Updated: 28 September 2019

Print version

CEE 370
Environmental Engineering Principles

Lecture #9

Material Balances I

Reading: Mihelcic & Zimmerman, Chapter 4

Davis & Masten, Chapter 4

9/25/19

- Gazette

gazettenet.com

NATION/WORLD

Zimbabwe's capital runs dry

Authorities shut down municipal water for 2 milion people

By **FARAI MUTSAKA**
Associated Press

HARARE, Zimbabwe — Tempers flared on Tuesday as more than 2 million residents of Zimbabwe's capital and surrounding towns found themselves without water after authorities shut down the main treatment plant, raising new fears about disease after a cholera outbreak while the economy crumbles even more.

Officials in Harare have struggled to raise foreign currency to import water treatment chemicals; about $2.7 million is needed per month. Meanwhile, water levels in polluted reservoirs are dropping because of drought.

For residents who have seen shortages of everything from medicines to bread to petrol in recent months, the latest indignity brought weariness and disgust.

"The toilets at school are just too filthy, people continue using them yet there is no water," said 12-year-old Dylan Kaitano, who was among many uniformed school children waiting in line at wells, some shoving in impatience. "I didn't go to school today because I have to be here."

Everyone living in Harare is affected, City Council spokesman Michael Chideme said, as residents turned to other options such as bottled water. He called it a dangerous situation because of the risk of water-borne diseases.

"It is a desperate situation," Deputy Mayor Enock Mupamaonde told The Associated Press outside the closed treatment plant. And more people are affected than thought, he said, estimating that another 2 million non-residents enter the city each day to use its services and conduct business.

At the Chivero reservoir, the city's main water supply, plastic bottles, vehicle tires and algae floated in the shallow water which was green and emitted a choking, foul smell.

Zimbabwe's capital now frequently records cases of diseases such as typhoid due to water shortages and dilapidated sewer infrastructure. Some residents for months have been forced to get water from shallow, unsafe wells and defecate in the open, while children pick their way across fetid yards.

The AP earlier this month watched some residents pump water then wait a half-hour for enough water to seep into a well to pump again.

"We are suffering," said Gladys Mupemhi, a resident of the low-income Kuwadzana suburb who said some people woke up at 4 a.m. on Tuesday to wait for hours in line. "We are only allowed a maximum of 20 liters of water per person, what can I do with 20 liters?"

Claudius Madondo, chairman of the residents association controlling the line, said nearby wells were no longer functioning, forcing the rationing. Some of the people waiting heckled him.

"Nothing is working in this country, how do we survive?" Hatineyi Kamwanda, another resident, said. "We can't even use the toilets, the children are not going to school because of this and now we fear cholera is going to hit us again.

"The president should treat us as human beings, we voted for him."

Twenty-six people died last year in a cholera outbreak, leading President Emmerson Mnangagwa to express dismay that Zimbabweans were suffering from a "medieval" disease.

The economic and social pressures follow Mnangagwa as he attends the annual United Nations gathering of world leaders this week.

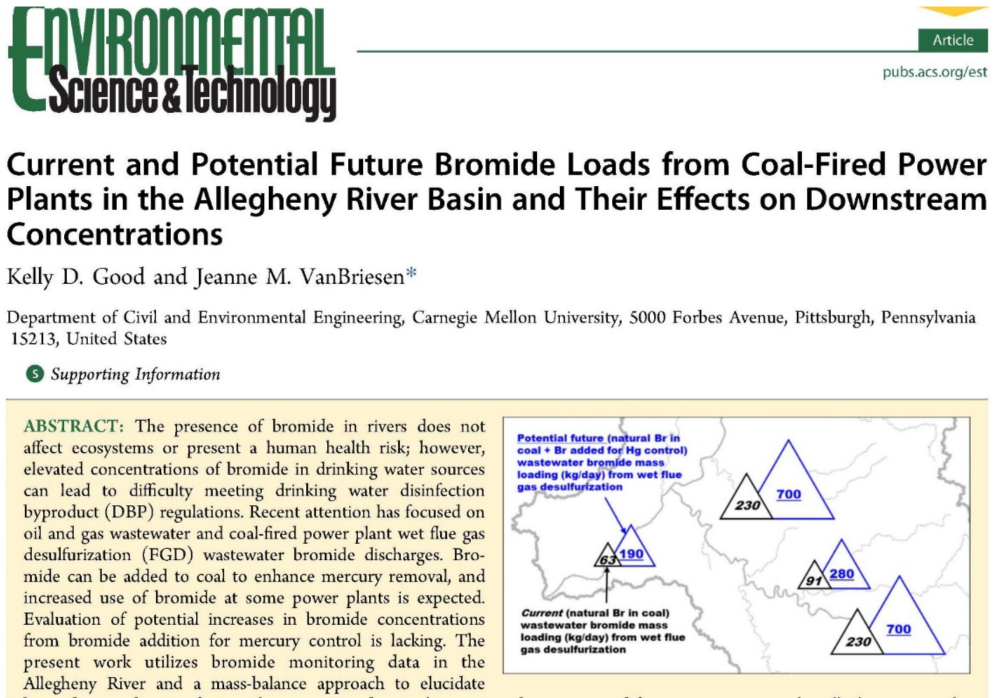
Zimbabwe once was a bright spot in southern Africa and a regional breadbasket but the economy has collapsed in recent years, and foreign currency is hard to come by. Prices for many basic items continue to rise, and the public health care system falters as some doctors and others say they can hardly afford the commute to work.

AP PHOTO

A woman heads home after fetching water at a borehole in Harare, Zimbabwe, Tuesday.

Pittsburgh Problem

- Bromide?



Environmental Science & Technology

Article

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Current and Potential Future Bromide Loads from Coal-Fired Power Plants in the Allegheny River Basin and Their Effects on Downstream Concentrations

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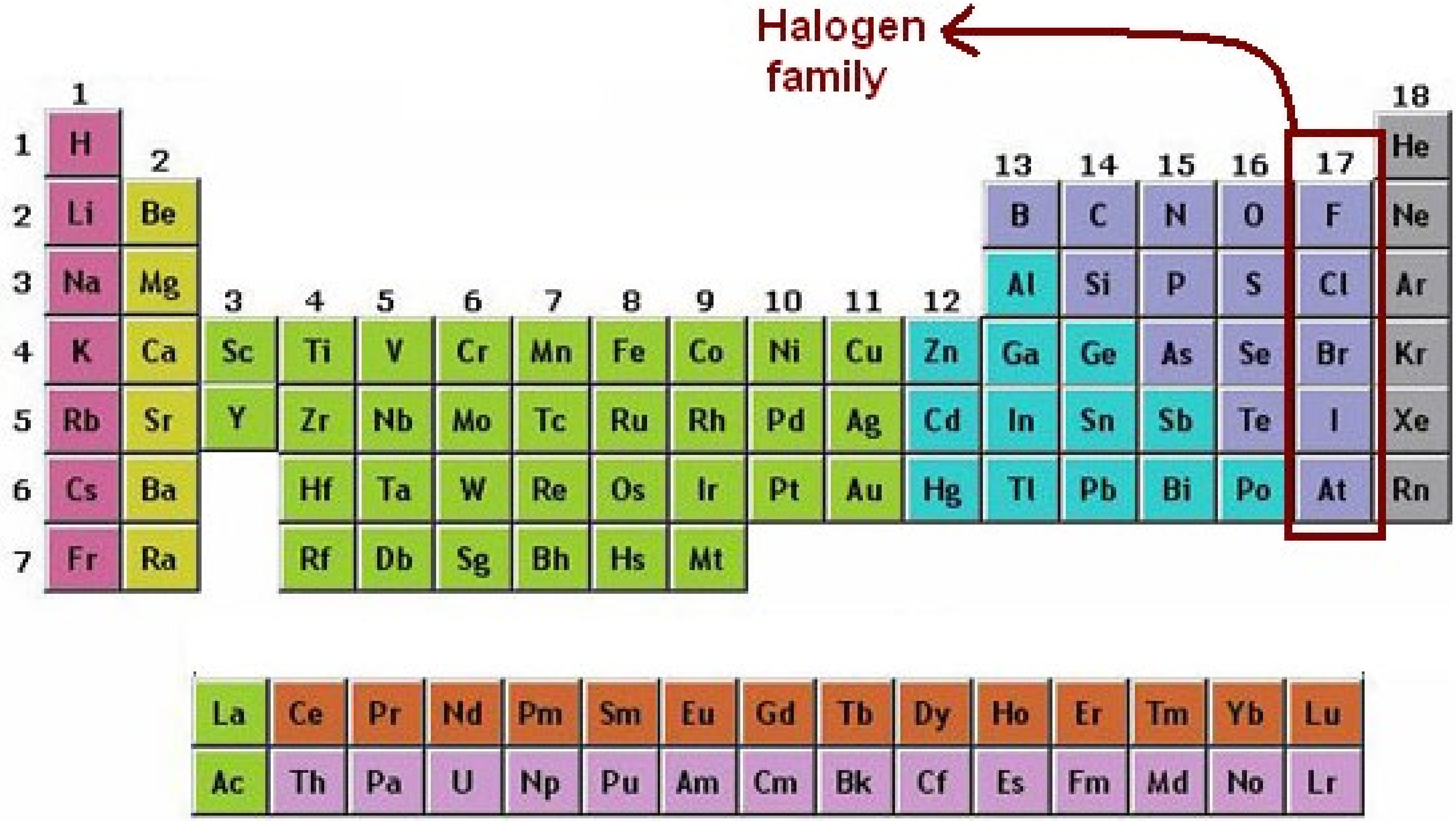
Ⓢ *Supporting Information*

ABSTRACT: The presence of bromide in rivers does not affect ecosystems or present a human health risk; however, elevated concentrations of bromide in drinking water sources can lead to difficulty meeting drinking water disinfection byproduct (DBP) regulations. Recent attention has focused on oil and gas wastewater and coal-fired power plant wet flue gas desulfurization (FGD) wastewater bromide discharges. Bromide can be added to coal to enhance mercury removal, and increased use of bromide at some power plants is expected. Evaluation of potential increases in bromide concentrations from bromide addition for mercury control is lacking. The present work utilizes bromide monitoring data in the Allegheny River and a mass-balance approach to elucidate

Why Bromide?

