

Introduction to Wastewater Treatment Processes

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Characterization of Domestic and Industrial Wastewaters

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1. Measurement of Concentration of Contaminants in Wastewaters

Contaminants in wastewaters are usually a complex mixture of organic and inorganic compounds. It is usually impractical, if not nearly impossible, to obtain complete chemical analysis of most wastewaters.

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For this reason, a number of empirical methods for evaluation of concentration of contaminants in wastewaters have been devised, the application of which does not require knowledge of the chemical composition of the specific wastewater under consideration. The most important standard methods for analysis of organic contaminants are described in Sections 2 and 3. For discussion of analytical methods for specific inorganic contaminants in wastewaters, determination of physical parameters (total solids, color, odor), and bioassay tests (coliforms, toxicity tests), the reader is referred to Ref. [13].

Special attention is given in this chapter to the biochemical oxygen demand of wastewaters (BOD). A mathematical model for typical BOD curves is discussed, as well as the evaluation of feasibility of biological treatment for an industrial wastewater (Sections 4–9). Average characteristics of municipal sewage and the procedure followed in industrial wastewater surveys are described in Sections 10 and 11. Since both flow rate and sewage strength may follow an aleatory pattern of variation, it may be desirable to perform a statistical correlation of such data. This subject is discussed in Section 12.

Analytical methods for organic contaminants are classified into two groups:

Group 1. Oxygen parameter methods

1. Theoretical oxygen demand (ThOD)
2. Chemical oxygen demand (COD) [standard dichromate oxidation method; permanganate oxidation test; rapid COD tests; instrumental COD methods ("AquaRator")]
3. Biochemical oxygen demand (BOD) (dilution methods; manometric methods)
4. Total oxygen demand (TOD)

Group 2. Carbon parameter methods

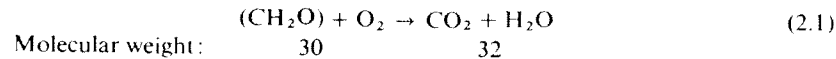
1. Theoretical organic carbon (ThOC)
2. Total organic carbon (TOC) (wet oxidation method; carbon analyzer determinations)

2. Measurement of Organic Content: Group 1—Oxygen Parameter Methods

2.1. THEORETICAL OXYGEN DEMAND (ThOD)

Theoretical oxygen demand (ThOD) corresponds to the stoichiometric amount of oxygen required to oxidize completely a given compound. Usually expressed in milligrams of oxygen required per liter of solution, it is a calculated value and can only be evaluated if a complete chemical analysis of the wastewater is available, which is very rarely the case. Therefore, its utilization is very limited.

To illustrate the calculation of ThOD, consider the simple case of an aqueous solution of a pure substance: a solution of 1000 mg/liter of lactose. Equation (2.1)* corresponds to the complete oxidation of lactose.



ThOD value is readily obtained from a stoichiometric calculation, based on Eq. (2.1):

$$\frac{30 \text{ (wt. lactose)}}{1000} = \frac{32 \text{ (wt. O}_2\text{)}}{\text{ThOD}}$$

$$\therefore \text{ThOD} = (32/30)1000 = 1067 \text{ mg/liter}$$

2.2. CHEMICAL OXYGEN DEMAND (COD)

Chemical oxygen demand (COD) corresponds to the amount of oxygen required to oxidize the organic fraction of a sample which is susceptible to permanganate or dichromate oxidation in an acid solution. Since oxidation performed in a COD laboratory test does not necessarily correspond to the stoichiometric Eq. (2.1), COD value is not expected to equal ThOD.

Standard COD tests (Sections 2.2.1 and 2.2.2) yield values which vary

TABLE 2.1
Average Values of Oxygen Parameters for Wastewaters as a Fraction of the Theoretical Oxygen Demand (Taken as 100)^a

ThOD	100
TOD	92
COD (standard method)	83
COD (rapid tests)	70
BOD ₂₀	
With nitrification	65
Nitrification suppressed	55
BOD ₅	
With nitrification	58
Nitrification suppressed	52

^a For carbon parameters the TOC represents an average of about 95% of the theoretical organic carbon (ThOC). Relationships between ThOD and ThOC are discussed in Section 3.

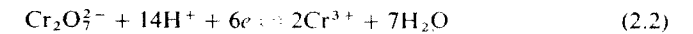
* For simplicity in Eq. (2.1), lactose was represented by one sugar unit (CH₂O). Multiplying this unit by a factor of 12 one obtains C₁₂H₂₄O₁₂, which is the molecular formula for lactose.

from 80–85% of the ThOD, depending on the chemical composition of the wastewater being tested. Rapid COD tests, discussed in Section 2.2.3, yield values equal to approximately 70% of ThOD value.

Approximate relationships between the various oxygen and carbon parameters are presented in Table 2.1, as estimated from a graph in Eckenfelder and Ford [4]. Values indicated in Table 2.1 are typical average values; correct relationships should be determined for the wastewater in question, as they are dependent upon its chemical composition. Thus, values in Table 2.1 are only utilized for rough estimates in the absence of actual data. Four types of COD tests are described next.

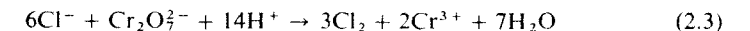
2.2.1. Standard Dichromate Oxidation Method [5, 8, 13]

The standard dichromate COD test is widely used for estimating the concentration of organic matter in wastewaters. The test is performed by heating under total reflux conditions a measured sample with a known excess of potassium dichromate (K₂Cr₂O₇), in the presence of sulfuric acid (H₂SO₄), for a 2-hr period. Organic matter in the sample is oxidized and, as a result, yellow dichromate is consumed and replaced by green chromic [Eq. (2.2)]. Silver sulfate (Ag₂SO₄) is added as catalyst.



Measurement is performed by titrating the remaining dichromate or by determining colorimetrically the green chromic produced. The titration method is more accurate, but more tedious. The colorimetric method, when performed with a good photoelectric colorimeter or spectrophotometer, is more rapid, easier, and sufficiently accurate for all practical purposes.

If chlorides are present in the wastewater, they interfere with the COD test since chlorides are oxidized by dichromate according to Eq. (2.3).



This interference is prevented by addition of mercuric sulfate (HgSO₄) to the mixture, as Hg²⁺ combines with Cl⁻ to form mercuric chloride (HgCl₂), which is essentially nonionized. A 10:1 ratio of HgSO₄:Cl⁻ is recommended. This corresponds to the following chemical reaction [Eq. (2.4)].

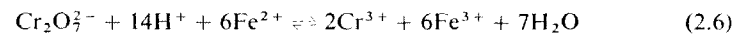


The presence of the Ag₂SO₄ catalyst is required for oxidation of straight-chain alcohols and acids. If insufficient quantity of HgSO₄ is added, the excess Cl⁻ precipitates the Ag₂SO₄ catalyst, thus leading to erroneously low values for the COD test. This corresponds to the following chemical reaction [Eq. (2.5)].

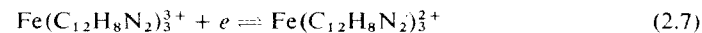


Standard ferrous ammonium sulfate $[\text{Fe}(\text{NH}_4)_2 \cdot (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ is used for the titration method. Ordinarily, standard ferrous sulfate loses strength with age, due to air oxidation. Daily standardization and mathematical correction in the calculation of COD to account for this deterioration are recommended [13]. Cadmium addition to the stock bottle of ferrous sulfate completely prevents deterioration. Ferrous sulfate available from Hach Chemical Company for the COD test is preserved in this manner, so that no further standardization checks are required.

The recommended procedure is to cool the sample after the 2-hr digestion with $\text{K}_2\text{Cr}_2\text{O}_7$, add five drops of ferroin indicator, and titrate with the standard ferrous ammonium sulfate solution until a red-brown color is obtained. The end point is very sharp. Ferroin indicator solution may be purchased already prepared (it is an aqueous solution of 1,10-phenanthroline monohydrate and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). The red-brown color corresponding to the end point is due to formation of a complex of ferrous ion with phenanthroline. Equation (2.6) corresponds to oxidation of ferrous ammonium sulfate by dichromate.



Equation (2.7) corresponds to formation of the ferrous-phenanthroline complex, which takes place as soon as all dichromate is reduced to Cr^{3+} , and therefore further addition of ferrous ammonium sulfate results in an excess of Fe^{2+} (ferrous ion).



phenanthroline-ferric phenanthroline-ferrous
(pale blue) (red-brown)

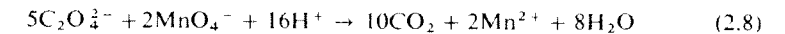
Details concerning preparation and standardization of reagents and calculation procedure are given in Refs. [5], [8], and [13]. Reproducibility of the COD test is affected by the reflux time. COD value obtained increases with reflux time up to about 7 hr and then remains essentially constant [4]. Instead of refluxing for 7 hr or more, a practical reflux time of 2 hr is recommended in the standard procedure.

2.2.2. Permanganate Oxidation Test

Recommended as the standard method until 1965, this test has been replaced by the dichromate test just described. This test utilizes potassium permanganate (KMnO_4) instead of dichromate as the oxidizing agent.

The wastewater sample is boiled with a measured excess of permanganate in acid solution (H_2SO_4) for 30 min. The pink solution is cooled and a known excess of ammonium oxalate $[(\text{NH}_4)_2\text{C}_2\text{O}_4]$ is added, the solution becoming colorless. Excess oxalate is then titrated with KMnO_4 solution until the pink

color returns. Oxalate used is calculated by difference, and permanganate utilized is calculated from simple stoichiometry. Equation (2.8) corresponds to oxidation of the oxalate.



2.2.3. Rapid COD Tests

Several rapid COD tests have been proposed involving digestion with dichromate for periods of time shorter than the 2 hr prescribed in the standard test. In one of these techniques, the wastewater is digested with the $\text{K}_2\text{Cr}_2\text{O}_7$ - H_2SO_4 - AgSO_4 solution at 165°C for 15 min. The solution is diluted with distilled water and titrated with ferrous ammonium sulfate, as in the standard method.

In this test, COD yield for domestic sludge corresponds to approximately 65% of the value obtained by the standard method. For other wastewaters, COD yield ratio between the rapid and the standard test varies depending on the nature of the wastewater.

2.2.4. Instrumental COD Methods [11, 14, 15]

Instrumental COD methods are very fast and yield reproducible results. In this section, the Precision AquaRator developed by the Dow Chemical Company and licensed to the Precision Scientific Company is described. The COD measurement requires only about 2 min and data are reproducible to within $\pm 3\%$ or better. Results correlate well with those of the standard COD method and are much more consistent than BOD tests, which typically vary by $\pm 15\%$.

The AquaRator is designed to measure oxygen demand in the range of 10–300 mg/liter. Samples of higher concentration are handled by preliminary dilution of the sample. A flow diagram of the Precision AquaRator is shown in Fig. 2.1.

A 20- μl sample (20×10^{-6} liter ≈ 0.02 cm^3), homogenized if necessary, is injected by a syringe into the Precision AquaRator. (See sample injection port, SIP.) The sample is swept through a platinum catalytic combustion furnace (SF) by a stream of dry CO_2 , which oxidizes the contaminants to CO and H_2O . Water is stripped out in a drying tube (DT), and reaction products are then passed through a second platinum catalytic treatment. The CO concentration is measured by an integral nondispersive infrared analyzer (IA), sensitized for carbon monoxide. The resultant reading is directly converted to COD by use of a calibration chart.

Carbon dioxide flow is set at approximately 130 cm^3/min by the flow control system. Any trace of oxygen present in the feed gas is reduced by a "purifying" carbon furnace (PCF), yielding a background gas stream of CO

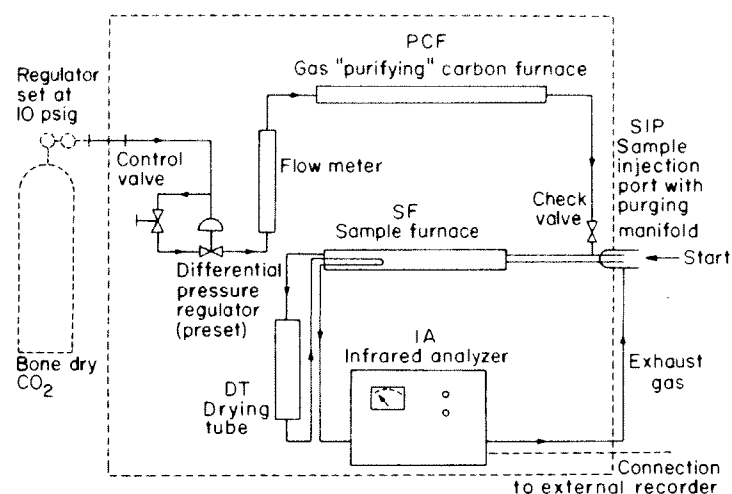
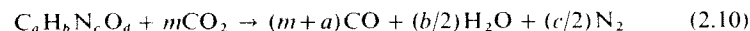
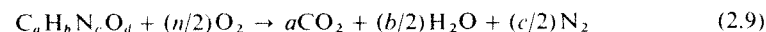


Fig. 2.1. Flow diagram of Precision AquaRator [11]. (Courtesy of Precision Scientific Company.)

and CO_2 which is indicated as a normal baseline of the recorder. The sample is injected into the sample furnace (SF), where contaminants and CO_2 react to form a typical mixture of CO , CO_2 , and H_2O . The infrared analyzer (IA) determines the increase of CO content in the gas stream, which is directly related to COD of the sample. Exhaust gas is then discharged through a sample inlet purging manifold.

The AquaRator theory is discussed in Stenger and Van Hall [14, 15]. Equations (2.9) and (2.10) indicate the types of reactions that take place when organic material is combusted in atmospheres of oxygen and carbon dioxide, respectively.



If oxygen required in Eq. (2.9) could be determined exactly, it would represent the ThOD of the sample. Ideally, the dichromate COD determination approaches this value, but some compounds are difficult to oxidize by the dichromate treatment. Oxidation which takes place in the AquaRator is more vigorous than dichromate oxidation, and thus results represent a more realistic level of oxygen demand of the contaminants present.

The originators of the method used in the AquaRator [14, 15] demonstrated that $(m+a)$ in Eq. (2.10) is equal to n in Eq. (2.9); that is, the number of moles of carbon monoxide produced is the same as the number of oxygen atoms

required. Therefore, instrument readings of carbon monoxide formed are directly related to chemical oxygen demand. Calibration is carried out by injecting standard solutions of sodium acetate trihydrate, for which oxygen demand in milligrams per liter can be calculated. A graph of oxygen demand vs. recorder output (chart divisions) is all that is required for determining the unknown contaminant demand.

2.3. BIOCHEMICAL OXYGEN DEMAND (BOD)

Biochemical oxygen demand is used as a measure of the quantity of oxygen required for oxidation of biodegradable organic matter present in the water sample by aerobic biochemical action. Oxygen demand of wastewaters is exerted by three classes of materials: (1) carbonaceous organic materials usable as a source of food by aerobic organisms; (2) oxidizable nitrogen derived from nitrite, ammonia, and organic nitrogen compounds which serve as food for specific bacteria (e.g., *Nitrosomonas* and *Nitrobacter*). This type of oxidation (nitrification) is discussed in Section 8; and (3) chemical reducing compounds, e.g., ferrous ion (Fe^{2+}), sulfites (SO_3^{2-}), and sulfide (S^{2-}), which are oxidized by dissolved oxygen.

For domestic sewage, nearly all oxygen demand is due to carbonaceous organic materials and is determined by BOD tests described in Sections 2.3.1 and 2.3.2. For effluents subjected to biological treatment, a considerable part of the oxygen demand may be due to nitrification (Section 8 of this chapter).

