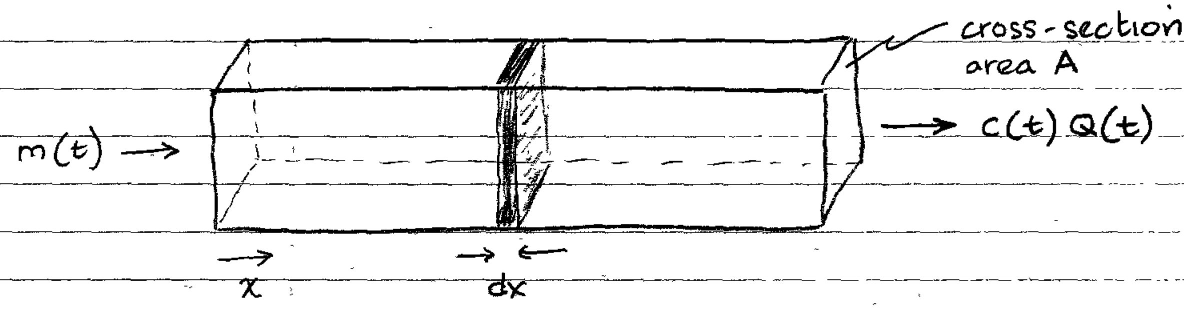
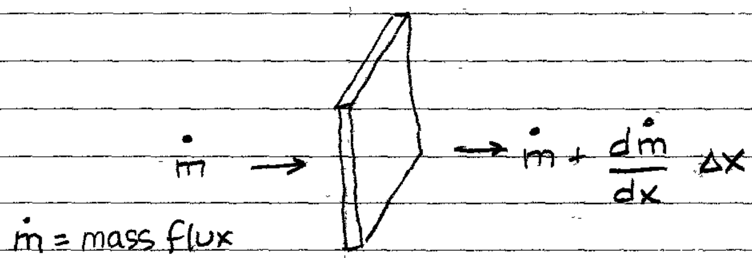
# Lecture 4 - Reactor vessels (con't)

## Dispersed flow reactor




Note: reactor is one-dimensional
Dimension $x$ factors into behavior

Solution for mass balance over slice dx




Slice experiences two mechanisms of mass transport:

1. Advection $= AUc$
2. Dispersion $= AD\frac{\partial c}{\partial x}$

$$\frac{\text{mass in}}{\text{unit time}} - \frac{\text{mass out}}{\text{unit time}} - \frac{\text{mass reacted away}}{\text{unit time}} = \frac{\text{change in mass}}{\text{unit time}}$$

$$\dot{m} - \left(\dot{m} + \frac{\partial \dot{m}}{\partial x}\right)\Delta x - \Delta V c K = \Delta V \frac{\partial c}{\partial t}$$

$$\dot{m} = Qc - AD\frac{\partial c}{\partial x} = AUc - AD\frac{\partial c}{\partial x}$$

$$\frac{\partial \dot{m}}{\partial x} = AU\frac{\partial c}{\partial x} - AD\frac{\partial^2 c}{\partial x^2}$$ assuming const A, U, D

Return to mass balance

$$\dot{m} - \left(\dot{m} + \frac{\partial \dot{m}}{\partial x}\right)\Delta x - \Delta \forall c K = \Delta \forall \frac{\partial c}{\partial t}$$

$$- AU \frac{\partial c}{\partial x} \Delta x + AD \frac{\partial^2 c}{\partial x^2} \Delta x - \Delta \forall c K = \Delta \forall \frac{\partial c}{\partial t}$$

Divide by $\Delta \forall$ and note $\frac{\Delta x}{\Delta \forall} = \frac{1}{A}$

$$- U \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} - Kc = \frac{\partial c}{\partial t}$$

$$\frac{\partial c}{\partial t} + U \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - KC$$

For steady state $\frac{\partial c}{\partial t} = 0$

For plug flow $D = 0$

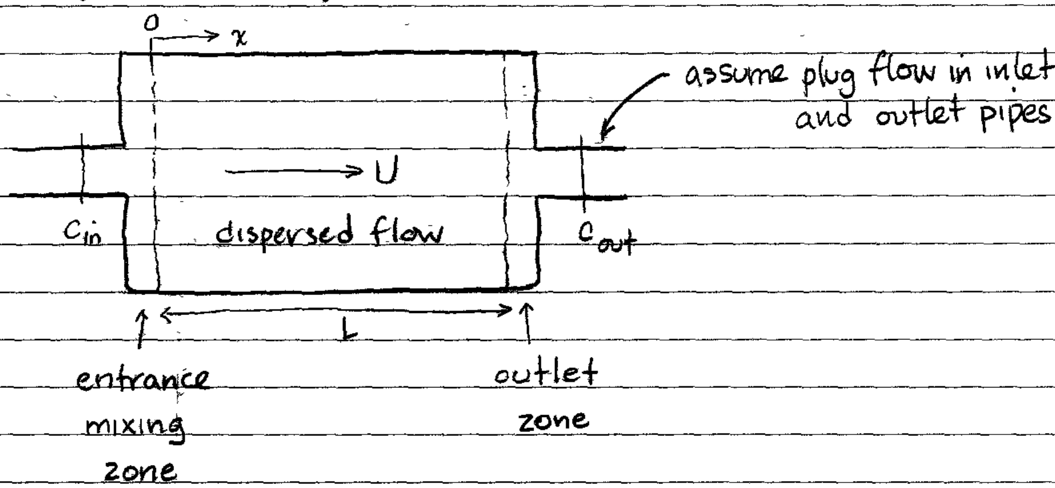
$$\rightarrow \quad U \frac{\partial c}{\partial x} = -KC$$

$$\frac{c(x)}{C_{in}} = e^{-\frac{Kx}{U}}$$

$$\frac{c}{C_{in}} = e^{-Kt_R} \quad \text{at outlet}$$

Solution for dispersed flow reactor with spike input

$$\frac{\partial c}{\partial t} + U\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} - Kc$$




For the configuration as sketched small inlet and outlet pipes relative to tank cross section, we can assume plug flow in the pipes (i.e. dispersion is negligible).

Therefore at inlet

$$Qc\Big|_{in} = Qc - DA\frac{\partial c}{\partial x}\Big|_{x=0}$$

At outlet:

$$Qc - DA\frac{\partial c}{\partial x}\Big|_{x=L} = Qc\Big|_{out}$$

At the outlet, we can assume dispersion into the pipe is much smaller than advection, therefore

$$Qc\Big|_{x=L} = Qc\Big|_{out}$$

or equivalently $\frac{\partial c}{\partial x} = 0$ at $x = L$

Thomas and McKee (1944) give solution to this equation for a spike input – see page 5 with $K=0$

The solution is a function of the Peclet Number, the ratio of advective mass flux to dispersive mass flux:

$$Pe = \frac{QL}{AD} = \frac{UL}{D}$$

The curves are used to estimate the dispersion coefficient for actual reactors by fitting the response curves to field data.
Notice that $Pe = 2$ curve is similar to radioactive tracer curve used to illustrate FMT

Note limiting cases:

as $D \rightarrow 0$ $Pe \rightarrow \infty$ Reactor is plug flow

as $D \rightarrow \infty$ $Pe \rightarrow 0$ Reactor is FMT

D is determined in practice by field tests but can be estimated with empirical equation by Liu (1977)

Longitudinal dispersion coefficient for open-channel flow:

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

$R_H$ = hydraulic radius

Reference: Liu, H., 1977. Predicting dispersion coefficient for streams. Journal of the Environmental Engineering Division, ASCE. Vol. 103, No. EE3, Pg. 59. February 1977.

