APPENDIX J

DYE TRACER TECHNIQUE TO ESTIMATE MEAN RESIDENCE TIME AND HYDRAULIC EFFICIENCY

J-1. Fluorescent Dyes.

a. General. Determination of retention time of ponded water is an important aspect of containment area design for retention of solids. Dye tracer studies may be undertaken to provide retention time data for better operation or management of existing dredged material containment areas. Various artificial tracers have been used to generate inflow and settling data characteristics. Radioactive tracers are effective; however, their use involves troublesome special handling and safety precautions. Commercially produced fluorescent dyes are easier and safer to handle and have been used extensively in inflow studies. Fluorescent materials used in tracing are unique in that they efficiently convert absorbed light into emitted light with a separate characteristic spectrum. Using the proper light source and filters, a fluorometer can measure small amounts of fluorescent material in a sample, Thus, when a fluorescent dye is mixed with a given parcel of water, that parcel may be identified and traced through a water system. The mean residence time and the amount of mixing of the water parcel in the system can be quantified by measuring the time variation of dye concentrations of the water leaving the system.

b. Physical-Chemical Considerations. For a given fluorescent dye, the interaction of the dye with surrounding environmental conditions should be considered. Use of a dye in nature's water normally is not affected by chemical changes. However, if the dye were to be used in waters having high chloride concentrations, the dye loss could be significant. Photochemical decay of dye concentration must also be considered when planning a dye tracer study. Factors influencing photochemical decay are light intensity, cloud cover, water turbidity, and water column depth. Other physical-chemical impacts on dyes are related pH, temperature, and salinity. Under acidic conditions, adsorption occurs more strongly, resulting in a reduction in fluorescence. A general rule of thumb on temperature impacts is that fluorescence decreases 5 percent for every 2° C increase in temperature. Tests have shown that dye decay occurs at a slower rate under saline conditions (7.02 metres sodium chloride solution) (item 30). Additional guidance for designing dye tracer studies and details of physical-chemical effects on dyes are found in items 1, 28, 11, 36, 30, 39, 38, and 8.

c. Dye Types. Fluorescent dyes have been used since the early 1900's. Several have been developed and used with varying degrees of success in the tracing of surface and ground waters. Smart and Laidlaw (item 30) evaluated eight dyes: Fluorescein, Rhodamine B, Rhodamine WT, Sulpho Rhodamine B, Lissamine FF, Pyramine, Amino G Acid, and Photine CU. Rhodamine B is stable in sunlight, but it is readily adsorbed to sediments in water. Rhodamine WT was developed specifically for water tracing and is recommended for such routine use.

J-2. Measurement Techniques.

a. Theory of Operation. Unlike sophisticated and complex analytical laboratory spectrofluorometers, filter fluorometers are relatively simple instruments. Basically, filter fluorometers are composed of six parts: a light (excitation energy) source, a primary or "excitation" filter, a sample compartment, a secondary or "emittance" filter, a photomultiplier, and a read-out device.

(1) When a fluorescent material is placed in a fluorometer, that spectral portion of the light source that coincides with the peak of the known excitation spectrum of the test material is allowed to pass through the primary filter to the sample chamber. This energy is absorbed by the fluorescent material, causing electrons to be excited to higher energy levels. In returning to its ground state, the fluorescent material emits light that is always at a longer wavelength and lower frequency than the light that was absorbed. It is this property that is the basis of fluorometry, the existence of a unique pair of excitation and emission spectra for different fluorescent materials. Finally, only a certain band of the emitted light, different from that used for excitation, is passed through the secondary filter to the photomultiplier, where a readout device indicates the relative intensity of the light reaching it. Thus, with different light sources and filter combinations, the fluorometer can discriminate between different fluorescent materials,

(2) The selection of light sources and filters is crucial since they determine the sensitivity and selectivity of the analysis. Fluorometer manufacturers recommend and supply lamps and filters for most applications, including Rhodamine WT applications.

