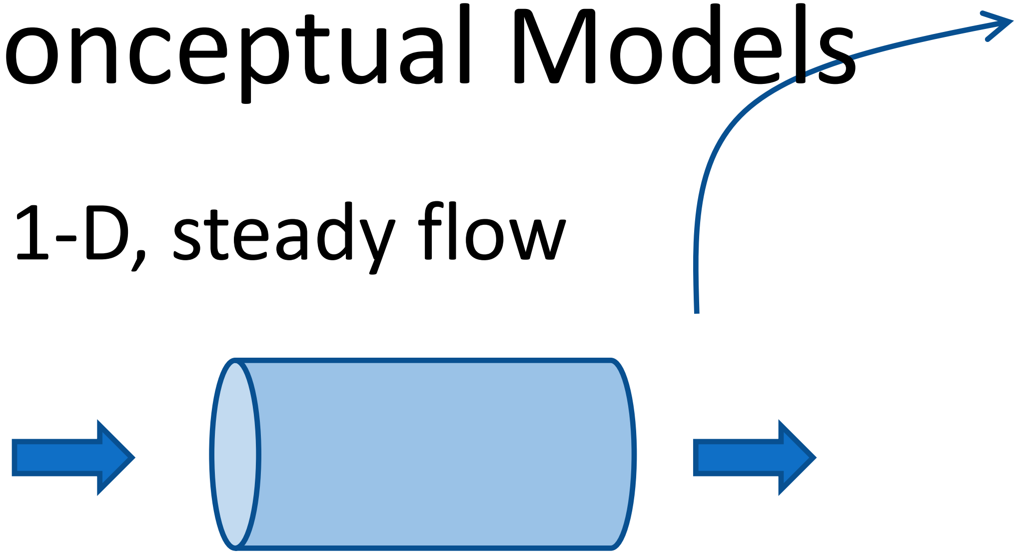


Permeable material that sorbs or breaks down contaminants on contact.

- Metallic iron→ reduce chlorinated solvents
- Limestone, phosphate→ precipitate metals
- Activated carbon, zeolites→ sorb contaminants
- Compost, mulch, sawdust→biodegradation

Idealized Conceptual Models

1. Reaction during 1-D, steady flow



$$\nabla \cdot \Gamma + \frac{\partial C}{\partial t} = R$$

$$\Gamma = qC = \frac{Q}{A} C$$

$$\nabla \cdot \Gamma = \frac{Q}{A} \nabla C = \frac{Q}{A} \frac{dC}{dx}$$

$$\frac{dC}{dt} = 0$$

$$R = -k_1 C n \qquad \frac{1}{T} \frac{M_s}{L_f^3} \frac{L_f^3}{L_c^3}$$

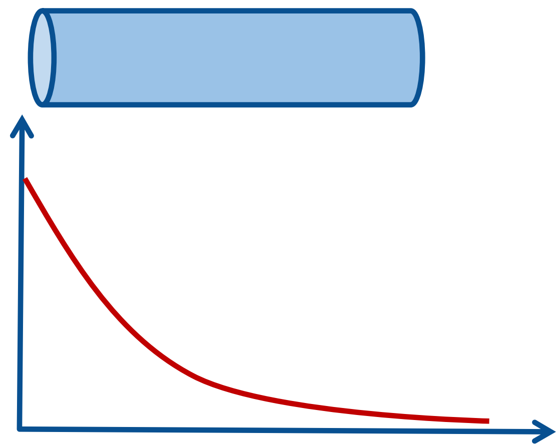
$$\nabla \cdot \Gamma + \frac{\partial C}{\partial t} = R \;\Rightarrow\; \frac{Q}{A} \frac{dC}{dx} = -k_1 C n$$