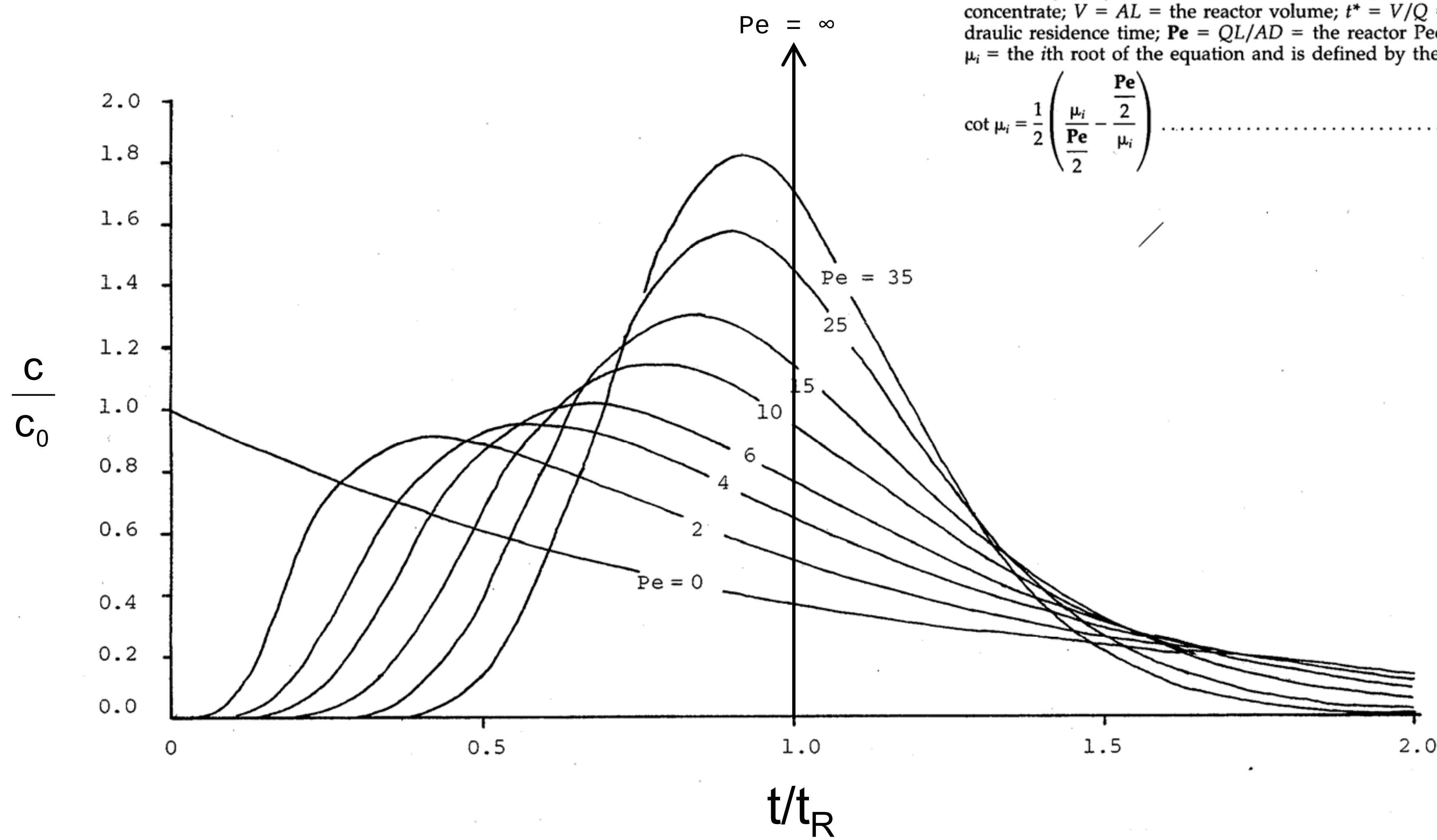
# Dispersed flow reactor response to spike input

The solution of Eq. 3 for a pulse concentrate input to a reactor with these boundary conditions is given by Thomas and McKee (19) as

$$\frac{c}{c_0} = 2\sum_{i=1}^{\infty}\left[\frac{\mu_i\left(\frac{\mathbf{Pe}}{2}\right)\sin\mu_i + \mu_i\cos\mu_i}{\left[\left(\frac{\mathbf{Pe}}{2}\right)^2 + \mu_i^2 + \mathbf{Pe}\right]}\cdot\exp\left(\frac{\mathbf{Pe}}{2} - \frac{\left(\frac{\mathbf{Pe}}{2}\right)^2 + \mu_i^2}{\mathbf{Pe}}\right)\frac{t}{t^*}\right] \quad (5)$$

in which $c_0 = M/V$ = a reference concentration; $M$ = the mass of input concentrate; $V = AL$ = the reactor volume; $t^* = V/Q$ = the reactor hydraulic residence time; $\mathbf{Pe} = QL/AD$ = the reactor Peclet number; and $\mu_i$ = the $i$th root of the equation and is defined by the implicit relation

$$\cot\mu_i = \frac{1}{2}\left(\frac{\mu_i}{\frac{\mathbf{Pe}}{2}} - \frac{\frac{\mathbf{Pe}}{2}}{\mu_i}\right) \quad (5a)$$



Wehner and Wilhelm solve the steady-state equation for continuous mass inflow (constant concentration)

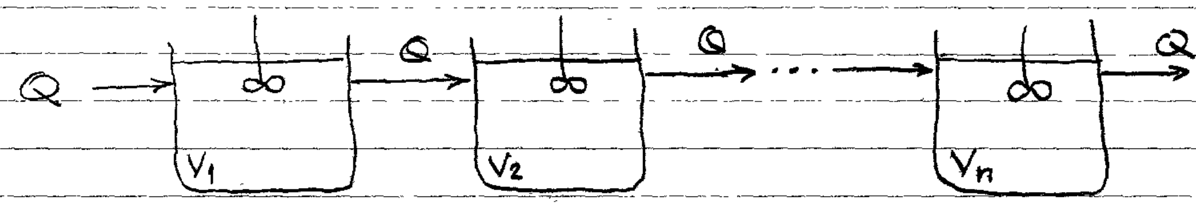
$$\frac{c_L}{c_0} = \frac{4a \exp(Pe/2)}{(1+a)^2 \exp(a\,Pe/2) - (1-a)^2 \exp(-a\,Pe/2)}$$

$$\text{where } a = \left(1 + \frac{4 k t_R}{Pe}\right)^{1/2}$$

Treatment efficiency varies between limit of Plug Flow Reactor ($Pe = \infty$) and Fully-mixed Tank ($Pe = 0$) – see graphs pg 7 and 8