- Brominated DBPs



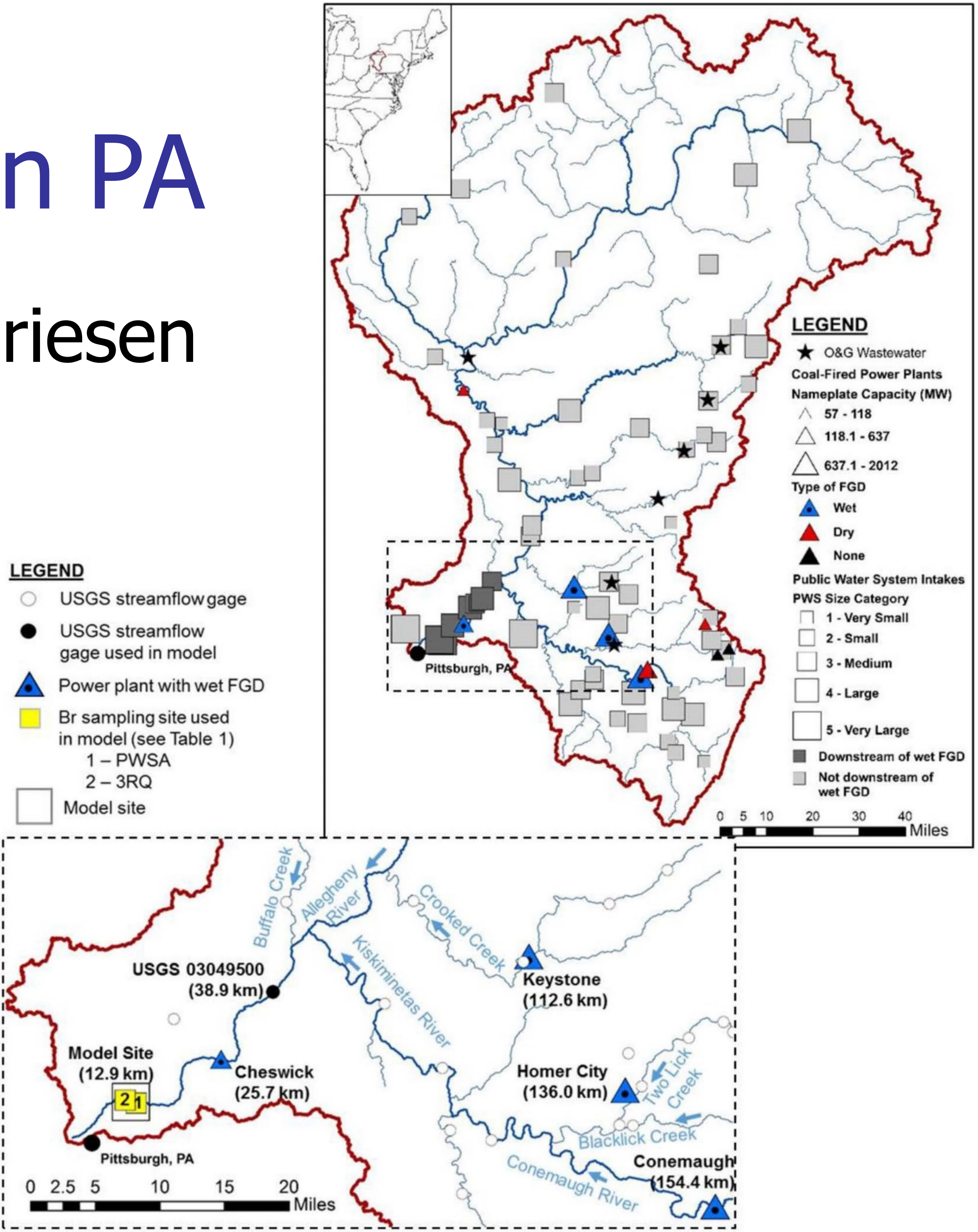
Halogen family

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt									

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Bromide in PA

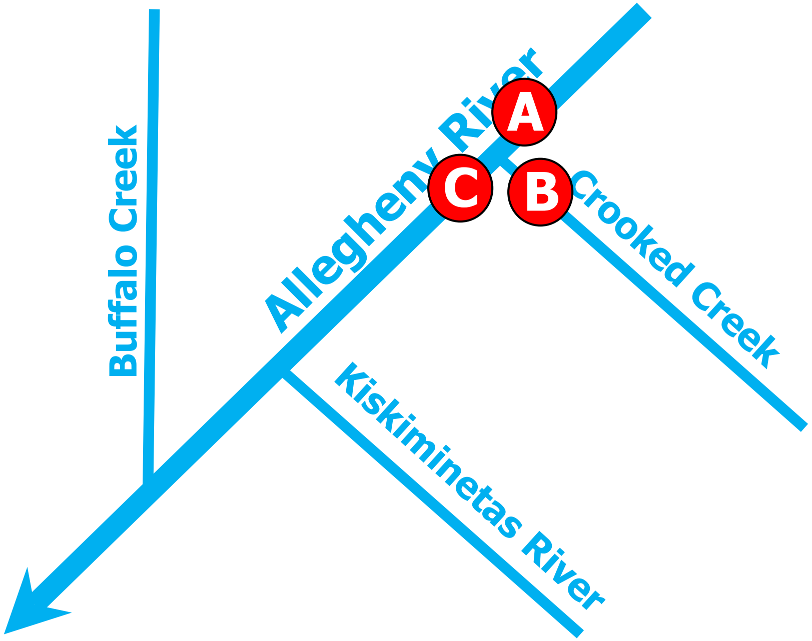
- Good & VanBriesen Publication



Downstream Bromide Levels

- Crooked Creek & Allegheny

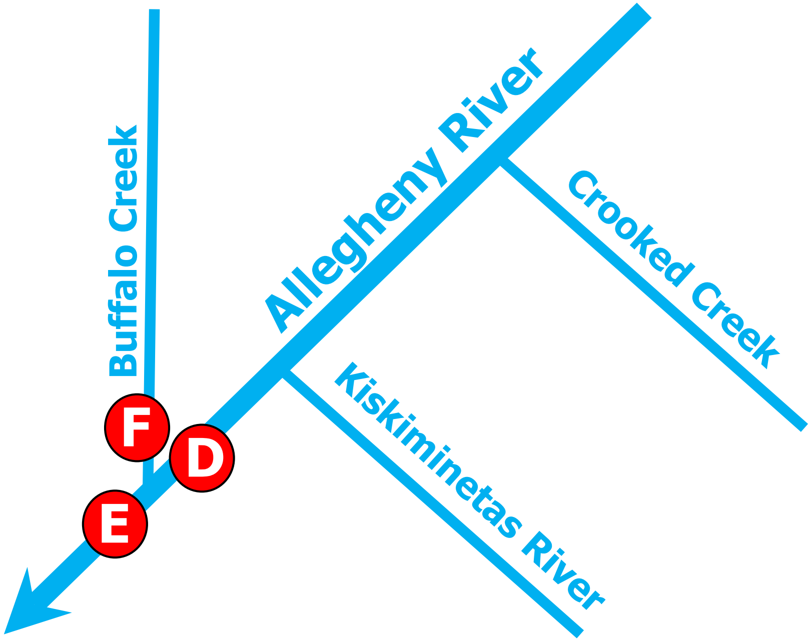
Location	**Q (m^3/s)**	**Br^- (µg/L)**
A	1000	5
B	100	200
C		



