6 Principles of Reactor Analysis and Mixing

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Terminology for Reactor Analysis and Mixing

Term	Definition
Agitation	Motion induced in a fluid to achieve flocculation, maintain particles in suspension, or promote mass transfer.
Batch reactor	Vessel in which reactants are introduced and reactions are allowed to proceed with no additional inputs to or outputs from the reactor during the reaction period.
Blending	Process of combining two liquid streams to achieve a specified level of uniformity as defined by the COV.
Completely mixed flow reactor (CMFR)	An ideal flow reactor in which the contents are continuously mixed and completely homogenous; no variation in concentration or other condition exists from one location to another in the reactor. Called continuously-stirred tank reactor (CSTR) in some older texts.
Coefficient of variation (COV)	Normalized standard deviation of the concentration in a stream used to define the uniformity (also homogeneity) of blending.
Conservative constituent	Constituent that does not react, transform, adsorb, or otherwise change as it passes through a reactor.

Term	Definition
Control volume	System in which a mass balance analysis is performed.
Diffusion	Movement of molecules from a higher concentration to a lower concentration due to Brownian motion.
Dispersion	Mixing in which a constituent is transported from a higher concentration to a lower concentration by eddies formed by turbulent flow or shearing forces between fluid layers.
Flow reactor	Reactor that operates on a continuous basis with flow into and out of the reactor.
Hydraulic residence time	Theoretical time that fluid remains in a reactor, defined as the reactor volume divided by the flow rate.
Mass balance analysis	Application of the law of conservation of mass, to account for changes in any component due to fluid flow, mass transfer, or chemical transformations.
Mean residence time	Average time that fluid remains in a reactor, defined as the first moment of tracer curve.
Mixer	Device used to bring about motion in a fluid for the purpose of agitation or blending.
Mixing	General term used to refer to agitation and blending
Nonconservative constituent	Constituent that reacts or transforms as it passes through a reactor.
Plug flow reactor (PFR)	An ideal flow reactor in which no dispersion, diffusion, or mixing of contents occurs in the axial direction.
Reactor	Tank, basin, or other vessel used in environmental and chemical engineering as a container in which chemical or biological reactions for treatment or transformation can take place.
Residence time distribution (RTD)	Probability distribution function that describes the range of time that fluid elements remain within a reactor.
Steady-state analysis	Analysis conducted when a reactor is operated for a long enough period of time with a constant influent concentration such that the concentration profile in the reactor does not change with time.
System boundary	Border used to identify all of the material flows into and out of a control volume.
Tracer, chemical	Conservative chemical used to assess the flow conditions through a reactor.
Velocity gradient G	Measure of the power input per unit volume $(P/\mu V)^{1/2}$

In the environment, many of the contaminants in water are removed grad-ually by naturally occuring physical, chemical, and biological processes. In water treatment, the same processes that occur in nature are carried out in vessels or tanks, commonly known as *reactors*. Through the use of engineered reactors, the processes used to treat water can be accelerated under con-trolled conditions. The rate at which such processes occur depends on the constituents involved and conditions in the reactor, including temperature and hydraulic (mixing) characteristics.

The topics presented in this chapter include (1) the types of reactors used in water treatment processes; (2) the mass balance analysis, which is the fundamental basis for the analysis of the physical, chemical, and biological processes used for water treatment; (3) ideal reactors used in modeling; (4) the modeling of reactions occurring in completely mixed batch reactors; (5) the modeling of reactions occurring in ideal continuous-flow reactors; (6) the use of tracer curves to characterize nonideal flow patterns; (7) the modeling of nonideal flow through reactors; (8) modeling the performance of nonideal reactors; (9) using tracer curves to model reactor performance; and (10) mixing.

6-1 Types of Reactors Used in Water Treatment

Unit operations and unit processes in water treatment can be carried out in a variety of reactors, which include large square and rectangular basins, cylindrical tanks, pipes, long channels, columns, and towers. Stoichiometric and kinetic descriptions of chemical reactions combined with knowledge of practical flow patterns provide the basis for reactor selection and design. Other factors to be considered include the quantity of material being processed and the structural requirements of the reactor selected (Froment and Bischoff, 1979; Kramer and Westerterp, 1963; Levenspiel, 1998; Green and Perry, 2007; Smith, 1981). The types of reactors and their applications and the hydraulic characteristics of reactors are introduced in this section.
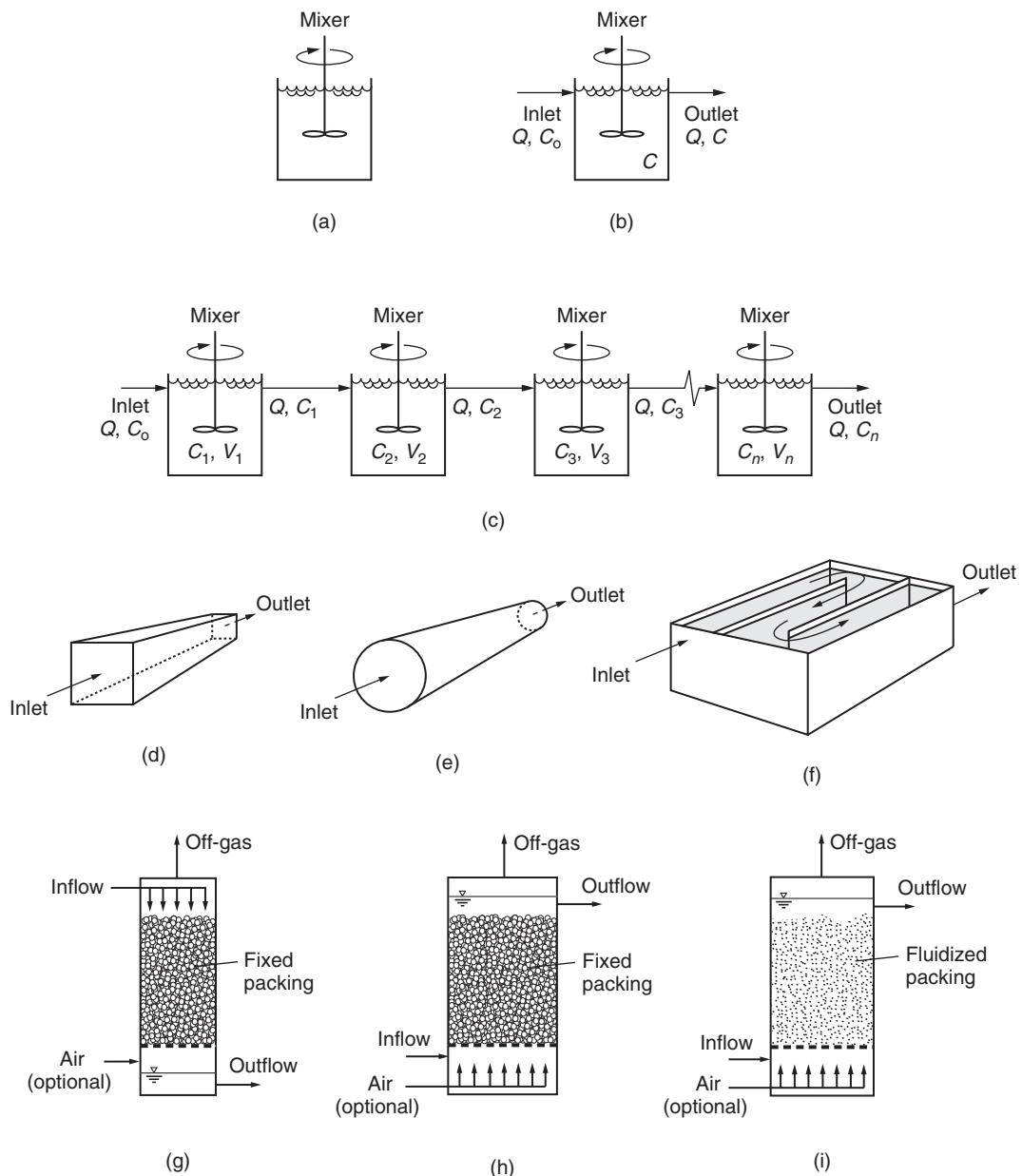
Types of Reactors   The reactors used for water treatment can be categorized based on the operation pattern, hydraulic characteristics, unit operation occurring, and entrance and exit conditions. Several types of reactors are shown on Fig. 6-1.

Reactors Characterized by Operation Pattern   Batch and continuous-flow reactors are the principal types of reactors. *Batch* reactors are characterized by noncontinuous operation (see Fig. 6-1a). Reactants are mixed together, and the reaction is allowed to proceed to completion. *Continuous-flow* reactors operate on a continuous basis with flow into and out of the reactor (see Fig. 6-1b). Continuous-flow reactors may also be arranged sequentially to change the flow characteristics (see Fig. 6-1c).

Batch reactors are used widely in the production of small-volume, spe-cialty chemicals in the chemical processing industries. However, the use

Figure 6-1
Typical reactors used in water treatment processes: (a) batch reactor; (b) continuous-flow mixed reactor; (c) continuous-flow mixed reactors in series, also known as tanks in series; (d) rectangular channel plug flow reactor; (e) circular pipe plug flow reactor; (f) serpentine configuration plug flow reactor; (g) packed-bed downflow reactor; (h) packed-bed upflow reactor; and (i) expanded-bed upflow reactor. (Adapted from Tchobanoglous et al., 2003.)

of batch reactors in water treatment applications is generally restricted to laboratory-scale investigations and chemical coagulant preparation. Continuous-flow reactors are used most commonly in full-scale water treatment plants because of the large volumes of water processed.

Reactors Characterized by Hydraulic Characteristics

Reactors used for carrying out reactions can be characterized as ideal or nonideal, according to the nature of the hydraulic and mixing conditions. In nonideal reactors, the hydraulic and mixing conditions tend to be complex (e.g., the mixing conditions in Lake Superior or a chlorine contact chamber). Ideal reactors are assumed to have uniform mixing and hydraulic conditions, depending on the specific reactor configuration. Common reactor configurations include (1) completely mixed batch reactors (CMBRs), (2) completely mixed flow reactors (CMFRs), and (3) plug flow reactors (PFRs). Reactor configurations are defined in Table 6-1 and discussed in detail in the following sections.

Table 6-1
Definition of reactors used in water treatment

Reactor	Definition
Ideal reactors	Reactors defined for purposes of modeling. Ideal assumptions, such as no dispersion or diffusion, are nearly achievable under closely controlled laboratory conditions. Definitions assume extreme fluid conditions, such as complete mixing or no mixing of reactants or products in the direction of flow.
Nonideal reactors	Mixing and/or the residence time distribution in the reactor does not meet ideal assumptions, for example, complete mixing. Often reactors that are used in practice are nonideal reactors.
Completely mixed batch reactor (CMBR)[a]	An ideal reactor in which no reactants or products flow into or out of the reactor. Complete mixing occurs instantaneously and uniformly throughout the reactor, and the reaction rate proceeds at the identical rate everywhere in the reactor.
Completely mixed flow reactor (CMFR)[b]	An ideal reactor in which reactants and products flow into and out of the reactor. Complete mixing occurs instantaneously and uniformly throughout the reactor. The reaction rate proceeds at the identical rate everywhere in the reactor, and the concentrations throughout the reactor are the same as the effluent concentration.
Plug flow reactor (PFR)	An ideal reactor in which fluid moves through the reactor as a plug and the fluid does not mix with fluid elements in front of or behind it. As a result, the reaction rate and concentrations of the reactants decrease as the fluid moves down the PFR. (Except for zero-order reactions) The composition at any travel time down the reactor is identical to the composition in the CMBR after the same period of time has passed.

[a]A CMBR may also be referred to as a batch reactor.
[b]A CMFR may also be referred to as a complete-mix reactor (CMR), continuous stirred-tank reactor (CSTR), constant-flow stirred-tank reactor (CFSTR), or backmix reactor.

Reactors may be classified according to the type of water treatment process to be carried out. Many reactions of importance in water treatment are heterogeneous because they consist of reactions occurring in more than one phase, so-called multiphase reactions. For example, ozone gas is sometimes mixed with water to achieve the transformation of some undesired constituent (e.g., oxidation of manganese or inactivation of pathogens). In other cases, a solid precipitate is formed that may be removed by sedimentation or filtration.

Reactors Characterized by Unit Process

   Various types of reactors are used to carry out multiphase reactions. Some reactors are used to mix reactants and to provide high contact areas between water and gas. Others are used for reactions that occur on or within the solid phase and some are used for precipitation reactions. Various multiphase reaction processes, the type of reactors used, and specific examples of the multiphase reactions used in water treatment processes are listed in Table 6-2.

REACTORS USED FOR MIXING
In reactors used for the mixing of reactants, the mixing can be either intense or slow depending upon the reactions desired. In the mixing of

Table 6-2
Examples of reactors used in water treatment

Process	Reactor Type	Examples
Oxidation	Stirred tanks, tanks in series, diffused gas contactors, Venturi reactor	Oxidation of iron, oxidation of manganese, dechlorination by SO_2, ozone reactions
Disinfection	Tanks with serpentine baffling, long channels, diffused gas contactors, pipes	Chlorination, ozonation, chlorine dioxide, chloramination
Coagulation and flocculation	Stirred tanks in series, sludge blanket reactors	Removal of particulates and NOM using Al(III) or Fe(III), removal of As(V)
Lime softening	Stirred tanks in series, recycle reactors, sludge blanket reactors, upflow fluidized beds	Removal of hardness
Air stripping	Packed tower, diffused gas contactors	VOC removal, CO_2 removal
Adsorption	Fixed-bed reactor, stirred tanks in series	SOC removal, taste and odor control
Ion exchange	Fixed-bed reactor, stirred tanks in series	Removal of hardness, nitrate, perchlorate, barium, NOM, etc.
Filtration	Fixed bed	Particulate removal, turbidity removal, microbial removal, assimiable organic carbon (AOC) removal
Membranes	Fixed bed	Particulate removal, microbial removal

coagulants, intense mixing is desirable to disperse the reactants quickly. Flocculation, on the other hand, requires moderate agitation to increase the rate of particle collision and formation of large aggregate particles. *Venturi reactors* are in-line mixers with a section of the pipe that is restricted to a throat section, where chemicals are applied. Mixing occurs in a turbulent region following the throat section. Venturi-type reactors are often used for injection of chlorine, carbon dioxide, and other soluble gases into water. *Static mixers* and *pumped flash mixers* are useful for rapid mixing of coagulants and polymers with large volumes of water. Various types of mixing devices are discussed further in Sec. 6-10.

REACTORS USED FOR CONTACT TIME
Reactors designed for a specified detention or reaction time are commonly known as *plug flow reactors* and are not subject to backmixing. For example, the disinfection of water is typically carried out by the exposure of the water to the disinfectant of interest for a specified duration of time. Sedimentation processes also require time for particles to fall out of solution. For reactions of this nature, where holding time is important, reactors may be designed as long, narrow channels (see Fig. 6-1d), long pipe or tubular vessels (see Fig. 6-1e), or a series of long channels (see Fig. 6-1f).

REACTORS USED FOR CONTACT BETWEEN WATER AND GAS
Packed columns consist of a cylindrical column containing appropriate packing materials that provide high interfacial areas between water and a gas, usually air. Packed columns are used for stripping of undesirable gases or volatile organic compounds (VOCs) from water. Two-phase flow in packed towers is typically countercurrent, with liquid entering at the top of the reactor and air forced in the bottom of the reactor (see Fig. 6-1g). As the liquid flows over the packing, a thin liquid film is produced and volatile compounds and gases are transferred into the gas phase. Other reactors used to contact water and gases include *bubble tanks*, where a gas is bubbled into the water in tanks, and *spray towers*, where water is sprayed into the air, used primarily for removal of volatile materials. Air–liquid contactors are discussed in Chap. 14.

REACTORS USED FOR REACTIONS OCCURRING ON OR WITHIN SOLID PHASE
In adsorption (see Chap. 15) and ion exchange (see Chap. 16), the reaction occurs on or within the solid phase of the adsorbent (e.g., activated carbon) or ion exchange resin, respectively. Reactors for adsorption and ion exchange may consist of a fixed bed (i.e., packed bed; see Fig. 6-1h without airflow) or a fluidized bed (i.e., the packing media is suspended in the reactor; see Fig. 6-1i without airflow). Filters (covered in Chap. 11) and membranes (covered in Chap. 12) can be used in a reactor to retain reactants and reaction products that must be removed from the water. Combined unit processes may also be occurring in a single reactor; for example, hybrid membrane adsorption reactors are used in water treatment processes (powdered activated carbon addition before ultrafiltration).

REACTORS WITH RECYCLE USED FOR PRECIPITATION REACTIONS
Recycle reactors operate with a portion of the flow returned to the reactor inlet. Such reactors are used principally for precipitation reactions in which a portion of the precipitated solids is recycled to accelerate the rate of precipitation as in softening.

Open- and closed-reactor terminology is used to describe the entrance and exit conditions when dispersion (longitudinal mixing caused by fluid turbulence) and molecular diffusion (see discussion in Sec. 6-7) are important reactant/product transport mechanisms. A reactor is classified as an *open* reactor when either dispersion or diffusion contributes to solute fluxes into and out of the reactor. An example of an open reactor is groundwater with a contaminant plume that moves with the bulk groundwater flow but also by diffusion. In such situations, the contaminants may be found upstream of the groundwater flow direction. Reactors in which neither dispersion nor diffusion contributes to solute flux into or out of the reactor are classified as *closed* reactors. Most reactors used in water treatment are closed reactors because reactants and products are typically conveyed into or out of basins by pipes and weirs and no backmixing can occur at the entrance or exit.

Reactors Characterized by Entrance and Exit Conditions

6-2 Mass Balance Analysis

The quantitative description of a water treatment process begins with an accounting of all materials that enter, leave, accumulate in, or are transformed within the boundaries of a system. The basis for this accounting procedure, known as a *mass balance*, is the law of conservation of mass, which accounts for changes in any component due to fluid flow, mass transfer, or chemical transformations. The materials involved in a system, the scale and system chosen to write a mass balance, and the general mass balance analysis are introduced in this section.

A constituent that passes through a processing system without reacting in the reactor and remains unchanged in total mass (but not perhaps in concentration) is known as a *conservative* constituent. Constituents that undergo reaction, are transformed, or accumulate within the reactor during processing, resulting in less mass exiting with the reactor effluent than entered, are known as *nonconservative* constituents. For example, the chloride ion will pass through a water filtration plant unchanged because this inorganic ion does not adsorb on particulate matter or undergo biological transformations. Thus, the chloride ion acts as a conservative constituent. On the other hand, the ferrous ion, an ion often found in ground and surface waters, undergoes oxidation and hydrolysis in the presence of oxygen or other oxidizing agents, leading to the formation and sedimentation of an insoluble precipitate at appropriate chemical conditions. Therefore, a ferrous ion is a nonconservative constituent.

Conservative and Nonconservative Constituents

Scale and System Selection
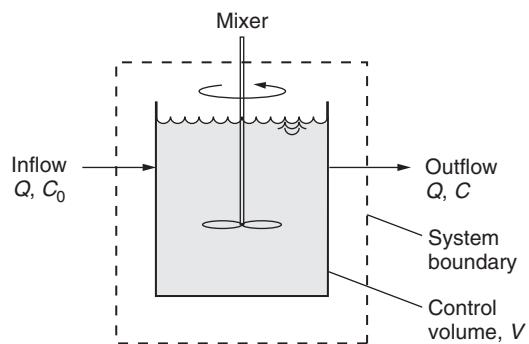
Accounting for the fate of a constituent in a water treatment plant or in an individual treatment process can be approached from various levels. While not commonly used in engineering design, the time and spatial variations of a constituent may be predicted based on forces operating at the ionic or molecular level. At the opposite extreme, it is possible to ignore all molecular interactions as well as the internal details of the system or unit and assume no local gradients of mass or temperature exist. The loss of mechanistic insight with this approach may still be correct, depending on what design issue is being investigated. Moreover, simpler approaches have the benefit of requiring much less complex mathematical analysis. Design based on mechanistic considerations is a desirable goal, but the complexity and uncertainty of the processes involved make mechanistic design unattainable in many cases, requiring the use of simplified but often still reasonable approaches. For example, if the amount of sludge that is generated by a coagulation/flocculation process is to be determined, then an overall mass balance on the process will be adequate. On the other hand, if the flocculator is to be designed for particle agglomeration and breakup on the microscale, then fluid velocity gradients in the flocculator on which microscale mixing occurs must be considered.

General Mass Balance Analysis

Two concepts needed to write a mass balance on a reactor include correct drawing of the system boundary and the choice of a time interval over which to write the mass balance. The *system boundary* is used to identify all of the material flows into and out of the system. The guiding principle in choosing the system is to have a uniform concentration (i.e., intensive properties such as concentration, temperature, and pressure are assumed isotropic) so that the kinetic expression can be evaluated at one concentration within the system. The actual volume in which change is occurring is often referred to as the *control volume*, and the control volume should be chosen so the mass flux (in and out) across the boundaries can be easily determined. A definition sketch of a control volume for a compeletely mixed reactor with inflow and outflow is shown on Fig. 6-2. For any control volume, a materials


Figure 6-2
Definition sketch for a materials balance analysis of a completely mixed continuous-flow reactor (CMFR).

balance can be expressed as

Mass of constituent entering system
  − mass of constituent leaving system
  − mass of constituent disappearing + mass of constituent   (6-1)
    appearing within system due to reaction
  = mass of constituent accumulation in system

The simplified word statement for the mass balance expression shown in Eq. 6-1 is written as

$$\text{In} - \text{out} - \text{loss} + \text{generation} = \text{accumulation} \qquad (6\text{-}2)$$

Mass may be transported across system boundaries by bulk fluid flow (advection) or by molecular diffusion or turbulent mixing (dispersion). The distinction between molecular diffusion and dispersion is described in detail in Sec. 6-7. Transformations or losses may occur because of chemical reactions and mass transfer between phases within the system boundaries. The spatial and temporal variation of the concentration of conservative and nonconservative constituents, depending on the scale of its application, can be determined using Eq. 6-1.

A mass balance on a single reaction only needs to be written for one component. The concentrations and pressures of the other components can be determined from the stoichiometry of the reaction, as shown previously in Chap. 5.

6-3 Hydraulic Characteristics of Ideal Reactors

Ideal reactors provide the basic conceptual foundation upon which an understanding of real reactors can be built. On the laboratory bench, with carefully managed conditions, reactors can be made to provide nearly ideal performance. For many processes, pilot-scale systems often come close to ideal performance as well. These ideal systems can be used to provide useful estimates of the performance of even the largest scale systems. Thus, a thorough understanding of the behavior of ideal reactors, including the necessary assumptions, is essential to testing and modeling full-scale process performance.

Completely Mixed Batch Reactor

When considering an ideal CMBR, the following assumptions are made: (1) the contents of the tank are completely uniform with no density gradients or dead space, (2) the probability of a particle of water being in any one part of the tank at any time is the same, (3) the temperature is uniform throughout the reactor, and (4) any chemical added to the contents is instantly and uniformly distributed throughout the reactor. A diagram sketch of the CMBR is shown on Fig. 6-3a.

Completely Mixed Flow Reactor

The assumptions made when modeling a CMFR are similar to those made for the CMBR, namely (1) the contents of the tank are completely uniform

Mixer

Tank contents are
completely mixed

(a)

Mixer

Inflow   Outflow

Tank contents are
completely mixed

Concentration of chemical
in mixing tank equal to
effluent concentration

(b)
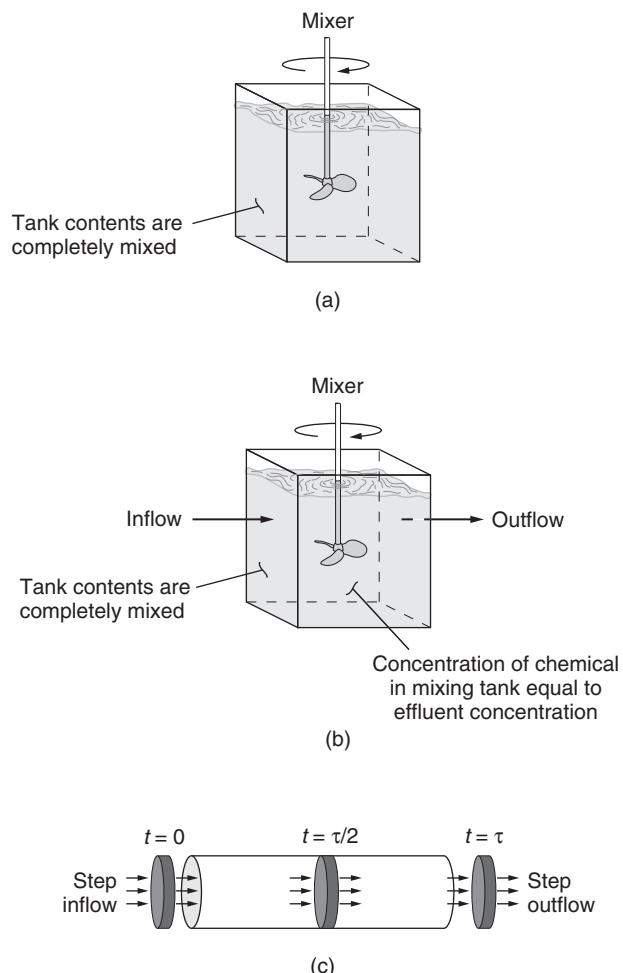
Figure 6-3
Concept diagrams for three ideal reactors:
(a) completely mixed batch reactor, (b) completely
mixed continuous-flow reactor, and (c) plug flow
reactor.

$t = 0$ $t = \tau/2$ $t = \tau$

Step
inflow

Step
outflow

(c)

with no density gradients or dead space, (2) the probability of a particle
of water being in any part of the tank at any time is the same, (3) the
temperature is uniform throughout the reactor, and (4) any chemical
added to the contents is instantly and uniformly distributed throughout
the reactor. Because of the first assumption of complete mixing, it is also
assumed that the effluent of a CMFR has precisely the same composition as
the contents. A diagram sketch of the CMFR is shown on Fig. 6-3b.

There are two important differences between the assumptions of the
CMBR and the CMFR when reactions are occurring in the reactor: (1) In
the CMBR all the reactants are in the reactor for the same residence time,
whereas in the CMFR the reactants are in the reactor for a variety of
residence times; and (2) in the CMBR the concentration of the reactants
changes with time as the reaction takes place, whereas in the CMFR the

concentration of all the reactants is the same throughout the reactor all the time (once the reactor has reached steady state).

Plug Flow Reactor

The water traversing an ideal PFR flows uniformly without mixing with the water in front of or behind it in the reactor. The plug flow concept can also be described as flow consisting of a series of plugs with the same diameter as the inside diameter of the reactor. Each time a new plug is introduced in one end of the reactor, another plug of the same size must exit the other end. If the plugs are introduced at a constant rate, then each plug is in the reactor for the same amount of time. Thus, the performance of a PFR is, by definition, precisely the same as the performance of a CMBR that has operated for the same period of time as the residence time of a PFR.
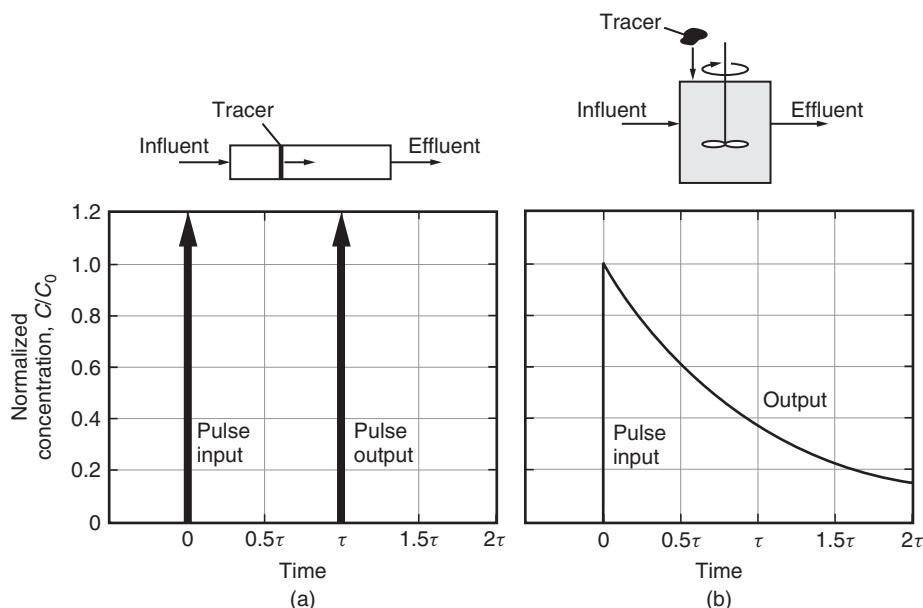
It is common for practitioners to conduct a bench-scale, batch experiment and then assume the same result will be obtained for the same conditions (e.g., chemical dosing, mixing intensity) and the same contact time in a full-scale continuous PFR facility, known as the plug flow assumption. The jar test, used to determine the optimum coagulant chemical dose, is an example of a bench-scale experiment. Reactors can be designed to operate as near-ideal PFRs; however, in many cases the performance is not ideal. Because of the desirable characteristics of the PFR for water treatment operations, it is important to understand what can be done to make a design approach plug flow and know when the plug flow assumption is erroneous. In addition, it is necessary to be able to estimate the performance of PFRs under nonideal conditions. A sketch of ideal flow in a PFR is shown on Fig. 6-3c.

Tracer Curves for Ideal Reactors

A tracer is a conservative chemical that is used to assess the flow conditions through a reactor. To compare the hydraulic performance of a continuous-flow reactor to the ideal model, a tracer is introduced into the reactor's influent, and its concentration is then observed in the reactor's effluent. Three techniques are used: (1) the instantaneous addition of a pulse or slug of tracer in the influent followed by observation of the same pulse as it exits the reactor, (2) the addition of the tracer at a steady rate followed by observation until the effluent of the reactor equals the influent concentration, or (3) the addition of a tracer at a steady rate until the effluent concentration equals the influent concentration, then a cessation of the tracer feed followed by continued observation until no tracer is found in the effluent. All three tracer addition methods yield information about the exit age distribution, the cumulative exit distribution, and the internal age distribution, respectively. Conducting tracer studies is discussed in greater depth in Sec. 6-6.

