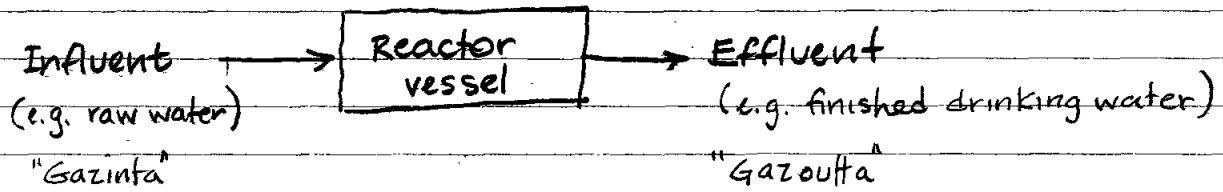
Lecture 3 - Reactor vessels

Reactor vessel – generic term to represent any natural water body or artificial tank or enclosure that receives and discharge water and within which one or more biogeochemical transformations occur such that the effluent liquid has characteristics that are different from the influent



Need to consider reactor hydraulics (flow through and mixing)

reactor chemical, biological, and physical reactions

reactor dimensionality – how many spatial dimensions are needed to represent the reactor mathematically

Also need to consider reaction dynamics

Types of reactions:

single step $A \rightarrow$ "not A"

$A + B \rightarrow C + D$

Two step $A + B \rightarrow E + F$ (slow)

$E + F \rightarrow C + D$ (fast)

Some reactions to not go to completion - equilibrium may not have been reached
→ This is typical of water and wastewater treatment processes

If reactions do not go to equilibrium rapidly, then we need to know kinetics to predict the state of the system (degree of treatment)

Types of Kinetics:

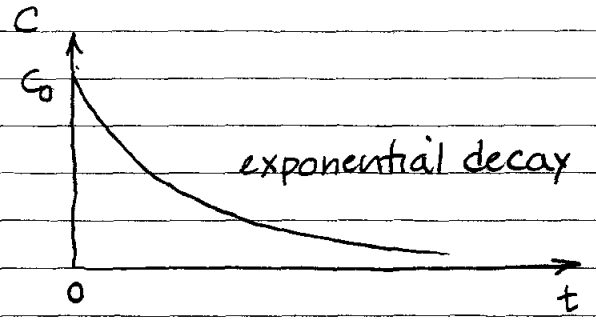
a. First-order

Rate of reaction is proportional to concentration

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

k = 1st-order reaction rate constant [1/T]

C = concentration (mass / unit volume) [M/L³]



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

$$\frac{dC}{C} = -K\,dt$$

take $\int$

$$\int \frac{dC}{C} = \ln C = \int -K\,dt = -Kt$$

$$\ln C = -Kt + \text{const}$$

$$C = e^{-Kt + \text{const}}$$

$$= e^{\text{const}}\, e^{-Kt} = C_0\, e^{-Kt}$$

C_0 ↑ initial conc.

b. second-order

Reactions involving two species A and B

$$\frac{dC_A}{dt} = -KC_AC_B$$

$$\frac{dC_B}{dt} = -KC_AC_B$$

K = second-order rate constant

units of $1/[\text{time} \cdot \text{conc}]$ or $[L^3/T \cdot M]$

e.g. 1/ time-moles

If $C_B \gg C_A$ then

$$\frac{dC_A}{dt} \approx -k' C_A$$

where $k' = kC_B$

k' is pseudo-1st-order rate constant [1/T]

kC_B is nearly constant (at least relative to C_A)

c. zero-order

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

Reaction rate is independant of concentration of reactant

Occurs with reactions in which a catalyst comes into play: reaction is limited by available reaction sites on the catalyst

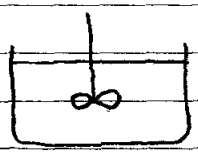
Usually, reactions in water and wastewater treatment are assumed to follow first-order reaction kinetics

Reactor vessels

Simplest reactor is the "fully-mixed tank" (FMT)