Idealized Conceptual Models

Case 1. Reaction during 1-D flow

$$\frac{dC}{dx} = -\frac{Ak_1 n}{Q} C \; ; \; C(0) = C_o$$

$$C = C_{in} e^{-\frac{k_1 n x}{q}} = C_{in} e^{-\frac{k_1 x}{v}}$$



Time scale for reaction $\frac{1}{k_1}$

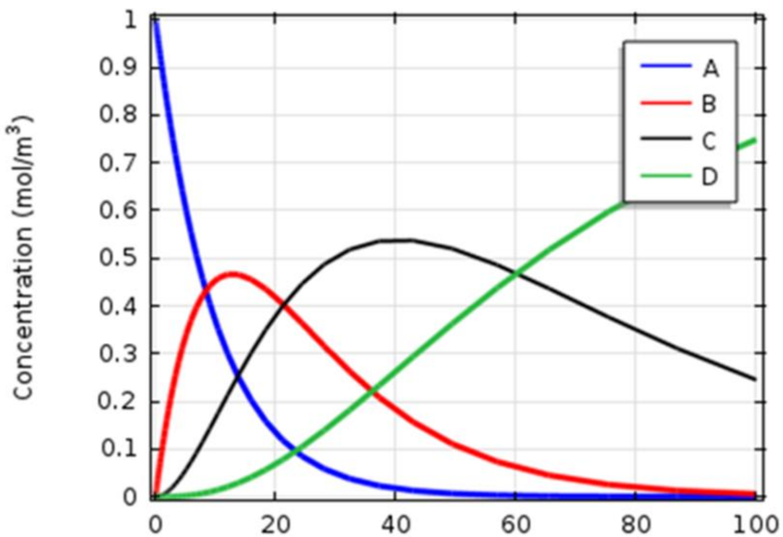
Time scale for advection (travel time): $\frac{L}{v} = \frac{Ln}{q}$

$$\frac{C}{C_{in}} = e^{-\frac{k_1 x}{v}} = e^{-\frac{k_1 n L}{q}\frac{x}{L}} = e^{-\frac{\text{travel time}}{\text{reaction time}}\frac{x}{L}} = e^{-Da_I x'}$$

More general case

other reactions, non-uniform v

First-order Decay Chain



Distance along flowpath

$$t = \frac{x}{v} = \int_0^x \frac{1}{v} dx$$ take integral along flowpath

Temporal changes map out to spatial zones

Non-ideal factors

Preferred flowpaths

Incomplete contact of reactants, affect k1

Non-ideal interface,

Water, precipitates, longer diffusion time

Storage along tube without reaction

Matrix diffusion

Reactions alter flow

Precipitation, dissolution, biofilm

Result:

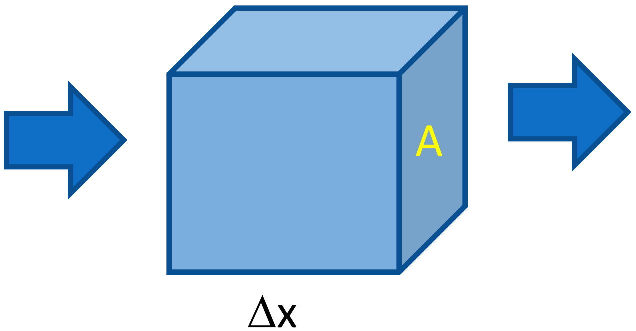
q, k_1, D change with time/space

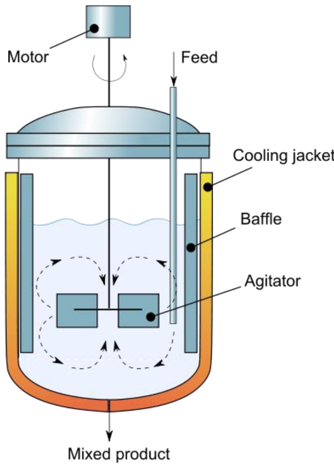
Idealized Conceptual Model

Case 2. Reaction in mixed region

CSTR, Lake, Ocean, pore

$$\nabla \cdot \Gamma + \frac{\partial C}{\partial t} = R$$



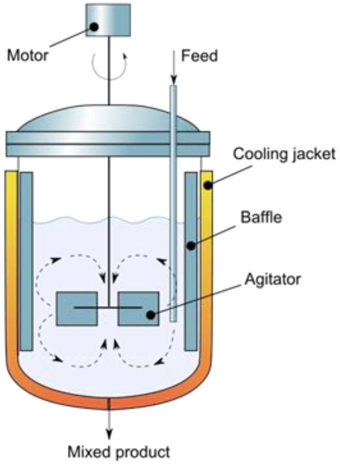


$$\Gamma = qC = \frac{Q}{A}C$$

$$\nabla \cdot \Gamma = \frac{Q}{A}\nabla C = \frac{Q}{A}\frac{\Delta C}{\Delta x} = \frac{Q}{V}\frac{(C - C_{in})}{}$$

