**Environmental Engineering Background**

There are three basic types of reactors: completely mixed batch reactors (CMBR), completely mixed flow reactors (CMFR) and plug flow reactors (PFR). In a CMBR, reactants are placed in a vessel and allowed to react until an endpoint is achieved. This reaction does not occur under steady-state conditions (i.e., concentrations are changing with time), but at any given instant the composition inside the vessel is assumed to be uniform. In a CMFR, reactants are fed continuously into a stirred tank and are thoroughly mixed throughout the tank. The concentrations of all reactants and products are assumed to be uniform inside the reactor, and therefore the concentration of any reactant/product in the outflow stream is the same as it is inside the reactor vessel. Also, the reactants in the inflow stream are assumed to be instantaneously mixed so that their concentrations decrease instantaneously to those inside the reactor. CMFRs generally operate at or close to steady state conditions; i.e., concentrations inside the reactor do not change over time. In a PFR, the reactants in the influent are assumed to move through the reactor as a “plug”, with no mixing occurring lengthwise through the reactor. This means that no element of fluid in the plug reaches the end of the reactor before any other, resulting in the same residence time in the reactor for all elements in that plug. While each plug is behaving as a batch reactor that is not at steady state, the reactor as a whole may be at steady state as long as influent conditions do not change.

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**Figure #1:** The three types of ideal reactors: a) completely mixed batch (CMBR), b) completely mixed flow (CMFR) & c) plug flow (PFR).
The use of CMBRs in water treatment applications is limited to laboratory scale experiments, due to the large volumes of water required for most treatment processes. However, CMBRs are widely used in the chemical processing industry, and sequencing batch reactors (SBRs) are used for wastewater treatment particularly at small plants. An example of a CMFR might be an activated sludge unit in a wastewater treatment plant; the return sludge is mixed with the influent sewage and usually complete mixing is maintained throughout the tank by the aeration system. A sedimentation basin or a trickling filter are examples of PFRs; in the former it is desirable for the fluid to move through the reactor as a plug so that settling can occur as a result of Stoke’s Law.

**Plug Flow Reactors**

A spike of dye introduced into the influent of a small basin under ideal conditions should move as a plug with no mixing in the direction of flow and no velocity gradients. With these conditions, if the concentration of the dye was monitored over time at the effluent side of the basin, the spike should appear after a set amount of time. Diffusion can cause some broadening of the spike, but if flow is laminar and uniform throughout the reactor then the peak will appear in the effluent at the theoretical detention time (see below). Ideal reactors are desirable because they are relatively easy to understand, and because they are more efficient than a reactor with non-ideal conditions. For example, in a sedimentation basin under ideal conditions, all particles would settle before they reached the end of the basin. Under non-ideal conditions, some fraction of the particles might flow through the reactor too quickly and not settle out.

**Theoretical Detention Time vs. Mean Detention Time**

The amount of time required for the reappearance of the spike could be calculated from the volume of the tank and the flow rate of the influent water as:

\[ \tau = \frac{V}{Q} \]

where \( \tau \) is the (theoretical) detention time, \( V \) is the volume of the tank and \( Q \) is the flow rate (volume time\(^{-1}\)) of the influent water. If the flow inside the tank should happen to deviate from plug flow, the spike of dye will appear as a dispersed concentration curve at the effluent outlet and it will probably not be centered at the theoretical detention time. Figure 2 (Levenspiel, 1972) compares a spike resulting from plug flow conditions and a concentration curve that results from a non-ideal reactor. The detention time of elements in a plug will vary in a non-ideal reactor. Therefore, the mean detention (residence) time, \( t_{avg} \), is calculated to represent the most likely amount of time that an element will spend in the reactor; it is equal to the time that it takes for 50% of the plug mass to exit the reactor. The plug mass can be estimated by integrating the area under the concentration curve (see Figure 2).

**Deviation from “Ideal” Reactors**

A spike of dye introduced into a tank may not appear in the effluent as a sharp spike for several reasons:

**Diffusion** - Spreading in both directions away from the spike center caused by the random motion of dye molecules undergoing collisions with each other.
**Short Circuiting** - This occurs when water flows preferentially through only a portion of the tank.

**Dead Zones** - Usually in the corners of the basin where low flow or no flow prevail.

![Figure #2: Ideal and non-ideal output for a Plug Flow Reactor.](image)

This laboratory will simulate a sedimentation basin as one example of a PFR taken from a water treatment process. Even the best designed basin will usually deviate from ideal conditions. A way to measure the amount of deviation occurring is by use of a tracer test to help determine the amount of non-ideality due to hydraulic effects. Several issues that can cause a tank to be non-ideal are addressed below.