2.3.1. BOD Dilution Test

Detailed description of the dilution test as well as preparation of reagents is given in Ref. [13]. Procedure is given below.

1. Prepare several dilutions of the sample to be analyzed with distilled water of high purity. Recommended dilutions depend on estimated concentration of contaminants responsible for oxygen demand. For highly contaminated waters, dilution ratios (ml of diluted sample/ml of original sample) may be of 100:1. For river waters, the sample may be taken without dilution for low pollution streams, and in other cases dilution ratios of 4:1 may be utilized.

2. Incubation bottles (250- to 300-ml capacity), with ground-glass stoppers are utilized. In the BOD bottle one places (a) the diluted sample (i.e., the "substrate"), (b) a *seed* of microorganisms (usually the supernatant liquor from domestic sewage), and (c) nutrient solution for the microorganisms. This solution contains sodium and potassium phosphates and ammonium chloride (nitrogen and phosphorus are elements needed as nutrients for microorganisms).

The pH of the solution in the BOD bottle should be about 7.0 (neutral).

Phosphate solution utilized is a buffer. For samples containing caustic alkalinity or acidity, neutralization to about pH 7 is made with dilute H_2SO_4 or NaOH prior to the BOD test.

For each BOD bottle a control bottle, which does not contain the substrate, is also prepared.

3. Bottles are incubated at 20°C . Each succeeding 24-hr period, a sample bottle and a corresponding control bottle are taken from the incubator, and dissolved oxygen in both is determined as described at the end of this section. The difference between concentrations of dissolved oxygen (mg/liter) in control bottle and in sample bottle corresponds to the oxygen utilized in biochemical oxidation of contaminants [Eq. (2.11)].

$$y \text{ (mg/liter)} = \text{DO (control bottle)} - \text{DO (sample bottle)} \quad (2.11)$$

Values of y (BOD, mg/liter) are plotted vs. incubation time t (days). A typical BOD curve for oxidation of carbonaceous materials is shown in Fig. 2.2. Curves for cases where nitrification takes place are discussed in Section 8.

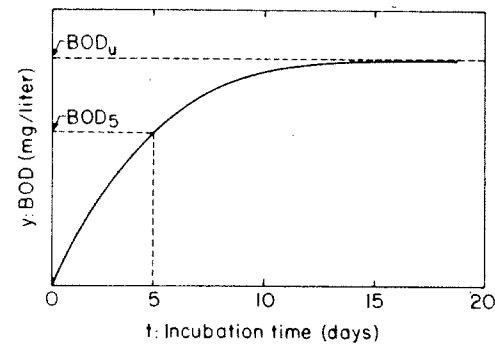


Fig. 2.2. Typical BOD curve for oxidation of carbonaceous materials.

Oxygen utilization in the BOD test is very slow. A typical curve (Fig. 2.2) only reaches the limiting BOD in about 20 days or more. This value is called *ultimate BOD*, denoted as BOD_u .

It is impractical to monitor continuously a process stream in terms of BOD because of the time factor involved in the test. In practice, BOD is reported in terms of 5-day BOD, denoted as BOD_5 (Fig. 2.2). Even 5 days is too long a period of time to wait for the result of a test.

It is important to notice that the value of BOD_u is not equal to ThOD, because in the BOD bottle not all substrate is oxidized. Ratios of values of BOD_u (or BOD_5) to ThOD depend on the chemical composition of the wastewater. Average values are given in Table 2.1.

The ratio of BOD_5 to BOD_u also varies according to the substrate. For

domestic sewage, this ratio is approximately 0.77 [Eq. (2.12)].

$$\text{BOD}_5/\text{BOD}_u = 0.77 \quad (2.12)$$

Considerable experience is required to obtain reliable results in the BOD dilution test. In general, reproducibility of results is not better than $\pm 15\%$. Some of the difficulties involved in the BOD dilution test are discussed in the next sections. Because of these fluctuations it is recommended that several BOD bottles be taken from the incubator every 24 hr and that statistical averaging of results be performed.

a. Ratio of COD and BOD_u

It has just been stated that values of BOD_u and ThOD are not equal. Similarly, the value of BOD_u is generally lower than that for COD obtained by the standard dichromate oxidation method, as indicated in Table 2.1. The reasons are that (1) many organic compounds which are oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$ are *not* biochemically oxidizable and (2) certain inorganic ions such as sulfides (S^{2-}), thiosulfates ($\text{S}_2\text{O}_3^{2-}$), sulfites (SO_3^{2-}), nitrites (NO_2^-), and ferrous ion (Fe^{2+}) are oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$, thus accounting for inorganic COD, which is not detected by the BOD test.

b. Effect of Seeding and Acclimation of Seed on the BOD Test

One of the most frequent reasons for unreliable BOD values is utilization of an insufficient amount of microorganism seed. Another serious problem for industrial wastes is acclimation of seed. For many industrial wastes, the presence of toxic materials interferes with growth of the microorganism population. BOD curves obtained exhibit a time lag period (Fig. 2.3).

Low BOD values are obtained if adequate corrective action is not taken. It becomes necessary to acclimate the microorganism seed to the specific

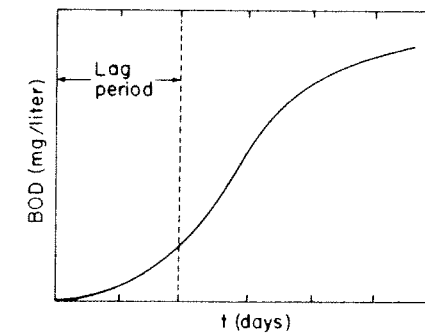


Fig. 2.3. Lag period in BOD test.

waste. This is achieved by starting with a sample of settled domestic sewage which contains a large variety of microorganisms, and adding a small amount of industrial effluent. Air is bubbled through this mixture. The operation is performed in bench scale reactors of either continuous or batch type. These reactors are described in Chapter 5, Section 6.1.

The process is repeated with gradual increase in the proportion of industrial waste to domestic sewage, until a microbial culture acclimated to the specific industrial waste is developed. This may be a long and difficult procedure for very toxic industrial wastewaters. When an acclimated culture has been developed, the BOD curve does not present a lag period, thus becoming a typical BOD curve of the general shape shown in Fig. 2.2.

c. Effect of Presence of Algae on the BOD Test

Presence of algae in the wastewater being tested affects the BOD test. If the sample is incubated in the presence of light, low BOD values are obtained owing to production of oxygen by photosynthesis, which satisfies part of the oxygen demand. On the other hand, if incubation is performed in darkness, algae survive for a while. Thus, short-term BOD determinations show the effect of oxygen on them. After a period in the dark, algae die and algal cells contribute to the increase of total organic content of the sample, thus leading to high BOD values. Therefore, the effect of algae on the BOD test is difficult to evaluate.

d. Glucose–Glutamic Acid Check

The quality of dilution water, which if contaminated leads to incorrect BOD values, the effectiveness of the seed, and the analytical technique are checked periodically by using pure organic compounds for which BOD is known or determinable. One of the most commonly used is a mixture of glucose ($C_6H_{12}O_6$) and glutamic acid [$HOOCCH_2CH_2CH(NH_2)COOH$]. A mixture of 150 mg/liter of each is recommended. Pure glucose has an exceptionally high oxidation rate with relatively simple seeds. When used with glutamic acid, the oxidation rate is stabilized and is similar to that of most municipal wastewaters. BOD of the standard glucose–glutamic acid solution is 220 ± 11 mg/liter. Any appreciable divergence from these values raises questions concerning quality of the distilled water or viability of the seeding material. If a variation greater than ± 20 –22 mg/liter occurs more frequently than 5% of the time, this indicates a faulty technique.

e. Determination of Dissolved Oxygen (DO)

The BOD dilution method requires determinations of the amount of dissolved oxygen. These determinations are performed by either titration or instrumental methods. The basic titration method is that of Winkler. Waste-

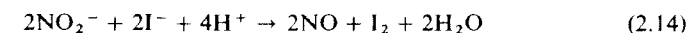
waters may contain several ions and compounds which interfere with the original DO determination. To eliminate these interferences, several modifications of the basic method have been proposed [13]. A brief description follows of the azide modification of Winkler's method, which effectively removes interference caused by nitrites. This is the most common interference found in practice. Other modifications to remove interferences are described in Ref. [13].

Winkler's method is based on oxidation of iodide ion (I^-), which is contained in the alkali–iodide–azide reagent, to iodine (I_2) by dissolved oxygen of the sample, and titration of the iodine by sodium thiosulfate ($Na_2S_2O_3$), utilizing starch as indicator. Oxidation is performed in acid medium (H_2SO_4) in the presence of manganese sulfate ($MnSO_4$). The alkali–iodide–azide reagent is a solution of NaOH, NaI, and NaN_3 (sodium azide).

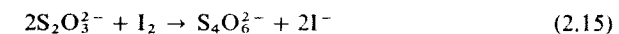
Equation (2.13) corresponds to the oxidation of I^- to I_2 .



Interference of nitrites is due to their oxidation to NO with formation of I_2 [Eq. (2.14)].



Titration of I_2 by thiosulfate corresponds to Eq. (2.15) [thiosulfate ($S_2O_3^{2-}$) is oxidized to tetrathionate ($S_4O_6^{2-}$)].



Starch yields a blue color in the presence of iodine. Titration with sodium thiosulfate is continued until the blue color disappears.

A variation of this procedure utilizes a new reagent (phenylarsine oxide, PAO) instead of sodium thiosulfate. This reagent has the advantage of being stable, whereas sodium thiosulfate deteriorates rapidly and should be re-standardized before each determination. A description of this improved procedure is found in Ref. [8].

Instrumental determination of dissolved oxygen is performed by DO analyzers. A diagram of a typical model of the instrument is shown in Fig. 2.4. The DO analyzer is a galvanic system which utilizes a cylinder-shaped lead anode surrounding a rod-shaped silver cathode. Both electrodes are covered by a layer of KOH electrolyte contained in a thin electrolytic pad. A plastic membrane covers the electrodes and electrolyte and serves as a selective diffusion barrier which is permeable to all gases, including molecular oxygen, but is virtually impermeable to ionic species which may be present in the wastewaters. To measure DO the probe is dipped into the sample. A cell current which is proportional to the oxygen concentration in the sample is measured directly in terms of mg/liter of dissolved oxygen by the needle in the oxygen

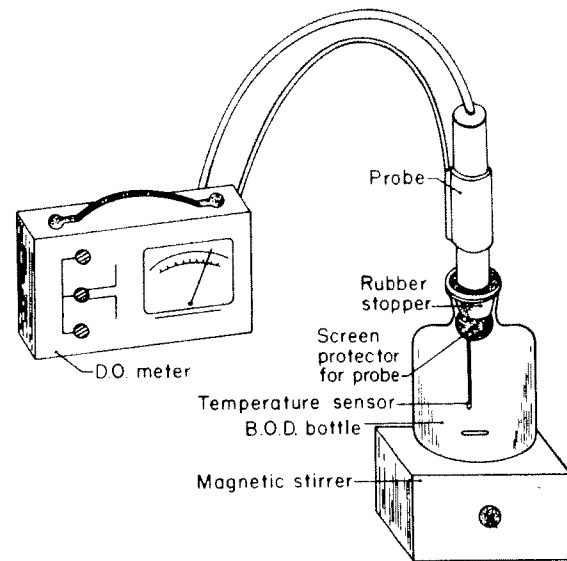


Fig. 2.4. Dissolved oxygen analyzer.

meter. The sample is constantly stirred during measurement, since only under these conditions is the current directly proportional to the oxygen concentration in the bulk of the test sample. Calibration of the DO analyzer is performed by measuring the DO of a sample of known oxygen content, which is determined by standard analytical methods (namely, the Winkler method) [13].

2.3.2. BOD Manometric Methods

The manometric apparatus described in this section is the Hach Model 2173 [7]. The Hach BOD apparatus has been compared with the standard dilution method under controlled laboratory conditions. In routine analysis it gives nearly equivalent results and precision. Since a physical change is observed, chemical laboratory analysis is not required. A diagram showing only one bottle is depicted in Fig. 2.5. The principle of operation is as follows: A measured sample of sewage or wastewater is placed in a bottle on the apparatus, which is connected to a closed-end mercury manometer. Above the sewage or water sample is a quantity of air (which contains approximately 21% oxygen by volume). Over a period of time bacteria in the sewage utilizes the oxygen to oxidize organic matter present in the sample, and thus dissolved oxygen is consumed. Air in the closed sample bottle replenishes the utilized oxygen, thus resulting in a drop of air pressure in the sample bottle. Mercury in the leg of the manometer connected to the bottle moves upward, as indicated by the arrow in Fig. 2.5. Thus, the pressure drop is registered on the mercury

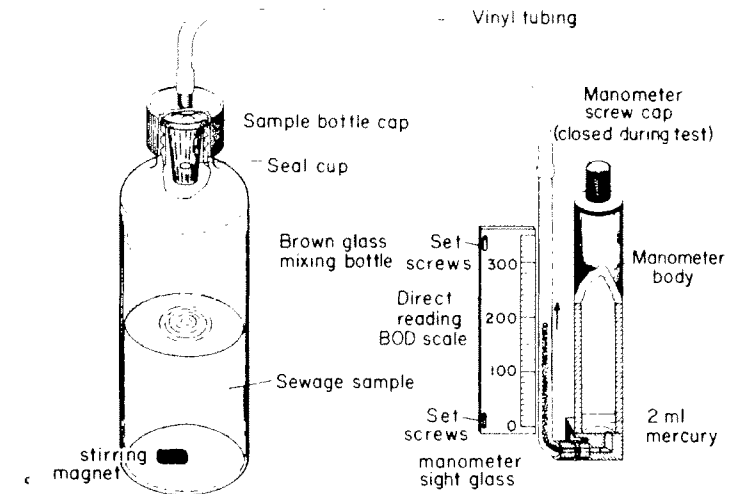


Fig. 2.5. Manometric BOD Apparatus (showing one cell) [7]. (Courtesy of Hach Chemical Company.)

manometer and read directly in mg/liter BOD. Prior to starting the test, set screws on the manometer scale are loosened and the zero mark is set at the top of the mercury column.

During the test period (5 days for BOD_5), the system is incubated at 20°C and the sample continually agitated by a magnetic stirring bar, which is rotated by a pulley system connected to a motor. Carbon dioxide is produced by oxidation of organic matter, and must be removed from the system so that it does not develop a positive gas pressure which would result in an error. This is accomplished by addition of a few drops of potassium hydroxide solution in the seal cup of each sample bottle. BOD readings are periodically checked by utilizing the standard glucose-glutamic acid solution.

When high oxygen demands are encountered the sample must be diluted. Accuracy of the manometric test is claimed as comparable to that of the dilution test.

2.4. TOTAL OXYGEN DEMAND (TOD) [6, 9, 17]

Usefulness of the standard COD method is due to the fact that results are obtained in 2 hr, rather than the 5 days taken for the common BOD measurement. However, the COD method is known *not* to oxidize contaminants as pyridine, benzene, and ammonia, although for many organic compounds oxidation has been reported as 95–100% of the theoretical.

Therefore, the search for improved analytical methods for determination of oxygen demand has focused on techniques [6] which are (1) meaningful and correlate with the accepted parameters for control and surveillance; (2) rapid, so results are known in minutes, not hours or days; and (3) truly adaptable to automation and continuous monitoring.

The Ionics model 225 Total Oxygen Demand (TOD) Analyzer determines total oxygen demand within 3 min. Figure 2.6 shows the functional elements of the system which includes the injection system, the combustion unit, the oxygen sensor assembly, and the recorder.