$$R = -k_1 C$$

Reaction in a mixed region



$$C = C_{in}\frac{1}{\left[1+\frac{k_1 V}{Q}\right]}\left(1-e^{-\frac{Q}{V}\left[1+\frac{k_1 V}{Q}\right]t}\right)+C_o e^{-\frac{Q}{V}\left[1+\frac{k_1 V}{Q}\right]t}$$

$$\frac{Q}{V} = \frac{1}{t_r} = \frac{1}{\text{residence time}}$$

$$k_1 = \frac{1}{\text{reaction time}}$$

$$\frac{Vk_1}{Q} = \frac{\text{residence time}}{\text{reaction time}} = Damkohler\ number\ \mathrm{Da}_{\mathrm{I}}$$

No reaction, k_1=0, conservative tracer

$$C = C_{in}\left(1-e^{-\frac{Q}{V}t}\right)+C_o e^{-\frac{Q}{V}t}$$

Residence Time Distribution

Pulse tracer test

$$\Delta M = C_{out}(t) Q \Delta t$$ increment of mass out

$$\frac{\Delta M}{M_T} = \frac{C_{out}(t) Q}{M_T} \Delta t$$ normalized

$$\frac{\Delta M}{M_T} = E(t) \Delta t$$ define RTD

$$E(t) = \frac{C_{out}(t) Q}{M_T}$$ Residence Time Distribution

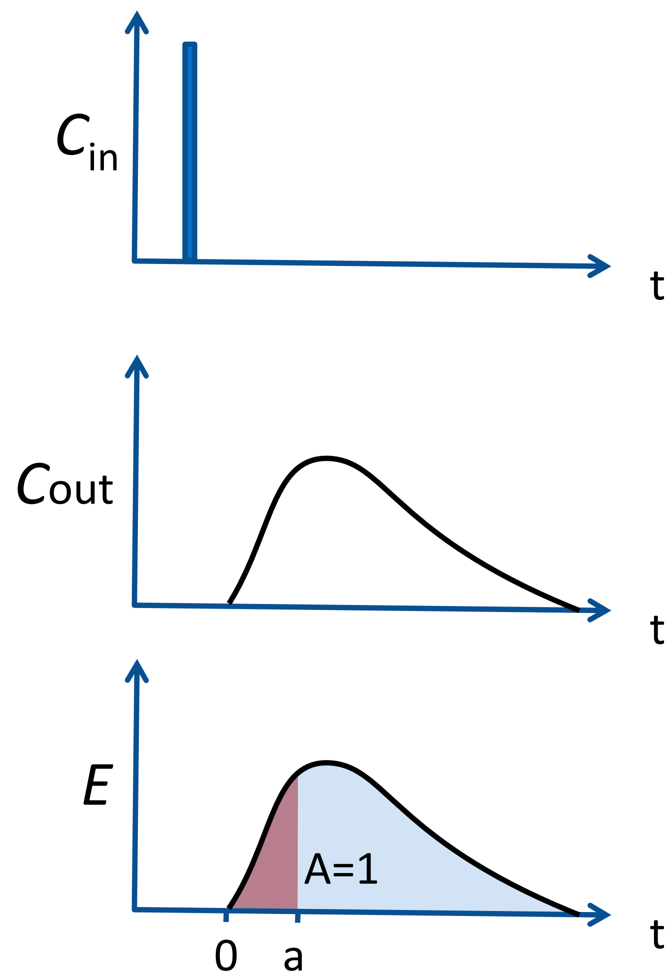
$$M_T = \int_0^\infty C_{out}(t) Q dt$$ Cumulative mass out