**Temperature Differences**
The addition of warm influent water to a basin containing cooler water can cause short circuiting of the warm water over the surface of the basin. This influent water reaches the effluent in a fraction of the theoretical detention time.

**Inlet Energy Dissipation**
Water carried in pipes to the sedimentation basin needs to maintain a velocity great enough for particulate matter to be held in suspension. This relatively fast moving water then needs to be slowed down and distributed over a broad area as it enters the basin. A plate containing evenly spaced holes, called a baffle, is used for such a purpose. If the energy of the influent is not dissipated adequately, jets of fast-moving water will carry the influent far into the reactor, and the result will be short-circuiting and a broad peak rather than a spike in the effluent.

**Outlet Currents**
Outlet currents of a clarifier are related to design of effluent weirs. If the length of an outlet weir is too short, outlet currents could form and sweep particles into the tank effluent. V-notch weirs
provide better lateral distribution of outlet flow and are therefore commonly used. In general, tank performance is primarily a function of temperature differences and inlet energy dissipation rather than outlet currents. Careful design of effluent weirs cannot be taken for granted, but will not overcome density currents created by other deficiencies.

Physical and chemical measurements

In this lab, two techniques will be used to track a spike input through a reactor. All groups will add a sudden input of dye that may be observed with the naked eye. However, to quantify the flow of dye, the absorbance of the effluent stream will be monitored. The amount of light that penetrates a solution is known as transmittance. Transmittance (T) is expressed as the ratio of the intensity of the transmitted light, I₀, and the intensity of the original light beam, I₀.

\[ T = \frac{I_t}{I_0} \]

Absorbance is related to transmittance; it is defined as:

\[ A = \log \left( \frac{1}{T} \right) \]

One may also recall from chemistry courses that absorbance follows Beer's Law:

\[ A = \text{C} \varepsilon \]

where \( C \) is concentration and \( \varepsilon \) is the extinction coefficient. In other words, absorbance is linearly proportional to concentration, and may be used as a measure of concentration.

The other tool that will be used to track the spike is conductivity. Conductivity is a measure of the ability of a solution to conduct electric current. The conductivity is proportional to the concentration of ions (charged atoms and molecules). Some groups will inject a sodium chloride (NaCl) solution together with the dye, and will monitor conductivity of the effluent to detect when the spike leaves the reactor. All groups will determine the theoretical and mean detention times and interpret the shape of the effluent peak in terms of the ideality of the reactor.

Statistics background

A. Distributions

The distribution of a data set refers to the frequency of occurrence of all values of the parameter of interest. Last week, we characterized the distribution only in terms of its central tendency, or mean, and its spread, quantified as the standard deviation. This week, we will examine the shape of the entire distribution, and review methods (graphical and numerical) for characterizing the shape. We will use an unconventional data set, the shape of the plume of dye leaving the reactor. What makes this unconventional is that we will use time as the dependent variable and concentration as the measure of the frequency (pdf) of occurrence of dye molecules.

Initially, the distribution of data is often viewed as a histogram, a plot of the frequency of occurrence vs. the values of the parameter of interest. A histogram of the measured MLSS values from a previous lab is shown below. To construct a histogram, data must be grouped into “bins” or ranges of parameter values; the histogram shows the number of measurements recorded within each subrange of parameter values (e.g., the number of samples with MLSS between 80 and 85 mg/L). Excel has a histogram function under the Data Analysis tools that are found under the Tools menu. The frequency of occurrence (y axis) could be expressed in a number of ways; in the graph below it is shown as number of occurrences, but it could be shown as a percentage of all measurements. For this lab, you cannot determine normality by plotting a histogram of concentrations; rather, it is the shape of the concentration vs. time curve that you are trying to compare with a normal distribution.

The histogram allows us to see the shape of the distribution and to make a preliminary assessment as to whether the data fit one of the standard distributions. The two most commonly
encountered standard distributions are the *normal* and *lognormal* distributions. The normal distribution is a symmetrical, bell-shaped distribution that is completely characterized by the mean and standard deviation. The equation describing the probability density function (i.e., frequency of occurrence) for a normal distribution is:

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left( -\frac{(x-\mu)^2}{2\sigma^2} \right)$$

The lognormal distribution can be described by the same function if $\log(x)$ is substituted for $x$ in the equation above and the mean and variance are computed for the log-transformed data.

![Histogram showing the distribution of MLSS values measured in 2008 CE3502 class.](image1)

**Figure 3.** Histogram showing the distribution of MLSS values measured in 2008 CE3502 class.

![Comparison of distribution of MLSS measurements with a normal distribution having the same mean and standard deviation.](image2)

**Figure 4.** Comparison of distribution of MLSS measurements with a normal distribution having the same mean and standard deviation.