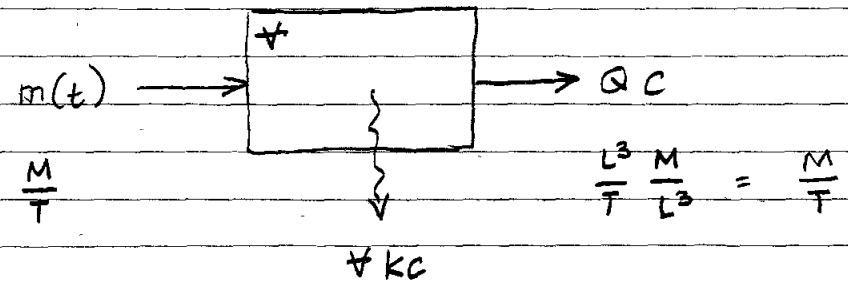
More formally called "continuous-flow stirred tank reactor" (CFSTR)

Diagrammatic representation.



Ideal CFSTR has uniform concentration within its confines - influent is mixed instantaneously and completely

Mass balance for CFSTR:



$m(t)$ - influent mass per unit time $= Q C_{in}$ $[M/T]$

$\forall$ - volume of tank $[L^3]$

Q - volumetric outflow from tank $[L^3/T]$

C - fully-mixed conc. within tank $[M/L^3]$

K - first-order rate constant $[1/T]$

$$m(t) \quad - \quad cQ \quad = \quad cK\forall \quad + \quad \frac{dC}{dt}\forall$$

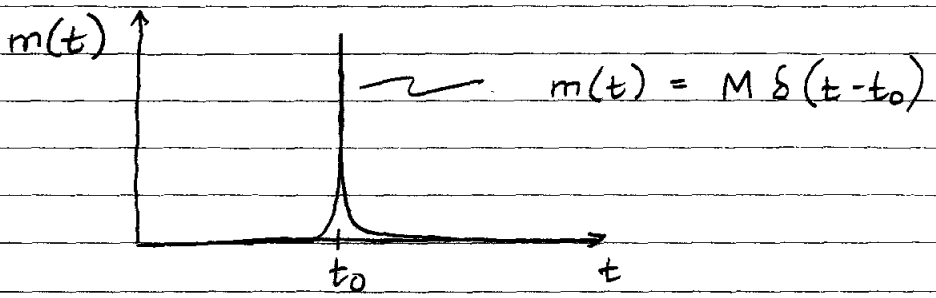
inflow mass per time	outflow mass per time	mass removed	change in mass in tank
$\left[\frac{M}{T}\right]$	$\left[\frac{M}{L^3}\frac{L^3}{T}\right]$	$\left[\frac{M}{L^3}\frac{1}{T}L^3\right]$	$\left[\frac{M/L^3}{T}L^3\right]$

$$\frac{m(t)}{\forall} - c\frac{Q}{\forall} = cK + \frac{dC}{dt}$$

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

$$\frac{dC}{dt} + c\left(K + \frac{1}{t_R}\right) = \frac{m(t)}{\forall}$$

Consider pulse injection ("spike" of mass)



$\delta(t-t_0)$ = Dirac delta function

$$\int_0^\infty \delta(t-t_0)\,dt = 1$$

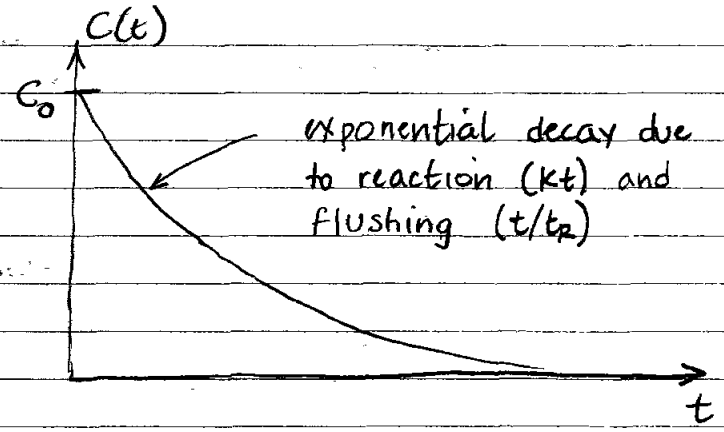
$$\delta(t-t_0) = \begin{cases} 0 & t \neq t_0 \\ \infty & t = t_0 \end{cases}$$