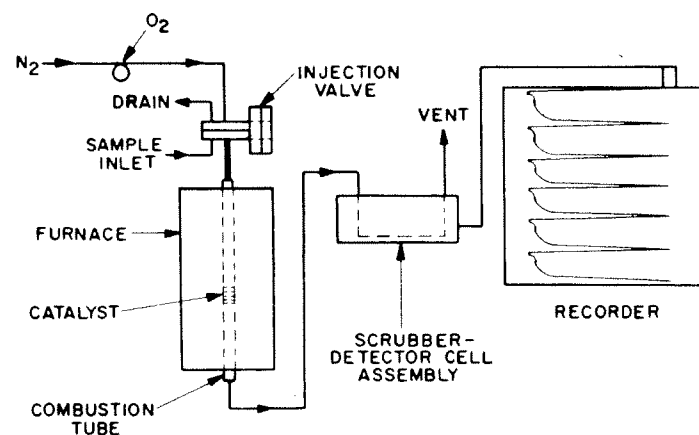


Fig. 2.6. Flow diagram for the TOD analyzer [6]. (Reprinted with permission. Copyright by The American Chemical Society.)

The wastewater sample is transmitted by an air-operated aspirator to the liquid injection valve. Upon actuation, the valve delivers a 20- μ l (0.02 cm³) sample into the combustion chamber. The sampling system is controlled by an adjustable program timer or by a manual pushbutton. A carrier gas (nitrogen) containing a small amount of oxygen of the order of 200 ppm is introduced simultaneously with the wastewater sample into the combustion chamber. The sample is vaporized and the combustible components are oxidized in a combustion tube. The tube, containing a platinum screen catalyst, is mounted in an electric furnace which is maintained at 900°C. As a result of the oxygen utilization in the combustion process, a momentary depletion of oxygen occurs in the inert gas stream. This depletion is accurately measured by passing the effluent through a platinum-lead fuel cell. Before entering the cell, the gas is scrubbed and humidified. Scrubbing is done by passing the gas through an aqueous caustic solution which removes carrier gas impurities harmful to the

detector cell and humidifies the gaseous sample. The fuel cell and scrubber are located in a thermostatically controlled and insulated chamber.

Fuel cell current output is a function of oxygen concentration. This is graphically monitored on a potentiometer recorder, with changes in current taking the form of recorder peaks. The recorder system includes an automatic zero circuit to maintain a constant baseline. Peaks recorded are linearly proportional to the reduced oxygen concentration in the carrier gas and the sample total oxygen demand. TOD measurement for unknown samples is determined by comparison of the recorded peak heights with a standard calibration curve. A typical calibration curve for standard solution analysis is shown in Fig. 2.7, which demonstrates the linearity of peak height vs. TOD.

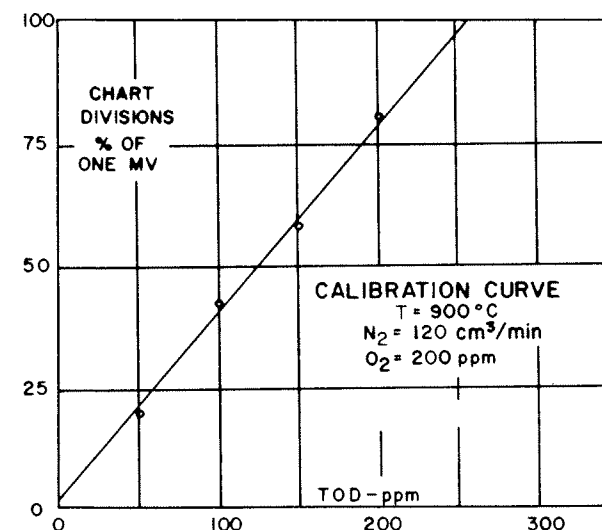
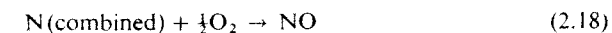


Fig. 2.7. Typical calibration curve for TOD analyzer [9]. (Courtesy of Ionics Incorporated.)

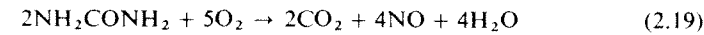
The TOD method measures the amount of oxygen consumed based on the following chemical reactions for the catalytic combustion process [Eqs. (2.16–2.18)].



Sulfurous compounds are oxidized to a stable condition consisting of a fixed

ratio of SO_2 to SO_3 . Molecular nitrogen, normally used as the carrier gas, does not react in the combustion process.

Equation (2.19) corresponds to a typical theoretical oxidation (for the case of urea).



Results of TOD analysis for a number of different compounds indicate that

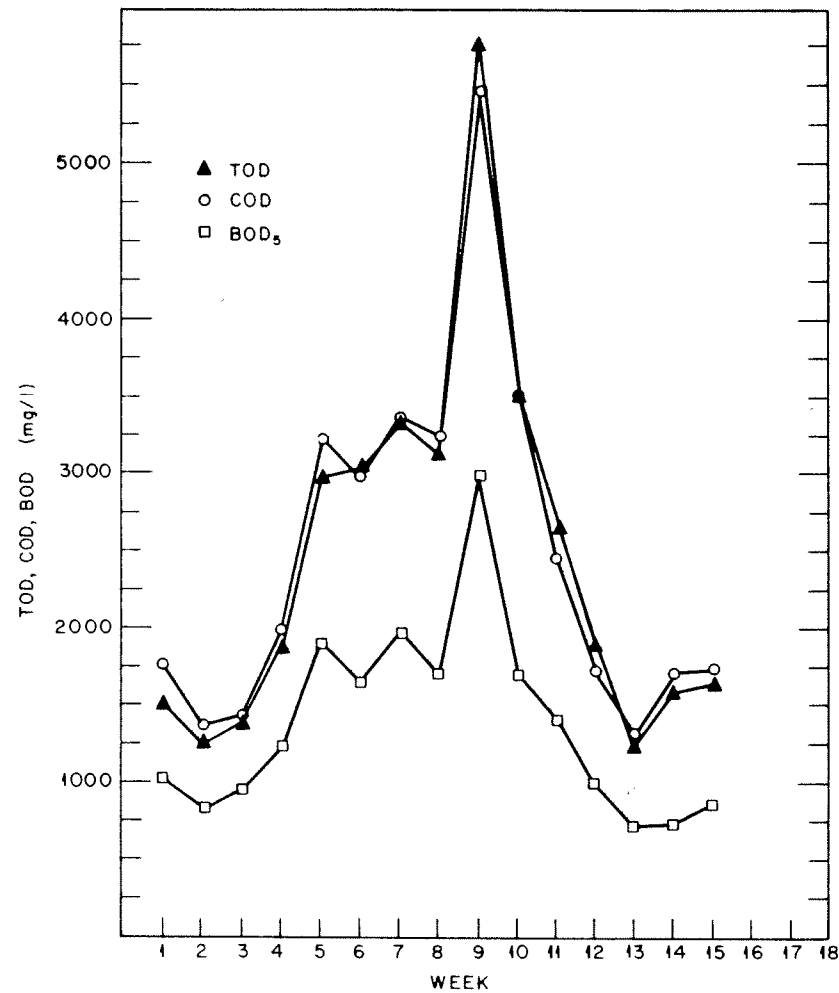


Fig. 2.8. Weekly analyses of a raw wastewater [17]. (Reprinted with permission. Copyright by The American Chemical Society.)

measured oxygen demand is usually closer to the theoretically calculated than is the case for chemical methods. These results are presented in Goldstein *et al.* [6]. None of the common ions normally found in water and wastewaters causes serious interference with TOD analyses [6].

Correlation of TOD analyses with COD has been checked for a number of typical waste streams [2, 3]. Figure 2.8 shows correlations of TOD, COD, and BOD₅ for a raw wastewater. Values of COD vs. TOD from Fig. 2.8 are plotted in Fig. 2.9, which shows a linear relationship. The relationship of TOD to COD or BOD₅ depends entirely on composition of the wastewater. Consequently, these ratios vary depending on the degree of biological treatment to which the wastewater is subjected.

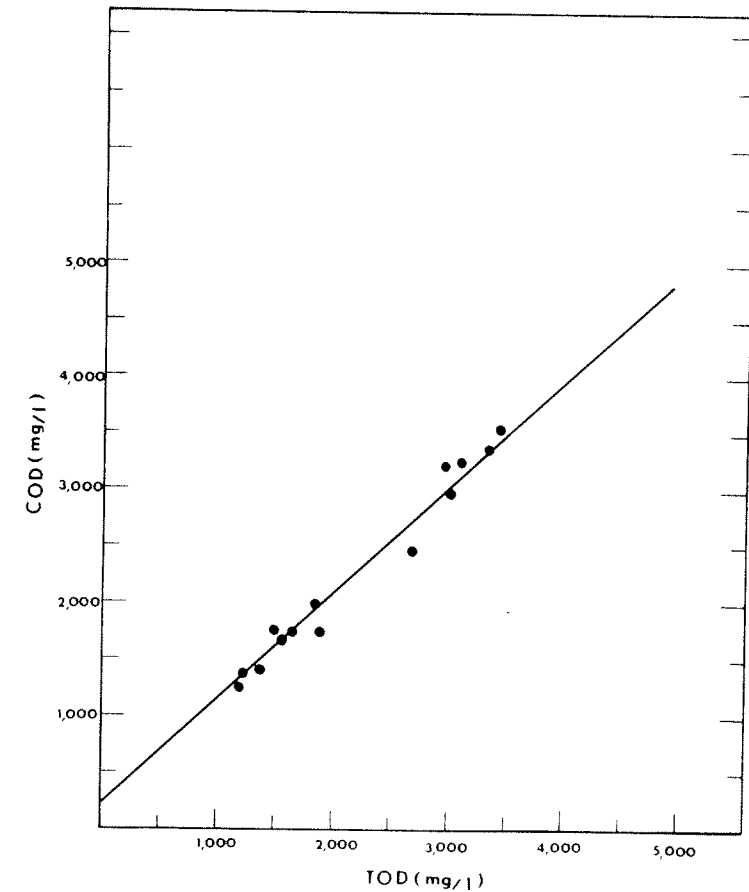
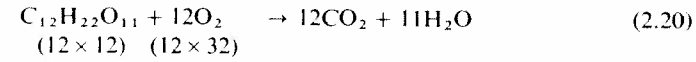


Fig. 2.9. The COD and TOD relationship of a raw wastewater [17]. (Reprinted with permission. Copyright by The American Chemical Society.)

3. Measurement of Organic Content: Group 2—Carbon Parameter Methods [2, 3]

Total organic carbon (TOC) tests are based on oxidation of the carbon of the organic matter to carbon dioxide, and determination of CO_2 either by absorption in KOH or instrumental analysis (infrared analyzer). Since theoretical oxygen demand (ThOD) measures O_2 and theoretical organic carbon (ThOC) measures carbon, the ratio of ThOD to ThOC is readily calculated from the stoichiometry of the oxidation equation.

Equation (2.20) corresponds to total oxidation of sucrose.



$$\therefore \text{ThOD/ThOC} = (12 \times 32)/(12 \times 12) = 2.67 \quad (2.21)$$

The ratio of molecular weights of oxygen to carbon is 2.67.

Thus, the theoretical ratio of oxygen demand to organic carbon corresponds to the stoichiometric ratio of oxygen to carbon for total oxidation of the organic compound under consideration. The actual ratio obtained from COD (or BOD) tests and TOC determinations varies considerably from this theoretical ratio (Section 3.3). Experimental determination of TOD is performed by either manual (wet oxidation) or instrumental methods.

3.1. WET OXIDATION METHOD FOR TOC

The manual or wet oxidation method for TOC consists of oxidation of the sample in a solution of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), fuming sulfuric acid (H_2SO_4), potassium iodate (KIO_3), and phosphoric acid (H_3PO_4). Oxidation products are passed through a tube containing KOH , where the carbon dioxide collected is determined by weighing the absorption tube before and after the experiment.

3.2. CARBON ANALYZER DETERMINATIONS [1]

The fundamental operating principle of TOC analyzers is combustion of organic matter to carbon dioxide and water. Combustion gases are then passed through an infrared analyzer, sensitized for carbon dioxide, and the response is recorded on a strip chart. A diagram of the Beckman model 915-A Total Organic Carbon (TOC) Analyzer is shown in Fig. 2.10. This instrument permits separate measurements for total carbon and inorganic carbon. Total carbon includes the carbon of organic materials and inorganic carbon in the form of carbonates (CO_3^{2-}), bicarbonates (HCO_3^-), and CO_2 dissolved in the sample. There are two separate reaction tubes: one operated

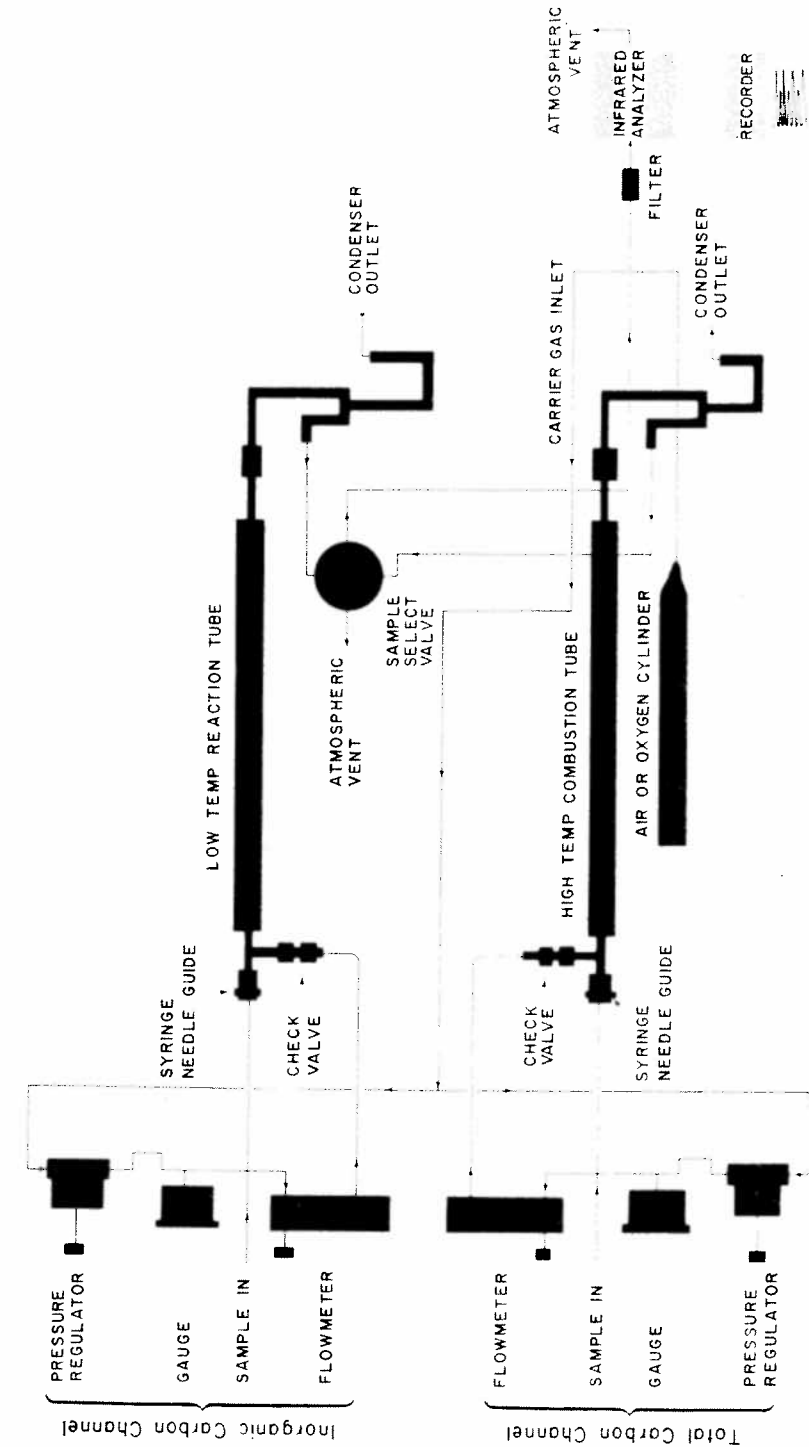


Fig. 2.10. Flow diagram of Beckman model 915-A Total Organic Carbon (TOC) Analyzer [1]. (Courtesy of Beckman Instruments, Inc.)

at high temperature (950°C) for measurement of total carbon and another operated at low temperature (150°C) for measurement of inorganic carbon.