(3) Two types of fluorometers are in common field use today. The standard instrument used in water tracing by many groups, including the USGS (Item 38), has been the Turner Model III manufactured by G. K. Turner Associates. Turner Designs has capitalized on recent advances in electronics and optics and developed a fluorometer, the Model 10 series, that is better adapted to field use than the Turner Model III, but is also more expensive.

b. Field Use. Once a fluorometer is calibrated, it must be decided where and how field samples will be analyzed--in situ or in a laboratory, continuously or discretely. During in situ analysis, the operation of the fluorometer in flow-through mode (where water from a given discharge point in the containment area is pumped continuously through the sample chamber in the fluorometer) is advantageous over its operation in cuvette mode (where a discrete sample is analyzed). Specifically, in situ flow-through analysis allows the homogeneity of fluorescence in the discharge to be easily observed, and eliminates the need for handling individual samples. Also, during in situ flow-through analysis, a strip chart recorder can be attached to the fluorometer, simplifying data collection by providing a continuous record of the fluorescence measured. During laboratory analysis, however, the flow-through system is seldom used, since discrete samples are homogeneous and usually lack the volume needed to fill the system. Instead, the fluorometer is operated in cuvette mode, where only a small portion of a sample is required for analysis.

(1) Each method of analysis also has its inherent problems. Laboratory analysis requires that discrete samples be collected, bottled, labeled, stored in the field, and then transported to the laboratory; this introduces many opportunities for samples to be lost through mislabeling, misplacement, or breakage. Also, the frequency of sampling may be insufficient to clearly define the changes in dye concentration as a function of time.

(2) In situ analysis, on the other hand, is usually performed under adverse environmental conditions--often at a fast pace, in a cramped and unsteady work space, or in less than ideal weather conditions. Thus, it is more likely that an error will occur during in situ analysis than during analysis in the controlled environment of a laboratory. It is also usually necessary to compute and apply many more temperature correction factors to fluorescence values during in situ analysis than during a laboratory analysis, since the samples to be analyzed in situ have not had a chance to reach a common temperature. This also increases the chances for error during analysis. In addition, in situ analysis is usually final. That is, if questions are raised about the validity of a measurement after the analysis, no sample is available for verification. In situ analysis may not be used when significant turbidity interference occurs.

(3) To minimize the risk involved in relying on either method alone, a combination of the two may be employed--a preliminary in situ analysis to help guide the sampling effort and a final laboratory analysis to ensure accurate results for quantitative analysis.

(4) Regardless of when and where fluorometric analysis takes place, several general precautionary measures should be taken to ensure that the analysis is reliable.

(a) The fluorometer should be accurately calibrated.

(b) Sample contamination should be avoided by rinsing or flushing the sample chamber between readings.

(c) The fluorometer operator should have experience with the instrument that is used. Experience can be gained through practice prior to the analysis.

(d) Sample temperatures should be observed and recorded during analysis to determine the necessary fluorescence correction factors.

(e) All information used to determine concentration units should be recorded (i.e., scale and meter or dial deflection).

(f) The calibration should be checked on a regular basis (every hour or so). This is especially important if the fluorometer is powered by a battery. When the battery is drained, readings are no longer accurate.

(5) For flow-through analysis in particular, all connections between the sampling hose, fluorometer, and pump must be tight to prevent air bubbles from entering the sample chamber. Air bubbles may also be introduced by a leaky pump seal. Thus, it is recommended that the pump be connected to the system

so that water is drawn up through the fluorometer to the pump. A screen placed at the intake end of the sampling hose will prevent sand and pebbles from altering the optics of the system, since they may scratch the glass in the sample chamber as they travel through the system.

(6) When analyzing samples in cuvette mode, the optics of the system may be distorted by scratches or smudges on the cuvette, making it necessary to wipe the cuvette clean prior to its insertion in the sample chamber. Once the cuvette is inside the warm sample chamber, a reading must be made quickly to prevent warming of the sample or condensation forming on the cuvette. Warming of the sample would cause a reduction in fluorescence, whereas condensation would distort the system optics.

(7) A person who has handled dye should never touch the fluorometer, or should use rubber gloves to handle dye and then discard them. Extremely small traces of dye on cuvettes or sample tubes can cause extremely large errors.

J-3. Sampling.

a. Sampling Equipment. The basic equipment needed to perform a dye tracer study includes the following:

(1) Fluorometers and accessories (filters, spare lamps, recorders, cuvettes, and sample holders). A spare fluorometer should be included if available, since the entire field study centers around its operation.

(2) Standard dye solutions for calibrating the fluorometers.

(3) Generators or 12-volt deep-cycle marine batteries (with charger) to power fluorometers and pumps, if the dye concentration is to be monitored continuously.