Solution for injection at $t = t_0 = 0$

$$C(t) = \frac{M}{\forall} \exp - \left(kt + \frac{t}{t_R} \right)$$

Define $C_0 = \frac{M}{\forall}$ conc at $t = 0$

$$c(t) = C_0 \exp - \left(Kt + \frac{t}{t_R} \right)$$



If $Q = 0$, $t_R \to \infty$ $\quad C(t) = C_0 e^{-kt}$

"Batch reactor"

If $K = 0$, $\quad C(t) = C_0 e^{-t/t_R}$

flushing of tank

Can consider both flushing and decay systematically by using the parameter Kt_R (Damköhler Number)

$$C(t) = C_0 \exp -\left(Kt + \frac{t}{t_R}\right)$$

$$= C_0 \exp - \left(Kt_R \cdot \frac{t}{t_R} + \frac{t}{t_R}\right)$$

$$= C_0 \exp - \left\{\frac{t}{t_R}\left(Kt_R + 1\right)\right\}$$

Higher K implies more rapid decrease in concentration with time - see graph pg 9

Note with $K=0$ $C/C_0 = 0.38$ at $t = t_R$ - most mass leaves system before nominal residence time

Many treatment units and natural water bodies approximate a FMT

Example: White, K.E., 1974. The use of radioactive tracers to study the mixing and residence time distributions in systems exhibiting three dimensional dispersion. Paper No. A6. Pp. A6-57 to A6-76. Proceedings of the First European Conference on Mixing and Centrifugal Separation, September 9-11, 1974, Cambridge, UK. BHRA Engineering, Cranfield, UK.

Lake used as "roughing" treatment (suspended sediment removal) for river water

Lake characteristics:

$\forall = 2000\ m^3$

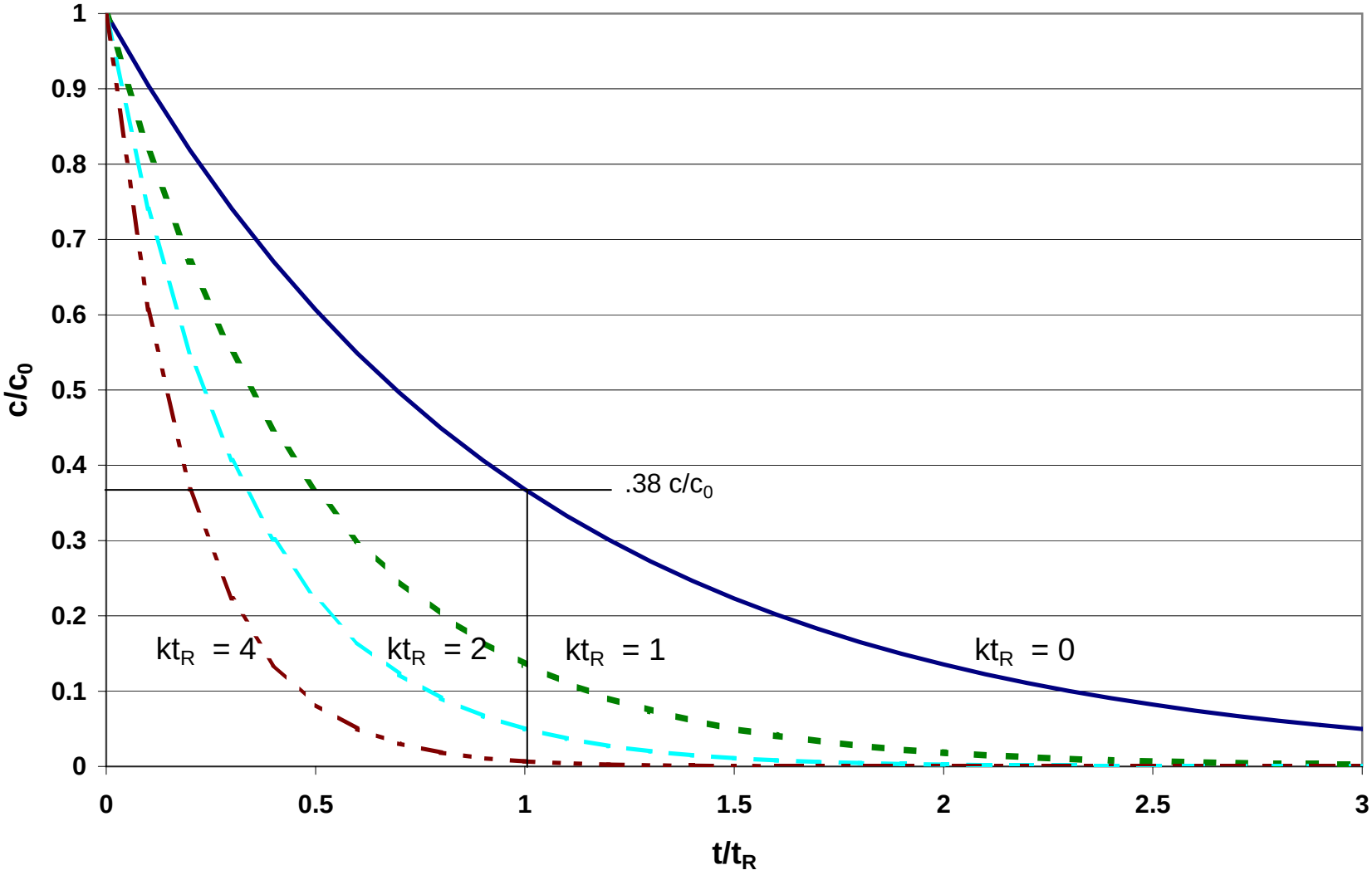
$h = 1\ m$

$w \hat{=} L \hat{=} 45\ m$

$Q = 0.055\ m^3/s$

$t_R = 10$ hours

Response of fully-mixed tank to pulse input



Spike injection of 38 mCi of radioactive bromine Br-82

Curie is quantity of radionuclide that undergoes 37×10^9 disintegrations per second

$$38\ mCi \times 37 \times 10^9\ dis/sec \longrightarrow 1.4 \times 10^9\ dis/sec\ (counts/sec)$$