Depending on range of analysis, a 20–200 μl water sample is syringe injected into a flowing stream of air and swept into a catalytic combustion tube containing a cobalt oxide-impregnated packing. The source of air which is used as carrier/oxidizer should be a low hydrocarbon, low CO_2 content cylinder. The combustion tube (high temperature combustion tube) is enclosed in an electric furnace thermostated at 950°C. Water is vaporized and all carbonaceous material is oxidized to CO_2 and steam. Airflow carries this cloud out of the furnace where the steam is condensed and removed. The CO_2 is swept into the nondispersive infrared analyzer.

Transient CO_2 is indicated as a peak on a strip chart recorder. Peak height is a measure of CO_2 present, which is directly proportional to the concentration of total carbon in the original sample and includes organic carbon, inorganic carbon, and CO_2 dissolved in the sample. By using standard solutions, the chart is calibrated in milligrams total carbon per liter of sample.

In a second operation, a sample of similar size is also syringe injected into a stream of air and swept into the second reaction tube (low temperature reaction tube), containing quartz chips wetted with 85% phosphoric acid. This tube is enclosed in an electric heater thermostated at 150°C, which is below the temperature at which organic matter is oxidized. The acid-treated packing causes release of CO_2 from inorganic carbonates, and the water is vaporized. Airflow carries the cloud of steam and CO_2 out of the furnace, where steam is condensed and removed. By previous repositioning of a dual channel selector valve, the CO_2 is swept into the infrared analyzer.

This quantity of CO_2 is also indicated on the strip chart recorder as a transient peak. Peak height is a measure of the CO_2 present, which is proportional to the concentration of inorganic carbonates plus CO_2 dissolved in the original sample. By using standard solutions, the chart is calibrated in milligrams inorganic carbon per liter of sample. Subtracting results obtained in the second operation from those in the first yields total organic carbon in milligrams TOC per liter of sample.

3.3. OXYGEN DEMAND–ORGANIC CARBON CORRELATION

The ratio ThOD/ThOC, which theoretically is equal to the stoichiometric ratio of oxygen to carbon for total oxidation of the organic compound under consideration, ranges in practice from nearly zero, when the organic matter is resistant to dichromate oxidation (e.g., pyridine), to values of the order of 6.33 for methane or even slightly higher when inorganic reducing agents are present. Table 2.2 presents relationships between oxygen demand and total carbon for several organic compounds.

Table 2.2
Relationships between Oxygen Demand and Total Carbon for Organic Compounds [3]

Substance	ThOD/ThOC (calculated)	COD/TOC (measured)
Acetone	3.56	2.44
Ethanol	4.00	3.35
Phenol	3.12	2.96
Benzene	3.34	0.84
Pyridine	3.33	—
Salicylic acid	2.86	2.83
Methanol	4.00	3.89
Benzoic acid	2.86	2.90
Sucrose	2.67	2.44

Correlation of BOD with TOC for industrial wastewaters is difficult because of their considerable variation in chemical composition. For domestic wastewaters a relatively good correlation has been obtained, which is represented by the straight line relationship given by Eq. (2.22).

$$\text{BOD}_2 = 1.87(\text{TOC}) - 17 \quad (2.22)$$

4. Mathematical Model for the BOD Curve

It is desirable to represent the BOD curve (Fig. 2.2) by a mathematical model. From kinetic considerations (Chapter 5, Section 3), the mathematical model utilized to portray the rate of oxygen utilization is that of a first-order reaction. Figure 2.2 reveals that the rate of oxygen utilization, given by the tangent to the curve at a given incubation time, decreases as concentration of organic matter remaining unoxidized becomes gradually smaller. Since there is a proportionality between the rate of oxygen utilization and that of destruction of organic matter by biological oxidation, rate equation [Eq. (2.23)] is written in terms of organic matter concentration (L ; mg/liter).

$$dL/dt = -k_1 L \quad (2.23)$$

where L is concentration of organic matter (mg/liter) at time t ; dL/dt , rate of disappearance of organic matter by aerobic biological oxidation ($dL/dt < 0$); t , time of incubation (days); and k_1 , rate constant (day^{-1}).

Separating variables L and t , and integrating from time zero corresponding to initial concentration of organic matter, L_0 , to a time t corresponding to concentration L [Eq. (2.24)]:

$$\ln(L/L_0) = -k_1 t \quad (2.24)$$

Changing to decimal logarithms [Eq. (2.25)]

$$\log(L/L_0) = -k_1 t / 2.303 \quad (2.25)$$

let $k_1/2.303 = k$. Then [Eq. (2.26)]

$$L/L_0 = 10^{-kt} \quad (2.26)$$

or

$$L = L_0 \cdot 10^{-kt} \quad (2.27)$$

Let y be the organic matter oxidized up to time t , i.e.,

$$y = L_0 - L \quad (2.28)$$

Conversely, y also measures the oxygen consumption up to time t , i.e., the ordinate of the BOD curve in Fig. 2.2 at time t . Combining Eqs. (2.28) and (2.27),

$$y = L_0(1 - 10^{-kt}) \quad (2.29)$$

which is the mathematical model for the BOD curve. From Eq. (2.29) it follows that for a very long oxidation period (i.e., $t \rightarrow \infty$), $y = L_0$. Therefore, k and L_0 measure, respectively, the rate of biochemical stabilization and the total amount of putrescible matter present.

From Eq. (2.27)

$$\log L = \log L_0 - kt \quad (2.30)$$

Equation (2.30) indicates that constants k and L_0 can be obtained from a semilogarithmic plot of L vs. t . Typical values of the rate constant k are presented in Chapter 5 for several types of wastewaters (Table 5.2, Section 5).

5. Determination of Parameters k and L_0

In application of Eq. (2.29) one usually has available a series of BOD measurements (y) at a sequence ($n = 1, 2, 3, \dots, x$) days. It is desired to determine the optimum values of parameters k and L_0 which satisfy Eq. (2.29) for the set of data. Thus, it is fundamentally a curve-fitting problem.

Several methods for calculating parameters k and L_0 have been proposed. Three of these, recommended by Eckenfelder [3], are (1) log-difference method, (2) method of moments [10], and (3) Thomas' graphical method.

5.1. LOG-DIFFERENCE METHOD

This method is based on the following considerations. Differentiating Eq. (2.29) with respect to t :

$$dy/dt = r = L_0(-10^{-kt})(\ln 10)(-k) \quad (2.31)$$

or

$$dy/dt = r = 2.303L_0k \cdot 10^{-kt} \quad (2.32)$$

where r is the rate of oxygen utilization. Taking decimal logarithms

$$\log r = \log(2.303L_0k) - kt \quad (2.33)$$

Equation (2.33) indicates that k and L_0 can be obtained from a semilog plot of r vs. t .

Step 1. Plot y (oxygen utilization) vs. t on cartesian coordinate paper. Draw a smooth best-fit curve through the points, discarding data which seem to be in error.

Step 2. Plot daily differences, $\Delta y/\Delta t$ vs. time (on semilog graph paper). Time intervals are usually taken as 0, 1, 2, 3, ... days, so that $\Delta t = 1$. Values of Δy 's are conventionally plotted vs. the time t corresponding to the middle of each interval (e.g., the value of Δy corresponding to interval 0-1 is plotted vs. $t = 0.5$).

Draw the best-fit straight line through these points.

Step 3. Calculation of k and L_0 . From the straight line drawn in Step 2, Eq. (2.33) yields:

$$k = -(\text{slope}) \quad (2.34)$$

$$\text{Intercept} = 2.303L_0k \quad (2.35)$$

$$\therefore L_0 = \text{intercept}/(2.303k) = \text{intercept}/(2.303)(-\text{slope}) \quad (2.36)$$

Therefore, k and L_0 are calculated from Eqs. (2.34) and (2.36), respectively.

Example 2.1

The data in Table 2.3 on oxygen utilization are available from BOD tests of a wastewater.

Obtain the values of k and L_0 in the BOD equation.

TABLE 2.3
BOD Tests of Wastewater

t (days)	y (mg/liter of BOD)
0	0.0
1	9.2
2	15.9
3	20.9
4	24.4
5	27.2
6	29.1
7	30.6

SOLUTION

Step 1. Data are plotted in Fig. 2.11. The curve is fairly smooth and the raw data are used in Step 2. If needed, smoothing is done by the best straight-line fit.

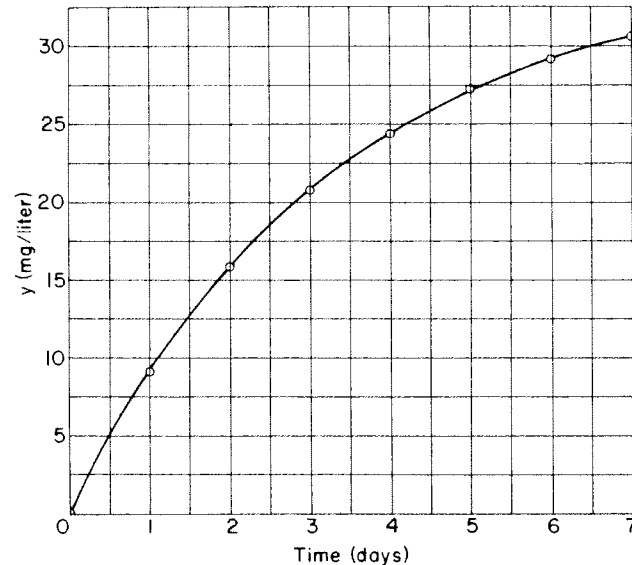


Fig. 2.11. Plot y vs. t (Example 2.1).

Step 2. Construct the difference table (Table 2.4). Values in column (3) are plotted vs. those in column (4) on semilog paper. This plot is shown in Fig. 2.12.

TABLE 2.4
Log-Difference Values from Table 2.3

(1) t (days)	(2) y (mg/liter)	(3) Δy (mg/liter) = $\Delta y/\Delta t$; since $\Delta t = 1$	(4) Mid-interval values of t
0	0	—	—
1	9.2	9.2	0.5
2	15.9	6.7	1.5
3	20.9	5.0	2.5
4	24.4	3.5	3.5
5	27.2	2.8	4.5
6	29.1	1.9	5.5
7	30.6	1.5	6.5

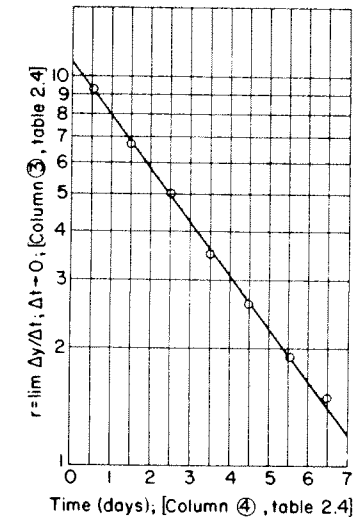


Fig. 2.12. Calculation of k and L_0 by the log-difference method.

Step 3. Calculate k and L_0 .

(a) *Calculation of k .* Base calculations on the coordinates of two points on the straight line (7, 1.2; 0, 10.9) and Eq. (2.34).

$$\text{Slope} = (\log 10.9 - \log 1.2)/(0 - 7) = -0.137$$

$$\therefore k = 0.137 \text{ day}^{-1}$$

(b) *Calculation of L_0 .* From Eq. (2.36)

$$L_0 = 10.9/(2.303 \times 0.137) = 34.5 \text{ mg/liter}$$

5.2. METHOD OF MOMENTS [10]

This method is of simple application once diagrams of $\sum y/L_0$ vs. k and $\sum y/\sum ty$ vs. k are constructed for an n -day sequence of BOD measurements. Equations are derived next for construction of Moore's diagrams for an n -day sequence of BOD measurements. These equations are applied to 7-, 5-, and 3-day sequences, yielding Figs. 2.13–2.15, respectively.

Consider BOD measurements taken over an n -day sequence, as indicated in Table 2.5. First, calculate ratio $\sum y/L_0$. The summation of entries in column (2) of Table 2.5 is [Eq. (2.37)]

$$\sum y = L_0[(1 + 1 + 1 + \dots + 1) - (10^{-k} + 10^{-2k} + 10^{-3k} + \dots + 10^{-nk})] \quad (2.37)$$

or

$$\sum y = L_0[n - (10^{-k} + 10^{-2k} + 10^{-3k} + \dots + 10^{-nk})] \quad (2.38)$$

TABLE 2.5
BOD Measurements, n -Day Sequence

(1) t (days)	(2) Eq. (2.29); $t = 1, 2, 3, \dots, n$; $y = L_0(1 - 10^{-kt})$	(3) = (1) \times (2) ty
1	$L_0(1 - 10^{-k})$	$L_0(1 - 10^{-k})$
2	$L_0(1 - 10^{-2k})$	$2L_0(1 - 10^{-2k})$
3	$L_0(1 - 10^{-3k})$	$3L_0(1 - 10^{-3k})$
4	$L_0(1 - 10^{-4k})$	$4L_0(1 - 10^{-4k})$
5	$L_0(1 - 10^{-5k})$	$5L_0(1 - 10^{-5k})$
6	$L_0(1 - 10^{-6k})$	$6L_0(1 - 10^{-6k})$
7	$L_0(1 - 10^{-7k})$	$7L_0(1 - 10^{-7k})$
—	—	—
—	—	—
n	$L_0(1 - 10^{-nk})$	$nL_0(1 - 10^{-nk})$
	$\sum y$	$\sum ty$

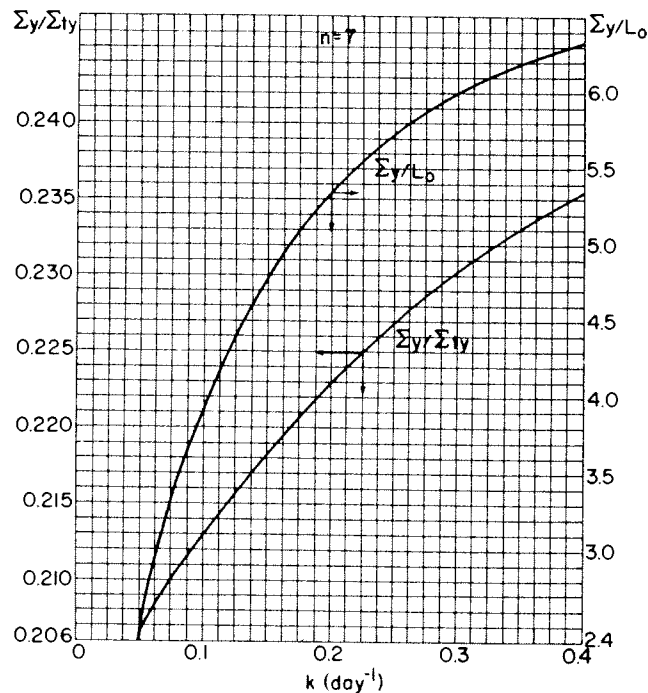


Fig. 2.13. Moore's method (7-day sequence).