(4) Sampling equipment--pump and hoses, automatic sampler or discrete sampler (e.g., a Van Dorn sampler), bottles, labels, waterproof markers.

(5) Temperature-measuring device for measuring sample temperatures, if the temperature of the samples being analyzed will vary significantly.

(6) Dye, dilution vessels, and injection equipment (e.g., bucket, pump, and hoses).

(7) Description and dimensions of the containment area and surveying equipment to measure dimensions of the containment area.

(8) Equipment and records to determine the flow rate of the effluent from the containment area (e.g., production records, dredge discharge rate, weir length, depth of flow over the weir, and head above the weir).

(9) Miscellaneous equipment (e.g., life jackets, tool kits).

(10) Data forms.

Additional equipment might include cameras, radios, rope, and lights. All equipment should be checked for proper performance prior to transporting to the field.

b. Preparatory Tasks.

(1) Prior to conducting the dye tracer study, the average discharge rate at all points of discharge from the containment area should be measured or estimated. Equipment should be prepared, calibrated, and installed to measure or estimate the discharge rate during the dye tracer study. If production records are to be used to estimate the discharge, the discharge should be correlated to production. The average discharge rate, $\bar{Q}$, is equal to the sum of the average discharge rate at each discharge point, $\bar{q}$.

(2) A survey of the containment area should be performed to determine the area, depth, and volume of ponding, V_p, at the site for determination of the theoretical residence time, T. The volume can be estimated from as-built or design drawings of the site, but the depth of fill and ponding should be verified in the field if an accurate estimate of the hydraulic efficiency is to be determined from the dye tracer study. The ponded volume is needed to estimate dye requirements. An accurate determination of the volume is not needed to determine only the mean residence time.

(3) Using the average discharge rate and the ponded volume, the theoretical residence time of the site should be computed to plan the duration of the dye tracer study and to determine the hydraulic efficiency.

$$T = V_p/\bar{Q} \qquad \text{(J-1)}$$

(4) The background fluorescence should be measured at the site. Background fluorescence is the sum of all contributions to fluorescence by materials other than the fluorescent dye. The best method to determine the background fluorescence is to measure the fluorescence of the discharge from the site several times prior to addition of dye at the inlet. If the background fluorescence is expected to be variable, the fluorescence of supernatant from the influent should be measured before and during the dye tracer study. The fluorescence of the water at the dredging site should not be used as the background fluorescence since some of the sediment that is mixed with the site water may remain suspended and exhibit fluorescence. Similarly, the sediment may release or adsorb fluorescent materials that would alter the fluorescence of the site water.

(5) The effect of turbidity on the measurement of fluorescence should be examined to determine whether the discharge samples should be filtered prior to measuring their fluorescence. Turbidity will reduce the fluorescence by absorbing and scattering the light from the fluorometer lamp. Filtering is necessary only when samples are highly turbid or when the turbidity varies significantly. The effect of turbidity can be tested very simply. A sample of the discharge is divided in half, and a small amount of dye is added to one of the portions. The fluorometer is blanked or zeroed on the portion without dye in it, and the fluorescence of the portion containing dye is measured. Next, both samples are filtered or centrifuged to remove the turbidity. The process is then repeated using the filtrates or supernatants--blanking the

fluorometer on the portion without dye in it and measuring the fluorescence of the portion containing dye. If the measured fluorescence of the sample without turbidity differed from the measured fluorescence of the sample with turbidity, then it is evident that turbidity affected the analysis. Alternatively, distilled water could be used as the blank when the turbidity or the background fluorescence is expected to vary significantly during the study.

c. Dye Dosage Requirements.

(1) Dye is usually released instantaneously as a slug in studies performed to measure the mean residence time or hydraulic efficiency of a basin. The dye marks a small parcel of water that disperses as the parcel passes through the basin. Ideally, the dispersion in a settling basin is kept very low, and the parcel moves as a slug through the basin by plug flow. In practice, the net flow-through velocity is very low, sufficiently low that the parcel would move by plug flow in the absence of external forces. However, containment areas are subject to wind forces that transform the basins into partially mixed basins where the velocities induced by wind are much greater than the net flow-through velocity. Consequently, the flow through the basin more closely represents completely mixed conditions than plug flow conditions. Therefore, the dye requirements are determined based on the assumption that the dye is completely mixed in the basin rather than longitudinally dispersed.