$$E(t) = \frac{C_{out}(t) Q}{\int_0^\infty C_{out}(t) Q dt}$$ Area = 1

if Q is constant

$$E(t) = \frac{C_{out}(t)}{\int_0^\infty C_{out}(t) dt}$$

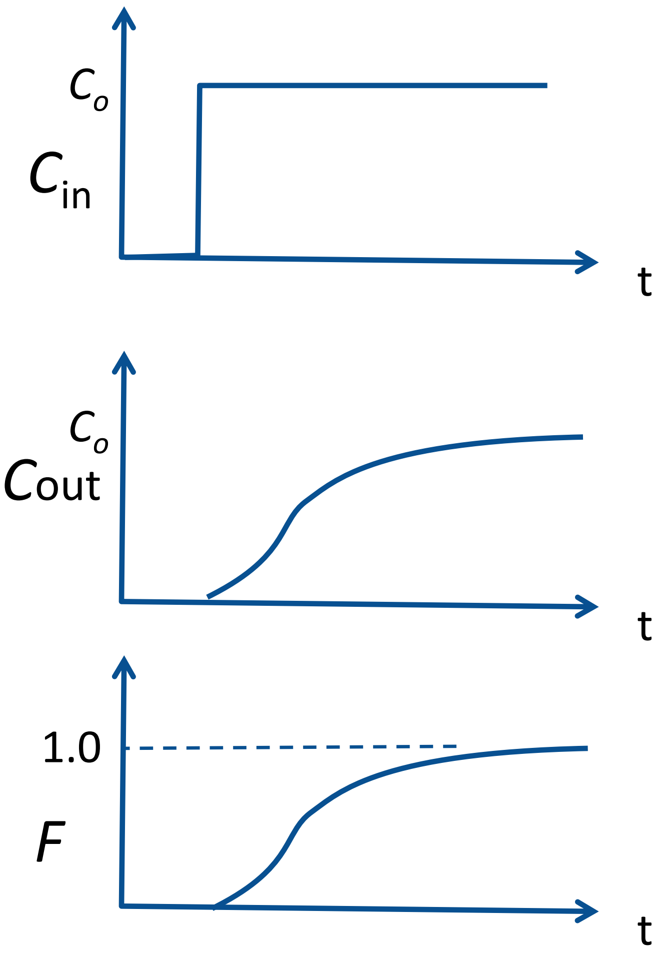
$$F(t) = \int_a^b E(t) dt$$ Cumulative RTD



Residence Time Distribution

Step tracer test

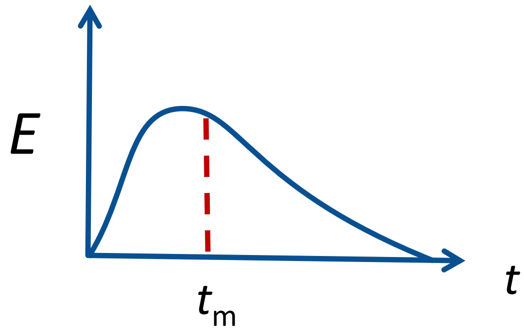
$$F(t) = \frac{C(t)}{C_o}$$ Cumulative RTD

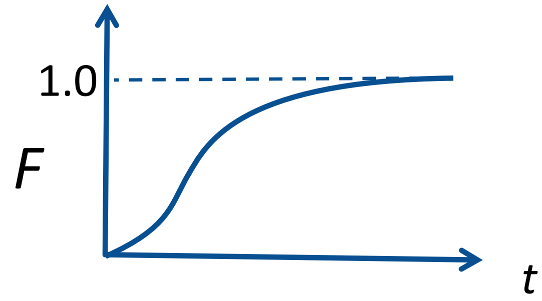


Residence Time Distribution

$$F(t) = \int_a^b E(t)dt$$ Cumulative RTD

$$E(t) = \frac{dF(t)}{dt}$$ RTD





Moments of RTD

mean residence time (first moment)

$$t_m = \int_0^\infty tE(t)dt$$

Variance of the residence time (second moment)