Many statistical analyses that we will learn later in the term assume that data follow a normal distribution, and for this reason it will be important to be able to test if data are normally distributed. There are many tests for normality, some being more complicated than others. Visually, a histogram (Fig. 3) can be inspected to see if the data are symmetrically distributed.
about the mean (i.e., if the mode = mean = median); you can do this test in this lab by seeing if the mode (high point on curve) occurs at the average residence time (see below). Another simple test is to compute the ratio s:μ (COV or RSD) where s is the standard deviation and μ is the mean; a value greater than 1.0 indicates the data are not normally distributed. One can also compare the histogram of the data with the probability density function (pdf) for a normal distribution. This is shown in Fig. 4 above for the MLSS results. For this lab, you could compare a calculated pdf for a normal distribution with your observed graph of concentration vs. time; you would use the average residence time as the mean, and you could try different values for the standard deviation to find the best fit with your curve.

Another widely used method for assessing the normality of the distribution is a probability plot. In a probability plot, the actual data are compared with those that would be expected if the data followed a normal distribution with the same mean and variance as the measured data. The MLSS data have been plotted on a probability plot in Fig. 5; to compute the “percentile” (P), the rank (r) of each data point is used:

\[ P(x) = \frac{r - 0.5}{n} \]

where n is the total number of data points. Next, using the Z table (standard normal distribution), the z value for each percentile (P(x)) is found; the percentiles are the area under the standard normal curve to the left of the corresponding z value. The z values may be converted back to the scale of the MLSS by multiplying by the standard deviation and adding the mean:

\[ z_i = \frac{Q_i - \mu}{\sigma} \quad \text{or} \quad Q_i = z_i \cdot \sigma + \mu \]

The Q values thus computed are equal to the expected values of MLSS were the MLSS normally distributed with mean of μ and standard deviation of σ. A plot of Q vs. MLSS should result in a straight line with slope of 1.0 if the data followed a perfect normal distribution. Some deviation is always observed, particularly for the largest and smallest values. The data in Figure 5 show an acceptable fit to a straight line; we would conclude that the data may be normally distributed.

You cannot easily construct a probability plot for the results from today’s lab.

![Figure 5. Probability plot for MLSS data. The expected values (Q_i) of MLSS for a normal distribution with mean 1600 mg/L and standard deviation of 420 mg/L are plotted against the measured values; the data lie acceptably close to the dashed 1:1 line. The solid line is the regression line whose equation is shown on the graph; the slope is acceptably close to 1.0.](image-url)
Experimental procedures

Equipment and supplies
Tank reactor       NaCl solution
Dye                Conductivity probe
1 5-mL syringe (for dye)     Watch or stopwatch
1 500-mL or 1000-mL graduated cylinder   Tape measure or meter stick
Thermometer        Vials
Beaker

Objective
The objectives of this lab are four-fold. First, observation of the concentration vs. time profile for a spike of dye (or salt) injected into a reactor will be made; second, determination if the dye/salt is a conservative tracer will be performed; third, mathematical and graphical determination of whether the conditions in the PFR are ideal or non-ideal will be performed; and finally, the data will be analyzed to see if the plume leaving the reactor has a normal or lognormal shape.

Stock Solution and Standard Curve
A stock solution of dye has been prepared by diluting 1 ml of dye to 1 liter of tap water (concentration equals $10^{-3}$). A standard curve of absorbance vs. dye concentration has been prepared using this stock solution. The standard curve and regression line can be found in Figure #3 on the next page.

!["Red" Dye Standard Curve](image)

Figure 3: Absorbance of a set of standard concentrations; regression is run through the origin.
Procedure
Approximate volume of tanks = 70 L
Flow rate (approx.) $\approx 1-7$ L/min

There will be four tanks in operation; one will have no baffle, two will have one baffle, and one will have two baffles. Each group will work with one of these tanks. Be sure to walk around and observe the other systems.

Eight groups will be measuring absorbance, and two groups will be measuring conductivity. The instructions for each of these measurements are slightly different; follow the instructions appropriate for your group.