(2) A typical dye tracer curve for a dredged material containment area, shown in Figure J-1, shows a residence time distribution that is characteristic of a partially mixed basin. Dye appears quickly at the discharge point at time t_i, and then shortly thereafter the peak concentration is discharged at time t_p. After the peak concentration reaches the discharge point, the dye concentration quickly decreases to about 30 to 60 percent of the peak concentration, depending on the wind and the theoretical residence time of the basin. The dye concentration then gradually decreases until all of the dye is finally discharged of time t_f. The mean residence time and theoretical residence time are shown in the figure as $\bar{t}$ and T, respectively. The residence time distribution indicates that some of the water short-circuits to the discharge point before the dye is completely mixed throughout the containment area. However, the dye becomes well mixed soon after the peak concentration is discharged, and then the dye concentration decreases gradually (instead of rapidly as it did before being completely mixed) to zero.

(3) Before determining the dye dosage requirements for a study, a standard calibration curve should be developed for the dye and the fluorometers to be used. This consists of plotting the fluorometer response for at least five known concentrations of dye. The design dye concentration is based on the ability to measure the dye concentration accurately for the length of the study, while not exceeding the maximum fluorometer response or excessively coloring the water.

(4) The dye dosage requirements are based on achieving an initial concentration of 30 parts per billion in a completely mixed basin. This concentration of Rhodamine WT corresponds to 30 percent of the full scale deflection of many commonly used fluorometers. With this quantity of dye, the peak