Radioactive Br has half-life of 35.4 hours

$$\frac{C}{C_0} = \frac{1}{2} = e^{-Kt_{1/2}}$$

$$t_{1/2} = \frac{-\ln 1/2}{K} = \frac{0.693}{K}$$

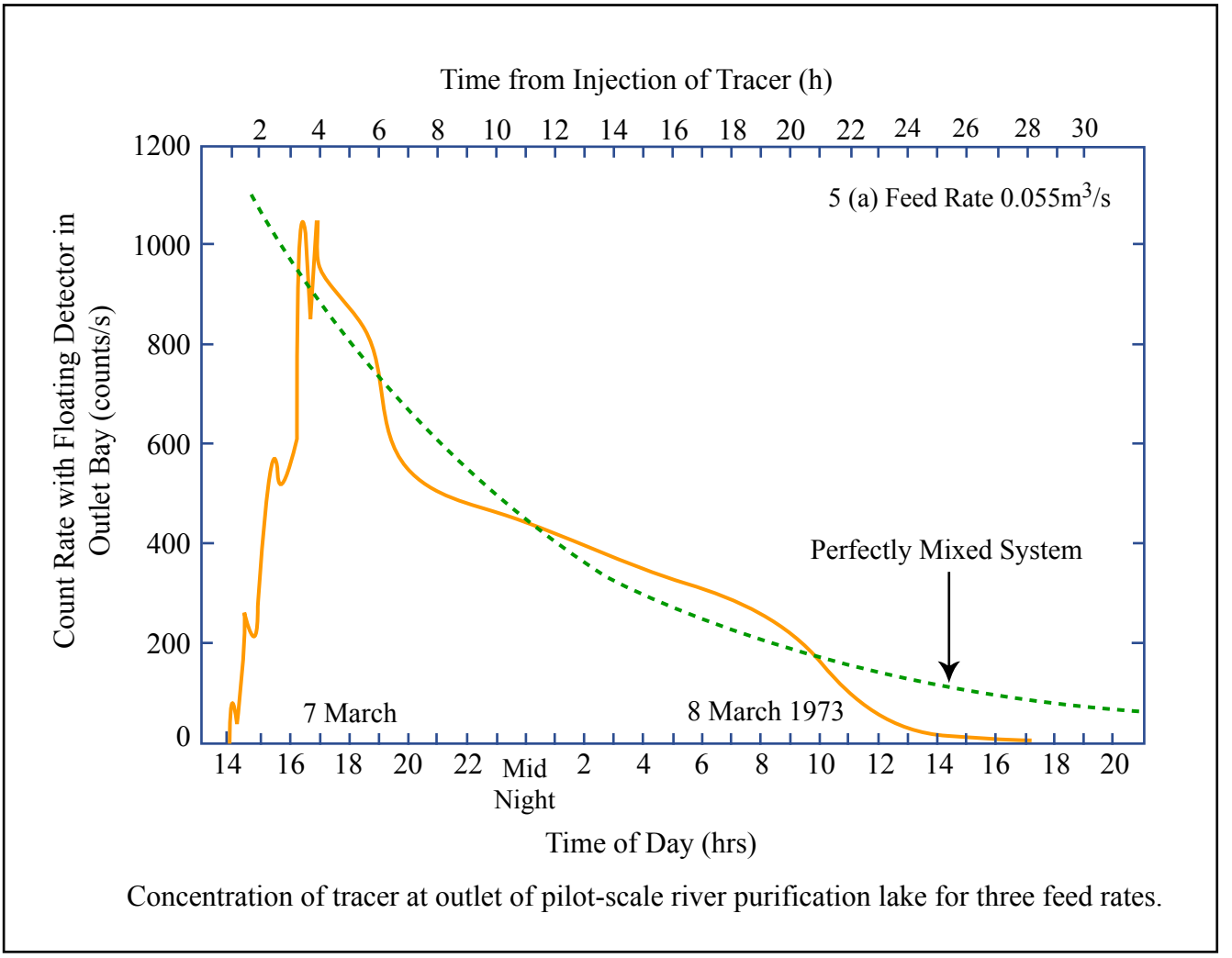
$$K = \frac{0.693}{t_{1/2}} = 0.02\ hr^{-1}$$

$$\therefore Kt_R = 0.02\ hr^{-1} \cdot 10\ hr = 0.2$$

Minor effect on behavior

Br-82 disintegrates to form Kr-82 and emit gamma and beta radiation

Translation of concentration in curies to counts in effluent (graph on page 11) is complicated function of detector type, radiation attenuation in water, detector configuration, radionuclide, etc. – Paper gives insufficient information to check FMT tank in graph



Concentration of tracer at outlet of pilot-scale river purification lake for three feed rates.

Figure by MIT OCW.

Adapted from: White, K. E. "The use of radioactive tracers to study mixing and residence-time distributions in systems exhibiting three-dimensional dispersion." In *First European Conference on Mixing and Centrifugal Separation*. Edited by N. G. Coles. Churchill Col, 1974.

How safe is Br-82?

EPA standards are concerned with exposure to radiation - MCL for beta emitters is 4 mrem per year

rem = Roentgen Equivalent Man

Measures dose of radiation to a person and accounts for energy of the radiation and how much is absorbed into body

(see www.physlink.com/Education/AskExperts/ae553.cfm

Conversion from Curie to rem is nuclide specific Conversion factors are given by National Bureau of Standards Handbook 69, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air or Water for Occupational Exposure"

Conversion factor for Br-82 is:

100 pCi/L → 4 mrem

See USEPA, 2000 Implementation Guidelines for Radionuclides. Report EPA-816-D-00-002. U.S. EPA Office of Water, Washington DC. December 2000. www.epa.gov/safewater/rads/draft_imp_guide.pdf

Assume 38 mCi fully mixed into 2000 m^3 volume:

$$C_o = 0.019 \frac{\mu Ci}{L} = 19 \frac{pCi}{L} \rightarrow 0.76 \text{ mrem}$$

safe to drink!