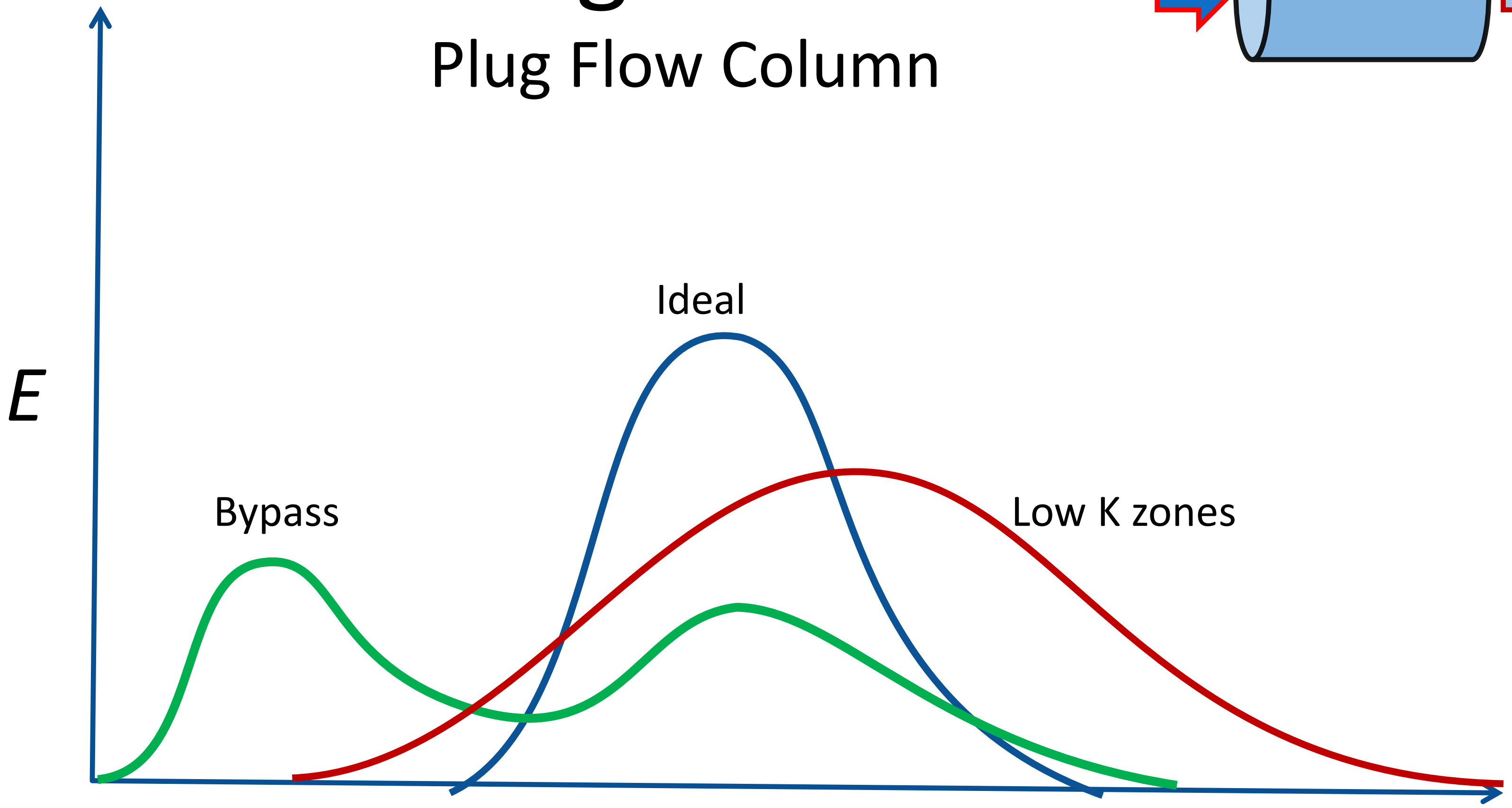
$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t)dt$$