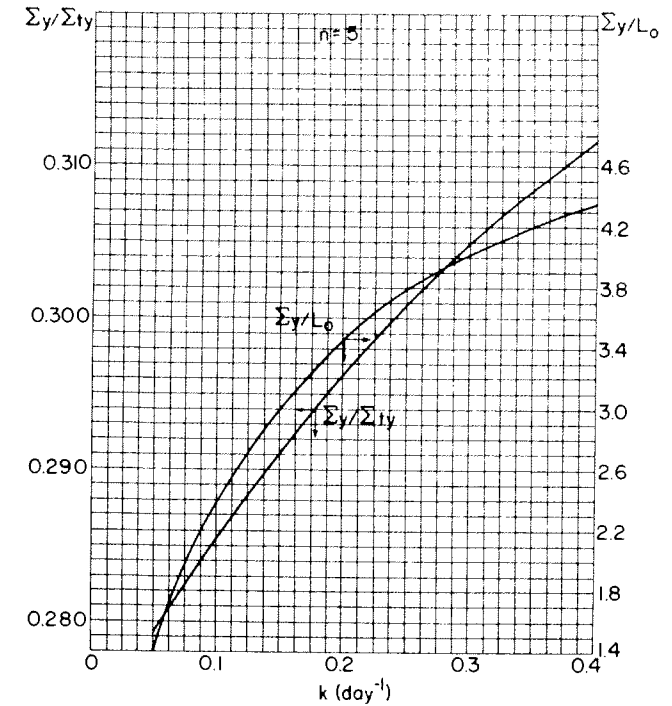


Fig. 2.14. Moore's method (5-day sequence).

The terms within parentheses in Eq. (2.38) form a geometrical progression for which the sum of terms is [Eq. (2.39)]

$$S = [(10^{-k})(10^{-nk} - 1)] / (10^{-k} - 1) \tag{2.39}$$

Substituting this value in Eq. (2.38) and solving for the ratio $\sum y/L_0$:

$$\sum y/L_0 = n - [10^{-k}(10^{-nk} - 1)] / (10^{-k} - 1) \tag{2.40}$$

From Eq. (2.40) it follows that for a given sequence of n days, the ratio $\sum y/L_0$ is only a function of k . Thus for a fixed n , one assumes values of k and plots a curve of $\sum y/L_0$ vs. k .

Now calculate ratio $\sum y/\sum ty$. $\sum y$ is obtained from Eq. (2.40), and $\sum ty$ corresponds to summation of entries in column (3) of Table 2.5.

$$\sum ty = L_0[(1 + 2 + 3 + \dots + n) - (10^{-k} + 2 \times 10^{-2k} + 3 \times 10^{-3k} + \dots + n \times 10^{-nk})] \tag{2.41}$$

or

$$\sum ty = L_0 \left(\sum_{i=1}^{i=n} i - \sum_{i=1}^{i=n} i \times 10^{-ik} \right) \tag{2.42}$$

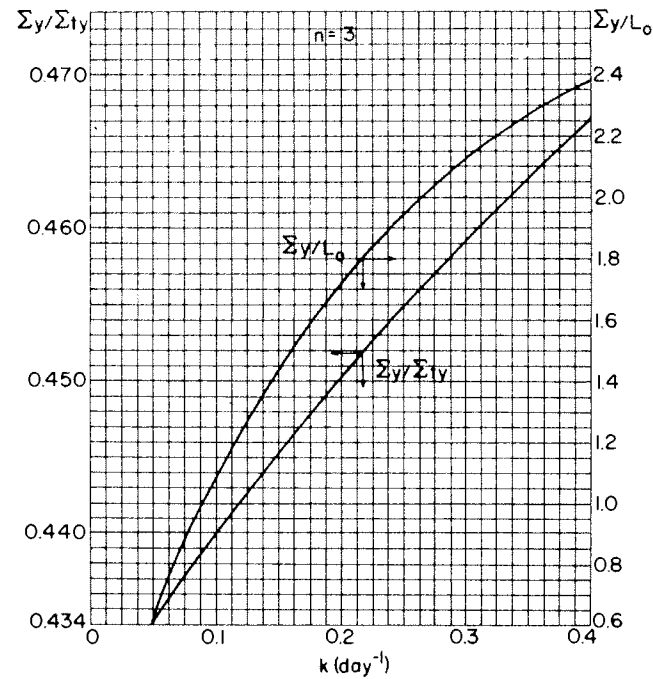


Fig. 2.15. Moore's method (3-day sequence).

Therefore, from Eqs. (2.40) and (2.42), ratio $\sum y/\sum ty$ is

$$\sum y/\sum ty = \frac{n - [10^{-k}(10^{-nk} - 1)/(10^{-k} - 1)]}{\sum_{i=1}^n i - \sum_{i=1}^n i \times 10^{-ik}} \quad (2.43)$$

From Eq. (2.43) it follows that for a given sequence of n days, ratio $\sum y/\sum ty$ is only a function of k . Thus for a fixed n , one assumes values of k and plots a curve of $\sum y/\sum ty$ vs. k from Eq. (2.43).

For specific cases such as the 7-day sequence, Eqs. (2.40) and (2.43) yield Eq. (2.44).

For $n = 7$

$$\sum y/L_0 = 7 - [10^{-k}(10^{-7k} - 1)/(10^{-k} - 1)] \quad (2.44)$$

$$\sum y/\sum ty = \frac{7 - [10^{-k}(10^{-7k} - 1)/(10^{-k} - 1)]}{28 - \sum_{i=1}^7 i \times 10^{-ik}} \quad (2.45)$$

where, in Eq. (2.45)

$$\sum_{i=1}^n i = \sum_{i=1}^7 i = 1 + 2 + 3 + 4 + 5 + 6 + 7 = 28$$

and

$$\sum_{i=1}^7 i \times 10^{-ik} = 10^{-k} + 2 \times 10^{-2k} + 3 \times 10^{-3k} + 4 \times 10^{-4k} + 5 \times 10^{-5k} + 6 \times 10^{-6k} + 7 \times 10^{-7k}$$

Figures 2.13-2.15 present graphs of $\sum y/L_0$ vs. k and $\sum y/\sum ty$ vs. k for 7-, 5-, and 3-day sequences, respectively. These figures are constructed from Eqs. (2.40) and (2.43), respectively, by assuming values of n (7, 5, 3) and k and calculating the corresponding ratios.

Application of Moore's diagram for calculation of parameters k and L_0 is illustrated by Example 2.2.

Example 2.2

Determine values of k and L_0 from the set of BOD determinations of Example 2.1.

SOLUTION

Step 1. Construct Table 2.6.

TABLE 2.6
Application of Moore's Method (Example 2.2)

t (days)	y (mg/liter BOD)	ty
0	0.0	0.0
1	9.2	9.2
2	15.9	31.8
3	20.9	62.7
4	24.4	97.6
5	27.2	136.0
6	29.1	174.6
7	30.6	214.2
	$\sum y = 157.3$	$\sum ty = 726.1$

Step 2. Calculate ratio $\sum y/\sum ty$.

$$\sum y/\sum ty = 157.3/726.1 = 0.217$$

Step 3. From Fig. 2.13 ($n = 7$) read for $\sum y/\sum ty = 0.217$.

$$k = 0.140 \text{ day}^{-1} \text{ (Abscissa of lower curve)}$$

From the ordinate of upper curve read

$$\sum y/L_0 = 4.62$$

$$\therefore L_0 = \sum y/4.62 = 157.3/4.62 = 34.05 \text{ mg/liter}$$

These values of k and L_0 agree closely with those calculated by the log-difference method in Example 2.1 ($k = 0.137 \text{ day}^{-1}$ and $L_0 = 34.5 \text{ mg/liter}$).

5.3. THOMAS' GRAPHICAL METHOD [16]

This is an approximate method which is justified since precision of the experimental results is often limited. The method is based on the similarity of the function

$$(1 - 10^{-kt}) \quad (2.46)$$

which is a factor of Eq. (2.29), and the function

$$2.3kt[1 + (2.3/6)kt]^{-3} \quad (2.47)$$

This similarity is seen in their respective series expansions, which are

$$(1 - 10^{-kt}) = (2.3kt)[1 - (1/2)(2.3kt) + (1/6)(2.3kt)^2 - (1/24)(2.3kt)^3 + \dots] \quad (2.48)$$

and

$$2.3kt[1 + (2.3/6)kt]^{-3} = (2.3kt)[1 - (1/2)(2.3kt) + (1/6)(2.3kt)^2 - (1/21.6)(2.3kt)^3 + \dots] \quad (2.49)$$

Comparison of the right-hand members of Eqs. (2.48) and (2.49) reveals that the first three terms in the two series within brackets are identical, and that the difference between the fourth terms is small. Replacing the function between parentheses in Eq. (2.29) by its approximation given by Eq. (2.47) yields Eq. (2.50).

$$y = L_0(2.3kt)[1 + (2.3/6)kt]^{-3} \quad (2.50)$$

from which, taking the inverse and rearranging,

$$t/y = [1 + (2.3/6)kt]^3 / 2.3kL_0 \quad (2.51)$$

Taking the cube root of both members of Eq. (2.51) and rearranging,

$$(t/y)^{1/3} = 1/(2.3kL_0)^{1/3} + [(2.3k)^{2/3}/6L_0^{1/3}]t \quad (2.52)$$

From Eq. (2.52), a plot of $(t/y)^{1/3}$ vs. t yields a straight line (Fig. 2.16 for Example 2.3) from which

$$\text{Slope} = B = (2.3k)^{2/3}/6L_0^{1/3} \quad (2.53)$$

$$\text{Intercept} = A = 1/(2.3kL_0)^{1/3} \quad (2.54)$$

From Eqs. (2.53) and (2.54) one obtains Eqs. (2.55) and (2.56).

$$k = 6B/2.3A = 2.61(B/A) \quad (2.55)$$

$$L_0 = 1/(2.3kA^3) \quad (2.56)$$

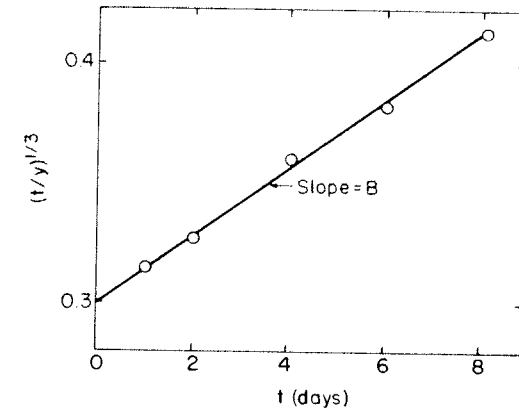


Fig. 2.16. Application of Thomas' method [14].

Application of this method is illustrated by Example 2.3.

Example 2.3 [16]

The BOD results tabulated below are observed on a sample of raw sewage at 23°C. Calculate parameters k and L_0 .

t (days)	y (BOD, mg/liter)
0	0
1	32
2	57
4	84
6	106
8	111

SOLUTION

Step 1. Construct Table 2.7.

TABLE 2.7
Application of Thomas' Method (Example 2.3)

(1) t	(2) y	(3) = (1) ÷ (2) t/y	(4) = [(3)] ^{1/3} $(t/y)^{1/3}$
0	0	—	—
1	32	0.03125	0.315
2	57	0.03509	0.327
4	84	0.04762	0.362
6	106	0.05660	0.384
8	111	0.07207	0.416

Step 2. Plot $(t/y)^{1/3}$ vs. t . The plot is shown in Fig. 2.16. From Fig. 2.16 obtain

$$A = 0.30 \quad (\text{intercept})$$

$$B = (0.416 - 0.300)/(8.0 - 0.0) = 0.0145 \quad (\text{slope})$$

Step 3. From Eqs. (2.55) and (2.56), obtain k and L_0 .

$$k = 2.61(0.0145/0.30) = 0.13 \text{ day}^{-1}$$

$$L_0 = 1/[2.3 \times 0.13(0.30)^3] = 124 \text{ mg/liter}$$

6. Relationship between k and Ratio $\text{BOD}_5/\text{BOD}_u$

Equation (2.29) is written as in Eq. (2.57) for $t = 5$ days, letting $y = \text{BOD}_5$ and $L_0 = \text{BOD}_u$.

$$\text{BOD}_5 = \text{BOD}_u(1 - 10^{-5k}) \quad (2.57)$$

from which

$$\text{BOD}_5/\text{BOD}_u = 1 - 1/10^{5k} \quad (2.58)$$

Assuming values of k , a curve of $\text{BOD}_5/\text{BOD}_u$ vs. k is plotted from Eq. (2.58). This curve rises with increasing k 's, reaching a plateau corresponding to an ordinate $\text{BOD}_5/\text{BOD}_u$ approaching unity for values of k beyond 0.3 [3].

From Eq. (2.58) for large values of k , $\text{BOD}_5/\text{BOD}_u$ approaches unity. This means that for a given substrate, if the rate of biochemical oxidation is very high, the value of BOD_5 is essentially equal to that of the ultimate BOD.

7. Environmental Effects on the BOD Test

The BOD test is affected by temperature and pH.

7.1. EFFECT OF TEMPERATURE

The reaction rate constant k is directly affected by temperature. The temperature dependence of k is given by the van't Hoff-Arrhenius equation [Eq. (2.59)].

$$d \ln k / dT = E / RT^2 \quad (2.59)$$

where k is reaction rate constant; T , absolute temperature; R , universal gas constant; and E , activation energy for the reaction (common values for wastewater treatment processes are in the range of 2000–20,000 cal/g mole). Integrating between limits [Eq. (2.60)]:

$$\ln(k_2/k_1) = [E(T_2 - T_1)] / (RT_1 T_2) \quad (2.60)$$

Since most wastewater treatment processes take place at nearly room temperature, the term $E/RT_1 T_2$ is nearly constant. Let it be denoted as C . Then [Eq. (2.61)]

$$\ln(k_2/k_1) = C(T_2 - T_1) \quad (2.61)$$

$$\therefore k_2/k_1 = e^{C(T_2 - T_1)} \quad (2.62)$$

Let $e^C = \theta =$ temperature coefficient. Then

$$k_2/k_1 = \theta^{(T_2 - T_1)} \quad (2.63)$$

The most usual application consists of estimation of constant k at a temperature T from its value determined experimentally at 20°C. From Eq. (2.63) we obtain Eq. (2.64).

$$k_T = k_{20} \theta^{(T - 20)} \quad (2.64)$$

where k_T is reaction rate at $T^\circ\text{C}$; k_{20} , reaction rate at 20°C; and T , temperature ($^\circ\text{C}$). Although θ is approximately constant, it varies slightly with temperature and its appropriate value should be selected. Values given below are those recommended by Schroepfer [12].

$$\theta = 1.135 \quad (4^\circ - 20^\circ\text{C})$$

$$\theta = 1.056 \quad (20^\circ - 30^\circ\text{C})$$

From Eq. (2.64) it follows that for a 10° rise in temperature the reaction rate nearly doubles.

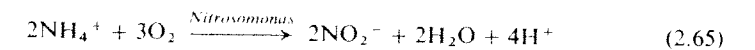
7.2. EFFECT OF pH

The standard BOD test specifies a pH of 7.2. If the pH is not 7.2, values of BOD_5 obtained are lower. It is recommended, therefore, to adjust the pH to 7.2. A typical curve of percentage of normal 5-day BOD vs. pH is presented by Eckenfelder and Ford [4]; its maximum (100%) corresponding to pH 7.2.

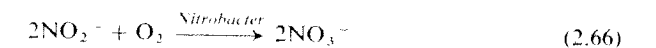
8. Nitrification

Equation (2.29) describes the oxidation of carbonaceous matter. Oxidation of nitrogenous material also contributes to oxygen demand if incubation is carried out for a sufficiently long period of time. This oxidation (referred to as nitrification) takes place in two steps:

1. Ammonium ion, NH_4^+ , is oxidized to nitrites in the presence of *Nitrosomonas* microorganisms [Eq. (2.65)].



2. Nitrites are then oxidized to nitrates in the presence of *Nitrobacter* microorganisms [Eq. (2.66)].



Rate constants, k , for nitrification are much lower than those for oxidation of carbonaceous matter. Although oxidation of carbonaceous and nitrogenous matter may occur simultaneously, nitrification normally does not begin until the carbonaceous oxygen demand is partially satisfied.