Consider FMT with continuous input of mass

$$m(t) = \text{const} = Q_i C_{in}$$

Initial condition $C = C_o$ at $t = 0$

C_{in} = const for $t \geq 0$

Solution:

$$c(t) = \frac{C_{in}}{1 + Kt_R}\left[1 - e^{-\left(t/t_R + Kt\right)}\right] + C_o e^{-\left(t/t_R + Kt\right)}$$

at $t \to \infty$ get steady-state solution

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

Treatment efficiency is removed conc $(C_{in} - C)$ over influent conc (C_{in})

$$\frac{C_{in} - C}{C_{in}} = 1 - \frac{1}{1 + Kt_R} = \frac{Kt_R}{1 + Kt_R} = \text{Efficiency}$$

Summary FMT or CFSTR

uniform conc in tank = conc in outflow

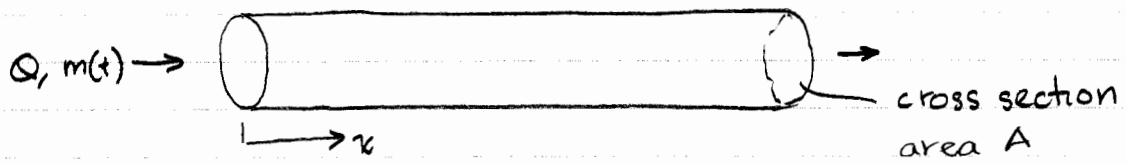
For const conc inflow $\frac{C}{C_{in}} = \frac{1}{1 + Kt_R}$

FMT is a zero-dimensional system: there is no influence of spatial dimensions on theoretical behavior

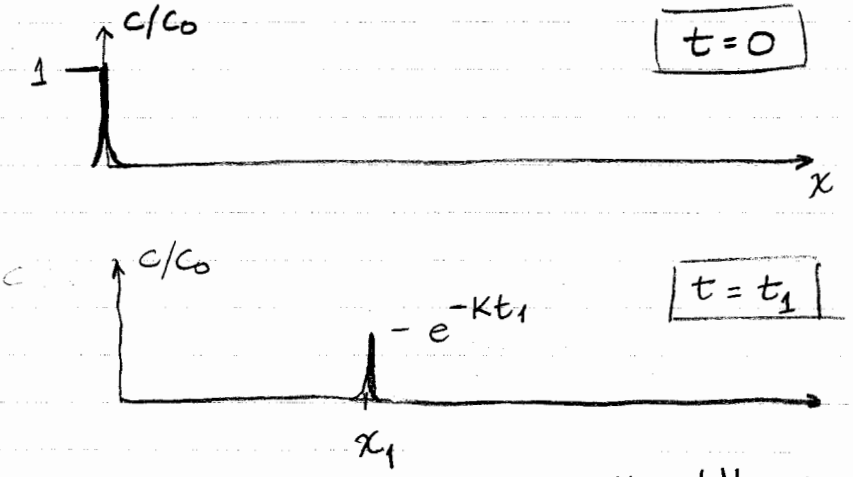
Plug flow reactor (PFR)

Exact opposite of FMT - Plug flow reactor has zero mixing

One-dimensional - long tank of small cross section



For spike input:



$$x_1 = Ut_1 = \frac{Q}{A} t_1$$

For PFR of volume $\forall$, residence time $t_R = \forall/Q$

For continuous inflow of Q with conc c_{in}, conc at outlet, C, is

$$C = c_{in}\, e^{-kt_R}$$

Efficiency $$\frac{c_{in} - C}{c_{in}} = 1 - e^{-kt_R}$$

Contrast performance of FMT with PFR

Same volume $\forall$, flow Q, residence time t_R, inflow conc C_{in}, 1st order decay coeff K