The tracer curves that occur from the addition of the same pulse input to both a PFR and a CMFR are illustrated on Fig. 6-4. A pulse that passes through the PFR has exactly the same shape it had initially and with a detention time $\tau = V/Q$ (volume/flow rate) after the tracer is added.

Figure 6-4
Tracer curves from ideal reactors: (a) plug flow reactor and (b) completely mixed flow reactor.

The tracer curve for a pulse input to a CMFR has a significantly different shape from that obtained for a PFR. The effluent tracer concentration from a CMFR instantly reaches a maximum as the tracer is uniformly distributed throughout the reactor and then gradually dissipates in an exponential manner as the tracer material leaves the effluent. The shape of the tracer curve is exponential because, as the tracer leaves the reactor, the concentration of the tracer is reduced, which in turn reduces the rate at which the tracer mass leaves the reactor. A mass balance analysis for a nonreactive substance (generation term is zero) can be used to determine the characteristics of a pulse tracer (in term is zero) in a CMFR:

$$\text{In} - \text{out} + \text{generation} = \text{accumulation}$$

$$0 - QC + 0 = V\frac{dC}{dt} \tag{6-3}$$

where Q = flow rate through reactor, L/s
        V = reactor volume, L
        C = effluent concentration of tracer at time t, mg/L
        t = time since slug of tracer was added to reactor, s

Equation 6-3 can be rearranged to obtain the expression

$$-\frac{Q}{V}dt = \frac{dC}{C} \tag{6-4}$$

At $t = 0^+$ (time immediately after tracer is added), the tracer slug has entered the reactor and is uniformly dispersed within the CMFR. Consequently, Eq. 6-4 may be integrated:

$$-\int_0^t \frac{Q\, dt}{V} = \int_{C_0}^C \frac{dC}{C} \tag{6-5}$$

where C_0 = initial mass of tracer added divided by volume of reactor, mg/L

The following expression is obtained after substitution of $\tau = V/Q$, the theoretical hydraulic detention time, into Eq. 6-5:

$$C = C_0 e^{-t/\tau} \tag{6-6}$$

where $\tau = V/Q$ = hydraulic detention time, s

The tracer curve shown on Fig. 6-4b may be obtained using the expression presented in Eq. 6-6.

In environmental engineering, it is common to employ a series of CMFRs to improve the hydraulic performance of a reactor. The improved efficiency that may be gained from CMFRs in series is discussed in Sec. 6-5. The impact of putting a few CMFRs in series (commonly known as tanks in series) on the tracer curve is described below. A definition sketch of CMFRs in series is shown on Fig. 6-5. The development of the CMFRs in series analysis is based on a constant total volume because the tank volume is an important factor controlling capital cost, and the purpose of the exercise is to determine if dividing that volume into several smaller compartments will improve efficiency. Assuming that both the total reactor volume and the mass of tracer added remain constant, the volume of each reactor is

Completely Mixed Flow Reactors in Series

$$V_R = \frac{V}{n} \tag{6-7}$$
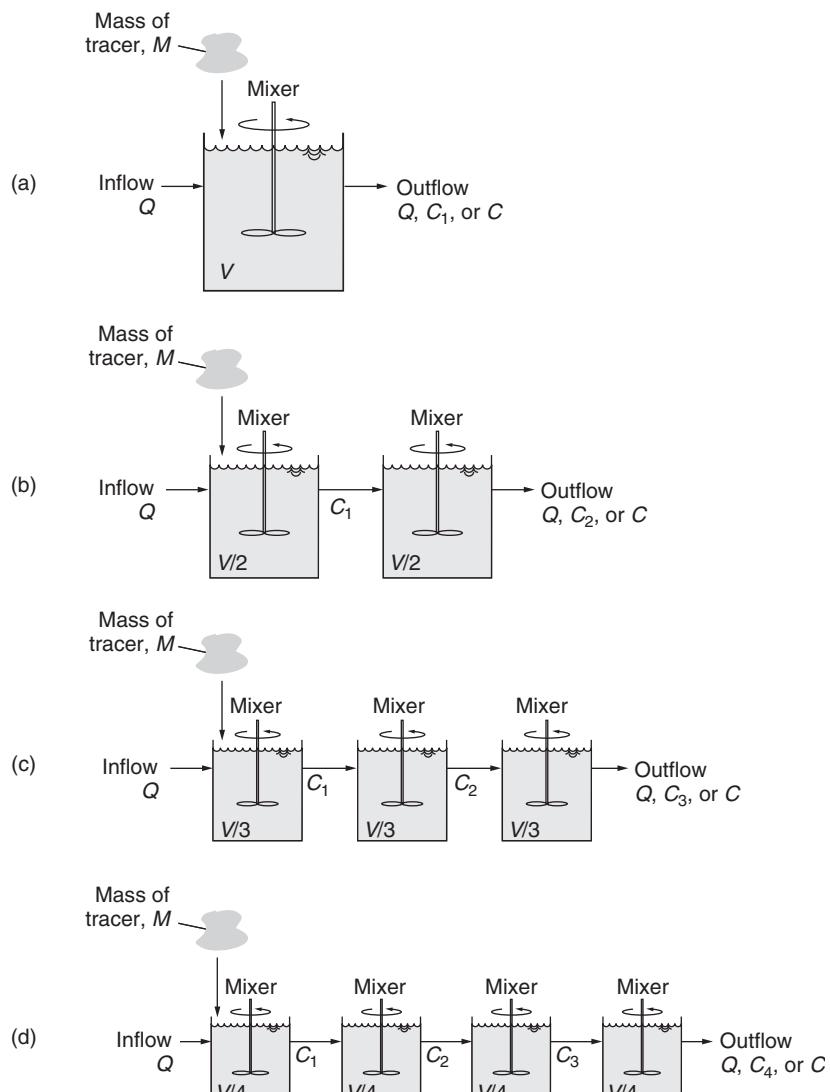
where V_R = volume of each reactor in series, m^3
V = total volume of all reactors in series, m^3
n = number of reactors in series

If the same mass of tracer is used in all tracer studies, the initial concentration of the tracer would be equivalent to the concentration that would result if the entire mass of tracer were placed in one tank having the same volume as all of the tanks in the series:

$$C_0^* = \frac{M}{V_R} \tag{6-8}$$

where M = mass of tracer added, g
C_0^* = initial concentration, mg/L (equivalent to g/m^3)

Figure 6-5
Definition sketch: comparing
a tracer test in (a) one,
(b) two, (c) three, or (d) four
CMFRs in series. Each series
receives the same mass dose
of tracer, M, and each series
has the same total volume, V.

If, however, all of the tracer is added to the first reactor, the initial concentration is given by the expression

$$C_0^* = \frac{nM}{V} = nC_0 \tag{6-9}$$

The mass balance (see Eq. 6-2) for a pulse input of conservative tracer in the first reactor in a series of n reactors incorporates the following assumptions: (1) the generation term can be assumed to be zero because the tracer substance is conservative (no reaction) and (2) the influent concentration

of tracer is zero because the tracer is added as a pulse input (single event). These assumptions result in the mass balance expression

$$0 - QC_1 + 0 = \frac{V}{n}\frac{dC_1}{dt} \tag{6-10}$$

where C_1 = effluent concentration exiting first reactor in series, mg/L

The expression shown in Eq. 6-10 can be simplified and rearranged for integration as

$$\int_{C_0^*}^{C_1} \frac{dC_1}{C_1} = -\int_0^t \frac{nQ}{V}dt \tag{6-11}$$

Integrating, as shown previously in Eq. 6-5, results in the expression

$$\ln\frac{C_1}{C_0^*} = -\frac{nQ}{V}t \tag{6-12}$$

Substituting nC_0 for C_0^*, the effluent concentration from the first CMFR in a series of ideal CMFRs as a function of time is written as

$$\frac{C_1}{C_0} = ne^{-(nQ/V)t} = ne^{-n\theta} \tag{6-13}$$

where θ = relative (normalized) detention time
   $= Qt/V = t/\tau$, dimensionless

For the second reactor in the series, the generation term is still zero. The influent concentration changes with time and is equal to the effluent concentration from the first CMFR in the series:

$$QC_1 - QC_2 + 0 = \frac{V}{n}\frac{dC_2}{dt} \tag{6-14}$$

The expression from Eq. 6-14 can be simplified and rearranged as

$$\frac{dC_2}{dt} + \frac{nQ}{V}C_2 = \frac{nQ}{V}C_1 \tag{6-15}$$

where C_2 = effluent concentration exiting second reactor in series, mg/L

Substituting Eq. 6-13 into Eq. 6-15 yields

$$\frac{dC_2}{dt} + \frac{nQ}{V}C_2 = \frac{nQ}{V}nC_0 e^{-(nQ/V)t} \tag{6-16}$$

The integrating factor method is used to solve Eq. 6-16. The method involves multiplying Eq. 6-16 by the integrating factor $e^{(nQ/V)t}$, which results in the expression

$$\frac{dC_2}{dt}e^{(nQ/V)t} + \frac{nQ}{V}e^{(nQ/V)t}C_2 = \frac{n^2Q}{V}C_0 e^{-(nQ/V)t}e^{(nQ/V)t} \tag{6-17}$$

The two terms on the left-hand side of Eq. 6-17 are the derivative of the product of the functions C_2 and $\exp[(nQ/V)t]$. Combining these terms yields

$$\frac{d\left[C_2 e^{(nQ/V)t}\right]}{dt} = \frac{n^2 Q}{V} C_0 \qquad (6\text{-}18)$$

Integrating Eq. 6-18 yields the following expression for the effluent concentration of tracer from the second CMFR in the series after some algebraic manipulation:

$$\frac{C_2}{C_0} = \frac{n^2 Qt}{V} e^{-(nQ/V)t} = n(n\theta) e^{-n\theta} \qquad (6\text{-}19)$$

Using the same approach as shown above, the effluent concentration for any number of reactors in series can be obtained. The corresponding effluent concentration expression for the third and fourth CMFRs in series is given by Eqs. 6-20 and 6-21, respectively:

$$\frac{C_3}{C_0} = \frac{n(n\theta)^2}{2} e^{-n\theta} \qquad (6\text{-}20)$$

$$\frac{C_4}{C_0} = \frac{n(n\theta)^3}{6} e^{-n\theta} \qquad (6\text{-}21)$$

where C_3 = effluent concentration exiting third reactor in series, mg/L

   C_4 = effluent concentration exiting fourth reactor in series, mg/L

The tracer curves from one, two, three, and four CMFRs in series, with each reactor series having an equivalent volume, are shown on Fig. 6-6. The tracer curve changes dramatically as the number of CMFRs increases. In addition, the use of CMFRs in series can also result in significant improvements in reactor performance, as discussed in the following sections.
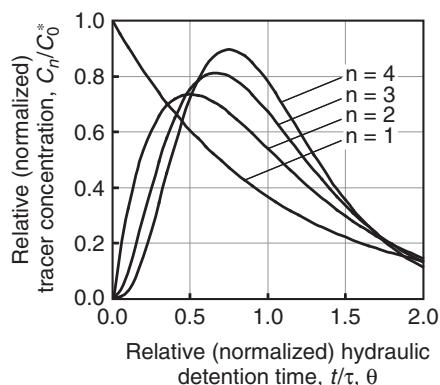
Figure 6-6
Tracer curves from one, two, three, and four CMFRs in series. Each series has the same total reactor volume and the same total mass of tracer added at the start.

6-4 Modeling Reactions in Completely Mixed Batch Reactors

The CMBR is the ideal reactor most widely used in the laboratory to gather and understand reaction data. The contents of the CMBR are mixed completely and the concentration is uniform throughout the reactor, as shown on Fig. 6-3a. The focus of this section is on modeling the reactions that occur in a CMBR.

For the system shown on Fig. 6-7, a boundary can be drawn around the system (see dashed line) and a mass balance can be written that accounts for the mass entering, leaving, reacting, or accumulating within that boundary during the time period from t to $t + \Delta t$:

Mass Balance Analysis

$$0 - 0 + \Delta t \; rV = N|_{t+\Delta t} - N|_t \qquad (6\text{-}22)$$

where

$$
\begin{aligned}
V &= \text{reactor volume, L} \\
\Delta t &= \text{time interval, s} \\
N|_{t+\Delta t} &= \text{amount of reactant in reactor evaluated at } t + \Delta t, \text{ mol} \\
N|_t &= \text{amount of reactant in reactor evaluated at } t, \text{ mol} \\
r &= \text{average reaction rate during interval from } t \text{ to } t + \Delta t, \\
&\quad \text{mol/L} \cdot \text{s}
\end{aligned}
$$

If Eq. 6-22 is rearranged and the limit as Δt approaches 0 is taken, the following general expression is obtained for a CMBR:

$$rV = \lim_{\Delta t \to 0} \left(\frac{N|_{t+\Delta t} - N|_t}{\Delta t} \right) = \frac{dN}{dt} \qquad (6\text{-}23)$$

Writing Eq. 6-23 in terms of concentrations yields

$$r = \frac{1}{V} \frac{dC \, V}{dt} = \frac{dC}{dt} + \frac{1}{V} \frac{C \, dV}{dt} \qquad (6\text{-}24)$$

where

$$
\begin{aligned}
C &= \text{concentration of reactant in CMBR, mol/L} \\
N &= \text{amount of reactant in reactor, mol} \\
t &= \text{time, s}
\end{aligned}
$$

Mixer

System boundary

Control volume, V
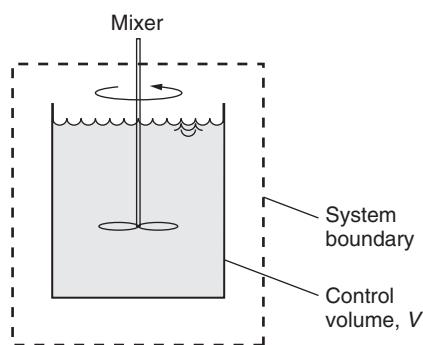
Figure 6-7
Definition sketch for mass balance analysis of batch reactor.

For a constant volume CMBR, Eq. 6-24 becomes

$$r = \frac{dC}{dt} \tag{6-25}$$

As shown in Eq. 6-25, C is a function of time. Equations 6-24 and 6-25 are valid regardless of the order of the reaction.

Reaction Rates in a Completely Mixed Batch Reactor

If the progress of a reaction is observed while it takes place in a CMBR, common kinetic rate expressions can be evaluated to determine the correlation between the data and the reaction kinetics. If the reaction is first order, Eq. 6-25 may be written as

$$r = -kC = \frac{dC}{dt} \tag{6-26}$$

where $k =$ first-order rate constant, s^{-1}

(a) $\ln(C)$ — y intercept = $\ln(C_0)$, Slope = k

(b) $1/C$ — Slope = k, y intercept = $1/C_0$

(c) C — y intercept = C_0, Slope = k

Time, t
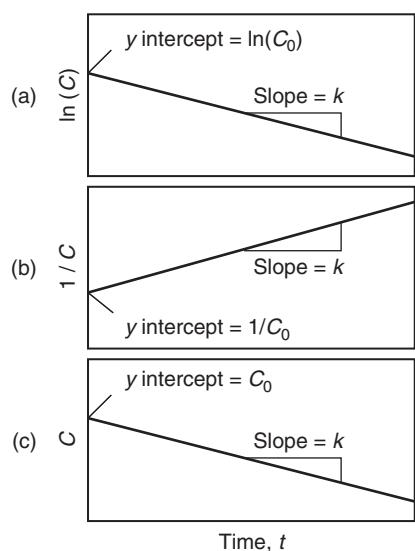
Figure 6-8
Graphical display of (a) first-, (b) second-, and (c) zero-order reactions.

Integrating the expression shown in Eq. 6-26 yields

$$\frac{C}{C_0} = e^{-kt} \tag{6-27}$$

where $C_0 =$ initial concentration, mol/L

Taking the natural logarithm of both sides, the following relationship is obtained:

$$\ln(C) - \ln(C_0) = -kt \tag{6-28}$$

For a first-order reaction, a plot of $\ln(C)$ as a function of t, as shown in Eq. 6-28, will result in a linear relationship. Such a plot is illustrated on Fig. 6-8a. The slope of the line in the plot is equal to the first-order rate constant k and the intercept is equal to $\ln(C_0)$.

Similar, straightforward graphical solutions can be demonstrated for reactions of zero order (Fig. 6-8c) and second order (Fig. 6-8b). Analytical solutions for all these reaction orders as well as for nth-order reactions are shown in Table 6-3. There is no linear graphical solution for an nth-order reaction, but a spreadsheet can be used to determine which reaction order results in the best fit.

Half-Life Concept for Irreversible Reactions

A widely used parameter to compare reaction rates is the half-life, the time within which half of the initial concentration of a reactant has disappeared, that is, $C/C_0 = 0.5$. For first-order, irreversible reactions, the half-life is obtained by rearrangement of Eq. 6-28 as follows:

$$\ln\left(\tfrac{1}{2}C_0\right) - \ln(C_0) = -kt_{1/2} \tag{6-29}$$

Equation 6-29 can also be written as

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k} \tag{6-30}$$

Example 6-1 Determination of reaction rate constant for decomposition of ozone

In laboratory experiments, ozone was added to a beaker (batch) of water and the concentration of ozone remaining was measured periodically. The initial concentration of ozone, C_0, was 5 mg/L for all experiments. The fraction of ozone remaining in the water at pH values of 7.6, 8.5, and 9.2 are presented in the following table (from Stumm, 1956):

Time, min	Ozone Concentration, C (mg/L)		
	pH = 7.6	pH = 8.5	pH = 9.2
0	5	5	5
1	4.95	—	4.25
2.3	—	4.15	—
5.5	—	—	2.1
6.8	4.55	—	—
7.4	—	3.05	—
8.9	—	2.75	—
9	4.35	—	1.1
14.3	—	2	—
18	3.7	—	—
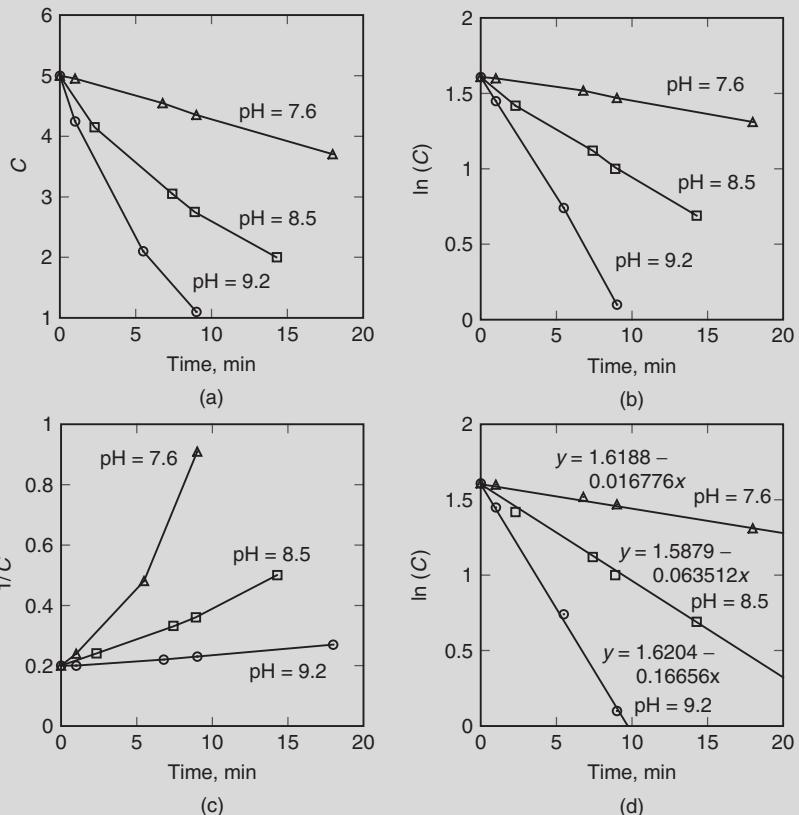
Determine the reaction order and reaction rate constant for the decomposition of ozone in water at three pH values (7.6, 8.5, and 9.2), considering zero-, first-, and second-order reactions.

Solution

1. Determine the order of the reaction by plotting various concentration quantities as a function of time.
   a. Construct a computation table for the values to be plotted.

Time, min	C			ln(C)			1/C		
	pH = 7.6	pH = 8.5	pH = 9.2	pH = 7.6	pH = 8.5	pH = 9.2	pH = 7.6	pH = 8.5	pH = 9.2
0	5	5	5	1.61	1.61	1.61	0.20	0.20	0.20
1	4.95	—	4.25	1.60	—	1.45	0.20	—	0.24
2.3	—	4.15	—	—	1.42	—	—	0.24	—
5.5	—	—	2.1	—	—	0.74	—	—	0.48
6.8	4.55	—	—	1.52	—	—	0.22	—	—
7.4	—	3.05	—	—	1.12	—	—	0.33	—
8.9	—	2.75	—	—	1.01	—	—	0.36	—
9	4.35	—	1.1	1.47	—	0.10	0.23	—	0.91
14.3	—	2	—	—	0.69	—	—	0.50	—
18	3.7	—	—	1.31	—	—	0.27	—	—

b. For a zero-order reaction, a plot of concentration C as a function of time t is shown in panel (a) of the figure below.

c. For a first-order reaction, a plot of the natural log of concentration, $\ln(C)$, as a function of time t is shown in panel (b) below.

d. For a second-order reaction, a plot of inverse concentration $1/C$ as a function of time t is shown in panel (c) below.

(a)

(b)

(c)

(d)

Because the plot constructed in panel (b) results in a linear relationship, ozone decomposition in water can be described using first-order kinetics.

2. Determine the reaction rate constants for each pH value. The reaction rate constant is determined by finding the slope of the best-fit line for the data. As shown in panel (d) above, the first-order reaction rate constants for the decomposition of ozone in water are 0.0168, 0.0635, and 0.167 min^{-1} for water with pH values of 7.6, 8.5, and 9.2, respectively.

Table 6-3
Solutions to reactions with different orders

Reaction Order	Rate Expression	Solution[a]	Units for Rate Constant
Zero order	$r = -k = \dfrac{dC}{dt}$	$C = C_0 - kt$	mol/L · s
First order	$r = -kC = \dfrac{dC}{dt}$	$C = C_0 e^{-kt}$	s^{-1}
Second order	$r = -kC^2 = \dfrac{dC}{dt}$	$\dfrac{1}{C} = \dfrac{1}{C_0} + kt$	L/mol · s
nth order	$r = -kC^n = \dfrac{dC}{dt}$	$C = \sqrt[-n+1]{(-n+1)\left(-kt + \dfrac{C_0^{-n+1}}{-n+1}\right)}$ $(n \geq 0, n \neq 1)$	$(L/mol)^n \cdot s^{-1}$

[a]For reactions in a PFR, the reaction time t is replaced by the hydraulic detention time τ ($\tau = V/Q$) in the solution equation.

Through a similar exercise, the half-life for a second-order irreversible reaction can be determined from the second-order rate expression solution given in Table 6-3. The half-life is inversely proportional to both the rate constant and the initial reactant concentration:
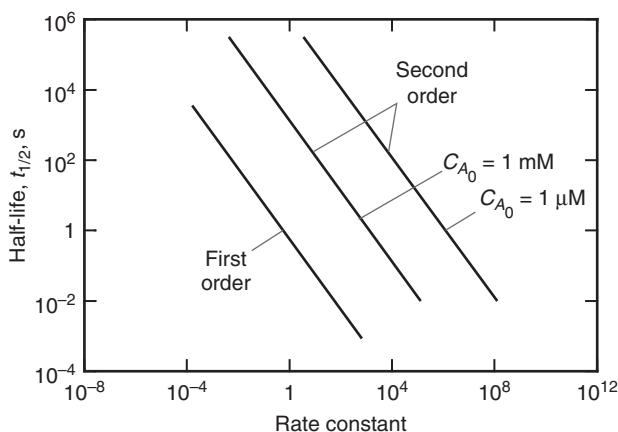
$$t_{1/2} = \frac{1}{kC_0} \tag{6-31}$$

Rate constants for common first-order reactions used in water treatment applications are listed in Table 6-4. Additional reaction rate constants can be found in compendiums in the literature (e.g., Hoffmann, 1981; Hoigne and Bader, 1983; Pankow and Morgan, 1981; Stumm and Morgan, 1996). The relationship between the half-life and the rate constant for first- and second-order reactions is illustrated on Fig. 6-9. Note that, where second-order reactions are concerned, the initial reactant concentration must be considered as well as the second-order rate constant.

Table 6-4
Selected first-order rate constants for reactions common to water treatment

Reaction	Conditions of Measurement	Rate Constant, s^{-1}	Reference
$Cl_2(aq) + H_2O \rightarrow HOCl + H^+ + Cl^-$	20°C	11	Eigen and Kustin (1962)
$SO_2(aq) + H_2O \rightarrow HOSO_3^- + H^+$	20°C	3.4×10^6	Eigen et al. (1961)
$CO_2(aq) + H_2O \rightarrow HCO_3^- + H^+$	20°C	0.02	Kern (1960)
$Al(H_2O)_6^{3+} \rightarrow [Al(H_2O)_5OH]^{2+} + H^+$	25°C, pH 4	4.2×10^4	Holmes et al. (1968)

Figure 6-9
Comparison of reaction half-life for first- and second-order reactions in water treatment (C_0 = initial concentration in reactor).

First-order reactions with rate constants greater than 1 s^{-1} are characterized as fast reactions. For example, the hydrolysis of chlorine in water has a first-order rate constant of 11 s^{-1} at 20°C (Eigen and Kustin, 1962). The reaction has a $t_{1/2}$ of 0.06 s and is essentially complete (99 percent conversion) in less than 0.5 s at a pH greater than 5. When the initial concentration is 10^{-3} mol/L or greater and the rate constant is greater than 10^2 L/mol·s, second-order reactions are also considered fast.

6-5 Modeling Reactions in Ideal Continuous-Flow Reactors

Models for ideal, continuous-flow reactors are useful for gaining an understanding of the behavior of reactors that are used in full-scale systems. The models for these systems are constructed easily and often provide practical estimates of full-scale behavior. The progress of reactions in CMFRs and PFRs with and without recycle are analyzed in this section. Although CFMRs in series will also be considered, combinations of CFMRs and PFRs will not be discussed. The student may want to seek other resources (Fogler, 1999; Levenspiel, 1998) to examine these questions, which can also have practical value.

Completely Mixed Flow Reactor

Four assumptions are made when considering an ideal CMFR (Sec. 6-3), and because of the assumption that the contents are mixed completely, it follows that the effluent has precisely the same composition as the reactor contents. Therefore, the rate of reaction in a CMFR proceeds according to the effluent concentration, resulting in the need for a larger reactor volume as compared to PFRs.

CMFR MASS BALANCE
Design of a CMFR is typically based on *steady-state* conditions, meaning the effluent concentration does not change with respect to time, there is no

accumulation, and reactor volume and flow rate are constant. Mathematically, this mass balance may be written as

$$Q\,(C_0 - C) + Vr|_C = 0 \tag{6-32}$$

where C_0 = influent concentration, which may be a function of time, mg/L

Q = flow rate, L/s

C = effluent concentration, mg/L

$r|_C$ = reaction rate in reactor at effluent concentration C, mg/L · s

V = reactor volume, L

In Eq. 6-32, the value of $r|_C$ will be less than zero if the component of interest is consumed by the reaction; the value of $r|_C$ will be greater than zero if the component of interest is produced by the reaction.

Dividing Eq. 6-32 by Q results in the expression

$$0 = C_0 - C + \frac{V}{Q}r|_C = C_0 - C + \tau r|_C \tag{6-33}$$

where τ = hydraulic detention time, which is equal to V/Q, s.

The hydraulic detention time or the volume of the reactor needed can be estimated if the chemical kinetics, treatment objective (effluent concentration), influent concentration, and flow rate are known, as follows:

$$\tau = \frac{C_0 - C}{-r|_C} \tag{6-34}$$

$$V = \frac{Q(C_0 - C)}{-r|_C} \tag{6-35}$$

The specific form that is taken by these equations depends on the rate of the reaction. The reaction rate takes different forms for zero-, first-, and second-order reactions, as shown in Table 6-3. Putting Eqs. 6-34 and 6-35 in proper form for these three reaction rates, the following expressions for determining the hydraulic detention time τ and volume V are obtained:

$$\tau = \frac{C_0 - C}{k} \qquad V = \frac{Q(C_0 - C)}{k} \quad \text{(zero order)} \tag{6-36}$$

$$\tau = \frac{C_0 - C}{kC} \qquad V = \frac{Q(C_0 - C)}{kC} \quad \text{(first order)} \tag{6-37}$$

$$\tau = \frac{C_0 - C}{kC^2} \qquad V = \frac{Q(C_0 - C)}{kC^2} \quad \text{(second order)} \tag{6-38}$$

where k = reaction rate constant (see Table 6-3 for units)

EXPRESSION OF CONCENTRATION IN TERMS OF REMOVAL

In many drinking water treatment operations, the focus is on removal of contaminants, so it is often relevant to determine the amount of

Example 6-2 Effluent concentration from a CMFR

A CMFR has an influent concentration of 200 mg/L and a first-order reaction rate constant of 4 d^{-1}. Assuming steady-state conditions, calculate the effluent concentration for a hydraulic detention time of 12 h. Calculate the required hydraulic detention time for an effluent concentration of 10 mg/L.