Upstream Bromide Levels

- Buffalo Creek contribution

Location	Q (m^3/s)	Br^- ($\mu g/L$)
D	1200	20
E	1400	80
F		



Basics

- Types of material balances
  - Mass Balance
    - Law of conservation of matter
  - Energy Balance
    - Law of conservation of energy
- General Approach
  - Define a control volume
  - Within that volume
    - Accumulation = Input – Output
    - Rate of Accumulation = Rate of Input – Rate of Output

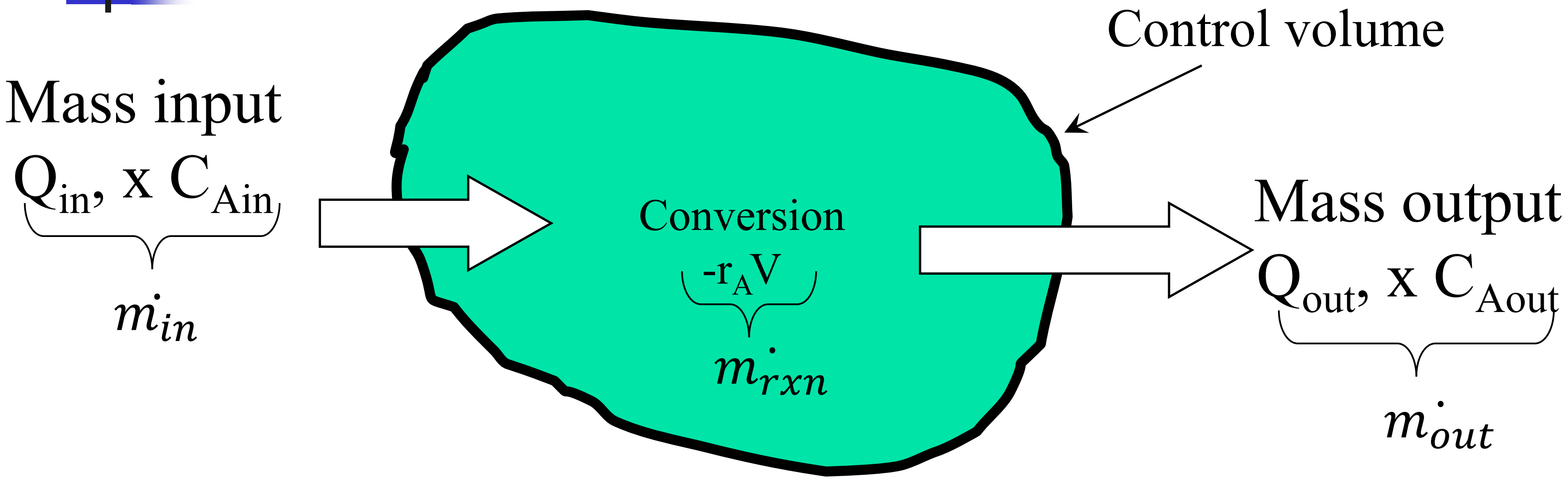
Mass Flux

- Rate of input/output
- Flux In: Flow entering a control volume

$$m_{in} = Q_{in} C_{in}$$

$$\left[\frac{mass}{time}\right] = \left[\frac{volume}{time}\right] x \left[\frac{mass}{volume}\right]$$

Mass Balances



System boundary
or
Control volume

Mass input

$$\underbrace{Q_{in},\ x\ C_{Ain}}_{\dot{m}_{in}}$$

Conversion

$$\underbrace{-r_A V}_{\dot{m}_{rxn}}$$

Mass output

$$\underbrace{Q_{out},\ x\ C_{Aout}}_{\dot{m}_{out}}$$

$$\left[\begin{matrix}\textbf{Accumulation}\\ \textbf{rate}\end{matrix}\right]_i = \left[\begin{matrix}\textbf{Input}\\ \textbf{rate}\end{matrix}\right]_i - \left[\begin{matrix}\textbf{Output}\\ \textbf{rate}\end{matrix}\right]_i - \left[\begin{matrix}\textbf{Conversion}\\ \textbf{rate}\end{matrix}\right]_i$$

$$\frac{dM}{dt} = \frac{d(VC)}{dt}$$

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

Mass Balances (cont.)

$$\frac{dM_A}{dt} = \sum_{i=1}^{n} (C_A Q)_{in} - \sum_{j=1}^{n} (C_A Q)_{out} - r_A V$$

where,

M_A = mass of a, [mass]

C_{Ain} = concentration of species A entering the system, [mass/volume]

C_{Aout} = concentration of species A leaving the system, [mass/volume]

Q_{in} = volumetric flow rate bulk mass entering the system, [volume/time]

Q_{out} = volumetric flow rate of bulk mass leaving the system, [volume/time]

r_A = reaction rate of species “A” forming something else, [mass/volume-time]

V = volume of reactor

And for a reaction of order “n”, $r_A = kC_A^n$

Mass Balances (cont.)

For systems at **steady state** with no accumulation, the time dependent term goes to zero and the equation reduces to:

$$\frac{dM_A}{dt} = 0 = \sum_{i=1}^{n} (C_A Q)_{in} - \sum_{i=1}^{n} (C_A Q)_{out} - r_A V$$

$$r_A V = \sum_{i=1}^{n} (C_A Q)_{in} - \sum_{i=1}^{n} (C_A Q)_{out}$$

Look at Example 4.1

Mass Balances (cont.)

Conservative substances are those that do not react. For these the value of r_A is zero and the mass balance equation reduces to:

$$\frac{dM_A}{dt} = \sum_{i=1}^{n} (C_A Q)_{in} - \sum_{i=1}^{n} (C_A Q)_{out}$$

And if the conservative substance is as steady state, the MB is even simpler:

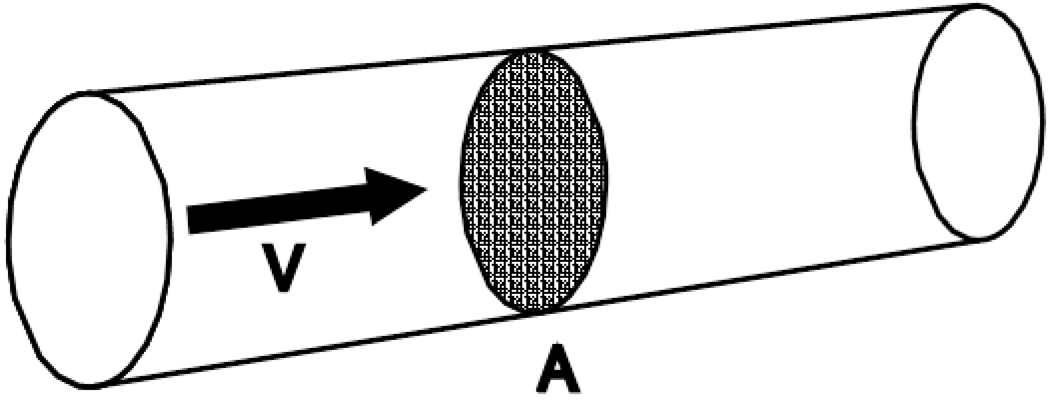
$$\sum_{i=1}^{n} (C_A Q)_{in} = \sum_{i=1}^{n} (C_A Q)_{out}$$

Analysis of Treatment Processes

- Basic Fluid Principles
  - Volumetric Flow Rate
  - Hydraulic Retention Time
- Conversion
- Mass Balances
- Reaction Kinetics and Reactor Design
  - Chemical Reaction Rates
  - Reactor Design
- Sedimentation Principles

Basic Fluid Principles

Volumetric Flow Rate



$$Q = Av$$

where,

Q = volumetric flow rate, [m^3/day, ft^3/s]
A = area across which the fluid passes, [m^2, ft^2]
v = fluid velocity, [m/d, ft/s]

Fluid Principles cont.

Hydraulic Retention Time

$$\mathbf{HRT = \theta = \frac{V}{Q}}$$

where,

θ = hydraulic retention time, [days]

V = volume, [m^3]

Q = volumetric flow rate, [m^3/day]