- Fully-mixed tanks in series

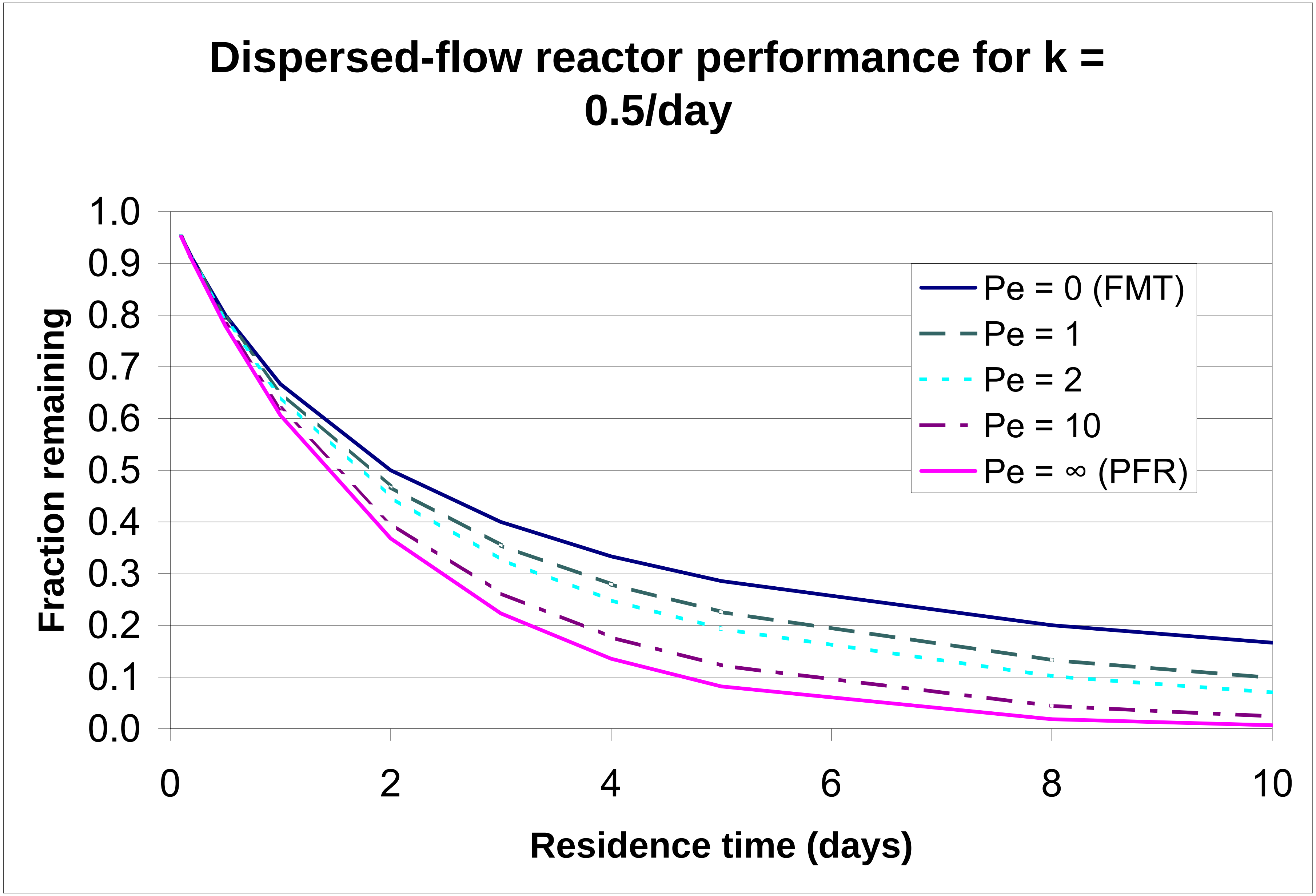
Can approximate dispersed-flow or even plug-flow reactors by putting FMT's in series:



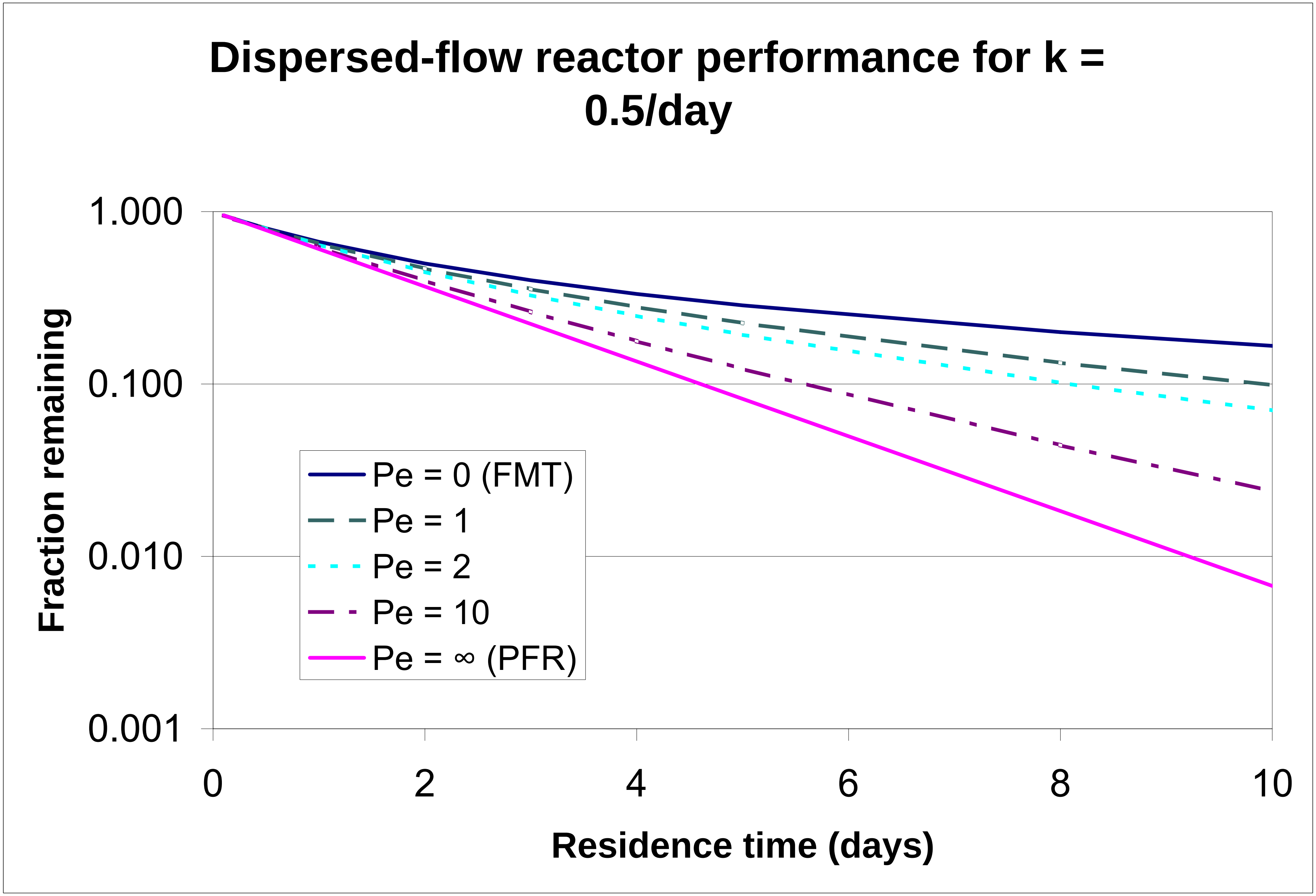

Consider mass balance for tank $i$ in series:

$$V_i \frac{dc_i}{dt} = Qc_{i-1} - Qc_i - V_i k c_i$$

| change in mass in tank | mass inflow | mass outflow | mass loss to reaction |
| --- | --- | --- | --- |