Groups measuring absorbance
1. If necessary, adjust the flow rate to obtain a constant level of water in your tank. Measure the effluent flow rate with a 1-liter (or 500-mL) graduated cylinder and a watch with a second hand. You might want to take the average of three measurements. Measure the dimensions of your tank, compute the volume and the theoretical retention time.
2. Measure the influent and effluent temperature.
3. Rapidly inject 3.0-5.0 ml of concentrated dye into the influent area of the tank using a hypodermic syringe. Record the volume injected and the time when the injection is made.
4. Take samples of the effluent at one-minute intervals. You have 10 vials in which to collect samples. This means that by the time the tenth sample is collected, the first vial must already have had its absorbance measured, be rinsed and be available for re-use. Measure and record the absorbance of the samples collected at the optimal wavelength of 522 nm (for this particular red dye). NOTE: You will use the standard curve above to determine dye concentrations for each sample. To measure absorbance:
   - Set the wavelength to the desired value of 522 nm;
   - With no cuvet present, set the % transmittance to 100%;
   - Switch to Absorbance;
   - Place cuvet with water in spectrophotometer, turn knob to set absorbance to zero;
   - Measure and record the absorbance of water in a second cuvet;
   - Use the second cuvet for all subsequent measurements of effluent absorbance;
   - Pour effluent sample from vial into cuvet, wipe with Kimwipe, measure and record absorbance;
   - Periodically, check that the absorbance of water in the first cuvet is still zero.
5. Continue taking samples of the effluent for absorbance measurements for a period of three times the theoretical detention time.
6. At the conclusion of the experiment, measure the flow rate and the influent and effluent temperatures again. Also, measure the temperature at 3 different places within the tank.
7. Wash all glassware including the hypodermic syringe.

Groups measuring conductivity
8. If necessary, adjust the flow rate to obtain a constant level of water in your tank. Measure the effluent flow rate with a 1-liter (or 500-mL) graduated cylinder and a watch with a
second hand. You may want to calculate the average of three measurements. Measure the
dimensions of your tank, compute the volume and the theoretical retention time.
9. Measure the influent and effluent temperature.
10. Pour a small volume of NaCl solution in a beaker and measure the conductivity.
11. Rapidly inject 3.0 ml of concentrated dye into the influent area of the tank using a
hypodermic syringe. Simultaneously, add 10-20 mL of saturated NaCl solution. Record the
time when the injection is made.
12. Measure the conductivity of the effluent at one-minute intervals by turning on the probe and
inserting it in the overflow weir by the drain hole.
13. Continue recording conductivity for a period of three times the theoretical detention time.
14. At the conclusion of the experiment, measure the flow rate and the influent and effluent
temperatures again. Also, measure the temperature at 3 different places within the tank.
15. Wash all glassware including the hypodermic syringe.

Results section
1. Using either the calibration graph provided for the dye or your conductivity measurement of
the saturated NaCl solution (360 g L^{-1}), convert all of your absorbance or conductivity values
to concentration units (mL/L or mg/L).
2. Create an x-y plot of dye or salt concentration (y axis) vs. time (x axis). On the graph, plot
the raw data as points. Does the shape of the plot appear to follow a normal distribution?
Present on the same plot a pdf for a normal distribution. Use the equation:

\[
f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(x - \mu)^2}{2\sigma^2}\right]
\]

Where \( x \) is time, \( \mu \) is set equal to \( t_{avg} \) (see below), and \( \sigma \) is chosen to match your data.
3. Find the Area under the Concentration vs. Time graph using rectangular approximation (use
of a spreadsheet is suggested).

\[
\text{Area} = \int_0^\infty C(t) \cdot dt = \sum_0^{i=t_{final}} C_i \Delta t_i = \sum_0^{t_{final}} \left[ \frac{(C_i + C_{i+1})}{2} \right] \cdot (t_{2i} - t_{1i})
\]

Where \( C_i = (C_1 + C_2)/2 \) and \( \Delta t = (t_2 - t_1) \).
4. Find the mean detention time \( t_{avg} \) of the fluid:

\[
t_{avg} = \int_0^\infty [t \cdot C(t) \ dt] \cdot \frac{1}{\text{Area}} = \sum_0^\infty [t_i \cdot C_i \Delta t_i] \cdot \frac{1}{\text{Area}}
\]

Where \( t_i = (t_1 + t_2)/2 \) and \( C_i \) & \( \Delta t \) are as above.
5. Find the volume of dye (or mass of salt) recovered:

\[
\text{Volume} = \text{Area} * (\text{average flowrate})
\]

Where the units are: Mass (mg) or Volume (mL), Area (mL/L * time), and flow rate (L/time).
6. You probably calculated a mass (volume) of tracer less than you actually injected. Calculate an average flow rate (L/hr) through the tank using the equation above and assuming that you recovered 100% of the amount injected; compare this calculated flow rate with your measured flow rate. Could an error in flow rate measurement explain why you did not recover 100% of the injected tracer?

Discussion
1. Does the reactor behave as an ideal PFR? Discuss how and why it differs from ideal PFR behavior.
2. Was the tracer conservative? Did you recover 100% of the tracer? If not, why?
3. Is the plume bell shaped (i.e., does it follow a normal distribution)? If not, why not? Does it follow a lognormal distribution?