Work out Example 7.1

Flux Density

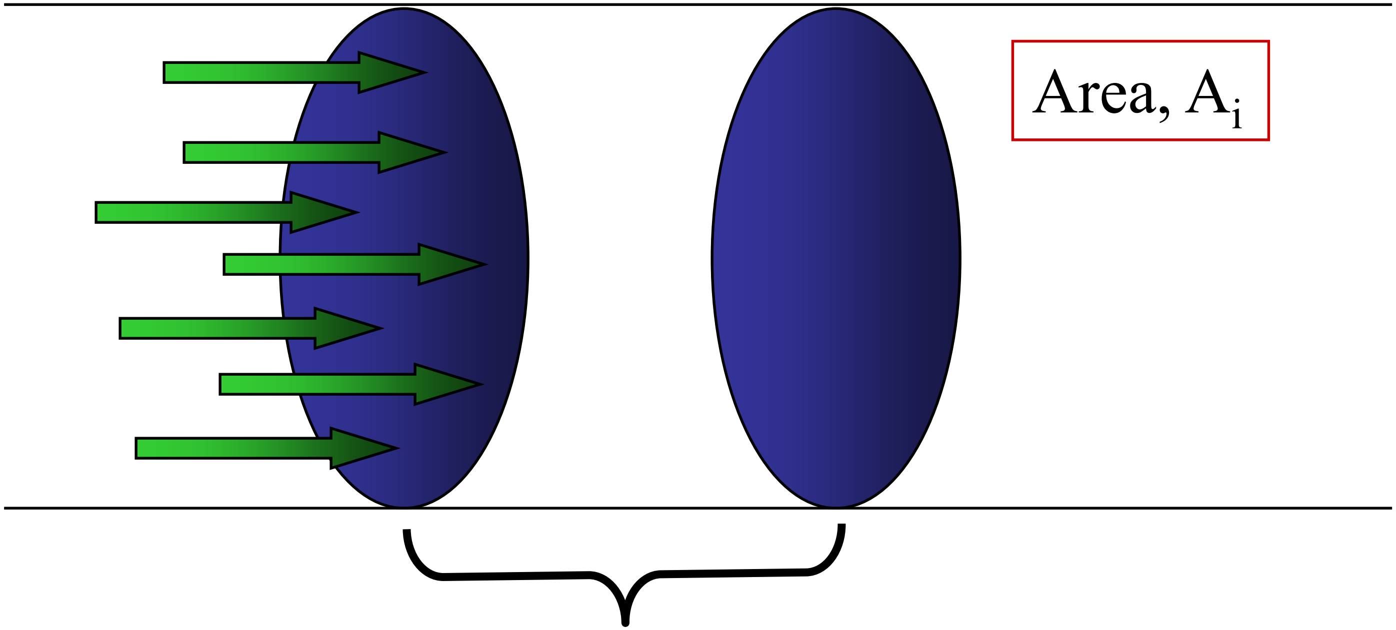
Flux is the movement of a mass past a surface, plane, or boundary.

$$J_i = \frac{M_i}{A_i \bullet t}$$

where,

J_i = flux density crossing the boundary i, [Kg/m^2-hr]
M_i = mass crossing the boundary i in time t, [Kg]
A_i = area of boundary i, [m]
t = time for the mass to cross the boundary i, [hr]

Flux (cont.)



Velocity, V_i

Area, A_i

Length L

If the right side of the above equation is multiplied by L/L, where L is the distance the approaching mass moves during time t, then the equation becomes:

Flux (cont.)

$$J_i = \frac{M_i}{A_i \, x \, t} \, x \, \frac{L}{L} = \frac{M_i}{A_i \, x \, L} \, x \, \frac{L}{t}$$

$$J_i = C_i V_i$$

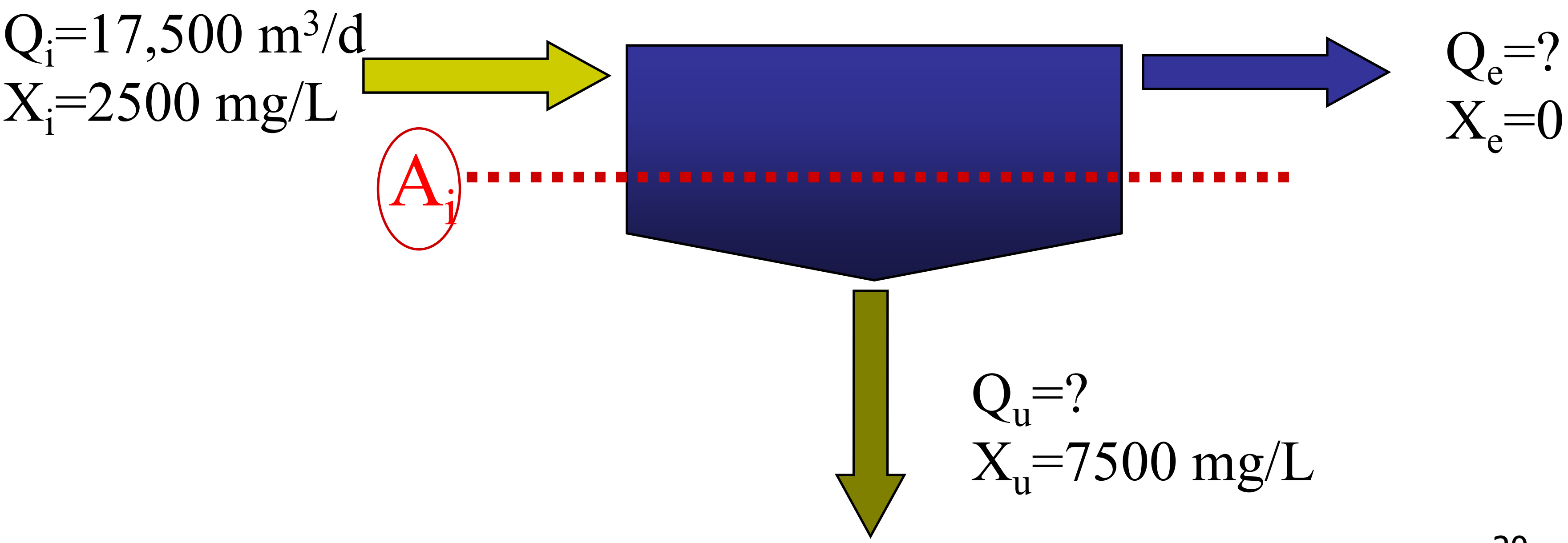
where,

C_i = the concentration of the material crossing the boundary i, [Kg/m^3]

V_i = the velocity of the material crossing the boundary i, [m/hr]

Clarifier Example

A 25 m diameter secondary clarifier has an influent solids concentration of 2500 mg TSS/L. The flowrate into the clarifier is 17,500 m^3/day. If the effluent solids are assumed to be zero, what return or recycle flow rate is required to attain a return solids concentration of 7500 mg TSS/L. Also, what is the solids flux across the boundary shown below.



Q_i=17,500 m^3/d
X_i=2500 mg/L

A_i

Q_e=?
X_e=0

Q_u=?
X_u=7500 mg/L

Clarifier example (cont.)

We can perform a mass balance to determine the underflow or recycle solids concentration, X_u. Assuming no accumulation in the sedimentation tank,

Mass in = Mass out

or

$$X_i Q_i = X_e Q_e + X_u Q_u$$

Since X_e is assumed to be zero,

$$Q_u = \frac{X_i Q_i}{X_u} = \frac{(2500 \text{ mg TSS/L})(17{,}500 \text{ m}^3/\text{d})}{7500 \text{ mg TSS/L}}$$

Clarifier example (cont.)

$$Q_u = 5{,}800 \ m^3/day$$

To determine the flux across A_i, we need the mass moving across i per day, or, $M_i = X_i V$

where V is the volume applied per time. If we choose one day for t, then, V is 17,500 m^3. Thus, the mass is,

$$M_i = (2500 \ mg\ TSS/L) \ x\ (17{,}500 \ m^3) \ x \ \frac{Kg}{10^6 \ mg} \ x \ \frac{10^3 \ L}{m^3} = 44{,}000 \ Kg$$

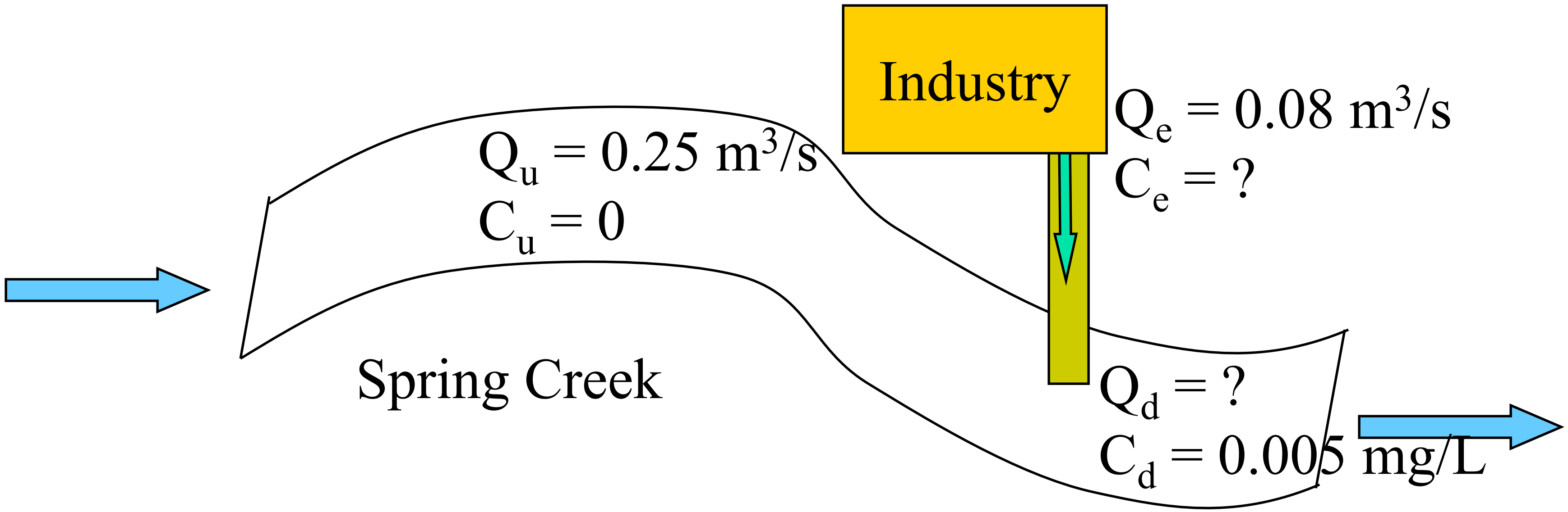
And the flux is:

$$J_i = \frac{43{,}750 \ Kg}{(\pi \ x \ (25 \ m/2)^2) \ x \ (1 \ day)}$$

$$J_i = 89 \ Kg/m^2\text{-}day = 3.7 \ Kg/m^2\text{-}hr$$

River Example

An industry is located adjacent to Spring Creek. The industry uses copper cyanide for plating both copper and brass. Estimate the maximum concentration of copper that can be discharged in the effluent in order to meet the required maximum concentration, C_d, of 0.005 mg Cu^{2+}/L in the stream. The upstream copper concentration is below the detection limit, i.e. C_u = 0 mg/L. Assume steady state conditions.