Dispersed-flow reactor performance for k = 0.5/day
Fraction remaining
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
Residence time (days)
Pe = 0 (FMT)
Pe = 1
Pe = 2
Pe = 10
Pe = ∞ (PFR)


Dispersed-flow reactor performance for k = 0.5/day
Fraction remaining
1.000
0.100
0.010
0.001
0
2
4
6
8
10
Residence time (days)
Pe = 0 (FMT)
Pe = 1
Pe = 2
Pe = 10
Pe = ∞ (PFR)

Divide by $\forall_i$ to get

$$\frac{dc_i}{dt} = \frac{c_{i-1} - c_i}{\forall_i / Q} - kc_i$$

$$= \frac{c_{i-1} - c_i}{t'_{R_i}} - kc_i$$

Assume all tanks of equal size $\forall$, $t'_{R_i} \rightarrow t'_R$

$t'_R$ = residence time of a single tank

Go back to solution for spike input to single tank:

$$c_1(t) = nc_o \exp - \left(kt + \frac{t}{t'_R}\right)$$

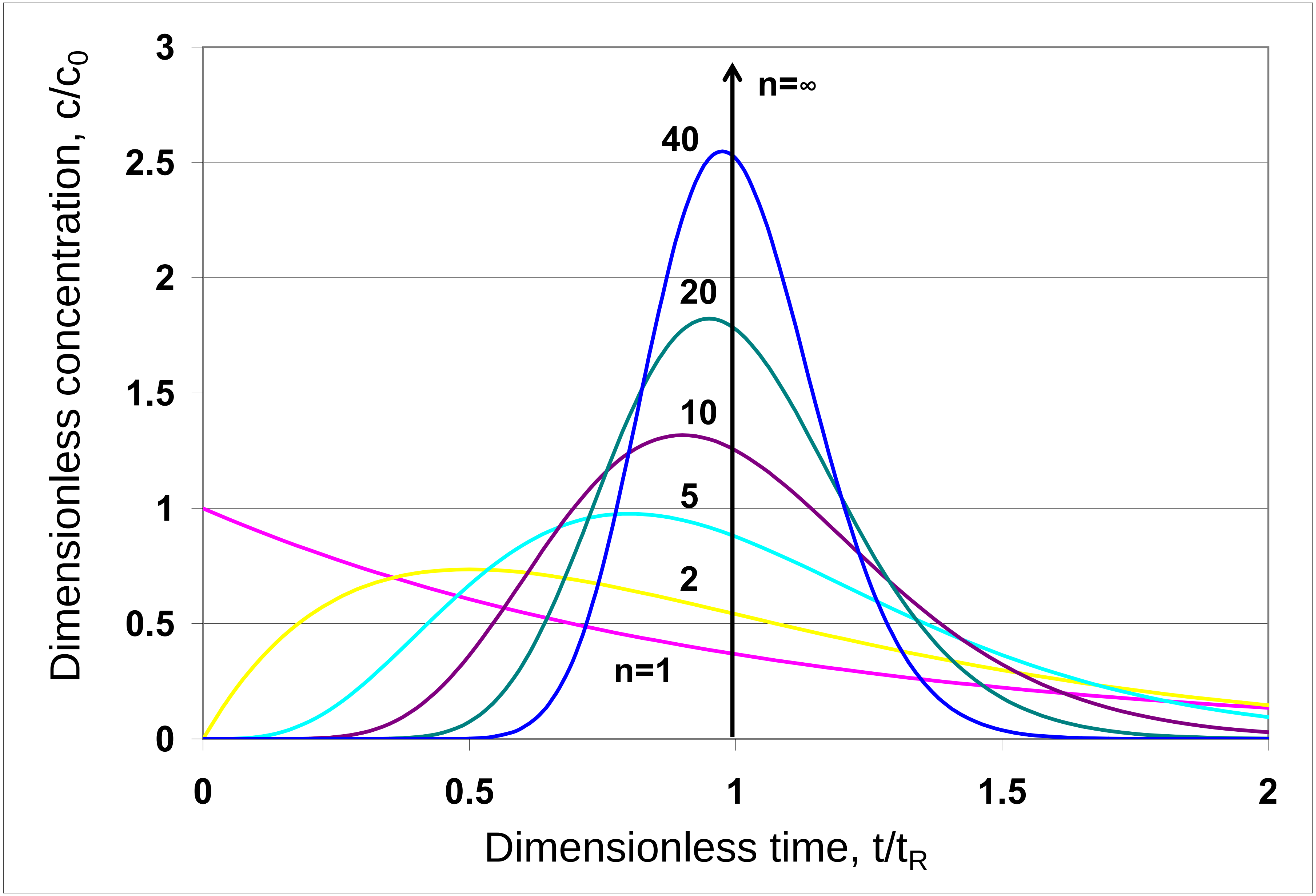
where $c_o = \frac{M}{n\forall}$

Solution for multiple tanks is done by Laplace transform (see O. Levenspeil and K.B. Bischoff, 1963. Patterns of flow in chemical process vessels. Advances in Chemical Engineering, Vol. 4)

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

Graph on page 10 shows solution for differents numbers of tanks with $k=0$

Peak concentration occurs at $\frac{t}{nt'_R} = \frac{n-1}{n} \rightarrow 1$ as $n \rightarrow \infty$



Dimensionless concentration, $c/c_0$
3
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
Dimensionless time, $t/t_R$
n=∞
40
20
10
5
2
n=1

Tanks in series behave like dispersed flow reactor – see figure on page 12

$$\mathbb{P}e \simeq 2n-1$$

For steady-state behavior solution for n tanks is straightforward

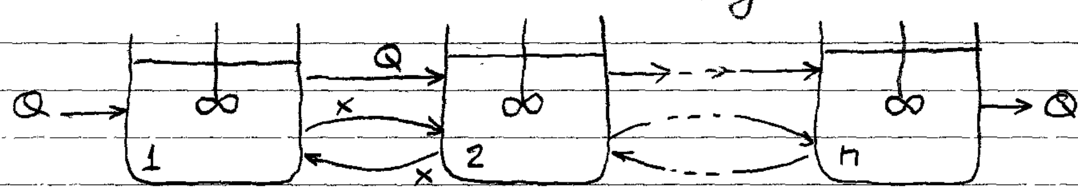
For 1 FMT $$\frac{c_1}{c_{in}} = \frac{1}{(1+kt_R')}$$