Solution

1. Determine the effluent concentration by rearranging Eq. 6-37. For steady state, the following result is obtained:

$$C = \frac{C_0}{1 + \tau k} = \frac{200 \text{ mg/L}}{1 + (4/\text{d})(0.5 \text{ d})} = 66.6 \text{ mg/L}$$

2. Determine the detention time using Eq. 6-37. The required hydraulic detention is given by the expression

$$\tau = \frac{C_0 - C}{kC} = \frac{(200 - 10) \text{ mg/L}}{(4/\text{d})(10 \text{ mg/L})} = \frac{190 \text{ mg/L}}{40 \text{ mg/L} \cdot \text{d}} = 4.75 \text{ d}$$

contaminant removal, that is,

$$\text{Removal} = R = 1 - \frac{C}{C_0} \qquad (6\text{-}39)$$

Each of the equations for detention time given above (Eqs. 6-36, 6-37, and 6-38) can be rearranged so that (1) the amount of contaminant removal for a reactor with a given detention time may be determined and (2) the detention time necessary for a specified degree of removal may be determined. For example, rearranging Eq. 6-36, the removal for a zero-order reaction may be defined as

$$1 - \frac{C}{C_0} = R = \frac{\tau k}{C_0} \qquad (6\text{-}40)$$

CMFR TANKS-IN-SERIES ANALYSIS

Treatment processes are frequently staged to meet treatment objectives (e.g., ozonation may be carried out in three or four consecutive stages). Staged treatment processes may be analyzed as tanks in series by building upon Eq. 6-32 developed for a single CMFR. The following analysis of CMFR in series is for first-order reactions, which are frequently encountered in water treatment engineering. The first step is to write Eq. 6-32 in terms of a rate law, instead of a reaction rate, and to include the number of equally sized tanks. The following expression is obtained for a first-order reaction for the first tank in a series of CMFRs.

$$0 = C_0 - C_1 - \frac{V}{nQ} k C_1 \qquad (6\text{-}41)$$

where C_1 = effluent concentration of first CMFR, mg/L

n = number of CMFRs

k = first-order reaction rate constant, s^{-1}

Rearranging Eq. 6-41 yields an expression to solve for C_1:

$$C_1 = \frac{C_0}{1 + (V/nQ)k} \tag{6-42}$$

Following the same steps, the expression for the effluent concentration of the second CMFR, C_2, can be obtained:

$$C_2 = \frac{C_1}{1 + (V/nQ)k} \tag{6-43}$$

Substituting the equation for C_1, Eq. 6-42, into Eq. 6-43 yields the expression

$$C_2 = \frac{C_0}{[1 + (V/nQ)k]^2} \tag{6-44}$$

A general expression for the effluent concentration of the nth equally sized CMFR, when the influent concentration is known, may be expressed as

$$C_n = \frac{C_0}{[1 + (V/nQ)k]^n} \tag{6-45}$$

The total volume required for n CMFRs in series may be determined by rearranging Eq. 6-45 as follows:

$$V = \left[\left(\frac{C_0}{C_n} \right)^{1/n} - 1 \right] \left(\frac{nQ}{k} \right) \tag{6-46}$$

UNSTEADY-STATE ANALYSIS

Reactors of concern in water treatment engineering typically operate at steady-state conditions. However, there are times that it is important to analyze reactors operating under unsteady-state conditions, such as when a reactor is first brought online. The unsteady-state analysis begins with a mass balance equation, which is written for a first-order reaction assuming constant volume and using detention time, $\tau = V/Q$, as follows:

$$\tau \frac{dC}{dt} = (C_0 - C) - \tau(kC) = C_0 - C(1 + k\tau) \tag{6-47}$$

The integral form of the mass balance analysis shown in Eq. 6-47 is expressed as

$$\int_{C_0^*}^{C} \frac{dC}{C_0 - C(1 + k\tau)} = \frac{1}{\tau} \int_0^t dt \tag{6-48}$$

where C_0^* = initial concentration in reactor at time zero, mg/L

Performing the integration of the unsteady-state mass balance results in the expression

$$-\left(\frac{1}{1 + k\tau} \right) \ln \left[\frac{C_0 - C(1 + k\tau)}{C_0 - C_0^*(1 + k\tau)} \right] = \frac{t}{\tau} \tag{6-49}$$

Solving Eq. 6-49 for C results in the final form of the unsteady-state mass balance:

$$C = \left(\frac{C_0}{1 + k\tau}\right) - \left[\left(\frac{C_0}{1 + k\tau}\right) e^{-(1+k\tau)t/\tau}\right] + (C_0^* e^{-(1+k\tau)t/\tau}) \tag{6-50}$$

The first term in Eq. 6-50 corresponds to the steady-state condition, and as $t \rightarrow \infty$, the second and third terms in Eq. 6-50 will drop out, indicating that the system has reached steady state.

TIME REQUIRED TO ACHIEVE STEADY STATE

When a process is brought online, it may be important to determine how long it will take for the process to achieve steady state. For instance, when bringing an ozone contactor online, it is important to know how long it will take for the effluent quality to meet treatment goals. To determine the time required to achieve steady state, the case of a first-order reaction is addressed. The initial concentration in the reactor (C_0^*) is set equal to the influent concentration (C_0) in Eq. 6-48 and the expression is integrated. The final form of the unsteady-state mass balance for this special condition is

$$C = \frac{C_0}{1 + k\tau} + \frac{k\tau C_0 e^{-(1+k\tau)t/\tau}}{1 + k\tau} \tag{6-51}$$

Equation 6-51 may now be simplified by dividing by C_0 and considering time as a fraction or multiple of the theoretical detention time, t/τ. The term t/τ, also known as normalized time, is used to allow comparison of reactors with different hydraulic detention times:

$$\frac{C}{C_0} = \frac{1}{1 + k\tau} + \frac{k\tau e^{-(1+k\tau)(t/\tau)}}{1 + k\tau} \tag{6-52}$$

As shown in Eq. 6-52, $k\tau$, which is the *Damköhler* number, is used to determine the dimensionless steady-state concentration and the profile of dimensionless concentration versus time.

In theory, it takes an infinite amount of time to achieve steady state; however, a reasonable steady state can generally be achieved within several detention times. To estimate an acceptable time, the following operational definition of steady state is introduced:

$$\frac{C}{C_0} - \frac{C_\infty}{C_0} \leq 0.01 \tag{6-53}$$

where C_∞ = steady-state concentration, mg/L

Substituting for $C_\infty/C_0 = 1/(1 + k\tau)$ and rearranging Eq. 6-53 yields the expression

$$\frac{C}{C_0} \leq 0.01 + \frac{1}{1 + k\tau} \tag{6-54}$$

The expression shown in Eq. 6-52 may be substituted for C/C_0 and Eq. 6-54 is rearranged to solve for time to steady state:

$$\frac{1}{1+k\tau} + \frac{k\tau e^{-(1+k\tau)(t/\tau)}}{1+k\tau} \leq 0.01 + \frac{1}{1+k\tau} \qquad (6\text{-}55)$$

The resulting expression for time to reach steady state is

$$\frac{t}{\tau} \geq \frac{1}{1+k\tau} \ln\left[\frac{100(k\tau)}{1+k\tau}\right] \qquad (6\text{-}56)$$

Based on the criterion developed in Eq. 6-53, operation times greater than those estimated using Eq. 6-56 will be adequate to achieve steady state. Using the expression for first-order reactions shown in Eq. 6-37, the term $k\tau$ can be substituted into Eq. 6-56, resulting in the equation

$$\frac{t}{\tau} \geq \frac{C_\infty}{C_0} \ln\left[100\left(1 - \frac{C_\infty}{C_0}\right)\right] \qquad (6\text{-}57)$$

To plot all possible scenarios, all possible Damköhler numbers need to be examined, which can be accomplished by plotting the number of hydraulic detention times that are required to achieve steady state as a function of the reduced steady-state concentration. As shown on Fig. 6-10, approximately 2.5 hydraulic detention times are adequate for all of the scenarios to achieve steady state. The time required to reach steady state for zero-order reactions can be computed using the procedure shown above, and the resulting equation is

$$\frac{t}{\tau} \geq -\ln\left(\frac{0.01}{1 - C_\infty/C_0}\right) \qquad (6\text{-}58)$$

A plot of hydraulic detention time versus reduced steady-state concentration for zero-order reaction is shown on Fig. 6-10. Approximately five hydraulic
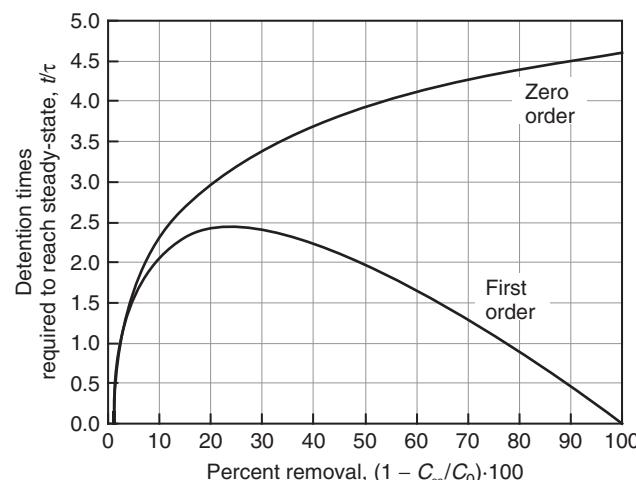

Figure 6-10
Number of detention times, τ, required to reach steady state. For purposes of this graph, steady state is defined as the condition when the effluent concentration is within 1 percent of long-term steady-state concentration.

detention times are adequate for all of the scenarios to achieve steady state, as shown on Fig. 6-10.

Plug Flow Reactor   In a PFR (see Fig. 6-3c), the fluid moves as a plug, and under perfect flow conditions there is no mixing in the axial direction, and there are neither velocity gradients nor concentration gradients in the direction perpendicular to flow. The PFRs of interest in water treatment engineering typically have a constant cross-sectional area (e.g., pipes, channels, or ditches), although a PFR can have a varying cross-sectional area, such as an irregularly shaped river (see Fig. 6-11). In general, a PFR usually requires less reactor volume than a CMFR for an equivalent degree of removal.

PFR MASS BALANCE

There are two possible points of view in which mass balances can be written for PFRs: (1) Eulerian and (2) Langrangian. For the Eulerian point of view, the observer is stationary and fluid flows through the system that the observer has chosen. For the Langrangian point of view, the observer moves with the fluid at its velocity and the system has no flow entering or leaving it.

The concentration in a PFR is dependent upon the independent variables of volume and time, and according to the mean-value theorem, there is at least one value of the dependent variable (C) that is equal to the mean value over the time and volume intervals $(t, t + \Delta t)$ and $(V, V + \Delta V)$, respectively. Thus, a general mass balance on the small element ΔV using the Eulerian point of view can be written as

$$\Delta t \, QC|_{V,t} - \Delta t \, QC|_{V+\Delta V,t} + r\Delta V\Delta t = \Delta V\big[C|_{t+\Delta t,V} - C|_{t,V}\big] \qquad (6\text{-}59)$$

where

Q = flow rate, L/s

Δt = elapsed time on interval $t \rightarrow t + \Delta t$, s

$C|_{V,t}$ = average concentration in reactor evaluated at V for interval $t \rightarrow t + \Delta t$, mg/L

$C|_{V+\Delta V,t}$ = average concentration in reactor evaluated at $V + \Delta V$ for interval $t \rightarrow t + \Delta t$, mg/L

r = average reaction rate on interval $t \rightarrow t + \Delta t$ in element ΔV, mg/L·s
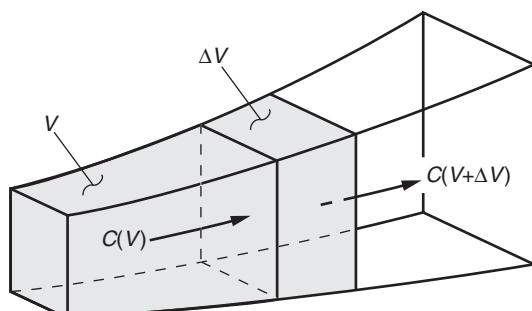

Figure 6-11
Illustration of plug flow reactor with variable cross-sectional area.

$$C|_{t+\Delta t,V} = \text{average concentration in element } \Delta V \text{ evaluated}$$
$$\text{at } t + \Delta t, \text{ mg/L}$$
$$C|_{t,V} = \text{average concentration in element } \Delta V \text{ evaluated}$$
$$\text{at } t, \text{ mg/L}$$

Dividing Eq. 6-59 by Δt and ΔV yields the equation

$$-\frac{QC|_{V+\Delta V,t} - QC|_{V,t}}{\Delta V} + r = \frac{C|_{t+\Delta t,V} - C|_{t,V}}{\Delta t} \tag{6-60}$$

Taking the limit as Δt and ΔV approach zero and assuming there is no volume change upon reaction (which is common for water treatment), the general material balance for a PFR is obtained as

$$-Q\frac{\partial C}{\partial V} + r = \frac{\partial C}{\partial t} \tag{6-61}$$

As shown in Eq. 6-61, the dependent variable C changes with the independent variables V and t. Consequently, one boundary condition and one initial condition are needed to solve this equation.

STEADY-STATE ANALYSIS

As discussed for the CMFR, when a reactor is operated for a long enough period of time with a constant influent concentration, it reaches steady state, meaning the concentration profile in the reactor does not change with time. As described in the following discussion, steady state will be established for a PFR after one hydraulic detention time. For steady-state operation, Eq. 6-61 may be written as

$$-Q\frac{\partial C}{\partial V} + r = \frac{\partial C}{\partial t} = 0 \tag{6-62}$$

The general equation for describing the fate of the component of interest in a PFR assuming steady state and constant Q is expressed as

$$\int_0^V dV = Q \int_{C_0}^C \frac{dC}{r} \tag{6-63}$$

The final form of the general equation is obtained by switching the order of the limits of integration (multiplying by -1):

$$V = Q \int_C^{C_0} \frac{dC}{-r} \tag{6-64}$$

In addition to calculating the volume of the reactor, the steady-state concentration profile in the reactor can be determined. For example, considering a first-order irreversible reaction, the following expression can be obtained for the concentration profile in the reactor by substituting the rate expression $r = -kC$ into Eq. 6-64 and performing the integration results in

$$C = C_0 e^{-k\tau} = C_0 e^{-k(V/Q)} \tag{6-65}$$

Example 6-3 Steady-state operation for PFR

For steady-state operation, calculate the required hydraulic detention time for a first-order reaction occurring in a PFR. The influent concentration of C_0 is 5 mg/L and the treatment objective is $C = 0.5$ mg/L. The reaction rate constant $k = 0.2$ min^{-1}. Compare the detention time required for a PFR to the time obtained for a CMFR at a flow rate of 25 L/min.

Solution

1. Determine the steady-state residence time and volume for the CMFR using Eq. 6-37. At steady state for a CMFR, the required residence time is estimated as

$$\tau_{CMFR} = \frac{C_0 - C}{kC} = \frac{(5 - 0.5)\ \text{mg/L}}{(0.2\ \text{min}^{-1})(0.5\ \text{mg/L})} = \frac{4.5\ \text{mg/L}}{0.1\ \text{mg/L} \cdot \text{min}} = 45\ \text{min}$$

   The required volume is calculated as

$$V_{CMFR} = Q\tau_{CMFR} = (25\ \text{L/min})(45\ \text{min}) = 1125\ \text{L}$$

2. Determine the steady-state residence time and volume for the PFR by rearranging Eq. 6-65. At steady state the required residence time and volume are as follows:

$$\tau_{PFR} = \frac{1}{k} \ln\left(\frac{C_0}{C}\right) = \frac{1}{0.2\ \text{min}} \ln\left(\frac{5\ \text{mg/L}}{0.5\ \text{mg/L}}\right) = 11.5\ \text{min}$$

$$V_{PFR} = Q\tau_{PFR} = (25\ \text{L/min})(11.5\ \text{min}) = 288\ \text{L}$$

3. Compare the PFR with the CMFR:

$$\tau_{CMFR} > \tau_{PFR}$$

$$V_{CMFR} > V_{PFR}$$

For a PFR with constant influent concentration steady state is achieved after an elapsed time equal to the hydraulic detention time because each fluid element travels through the reactor for one detention time.

Comparison of Residence Time and Volume Required for PFRs and CMFRs

It is important to compare the residence time and volume required for PFRs to CMFRs to evaluate the efficiency of reactors. The results differ greatly for irreversible reactions, as discussed below. As defined in Chap. 5, irreversible reactions are reactions that do not proceed in the reverse direction at any measurable rate. In such reactions the concentration of reactants decreases with time, and the reaction rate decreases from its initial value.

A PFR is much more efficient as compared to a CMFR for irreversible reactions, as may be determined by comparing the rates at which the reaction proceeds in a PFR versus a CMFR. In the CMFR, the rate of reaction proceeds at a rate governed by the concentration within the reactor, which corresponds to the effluent concentration. At the inlet of a PFR, the reaction proceeds at a rate governed by the influent concentration, and the rate declines as the fluid moves through the reactor. The final reaction rate in a PFR is governed by the effluent concentration. Effluent concentrations as a function of reactor volume required for PFRs and CMFRs are compared on Fig. 6-12. For a PFR, the concentration profile illustrated on Fig. 6-12 corresponds to the concentration within the reactor, whereas the concentration profile in a CMFR is a horizontal line corresponding to the effluent concentration. For any irreversible reaction of order greater than zero, the reaction rate will proceed at its lowest rate for the CMFR and the highest rate for the PFR.

The equation to determine V or τ for nth order ($n \geq 0, n \neq 1$) can be obtained by substituting the appropriate rate expression into Eq. 6-64:

$$V = Q \int_C^{C_0} \frac{dC}{kC^n} = \frac{Q}{k} \left. \frac{C^{-n+1}}{-n+1} \right|_C^{C_0} = \frac{Q}{k} \left(\frac{C_0^{-n+1}}{-n+1} - \frac{C^{-n+1}}{-n+1} \right) \qquad (6\text{-}66)$$

$$\tau = \frac{V}{Q} = \frac{1}{k} \left(\frac{C_0^{-n+1}}{-n+1} - \frac{C^{-n+1}}{-n+1} \right) \qquad (6\text{-}67)$$

where V = reactor volume, L
  Q = flow rate, L/s
  C_0 = influent concentration, mg/L
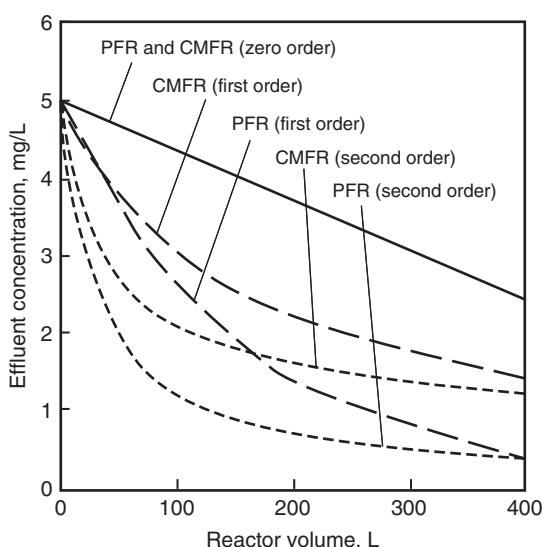
Figure 6-12
Effluent concentration as function of reactor volume for PFRs and CMFRs with zero-, first-, and second-order reactions occurring. The curves were generated using a flow $Q = 26.3$ L/min, rate constant $k = 0.168$ min^{-1}, and initial concentration $C_0 = 5$ mg/L.

C = effluent concentration, mg/L
k = reaction rate constant, $(\text{mg/L})^{-n+1}/\text{s}$
n = reaction order
τ = hydraulic detention time, s

The PFR and CMFR equations are now used to represent the volume of a CMFR divided by the volume of a PFR versus percent removal, as presented on Fig. 6-13. As the percent removal increases, the volume required for a CMFR compared to a PFR increases. The CMFR volume also increases relative to a PFR as the reaction order increases.

A graphical representation of the hydraulic detention time of the CMFR and PFR, as given by the following equations, is shown on Fig. 6-14a:

$$\tau_{\text{CMFR}} = \frac{V_{\text{CMFR}}}{Q} = \frac{C_0 - C}{-r} \qquad (6\text{-}68)$$

$$\tau_{\text{PFR}} = \frac{V_{\text{PFR}}}{Q} = \int_C^{C_0} \frac{dC}{-r} \qquad (6\text{-}69)$$

The hydraulic detention time of a CMFR can be computed as the area of a rectangle with a base equal to $C_0 - C$ and a height equal to $-1/r$. The hydraulic detention time of a PFR is equal to the area under the $-1/r$ curve from C to C_0.

It should be noted that a monotonically decreasing function for $-1/r$ versus C is obtained for reaction order n greater than zero, with the decrease being larger as n increases. Accordingly, there is a greater difference in the volumes of a CMFR and a PFR for a second-order reaction as compared to a first-order reaction. There would be no difference for a zero-order reaction; consequently, the residence times would be identical for a CMFR and a PFR.
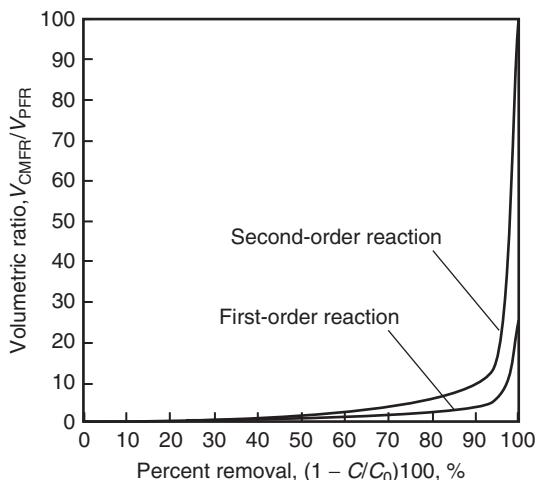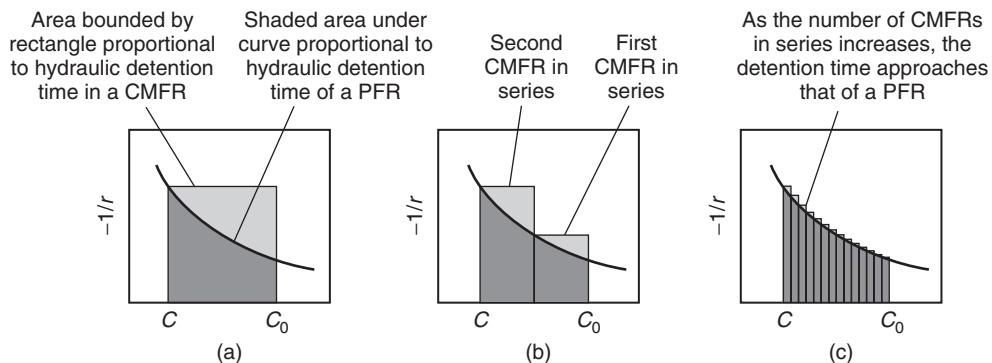
Figure 6-13
Plot of volume of CMFR divided by volume of PFR as function of percent removal.

Figure 6-14
Comparison of detention time required for CMFR as compared to PFR: (a) for one CMFR, (b) for two CMFRs in series, and (c) for multiple CMFRs in series.

As shown on Fig. 6-14b, the hydraulic detention time and reactor volume are reduced for two CMFRs in series. The use of multiple CMFRs in series can approach the efficiency of a PFR, as shown on Fig. 6-14c.

The notation for determining chemical conversion in reactors with recycle is shown on Fig. 6-15. A portion of the throughput Q is diverted from the reactor effluent and recycled to the influent at a rate q. A portion of the solids may also be wasted from the recycle stream using a separation device such as a clarifier.

Reactors with Recycle

COMPLETELY MIXED FLOW REACTORS WITH RECYCLE
A steady-state materials balance around the CMFR of volume V (see Fig. 6-15) yields

$$QC_0 - [(Q - q_w)C + q_wC] - kCV = 0 \qquad (6\text{-}70)$$

where
Q = flow rate, L/s
C_0 = influent concentration, mg/L
q_w = waste flow rate, L/s
C = effluent concentration, mg/L
k = reaction rate constant, s^{-1}
V = reactor volume, L
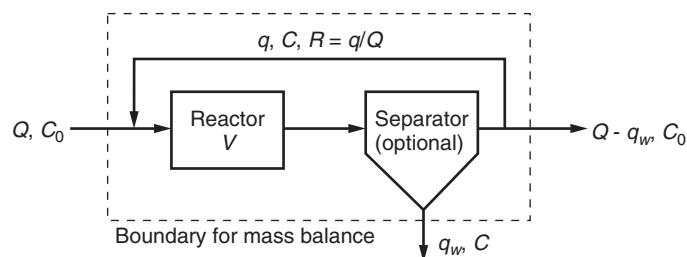
Figure 6-15
Notation used for materials balance for reactor with recycle and solids separator.

The mass balance given by Eq. 6-70 may be simplified to the expression

$$\tau_{CMFR} = \frac{1}{k}\left(\frac{C_0}{C} - 1\right)$$ (6-71)

where τ_{CMFR} = residence time for CMFR, s
        k = reaction rate constant, s^{-1}

Equation 6-71 is identical to Eq. 6-34 for a CMFR with first-order kinetics. However, the rate constant k for the heterogeneous reaction in Eq. 6-71 depends on the concentration of solids in the reactor; the reaction rate would be higher if some solids were recycled and they catalyzed the reaction.

Plug Flow Reactors with Recycle

The steady-state materials balance for the PFR with recycle around the fluid element dV may be written as

$$(Q + q)\,dC = r\,dV$$ (6-72)

where q = recycle flow rate, L/s
        r = reaction rate, mg/L·s

Separating variables and integrating between the influent concentration with recycle C_I and C, the following equation for first-order kinetics is obtained:

$$\tau_{reactor} = \left(\frac{1+R}{k}\right)\ln\left(\frac{C_I}{C}\right)$$ (6-73)

where $\tau_{reactor}$ = residence time for PFR with recycle, s
        R = recycle ratio, q/Q
        k = reaction rate constant, s^{-1}
        C_I = influent concentration with recycle, mg/L
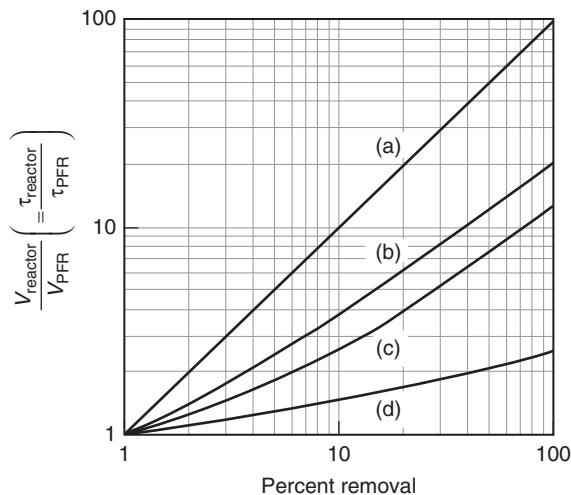
An expression for the influent concentration with recycle can be derived from the mass balance:

$$C_I = \frac{C_0 Q + qC}{Q + q}$$ (6-74)

The residence time for a PFR with recycle may be determined using the equation

$$\tau_{reactor} = \frac{1+R}{k}\ln\left(\frac{C_0/C + R}{1 + R}\right)$$ (6-75)

With no recycle ($R = 0$), the expected design equation for an ideal PFR is obtained. At the other extreme, with $R \to \infty$, the reactor approaches the CMFR model. The recycle reactor is thus a model of fluid behavior lying between the two extremes of complete mixing and no mixing. The residence time for a given reactor, $\tau_{reactor}$, is compared to τ_{PFR} on Fig. 6-16. At the 95 percent conversion level (fraction of reactant remaining is 0.05), 100 percent recycle (PFR recycle $R = 1$) increases the required reactor volume by a factor of approximately 4 ($\tau_{reactor}/\tau_{PFR} \approx 4$). For the same

$$\frac{V_{reactor}}{V_{PFR}}\left(=\frac{\tau_{reactor}}{\tau_{PFR}}\right)$$

Percent removal

Figure 6-16
Impact of reaction order, reactor type, and required removal on reactor volume: (a) CMFR with second-order reaction, (b) CMFR with first-order reaction, (c) PFR with recycle $R = 1$, and first-order reaction, and (d) three CMFRs in series with first-order reaction.

95 percent conversion level, a CMFR would need to be approximately 6 times larger than a PFR for a first-order reaction and approximately 20 times larger than a PFR for a second-order reaction. As R decreases, a smaller reactor volume is required. Thus, a PFR recycle reactor should be designed with an efficient solids separator to ensure minimum recycle ratios that are consistent with the levels of solids required in the reactor. Complete process design also requires a mass balance on solids (Ferguson et al., 1973). As discussed for the CMFR with recycle, a PFR with solids recycle could have a smaller reactor volume if the recycled solids catalyzed the reaction.

6-6 Using Tracers to Characterize Hydraulic Performance of Nonideal Reactors

Water treatment facilities include the largest continuous-flow reactors in use today, and as the scale of continuous-flow reactors increases, their departure from the ideal flow behavior increases. The nonideality associated with large reactors has important implications for the treatment of drinking water because drinking water treatment plants include the largest engineered continuous-flow reactors in existence, far larger than most of the reactors of interest in chemical engineering. As a result, understanding nonideality is critical to the proper design of water treatment processes. There are two important ways in which real continuous-flow reactors behave differently than the ideal reactors discussed in the previous sections: (1) They exhibit nonideal flow behavior and tracer curves that deviate from the ideal curves shown on Fig. 6-4, and (2) the contents of nonideal reactors are not perfectly homogeneous, that is, they are not uniformly mixed to the molecular level.

Although much is known about the residence time distribution (RTD) behavior of flow through different reactor types, it is difficult to design a reactor and know the specific RTD that will result once flow passes through it at full scale. In the long term, computational fluid dynamics (CFD) promises to change this situation, but at the present time, if a reactor's application requires that its RTD be known, then tracer tests must be conducted in the full-scale reactor to measure the RTD directly. Tracer tests are also necessary to confirm the RTD of pilot-scale and demonstration-scale reactors and to develop data that can be used to predict the impact of design changes on performance. However, if the RTD is determined for a large-scale reactor, it may be possible to determine how to modify it to improve its performance by using baffles, turning vanes, and the like to make it perform closer to a PFR. Conducting and evaluating tracer tests are discussed in this section.