Solution to River Ex.

We first use a mass balance on the flow into and out of the system. The flow after discharge can be calculated by a mass balance on the water entering and leaving the system (the concentration of water in water is unity, and thus cancels):

$$Q_d = Q_u + Q_e$$

where the "e" subscript indicates effluent, the "u" subscript indicates up-stream, and the "d" subscript indicates down-stream.

$$Q_d = 0.25 \ m^3/\mathrm{sec} + 0.08 \ m^3/\mathrm{sec} = 0.33 \ m^3/\mathrm{sec}$$

Solution to River Ex. (cont.)

The allowable concentration of copper in the effluent can then be determined by a mass balance on copper entering and leaving the system:

$$\mathbf{Q_u C_u + Q_e C_e = Q_d C_d}$$

Solving for C_e (two equations and two unknowns):

$$C_e = \frac{Q_d C_d - Q_u C_u}{Q_e}$$

$$C_e = \frac{0.33\, {}^{m^3}\!/\!_s\; 0.005\, {}^{mg}\!/\!_L + 0.25\, {}^{m^3}\!/\!_s\; 0\, {}^{mg}\!/\!_L}{0.08\, {}^{m^3}\!/\!_L}$$

$$\mathbf{C_e = 0.021\ mg/L}$$

Reactor Kinetics

- Batch Reactors
    - Pg 129
- Continuous Flow
  - Completely Mixed (CMFR)
    - Pg 122-129
  - Plug Flow (PFR)
    - Pg 130-131
  - Mixed Flow (non-ideal)

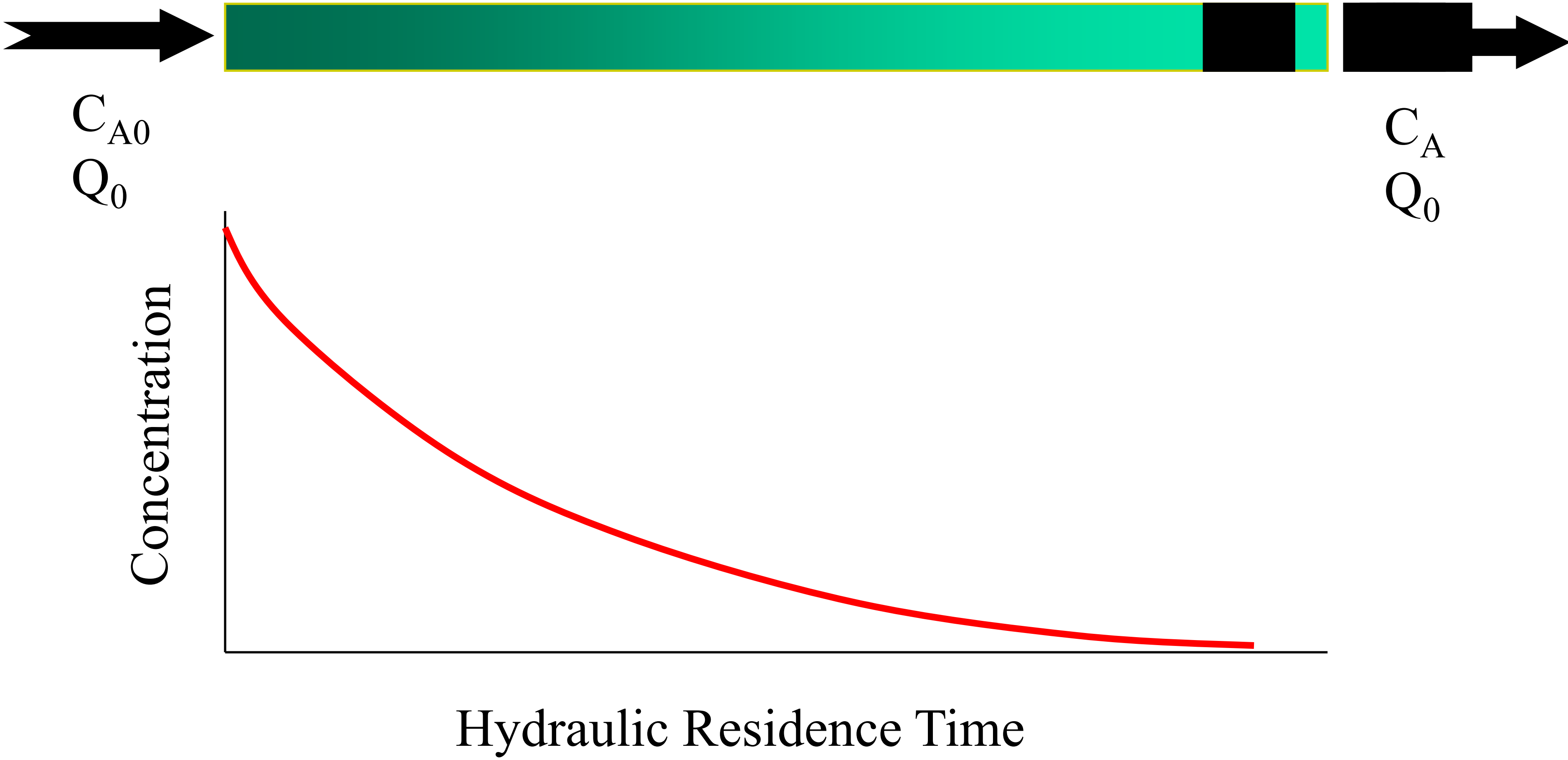
Reactor Question

- Which type of reactor is more effective?
  - A. Plug Flow Reactor (PFR)
  - B. Completely Mixed Flow Reactor (CMFR)
  - C. Batch Reactor (BR)
  - D. Depends on the reaction order
  - E. Both PFR and BR

Plug Flow Reactors

- Like laminar flow through a pipe
- Examples
  - Long, narrow Rivers
  - Packed tower biofilters
  - Drinking water distribution pipes

Plug Flow Reactors



PFR's (cont.)

- Minimal or no axial or longitudinal mixing
- As a slice of fluid progresses through the reactor, the reactants are converted to products. The reaction in the slice of fluid is analogous to the reaction in a batch reactor. The difference is that the fluid in this case is actually flowing through the reactor. The hydraulic residence time, θ, is the amount of time it takes the slice of fluid travel completely through the PFR. Thus, the mass balance equation for the PFR is:

$$\begin{bmatrix}\textbf{Accumulation}\\\textbf{rate}\end{bmatrix}_i = \begin{bmatrix}\textbf{Input}\\\textbf{rate}\end{bmatrix}_i - \begin{bmatrix}\textbf{Output}\\\textbf{rate}\end{bmatrix}_i - \begin{bmatrix}\textbf{Conversion}\\\textbf{rate}\end{bmatrix}_i$$

Input and output are set to zero because nothing crosses the boundaries of the slug of water as it moves along the reactor

$$\frac{dM_A}{dt} \equiv V\frac{dC_A}{dt} = 0 - 0 - r_A V$$
$$= -kC_A V$$

$$\frac{dC}{dt} = -kC_A$$
$$C_A = C_{A_O} e^{-kt}$$

$$C_A = C_{A_O} e^{-k\theta}$$

Fluid Principles cont.