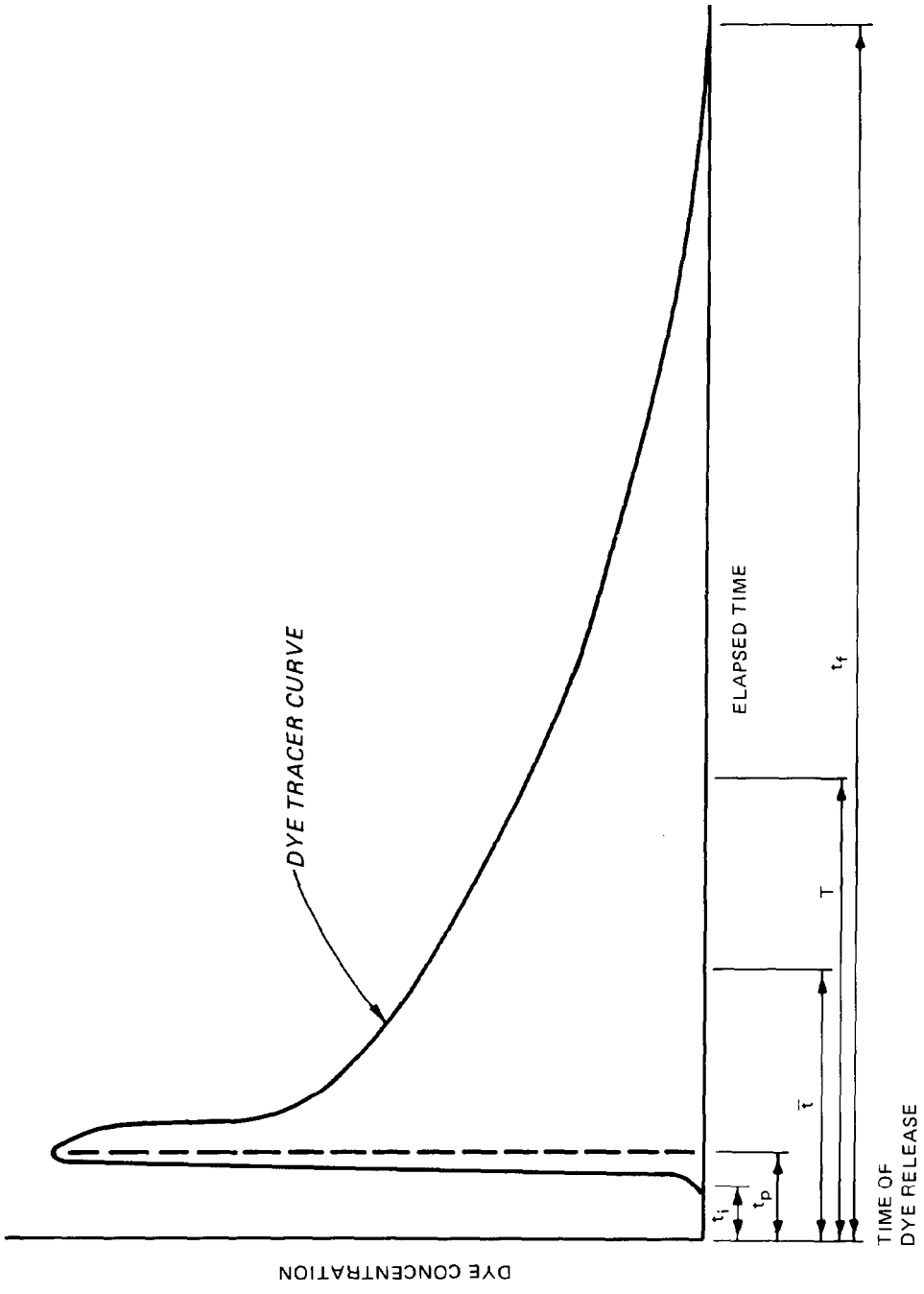

Figure J-1. A typical plot of the residence time distribution for dredged material containment areas

concentration will generally be less than 100 parts per billion (or 100 percent of the maximum fluorometer response) except for very small containment areas (<15 acres) or for areas with very bad channeling and short-circuiting. Since the peak concentration may exceed the capacity of the fluorometer, discrete samples should be taken during the period when the peak concentration is being discharged. These samples may be diluted to measure the peak concentration.

(5) The dye dosage requirements are computed as follows:

$$\text{Dye Dosage, lb} = 0.00272\ (C_o,\ \text{ppb})\ (V_p\ ,\ \text{acre-ft}) \qquad \text{(J-2a)}$$

$$= 6.24 \times 10^{-8}\ (C_o\ ,\ \text{ppb})\ (V_p\ ,\ \text{cu ft}) \qquad \text{(J-2b)}$$

$$= 2.21 \times 10^{-9}\ (C_o,\ \text{ppb})\ (V_P,\ \text{litres}) \qquad \text{(J-2c)}$$

where

C_o = desired dye concentration (generally 30 parts per billion for Rhodamine WT)

V_p = ponded volume

Dye Dosage = quantity in pounds of pure dye to be added to containment area

(6) Fluorescent dyes are not generally produced at 100 percent strength. Rhodamine WT is typically distributed at 20 percent dye by weight. Consequently, the quantity of manufacturer stock dye would be five times as large as computed in Equation J-2.

$$\text{Stock Dye Dosage} = \frac{\text{Dye Dosage}}{\text{Stock Concentration}} \qquad \text{(J-3)}$$

where the stock concentration is the fractional dye content by weight.

(7) The volume of stock dye required can be computed as follows:

$$\text{Volume of Stock Dye} = \frac{\text{Stock Dye Dosage}}{\text{Specific Weight}} \qquad \text{(J-4)}$$

The specific weight of liquid Rhodamine WT dye at a concentration of 20 percent by weight is about 1.19.

d. Dye Addition. The dye should be added to the influent stream in liquid form in a quantity and manner that is easy to manage. If the dye comes in solid form, it should be dissolved prior to adding it. Solid dye is easier to transport, but it is often inconvenient to dissolve at field locations. The dye may be diluted to a volume that will ensure good mixing with the influent stream, but the quantity should not be so large that it takes more than about 5 or 10 minutes to add the dye. The dye may be pumped into the influent pipe or poured into the influent jet or pool. Greater dilutions should be used to ensure good mixing if the dye is to be poured into the influent. Care must be taken that the dye is distributed so that it flows into the containment area in the same manner that the influent does.

e. Sampling Procedures.

(1) Sampling should be conducted at all points of discharge from the containment area.

(2) The dye concentration may be measured continuously at the discharge, or discrete samples may be collected throughout the test. Discrete samples must be taken when turbidity interference occurs, since the samples must be filtered or centrifuged. Discrete samples should be taken when the dye is being measured continuously to provide a backup in the case of equipment malfunction and to verify the results of the continuous monitor.

(3) The sampling frequency should be scheduled to observe any significant change in dye concentration (about 5 to 10 percent of the peak dye concentration). Sampling should be more frequent near the start of the test, when dye starts to exit from the containment area, and when the peak dye concentration passes the discharge points. About 40 carefully spaced samples should clearly define the residence time distribution or dye tracer curve.