Skewness of the residence time (third moment)

$$s^3 = \frac{1}{\sigma^{3/2}} \int_0^\infty (t - t_m)^3 E(t)dt$$

Diagnostics

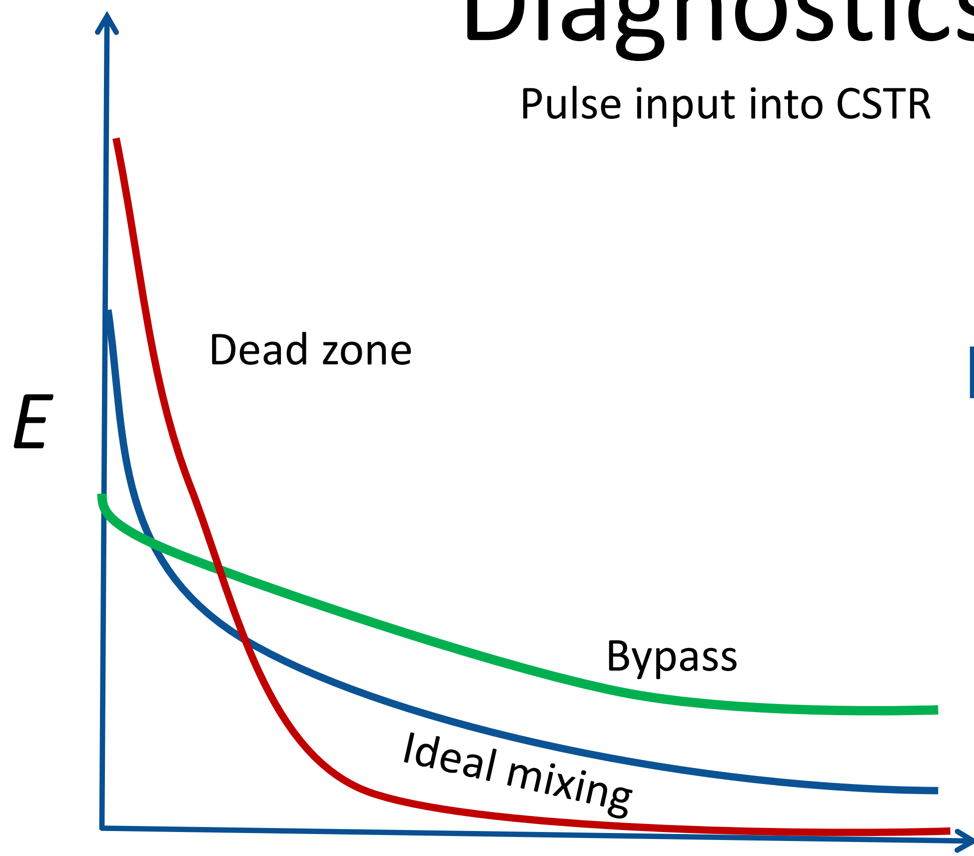
Plug Flow Column

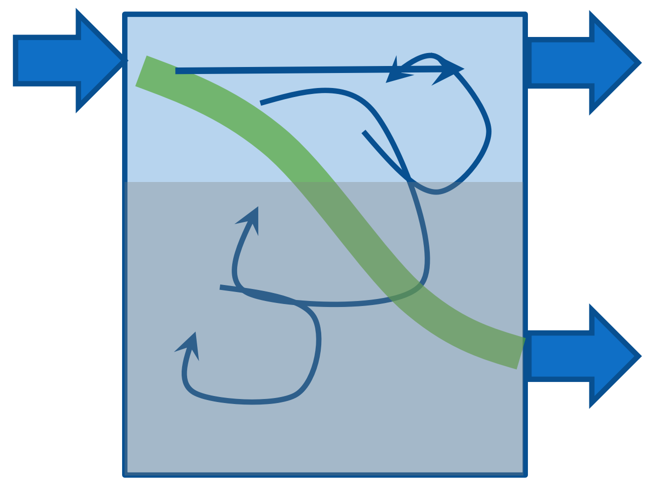


How to use moments to diagnose?

Diagnostics

Pulse input into CSTR





Residence time and Reaction

- Residence time = time molecule in reactor
- First-order rxn only depends on residence time
- Other rxn also depend on mixing
- Macro-mixing→flow paths
- Micro-mixing→mechanical dispersion, diffusion