Methodology for Tracer Testing
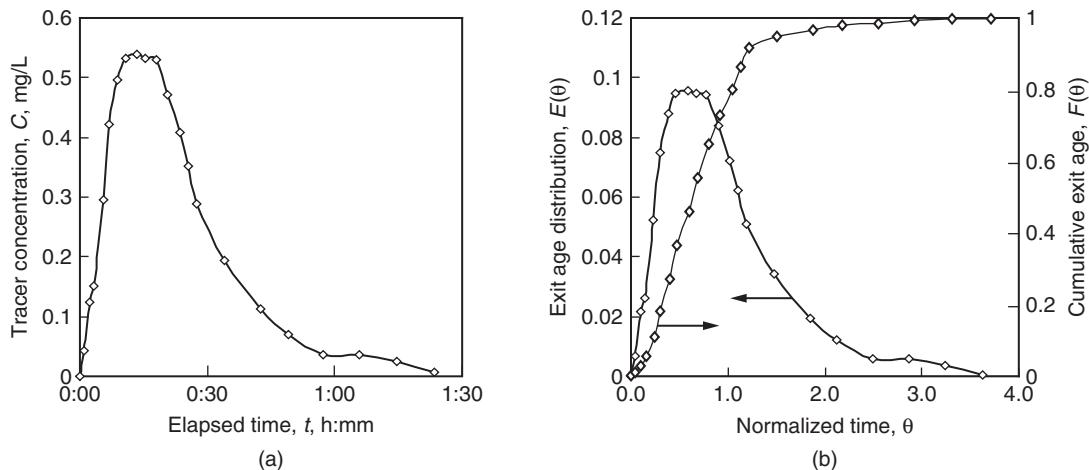
The basic technique used to conduct a tracer study is to introduce the tracer at the reactor inlet and measure the response at the outlet. A tracer is a conservative element, typically a dye or salt solution. The tracer concentration may be measured using a spectrophotometer if a dye is used, a conductivity meter, or specific ion measurements (e.g., flouride or lithium) if salts are used. Application may be all at once (slug or pulse input) or pumped continuously (step input), resulting in different tracer output curves. When the tracer is applied through a step input, a second tracer curve may be obtained after the tracer input is stopped by recording the tracer disappearance, referred to as a step-down tracer study. Effluent samples can be collected manually as grab samples at specified time intervals or by using an autosampler coupled with a detection instrument for automated sampling. Sampling should be performed frequently enough so that the tracer response may be properly characterized.

Analysis of Tracer Data

The tracer curve resulting from a step or pulse input, generally a plot of tracer concentration exiting the reactor as a function of time, is known as the C curve, as shown on Fig. 6-17a. To standardize the analysis of tracer curves, tracer data must be normalized in two ways: (1) with respect to the residence time and (2) with respect to the output concentration.

NORMALIZED TIME

The theoretical hydraulic residence time τ in any reactor is equal to the reactor volume divided by the bulk flow rate. For a perfect tracer in an ideal reactor, the mean residence time $\bar{t}$ is equal to τ (Fogler, 1999; Trussell et al., 1979). However, reactors are not perfect, and as a result, the measured mean residence time is always less than τ. The principal cause of this deviation is the presence of dead spaces in the reactor (spaces that do not mix well with the remainder of the contents) where the volume is not used. Thus, the effective volume of the reactor is smaller than the actual volume,

Figure 6-17
Results of tracer test from three CMFRs in series: (a) concentration C as function of time and (b) exit age distribution E and cumulative exit age distribution F.

and the mean residence time is smaller than τ. When chosing a tracer, care must be taken that the tracer does not adsorb on the walls of the vessel because adsorption can cause the mean residence time to be less than τ. It is important that $\bar{t}$, not τ, be used in normalizing tracer curves. The mean residence time is determined from the results of the tracer study in the following manner:

$$\bar{t} = \frac{\displaystyle\int_0^\infty Ct\,dt}{\displaystyle\int_0^\infty C\,dt} \tag{6-76}$$

where $\bar{t}$ = mean residence time of tracer in reactor, min or s
C = concentration exiting reactor at time t, mg/L
t = time since addition of tracer pulse to reactor's entrance, min or s

The denominator in Eq. 6-76 corresponds to the area under the concentration-versus-time curve. The normalized time is determined with the following expression:

$$\theta = \frac{t}{\bar{t}} \tag{6-77}$$

where θ = normalized time, dimensionless

NORMALIZATION CONCENTRATION
The measured concentration must be normalized such that the possibility for all measurements is 1.0. To normalize the concentration, the measured

tracer concentration is divided by the total mass concentration.

$$C_N = \int_0^\infty C \, d(\theta) \tag{6-78}$$

$$1 = \int_0^\infty \frac{C}{C_N} d(\theta) \tag{6-79}$$

where C_N = total mass concentration of tracer recovered, mg/L

Just as τ cannot be used in place of $\bar{t}$ for normalization of the detention time, neither can the mass of tracer injected be used to normalize the concentration. The recovery of the tracer is always somewhat less than the mass injected, and the mass recovered in the measurements must be used for normalization. Nevertheless, a carefully conducted tracer study will normally account for more than 95 percent of the mass of the tracer applied, and when this is not the case, it is cause for reexamination of the entire study.

EXIT AGE DISTRIBUTION

The normalized curve for the pulse tracer study is referred to as the exit age distribution $E(\theta)$, and the normalized curve of the step input tracer study is referred to as the cumulative exit age distribution $F(\theta)$. It is also possible to do a continuous tracer study with a step down in concentration. In this case, the normalized curve is referred to as the cumulative internal age distribution $I(\theta)$. The exit age distribution is the most convenient form for performing reactor calculations and provides a distribution of the ages of the fluid elements that leave the reactor.

The exit age distribution is related to the cumulative exit age distribution and the cumulative internal age distribution by the equation

$$E(\theta) = \frac{dF(\theta)}{d\theta} = -\frac{dI(\theta)}{d\theta} \tag{6-80}$$

The exit age distribution curve has the the following important properties:

1. The integral $\int_\theta^{\theta+\Delta\theta} E(\theta) \, d\theta$ equals the fraction of material leaving the reactor having ages between θ and $\theta + \Delta\theta$.
2. The probability of having all possible ages is 1.0, that is, $1.0 = \int_0^\infty E(\theta) \, d\theta$.
3. The fraction older than a specified age, θ_2, is $\int_{\theta_2}^\infty E(\theta) \, d\theta$.
4. The fraction younger than a specified age, θ_2, is $\int_0^{\theta_2} E(\theta) \, d\theta$.

COMPUTATION OF EXIT AGE DISTRIBUTION CURVE

The exit age distribution for a CMFR is given by the expression

$$E(\theta) = \frac{C}{C_N} = \frac{C_0 e^{-\theta}}{\displaystyle\int_0^\infty C_0 e^{-\theta} d(\theta)} = e^{-\theta} \tag{6-81}$$

The exit age distribution and cumulative exit age for the tracer curve presented on Fig. 6-17a are shown on Fig. 6-17b. In principle, the exit age distribution for a PFR tracer study should show a very high concentration spike at the hydraulic detention time of the reactor, and the area under the exit age distribution $E(\theta)$ must be 1. Accordingly, the exit age distribution for a PFR is given by the expression

$$E(\theta) = \delta(1 - \theta) \tag{6-82}$$

where $\delta(1 - \theta) =$ Dirac delta function

The Dirac delta function $\delta(x)$ has the following operational definition:

$$1 = \int_0^\infty \delta(1 - \theta)\, d\theta \qquad \delta(1 - \theta) = 0 \quad \text{for} \quad \theta \neq 1$$

and

$$\delta(1 - \theta) = \delta(0) = \infty \quad \text{for} \quad \theta = 1 \tag{6-83}$$

Conceptually, the Dirac delta function has an infinite height, infinitesimally small base, and an area of 1.0. The Dirac delta function is commonly used in calculus and is defined as

$$\int_0^\infty y(x)\delta(x_0)\, d\theta = y(x_0) \tag{6-84}$$

where $x, x_0 =$ independent variables

The term $\delta(x)$ is not evaluated except when it is used in an integral. Use of the delta function is similar to the use of imaginary numbers such as $\sqrt{-1}$ because the products of imaginary numbers are always evaluated and the mathematical representation of the numbers is needed before they are multiplied with one another.

Because not all of the tracer will be recovered, the following steps are followed to obtain the exit age distribution from a pulse tracer study:

1. Determine the mean detention time using Eq. 6-76.
2. Compare the mean detention time with the hydraulic detention time and determine if there is any short circuiting. If there is short circuiting, evaluate whether modification to the reactor can eliminate this and improve performance.
3. Determine the normalization concentration using the equation

$$C_N = \int_0^\infty Cd\left(\frac{t}{\bar{t}}\right) = \frac{\int_0^\infty C\, dt}{\bar{t}} \tag{6-85}$$

4. Replot the tracer study as $E(\theta) = C/C_N$ versus $\theta = t/\bar{t}$.

COMPUTATION OF VARIANCE

The variance σ_t^2, the second moment about the mean of the data, is used to deteremine the spread of the tracer curve using the following equation:

$$\sigma_t^2 = \frac{\int_0^\infty (t - \bar{t})^2 C\, dt}{\int_0^\infty C\, dt} \tag{6-86}$$

where $\sigma_t^2 =$ variance with respect to t, $\min^2$

The variance can also be calculated from the exit age distribution as follows:

$$\sigma_\theta^2 = \int_0^\infty E(\theta)\,(\theta - 1)^2\, d\theta = \frac{\sigma_t^2}{\bar{t}^2} \tag{6-87}$$

where $\sigma_\theta^2 =$ variance with respect to θ, dimensionless

Example 6-4 Calculation of exit age distribution for pulse tracer study

A pulse study on an open-channel reactor (PFR) was conducted and the results are reported in the table below. Plot the tracer curve and normalized RTD curve and determine the variance of the tracer data.

Time, min	C, mg/L	Time, min	C, mg/L	Time, min	C, mg/L
0	0	64	34	90	31
10	0	65	38	95	21
20	1	66	46	100	15
30	2	68	58	105	10
40	4	70	62	110	6
50	9	71	63	120	3
55	15	72	63	130	1
60	24	75	64	140	0
62	28	80	58		
63	30	85	45		

Solution

1. The tracer curve is shown on panel (a) of the figure in step 2e below.
2. Construct a plot of the normalized RTD curve.
   a. Set up a computation table to determine the mean detention time (used for normalizing time data) using Eq. 6-76:

$$\bar{t} = \frac{\int_0^\infty Ct\,dt}{\int_0^\infty Ct\,dt} \approx \frac{\sum \overline{Ct}\Delta t}{\sum \overline{C}\,\Delta t}$$

The summation is shown in the table given below.

t, min	C, mg/L	$\left(\frac{C_{i-1}+C_i}{2}\right)\Delta t$	$\left(\frac{C_{i-1}t_{i-1}+C_it_i}{2}\right)\Delta t$	t, min	C, mg/L	$\left(\frac{C_{i-1}+C_i}{2}\right)\Delta t$	$\left(\frac{C_{i-1}t_{i-1}+C_it_i}{2}\right)\Delta t$
0	0	—	—	70	62	120	8,284
10	0	0	0	71	63	62.5	4,407
20	1	5	100	72	63	63	4,505
30	2	15	400	75	64	190.5	14,004
40	4	30	1,100	80	58	305	23,600
50	9	65	3,050	85	45	257.5	21,163
55	15	60	3,188	90	31	190	16,538
60	24	97.5	5,663	95	21	130	11,963
62	28	52	3,176	100	15	90	8,738
63	30	29	1,813	105	10	62.5	6,375
64	34	32	2,033	110	6	40	4,275
65	38	36	2,323	120	3	45	5,100
66	46	42	2,753	130	1	20	2,450
68	58	104	6,980	140	0	5	650
Total						2,148.5	164,627

$$\bar{t} \approx \frac{\sum \overline{Ct}\,\Delta t}{\sum \overline{C}\,\Delta t} = \frac{164{,}627}{2148.5} = 76.6\,\text{min}$$

b. Determine the value to be used for normalization of the tracer concentration C_N using Eq. 6-85:

$$C_N = \int_0^\infty Cd\left(\frac{t}{\bar{t}}\right) = \frac{\int_0^\infty C\,dt}{\bar{t}} \approx \frac{\sum \overline{C}\Delta t}{\bar{t}} = \frac{2148.5}{76.6} = 28\,\text{mg/L}$$
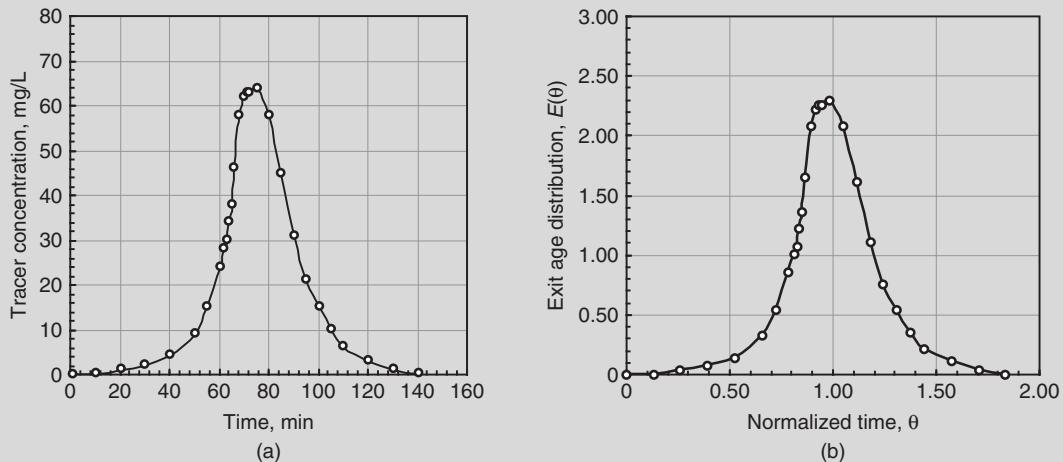
c. Use $\bar{t}$ and C_N to normalize the original tracer study data:

$$\theta = \frac{t}{\bar{t}} = \frac{t}{76.6} \quad \text{and} \quad E(\theta) = \frac{C}{C_N} = \frac{C}{28}$$

d. Set up a computation table to determine the values to be used for plotting the RTD curve.

t, min	C, mg/L	θ	E(θ)	t, min	C, mg/L	θ	E(θ)
0	0	0.00	0.00	70	62	0.91	2.21
10	0	0.13	0.00	71	63	0.93	2.25
20	1	0.26	0.04	72	63	0.94	2.25
30	2	0.39	0.07	75	64	0.98	2.28
40	4	0.52	0.14	80	58	1.04	2.07
50	9	0.65	0.32	85	45	1.11	1.61
55	15	0.72	0.54	90	31	1.17	1.11
60	24	0.78	0.86	95	21	1.24	0.75
62	28	0.81	1.00	100	15	1.30	0.54
63	30	0.82	1.07	105	10	1.37	0.36
64	34	0.83	1.21	110	6	1.43	0.21
65	38	0.85	1.36	120	3	1.56	0.11
66	46	0.86	1.64	130	1	1.69	0.04
68	58	0.89	2.07	140	0	1.83	0.00

e. The final exit age distribution is shown in panel (b) below.

(a)

(b)

3. Compute the variance using Eqs. 6-86 and 6-87:

$$\sigma_t^2 = \frac{\int_0^\infty (t - \bar{t})^2 \, C \, dt}{\int_0^\infty C \, dt} \approx \frac{\sum \overline{(t - \bar{t})^2 \, C} \, \Delta t}{\sum \overline{C} \, \Delta t}$$

$$\sigma_\theta^2 = \frac{\sigma_t^2}{\bar{t}^2}$$

Set up a computation table to compute the terms needed to determine the variance.

t, min	C, mg/L	$\bar{C}\,\Delta t^a$	Term^b	t, min	C, mg/L	$\bar{C}\,\Delta t^a$	Term^b
0	0	—	—	70	62	120	7,176.5
10	0	0	0.0	71	63	62.5	2,416.4
20	1	5	16,075.5	72	63	63	1,720.4
30	2	15	37,886.0	75	64	190.5	2,367.1
40	4	30	48,750.9	80	58	305	2,040.7
50	9	65	59,024.7	85	45	257.5	9,324.2
55	15	60	33,703.4	90	31	190	21,452.2
60	24	97.5	34,398.2	95	21	130	31,283.7
62	28	52	12,746.8	100	15	90	37,933.6
63	30	29	5,842.1	105	10	62.5	40,375.0
64	34	32	5,558.8	110	6	40	36,651.3
65	38	36	5,344.4	120	3	45	61,384.2
66	46	42	5,235.8	130	1	20	42,324.6
68	58	104	9,660.1	140	0	5	14,203.5
						2,148.5	584,880.0

$^a\bar{C}\,\Delta t = \left(\frac{C_{i-1}+C_i}{2}\right)\Delta t.$

$^b\left\{\left[(t_{i-1}-\bar{t})^2 C_{i-1} + (t_i-\bar{t})^2 C_i\right]/2\right\}\Delta t.$

$$\sigma_t^2 = \frac{\sum \overline{(t-\bar{t})^2 C}\,\Delta t}{\sum \bar{C}\,\Delta t} = \frac{584,880}{2,148.5} = 272.2\ \text{min}^2$$

$$\sigma_t = 16.50\ \text{min}$$

$$\sigma_\theta^2 = \frac{\sigma_t^2}{\bar{t}^2} = \frac{272.2\ \text{min}^2}{(76.6\ \text{min})^2} = 0.0464$$

$$\sigma_\theta = 0.221$$

Comment

The numerical integration in this example was carried out using the trapezoidal rule. It should be noted that other methods of integration, including the rectangular, Simpson, and Durand rules as well as more complex methods, may be used.

Parameters Used to Characterize Tracer Results

For some time, the environmental engineering community has understood that the RTD of a reactor, particularly a disinfection contactor, is important. As a result, tracer curves have been used to characterize these reactors and aid in understanding their performance. As this understanding has grown more sophisticated, a number of indices have been used to characterize reactors and their tracer results. Some of the most commonly used terms are summarized in Table 6-5. By far the most commonly used term to characterize reactors is the hydraulic detention time τ, and it is clear that

Table 6-5
Terms used to characterize tracer curves

Term	Definition
d	Dispersion number. Measures dispersion in reactor. For an ideal PFR, $d = 0$. For an ideal CMFR, $d = \infty$
Pe	Peclet number; Pe $= 1/d$
τ	Theoretical hydraulic residence time ($\tau = V/Q$)
t_i	Time at which tracer first appears
θ	Normalized detention time ($t/\bar{t} \approx t/\tau$)
t_p, t_{modal}	Time at which peak concentration of tracer is observed (mode)
$\bar{t}$	Mean residence time, centroid of pulse tracer curve
t_{10}, t_{50}, t_{90}	Time at which 10, 50, and 90% of tracer has passed through reactor or when 10, 50, and 90% of the fluid has passed through the reactor
t_{90}/t_{10}	Morrill dispersion index (MDI)
t_i/τ	Index of short circuiting. In an ideal PFR, the ratio is 1 and approaches zero with increased short circuiting
t_p/τ	Index of modal retention time. Ratio is 1 in an ideal PFR and zero in an ideal CMFR. For values of the ratio greater than or less than 1.0, the flow distribution in the reactor is not uniform
$\bar{t}/\tau$	Index of average retention time; reflects the volume of the reactor that is not used as the fluid passes through the reactor. This volume is sometime called dead volume. If the ratio is 1.0, there is no dead volume in the reactor
t_{50}/τ	Index of mean retention time. The ratio t_{50}/τ is a measure of the skew of the $E(\theta)$ curve. A value of t_{50}/τ of less than 1.0 corresponds to an $E(\theta)$ curve that is skewed to the left. Similarly, for values greater than 1.0 the $E(\theta)$ curve is skewed to the right
n	Equivalent number of tanks in series in TIS model

τ has great significance. Of the remaining indices, the most important are probably the dispersion number d; the Peclet number Pe; the equivalent number of tanks in series (TIS), n; and t_{10}. The dispersion number, the Peclet number, and the equivalent number of tanks in series are important because these can be used in the single-parameter models as a comprehensive measure of dispersion, as discussed in Sec. 6-7. The time for 10 percent of the tracer to pass through the reactor, t_{10}, is important because the U.S. EPA uses that measurement for regulating the performance of disinfection reactors for drinking water.

6-7 Modeling Hydraulic Performance of Nonideal Reactors

As described in Sec. 6-6, the flow in real reactors is not ideal and RTD curves are used to characterize the nonideal flow. In nonideal reactors, the mixing conditions are complex and flow behavior often deviates substantially from the assumptions of ideal flow. The nonideal reactor analysis in this section includes (1) the factors that cause nonideal flow; (2) distinction between molecular diffusion, turbulent diffusion, and dispersion; and (3) models used for characterizing nonideal flow and predicting nonideal reactor performance.

Mixing at two scales dramatically affects reactor efficiency. At the microscale ($<\sim$500 μm), there is concern about mixing reactants in the influent such that there is a uniform concentration of the reactants entering the reactor. At the macroscale, there is concern about how long different fluid elements (which are presumed uniform in concentration at the microscale) reside in the reactor. There are three principal types of nonideal fluid behavior at the macroscale in processing equipment: (1) inadequate initial blending, (2) short circuiting, and (3) diffusion and dispersion. Ultimately, nonideal flow can cause decreased removal efficiencies or the formation of undesirable by-products.

Causes of Nonideal Flow

INADEQUATE INITIAL BLENDING
Nonideal flow in reactors may be caused by inadequate initial blending of reacting components as they enter the reactor. As blending of miscible fluids and soluble components will occur, the initial mixing issue becomes a question of whether the blending is accomplished fast enough relative to the speed of the reactions taking place. Blending is addressed in greater depth in Sec. 6-10.

SHORT CIRCUITING
Short circuiting is characterized by a segment of the fluid stream having a residence time considerably shorter than the mean hydraulic residence

time. Short circuiting is a common design issue in CMFRs, rectangular basins, and packed columns or towers, and it is particularly important in processes where a high level of removal is required, such as disinfection (e.g., 99.99 percent inactivation). The impact of short circuiting on processes with low versus high removal requirements is compared in Sec. 13-4. Short circuiting may develop within the reactor due to poor fluid mechanical design of (1) internal packing material, (2) inlet and outlet structures, and (3) the aspect ratio of the reactor itself (length as compared to depth and width with a larger aspect ratio being most desirable). Short circuiting also occurs when circulation patterns develop due to wind or density differences due to temperature or the concentration of dissolved or suspended materials. For example, when the flow entering the reactor is warmer than the flow in the reactor, a portion of flow can travel to the outlet across the top of the reactor. Short circuiting also occurs in sedimentation basins due to the greater bulk density of the sludge with respect to the bulk water above it. In shallow reactors, wind can transport a portion of the incoming flow to the outlet, resulting in an observed detention time that is shorter than the theoretical residence time of the reactor. Wind can also cause backmixing. However, as discussed later, velocity gradients and short circuiting can be overcome by using baffles, increasing the aspect ratio of the reactor, and proper orientation of basins relative to the prevailing winds or covering them.

DIFFUSION AND DISPERSION
In addition to improper initial blending and short circuiting, diffusion and dispersion can contribute to the nonideal flow observed in reactors. In general, diffusion involves the movement of a constituent from a higher concentration to a lower concentration as a result of collisions with fluid molecules that move by Brownian motion. Dispersion is the mixing brought about by physical processes such as turbulence and velocity gradients.

Diffusion
Molecular diffusion occurs when dissolved constituents or very small particles move randomly within the water matrix as a result of collisions with water molecules that move randomly. This random motion is generally referred to as Brownian motion. Because molecular diffusion does not depend on any bulk movement of the water, it can occur both under laminar and turbulent flow conditions. Molecular diffusion is irreversible and is different for different constituents. Mass transfer brought about by molecular diffusion is described by Fick's law, which is considered in Chap. 7.

Dispersion
The mixing process whereby a constituent is transported from a higher concentration to a lower concentration, by eddies formed by turbulent

flow or shearing forces between fluid layers is known as dispersion. Eddies can vary in size from microscale to macroscale to large circulation patterns in the ocean. Microscale mass transport is only by molecular diffusion, whereas in the macroscale mass transport can be by both molecular and dispersion, with the latter predominating. Kolmogorov (1941a,b,c), as discussed in Sec. 6-10, identified the dividing line between the microscle and macroscale and suggested a method for determining the size of the smallest eddy that could be generated as a function of the amount of energy dissipated. Dispersion is considered further in Sec. 6-10.

The constituent mixing that results from the shearing forces between fluid layers and by the random fluid motion of turbulence is also known as dispersion. The parabolic distribution of flow velocities that occurs in pipe flow is a classic example of the shearing that occurs between fluid layers and is known as Taylor dispersion. Dispersion occurs mainly in tanks, channels, pipes, or columns and is characterized by longitudinal mixing, which distorts the flat velocity profile (perpendicular to the direction of flow) that is assumed for an ideal PFR. Because dispersion coefficients are dominated by the character of turbulence at the macroscale, they are identical for all constituents, and tracer studies can be conducted using a dye or salt solution. Typical values of some observed dispersion coefficients E are illustrated on Fig. 6-18. Representative values for molecular diffusion are shown in the lower left on Fig. 6-18.

Models Used to Describe Nonideal Flow

When an engineer designs a large reactor for water treatment, nonideal flow is almost always a design issue. To ensure that the reactor will perform as intended, it is important that the design engineer consider impacts that
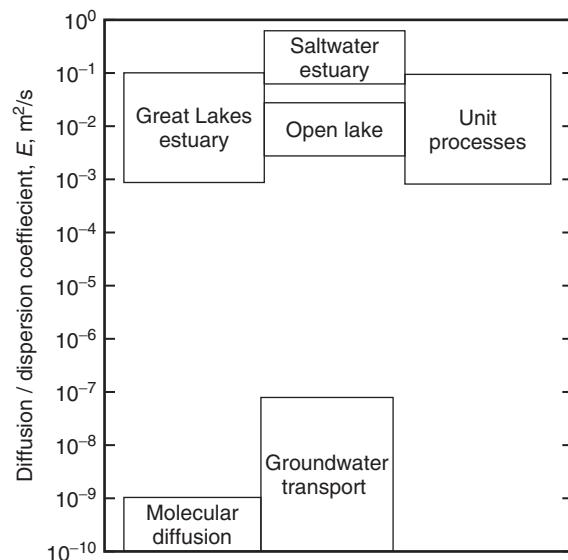

Figure 6-18
Observed coefficients of dispersion and molecular diffusion.

nonideal flow might have on reactor performance. Considering nonideal effects on reactors occurs through two important steps: (1) understanding the impact of reactor design on nonideal flow and (2) understanding the impact of nonideal flow on reactor performance. Neither of these tasks is accomplished easily, but understanding the impact of reactor design on nonideal flow presents a particular challenge. Usually, the approach taken is to (1) construct a model of the RTD in the reactor as a way of understanding its nonideal behavior and then (2) use the RTD model to predict the impact on reactor performance. Two single-parameter models are typically used to model RTD: (1) the dispersion model or dispersed-flow model (DFM) and (2) the tanks-in-series (TIS) model. Once a reactor has been built, it is common to conduct a tracer study to determine the actual RTD of the reactor and then to see how well that RTD can be fit to one of these single-parameter models. The DFM and the TIS model are introduced in the following discussion.

DISPERSED-FLOW MODEL

If longitudinal dispersion is the main cause for deviation from ideal flow in a conduit reactor (i.e., a tube, pipe, or channel), then the following mass balance may be established, assuming a constant cross-sectional area and no short circuiting in the reactor:

$$
\left(QC|_{z,t} - E \cdot a \left. \frac{\partial C}{\partial z} \right|_{z,t} \right) \Delta t - \left(QC|_{z+\Delta z,t} - E \cdot a \left. \frac{\partial C}{\partial z} \right|_{z+\Delta z,t} \right) \Delta t
$$

$$
+ r \cdot a \cdot \Delta z \, \Delta t = a \cdot \Delta z [C|_{t+\Delta t,z} - C|_{t,z}] \tag{6-88}
$$

where
$\quad Q =$ flow rate, L/s
$\quad \Delta t =$ elapsed time on interval $t \to t + \Delta t$, s
$\quad C|_{z,t} =$ average concentration in reactor evaluated at z for interval $t \to t + \Delta t$, mg/L
$\quad C|_{z+\Delta z,t} =$ average concentration in reactor evaluated at $z + \Delta z$ for interval $t \to t + \Delta t$, mg/L
$\quad E =$ dispersion coefficient, m^2/s
$\quad a =$ cross-sectional area of reactor, m^2
$\quad \left. \frac{\partial C}{\partial z} \right|_{z,t} =$ change in concentration with position in reactor evaluated at z for the interval $t \to t + \Delta t$, mg/L·m
$\quad \left. \frac{\partial C}{\partial z} \right|_{z+\Delta z,t} =$ change in concentration with position in reactor evaluated at $z + \Delta z$ for interval $t \to t + \Delta t$, mg/L·m
$\quad r =$ average reaction rate on interval $t \to t + \Delta t$ in element, mg/L·s
$\quad \Delta z =$ length of element, m
$\quad C|_{t+\Delta t,z} =$ average concentration in element evaluated at $t + \Delta t$, mg/L
$\quad C|_{t,z} =$ average concentration in element evaluated at t, mg/L

In Eq. 6-88, there are values of the dependent variable that are equal to the mean value over the intervals $(t, t + \Delta t)$ or $(z, z + \Delta z)$, which can be inferred from the mean-value theorem. For this reason, the dependent values are evaluated somewhere located in the intervals $(t, t + \Delta t)$ and $(z, z + \Delta z)$. When taking the limit as Δt and Δz approach zero, they are evaluated at t and z because they were contained on the intervals. Dividing by $a \, \Delta z$ and Δt, multiplying by τ, taking the limit as $\Delta z \to 0$, $\Delta t \to 0$, and rearranging, the following expression is obtained:

$$-\frac{\partial C}{\partial (z/L)} + \left(\frac{E}{vL}\right) \frac{\partial^2 C}{\partial (z/L)^2} + r\tau = \frac{\partial C}{\partial (t/\tau)} \tag{6-89}$$

where L = length of reactor, m
 v = average fluid velocity (Q/a), m/s
 τ = hydraulic detention time, s

To evaluate the RTD, it is assumed that the tracer does not participate in any reactions (i.e., a conservative tracer). Thus, Eq. 6-89 can be rearranged to the following:

$$-\frac{\partial C}{\partial \bar{z}} + \frac{1}{\mathrm{Pe}} \frac{\partial^2 C}{\partial \bar{z}^2} = \frac{\partial C}{\partial (t/\tau)} \tag{6-90}$$

where   Pe = Peclet number = vL/E, dimensionless
 $\bar{z}$ = dimensionless length $(\bar{z} = z/L)$

The Peclet number is the ''single parameter'' of the DFM. Specifying the Peclet number is concomitant with specifying the entire RTD. Conceptually, the Peclet number is the ratio between mass transport by advection to dispersion:

$$\mathrm{Pe} = \frac{vL}{E} = \frac{\text{rate of transport by advection}}{\text{rate of transport by dispersion}} \tag{6-91}$$

High Peclet numbers result when advection controls mass transport within the reactor because dispersion and advection act in parallel. As the Peclet number approaches infinity, transport is only by advection; no axial dispersion occurs and the reactor performance approaches that of a PFR. Conversely, for a Peclet number approaching zero, there is no transport by advection; only axial dispersion occurs and the reactor performance approaches that of a CMFR.