FMT $$\frac{C}{C_{in}} = \frac{1}{1+Kt_R}$$

PFR $$\frac{C}{C_{in}} = e^{-Kt_R}$$

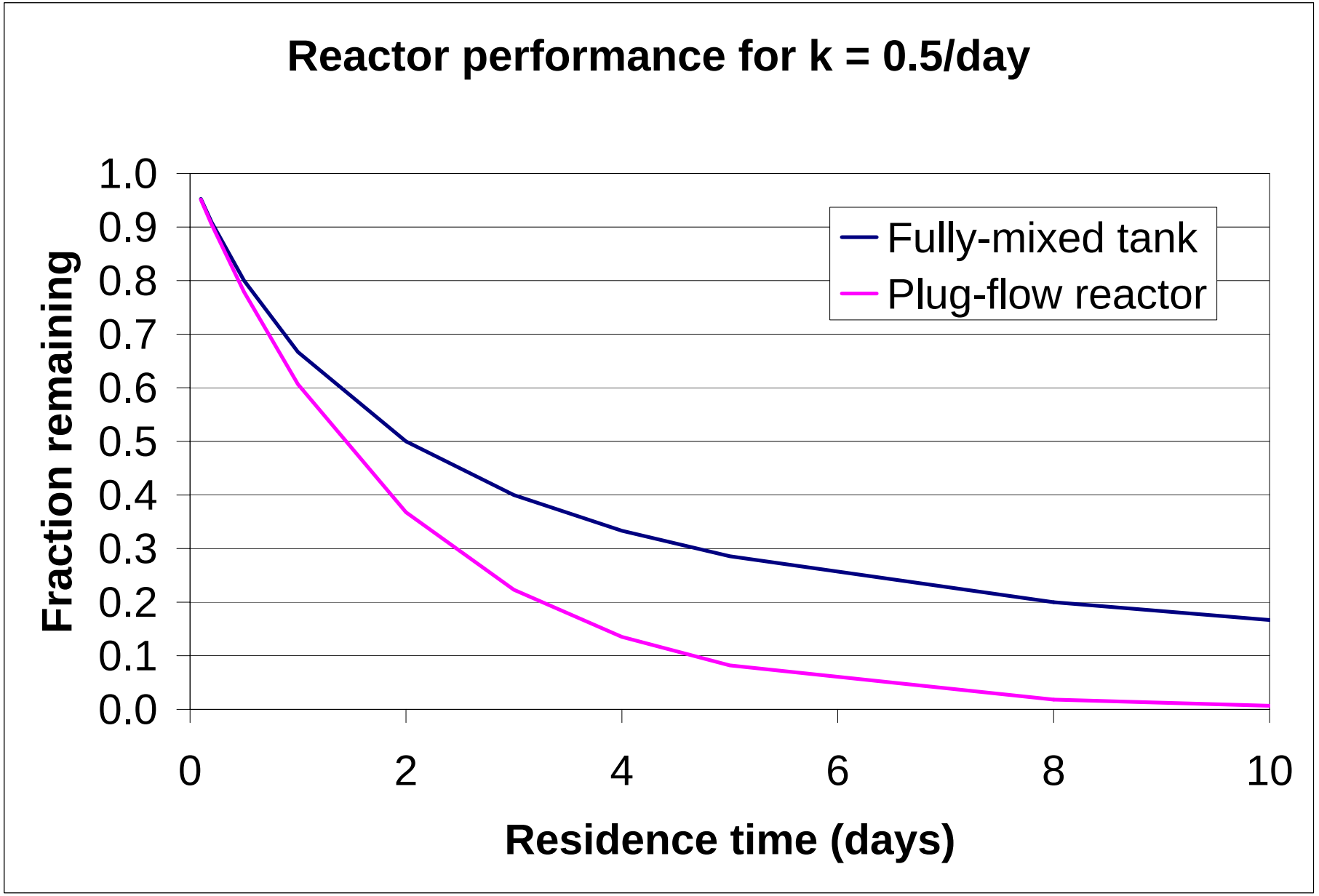
Plot on page 16 shows that for same residence time, the plug-flow reactor gives superior treatment

Plug flow is difficult to achieve in practice – often use baffles to approach plug flow

Examples: chlorine contact chamber in Lynn WWTP photos in Lecture 1

Page 17 - cooling pond at Dresden Nuclear Power Plant

In actual fact, if we injected spike of fluid into long narrow reactor, there would be mixing with adjacent fluid → dispersion


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)
Fully-mixed tank
Plug-flow reactor

Chlorine contract chambers at Lynn WWTP

Cooling pond at Dresden Nuclear Power Plant