A typical BOD curve for a wastewater showing carbonaceous oxidation and nitrification phases is shown in Fig. 2.17. Nitrification is suppressed by

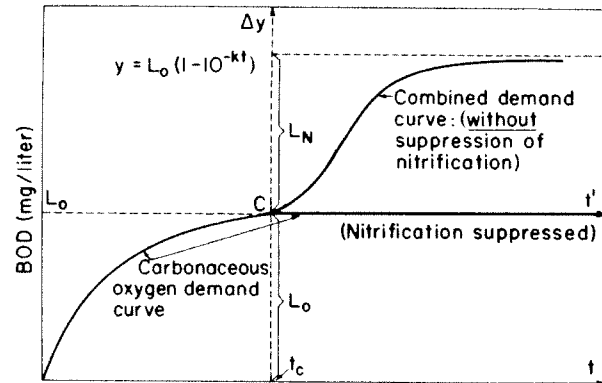


Fig. 2.17. Carbonaceous and nitrogenous BOD.

addition of certain chemicals (e.g., methylene blue, thiourea). If this is done, the BOD curve thus obtained approaches a limiting ordinate L_0 (ultimate carbonaceous demand), as indicated in Fig. 2.17. Beyond time t_c , the carbonaceous oxygen demand is essentially satisfied, so the ordinate value becomes constant at L_0 . If, on the other hand, nitrification is not suppressed beyond $t = t_c$, the effect of nitrification is superimposed on the carbonaceous oxygen demand to yield the combined oxygen demand curve (carbonaceous + nitrification demand).

The carbonaceous oxygen demand curve is described by Eq. (2.29). If a translation of coordinate axes is performed so that the origin of the new system of coordinates coincides with point C (system Δy vs. t'), the equation for the nitrification oxygen demand curve [Eq. (2.67)] is written as

$$\Delta y = L_N(1 - 10^{-k_N t'}) \quad (t > t_c) \quad (2.67)$$

where $t' = t - t_c$. Thus

$$\Delta y = L_N[1 - 10^{-k_N(t-t_c)}] \quad (2.68)$$

where k_N is the rate constant for nitrogenous demand and L_N the ultimate nitrogenous demand. The abscissa axis of the coordinate system Δy vs. t' essentially coincides with the carbonaceous oxygen demand curve beyond $t = t_c$.

Equations (2.29) and (2.69) for combined oxygen demand curve are

For $t < t_c$ (carbonaceous oxygen demand only)

$$y = L_0(1 - 10^{-kt}) \quad (2.29)$$

For $t > t_c$

$$y = \underbrace{L_0(1 - 10^{-kt})}_{\text{for } t > t_c, \text{ } L_0(1 - 10^{-kt}) \rightarrow L_0} + \underbrace{L_N[1 - 10^{-k_N(t-t_c)}]}_{\text{increment } \Delta y \text{ due to nitrogenous demand}} \quad (2.69)$$

Values of parameters k_N and L_N are determined by any of the methods previously discussed with reference to the new system of coordinates [i.e., Eq. (2.68)].

9. Evaluation of Feasibility of Biological Treatment for an Industrial Wastewater

9.1. INTRODUCTION

Frequently, it is necessary to conduct treatability studies for streams of industrial wastewaters, since they may contain toxic substances which have an adverse effect on biological systems. The problem of acclimation of microorganism seed to toxic substances is discussed in Section 2.3.1. Two types of tests to evaluate the feasibility of biological treatment for industrial wastewater [4] are (1) manometric techniques (*Warburg respirometer*), and (2) batch reactor evaluation.

9.2. WARBURG RESPIROMETER

A schematic diagram of the Warburg respirometer is shown in Fig. 2.18. The principle of operation, which consists in respiring a wastewater sample in a closed air atmosphere at constant temperature, is identical to that of the BOD manometric apparatus (Section 2.3.2). Oxygen utilized is measured with respect to time by noting the decrease in pressure of the system at constant volume. The CO_2 evolved is absorbed by a solution of KOH; thus the decrease in pressure is a measure of oxygen consumption only.

Steps in the operational procedure are given below [4].

1. The wastewater sample is placed in the sample flask with the required volume of biological seed. The sample flask is immersed in a constant temperature bath and agitated by a shaking mechanism.

2. A 20% solution of KOH is placed in the center well (about one-quarter full). Insert a strip of folded filter paper inside the center well to enhance the alkali absorption of carbon dioxide. The paper soaks up KOH solution and in this way a larger alkali surface becomes available for absorption of carbon dioxide.

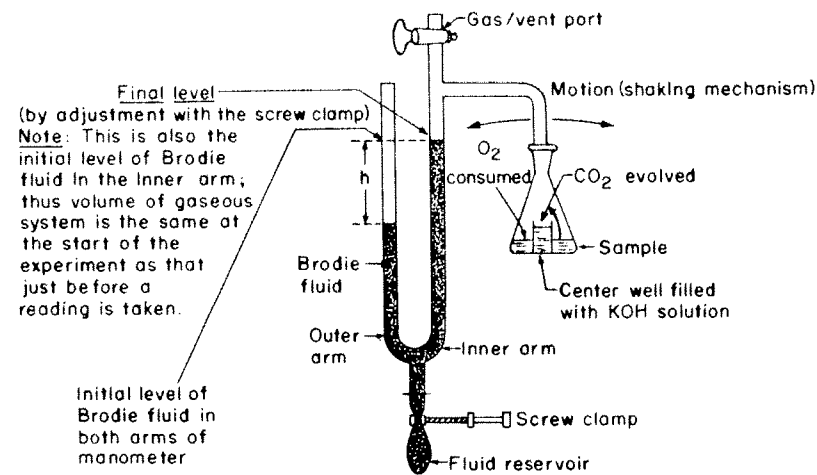


Fig. 2.18. Schematic diagram of Warburg respirometer.

3. Set up a reference flask ("thermobarometer") by adding to a sample flask only distilled water. The volume of distilled water equals the total waste seed volume in each of the test flasks. This reference flask is used for correction due to changes of atmospheric pressure during the time of the experiment, hence the name "thermobarometer."

4. Shake the system* with the gas vent port open for approximately 5 min. The level of the manometric fluid (Brodie's fluid) is the same in both arms of the manometer when equilibrium is reached. Adjust the manometric fluid to the reference mark in the inner arm of the manometer, with the gas vent port open. Adjustment of the level of the manometric fluid is made by means of a screw clamp, thus permitting adjustment of the height of manometric liquid within the two arms of the manometer. Stop the shaking and check all fittings.

5. Close the gas vent port, turn on the shaking assembly, and take readings at selected time intervals. Prior to a reading, turn the shaker off and adjust level of Brodie's fluid in the inner arm to the reference mark. Thus, the volume of the gaseous system is the same at the start of the experiment as that just before a reading is taken.

6. The reference flask readings serve the purpose of correcting for atmospheric pressure changes during the test. If the fluid in the outer arm of the

* Shaking is necessary because a film with a depleted oxygen concentration forms at the interface between the gas phase and the liquid sample if there is no agitation. This slows down the rate of oxygen utilization. Shaking provides for film renewal so that the liquor is always in contact with a gas phase rich in oxygen.

manometer attached to the thermobarometer flask rises, there has been a decrease in atmospheric pressure, and the observed reading must be added to the test value. If, on the other hand, the fluid in the outer arm of the manometer falls, there has been an increase in atmospheric pressure, and the observed reading must be subtracted from the test value.

$$\text{Sample reading } (h) = P_{at} - P_{system} \quad (2.70)$$

where P_{at} is the value of atmospheric pressure at start of experiment. During an experiment if the atmospheric pressure (P_{at}) rises, the calculated h [Eq. (2.70)] would be higher than the true value unless the appropriate correction is subtracted.

7. Once the substrate has been utilized, oxygen uptake stabilizes and the test series is terminated.

The cumulative oxygen uptakes (milligrams of oxygen per liter of solution) are then plotted vs. time (hr). A typical graph obtained for a toxic wastewater stream is shown in Fig. 2.19. This stream is added to domestic sewage (indicated as "seed" in Fig. 2.19) in increasingly larger proportions.

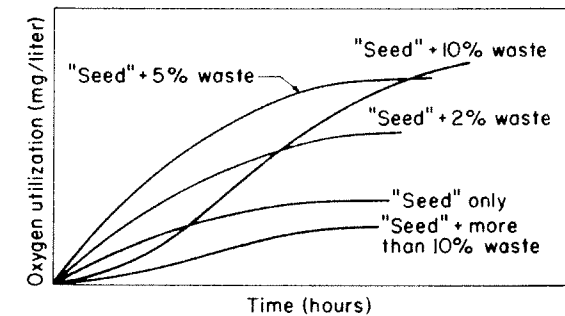


Fig. 2.19. Oxygen uptakes at different wastewater concentrations.

Figure 2.19 indicates that this specific wastewater is toxic or inhibitory when its concentration exceeds 10% in volume, in which case the oxygen uptake suffers a large drop.

Calculation of Oxygen Uptake (mg O_2 /Liter of Sample) from the Reading h (cm)

In this calculation procedure, it is assumed that atmospheric pressure has not changed during the time of experiment [if it does, correct as indicated in Step 6, Eq. (2.70)]. At the beginning of the experiment, the ideal gas law is applied to the air in the closed system, i.e.,

$$P_1 V = N_1 RT \quad (2.71)$$

where P_1 is the atmospheric pressure at start of experiment (cm of Brodie's fluid)*; V the gas volume in closed system (ml); T the temperature of constant temperature bath ($^{\circ}\text{K}$); N_1 the g moles of air at the beginning of experiment in closed system; and R the universal gas constant.†

From Eq. (2.71) we derive Eq. (2.72).

$$N_1 = P_1 V/RT \quad (2.72)$$

At the time a reading (h) is taken (Fig. 2.18)

$$P_2 V = N_2 RT \quad (2.73)$$

where P_2 is the system pressure ($P_2 < P_1$); V the volume of gas phase in system (kept constant by adjustment with the screw clamp); and N_2 the g moles of gas phase in closed system at time of reading. For $N_2 < N_1$ due to oxygen absorption, then

$$N_2 = N_1 - x \quad (2.74)$$

where x is g moles of O_2 adsorbed.

From Eq. (2.73)

$$N_2 = P_2 V/RT \quad (2.75)$$

Equating Eqs. (2.74) and (2.75) and solving for x :

$$x = N_1 - (P_2 V/RT) \quad (2.76)$$

Substituting in Eq. (2.76) N_1 by its value given by Eq. (2.72):

$$x = (V/RT)(P_1 - P_2) \quad (2.77)$$

where $(P_1 - P_2)$ equals the height h of Brodie's fluid (Fig. 2.18). Therefore,

$$x = (V/RT)h \quad (\text{g moles } \text{O}_2) \quad (2.78)$$

If V_s is the volume of the wastewater sample in ml, oxygen utilization in mg/liter is

$$\begin{aligned} \text{Oxygen utilization} &= (Vh/RT) \text{ g moles } \text{O}_2 \times \frac{1}{(V_s \times 10^{-3}) \text{ liter}} \\ &\times \frac{32 \text{ g}}{\text{g mole } \text{O}_2} \times 10^3 \frac{\text{mg}}{\text{g}} \end{aligned}$$

* Specific gravity of Brodie's fluid is 1.001 at 0°C (with respect to water at 4°C). Therefore, normal atmospheric pressure is equivalent to a column of Brodie's fluid (at 0°C) of height equal to

$$\begin{aligned} &76.0 \text{ cm Hg} \times 13.6 \text{ cm water/cm Hg} \times \text{cm Brodie's fluid}/1.001 \text{ cm water} \\ &= (76.0 \times 13.6)/(1.001) = 1032.6 \text{ cm Brodie's fluid at } 0^{\circ}\text{C} \end{aligned}$$

$$\begin{aligned} \dagger R &= P_0 V_0/T_0 = \frac{(1032.6 \text{ cm Brodie})(22,412 \text{ ml/g mole})}{273.2^{\circ}\text{K}} \\ &= 84,709 \text{ (cm Brodie)(ml)/(g mole)(}^{\circ}\text{K)} \end{aligned}$$

or

$$\text{Oxygen utilization} = 32 \times 10^6 (V/V_s)(h/RT) \quad (\text{mg/liter}) \quad (2.79)$$

where V is the gas volume in closed system (ml); V_s the volume of wastewater sample (ml); h the reading (cm of Brodie's fluid) (Fig. 2.18); R the universal gas constant [84,709 (cm Brodie)(ml)/(g mole)($^{\circ}\text{K}$)]; and T the temperature of bath ($^{\circ}\text{K}$).

9.3. BATCH REACTOR EVALUATION

A series of batch biological reactors (bench scale) are used to accomplish essentially the same objective as the Warburg respirometer. A battery of batch reactors recommended for this type of work is shown in Fig. 5.2 and described in Section 3.1 of Chapter 5.

An acclimated seed is added to the series of reactors. Various concentrations of a wastewater are then added to each reactor. The mixed contents are aerated for 2-3 days. The apparent toxicity is evaluated, samples are withdrawn at the end of 1, 2, 4, 8, 12, and 24 hr of aeration, and COD or BOD removal tests are performed. Typical BOD curves obtained in this manner are similar to the ones shown in Fig. 2.19.

10. Characteristics of Municipal Sewage

Municipal sewage is composed mainly of organic matter, either in soluble or colloidal form or as suspended solids. Eckenfelder [3] reports of analysis of data on municipal sewage for a survey which included 73 cities in 27 states of the United States. Some average per capita values from this survey are

Flow: 135 gal/(capita)(day)

BOD₅: 0.2 lb/(capita)(day) = 90.7 g/(capita)(day)

Suspended solids: 0.23 lb/(capita)(day) = 104 g/(capita)(day)

For a city of one million people, the following values are obtained by prorating this per capita data.

Flow: 135 Mgal/day \times 8.34 lb/gal = 1126 Mlb/day

BOD₅: 200,000 lb/day

or in terms of mg/liter

BOD₅: 200,000 lb/day \times day/1126 Mlb = 178 lb/Mlb = 178 ppm \approx 178 mg/liter*

* Since most wastewaters contain small concentrations of soluble (and/or insoluble) matter, wastewater density is taken hence as equal to that for pure water, i.e., approximately 1 mg/liter. Consequently, mg/liter becomes essentially equivalent to parts per million (ppm), since 1.0 mg/liter \approx 1.0 mg/10³ g = 1.0 g/10⁶ g = 1.0 ppm.

Presence of industrial wastes in a municipal sewage system may change these values considerably.

11. Industrial Wastewater Surveys

The procedure to be followed in industrial wastewater surveys has been described in Chapter 1 (Section 2.5.2, Step 1). A complete sewer map of the plant is developed. For accomplishing this objective, sampling and measuring stations are located in the plant, including all significant sources of wastewaters. Analyses to be run are selected and sampling and analyses schedules carefully planned. Material balances, including both process and sewer lines, are written.

Statistical plots for all significant characteristics are prepared. Whenever possible, these statistical plots are related to production, that is, gal/ton of product or lb BOD/ton of product. This permits extrapolation to other production schedules. Sources for wastewater segregation, reuse, and recirculation are identified.

Flow measurements of wastewater streams are performed by a variety of methods, which are summarized by Eckenfelder [3].