Often the dispersion number d is used in place of the Peclet number. The relationship between the dispersion number and the Peclet number is as follows:

$$d = \frac{1}{\mathrm{Pe}} \tag{6-92}$$

where d = dispersion number, dimensionless

The Peclet number and dispersion number are both used in environmental literature, and, therefore, it is important to understand the relationship between these two parameters. The dispersion number and DFM are also

used in Chaps. 8 and 13. To solve Eq. 6-90, one initial condition and two boundary conditions are needed (Fogler, 1999). The boundary conditions, which apply to either steady-state or unsteady-state conditions, are discussed below.

Open and closed systems and the DFM model
There are two well-known approaches to the boundary conditions for the DFM model, the closed-system approach and the open-system approach. The differences between the open and closed models are shown on Fig. 6-19. For the closed-system model, it is assumed that plug flow occurs in and out of the reactor and dispersed flow occurs within the reactor. For the open-system model, it is assumed that dispersed-flow conditions are present throughout; that is, the reactor is essentially a segment of flow with characteristics common to the flow preceding and following it. Most unit operations used in environmental engineering are better approximated by the closed-system assumptions, although, as will be shown later, the differences between these models are not very significant when the Peclet number is greater than approximately 40 (when the dispersion number is below approximately 0.025), and most engineered PFRs exceed this performance.

Solving DFM for a closed-flow system
For a closed reactor it is assumed that plug flow conditions exist before the entrance (advection only) and dispersed-flow conditions exist after the
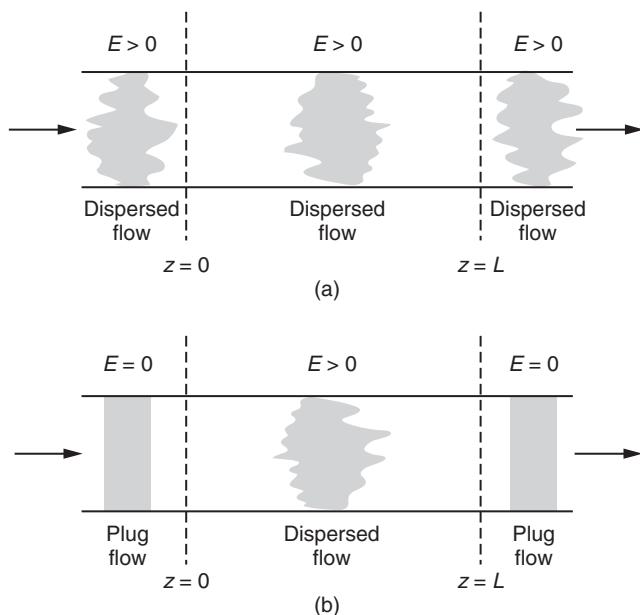
Figure 6-19
Illustration of boundary conditions for dispersion model: (a) open system and (b) closed system.

entrance (advection and dispersion). Thus, the following mass balance can be written at the entrance to the reactor:

$$QC|_{z=0^-} = QC|_{z=0^+} - E \cdot a \left. \frac{\partial C}{\partial z} \right|_{z=0^+} \qquad (6\text{-}93)$$

where $QC|_{z=0^-}$ = mass of tracer that enters reactor, or QC_0, mg/s
$\quad\quad\quad QC|_{z=0^+}$ = advective transport of tracer evaluated at $z = 0^+$, mg/s
$\quad\quad z = 0^-, 0^+$ = location just before and just after entrance of reactor

Recognizing that the velocity v is equal to flow divided by the cross-sectional area, Q/a, Eq. 6-93 may be rewritten as

$$\left. \frac{\partial C}{\partial z} \right|_{z=0^+} = \frac{v}{E} \left(C|_{z=0^+} - C|_{z=0^-} \right) \qquad (6\text{-}94)$$

The final form of the boundary condition is given by the expression

$$\left. \frac{\partial C}{\partial (z/L)} \right|_{z=0^+} = \frac{vL}{E} \left(C|_{z=0^+} - C_0 \right) = \text{Pe} \left(C|_{z=0^+} - C_0 \right) \qquad (6\text{-}95)$$

As shown in Eq. 6-95, there is a discontinuity in the concentration at the entrance of the reactor. Also for a closed system, it is assumed that dispersed-flow conditions exist before the exit (advection and dispersion) and plug flow conditions exist after the exit (advection only). Thus, a mass balance on the exit of a closed reactor yields

$$QC|_{z=L^-} - (E \cdot a) \left. \frac{\partial C}{\partial z} \right|_{z=L^-} = QC|_{z=L^+} \qquad (6\text{-}96)$$

where $QC|_{z=L^-}$ = advective transport of tracer evaluated at $z = L^-$, mg/s
$\quad\quad\quad QC|_{z=L^+}$ = mass of tracer that leaves reactor, mg/s
$\quad\quad\quad\quad\quad\quad C$ = effluent concentration, mg/L
$\quad\quad z = L^-, L^+$ = locations just before and just after exit of reactor

Unlike the entrance of the reactor, there cannot be a discontinuity in concentration at the exit, and therefore the final form of the boundary condition is given by the following expressions:

$$\left. \frac{\partial C}{\partial z} \right|_{z=L} = 0 \qquad (6\text{-}97)$$

$$C|_{L^-} = C|_{L^+} \qquad (6\text{-}98)$$

Thomas and McKee (1944) developed a solution for a closed reactor for a conservative or nonreacting tracer, which has been modified in terms of the Peclet number:

$$\frac{C}{C_0} = 2 \sum_{i=1}^{\infty} b \left[\frac{a \sin b + b \cos b}{a^2 + 2a + b^2} \right] \exp \left[a - \frac{(a^2 + b^2)\, \theta}{2a} \right] \qquad (6\text{-}99)$$

where C = effluent concentration of nonreactive tracer, mg/L

C_0 = initial concentration of tracer in reactor, mg/L

$$b = \cot^{-1}\left[\frac{(b/a) - (a/b)}{2}\right]$$

$a = \text{Pe}/2 = \frac{1}{2}d$

Pe = Peclet number, dimensionless (see Eq. 6-91)

θ = normalized detention time, $t/\bar{t}$

To fit the closed-system DFM to an existing reactor, a pulse tracer study is conducted to obtain the exit age distribution. In turn, the tracer data can be fit with Eq. 6-99 to determine Pe. For a corresponding set of C/C_0 and θ values, a Pe is assumed and Eq. 6-99 is solved by successive numerical approximation. The process is repeated until a value of Pe is found such that Eq. 6-99 closely approximates the tracer curve.

Because of the difficulty in solving Eq. 6-99 and because it is easier to determine the variance of the tracer curve, the dispersion may be estimated using the following expression, which relates the Pe to σ_θ^2 (Fogler, 1999):

$$\sigma_\theta^2 = \frac{\sigma_t^2}{\bar{t}^2} = \left(\frac{2}{\text{Pe}}\right) - \left[2\left(\frac{1}{\text{Pe}}\right)^2\left(1 - e^{-\text{Pe}}\right)\right] \tag{6-100}$$

where σ_θ^2 = variance with respect to θ

σ_t^2 = variance with respect to t

Consequently, a determination from variance is often used in spite of the inaccuracies that can result from determining σ_θ^2 from experimental data. For example, small concentrations far from the centroid can have a large impact on the value of σ_θ^2. Thus, for accurate estimates of reaction performance, Eq. 6-99 should be fit to the data to determine the Pe.

Solving DFM for an open-flow system

For an open system it is assumed that dispersed-flow conditions exist before and after the entrance (advection and dispersion). Thus, the following mass balance can be written at the entrance to the reactor:

$$QC|_{z=0^-} - E \cdot a \left.\frac{\partial C}{\partial z}\right|_{z=0^-} = QC|_{z=0^+} - E \cdot a \left.\frac{\partial C}{\partial z}\right|_{z=0^+} \tag{6-101}$$

The final form of the boundary condition at the entrance to the reactor is given by

$$C|_{z=0^-} - \frac{1}{\text{Pe}}\left.\frac{\partial C}{\partial (z/L)}\right|_{z=0^-} = C|_{z=0^+} - \frac{1}{\text{Pe}}\left.\frac{\partial C}{\partial (z/L)}\right|_{z=0^+} \qquad C|_{z=0^-} = C|_{z=0^+}$$

$$\tag{6-102}$$

Similarly, a mass balance at the exit of an open reactor yields the final form of the boundary condition:

$$C|_{z=L^-} - \frac{1}{\text{Pe}}\left.\frac{\partial C}{\partial (z/L)}\right|_{z=L^-} = C|_{z=L^+} - \frac{1}{\text{Pe}}\left.\frac{\partial C}{\partial (z/L)}\right|_{z=L^+} \qquad C|_{z=L^-} = C|_{z=L^+}$$

$$\tag{6-103}$$

It is important to realize that $C|_{z=0^-}$ and $C|_{z=0^+}$ are not equal to the influent concentration into the reactor because dispersion transports the substance upstream and downstream.

If Eq. 6-90 is solved for a nonreactive tracer ($r = 0$) in an open reactor, the following expression for $E(\theta)$ is obtained (Levenspiel and Smith, 1957):

$$E(\theta) = \frac{1}{\sqrt{4\pi\theta(1/\mathrm{Pe})}} e^{-\mathrm{Pe}(1-\theta)^2/4\theta} \tag{6-104}$$

For low dispersion (high Pe), Eq. 6-104 simplifies to the following:

$$E(\theta) = \frac{1}{\sqrt{4\pi(1/\mathrm{Pe})}} e^{-\mathrm{Pe}(1-\theta)^2/4} \tag{6-105}$$

The mean detention time $\bar{t}$ for an open reactor is longer than the theoretical hydraulic detention time τ because some of the tracer can migrate upstream of the reactor. The mean detention time can be determined using the expression

$$\bar{t} = \left[1 + \left(\frac{2}{\mathrm{Pe}}\right)\right]\tau \tag{6-106}$$

where $\bar{t} = $ centroid of tracer curve $= \int_0^\infty Ct\,dt / \int_0^\infty C\,dt$
  $\tau = $ hydraulic detention time $= V/Q$

It has been shown that the following relationship between the Pe and σ_θ^2 applies to open systems (Fogler, 1999):

$$\sigma_\theta^2 = \frac{\sigma_t^2}{\bar{t}^2} = \frac{2}{\mathrm{Pe}} + 8\left(\frac{1}{\mathrm{Pe}}\right)^2 \tag{6-107}$$

To fit the open-system DFM to an existing reactor, a pulse tracer study is conducted to obtain the exit age distribution. The Peclet number may be estimated in two ways: from the variance of tracer data using Eq. 6-107 or by directly fitting the tracer data to Eq. 6-104. As discussed for the closed reactor system, the latter approach usually results in a superior fit and should be used to determine the Peclet number whenever possible.

TANK-IN-SERIES MODELS

The analysis summarized in Eq. 6-21 can be used to show that the exit age distribution for a cascade of n CMFRs in series is given by the following expression (Levenspiel, 1998):

$$E(\theta)_n = \frac{n(n\theta)^{n-1}}{(n-1)!} e^{-n\theta} \tag{6-108}$$

where $E(\theta)_n = $ exit age distribution for n tanks in series
  $\theta = $ relative residence time $= t/\bar{t}$, dimensionless

The variance can be determined using the expression

$$\sigma_\theta^2 = \frac{1}{n-1} \tag{6-109}$$

where $\sigma_\theta^2 = $ variance with respect to θ

To fit the TIS model to an existing reactor, a pulse tracer study is conducted to obtain the exit age distribution. The tracer data can be fit with Eq. 6-108 to determine n. Once the value of n has been estimated using this method, Eq. 6-108 can be used to construct a curve of $E(\theta)$ as a function of θ. Again, under conditions of low dispersion (high n), the results of the TIS model approach those of the DFM. Under these conditions, the following relationship may be used:

$$n = \tfrac{1}{2}\mathrm{Pe} + 1 \approx \tfrac{1}{2}\mathrm{Pe} \qquad (6\text{-}110)$$

For Pe numbers of 5, 10, and 25, n is equal to 3.5, 6.0, and 13.5, respectively. The results obtained using the TIS and DFM methods are similar; however, it is much easier to use the TIS method as compared to the DFM method. Fortunately, the equivalence can be drawn between the number of tanks for the TIS model and the Pe number used in the closed-flow DFM method (see Eq. 6-100), as shown in Eqs. 6-111 and 6-112 for a large Pe:

$$\sigma_\theta^2 \approx \frac{1}{n} \approx \left\{ \left(\frac{2}{\mathrm{Pe}}\right) - \left[2\left(\frac{1}{\mathrm{Pe}}\right)^2 (1 - e^{-\mathrm{Pe}}) \right] \right\} \qquad (6\text{-}111)$$

$$n \approx \frac{1}{(2/\mathrm{Pe}) - 2(1/\mathrm{Pe})^2(1 - e^{-\mathrm{Pe}})} \approx \frac{\mathrm{Pe}}{2} \qquad (6\text{-}112)$$

The result shown in Eqs. 6-110 and 6-112 can be used to develop an appreciation for the magnitude of the Pe number. For example, a Pe of 20, 50, or 100 would correspond to 10, 20, or 50 tanks in series, respectively.

Example 6-5 Determination of single-parameter fit to RTD

Using the tracer data analysis shown in Example 6-4, estimate the Peclet number and dispersion number for the open-flow DFM by fitting the model to Eq. 6-104 and also the number of tanks in series by fitting the data to Eq. 6-108. Plot the resulting exit age curves and compare them to the original data.

Solution

1. Determine the Peclet number for the open-flow DFM by fitting Eq. 6-104 to the $E(\theta)$ curve shown in Example 6-4.

2. Determine the number of tanks in series for the tanks-in-series model by fitting Eq. 6-108 to the $E(\theta)$ curve shown in Example 6-4.

   Both fits are accomplished by setting up the data and the equation on a spreadsheet and finding the value of Pe (Eq. 6-104) or n (Eq. 6-108) that minimizes the sum of squares of the differences
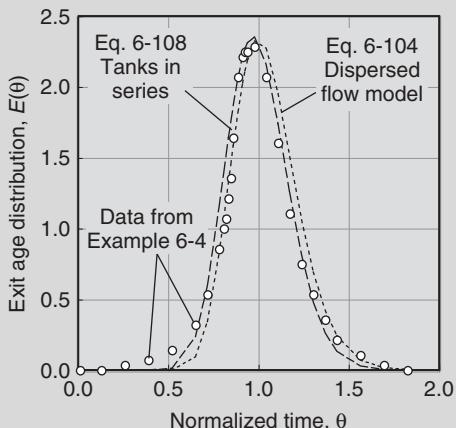
between the model and the data. The results of these calculations are shown in the table below.

θ	E(θ)	Eq. 6-104	[col. 2 – col. 3]²	Eq. 6-108	[col. 2 – col. 5]²
0.013	0.00	0.00	0.0000	0.00	0.0000
0.130	0.00	0.00	0.0000	0.00	0.0000
0.261	0.04	0.00	0.0016	0.00	0.0016
0.391	0.07	0.00	0.0049	0.00	0.0049
0.522	0.14	0.00	0.0190	0.01	0.0156
0.652	0.32	0.13	0.0372	0.25	0.0045
0.717	0.54	0.42	0.0145	0.62	0.0062
0.782	0.86	0.94	0.0069	1.16	0.0925
0.808	1.00	1.20	0.0385	1.41	0.1647
0.821	1.07	1.33	0.0652	1.53	0.2075
0.834	1.21	1.45	0.0594	1.64	0.1869
0.847	1.36	1.58	0.0481	1.75	0.1554
0.860	1.64	1.70	0.0036	1.86	0.0483
0.887	2.07	1.93	0.0206	2.05	0.0003
0.913	2.21	2.10	0.0113	2.19	0.0003
0.926	2.25	2.17	0.0058	2.24	0.0000
0.939	2.25	2.23	0.0004	2.28	0.0011
0.978	2.28	2.32	0.0013	2.32	0.0015
1.043	2.07	2.20	0.0157	2.13	0.0033
1.108	1.61	1.84	0.0526	1.72	0.0130
1.173	1.11	1.39	0.0787	1.25	0.0199
1.239	0.75	0.96	0.0434	0.82	0.0045
1.304	0.54	0.62	0.0059	0.49	0.0024
1.369	0.36	0.37	0.0002	0.27	0.0076
1.434	0.21	0.21	0.0000	0.14	0.0048
1.565	0.11	0.06	0.0025	0.03	0.0063
1.695	0.04	0.01	0.0006	0.01	0.0012
1.825	0.00	0.00	0.0000	0.00	0.0000

sum = 0.5377
Pe = 67.0

sum = 0.9544
n = 33

3. Determine the dispersion number from the Peclet number using Eq. 6-92:

$$d = \frac{1}{Pe} = \frac{1}{67} = 0.0149$$

4. A plot comparing the exit age data with the results of the two models is illustrated below.


Comment
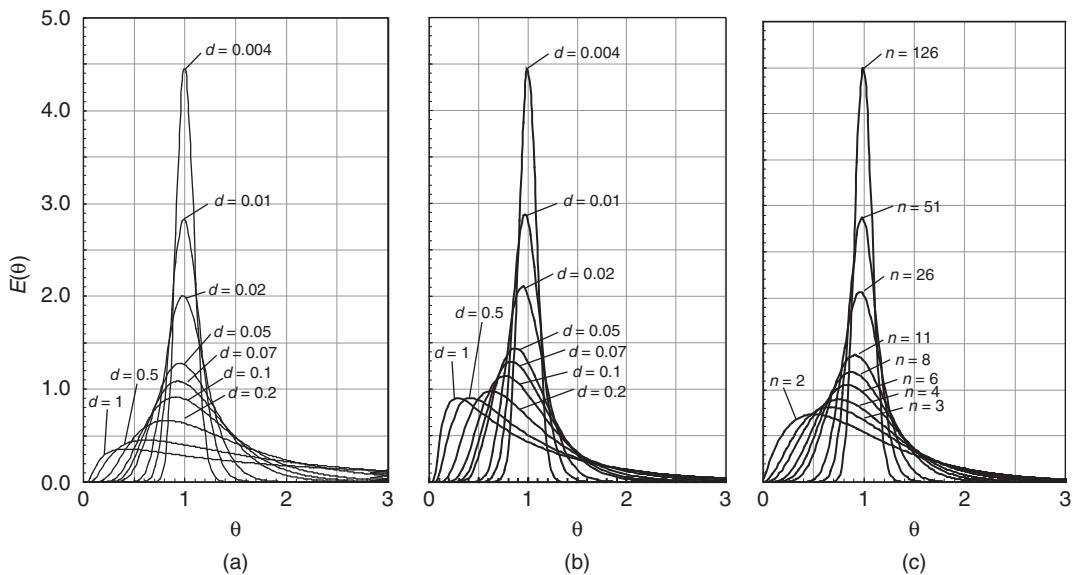
Both the TIS and DFM models fit the data well, except for the data for small exit ages. The fluid that exits the reactor with small residence times can have a large influence on reactor performance.

Application of RTDs and t_{10} Concept

The RTDs for the three models, closed-flow DFM, open-flow DFM, and TIS model, are displayed on Fig. 6-20. Under conditions where dispersion is high (high d for the DFM or low n for the TIS model), these three models produce significantly different RTDs, as shown on Fig. 6-20. Under conditions where dispersion is low (low d for the DFM or high n for the TIS model), these models produce RTDs that are nearly identical.

In subsequent sections it will be shown that the entire RTD is useful in evaluating the expected performance of a given reactor design. However, RTDs are complicated, and their use in evaluating reactor performance, while the best available technology, is also somewhat more complicated than just assuming that an actual reactor performs similar to a PFR with a certain residence time that is determined by a tracer study. As a result, regulatory authorities often regulate reactor design using certain simplified performance criteria. For example, in disinfection practice (see Chap. 13), it is assumed that the effective contact time corresponds to the length of time it takes for the first 10 percent (θ_{10}) of a tracer to pass through the reactor. This approach is conservative because credit is only received for θ_{10} and not θ_{50}, which corresponds to the actual residence time.

Each RTD model discussed was examined to assess the impact of reactor dispersion on θ_{10}, the fraction of the reactor's theoretical detention time

Figure 6-20
Comparison of $E(\theta)$ curves for (a) DFM open system, (b) DFM closed system, and (c) TIS model.

that would be allowed as credit by the U.S. EPA rules (see example for open-system DFM on Fig. 6-21a). A plot of θ_{10} $(t_{10}/\bar{t})$ as a function of increasing dispersion for all three RTD models is displayed on Fig. 6-21b. Note that the TIS model does not allow for direct application of the dispersion or Peclet numbers, so an approximate transformation represented by Eq. 6-110 was used for comparison purposes. As expected, the θ_{10} value drops consistently as dispersion increases. For example, credit would be received for more than 80 percent of the residence time of the reactor for low dispersion $(d < 0.01, \text{Pe} > 100, n > 50)$ to as low as 25 to 50 percent of the residence time for reactors with high dispersion $(d > 0.3, \text{Pe} < 3, n < 2 \text{ or } 3)$. A credit of 80 percent or more would correspond to a well-designed reactor.

Extensive studies have been conducted to determine the dispersion in open-channel flow. The dispersion in an existing reactor can be determined using a tracer study; however, when designing facilities, it is useful to be able to predict the dispersion. Davies (1972) proposed the following relationship for flow in an open channel and a high Reynolds number, which can be used to estimate the dispersion coefficient:

Predicting Dispersion in a Channel

$$E = 1.01v(\text{Re})^{0.875} \qquad (6\text{-}113)$$

where
$E =$ coefficient of dispersion, m^2/s
$v =$ kinematic viscosity, m^2/s
$\text{Re} =$ Reynolds number $= 4vR_h/v$, dimensionless
$v =$ velocity in open channel, m/s
$R_h =$ hydraulic radius $=$ sectional area/wetted perimeter, m
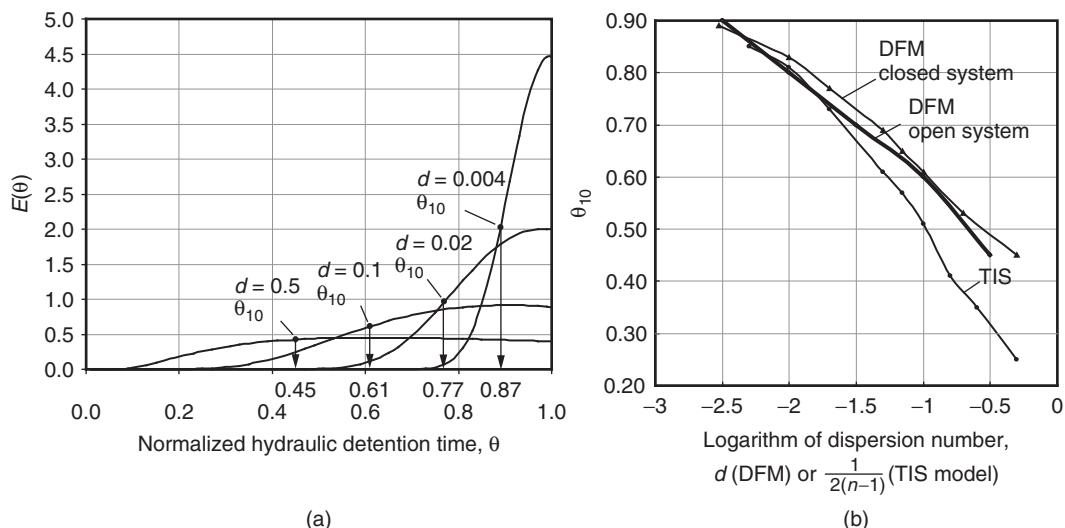
Figure 6-21
Dispersion and θ_{10}. (a) Analyzing effect of dispersion on θ_{10} using DFM model for open system. (b) Relationship between increasing dispersion and θ_{10} for three models: DFM closed system, DMF open system, and TIS model.

Other models developed for the dispersion coefficient are based on the Taylor equation and are discussed in Chap. 13.

Example 6-6 Estimate of dispersion in open channel

For an open-channel PFR with a water flow rate of 4320 m^3/d, estimate the dispersion number and t_{10}. Assume that $\bar{t} \cong \tau$ and that the channel has a length of 40 m, a width of 3 m, and a water depth of 3 m. Use a kinematic viscosity of 1.003×10^{-6} m^2/s for the water. Assume the dispersion in the channel can be estimated accurately using Eq. 6-113 and that the RTD in the channel can be predicted using the open-flow DFM model (Eq. 6-104).

Solution

1. Estimate the dispersion number.
   a. To apply Eq. 6-113, compute the Reynolds number Re:

$$\text{Average water velocity } v = \frac{(4320 \text{ m}^3/\text{d})(1 \text{ d}/86{,}400 \text{ s})}{3 \text{ m} \times 3 \text{ m}}$$

$$= 0.0056 \text{ m/s}$$

$$\text{Hydraulic radius } R_h = \frac{3 \text{ m} \times 3 \text{ m}}{3 \text{ m} + 3 \text{ m} + 3 \text{ m}} = 1 \text{ m}$$

Reynolds number $\mathrm{Re} = \dfrac{4vR_h}{v} = \dfrac{(4)(0.0056 \text{ m/s})(1 \text{ m})}{1.003 \times 10^{-6} \text{ m}^2/\text{s}}$

$= 22{,}156$

b. Compute the coefficient of dispersion E:

$E = 1.01v(\mathrm{Re})^{0.875} = (1.01)(1.003 \times 10^{-6} \text{ m}^2/\text{s})(22{,}156)^{0.875}$

$= 0.00643 \text{ m}^2/\text{s}$

c. Compute the dispersion number using Eqs. 6-91 and 6-92:

$d = \dfrac{E}{vL} = \dfrac{0.00643 \text{ m}^2/\text{s}}{(0.0056 \text{ m/s})(40 \text{ m})} = 0.0289$

2. Estimate t_{10}.

a. Determine the Peclet number from the dispersion number using Eq. 6-92:
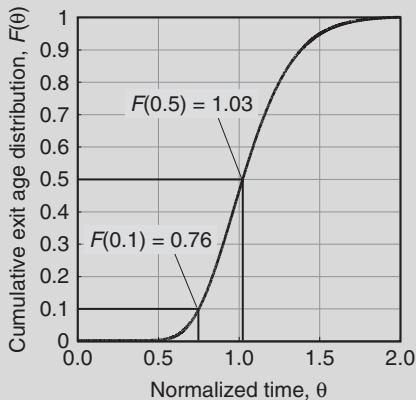
$\mathrm{Pe} = \dfrac{1}{d} = \dfrac{1}{0.0289} = 34.5$

b. Set up a table to compute the cumulative exit age distribution $F(\theta)$ using Eq. 6-104 to find $E(\theta)$ from θ and Eq. 6-80 to convert $E(\theta)$ to $F(\theta)$:

θ	$E(\theta)$	$\bar{E}(\theta)$	$\bar{E}(\theta)\Delta\theta^a$	$F(\theta)$	θ	$E(\theta)$	$\bar{E}(\theta)$	$\bar{E}(\theta)\Delta\theta^a$	$F(\theta)$
0.0									
0.1	0.000	0.0	0.0	0.0	1.4	0.522	0.6607	0.0661	0.9008
0.2	0.000	0.0	0.0	0.0	1.5	0.320	0.4212	0.0421	0.9429
0.3	0.000	0.0	0.0	0.0	1.6	0.187	0.2539	0.0254	0.9683
0.4	0.001	0.0005	0.0001	0.0001	1.7	0.105	0.1463	0.0146	0.9829
0.5	0.031	0.0161	0.0016	0.0017	1.8	0.057	0.0811	0.0081	0.9910
0.6	0.213	0.1222	0.0122	0.0139	1.9	0.030	0.0436	0.0044	0.9954
0.7	0.652	0.4328	0.0433	0.0572	2.0	0.016	0.0228	0.0023	0.9977
0.8	1.204	0.9280	0.0928	0.1500	2.1	0.008	0.0117	0.0012	0.9989
0.9	1.589	1.3963	0.1396	0.2896	2.2	0.004	0.0059	0.0006	0.9994
1.0	1.659	1.6241	0.1624	0.4520	2.3	0.002	0.0029	0.0003	0.9997
1.1	1.462	1.5609	0.1561	0.6081	2.4	0.001	0.0014	0.0001	0.9999
1.2	1.135	1.2989	0.1299	0.7380	2.5	0.000	0.0007	0.0001	0.9999
1.3	0.800	0.9675	0.0967	0.8347	2.6	0.000	0.0003	0.0000	1

[a] $\Delta\theta = 0.1$.

c. Plot the cumulative exit age distribution and estimate the value of θ at $F(\theta) = 0.10$. As shown in the plot below, the value of θ at $F(\theta) = 0.10$ is 0.76.

d. Determine the hydraulic detention time for the basin.

$$\tau = \frac{V}{Q} = \frac{360 \text{ m}^3}{3 \text{ m}^3/\text{min}} = 120 \text{ min}$$

e. Determine the mean residence time. The mean residence time is equal to the hydraulic detention time as given in the problem statement. Because there is no short circuiting, Eq. 6-106 should be used to estimate $\bar{t}$, but the open-flow DFM model was used to simulate a closed-flow DFM model because it is simpler to use and yields similar results at high Pe values.

$$\bar{t} = \tau \quad \text{and} \quad \bar{t} = 120 \text{ min}.$$

f. Estimate t_{10}.
From the above plot, $F(0.10) = 0.76$
Therefore, by EPA's definition $t = t_{10}$ when $\theta_{10} = 0.76$.
Substituting into to Eq. 6-77 and rearranging,

$$t_{10} = \bar{t} \times \theta_{10} \quad \text{or} \quad t_{10} = 120 \times 0.76 = 91 \text{ min}$$

The influence of the aspect ratio can be determined by examining Eq. 6-113. If it is assumed that the Reynolds number is raised to the power of 1.0, the following expressions can be derived:

$$\text{Pe}_{R_h} = \frac{vR_h}{E} = 0.25 \tag{6-114}$$

$$\text{Pe}_L = \text{Pe}_{R_h} \frac{L}{R_h} \tag{6-115}$$

where Pe_{R_h} = Peclet number based on hydraulic radius

As shown in Eq. 6-115, the Pe number increases as the L/R_h increases. Thus, if the L/R_h is 400, which corresponds to a long conveyance channel, the Pe number would be 100, which corresponds to a θ_{10} of 0.8.