For 2 FMTs $$\frac{c_2}{c_1} = \frac{1}{(1+kt_R')}$$

$$\frac{c_2}{c_{in}} = \frac{1}{(1+kt_R')^2}$$

For n FMTs $$\frac{c_n}{c_{in}} = \frac{1}{(1+kt_R')^n}$$

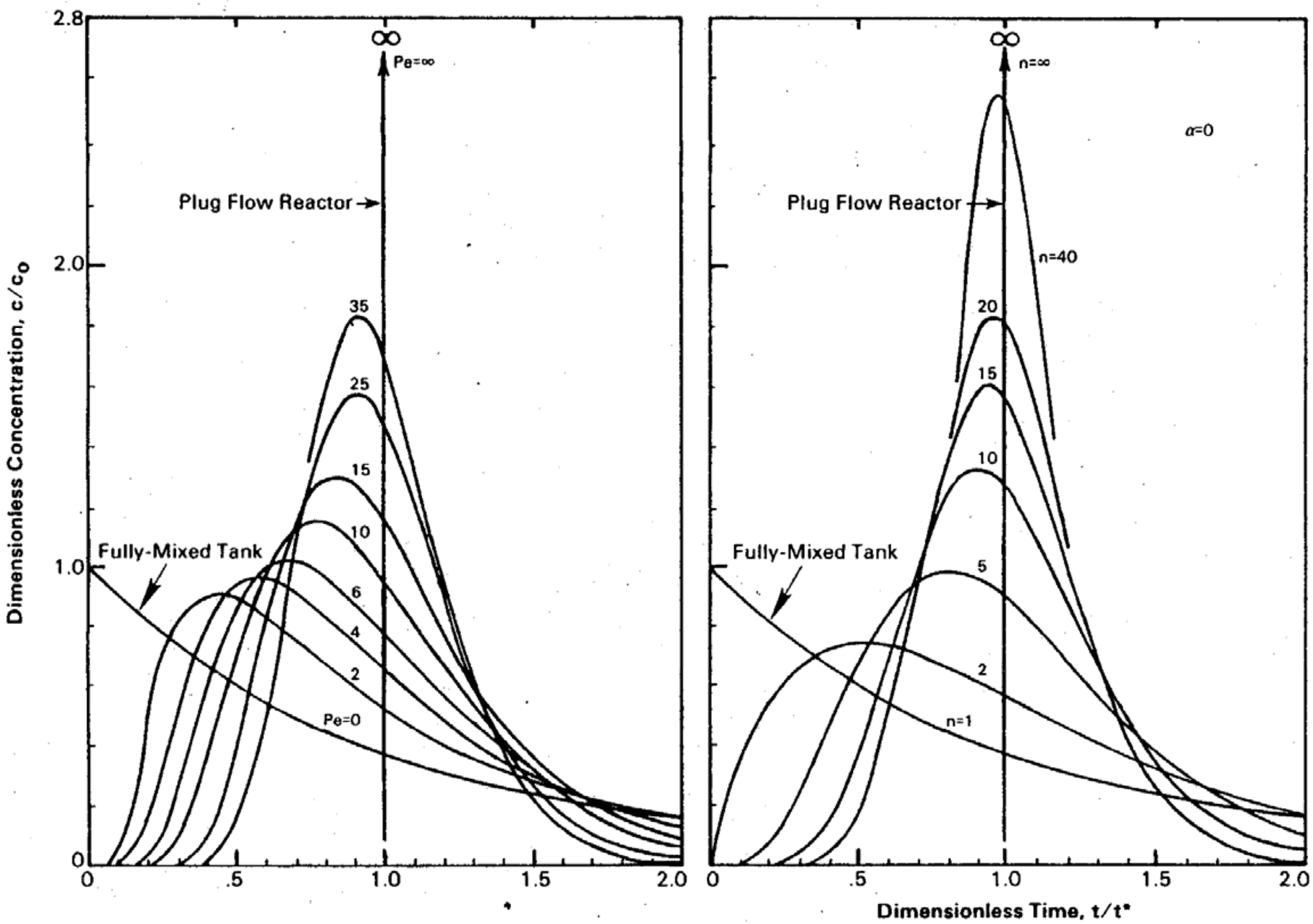
Can also consider FMTs with exchange flow:




Exchange flow creates the effect of additional mixing and in the limit of infinite exchange flow makes a tanks-in-series reactor look like a FMT

Figure on page 13 shows response of 10 tanks in series under variable exchange flow

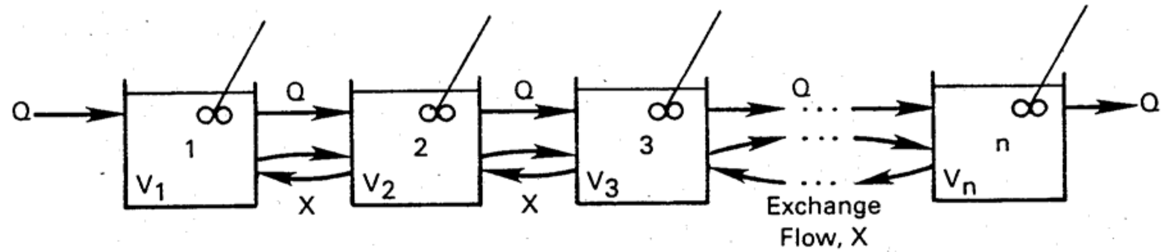
# Tanks-in-series compared to dispersed flow reactor