1. Installation of weirs for flow in open channels and partially filled sewers
2. Bucket and stopwatch method, suitable for low flow rates and/or intermittent discharges. In the latter case, flow rate and duration of operation are determined
3. Pumping duration and rate. Flow is estimated from the characteristic curves of the pump
4. Timing a floating object between two fixed points along the course. This method is applied to partially filled sewers. Depth of flow in the sewer is also measured. Average velocity is estimated from surface velocity, which is the one directly measured. For laminar flow the average velocity is approximately 0.8 times the surface velocity. Flow is then evaluated from the knowledge of this average velocity
5. Examination of plant water use records. Taking into account water losses in product or due to evaporation, this method leads to approximate estimates
6. Timing change of level in tanks or reactors, used primarily for batch operation discharges

12. Statistical Correlation of Industrial Waste Survey Data

Industrial wastewater discharges are highly variable in volume and composition and are appropriately treated by statistical analysis. Probability plots are used when dealing with statistics of events which fall into the bell-shaped probability curve so familiar to statisticians. A plot of data on prob-

ability-type graph paper straightens out the probability curve, leading to a straight line plot (linearization of the data). The straight line thus obtained is referred to as Henry's line. Therefore, if a series of experimental data is plotted on this paper and the result is a straight line, this indicates a random distribution of experimental data.

Probability graph paper utilized in this work is illustrated in Fig. 2.20. The abscissa is a probability scale and the ordinate is a logarithmic one.

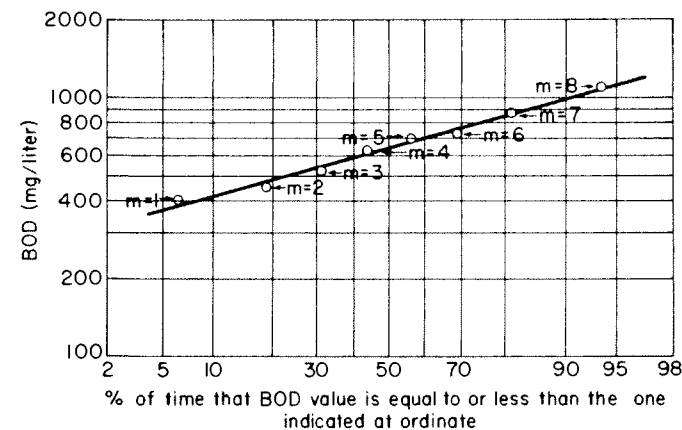


Fig. 2.20. Probability plot for Example 2.4 (Method 1).

Two methods for statistical correlation of industrial waste survey data are recommended by Eckenfelder [3].

Method (1) is recommended for small amounts of data (i.e., less than 20 datum points).

Step 1. Arrange data in increasing order of magnitude.

Step 2. Let n be the total number of points and m the assigned serial number from 1 to n . Tabulate data (in increasing order of magnitude) vs. m .

Step 3. Plotting positions (abscissas of the probability plot) are determined from

$$\text{Frequency} = (100/n)(m - 0.5)$$

This quantity is equivalent to the percent occurrence of the value plotted in the ordinate, i.e., percent of time that the value in question is equal to or less than the reading of the ordinate. The position of the best-fit line is judged by eye or the least-squares method is used. Application of method (1) is illustrated by Example 2.4.

Example 2.4

The following BOD data (mg/liter) arranged in increasing order of magnitude was obtained for an industrial stream [column (1) of Table 2.8]. Plot Henry's line by the method described.

TABLE 2.8
Calculations for Example 2.4

(1) Step 1, BOD (mg/liter)	(2) Step 2 ($n = 8, m = 1, 2, \dots, 8$), values of m	(3) Frequency = $(100/n)(m-0.5)$, % time equal to or less than
400	1	6.25
450	2	18.75
520	3	31.25
630	4	43.75
700	5	56.25
730	6	68.75
860	7	81.25
1100	8	93.75

SOLUTION The procedure is indicated in Table 2.8 and Fig. 2.20. The probability of occurrence of any value is now estimated. For example, from Fig. 2.20 the BOD is equal to or less than 1000 mg/liter 90% of the time.

A statistical analysis of the various waste characteristics provides a basis for choice of design values. For example, the hydraulic capacity of a plant is selected in excess of the 99% frequency (here the ordinate is flow rate). On the other hand, sludge-handling facilities are usually designed on the basis of the 50% frequency.

Method (2) is employed when a large number of data (more than 20 datum points) have to be analyzed. Calculate the plotting position [column (3) of Table 2.8] from

$$\text{Frequency} = m/(n+1)$$

Otherwise, the procedure is the same as in method (1).

Problems

I. The following BOD data are given:

t (days)	BOD (mg/liter)
1	6.5
2	11.0
3	15.0
4	18.0
5	20.0
6	22.0
7	23.0
8	24.0
9	25.0
10	26.0

- Plot the BOD curve.
- Calculate the values of parameters k and L_0 by the following methods:
 - Log-difference method
 - Moore's method of moments, utilizing 3-, 5-, and 7-day sequences
 - Thomas' graphical method

Tabulate values obtained under (a), (b), and (c). Compare values of L_0 with that obtained by visual extrapolation of the curve.

II. For a wastewater, $k = 0.1$ (decimal log basis) and the 5-day BOD is 200 mg/liter. Estimate the 1-day BOD and the ultimate demand (L_0). What is the 5-day BOD if the incubation is at 30°C instead of the conventional temperature of 20°C?

III. Determine ThOD for alanine [$\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$] (in g O_2 /g mole of alanine) using the following assumptions:

- Carbon atoms are oxidized to CO_2 while nitrogen is converted to ammonia.
- Ammonia is then oxidized to HNO_2 in the presence of nitrite-forming bacteria.
- Finally, HNO_2 is oxidized to HNO_3 in the presence of nitrate-forming bacteria. ThOD is the sum of the oxygen required for these three steps.

IV. Nine determinations of suspended solids (ppm) in a waste stream yield the following results, arranged in order of increasing magnitude: 48, 83, 85, 102, 130, 134, 153, 167, and 180.

- Linearize the distribution by a probability plot.
- What is the probability of occurrence of a suspended solid (SS) value equal to or less than 200 ppm?

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1. Introduction

Selection of a wastewater treatment process or sequence of processes depends on a number of factors, i.e., (1) characteristics of the wastewater, e.g., BOD, % of suspended solids, pH, presence of toxic materials; (2) required effluent quality; (3) cost and availability of land, e.g., certain biological processes (stabilization ponds) are only economically feasible if low cost land is available; and (4) consideration of a possible future upgrading of water quality standards, necessitating design of a more sophisticated type of treatment for future use.

Pretreatment of wastewater implies removal of suspended solids or con-

ditioning of wastewater for discharge into either a receiving body of water or a secondary treatment facility through neutralization and/or equalization. Types of primary treatment discussed in this chapter are (1) screening, (2) sedimentation, (3) flotation, and (4) neutralization and equalization.

2. Screening

Screening is employed for removal of suspended solids of various sizes. Screen openings range in size depending on their purpose, and cleaning of screens is done either manually or mechanically. Screenings are disposed of by burial, incineration, or anaerobic digestion. Screens are classified as fine and coarse.

Fine screens have openings of 3/16 in. or smaller. They are usually made of steel mesh or perforated steel plates and sometimes used instead of sedimentation tanks. However, whereas they remove from 5 to 25% of suspended solids, 40–60% is removed by sedimentation. For this reason, and also because clogging is frequently a problem, use of fine screens is not very common.

Coarse screens have openings ranging from 1.5 to 3.0 in. They are used as protecting devices so that large suspended solids do not damage pumps and other equipment.

Sometimes shredders are used instead of coarse screens. These devices tear down suspended solids, which are then removed by sedimentation.

3. Sedimentation

3.1. INTRODUCTION

Sedimentation is utilized in wastewater treatment to separate suspended solids from wastewaters. Removal by sedimentation is based on the difference in specific gravity between solid particles and the bulk of the liquid, which results in settling of suspended solids.

In some cases, sedimentation is the only treatment to which the wastewater is subjected. Sedimentation is also utilized in one or more steps of a treatment sequence. In a typical activated sludge plant, sedimentation is utilized in three of the treatment steps: (1) in grit chambers, in which inorganic matter (e.g., sand) is removed from the wastewater; (2) in the primary clarifier, which precedes the biological reactor, solids (organic and others) are separated; and (3) in the secondary clarifier, which follows the biological reactor, the biological sludge is separated from the treated effluent.

3.2. TYPES OF SETTLING

Three types of settling are recognized depending on the nature of solids present in the suspension.

1. *Discrete settling.* Particles being settled keep their individuality, i.e., they do not coalesce with other particles. Thus, the physical properties of the particles (size, shape, specific gravity) are unchanged during the process. The settling of sand particles in grit chambers is a typical example of discrete settling.

2. *Flocculent settling.* Agglomeration of the settling particles is accompanied by changes in density and settling velocity. The sedimentation occurring in primary clarifiers is an example.

3. *Zone settling.* Particles form a lattice (or blanket) which settles as a mass exhibiting a distinct interface with the liquid phase. Examples include sedimentation of activated sludge in secondary clarifiers and that of alum flocs in water treatment processes.

3.3. THEORY OF DISCRETE SETTLING

The fundamental relationship for settling of discrete particles is Newton's law, which is based on the assumption that particles are spherical with a uniform diameter. When a particle settles, it accelerates until the forces promoting settling, i.e., the particle effective weight, are balanced by the drag or frictional resistance of the liquid. When this equality is achieved, the particle reaches a constant settling velocity called the terminal or settling velocity of the particle.*

Consider the particle in Fig. 3.1, which has reached its terminal velocity, and write the appropriate force balance. The force promoting sedimentation, i.e., the effective weight of the particle, is the difference between its actual weight and the hydrostatic lift:

$$F_s = v\rho_s g - v\rho_L g = (\rho_s - \rho_L)gv \quad (3.1)$$

where F_s is the particle effective weight; ρ_s the particle density; ρ_L the liquid density; g the acceleration of gravity; and v the particle volume, $\frac{1}{6}\pi d^3$, where d is the diameter of the spherical particle.

The drag force impeding sedimentation is

$$F_D = C_D A(\rho_L V^2/2) \quad (3.2)$$

where F_D is the drag force; C_D the drag coefficient; A the projected area of the particle, $A = \frac{1}{4}\pi d^2$; and V the relative velocity between particle and fluid.

For the condition defining the terminal velocity, equate Eqs. (3.1) and (3.2).

$$(\rho_s - \rho_L)gv = C_D A(\rho_L V_s^2/2)$$

where

$$V = V_s = \text{settling velocity}$$

* This results from force = (mass) (acceleration). Thus zero acceleration corresponds to a net force of zero, i.e., a perfect balance of forces.

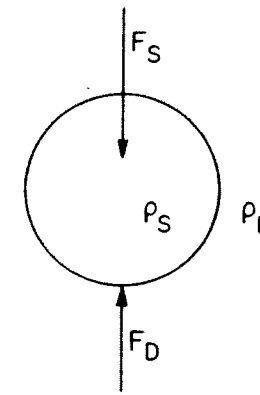


Fig. 3.1. Discrete settling of a particle.

Substituting $v = \frac{1}{6}\pi d^3$, $A = \frac{1}{4}\pi d^2$, and solving for the terminal velocity, V_s [Eq. (3.3)]:

$$V_s = \left[\frac{4}{3}(g/C_D) \frac{\rho_s - \rho_L}{\rho_L} \cdot d \right]^{1/2} \quad (3.3)$$

which is Newton's law.

For spherical particles, the drag coefficient C_D is related to the Reynolds number N_R defined in Eq. (3.4).

$$N_R = dV_s\rho_L/\mu_L \quad (3.4)$$

where d is the diameter of sphere, V_s the terminal velocity (settling velocity), and ρ_L and μ_L the density and viscosity of liquid. This relationship is shown in Fig. 3.2.*

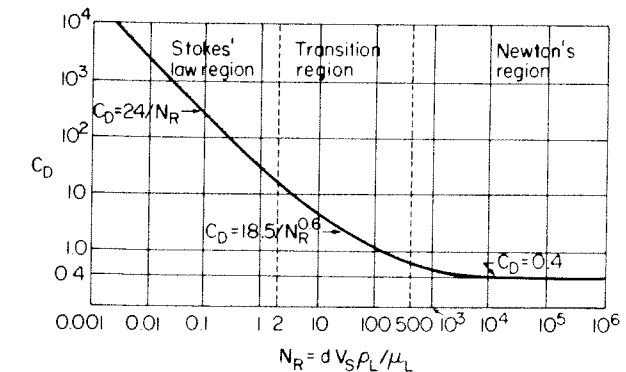


Fig. 3.2. Correlation for drag coefficient for spherical particles.

* For nonspherical particles Fig. 3.2 is plotted as a family of curves, each curve corresponding to specified value of a parameter defined as sphericity [sphericity, ψ = (surface area of a sphere having same volume as particle)/(surface area of particle)]. See Waddell [8].

In general, the drag coefficient C_D is approximated by

$$C_D = b/N_R^n \quad (3.5)$$

where coefficients b and n for the different regions of Fig. 3.2 are indicated in Table 3.1. The approximate relationship between C_D and N_R given by Eq.

TABLE 3.1
Drag Coefficient C_D

Region	b	n	$C_D = b/N_R^n$
Stokes' law $N_R < 2$	24	1.0	$C_D = 24/N_R$
Transition $2 < N_R < 500$	18.5	0.6	$C_D = 18.5/N_R^{0.6}$
Newton's $N_R > 500$	0.4	0.0	$C_D = 0.4$

(3.5) is written in logarithmic form for the three regions indicated in Fig. 3.2.

Stokes' region: $C_D = 24/N_R$
 $\therefore \log C_D = -\log N_R + \log 24$

Transition region: $C_D = 18.5/N_R^{0.6}$
 $\therefore \log C_D = -0.6 \log N_R + \log 18.5$

Newton's region: $C_D = 0.4$
 $\therefore \log C_D = \log 0.4 = 0.0 \log N_R + \log 0.4$

Thus the curve in Fig. 3.2 is approximately replaced by three segments of straight line with slopes of, respectively, -1 , -0.6 , and 0.0 .

Many sedimentation problems in wastewater treatment occur in Stokes' region. Substituting $C_D = 24/N_R = 24\mu_L/dV_S\rho_L$ in Eq. (3.3) and simplifying, Stokes' law is obtained.

$$V_S = 1/18 \cdot \frac{\rho_S - \rho_L}{\mu_L} \cdot gd^2 \quad (3.6)$$

For a specific problem in Stokes' region (ρ_S , ρ_L , and μ_L fixed) Eq. (3.6) is written as [Eq. (3.7)]

$$V_S = Kd^2 \quad (3.7)$$

(where K is a constant), which in logarithmic form becomes [Eq. (3.8)]

$$\log V_S = 2 \log d + \log K = 2 \log d + C \quad (C \text{ is a constant}) \quad (3.8)$$

Thus, a logarithmic plot of V_S vs. d yields a straight line of slope equal to 2.0 for Stokes' region.

For a specific problem in Newton's region, since C_D is a constant ($C_D = 0.4$), Eq. (3.3) yields Eq. (3.9).

$$V_S = K'd^{1/2} \quad (3.9)$$

(where K' = a constant) which in logarithmic form becomes Eq. (3.10).

$$\log V_S = \frac{1}{2} \log d + \log K' = \frac{1}{2} \log d + C' \quad (3.10)$$

where C' is a constant. Thus, a logarithmic plot of V_S vs. d yields a straight line of slope equal to $\frac{1}{2}$ for Newton's region.