When designing reactors for water treatment, there are generally two types of reactors: (1) a well-mixed reactor in which mixing is mechanically forced for a number of reasons (e.g., to blend chemicals, as discussed in Sec. 6-10, to strip volatile compounds, or to prevent particle settling) and (2) a reactor mixed by the flow through the process equipment (e.g., channels, ditches, or pipes).

Improving Reactor Performance

IMPROVING CMFR PERFORMANCE

Generally, the performance of well-mixed reactors can be improved by inserting baffles in the reactor and converting the reactor from one CMFR to multiple CMFRs. The improvement in reactor performance expected after dividing a CMFR into multiple CMFRs may be estimated with the TIS model described previously. Procedures used to obtain adequate mixing are discussed in Sec. 6-10.

IMPROVING PFR PERFORMANCE

The methods used to improve the performance of a PFR are different than those described for the CMFR. If the fluid velocity is low or the inlet and outlet hydraulics are poor, as shown on Fig. 6-22a, dead volume and
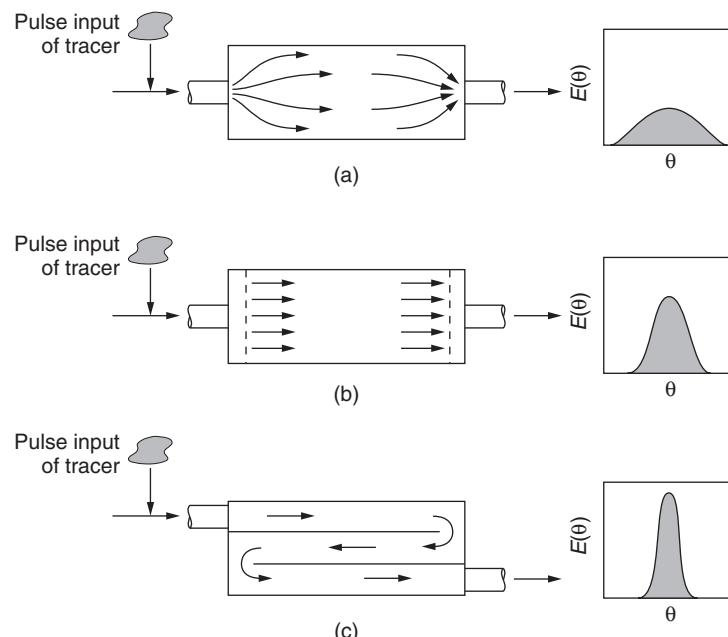

Figure 6-22
Improvement of reactor performance of a basin: (a) original basin with poor inlet hydraulics, (b) basin with improved inlet and outlet hydraulics, and (c) basin with insertion of baffles to increase aspect ratio.

short circuiting can occur. The solution to improving process performance is to distribute the flow uniformly at the inlet and outlet, such as with diffuser baffles, as shown on Fig. 6-22b. For nonsedimentation processes, reactor performance can be improved by installing baffles in the basin so that the flow serpentines through the basin, as shown on Fig. 6-22c. Increasing velocity by inserting baffles that are shown on Fig. 6-22c is not recommended for sedimentation processes, and is discussed in Chap. 10, because sedimentation processes need quiescent conditions. Tracer studies and nonideal flow models can be used to evaluate such improvements. Baffle installation as shown on Fig. 6-22c increases the reactor length-to-depth or length-to-width ratio and the impact of the aspect ratio can then be evaluated.

Turning vanes, hammer heads, filets, and submerged baffles after each turn can be used to minimize short circuiting and improve reactor performance. These features and other techniques are discussed in Chap. 13 because of the importance of minimizing dispersion in disinfection contactors. Chapter 13 also discusses approaches to design to achieve a specific level of dispersion.

6-8 Modeling Reactions in Nonideal Reactors

The modeling of chemical reactions occurring in ideal reactors was introduced in Secs. 6-4 and 6-5. However, the nonideal nature of the hydraulics of real reactors, as described in Secs. 6-6 and 6-7, affects the actual performance. Therefore, it is necessary to describe the performance of reactors in terms of the nonideal nature of reactor hydraulics. When a tracer curve is not available, the DFM and TIS model, introduced in Sec. 6-7, may be used with appropriate kinetic expressions to model reactor performance, as described below.

Dispersed-Flow Model Applied to a Reactive System

The dispersed-flow model, presented in Sec. 6-7, can be used with appropriate reaction kinetics to predict reactor performance. Steady state can only exist for a constant influent concentration, and at steady state, Eq. 6-89 becomes

$$\left(\frac{1}{\text{Pe}}\right)\frac{d^2C}{d\bar{z}^2} - \frac{dC}{d\bar{z}} - k\tau C^n = 0 \qquad (6\text{-}116)$$

where $\text{Pe} =$ Peclet number, dimensionless
$C =$ effluent concentration, mg/L
$\bar{z} =$ dimensionless length $= z/L$, dimensionless
$L =$ length of reactor, m
$k =$ rate constant, $(\text{mg/L})^{-n+1}/\text{s}$
$\tau =$ hydraulic detention time, s
$n =$ reaction order

If the dimensionless normalized concentration $\overline{C}$ is introduced into Eq. 6-116, the following expression is obtained:

$$\left(\frac{1}{\mathrm{Pe}}\right)\frac{d^2\overline{C}}{d\overline{z}^2} - \frac{d\overline{C}}{d\overline{z}} + k\tau C_0^{n-1}\overline{C}^n = 0 \qquad (6\text{-}117)$$

where $\overline{C}$ = normalized concentration = C/C_0, dimensionless
C_0 = initial concentration, mg/L

In Eq. 6-117, the effluent concentration is governed by three dimensionless groups: the Damköhler number $(k\tau C_0^{n-1})$, the Peclet number (Pe), and the reaction order (n).

Equation 6-117 has been solved analytically by Danckwerts (1953) and Wehner and Wilhelm (1958) for a first-order reaction. For reactors that are either open or closed, the solution is

$$\frac{C}{C_0} = \frac{4a\exp(\mathrm{Pe}/2)}{\left[(1+a)^2\exp(a\,\mathrm{Pe}/2)\right] - \left[(1-a)^2\exp(-a\,\mathrm{Pe}/2)\right]} \qquad (6\text{-}118)$$

where $a = \sqrt{1 + 4k\tau(1/\mathrm{Pe})}$

A generalized plot of Eq. 6-118 is presented on Fig. 6-23 for values of the Damköhler number $(k\tau)$ and dispersion number of interest in water treatment. The design engineer can control the product $k\tau$ by adjusting the design hydraulic detention time τ. The Peclet number can also be controlled to some extent by the details of the design of the reactor itself (e.g., baffling, aspect ratio). For example, if the value of $k\tau$ is equal to 4, then the best performance that could be achieved with a PFR would be
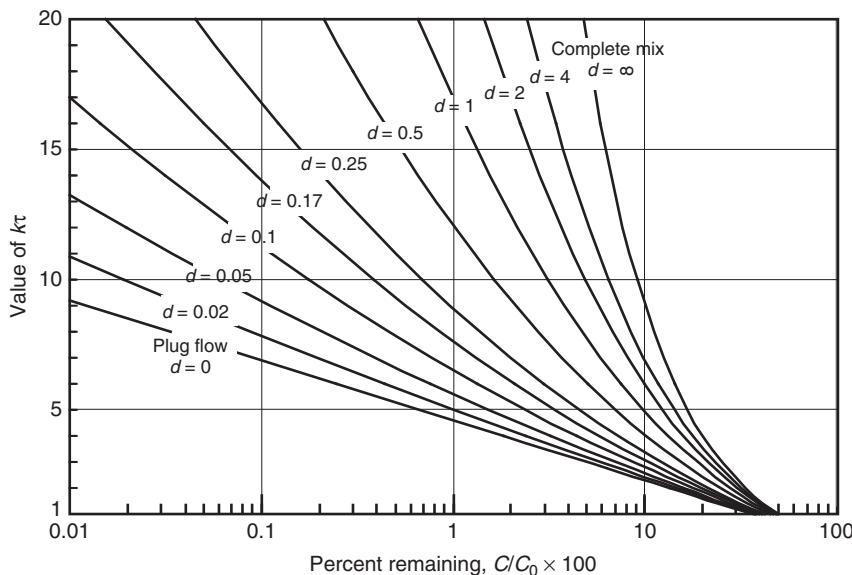

Figure 6-23
Reactor performance as function of Damköhler number and dispersion number (inverse of Peclet number) for first-order reaction.

Example 6-7 DFM calculation for first-order reaction

Using the DFM for a closed reactor and exit age distribution shown in Example 6-5, compare the reactor removal efficiency for a PFR and a CMFR. Use the following values for the calculations:

$$C_0 = 200 \text{ mg/L} \qquad k = 0.0746 \text{ min}^{-1} \qquad -r = kC$$

$$\bar{t} = 76.6 \text{ min (calculated in Example 6-4)}$$

Solution

1. Compute the reactor removal efficiency. For a first-order reaction, the Damköhler number is

$$k\tau \simeq k\bar{t} = (0.0746)(76.6) = 5.72$$

Use Eq. 6-118 to solve for C/C_0 (Pe = 67 from Example 6-5):

$$a = \sqrt{1 + 4k\tau \left(\frac{1}{\text{Pe}}\right)} = \sqrt{1 + 4(0.0746)(76.6)\left(\frac{1}{67}\right)} = 1.16$$

$$\frac{C}{C_0} = \frac{4a \exp(\text{Pe}/2)}{[(1+a)^2 \exp(a\,\text{Pe}/2)] - [(1-a)^2 \exp(-a\,\text{Pe}/2)]}$$

$$= \frac{4(1.16)\exp(67/2)}{[(1+1.16)^2 \exp(1.16\times67/2)] - [(1-1.16)^2 \exp(-1.16\times67/2)]}$$

$$= 0.0050$$

$$C = 1.0 \text{ mg/L}$$

Alternatively, C/C_0 may be estimated using Fig. 6-23; however, because the dispersion number is low, the use of Fig. 6-23 is limited.

2. Compare the reactor removal efficiency with a PFR and a CMFR.
   a. The effluent concentration for a PFR with a mean detention time equal to the hydraulic detention time is determined using Eq. 6-65:

$$\frac{C}{C_0} = e^{-k\bar{t}} = e^{-(0.0746)(76.6)} = 0.00330 \quad \text{or} \quad C = 0.66 \text{ mg/L}$$

The ratio C/C_0 may also be determined using Fig. 6-23; $C/C_0 \simeq 0.0035$ for a PFR when d approaches zero (Pe = ∞).
   b. The effluent concentration for a CMFR with a mean detention time equal to the hydraulic detention time is determined by

rearranging Eq. 6-37:

$$\frac{C}{C_0} = \frac{1}{1 + k\bar{t}} = 0.149 \quad \text{or} \quad C = 29.8 \text{ mg/L}$$

Here, C/C_0 may also be determined using Fig. 6-23; $C/C_0 \simeq 0.14$ for a CMFR when d approaches infinity (Pe $= 0$).

Comment

In this example, a Pe value of 67 (which corresponds to 33 reactors in series in the TIS model) yields an effluent concentration that is double that of an ideal PFR. For disinfection where reductions of 99.99 percent or greater may be required, reactors with very high Pe or low dispersion numbers must be used (see Chap. 13).

98 percent (2 percent remaining), and if the reactor Peclet number was equal to 2 (dispersion number equals 0.5), the best peformance that could be achieved is 90 percent (10 percent remaining). Also, as shown on Fig. 6-23, when removal requirements are modest (less than 50 percent), the Peclet number for the reactor does not make a great deal of difference. On the other hand, when removal requirements are more stringent, maintaining a high Pe (low dispersion) is a critical design requirement.

For second-order reactions, Eq. 6-115 can only be solved numerically. The correspoding results for the DFM for a second-order reaction are displayed on Fig. 6-24.

The reactor performance for the TIS model can be estimated from mass balances for a number of tanks in series. For a first-order reaction, the following expression is obtained:

Tanks-in-Series Model Applied to a Reactive System

$$\frac{C}{C_0} = \frac{1}{(1 + k\tau/n)^n} \tag{6-119}$$

For a second-order reaction, the following equation can be used for n tanks by calculating the effluent concentration from tank i from the previous tank:

$$\frac{C_i}{C_{i-1}} = \frac{-1 + \sqrt{1 + 4k\tau C_{i-1}/n}}{2k\tau C_{i-1}/n} \tag{6-120}$$

where $i =$ intermediate tank in series of n tanks
$C_i =$ concentration exiting tank i, mg/L
$C_{i-1} =$ initial concentration entering tank i, mg/L
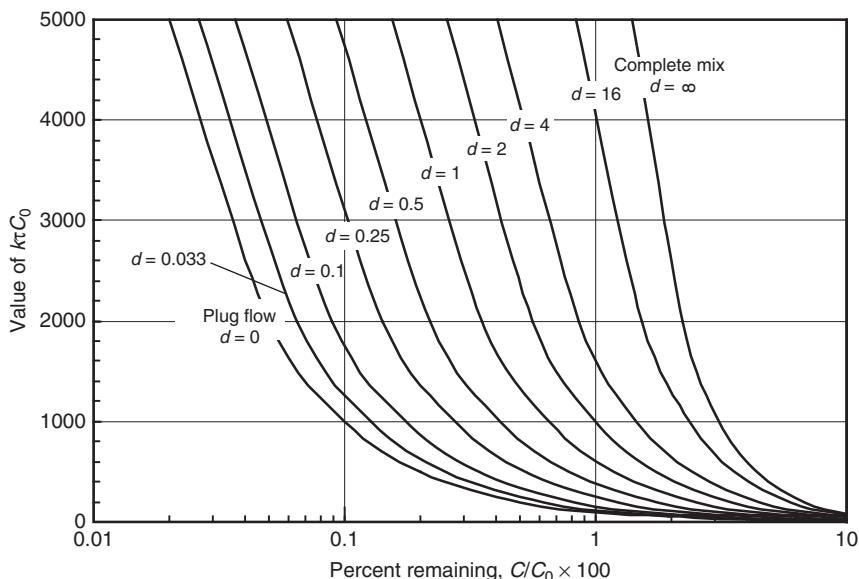
Figure 6-24
Reactor performance as
function of Damköhler
number and dispersion
number (inverse of
Peclet number) for
second-order reaction.
(Adapted from Levenspiel
and Bischoff, 1959.)

Example 6-8 Tank-in-series model calculation

Calculate the performance for the reactor evaluated in Example 6-7 for a
first-order reaction using the TIS model and compare to the results from
the DFM. Estimate the reactor performance for a PFR and a CMFR with the
identical hydraulic detention times.

Solution

1. Determine the reactor removal efficiency for a TIS model with $n = 33$
tanks (see Example 6-5) using Eq. 6-119 for the TIS model:

$$\frac{C}{C_0} = \frac{1}{(1 + k\tau/n)^n} = \frac{1}{(1 + 5.72/33)^{33}} = 0.00512$$

$$C = 1.02 \text{ mg/L}$$

2. The results from TIS and DFM analysis and the estimated performance
of a reactor for a PFR and a CMFR with the identical hydraulic detention
time are compared in the following table:

	TIS	DFM	PFR	CMFR
C, mg/L	1.02	1.00	0.66	29.8

> **Comment**
>
> As summarized in the table above, the reactor performance predicted using the TIS and DFM models is similar. In addition, the performance is closer to that of a PFR than to a CMFR because the Pe and number of tanks in series is large.

6-9 Using Tracer Curves to Model Reactions in Reactors

The DFM and TIS models presented in the previous sections are useful for generating RTD curves when actual tracer response data are not available. The DFM and TIS model can also be used for modeling reactions, where it is assumed that homogeneous conditions exist on the molecular scale (microscale). However, when a tracer curve obtained from a reactor study or CFD calculation is available, the segregated-flow model (SFM) may be used to model reactions. The SFM, limitations of the SFM, and comparison of the SFM and various nonideal flow models are presented in this section.

Segregated-Flow Model

The assumption in the SFM is that all fluid elements are segregated, meaning they do not mix or interact with each other. Consequently, the performance of a real reactor can be determined by estimating the amount of reaction that would take place for each fluid element and then mixing the elements at the end of the reactor. For an exit age distribution as shown on Fig. 6-25, the SFM is obtained by approximating the real reactor as numerous batch or plug flow reactors that have different residence times and exit age characteristics. The normalized curve for the pulse tracer study, $E(\theta)$, is used to determine the amount of fluid that has a particular age.

For development of the SFM, performance for a real reactor is estimated in terms of C/C_0. The contribution for fluid element 9 (see Fig. 6-25) is given by the expression

$$\begin{pmatrix} C/C_0 \text{ from CMBR or PFR} \\ \text{with detention time } \theta_9 \end{pmatrix} \times \begin{pmatrix} \text{fraction of exit stream} \\ \text{that has age } \theta_9 \end{pmatrix} = R(\theta_9)E_9\,\Delta\theta_9$$

(6-121)
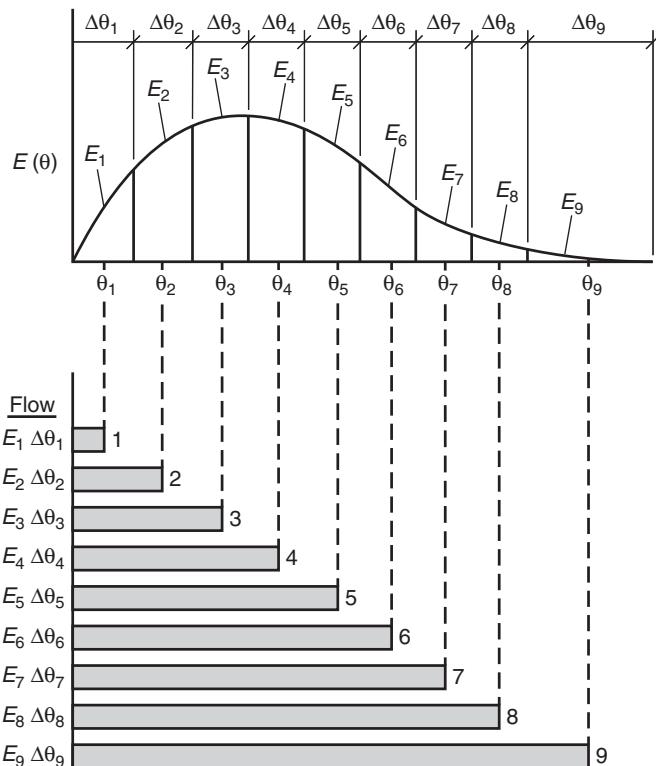
where
θ_9 = exit age for fluid element 9
$R(\theta_9)$ = dimensionless effluent concentration for fluid element 9, which equals effluent concentration divided by influent concentration leaving ideal PFR or CMBR with hydraulic detention time that corresponds to θ_9
E_9 = exit age distribution for fluid element 9
$E_9\Delta\theta_9$ = fraction of exit stream that has age θ_9

Figure 6-25
Definition sketch for SFM. Flow at each average θ corresponds to flow in ideal plug flow or batch reactor.

To determine the reactor performance, sum the contribution of each PFR as follows:

$$\frac{\overline{C}}{C_0} = R(\theta_1)E_1\,\Delta\theta_1 + R(\theta_2)E_2\,\Delta\theta_2 + \cdots + R(\theta_9)E_9\,\Delta\theta_9 \qquad (6\text{-}122)$$

where $\overline{C}$ = average effluent concentration, mg/L

In theory, an infinite number of small PFRs is needed, and taking the limit $N \to \infty$, the following expression is obtained:

$$\frac{\overline{C}}{C_0} = \sum_{i=1}^{N} R(\theta_i)E(\theta_i)\,\Delta\theta_i = \int_0^\infty R(\theta)E(\theta)\,d\theta \qquad (6\text{-}123)$$

The parameter $R(\theta)$ can be obtained by substitution of $\theta\overline{t}$ for τ in the following general expression for any order kinetics. The expressions given

previously in Table 6-3 can also be used.

$$\tau = - \int_{C_0}^{C} \frac{dC}{-r} \tag{6-124}$$

For example, the following expressions are obtained for first- and second-order reactions:

$$R(\theta) = \begin{cases} e^{-k\theta\bar{t}} & \text{(first order)} \tag{6-125} \\ \dfrac{1}{1 + k\bar{t}C_0\theta} & \text{(second order)} \tag{6-126} \end{cases}$$
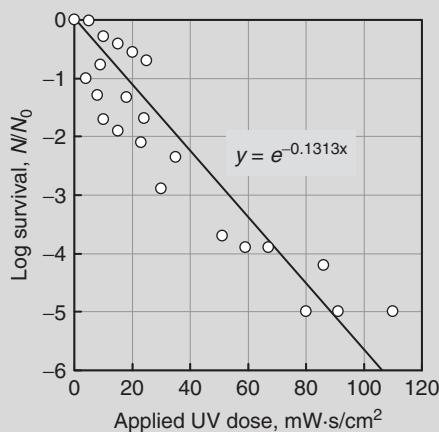
The SFM can be used when $E(\theta)$ and $R(\theta)$ are known. For example, SFM applies when there is batch rate data because $R(\theta)$ is identical to the result that would be expected from a batch reactor. To convert C/C_0 versus time to C/C_0 versus θ, divide the elapsed time in the batch reactor study by $\bar{t}$. The SFM can also be used for sedimentation basins with $R(\theta)$ determined from settling column tests, where the settling column has a depth equal to the settling zone in the sedimentation basin.

Example 6-9 Evaluation of UV disinfection process using SFM

A UV disinfection process takes place in a pipe that contains UV lamps. The pipe is 1 m long with a diameter of 0.3 m. The process flow rate is 1000 m^3/d and the average UV intensity in the reactor is 15 mW/cm^2. The results of a tracer study conducted on the UV disinfection reactor are shown in the following table:

Time, s	Normalized Time, θ	$E(\theta)$	Time, s	Normalized Time, θ	$E(\theta)$
0.0	0.000	0.000	9.0	1.400	0.466
0.6	0.100	0.000	9.7	1.500	0.309
1.3	0.200	0.001	10.3	1.600	0.196
1.9	0.300	0.017	11.0	1.700	0.120
2.6	0.400	0.101	11.6	1.800	0.071
3.2	0.500	0.314	12.3	1.900	0.040
3.9	0.600	0.647	12.9	2.000	0.022
4.5	0.700	1.006	13.6	2.100	0.012
5.2	0.800	1.273	14.2	2.200	0.006
5.8	0.900	1.376	14.8	2.300	0.003
6.5	1.000	1.313	15.5	2.400	0.002
7.1	1.100	1.134	16.1	2.500	0.001
7.7	1.200	0.901	16.8	2.600	0.000
8.4	1.300	0.668			

The UV dose–response curve for a certain microorganism has been deter-
mined and the results are shown in the following plot:

The average concentration of the microorganism in the influent to the UV
reactor, N_0, is $0.1\ L^{-1}$. Estimate the concentration of the microorganism in
the effluent from the UV disinfection process using the SFM.

Solution

1. Set up a table to compute the number of organisms surviving the
   disinfection process.
   a. Compute the unit exit age distribution $E(\theta)\,\Delta\theta$ with a $\Delta\theta$ value of
      0.1. For the time step $t = 2.6$,

   $$E(\theta)\,\Delta\theta = (0.101)(0.1) = 0.0101$$

   b. Estimate the applied dose. The applied dose is determined by
      multiplying the average UV intensity in the reactor by the corre-
      sponding time step. For the time step $t = 2.6$,

   $$\text{Applied dose} = (15\ \text{mW/cm}^2)(2.6\ \text{s}) = 39.0\ \text{mW} \cdot \text{s/cm}^2$$

   c. Estimate the fraction of organisms surviving at the applied dose,
      $R(\theta)$. The fraction of organisms surviving is a function of the applied
      dose, and the relationship is given in the problem statement. Use
      the curve fit to determine the survival. For the time step $t = 2.6$,

   $$\text{Estimated survival, } N/N_0 = e^{(-0.1313 \times 39.0\ \text{mW} \cdot \text{s/cm}^2)} = 0.0060$$

d. Compute the number of organisms surviving. The number of organisms surviving may be determined by multiplying the fractional survival N/N_0 at each time step by the average influent concentration and the unit exit age distribution. For the time step $t = 2.6$,

$$\text{Microorganisms surviving} = (0.0101)(0.0060)(0.1 \text{ L}^{-1})$$
$$= 6.03 \times 10^{-6} \text{ L}^{-1}$$

e. Summarize the computations in a table.

Time, s	Normalized Time, θ	$E(\theta)$	$E(\theta)\,\Delta\theta$	Applied Dose, $mW \cdot s/cm^2$	Estimated Survival, $R(\theta)$, N/N_0	Effluent Microorganism Concentration, L^{-1}
0.0	0.000	0.000	0	0.0	1.0000	0.000000
0.6	0.100	0.000	2.617×10^{-7}	9.7	0.2805	0.000000
1.3	0.200	0.001	8.921×10^{-5}	19.4	0.0787	0.000007
1.9	0.300	0.017	1.712×10^{-3}	29.0	0.0221	0.000038
2.6	0.400	0.101	1.012×10^{-2}	38.7	0.0062	0.000063
3.2	0.500	0.314	3.138×10^{-2}	48.4	0.0017	0.000055
3.9	0.600	0.647	6.467×10^{-2}	58.1	0.0005	0.000032
4.5	0.700	1.006	1.006×10^{-1}	67.8	0.0001	0.000014
5.2	0.800	1.273	1.273×10^{-1}	77.4	0.0000	0.000005
5.8	0.900	1.376	1.376×10^{-1}	87.1	0.0000	0.000001
6.5	1.000	1.313	1.313×10^{-1}	96.8	0.0000	0.000000
7.1	1.100	1.134	1.134×10^{-1}	106.5	0.0000	0.000000
7.7	1.200	0.901	9.009×10^{-2}	116.2	0.0000	0.000000
8.4	1.300	0.668	6.677×10^{-2}	125.8	0.0000	0.000000
9.0	1.400	0.466	4.663×10^{-2}	135.5	0.0000	0.000000
9.7	1.500	0.309	3.095×10^{-2}	145.2	0.0000	0.000000
10.3	1.600	0.196	1.964×10^{-2}	154.9	0.0000	0.000000
11.0	1.700	0.120	1.199×10^{-2}	164.6	0.0000	0.000000
11.6	1.800	0.071	7.067×10^{-3}	174.2	0.0000	0.000000
12.3	1.900	0.040	4.040×10^{-3}	183.9	0.0000	0.000000
12.9	2.000	0.022	2.246×10^{-3}	193.6	0.0000	0.000000
13.6	2.100	0.012	1.218×10^{-3}	203.3	0.0000	0.000000
14.2	2.200	0.006	6.454×10^{-4}	213.0	0.0000	0.000000
14.8	2.300	0.003	3.351×10^{-4}	222.6	0.0000	0.000000
15.5	2.400	0.002	1.707×10^{-4}	232.3	0.0000	0.000000
16.1	2.500	0.001	8.548×10^{-5}	242.0	0.0000	0.000000
16.8	2.600	0.000	4.212×10^{-5}	251.7	0.0000	0.000000
			1			0.000214

2. Estimate the concentration of microorganisms in the process effluent. Summing the values of effluent microorganism concentration for all time steps results in a value of 0.000214 L^{-1}. For a flow rate of 1000 m^3/d, the total number of organisms that can pass through the reactor without being inactivated in one day is

$$\text{Microorganism concentration 1 d flow} = (0.000214\ L^{-1})(10^6\ L/d)$$

$$= 214\ d^{-1}$$

Comment

Because of the nonideal hydraulics in the reactor, it is possible for some of the water to pass through before the detention time required for adequate treatment. Because some microorganisms can cause illness even at low dosages, reactor performance is critical to ensure safe water.

Limitations of SFM Application

The SFM is valid for any shape of reactor and has the following limitations:

1. The SFM can be used to obtain an exact solution for a first-order reaction.
2. For a zero-order reaction, the effluent concentration is identical for both PFRs and CMFRs. Mixing has no impact on the reactor performance and maximum performance can be obtained as long as $\bar{t} = \tau$.
3. For reaction orders greater than 1.0, the effluent concentration calculated using the SFM is less than the actual effluent concentration and represents the lower bound of the effluent concentration (the best possible performance).
4. For reaction orders less than 1.0, the effluent concentration calculated by the SFM is greater than the actual effluent concentration and represents the upper bound of the effluent concentration (the worst possible performance).

A comparison of the differences between the actual and calculated effluent concentration for a CMFR when using the SFM for reaction orders greater than 1 and less than 1 are presented in the following discussion.

REACTION ORDERS GREATER THAN 1

For a second-order reaction in a CMFR, the effluent concentration from a CMFR is given by the expression

$$\frac{C}{C_0} = \frac{-1 + \sqrt{1 + 4k\tau C_0}}{2k\tau C_0} \tag{6-127}$$

where k = reaction rate, L/mg·s
      τ = hydraulic detention time, s

For $k\tau C_0 = 1$, the resulting value of C/C_0 is 0.618, as computed using Eq. 6-125. The terms that appear in the SFM approximation of a CMFR are

$$R(\theta) = \frac{1}{1 + k\tau C_0 \theta} \tag{6-128}$$

$$E(\theta) = e^{-\theta} \tag{6-129}$$

The SFM approximation for a CMFR with $k\tau C_0 = 1.0$ results in the expression

$$\frac{\overline{C}}{C_0} = \int_0^\infty \left[\left(\frac{1}{1 + k\tau C_0 \theta} \right) e^{-\theta} \right] d\theta = 0.596 \tag{6-130}$$

Thus, for a second-order reaction, the SFM method predicts a lower concentration than a mass balance on a CMFR. The difference between Eqs. 6-130 and 6-127 is shown as line (a) on Fig. 6-26. As shown, the concentration predicted by the SFM is consistently lower than the result for a CMFR. The reason the SFM predicts a lower concentration for a second-order reaction is because less backmixing occurs as the performance approaches ideal plug flow. Under ideal conditions, the results from the SFM analysis will be identical to the analytical solution for a PFR.