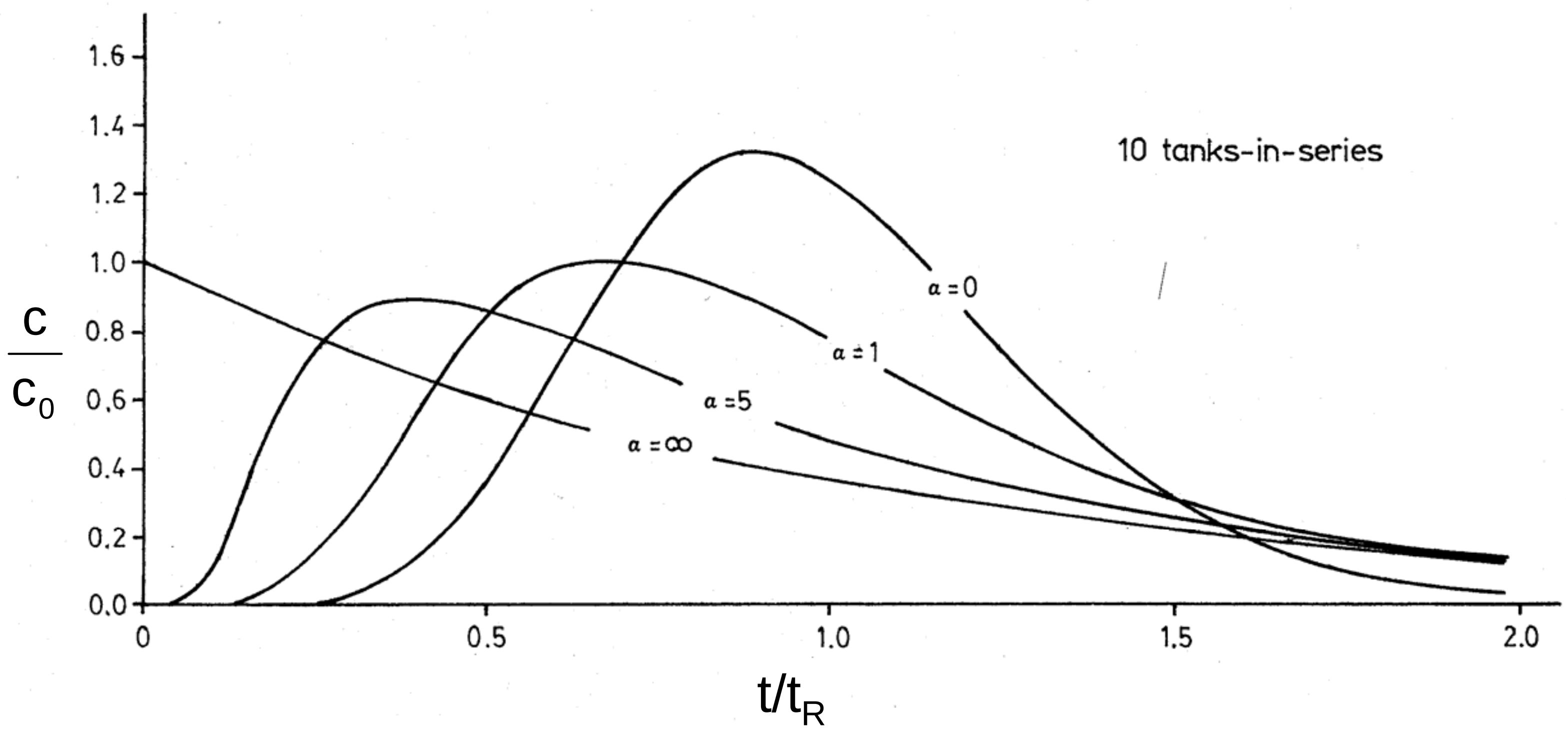



Dispersed flow

Tanks-in-series

# Tanks-in-series with exchange flow



Models illustrate that reactors, even if intended to behave one way, are not so different from other reactors

Plug flow reactor ≈ dispersed flow reactors

FMTs in series → plug flow reactor in limit

≈ dispersed flow reactor

PFR provides better treatment than PFR and DFR in theory, but practice may be different

Achieving FMT thwarted by:

Short circuiting from inlet to outlet with consequent dead zones

Achieving PFR thwarted by:

Initial mixing zone
Mixing / dispersion in reactor

Behavior of real reactors needs to be assessed by tests with tracers

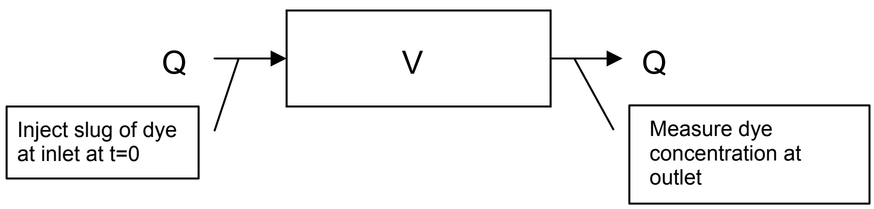
## Residence Time Distributions

We have seen two extreme ideals:

Plug Flow – fluid particles pass through and leave reactor in same sequence in which they enter

Stirred Tank Reactor – fluid particles that enter the reactor are instantaneously mixed throughout the reactor

Residence time distribution - RTD(t) – represents the time different fractions of fluid actually spend in the reactor, i.e. the probability density function for residence time

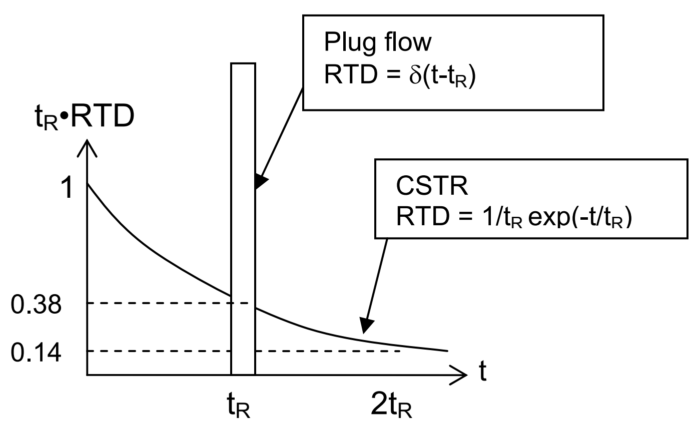



$$\mathrm{RTD}(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt} \quad \text{(for steady flow)}$$

Note units - RTD is in inverse time

by definition: $\int_0^\infty \mathrm{RTD}(t)\,dt = 1$ (i.e., total probability = 1)

$$t_D = \int_0^\infty t\,\mathrm{RTD}(t)\,dt$$ = first moment of RTD = tracer detention time




RTD math:

Dirac delta function (or unit impulse function)

Represents a unit mass concentrated into infinitely small space resulting in an infinitely large concentration

$\delta(t) = \infty$ at t = 0, 0 at $t \neq 0$

$$\int_{-\infty}^{\infty} \delta(t)dt = 1$$

Can think of Dirac delta function as extreme form of Gaussian

$M_0\delta(t-\tau)$ is spike of mass $M_0$ at time $\tau$

Plug Flow

$RTD(t) = \delta(t-t_R)$ with implied units of $t^{-1}$

$$\int_0^{\infty} RTD(t)dt = \int_0^{\infty} \delta(t-t_R)dt = 1 \quad \text{zeroth moment}$$

Note lower limit is 0 and not $-\infty$ since you can't have negative residence time (i.e., fluid leaving before it entered)

$$t_D = \int_0^{\infty} t\,RTD(t)dt = \int_0^{\infty} t\,\delta(t-t_R)dt = t_R \quad \text{first moment (mean) = tracer detention time}$$

CFSTR

$RTD(t) = \exp(-t/t_R) / t_R$ units of $t^{-1}$

$$\int_0^{\infty} RTD(t)dt = \int_0^{\infty} \frac{\exp(-t/t_R)}{t_R}dt = -t_R\left[\frac{\exp(-t/t_R)}{t_R}\right]_0^{\infty} = -t_R\left[0 - \frac{\exp(0)}{t_R}\right] = 1$$

$$t_D = \int_0^{\infty} t\,RTD(t)dt = \int_0^{\infty} t\,\frac{\exp(-t/t_R)}{t_R}dt = \frac{1}{t_R}\left[\frac{\exp(-t/t_R)}{1/t_R^2}\left(-t/t_R - 1\right)\right]_0^{\infty}$$

$$= t_R\left[0 - \exp(0)(-0-1)\right] = t_R$$

| Note: from CRC Tables: $\int xe^{ax}dx = \frac{e^{ax}}{a^2}(ax-1)$ |
|---|

## Control Volume Models and Time Scales for Natural Systems

What are actual systems like? Plug flow or Stirred reactor

It depends upon the time scales:

Mixing time for plug flow reactor is infinite: it never mixes

Mixing time for stirred reactor is zero: it mixes instantaneously

When are these assumptions realistic?