Hydraulic Retention Time

$$\mathbf{HRT} = \theta = \frac{\mathbf{V}}{\mathbf{Q}}$$

where,

θ = hydraulic retention time, [days]

V = volume, [m^3] of reactor or reactor segment

Q = volumetric flow rate, [m^3/day]

And so it becomes:

$$\frac{C_A}{C_{Ao}} = e^{-kV/Q}$$

or:

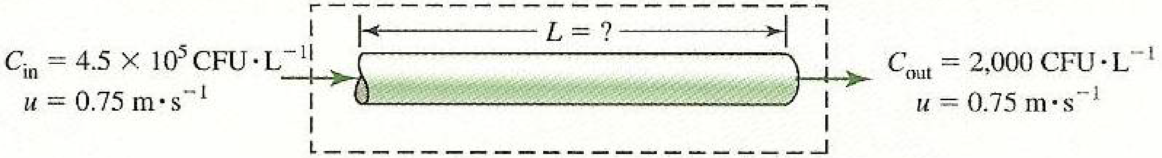
$$\ln\left(\frac{C_A}{C_{Ao}}\right) = -k\frac{V}{Q} = -k\frac{L}{u}$$

PFR Example

- Disinfection (example)

A wastewater treatment plant must disinfect its effluent before discharging the wastewater to a near-by stream. The wastewater contains 4.5×10^5 fecal coliform colony-forming units (CFU) per liter. The maximum permissible fecal coliform concentration that may be discharged is 2000 fecal coliform $\text{CFU} \cdot \text{L}^{-1}$. It is proposed that a pipe carrying the wastewater be used for disinfection process. Determine the length of pipe required if the linear velocity of the wastewater in the pipe is $0.75 \text{ m} \cdot \text{s}^{-1}$. Assume that the pipe behaves as a steady-state plug-flow system and that the reaction rate constant for destruction of the fecal coliforms is 0.23 min^{-1}.

The mass balance diagram is sketched here. The control volume is the pipe itself.

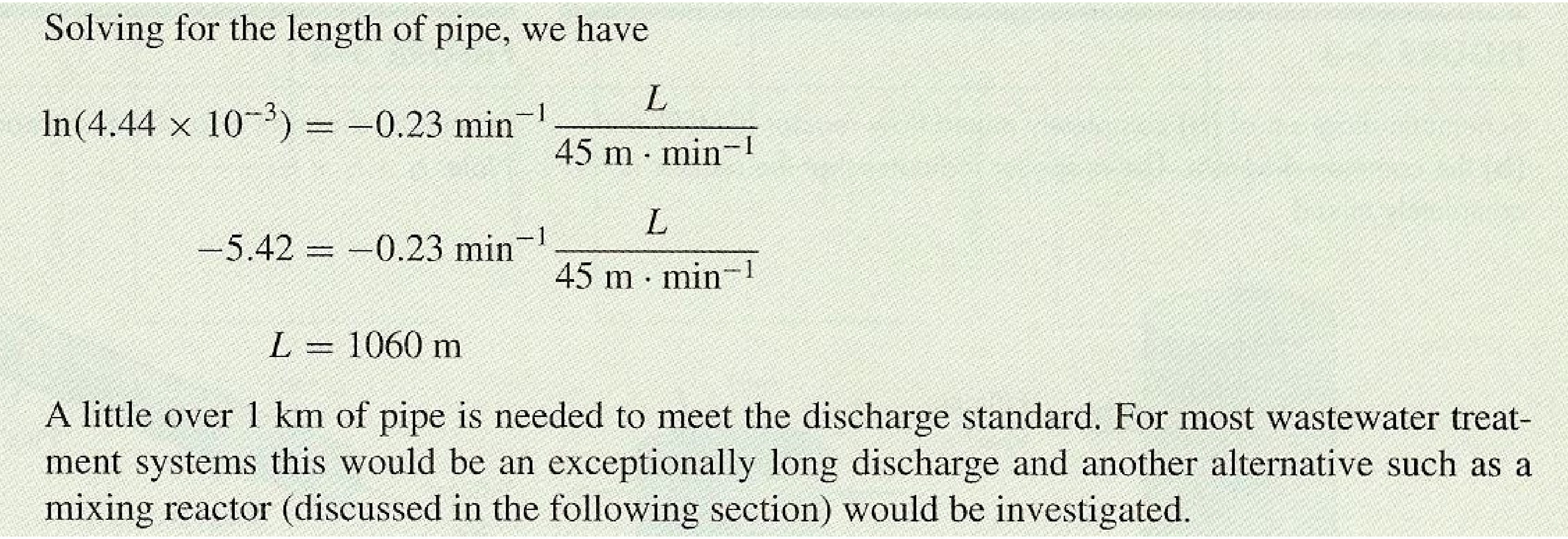


Using the steady-state solution to the mass-balance equation, we obtain

$$\ln \frac{C_{out}}{C_{in}} = -k \frac{L}{u}$$

$$\ln \frac{2000 \text{ CFU} \cdot \text{L}^{-1}}{4.5 \times 10^5 \text{ CFU} \cdot \text{L}^{-1}} = -0.23 \text{ min}^{-1} \frac{L}{(0.75 \text{ m} \cdot \text{s}^{-1})(60 \text{ s} \cdot \text{min}^{-1})}$$

PFR Example (cont.)



Solving for the length of pipe, we have

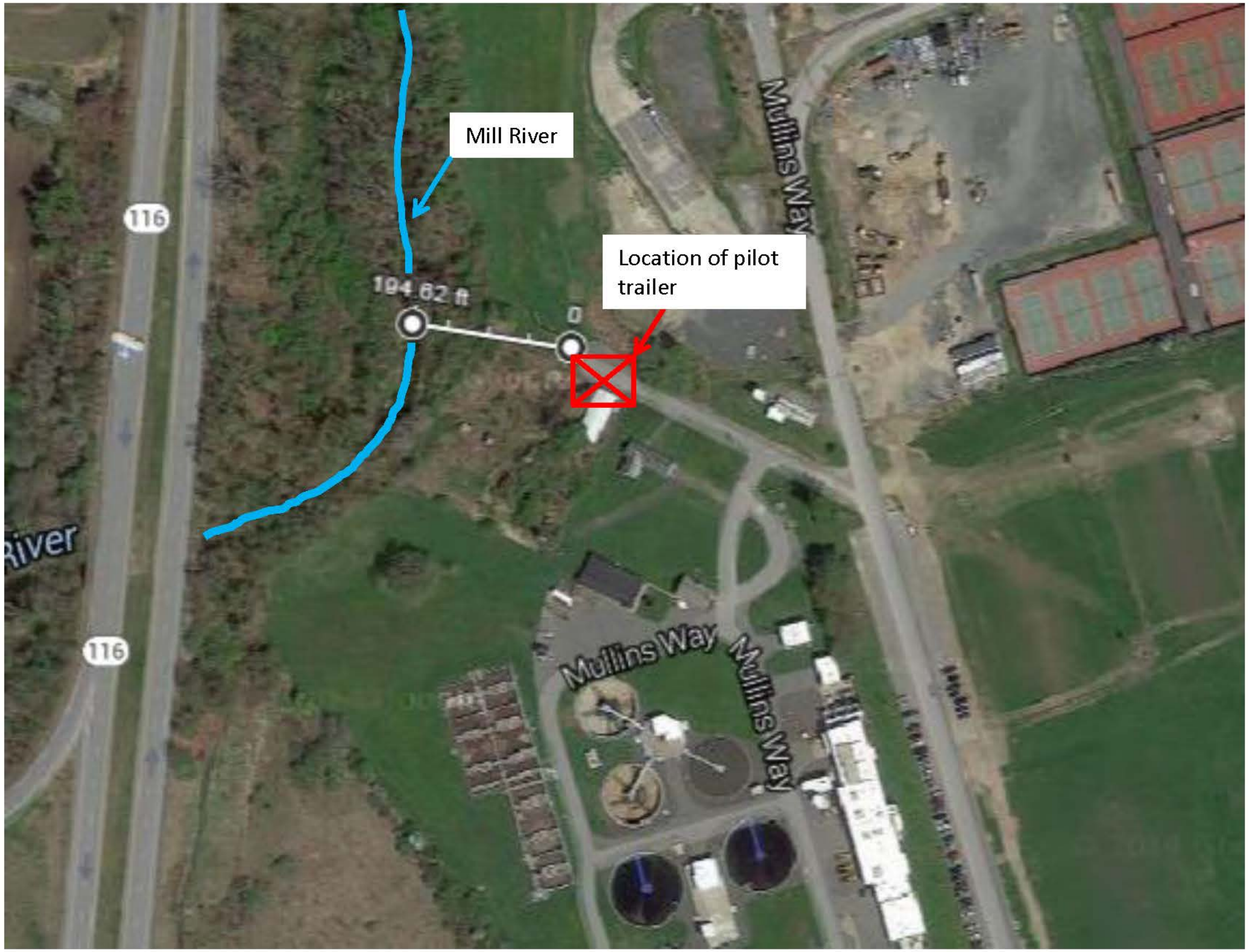
$$\ln(4.44 \times 10^{-3}) = -0.23\ \text{min}^{-1} \frac{L}{45\ \text{m} \cdot \text{min}^{-1}}$$

$$-5.42 = -0.23\ \text{min}^{-1} \frac{L}{45\ \text{m} \cdot \text{min}^{-1}}$$

$$L = 1060\ \text{m}$$

A little over 1 km of pipe is needed to meet the discharge standard. For most wastewater treatment systems this would be an exceptionally long discharge and another alternative such as a mixing reactor (discussed in the following section) would be investigated.