ORDERS LESS THAN 1

For reaction orders less than 1.0, such as $n = 0.5$, the following relationship for $R(\theta)$ is obtained from a PFR mass balance:

$$R(\theta) = \left(1 - \frac{k\tau\theta}{2C_0^{0.5}} \right)^2 \tag{6-131}$$
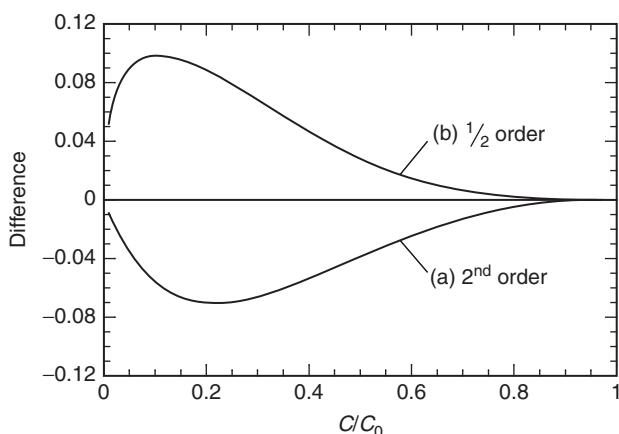
Figure 6-26
Difference between the actual effluent concentration for a CMFR and the SFM for: (a) a second-order reaction rate and (b) a half-order reaction rate.

The SFM approximation to a CMFR is given by the expression

$$\frac{\overline{C}}{C_0} = \int_0^\infty \left[\left(1 - \frac{k\tau\theta}{2C_0^{0.5}} \right)^2 e^{-\theta} \right] d\theta \tag{6-132}$$

However, a reasonable result of Eq. 6-130 cannot be obtained using the range of integration from zero to infinity because the value of $k\tau\theta/(2C_0^{0.5})$ needs to be between zero and unity (otherwise the effluent concentration is negative). Therefore, the SFM approximation for a CMFR with a reaction order of 0.5 is modified to

$$\frac{\overline{C}}{C_0} = \int_0^{(1/L)} \left[(1 - L\theta)^2 e^{-\theta} \right] d\theta \tag{6-133}$$

where $L = k\tau/(2C_0^{0.5})$

For $L = 0.5$ the resulting value of $\overline{C}/C_0$ is 0.432, as computed using Eq. 6-133.

For a CMFR using a conventional mass balance approach, the following expressions are obtained:

$$\tau = \frac{V}{Q} = \frac{C_0 - C}{kC^{0.5}} \tag{6-134}$$

$$\frac{C}{C_0} = \frac{1}{2} \left[2 + \frac{\tau^2 k^2}{C_0} - \sqrt{\left(2 + \frac{\tau^2 k^2}{C_0} \right)^2 - 4} \right] \tag{6-135}$$

For $k\tau/2C_0^{0.5} = 0.5$ (equal to $\tau^2 k^2/C_0 = 1$), the resulting value of C/C_0 is 0.382, as computed using Eq. 6-135.

Thus, for a half-order reaction, the SFM method predicts a higher concentration than a mass balance on a CMFR. The difference between Eq. 6-133 and 6-135 is shown as line (b) on Fig 6-26. As shown on Fig. 6-26, the SFM consistently predicts a larger concentration than a mass balance on a CMFR. This difference is the maximum difference that can be expected using the SFM for a half-order reaction.

As shown in the analysis presented above, the differences for 0.5 and second orders represent the maximum difference between the SFM and a given reactor's actual performance, respectively. The SFM predicts an exact answer for any reaction order when used to simulate a PFR $[E(\theta) = \delta(1)]$. Accordingly, the SFM would predict reactor performance that is closer to the observed reactor performance as the reactor backmixing decreased to that of a PFR (no backmixing).

6-10 Mixing Theory and Practice

Mixing is a central part of water treatment. In some unit operations, mixing has a profound impact on the course of the reactions of interest. In other unit operations, understanding mixing is an important adjunct to

process control. In still others, mixing energy actually contributes to the rate of the reaction (e.g., flocculation). In the early days, the design and implementation of mixing facilities was a haphazard processes. Even today, there is a great deal of art in designing mixing facilities. Nevertheless, as discussed below, scientific tools are available that can be used to improve the design of these facilities.

Two types of mixing are applied in water treatment: (1) agitation and (2) blending. Each is considered separately in the following discussion.

Types of Mixing

AGITATION (FLUID)

Agitation is the term used to describe the motion induced in a fluid to promote processes such as flocculation, to maintain particles in suspension, and for mass transfer such as aeration. In flocculation, the water is agitated to bring about contact between particles, after the chemistry (coagulation) has been used to neutralize their natural repulsion to each other. To design mixing facilities for flocculation it is important to know (1) the particle size distribution of the particles to be flocculated and (2) the degree of agitation necessary to bring about particle contact. The subject of flocculation is considered in greater detail in Chap. 10. Agitation is also used to prevent particles from settling in equalization and related facilities (also covered in Chap. 10). Mass transfer reactions are enhanced by agitation such as occurs as water falls over a cascade of stairs or when air is bubbled through water for the addition of oxygen or to remove supersaturated gases from solution. Mass transfer reactions are discussed further in Chap. 7.

BLENDING

The process of combining two or more liquid streams to achieve a specified level of uniformity is known as *blending*. To design mixing facilities, for the purposes of blending, it is important to (1) understand how to estimate the thoroughness of the blending required so that process sampling, analysis, and control can be accomplished (e.g., chlorination, pH control, or fluoridation) and (2) identify those situations where the speed and thoroughness of blending both have important impacts on process efficiency and effectiveness (e.g., coagulation with Al^{3+} or Fe^{3+} or disinfection of secondary effluent with chlorine). Significant differences in approach result from these different design objectives.

Because of their large size, virtually all water treatment processes take place in turbulent flow. As a result, to better understand mixing in water treatment, it is helpful to gain a conceptual understanding of turbulence. Thus, before discussing mixing for agitation and blending, the nature of turbulence is explored briefly below.

Some Fundamentals of Mixing

INTRODUCTION TO TURBULENCE

It is helpful to think of turbulent flow as consisting of a cascade of eddies—more specifically a cascade of energy from large eddies to small eddies. Kinetic energy imparted to the water through physical action (a pump, a mixer, falling over a weir, etc.) imparts momentum to large segments of water, creating the large eddies moving in a direction consistent with the motive force; however, the structure of water is such that, as these large eddies move around, their energy is immediately transferred to smaller eddies. Once the eddies become small enough, inertial forces are overcome by the viscous nature of water and they can get no smaller. This cascade of eddies and the significance of the different zones of turbulent flow are illustrated on Fig. 6-27.

The immediate turbulence resulting from the motion-inducing device is anisotropic (energy of motion is in one direction or another), but once the energy from this source has been relayed down to smaller eddies, the turbulence becomes isotropic (energy of motion is equal in all directions). The velocity gradients necessary for flocculation (see Sec. 9-6) are present under both anisotropic and isotropic turbulence, but the large-scale shear forces responsible for floc breakup are mostly found in anisotropic flow.
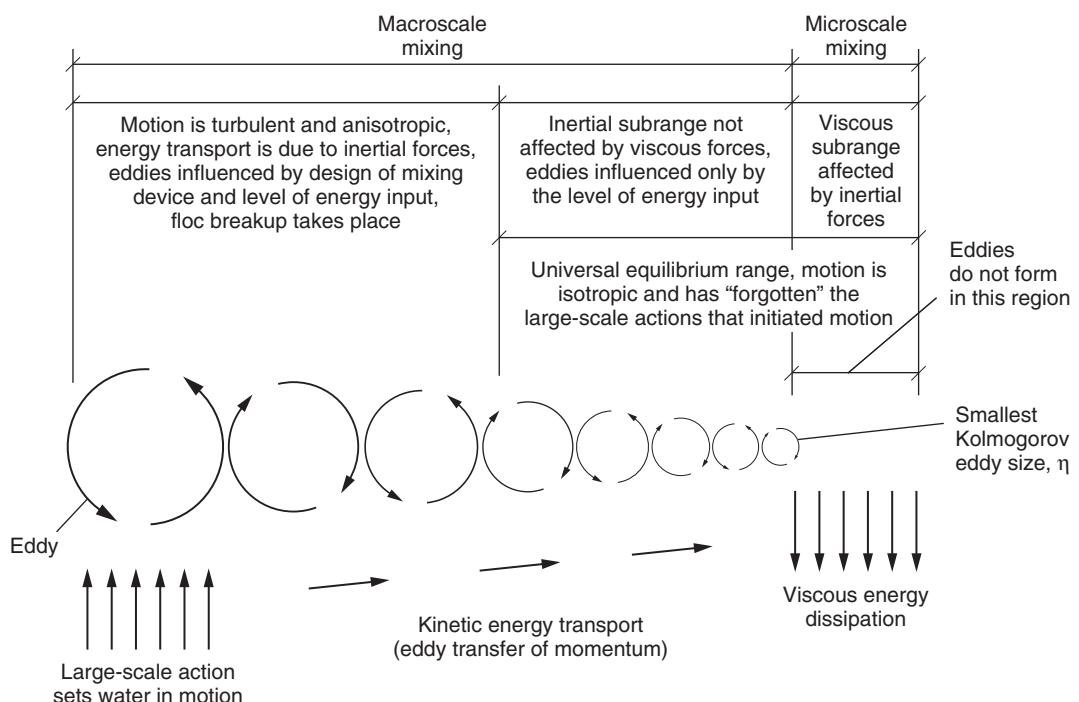

Figure 6-27
Overview of turbulence as it relates to mixing. (Adapted from Stanley and Smith, 1995.)

The design of the mixing equipment for flocculation involves a trade-off between flocculation and floc breakup.

MIXING AND SCALE OF TURBULENCE
The largest eddies start out approximately one-half to one-third the dimension of the mixing device, and the size of the smallest eddies is determined by the boundary between turbulent and viscous flow. The size of the smallest eddy is considered the dividing line between the microscale and macroscale. In the macroscale, mass transfer takes place both by turbulent diffusion and molecular diffusion, but turbulent diffusion is dominant. In the microscale, mass transfer takes place only by molecular diffusion. As more energy is input to the system, the dividing line between the microscale and the macroscale becomes increasingly smaller; that is, the smallest eddies get even smaller. A Russian mathematician named Kolmogorov recognized this dividing line and suggested that the diameter of the smallest eddy, η, could be estimated from the amount of energy being dissipated in the system (Kolmogorov 1941a,b,c):

$$\eta = \left(\frac{v^3}{\varepsilon}\right)^{1/4} \tag{6-136}$$

where η = diameter of smallest eddy, m
v = kinematic viscosity, m^2/s
ε = energy dissipation rate at point of interest, $J/kg \cdot s$

The energy dissipation rate in a mixing vessel, ε, is not uniform throughout the vessel, but because energy must be dissipated at the same rate at which it is input to the system, the overall average rate of energy dissipation, $\bar{\varepsilon}$, is equal to the power input:

$$\bar{\varepsilon} = \frac{P}{M} \tag{6-137}$$

where $\bar{\varepsilon}$ = average energy dissipation per unit mass for vessel, $J/kg \cdot s$
P = power of mixing input to entire mixing vessel, J/s
M = mass of water in mixing vessel, kg
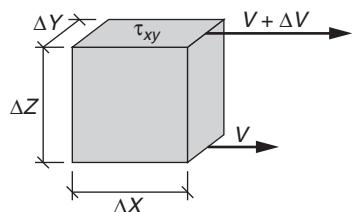
CAMP–STEIN ROOT-MEAN-SQUARE VELOCITY GRADIENT
About the same time as Kolmogorov did his work, Camp and Stein (1943) proposed a similar parameter, the root-mean-square (RMS) velocity gradient $\overline{G}$. Camp and Stein proposed that $\overline{G}$ could be used as a design parameter for flocculation facilities and that the speed of flocculation is directly proportional to the velocity gradient. In subsequent studies it was demonstrated that the direct proportionality that Camp and Stein hypothesized occurred with both metal ion coagulants (Harris et al., 1966) and polymers (Birkner and Morgan, 1968) at both bench and pilot scale (Harris et al., 1966).

Camp and Stein (1943) developed a simple equation for $\overline{G}$ by equating the velocity gradient to the power dissipated per unit volume (P/V).

Figure 6-28
Schematic of forces acting on fluid
element in flocculator.

Consider the fluid element illustrated on Fig. 6-28 and the forces acting on it. The shear stress in the x–y plane, τ_{xy}, is due to the velocity gradient in the z direction, and the force exerted on it is given by the expression

$$\text{Force} = \tau_{xy}\,\Delta x\,\Delta y = \mu\frac{dv}{dz}\Delta x\,\Delta y \qquad (6\text{-}138)$$

where μ = dynamic viscosity of water, $N \cdot s/m^2$ and Δx, Δy, Δz are fluid element dimensions on Fig. 6-28. The product of force and velocity is power, so, using the velocity increment due to the shear stress in the fluid element, the power per unit volume can be written as

$$\frac{P}{V} = \frac{\text{Force} \times \text{velocity}}{\Delta x\,\Delta y\,\Delta z} = \frac{\left[\mu\,(dv/dz)\,\Delta x\,\Delta y\right]\left[(dv/dz)\,\Delta z\right]}{\Delta x\,\Delta y\,\Delta z} = \mu\left(\frac{dv}{dz}\right)^2$$
$$(6\text{-}139)$$

where P/V = power dissipated in selected fluid element, $J/m^3 \cdot s$

Under turbulent-flow conditions, the velocity gradient is not well defined and varies both in time and space throughout the flocculation vessel. Camp and Stein proposed that the velocity gradient, averaged over the volume of the entire vessel, could be used as a design parameter for flocculation. They named the parameter the RMS velocity gradient. Rearranging Eq. 6-139 and defining the RMS velocity gradient dv/dz as $\overline{G}$,

$$\overline{G} = \sqrt{\frac{P}{\mu V}} \qquad (6\text{-}140)$$

where $\overline{G}$ = global RMS velocity gradient (energy input rate), s^{-1}
P = power of mixing input to vessel, J/s (same as P in Eq. 6-137)
V = volume of mixing vessel, m^3

The Camp–Stein RMS velocity gradient $\overline{G}$ has since become a widely adopted standard used by engineers for assessing energy input in all kinds of mixing processes, particularly flocculation, and $\overline{G}$ is the parameter that will be used to characterize mixing energy throughout this book.

Example 6-10 Determination of relationship between smallest eddy size η and $\overline{G}$ for water at 10°C

Find the relationship between η and $\overline{G}$ and then produce a semilog plot of this relationship for water at $10°C$ and for $\overline{G}$ values between 1 and 1000 s^{-1}. At $10°C$ the kinematic viscosity of water is 1.31×10^{-6} m^2/s. Assume that all the energy is dissipated uniformly throughout the vessel (e.g., $\varepsilon \cong \overline{\varepsilon}$).

Solution

1. Develop a relationship between η and $\overline{G}$.
   a. Solving Eq. 6-137 and Eq. 6-140 for P and setting them equal to each other yields

   $$M\overline{\varepsilon} = \overline{G}^2 \mu V$$

   b. Rearranging gives

   $$\overline{\varepsilon} = \nu\overline{G}^2$$

   where $$\nu = \frac{\mu}{\rho} = \frac{\mu V}{M}$$
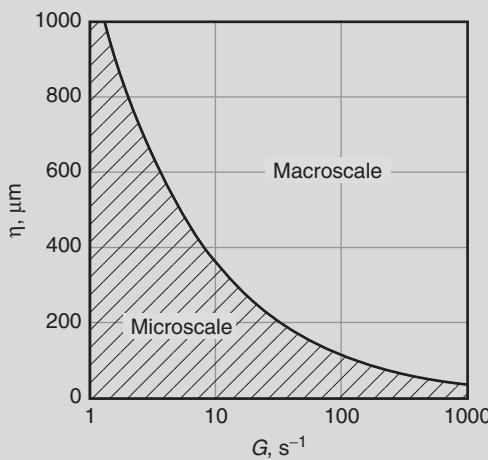
   c. Rearrange Eq. 6-136 to yield

   $$\varepsilon = \frac{\nu^3}{\eta^4}$$

   d. Assuming $\varepsilon \cong \overline{\varepsilon}$, equating the equations from steps b and c yields

   $$\eta = \left(\frac{\nu}{\overline{G}}\right)^{1/2}$$

   $$= \left[\frac{\left(1.31 \times 10^{-6}\ \text{m}^2/\text{s}\right)}{\overline{G},\ \text{s}^{-1}}\right]^{1/2}$$

2. Substitute values for $\overline{G}$ between 1 and 1000 s^{-1} in the expression developed above and plot the results. The required plot is given below.

**Uniformity
and Time Scales
in Mixing**

One of the principal objectives of mixing, as noted previously, is the blending of two flows, usually the blending of a small flow of chemical solution with the much larger flow of the water to be treated. The greater the difference in the flow of the water to be treated and the flow of the chemical being blended, the more difficult the blending is to accomplish. There are two ways that the degree of blending can be assessed: (1) the uniformity of the concentration of components in solution with time (both in time and in space) and (2) the time it takes to accomplish a specified level of uniformity. The uniformity of blending with time and/or space is generally addressed by specifying an objective for the variation of the concentration of the chemical to be blended.

In water treatment there are two principal circumstances when blending is important: (1) blending must be achieved before samples can be taken for the analysis that confirms that the quality of the blend meets the goals (e.g., before chlorine residual analysis) and (2) rapid blending must be achieved with water treatment chemicals that involve irreversible competitive consecutive reactions (e.g., coagulation with alum or ferric chloride or the breakpoint reactions between chlorine and ammonia described in Chap. 13).

UNIFORMITY OF BLENDING

When a chemical is to be added to a water stream and blending is required, there are two tasks that must be addressed: (a) specifying the uniformity of the blend produced and (b) specifying the magnitude of the task that the mixer must accomplish. Assessing the uniformity of the blend can be determined with respect to variations in time and/or space, but it is most often determined in the context of variation in time. Important variations in the concentration with time are identified on Fig. 6-29. The standard deviation is

$$\sigma = \sqrt{\frac{\sum_{t=1}^{n} \left(C_t - \overline{C}\right)^2}{n-1}} \tag{6-141}$$

where C_t = instantaneous concentration at time t, mg/L

$\overline{C}$ = average concentration mg/L, and

σ = standard deviation of the concentration in the stream

n = number of samples of concentration

When the uniformity of the blend is specified, the standard deviation is usually normalized to the average concentration. This normalized standard deviation is usually identified as the coefficient of variation (COV):

$$COV = \left(\frac{\sigma}{\overline{C}}\right) \times 100\% \tag{6-142}$$
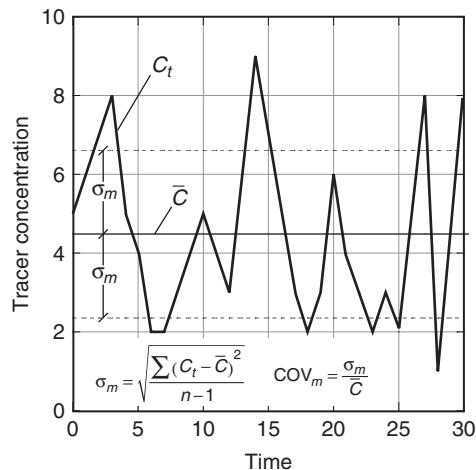
Figure 6-29
Illustration of typical concentration variation immediately downstream of tracer addition point.

where   COV = coefficient of variation with time

σ = standard deviation of concentration, mg/L

$\overline{C}$ = average concentration over time, mg/L

An analogous exercise can be used to estimate the quality of a blend in space, for example, samples taken across the cross section of flow a specified distance downstream of the point of chemical addition.

The magnitude of the blending that must be accomplished is determined by the COV that is sought in the design and the segregation of the unmixed streams. Danckwerts (1952) defined the term *intensity of segregation I_s* as given by Eq. 6-143 to characterize the state of blending:

$$I_s = \left(\frac{\sigma_m}{\sigma_u} \right)^2 \tag{6-143}$$

where I_s = Danckwerts' intensity of segregation

σ_m = standard deviation of concentration in blended stream

σ_u = standard deviation between two streams in unblended condition

Danckwerts' intensity of segregation I_s is a description of the degree to which the two streams have been blended. The general description of how completely the streams are blended can be put in the following way:

When $I_s = 0$, the two streams are blended completely.

When $I_s = 1$, the two streams are completely unblended.

The term I_s can also be used to specify what a mixing device must accomplish. The value of I_s for a mixer can be determined from Eq. 6-143 if σ_u is known and a decision is made on the σ_m to be specified.

The standard deviation between the two unblended streams, σ_u, can be estimated on the basis of their relative flow rates. When chemical A is being added to a stream of water, the volume fraction of the chemical solution being added to the original water stream can be estimated as follows:

$$\overline{X}_A = \frac{Q_A}{Q_w + Q_A} \qquad (6\text{-}144)$$

By definition,

$$\overline{X}_w = 1 - \overline{X}_A \qquad (6\text{-}145)$$

where $\overline{X}_A$ = volume fraction of stream containing chemical A in unblended condition

Q_A = flow rate of solution stream of chemical A, m^3/s

Q_w = flow rate of water stream being treated, m^3/s

$\overline{X}_w$ = volume fraction of water in unblended condition

and if it is assumed that a large number of random samples are taken from the two streams, it can be shown that

$$\sigma_{u(\text{vol})} \cong \sqrt{\overline{X}_A \left(1 - \overline{X}_A\right)} \qquad (6\text{-}146)$$

where $\sigma_{u(\text{vol})}$ = standard deviation of concentrations before blending (expressed as volume fraction)

When designing systems to dose chemicals in a water treatment plant, concentration data are often more readily available than flow rate data. A mass balance can be used to relate the flows and concentrations:

$$Q_A C_A = Q_w C_{\text{dose}} \qquad (6\text{-}147)$$

or

$$\frac{Q_A}{Q_w} = \frac{C_{\text{dose}}}{C_A} \qquad (6\text{-}148)$$

where Q_A = flow rate of feed stream for chemical A, m^3/s

Q_w = flow rate of water stream being treated, m^3/s

C_A = concentration of chemical A in feed stream, kg/m^3

C_{dose} = dose of chemical A to be applied to water stream, kg/m^3

The volume fraction can then be found by substituting Eq. 6-148 into Eq. 6-144:

$$\overline{X}_A = \frac{C_{\text{dose}}}{C_A + C_{\text{dose}}} \qquad (6\text{-}149)$$

The application of the above equations is illustrated in Example 6-11.

TIME REQUIRED TO ACCOMPLISH BLENDING

The uniformity of the blend is important, but the time required to accomplish blending is equally important. There are two circumstances where the time required to meet a blending goal, t_b, is important: (1) when blending must be complete for purposes of analysis and control and (2) when blending must be completed rapidly to prevent adverse outcomes.

Example 6-11 Estimating value of I_s

A water treatment plant must dose the water with 30 mg/L of alum so that the coefficient of variation of the blend is 5 percent or less (COV $\leq$ 5 percent). Estimate the I_s that characterizes the magnitude of the blending job (the mixer's specification). It may be assumed that the alum solution has a strength of 651 g/L. *Hint:* Both σ_u and σ_m must be on the same basis. Because σ_u is estimated as a volume fraction ($\sigma_{u(vol)}$), σ_m must also be expressed as a volume fraction ($\sigma_{m(vol)}$) for I_s to be properly determined.

Solution

1. Determine the volume fraction using Eq. 6-149:

$$\overline{X}_A = \frac{C_{dose}}{C_A + C_{dose}}$$

As $C_A \gg C_{dose}$,

$$\overline{X}_A \cong \frac{C_{dose}}{C_A} = \frac{30 \text{ mg/L}}{651{,}000 \text{ mg/L}} = 4.61 \times 10^{-5}$$

2. Estimate the standard deviation of the concentration using Eq. 6-142: (Eq. 6-142 is equally valid whether concentration or volume fraction is used).

$$\text{COV} = 5\% = \frac{\sigma_{m(vol)}}{\overline{X}_A} \times 100\%$$

$$\sigma_{m(vol)} = 0.05 \times 4.61 \times 10^{-5} = 2.30 \times 10^{-6}$$

3. Determine the uniformity of the unblended streams. Substituting 4.61×10^{-5} into Eq. 6-146 results in the unblended uniformity on a volume fraction basis ($\sigma_{u(vol)}$):

$$\sigma_{u(vol)} = \sqrt{4.61 \times 10^{-5} \left(1 - 4.61 \times 10^{-5}\right)} = 0.00679$$
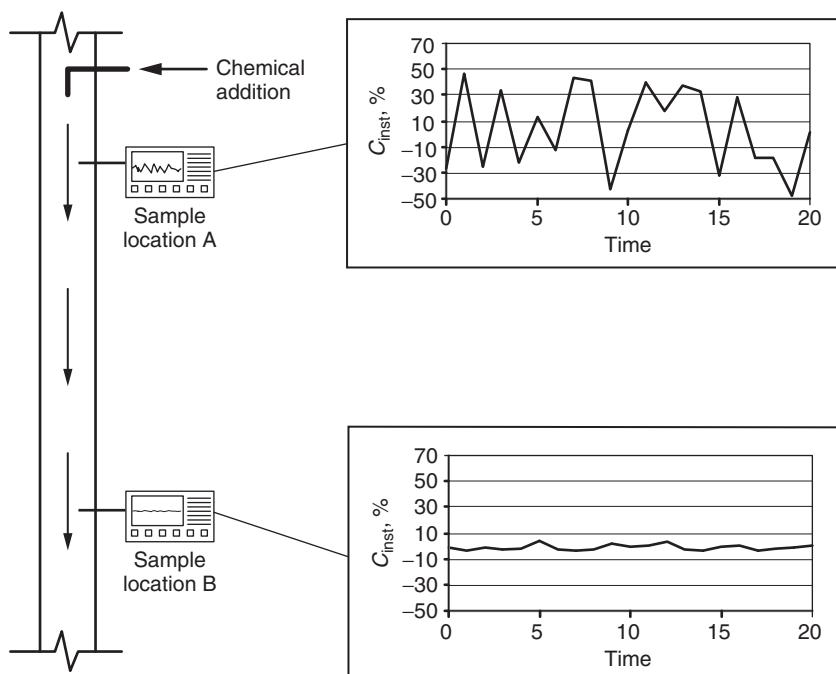
4. Determine the intensity of segregation using Eq. 6-143:

$$I_s = \left(\frac{2.30 \times 10^{-6}}{0.00679}\right)^2 = \left(3.39 \times 10^{-4}\right)^2 = 1.15 \times 10^{-7}$$

Blending time and control

A situation where blending must be complete for purposes of analysis and control is illustrated on Fig. 6-30. As shown, a simple point discharge is introduced into a conduit, and the variation of concentration is observed

Figure 6-30
To achieve reliable
monitoring for control, the
downstream sampling point
must be beyond the point
where uniform blending is
achieved.

at two sampling points downstream. Sampling at point A, the signal that
is generated would make control very difficult. Sampling at point B solves
this problem, but at the expense of time. Sampling at point B introduces
another control problem, the travel time from point A to point B. When a
chemical feed is simply discharged into turbulent flow in a pipe or channel,
a travel distance of as much as 100 conduit diameters in length may be
required before acceptable blending is achieved. When such travel distances
are not acceptable, a special mixing or blending device is required. The
design engineer needs to know where the blend will be sufficiently uniform
and what may be done if uniformity is not achieved soon enough.

Rapid blending
When irreversible competitive consecutive reactions are involved, it is often
important to accomplish blending rapidly to avoid adverse outcomes. It is
also important that blending be accomplished in a manner that prevents
backmixing (recirculation) so that components already formed do not gain
access to the chemical being added a second time. Put another way, the
two components must be rapidly blended across the flow cross section.
A relatively simple model for characterizing situations where rapid mixing
is important was proposed by Toor (1969). Toor proposed that reactions

be broken into three classes:

$$\frac{t_k}{t_b} \gg 1 \text{ (slow reaction)} \tag{6-150}$$

$$\frac{t_k}{t_b} \approx 1 \text{ (moderate reaction)} \tag{6-151}$$
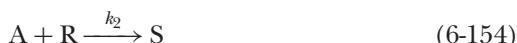
$$\frac{t_k}{t_b} \ll 1 \text{ (fast reaction)} \tag{6-152}$$

where t_k = time characteristic of reaction of interest, e.g., reaction half-life, s

t_b = time characteristic of blending, e.g., time required to achieve COV < 5 percent, s

For slow reactions $(t_k \gg t_b)$, blending is generally accomplished at the molecular level before the reaction of interest makes significant progress. With moderate reactions $(t_k \sim t_b)$, the reaction occurs at the same pace as blending, and with fast reactions $(t_k \ll t_b)$ the state of the reaction at any moment in time is limited by the remaining segregation, that is, the degree to which the blending is not yet complete. To make deliberate decisions about rapid blending, information must be available on both the time characteristic of the reaction t_k and the time characteristic of mixing t_b.

Toor recognized that comparing t_k and t_b alone is not enough to make sound decisions about the importance of rapid blending. For example, when a simple, reversible reaction with no competitive side reactions is being considered, the outcome will be the same no matter how fast is the blending. The outcome of fast, competitive, consecutive, poorly reversible reactions can be markedly influenced by the time of blending. Consider the following competitive, consecutive model reactions (Toor, 1969):

$$A + B \xrightarrow{k_1} R \tag{6-153}$$

$$A + R \xrightarrow{k_2} S \tag{6-154}$$

Consider the case where a concentrate of chemical A is being added to a dilute solution of chemical B and the objective is to produce product R, that is, S is considered an undesirable by-product. When mixing is slow $(t_b \gg t_k)$, B is soon depleted in the A-rich zones of the mixture and the formation of S is favored. When blending is fast $(t_b \ll t_k)$, the formation of R is favored unless too much A is added.

The time characteristic of blending t_b increases with the scale of the water stream being treated. For example, in a 0.007- to 0.03-ML/d pilot plant, t_b ranges from 0.1 to 1 s. Whereas in treatment plants with capacities of 10, 100, and 1000 ML/d, with efficient blending, t_b is on the order of 3, 10, and 30 s, respectively. When rapid blending is expected to be important, large-scale testing is important.