We need to estimate the time of the real system to mix - $t_{MIX}$ compared to time to react

If $t_{MIX} << t_R \rightarrow$ stirred reactor

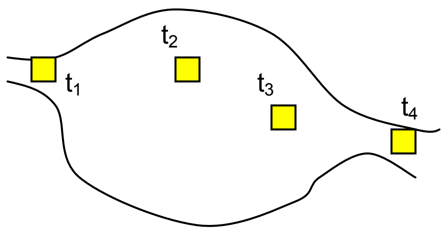
If $t_{MIX} >> t_R \rightarrow$ plug flow reactor

## Residence Time and Reactions

RTD provides a means to estimate pollutant removal

Consider a $1^{st}$-order reaction: $C(t) = C_0 \exp(-kt)$

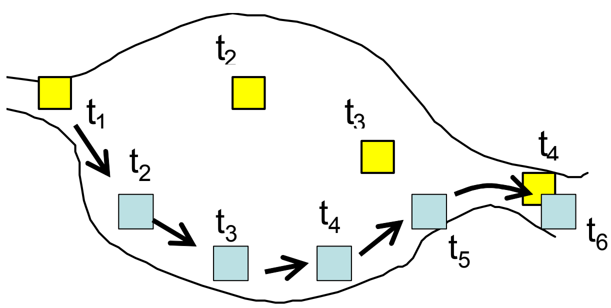
This reaction applies to any water mass entering and exiting the system – view from Lagrangian perspective (i.e., following the parcel of water)




Exit concentration:
$C_e = C_0 \exp(-kt_4)$

Consider a different parcel, taking a longer route:

Exit concentration $C_e=C_0 \exp(-kt_6)$ where $t_6 > t_4$



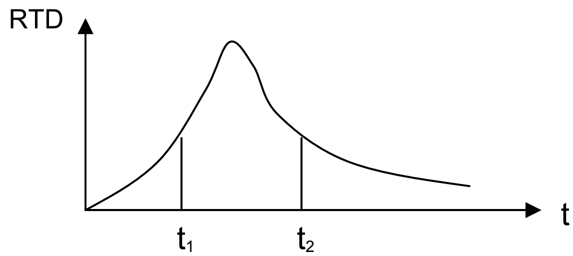

If a plug flow model applies, the exit concentration is simple: all parcels exit at exactly $T_R$

In a natural system, it is not perfect plug flow, therefore look at RTD

RTD gives the probability that the fluid parcel requires a given amount of time to pass system

On average:

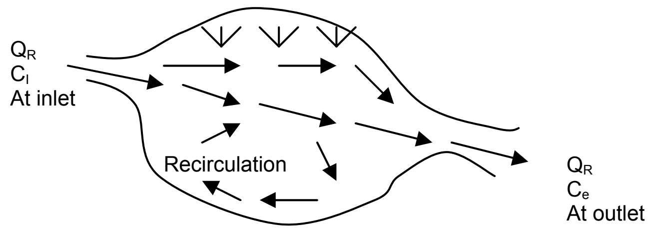
$$C_e = \int_0^{\infty} RTD(t)\, C_0 \exp(-kt)dt$$




At $t_1$ $C_e = C_0 \exp(-kt_1)$

At $t_2$ $C_e = C_0 \exp(-kt_2)$

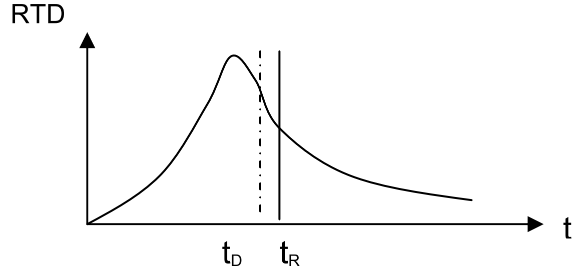
## Residence Time Distribution for Real Systems




Real circulation has:

Short circuiting
Dead zones (exclusion zones)

RTD from tracer study ≠ plug flow <u>or</u> stirred tank reactor




Detention time, $T_D$

$$t_D = \int_0^\infty t\,RTD(t)\,dt$$

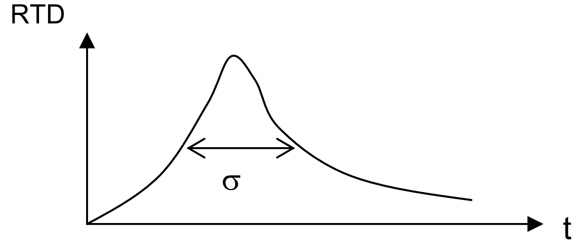
Note distinction with hydraulic residence time, $t_R = V/Q$

$t_D = t_R$ if and only if there are no exclusion zones

Variance of RTD is a measure of mixing

$$\sigma^2 = \int_0^\infty (t - t_D)^2 RTD(t)\,dt$$

As a dimensionless number, $d = \left(\frac{\sigma}{t_D}\right)^2$




As $\sigma \to 0$, no mixing, plug flow
As $\sigma \to \infty$, complete mixing, CFSTR

## Residence Time Distribution for Real Systems

Review some concepts:

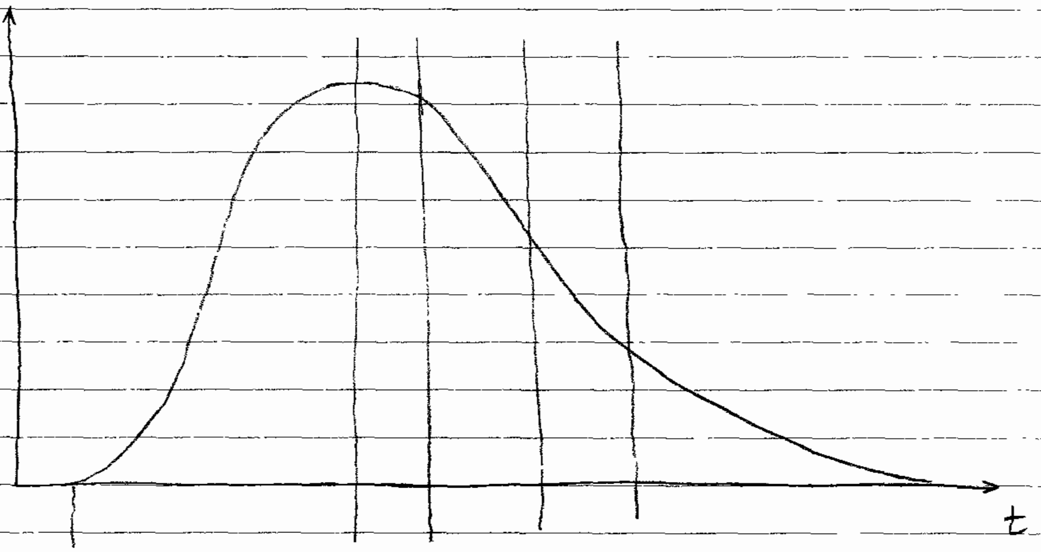
- Two models for mixing
  - Plug flow
  - Stirred reactor
- Time scales:
  - $t_R = V/Q$ mean hydraulic residence time (nominal residence time)
  - $t_{REACTION} = 1/k$ (or for 95% complete reaction or removal 3/k)
  - $t_{ADV} = L/u$
- Limitations of $t_R$ in describing residence times of true systems because of dead zones, recirculation, short circuiting

Consider alteration of the real system:

- Add berms to control circulation!