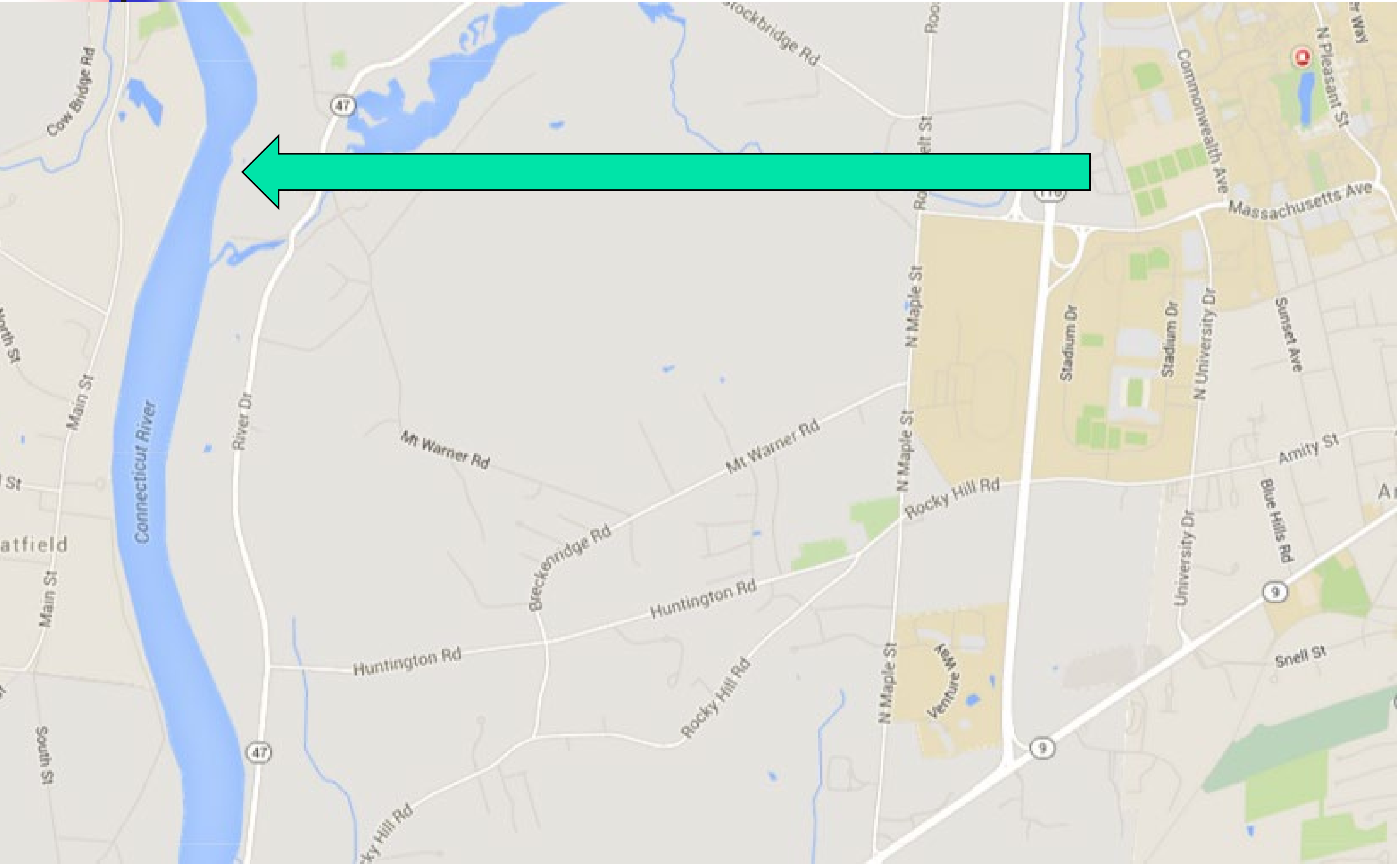
Amherst WWTP & Mill River



Map #1 – plan view of site

Mill River

Discharge to CT River

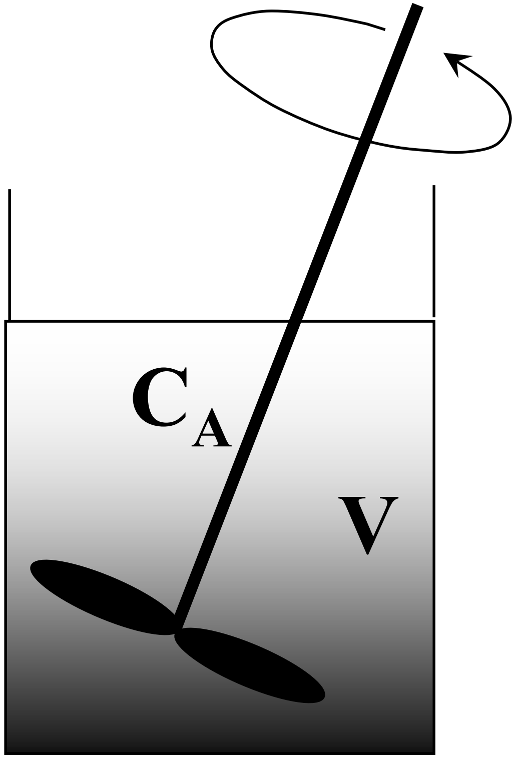


Batch Reactors

General Reactor mass balance

$$\frac{dM_A}{dt} = \sum_{i=1}^{n}(C_{Ai}Q_i)_{in} - \sum_{j=1}^{n}(C_{Aj}Q_j)_{out} - r_A V$$

Batch reactors are usually filled, allowed to react, then emptied for the next batch – “Fill & Draw”



Because there isn’t any flow in a batch reactor:

$$\frac{1}{V}\frac{dM_A}{dt} = -r_A$$

And:

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

Which for a 1st order reaction is:

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

Batch Reactor Example

A wastewater contains contaminant "A" with an initial concentration of 1200 mg/L. It is to be treated in a batch reactor. The reaction of A to products is assumed to be first order. The rate constant, k, is 2.5/day. Determine the time required to convert 75 percent of A to products. Plot the conversion of A versus time for the first 10 days.

$$r_A = kC_A$$

So:

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

$$-kt\Big]_0^t = \ln C\Big]_{C_{Ao}}^{C_A}$$

$$\mathbf{C_A = C_{Ao}e^{-kt}}$$

Batch Reactor Example (cont.)

$$t = \frac{\ln\left(\frac{C_A}{C_{Ao}}\right)}{-k}$$

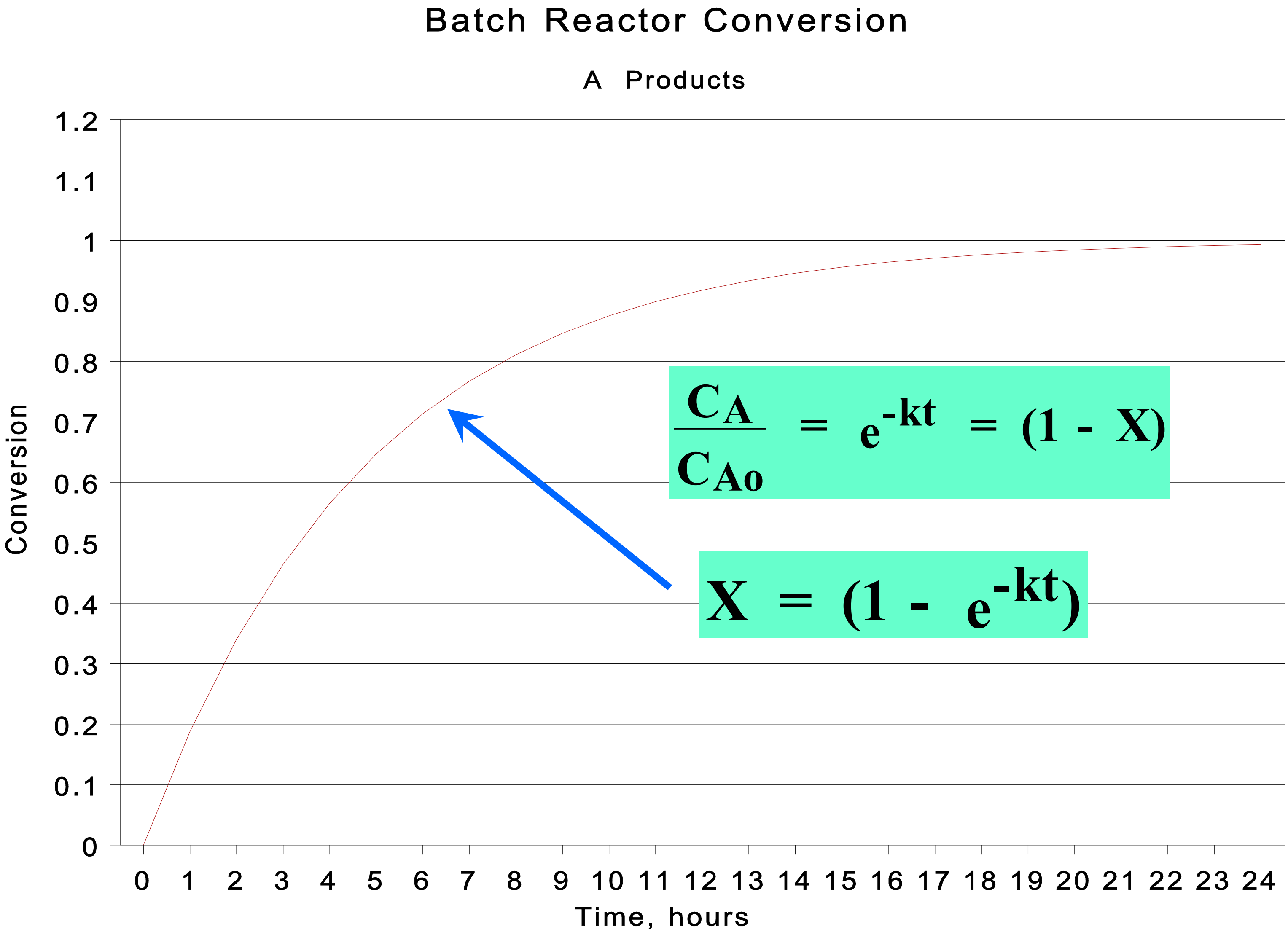
$$C_A = C_{Ao}(1 - X) = 1200\ \text{mg/L} \times (1 - 0.75)$$