Table 6-6
Blending assessment of some typical reactions

Example Reactions	Blending Time, s	Is Rapid Initial blending Important?	Comments
Coagulation with Fe^{3+} or Al^{3+}	<0.3	Yes	Fast, poorly reversible, competitive, consecutive
pH adjustment	≪1	No	Fast, easily reversible
$CaCO_3$ nucleation	~20	Perhaps	Somewhat fast, poorly reversible
HOCl/NOM to DBPs	~90,000	No	Very slow, not reversible, competitive, consecutive
Chlorine hydrolysis	0.06	Yes	Fast, easily reversible, Cl_2 has low solublity
Chlorine/ammonia (high Cl_2/N)	<0.1–2000	Yes	Fast in early stages, poorly reversible, competitive, consecutive
Chlorine/ammonia (low Cl_2/N)	10,000–1,000,000	No	Extremely slow, poorly reversible, competitive, consecutive
HOCl/coliform	~10	No	Fast, persistent residual kill
HOCl/*Giardia*	~200	No	Slow, persistent residual kill
HOCl/*Cryptosporidium*	~90,000	No	Slow, persistent residual kill

Several reactions commonly encountered in the treatment of drinking water are summarized in Table 6-6. Three reactions are discussed further below: (1) the addition of sulfuric acid to reduce the pH, (2) the reaction of chlorine with NOM, and (3) the reaction of chlorine with ammonia to form chloramines:

1. *pH adjustment with H_2SO_4*. This reaction is extremely fast $(t_k \ll t_b)$. The reaction is also reversible. The time of blending will control the apparent rate of the reaction, but the outcome will be the same for any reasonable mixing time. Thus, it is only important that blending be complete before the water is sampled and analyzed for pH or before another reaction is introduced, which depends on the pH goal being sought.

2. *Chlorination of NOM to form DBPs*. Though hardly simple, the reaction of chlorine with NOM is generally regarded as slow. The time for completion is generally 10 to 20 h or more. The time of blending is rarely more than a few minutes. Thus, $t_k \gg t_b$, and this is a slow

reaction where the speed of initial blending would not be of great importance.

3. *Reaction of chlorine with ammonia to form chloramines.* These reactions are discussed further in Chaps. 8 and 13. They consist of a series of competitive, consecutive reactions some of which are very fast and many of which are poorly reversible (Saunier and Selleck, 1979; Wei and Morris, 1974). Consequently, blending can and does have a great impact on the outcomes achieved.

All the discussion so far has been concerned with managing the dispersion created by the turbulence at the macroscale (turbulent diffusion) to accomplish a specified level of blending. When rapid blending is being pursued for the purposes of facilitating chemical reactions, blending must be accomplished to the molecular level. Consequently, diffusion must be responsible for transport of the treatment chemical within the microscale. The time scale that is required for this transport into the smallest eddies can be estimated by using the following expression (Crank, 1979):

Blending below Microscale

$$t_d = \frac{3R^2}{4D_l} \qquad (6\text{-}155)$$

where t_d = time for molecules to diffuse in or out of eddy, s

R = radius of eddy, m

D_l = liquid diffusivity of chemical molecule ($\sim 10^{-9}$ m^2/s)

Earlier in this section it was shown that eddy size is influenced by the energy input and that the eddy diameter is equal to the Kolmogorov microscale η, introduced previously in the earlier subsection on mixing and the scale of turbulence (Logan, 1999). Hence the radius of the smallest eddy is equal to half of η:

$$R_{\text{avg}} = \tfrac{1}{2}\eta \qquad (6\text{-}156)$$

where R_{avg} = radius of smallest eddy, m

Expressing energy input in terms of the Camp–Stein $\overline{G}$ and combining Eqs. 6-136, 6-137, 6-140, and 6-155, it can be demonstrated that the product $\overline{G}t_d$ that must be sustained to ensure that mixing occurs throughout the microscale can be calculated as shown below for 10°C:

$$\overline{G}t_d = \frac{3v}{16D_t} \cong \frac{3 \times 1.31 \times 10^{-6} \text{ m}^2/\text{s}}{16 \times 10^{-9} \text{ m}^2/\text{s}} = 246 \qquad (6\text{-}157)$$

Obtaining the engineering data necessary for the design of a mixing device using intensity of segregation I_s is not very easy for the following reasons: (1) most of the work on specification of blending has been done in the

Mixing Devices Used for Blending

chemical engineering field, (2) even in that field the important blending problems are in laminar flow in liquids and turbulent-flow studies are largely limited to combustion, and (3) the mixing devices used in chemical engineering are designed to handle much smaller flows.

As a result, environmental engineers more commonly rely on mixing devices that are designed to achieve a certain intensity of mixing ($\overline{G}$) rather than mixing devices designed to produce a specified quality of mix (COV < 5 percent) (Kawamura, 2000). Several of the devices that are commonly used are described in Table 6-7 and illustrated on Fig. 6-31. The advantages and disadvantages of the various devices are also noted in Table 6-7.

Nevertheless, design data for the intensity of segregation approach are available for some devices. In the remainder of this chapter, the limited design data available are used to highlight some key design issues.

**Design of Mixers to Achieve a Specified Blend**

The design of mixers to achieve a specified blend is discussed briefly below. The design is based on the principles described earlier and published statistics on four mixing devices that are useful for blending for control or rapid mixing in small facilities. Unfortunately, design information is not available for devices used for the rapid mixing of flow streams, which

Table 6-7
Rapid mixing devices that avoid or minimize backmixing

Mixing Device	Advantages	Disadvantages	Upper Flow Limit, ML/d[a]
Centerline diffuser	Simple, reliable, inexpensive, data for Eq. 6-158 available	Turbulence is essential	5
Venturi injector	Simple, reliable	Data for Eq. 6-158 not available, subject to clogging	30
Static mixer	Simple, reliable, data for Eq. 6-158 available	Expensive, subject to clogging	100
Axial pumped jets	Can be simple, reliable	Data for Eq. 6-158 not available, subject to clogging, some backmixing	100
Lateral pumped jets	Can be simple, reliable	Data for Eq. 6-158 not available, subject to clogging	150
Conventional stirred tanks	Familiar, can be effective at blending	Expensive to maintain, high energy costs, extensive backmixing	150

[a]Approximate upper limit for efficient mixing in reasonable time. Above these limits, multiple units in parallel are recommended.
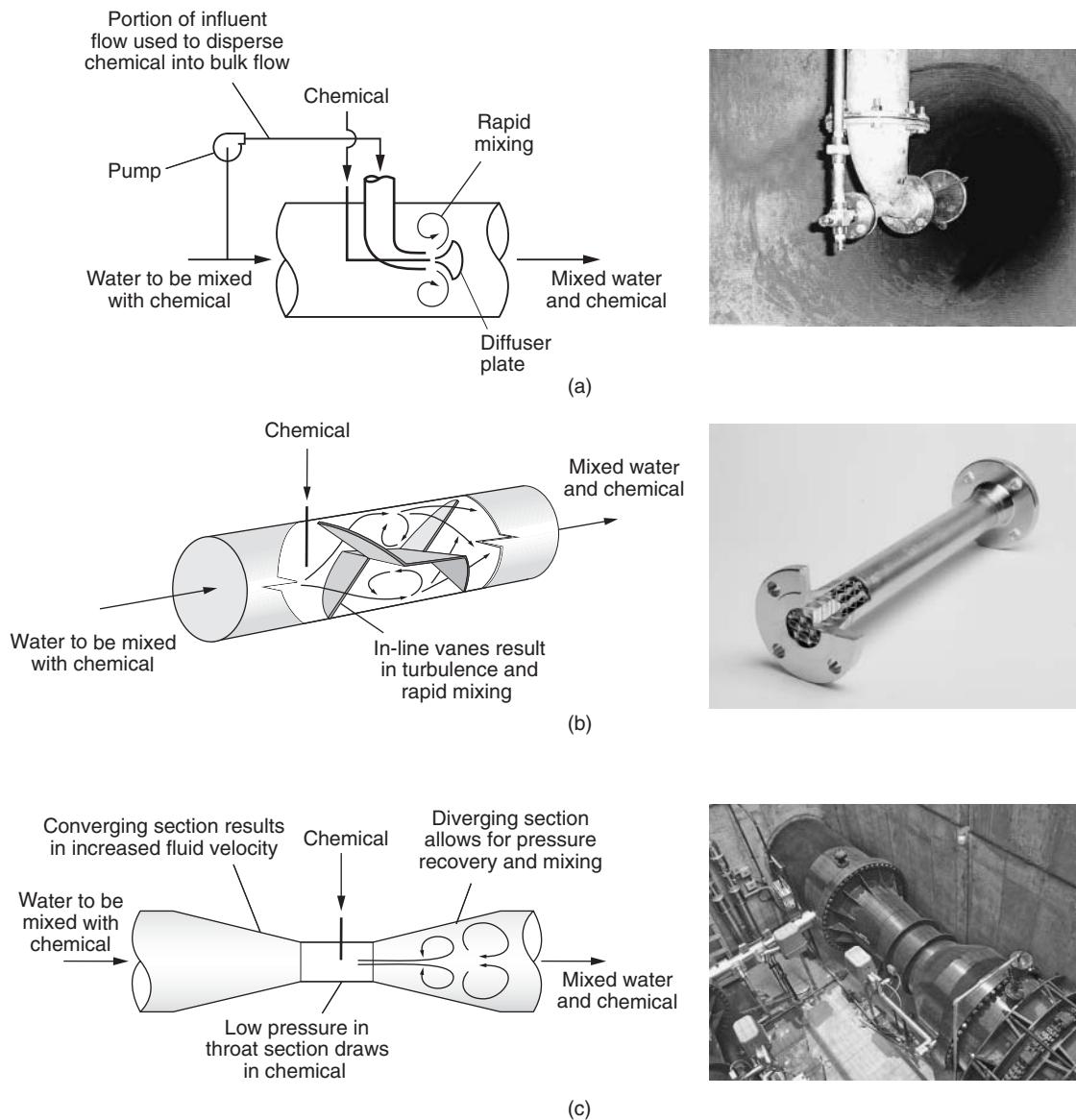
Figure 6-31
Illustrations of blending approaches used in water treatment: (a) pumped flash mixer, (b) in-line static mixer, and (c) in-line Venturi mixer.

are the size of those found in the larger full-scale water treatment plants. For these designs, empirical rules are generally used, although there is increasing interest in applying computational fluid dynamics (DuCoste and Oritz, 2003). Despite these limitations, the illustrative calculations are given here because they demonstrate important features regarding the scalability of rapid mixing.

Godfrey (1985) proposed the following related rules for modeling a variety of mixers that operate in the centerline of pipe flow: (1) a centerline discharge, (2) a Kenics static mixer, (3) a Koch static mixer, and (4) a pipe with trapezoidal baffles:

$$\left(\frac{\sigma_b}{\sigma_u}\right)_{AR=L/D} = \left(\frac{\sigma_b}{\sigma_u}\right)_{AR=1}^{L/D} \tag{6-158}$$

where $(\sigma_b/\sigma_u)_{AR=L/D} = \sigma_b/\sigma_u$ achieved by mixer with length-to-width ratio (aspect ratio, AR) equal to L/D

$(\sigma_b/\sigma_u)_{AR=1} = \sigma_b/\sigma_u$ achieved by mixer with aspect ratio of unity

L = length of mixer, m

D = diameter of mixer, m

$$(N_{VH})_{AR=L/D} = \frac{L}{D}(N_{VH}) \, AR = 1 \tag{6-159}$$

where $(N_{VH})_{AR=L/D}$ = number of velocity heads lost through mixer with aspect ratio equal to L/D

$(N_{VH})_{AR=1}$ = number of velocity heads lost through mixer with aspect ratio of unity

Godfrey (1985) reported values for $(\sigma_b/\sigma_u)_{AR=1}$ and $(N_{VH})_{AR=1}$ for four mixing devices as shown in Table 6-8.

Equation 6-159 can be used to estimate the L/D of the mixing device required to meet a specified level of uniformity, $(\sigma_b\sigma_u)_{AR=L/D}$, and Eq. 6-158 can be used to estimate the head loss that will occur through the device. The mixing time required to meet the specified level of uniformity, t_b, is the time it takes for the water to pass through the mixer and is determined from the velocity of flow and the length of the mixer.

Table 6-8

Performance and design parameters for mixing devices

Mixing Device	$(\sigma_b/\sigma_u)_{AR=1}$	$(N_{VH})_{AR=1}$
Pipeline	0.95	0.02
Koch static mixer	0.21	3.8
Kenics static mixer	0.63	2.0
Trapezoidal baffles	0.38	6.6

Example 6-12 Design of static mixer to achieve specified degree of blending

A pilot plant is to be designed to add 30 mg/L of alum to a design flow of 5 L/min. The blend specification is that COV $\leq$ 5 percent. Estimate the length of a static mixer required for this degree of blending. Use a design velocity of $\leq$2 m/s. Assume that the mixing device inserts come in units 1.5 diameters in length and are available in diameters of 12.5 and 20 mm. Use a whole number of inserts to achieve a reasonable safety factor. Finally, estimate the length of time required for the water to achieve the required degree of blending and the head loss through the mixer.

Solution

1. Determine the mixer diameter using a design velocity $\leq$2 m/s:
   a. The area of the pipe is

   $$A_{pipe} = \frac{Q}{V}$$

   $$= \frac{(5 \text{ L/min}) \left(1 \text{ m}^3/1000 \text{ L}\right)}{(2 \text{ m/s}) (60 \text{ s/min})} = 4.17 \times 10^{-5} \text{ m}^2$$

   b. The corresponding pipe diameter is

   $$d_{pipe} = \sqrt{\frac{4A_{pipe}}{\pi}} = \sqrt{\frac{4 \times 4.17 \times 10^{-5} \text{ m}^2}{\pi}} = 0.0073 \text{ m} = 7.3 \text{ mm}$$

   A pipe diameter of 12.5 mm (0.5 in.) is about the minimum practical size to use in a pilot plant. Choose $D_{mixer} = 12.5$ mm.

2. Determine the number of mixer inserts:
   a. From Example 6-11, the value of the intensity of segregation $[I_s]_{mixer}$ is 1.15×10^{-7}. Thus, from Eq. 6-143,

   $$\left(\frac{\sigma_b}{\sigma_u}\right)_{mixer} = \sqrt{1.15 \times 10^{-7}} = 3.39 \times 10^{-4}$$

   Substituting into Eq. 6-158, yields

   $$3.39 \times 10^{-4} = (0.21)^{L/D} \quad \text{and} \quad \frac{L}{D} = 5.12$$

  b. According to the problem statement, these mixing devices come with standard length inserts of $L/D = 1.5$. One mixer insert will provide $L/D = 1.5$. Four will provide $L/D = 6$. Use four inserts.

3. Estimate blending time t_m to meet the blend requirement:
   a. The total length of the mixer is $4 \times 1.5 \times 0.0125 = 0.075$ m. The velocity v in the mixer will be

$$v = \frac{Q}{A} = \frac{(5 \text{ L/min})\left(1 \text{ m}^3/1000 \text{ L}\right)}{\left[\pi \times (0.0125 \text{ m})^2/4\right](60 \text{ s/min})} = 0.679 \text{ m/s}$$

   b. The blending time is

$$t_m = \frac{0.075 \text{ m}}{(0.679 \text{ m/s})} = 0.11 \text{ s}$$

4. Determine the total head loss:
   a. The velocity head is

$$\text{Velocity head} = \frac{v^2}{2g} = \frac{(0.679 \text{ m/s})^2}{2\,(9.8 \text{ m/s}^2)} = 0.0235 \text{ m}$$

   b. From Gray's data,

$$\left[N_{\text{VH}}\right]_{\text{AR}=1} = 3.8$$

   The total head loss is

$$\Delta H_L = 0.0235 \times 3.8 \times 6 = 0.54 \text{ m}$$

Comment

It seems practical to meet this blending specification with $t_b \sim 0.1$ s at the small scale of this pilot plant. Further analysis will show that using the same static mixer takes much more time and head loss at full scale.

Design of Blending for Process Control

Equation 6-158 along with the $(\sigma_b/\sigma_u)_{\text{AR}=1}$ value for flow in a straight pipe or channel can be used to estimate the blending requirements for process control. However, the value of $(\sigma_b/\sigma_u)_{\text{AR}=1}$ given above is an approximation, and field measurement can often provide a more accurate estimate. Likewise, field measurements of the blending being achieved in a channel can be used to evaluate alternatives for remediating control problems.

Example 6-13 Blending to achieve process control

In a large water treatment plant with a flow of 200 ML/d, hydrofluosilicic acid is added to the product water. The acid is added, with mixing, at the beginning of a 100-m (328-ft) channel and the fluoride residual is monitored 23 m (75 ft) downstream of the point of addition. Unfortunately, the COV of the fluoride signal at the monitoring point is unacceptably high for control purposes (25 percent). Estimate how far down the channel the sample point would have to be moved to meet a COV criterion of 5 percent. Also estimate the water travel time between the point of fluoride addition and the point of fluoride analysis. The hydrofluosilicic acid solution has a fluoride concentration of 220 g/L. *Hint:* It is possible to estimate $[I_s]_{mixer}$ by assuming that segregation will decline as the water flows down the channel as it would in a pipe. The channel has a depth of 3 m. The depth should be used as D in Eqs. 6-157 and 6-158. The width of the channel is also 3 m.

Solution

1. Using Eq. 6-142, the COV downstream of the old monitor ($COV_{old\ monitor}$) and the COV downstream of the new monitor ($COV_{new\ monitor}$) can be used to relate the standard deviation downstream of the old monitor ($\sigma_{old\ monitor}$) to the standard deviation downstream of the new monitor ($\sigma_{new\ monitor}$):

$$\frac{COV_{new\ monitor}}{COV_{old\ monitor}} = \frac{\left(\sigma_{new\ monitor}/\overline{C}\right) \times 100\%}{\left(\sigma_{old\ monitor}/\overline{C}\right) \times 100\%} = \frac{\sigma_{new\ monitor}}{\sigma_{old\ monitor}}$$

Thus

$$\frac{\sigma_{new\ monitor}}{\sigma_{old\ monitor}} = \frac{COV_{new\ monitor}}{COV_{old\ monitor}} = \frac{5\%}{25\%} = 0.2$$

2. Estimate the required length L:
   a. Estimate the L/D value using Eq. 6-158:

$$\left(\frac{\sigma_b}{\sigma_u}\right)_{AR=L/D} = \left(\frac{\sigma_b}{\sigma_u}\right)_{AR=1}^{L/D}$$

$$\left(\frac{\sigma_b}{\sigma_u}\right)_{AR=L/D} = \frac{\sigma_{new\ monitor}}{\sigma_{old\ monitor}} = 0.2$$

$$0.2 = \left(\frac{\sigma_b}{\sigma_u}\right)_{AR=1} = 0.95^{L/D}$$

Taking the logarithm of both sides and rearranging,

$$\frac{L}{D} = \frac{-0.699}{-0.0223} = 31.4$$

b. The required length L is

$$L = 31.4 \times 3 = 94 \text{ m}$$

Thus, the sampling point will have to be moved 71 m (94 − 23) downstream from the current monitoring point.

3. Estimate the water travel time, t_b:
   a. Estimate the velocity in the channel:

$$v = \frac{Q}{A} = \frac{(200 \text{ ML/d})\left(1 \text{ m}^3/1000 \text{ L}\right)\left(10^6 \text{ L/1 ML}\right)}{3 \text{ m} \times 3 \text{ m}}$$

$$= 2.2 \times 10^4 \text{ m/d} = 15.4 \text{ m/min}$$

   b. The blending time is

$$t_b = \frac{L}{v} = \frac{0.94 \text{ m}}{15.4 \text{ m/min}} = 6.1 \text{ min}$$

Problems and Discussion Topics

6-1   Derive the solution to mass balance equations for the second- and nth-order reactions occurring in a CMBR.

6-2   A second-order irreversible elementary reaction 2A → products is carried out in a batch reactor. For a certain set of conditions, it is found that it took 20 min for a reaction to reach 60 percent completion. What would be the time required to reach the same degree of completion if (a) the initial concentration of A were doubled and (b) the reaction rate constant were doubled?

6-3   A first-order reaction A → products is to be carried out in a CMFR. The reaction rate constant was determined to be 1.0 h^{-1}. What is the residence time required for 90 percent conversion of the reactant provided there are no changes in temperature and density of the system?

6-4   A given reactant decomposes in water with a second-order rate constant of $k = 0.43 \text{ L/mol} \cdot \text{s}$. If a feed stream with an initial concentration of 1.0 mol/L is passed through a CMFR at the rate of $0.1 \text{ m}^3/\text{s}$, what will be the reactor volume required for 90 percent decomposition of the reactant?

6-5   If two CMFRs in series each having one-half the volume calculated in Problem 6-4 were used, what would be the resulting percent decomposition of the reactant?

6-6   Derive and solve the differential equation that can be used to describe the effluent concentration leaving a CMFR for a first-order reaction. Assume $C_0^* = C_0$.

6-7   Rearrange the solution obtained in Problem 6-6 and solve for the time (expressed as multiples of the hydraulic detention time) required after startup such that the effluent concentration is within 1 percent of the steady-state value C_∞:

$$\frac{C - C_\infty}{C_0} \leq 0.01$$

Plot the time required to achieve the above criteria versus the ratio of the steady-state concentration to the influent concentration. Is there a maximum time?

6-8   A reaction follows the rate expression of $r = -kC^{1.5}$. The feed concentration is 1 mol/L and the reaction rate constant k was determined to be 1.0 $(L/mol)^{1/2}/h$. For a flow rate of 100 L/h, compute the volume requirement for a CMBR at 95 percent conversion if the down time for the CMBR is 1 h between batches? What is the volume requirement for a CMFR at 95 percent conversion? What is the volume requirement for a PFR at 95 percent conversion?

6-9   If A → products follows a second-order reaction mechanism, what is the volume requirement for a CMFR as compared to a PFR for 95 percent conversion of A? How could the volume efficiency be improved?

6-10 Because of the ease of construction and operation of a CMFR, its use is sometimes preferred over a PFR. For the following conditions, indicate the preferred reactor (PFR or CMFR), where an additional CMFR volume requirement of 25 percent is acceptable. Justify each answer by computing the volume requirements for the CMFR and PFR under each condition presented in the table below.

Reaction Order	Degree of Completion of Reaction, %	PFR	CMFR
2	99		
1	99		
0	99		
0	10		
1	10		

Reaction Order	Degree of Completion of Reaction, %	PFR	CMFR
2	10		
0	40		
1	40		
2	40		
$\frac{1}{3}$	40		

6-11   Explain graphically using a plot of $-1/r$ versus concentration of reactants as a function of time why the PFR is more efficient in terms of volume requirements than the CMFR when the order of the reaction is greater than zero. Also show graphically why a large number of equal-volume CMFRs connected in series can achieve the same volume efficiency as a PFR.

6-12   The following kinetic data were obtained to determine the order of reaction with respect to one reactant. Determine the reaction order that yields the best fit and estimate the rate constant for the reaction.

Time, min	Concentration, mg/L
0	40.00
1	31.50
2	21.50
3	17.85
4	12.16
5	10.08
6	6.84
7	5.25
8	4.30
9	2.95
10	2.42

6-13   The reaction A → B is autocatalytic (i.e., the product itself is also participating in the reaction), yielding a rate expression of the form

$$r_A\,(\text{mol/L} \cdot \text{min}) = -kC_A C_B \qquad k = 0.05 \text{ L/mol} \cdot \text{min}$$

a. Calculate the residence time required in a CMFR at steady state to achieve 80 percent conversion of A when the feed concentration of A and B are 2 mol/L and 0.05 mol/L.

b. Because the reaction follows second-order kinetics, a PFR should in theory yield a lower residence time and thus require a smaller reactor volume than a CMFR. Is a PFR preferred over a CMFR for the case of an autocatalytic reaction? State clearly the reasons for either recommending or not recommending a PFR, based

on a plot of $-1/r_A$ versus concentration. What combination of reactors will result in the smallest volume?

6-14 Derive the exit age distribution for n reactors (tanks) in series.

6-15 Calculate the effluent concentration C using the DFM for a second-order reaction in the case of a closed reactor. Assume Pe = 0.4, $\tau = 10$ min, $k = 0.05$ L/mg $\cdot$ min, and $C_0 = 2000$ mg/L.

6-16 Consider a PFR in which the conversion (extent of reaction) is 99.5 percent for a first-order reaction.
  a. What would be the conversion in a completely mixed flow reactor of the same volume?
  b. What would be the conversion in that reactor if the dispersion number $E/vL = 1$?
  c. What would the conversion be if the length was doubled but the residence time remained the same? (Assume E is the same as the original.)
  d. What would the conversion be if the length was halved and the residence time remained the same? (Assume E is the same as the original reactor.)
  e. Suppose it is desired to obtain 95 percent conversion in this nonideal reactor system with $E/vL = 1$. How many times larger than the volume of a PFR would be needed in the real reactor?

6-17 Rework Problem 6-16 for second-order kinetics.

6-18 Derive the expression to obtain the effluent concentration for n reactors (tanks) in series for a second-order reaction.

6-19 The following concentration data expressed in mg/L were obtained from tracer studies conducted on five different reactors. For a given reactor (to be selected by the instructor), plot the tracer curve, the normalized RTD curve, and the cumulative RTD curve.

Time, min	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Reactor 5
0	0	0	0	0	0
10	0	2	0	0	0
20	1	5.4	0	0	0
30	2	8.4	0.1	0	0
40	5.1	11.4	0.2	0	0
50	8.9	13	0.5	0	2
60	11.2	12.1	6.3	0	6.2
70	10.5	9.3	15.2	4.5	13
80	9.2	7.2	18.1	9	10.4
90	8	5.2	8.5	14.1	5.1
100	6.5	3.6	3.2	15.6	2.8
110	5	2.5	1.8	12.9	1.1
120	3.5	1.4	1.2	9.2	0.5

Time, min	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Reactor 5
130	2	0.9	0.8	5.3	0.4
140	1.4	0.4	0.6	2.3	0.1
150	0.8	0.1	0.3	1.1	0
160	0.4	0	0.2	0.8	0
170	0.2	0	0.2	0.5	0
180	0	0	0.1	0.2	0
190	0	0	0	0.1	0
200	0	0	0	0	0

6-20   Using the data provided in Problem 6-19, compute the dispersion number, Peclet number, and equivalent number of tanks in series for the selected reactor (to be selected by the instructor). Plot the results of the single-parameter model and compare to the actual data.

6-21   Using the tracer data (to be selected by the instructor) provided in Problem 6-19, calculate the expected effluent concentration using the TIS model assuming a first-order reaction rate constant $k = 0.2$ min^{-1}.

6-22   Using the tracer study results given in Problem 6-19 (reactor data to be selected by the instructor), determine the expected effluent concentration using the SFM. Assume a first-order reaction with the rate constant $k = 0.2$ min^{-1}.

6-23   For a reaction A $\rightarrow$ P, $C_0 = 100$ mg/L:

a. Calculate the rate constants for first- and second-order kinetics assuming a PFR with the same detention time calculated in Problem 6-19 and an effluent concentration $C = 0.5$ mg/L.

b. Using figures developed for the DFM, calculate the expected effluent concentrations for first- and second-order kinetics. Use the rate constants determined in (a) above and the Pe number determined in Problem 6-20.

c. Calculate the expected effluent concentration for first- and second-order kinetics using the TIS model. Use the rate constants determined in (a) above and the tank number determined in Problem 6-20.

d. Calculate the expected effluent concentration at steady state for the SFM using second-order kinetics and the rate constants in (a) above.

6-24   Consider an open channel with the following characteristics: (a) depth = width = 2 m, (b) depth = width = 2.5 m, and (c) depth = width = 3 m. The flow rate is 4 m^3/s and the detention time is 60 s. If a first-order irreversible reaction is occurring with a rate constant equal to 0.1 s^{-1}, determine the expected effluent concentration C/C_0 for the various channel widths. Comment on the impact of

increasing the aspect ratio on reactor performance. Use Eq. 6-113 to estimate the dispersion factor. Assume the kinematic viscosity of water is 1.003×10^{-6} m^2/s.

6-25   For a reactor with a length of 25 m, depth of 3.5 m, flow rate of 2.5 m^3/min, and width of 2, 3, 4, or 5 m (to be selected by the instructor), estimate the dispersion number, hydraulic detention time, and θ_{10} value. Assume the kinematic viscosity of water is 1.003×10^{-6} m^2/s.

6-26   Using the following dose–response data for a particular microorganism found in a water supply, apply the SFM to the reactor from Problem 6-19 (to be selected by the instructor) to estimate the effluent concentration:

Exposure Time, min	Number of Organisms Remaining, No./100 mL
0	100,000
10	10,000
20	1,000
30	100
40	10
50	1
60	0.1
70	0.01
80	0.001
90	0.0001

6-27   A treatment plant has been designed with the capability to add hydrofluosilicic acid. The mixer installed at the point of chemical addition is warranted to achieve a COV of ≤ 5 percent across the cross section of flow at the point where the automatic analyzer draws samples for analysis. In a performance test during plant startup (commissioning) samples were taken at nine representative points across the cross section and the results are reported below. Determine if the mixer is meeting its specification.

Sample Point	Fluoride, mg/L
1	1.02
2	1.20
3	0.95
4	0.90
5	1.10
6	0.85
7	0.95
8	0.98
9	0.95

6-28 A water treatment plant is to be designed to add 30 mg/L of alum that has a strength of 651 g/L to a design flow of 50 ML/min. The blend specification is for a COV value of ≤ 5 percent. Estimate the length of a Koch static mixer required for this application. Use a design velocity of 2 m/s. Assume that the mixer inserts come in units 1.5 diameters in length and are available in diameters of 12.5 and 20 mm. Use a whole number of inserts to achieve a reasonable safety factor. Finally, estimate the length of time required for the water to achieve the mixing and the head loss through the mixer.

6-29 Derive Eq. 6-146 for σ_u, the standard deviation of the volume fraction of two unmixed streams. *Hint 1:* Assume that 1000 samples are taken at random from the two streams and calculate the standard deviation of each. *Hint 2:* Samples drawn from Q_a will have a volume fraction equal to 1, whereas samples drawn from Q_w will have a volume fraction of Q_a equal to 0.

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