# Tracer curve analysis

## characteristic times for tracer curves at tank outlet




$t_i$ time of initial tracer appearance

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

= tracer detention time or mean residence time
Camp (1946) calls this $T_G$, the center of gravity of the concentration curve.

$T_R = \forall / Q$ = hydraulic residence time

$t_{50}$ or $t_{median}$ = median residence time, time at which 50% of mass has exited reactor
Camp (1946) calls this $T_A$, the center of area of the concentration curve

$$\int_0^{t_{50}} \frac{C(t)}{C_0}\, dt = 0.5$$

$t_p$ — time of peak concentration or mode

Relationship between various times indicates how far from "ideal" reactor is performing

Possible causes of non-ideal flow

Short circuiting — density currents, wind-driven currents can cause flow to go directly from inlet to outlet, by-passing much of tank volume

If $\frac{t_{50}}{T_R} < 1$ short circuiting is occurring (the lower the value, the worse the short circuiting)

Reynolds/Richards pg. 254 call this $\frac{\text{Median } t}{\text{Theoretical } t}$

Dead zones — corners, stagnant zones, swirling eddies are parts of tank not contributing much to treatment, shortening effective detention time

If $\frac{T_D}{T_R} < 1$ dead zones

R/R call this $\frac{\text{Mean } t}{\text{Theoretical } t}$

Other indications

$T_D$ variable over multiple tests – unstable flow

$\frac{t_i}{T_R} < 1$ Indicates dispersion and/or short circuiting

Camp (1946) pg 23 shows some examples:

| | | $t_{50}/T_R$ | $t_i/T_R$ |
|---|---|---|---|
| A. | Ideal FMT | 0.693 | 0 |
| B. | 200-ft diameter radial flow tank for Detroit Sewage Treatment Works | 0.831 | 0.14 |
| C. | Wide rectangular tank in Detroit Springwells Filtration Plant | 0.925 | 0.3 |
| D. | Narrow rectangular tank at Detroit Sewage Treatment Works | 0.903 | 0.52 |
| E. | Baffled tank with 15 passes (close to plug flow) | 0.988 | 0.74 |
| F. | Ideal plug flow | 1 | 1 |

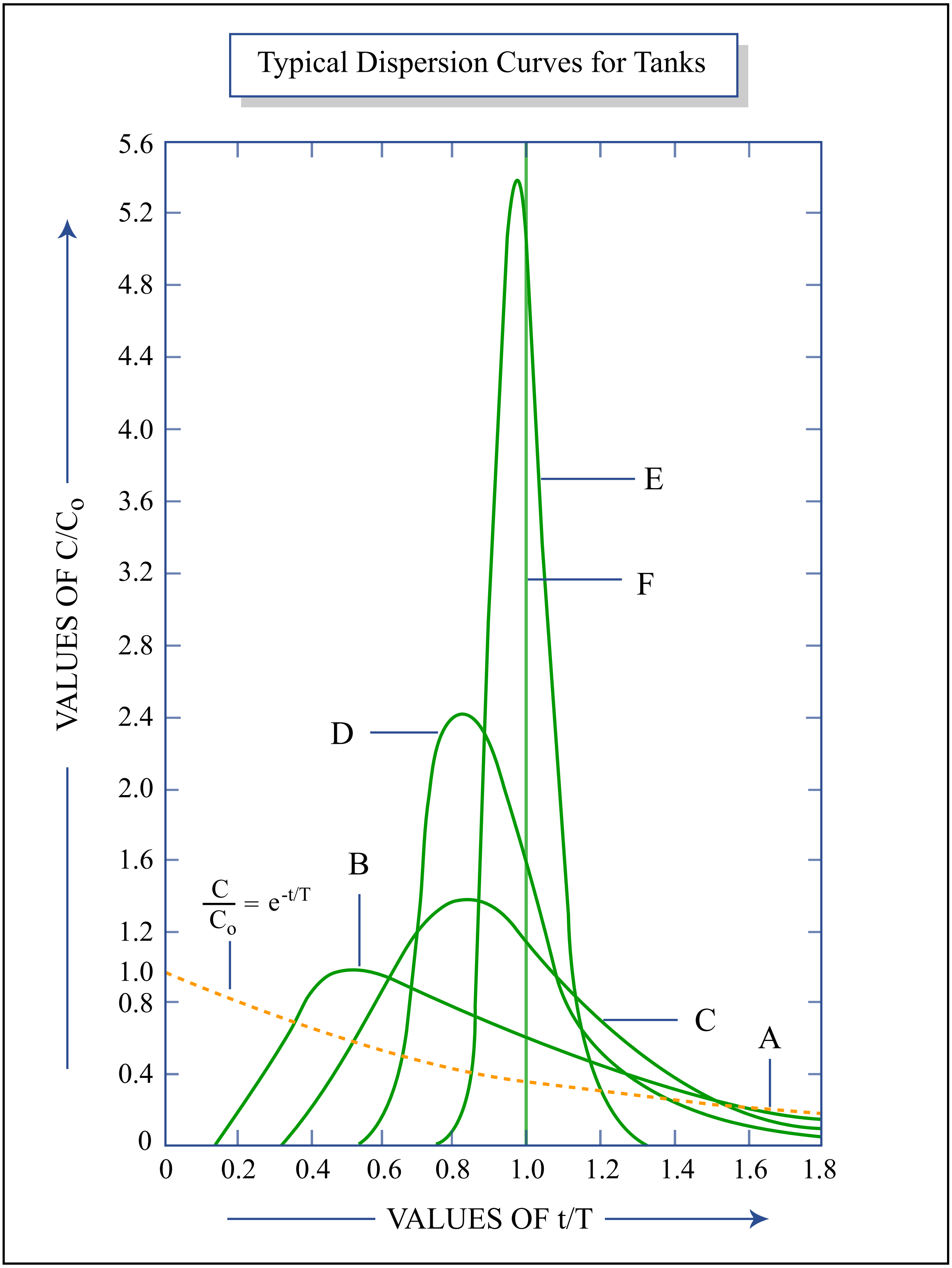



Figure by MIT OCW.

Adapted from: Camp, T. R. "Sedimentation and the design of settling tanks." *Transactions ASCE* 111 (1946): 895-936.