(4) The sampling duration should be sufficiently long to permit the dye concentration to decrease to 10 percent of the peak concentration or less. For planning purposes, the duration should be at least about 2.5 times the theoretical residence time.

(5) The flow rate at all points of discharge from the containment area should be measured. If the flow rate varies significantly (more than 20 percent of average), the flow rate should be measured periodically throughout the test. Production records may be used to provide an indication of the variability of the flow rate. The flow rate over weirs may be estimated by measuring the depth of flow over the weir and the length of the weir crest and applying the weir formula for sharp-crested weirs:

$$Q = 3.3\ LH^{3/2} \qquad \text{(J-5)}$$

or

$$Q = 2.6\ Lh^{3/2} \qquad \text{(J-6)}$$

where:

Q = flow rate, cubic feet per second
L = weir crest length, feet
H = static head above weir crest, feet
h = depth of flow above weir crest, feet

J-4. Data Analysis.

a. Data Reduction. The data should be tabulated in the following form:

Sample	Time from Dye Addition	Flow Rate	Dye Concentration Above Background	Time Interval
i	t_i	Q_i	C_i	Δt_i

Column 1 is the number of the sample, i . If the dye concentration was monitored continuously, discrete points on the dye concentration curve may be used as samples. Column 2 is the time, t_i , that elapsed between the time that the dye was added to the influent and the sample was taken from the effluent.

Column 3 is the flow rate, Q_i , at the time that the sample was taken. The flow rate is needed only when the flow rate is not constant during the test. Column 4 is the dye concentration of the sample discounted for the background fluorescence, C_i ; that is:

$$C_i = C_{si} - C_{bi} \tag{J-7}$$

where

C_i = dye concentration discounted for background fluorescence of sample i

C_{si} = measured fluorescence of sample i

C_{bi} = background fluorescence at time t_i

If the background fluorescence does not vary, C_{bi} would be a constant and may be eliminated from the expression for calculating C_i if the fluorometer is blanked or zeroed with the site water. Column 5 is the interval of time, Δt_i , over which the sample is representative of the results. The value of this interval is one-half of the interval between the times when the samples immediately preceding and following the sample of interest were taken.

$$\Delta t_i = \frac{t_{i+1} - t_{i-1}}{2} \tag{J-8}$$

where

Δt_i = time interval over which sample i is representative

t_{i+1} = time when the following sample was taken

t_{i-1} = time when the preceding sample was taken

A data table is produced for each point of discharge.

b. Determination of Mean Residence Time.

(1) After generating the data tables, the mean residence time is computed as follows:

$$\bar{t} = \frac{\sum_{i=0}^{n} t_i \, C_i \, Q_i \, \Delta t_i}{\sum_{i=0}^{n} C_i \, Q_i \, \Delta t_i} \tag{J-9}$$

where:

$\bar{t}$ = mean residence time
n = total number of samples

(2) If the flow rate is nearly constant throughout the test, the equation may be simplified to:

$$\bar{t} = \frac{\sum_{i=0}^{n} t_i \, C_i \, \Delta t_i}{\sum_{i=0}^{n} C_i \, \Delta t_i} \qquad \text{(J-10)}$$

(3) If the sampling interval is constant (i.e., Δt_i = constant) but the flow rate is not constant, the equation may be simplified to:

$$\bar{t} = \frac{\sum_{i=0}^{n} t_i \, C_i \, q_i}{\sum_{i=0}^{n} C_i \, q_i} \qquad \text{(J-11)}$$

(4) If both the sampling interval and the flow rate are constant, the equation may be simplified to:

$$\bar{t} = \frac{\sum_{i=0}^{n} t_i \, C_i}{\sum_{i=0}^{n} C_i} \qquad \text{(J-12)}$$

c. Determination of Hydraulic Efficiency.

(1) The hydraulic efficiency is the ratio of the mean residence time to the theoretical residence time where:

$$\text{Hydraulic Efficiency} = \frac{\bar{t}}{T} \qquad \text{(J-13)}$$

(2) The correction factor for containment area volume requirements is equal to the reciprocal of the hydraulic efficiency. This correction is applied by multiplying the volume by the correction factor.

$$\text{Hydraulic Efficiency Correction Factor for Volume Requirements} = \frac{1}{\text{Hydraulic Efficiency}} \quad \text{(J-14)}$$