$$C_A = 300\ \text{mg/L}$$

$$t = \frac{\ln\left(\frac{300\ \text{mg/L}}{1200\ \text{mg/L}}\right)}{-2.5/\text{day}}$$

$$t = 0.55\ \text{days}$$

Batch Reactor Example (cont.)



$$\frac{C_A}{C_{Ao}} = e^{-kt} = (1 - X)$$

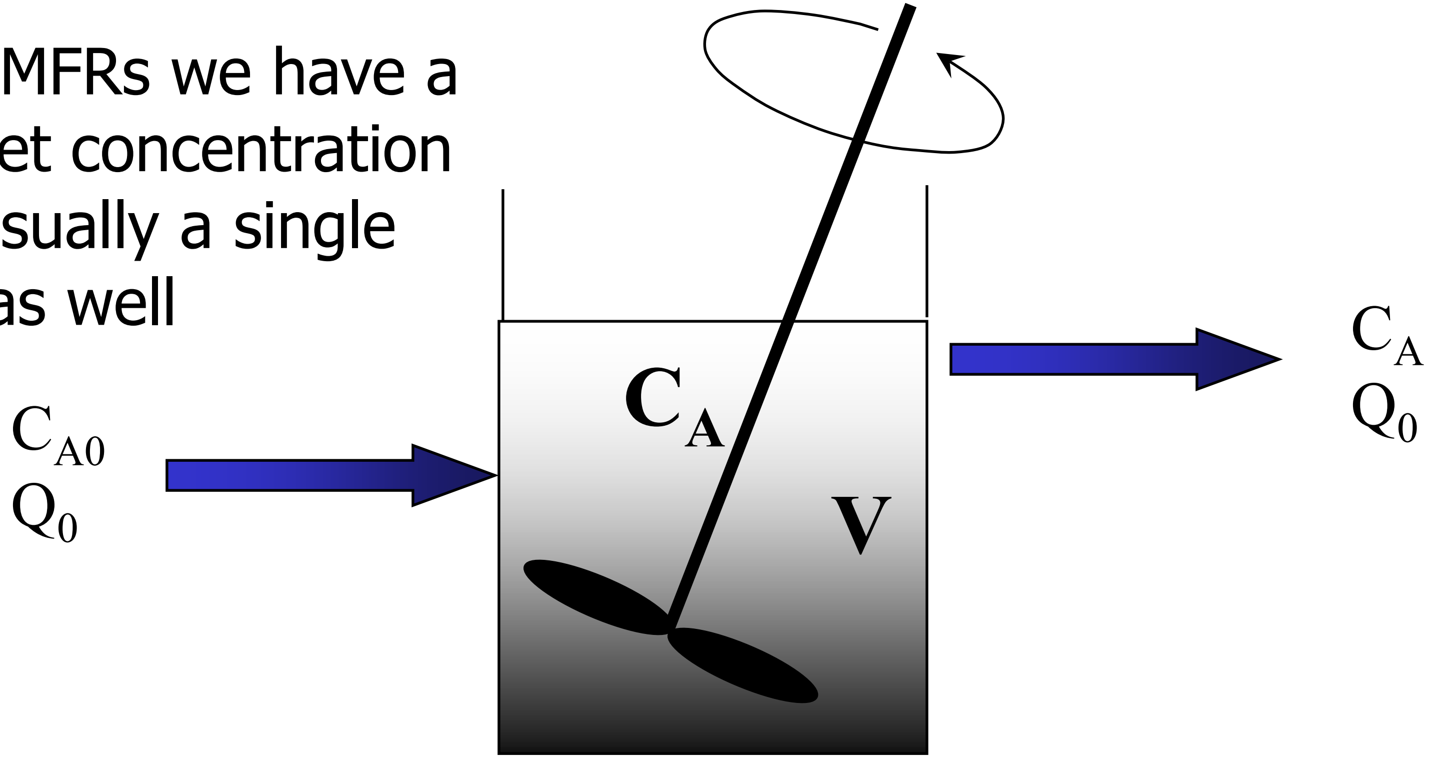
$$X = (1 - e^{-kt})$$

CMFR (completely mixed)

General Reactor mass balance

$$\frac{dM_A}{dt} = \sum_{i=1}^{n}(C_{Ai}Q_i)_{in} - \sum_{j=1}^{n}(C_{Aj}Q_j)_{out} - r_A V$$

But with CMFRs we have a single outlet concentration (C_A) and usually a single inlet flow as well



CMFR at SS

And at SS, $dM_A/dt = 0$, so:

$$r_A V = C_{Ao} Q_o - C_A Q_o$$

where,

Q_o = volumetric flow rate into and out of the reactor, [volume/time]

C_{Ao} = reactant concentration entering the reactor, [mass/volume]

C_A = reactant concentration in the reactor and in the effluent, [mass/volume]

V = reactor volume, [volume]

$$r_A = \frac{(C_{Ao} Q_o - C_A Q_o)}{V}$$

And if we define the hydraulic residence time:

$$\boldsymbol{\theta = \frac{V}{Q}}$$

$$r_A = \frac{C_{Ao} - C_A}{\theta}$$

CMFR with 1st order reaction

- From the general equation

$$r_A = \frac{C_{Ao} - C_A}{\theta}$$

- We get:

$$kC_A = \frac{C_{Ao} - C_A}{\theta}$$

- or

$$kC_A = \frac{C_{Ao} - C_A}{V/Q}$$

$$\frac{V}{Q} kC_A = C_{Ao} - C_A$$

$$C_A + \frac{V}{Q} kC_A = C_{Ao}$$

$$C_A = \frac{C_{Ao}}{1 + \left(V/Q \right) k}$$

$$C_A = \frac{C_{Ao}}{1 + k\theta}$$

CMFR SS Example #1

A CMFR is used to treat a wastewater that has a concentration of 800 mg/L. The hydraulic detention time of the wastewater in the reactor is 6 hours. The chemical reaction is an elementary irreversible second order reaction:

$$2A \xrightarrow{k} \text{Products}$$

The reaction constant, k, is 3.7 L/mg-day. Determine the conversion, X, for the process.

CMFR SS Example #1 (cont.)

The first step is to determine the reactor mass balance and the kinetic expressions. The reaction is second order irreversible so the kinetic expression is:

$$\mathbf{r_A = kC_A^2}$$

The mass balance for a CMFR is:

$$r_A = \frac{(C_{Ao} - C_A)}{\theta}$$

And:

$$\frac{(C_{Ao} - C_A)}{\theta} = kC_A^2$$

Rearranging, we obtain a quadratic equation with C_A as the unknown:

$$\mathbf{k\theta C_A^2 + C_A - C_{Ao} = 0}$$

CMFR SS Example #1 (cont.)

If the values for k, θ, and C_{Ao} are substituted into the relationship, the effluent concentration can be determined. It is 29 mg/L. The conversion can now be calculated:

$$X = \frac{(C_{Ao} - C_A)}{C_{Ao}} = \frac{(800\ mg/L - 29\ mg/L)}{800\ mg/L}$$

$$X = 0.96$$

Reactor Question

- For a first order reaction, which type of reactor is more effective?
  - A. Plug Flow Reactor (PFR)
  - B. Completely Mixed Flow Reactor (CMFR)
  - C. Batch Reactor (BR)
  - D. All are the same
  - E. Both PFR and BR

- To next lecture