For the transition region, $C_D = 18.5/N_R^{0.6} = (18.5\mu_L^{0.6})/(d^{0.6}V_S^{0.6}\rho_L^{0.6})$. Substituting this value in Eq. (3.3) and simplifying, one obtains Eq. (3.11).

$$V_S = [(4g/55.5)(\rho_L^{0.6}/\mu_L^{0.6})(\rho_S - \rho_L)/\rho_L]^{1/4} d^{1.143} = K''d^{1.143} \quad (3.11)$$

where K'' is a constant. In logarithmic form this becomes [Eq. (3.12)]

$$\log V_S = 1.143 \log d + \log K'' = 1.143 \log d + C'' \quad (3.12)$$

where C'' is a constant. Thus, a logarithmic plot of V_S vs. d yields a straight line of slope 1.143 for the transition region. The logarithmic plot of V_S vs. d for the three regions is shown in Fig. 3.3. Even in the case of grit chambers, the theory just outlined suffers from two serious limitations: (1) grit particles are seldom spherical, and (2) grit particles do not have uniform density.

A graph corresponding to Eq. (3.3) is plotted in Fig. 3.4, giving the relationship between particle diameter and velocity V_S . Particles of specific gravities 1.001, 1.01, and 2.65 are considered in plotting Fig. 3.4. Value 2.65 corresponds to the specific gravity of typical sand. The liquid used is water at temperatures indicated, corresponding to respective values of ρ_L , μ_L . Values of C_D are obtained from Fig. 3.2 by a trial and error procedure: (1) for specified particle

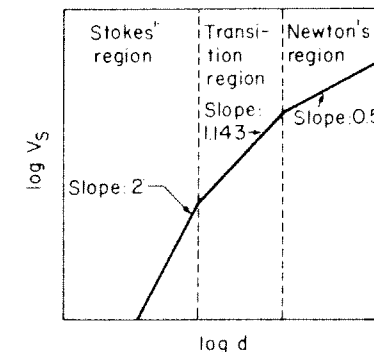


Fig. 3.3. Logarithmic plot of V_S vs. d .

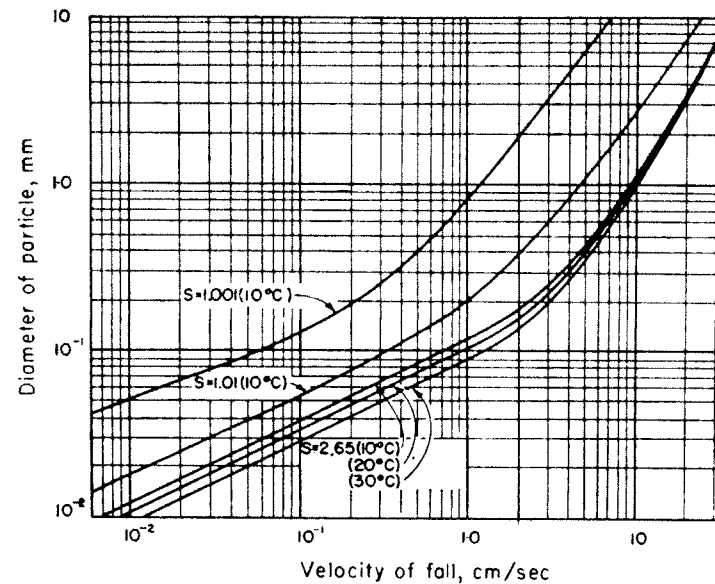


Fig. 3.4. Relation between settling velocity and particle diameter [4].

diameter and temperature (ρ_L and μ_L fixed) assume a settling velocity V_S ; (2) Calculate N_R based upon this assumed velocity; (3) From Fig. 3.2 read C_D ; and (4) From Eq. 3.3 recalculate V_S . If it agrees with the value assumed in (1) calculations are consistent. Otherwise, iteration is continued until agreement is obtained.

Figure 3.4 is constructed in this manner. Since construction is based upon the actual curve of C_D vs. N_R (i.e., Fig. 3.2), the lines in Fig. 3.4 exhibit some curvature, by contrast with the three straight line segments in Fig. 3.3 [construction of which is based on the approximate relationships given by Eqs. (3.8), (3.10), and (3.12)]. As an approximation, however, curves in Fig. 3.4 are replaceable by three straight line segments.

3.4. THE IDEAL SEDIMENTATION TANK CONCEPT

This concept, developed by Hazen [5] and Camp [1], is the basis for arriving at relationships utilized in the design of sedimentation tanks. The model chosen for a sedimentation tank consists of four zones (Figs. 3.5 and 3.6).

1. Inlet zone. Here the flow becomes quiescent. It is assumed that at the limit of this zone (i.e., along vertical line $x\tau$) particles are uniformly distributed across the influent cross section.

2. Sedimentation zone. A particle is assumed to be removed from suspension once it hits the bottom of this zone (horizontal line τy).

3. Sedimentation

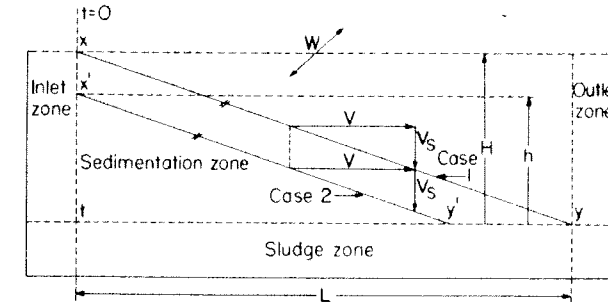


Fig. 3.5. Model of a sedimentation tank with discrete settling particles (Cases 1 and 2).

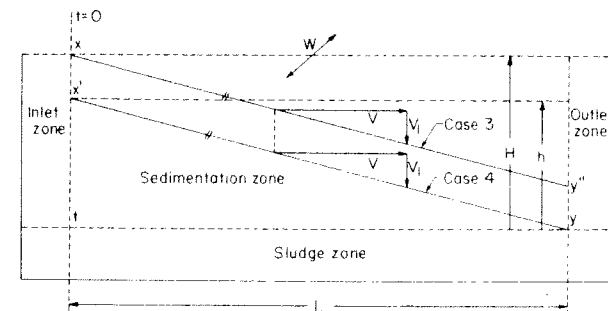


Fig. 3.6. Model of a sedimentation tank with discrete settling particles (Cases 3 and 4).

3. Outlet zone. Wastewater is collected here prior to transfer to the next treatment.

4. Sludge zone. This zone is provided for sludge removal.

Settling paths of particles entering the sedimentation zone at points x and x' for discrete settling are indicated by lines xy and $x'y'$ in Fig. 3.5 and lines $x\tau''$ and $x'\tau'$ in Fig. 3.6. These settling paths are the net result of two velocity vector components:

1. Flow-through velocity V [Eq. (3.13)]

$$V = Q/A' = Q/WH \quad (3.13)$$

where V is the flow-through velocity (ft/sec); Q the flow rate (ft³/sec); A' the vertical cross-sectional area of sedimentation zone, namely $A' = WH$ (ft²) (refer to Fig. 3.7); W the width of sedimentation zone (ft); and H the depth of sedimentation zone (ft).

2. Settling velocity, indicated by either vectors V_S or V_1 in Figs. 3.5 and 3.6, respectively.

For discrete settling the settling velocity is constant for any specific settling

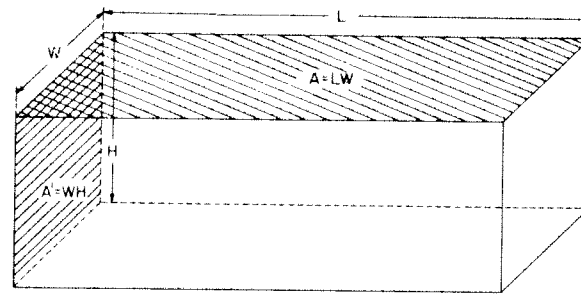


Fig. 3.7. Geometry of the sedimentation zone.

path, i.e., V_s and V_1 do not vary along their respective paths. This is due to the fact that a discrete particle is unhindered by neighboring ones (no coalescence), so it settles with a uniform velocity, read from Fig. 3.4, as a function of the particle diameter.

For flocculent settling the situation is different. Figure 3.8 illustrates a typical sedimentation path of flocculent settling (Section 3.5). As coalescence

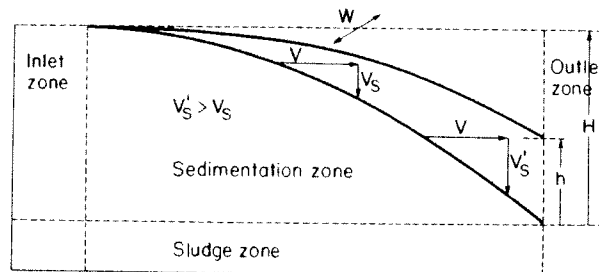


Fig. 3.8. Model of a sedimentation tank for flocculent settling.

with neighboring particles takes place, the effective diameter of the particle increases, and thus its settling velocity V_s also increases. The net result is that settling paths are curved in contrast with straight line paths for discrete settling.

Consider the following cases with reference to Figs. 3.5 and 3.6, keeping in mind that a particle is assumed to be removed from the suspension once it hits the bottom of the sedimentation zone.

Case 1 (Fig. 3.5). A particle which at time zero ($t = 0$) is located at point x and possesses a settling velocity V_s (and diameter d_s read from Fig. 3.4). This particle is removed, since it touches the bottom of the sedimentation zone at y (path xy).

Case 2 (Fig. 3.5). A particle which at $t = 0$ is located at x' on the same vertical line as x but below x , and has a settling velocity V_s (or greater than V_s). This particle is also removed since it hits the bottom of the sedimentation zone

to the left of point y (at y'). If the settling velocity is greater than V_s the particle touches the bottom of the sedimentation zone to the left of y' . Figure 3.6 portrays the case of particles with a diameter d_1 ($d_1 < d_s$), possessing a settling velocity V_1 ($V_1 < V_s$). (Settling velocity V_1 is read from Fig. 3.4 for $d = d_1$.) These particles are shown separately in Fig. 3.6 simply to avoid overcrowding of the diagram. In fact they are together in the slurry with particles of settling velocity V_s .

Case 3 (Fig. 3.6). A particle which at $t = 0$ is located at x and has a settling velocity V_1 (where $V_1 < V_s$). This particle is not removed since it does not reach the bottom of the sedimentation zone (i.e., line ty) in time for removal (sedimentation path xy'').

Case 4 (Fig. 3.6). A particle with settling velocity V_1 (where $V_1 < V_s$) and situated at x' at $t = 0$. This particle is removed (sedimentation path $x'y$). Consider now the settling velocity V_s . From Eq. (3.13)

$$Q = VA' = VWH \quad (3.14)$$

From consideration of similar triangles in Fig. 3.5

$$V = V_s(L/H) \quad (3.15)$$

Substitution of Eq. (3.15) in Eq. (3.14) and simplification leads to

$$Q = V_s LW = V_s A \quad (3.16)$$

where $A = LW =$ horizontal cross-sectional area of the sedimentation zone (ft^2) (Fig. 3.7).

From Eq. (3.16)

$$V_s = Q/LW = Q/A \quad (3.17)$$

From Eq. (3.17) it follows that the settling efficiency is a function of the horizontal cross-sectional area, rather than of the depth H . Thus, in principle, it is advisable to utilize sedimentation tanks of high surface area A and low depths. The only reasons for using a reasonable depth are (1) to satisfy depth requirements in order to provide for mechanical rakes utilized for removal of settled sludge, and (2) the horizontal component of velocity (flow-through velocity V) must be kept within certain limits to prevent scouring the particles which have settled.

From Eq. (3.13) it follows that H should not be too low since V would rise above the scour velocity. The subject of scour velocity is discussed in this section. Scour occurs when flow-through velocity V is sufficient to suspend previously settled particles. Scour is not usually a problem in large settling tanks, but it can be an important factor in grit chambers and narrow channels.

The two fundamental premises of the ideal tank concept are (1) uniform distribution of particles across the influent cross section (i.e., along vertical

line xt) and (2) assumption that a particle is considered removed when it reaches the bottom of the sedimentation zone (i.e., horizontal line ty).

Keeping in mind these two premises, two corollaries follow: (1) All particles with a settling velocity equal to or greater than V_s are removed; and (2) all particles with a settling velocity less than V_s (such as V_1 in Fig. 3.6) are removed in a proportion given by the ratio V_1/V_s .

From geometric consideration of the particle path (Figs. 3.5 and 3.6) touching point y at the bottom of the sedimentation tank (particles with settling velocity V_s in Fig. 3.5 following path xy , and particles with settling velocity V_1 in Fig. 3.6 following path $x'y$), one writes [Eq. (3.18)]

$$V_1/V_s = h/H \quad (3.18)$$

For example, if $H = 100$ in. and $h = 75$ in., then

$$V_1/V_s = 75/100 = 0.75$$

or 75% of the particles with a settling velocity V_1 are removed, i.e., those which at time $t = 0$ are at a height x' or below. The remaining particles with settling velocity V_1 , i.e., those situated between x and x' at time $t = 0$, are *not* removed.

The overflow rate defined as

$$Q/A = \text{ft}^3/(\text{ft}^2)(\text{hr}) = \text{ft}/\text{hr}$$

is defined as the settling velocity V_s of a particle that settles through a distance exactly equal to the effective depth of the tank during the theoretical detention period. This results from the definition of detention period:

$$t = \text{detention period} = (\text{volume of tank})/Q = HA/Q \quad (A = LW) \quad (3.19)$$

From Eq. (3.19) it follows that a settling velocity V_s defined as $V_s = H/t$ is equivalent to the overflow rate, since

$$V_s = H/t = H/(HA/Q) = Q/A$$

which is Eq. (3.17).

The *scour velocity* V_c is the value of the flow-through velocity V [Eq. (3.20)],

$$V = V_c = Q/A' = Q/WH \quad (3.20)$$

for which "previously settled" particles are scoured away.*

* The words "previously settled" are placed in quotes because a particle which is scoured away never actually settles. Mentally one separates the processes of settling and scouring and imagines that a particle settles and subsequently is scoured away. This reasoning is compatible with the hypothetical resolution of the velocity trajectory into vectors V (flow-through velocity) and V_s (settling velocity).

The scour velocity is estimated by the following empirical equation [Eq. (3.21)] [1]:

$$V_c = [8\beta g d(s-1)/f]^{1/2} \quad (3.21)$$

where V_c is the velocity of scour (mm/sec); i.e., flow-through velocity required to scour all particles of diameter d or smaller; β the constant (0.04 for ungranular sand, 0.06 for nonuniform sticky material); f the Weisbach-D'Arcy friction factor (0.03 for concrete); g the acceleration of gravity (mm/sec²) (normal: 9800 mm/sec²); d the particle diameter (mm) (particles with diameter d or less than d are scoured away); and s the specific gravity of particle.

Example 3.1

Consider a suspension of sand ($s = 2.65$) in water at 20°C with a uniform particle size ($d = 0.07$ mm). Flow is 1.0 Mgal/day.

1. Calculate the settling tank surface (horizontal cross section) for obtaining removal of 70% of the particles.

2. Suppose that instead of a uniform particle diameter, there is, besides particles of $d = 0.07$ mm, another set with a uniformly larger diameter, which are completely removed in the settling tank designed for 70% removal of the particles with $d = 0.07$ mm. Determine what is the minimum particle diameter for total removal.

3. For case (2), determine the flow-through velocity V_c so that all particles of lower settling velocity than those completely removed are scoured away. What combination of length, width, and depth for the settling tank meets these requirements?

SOLUTION: Part 1

Step 1. From Fig. 3.4 [for $d = 0.07$ mm and $s = 2.65$ (at 20°C)], read

$$V_s = 0.45 \text{ cm/sec}$$

or

$$V_s = 0.45 \text{ cm/sec} \times \text{ft}/30.48 \text{ cm} \times 3600 \text{ sec/hr}$$

$$V_s = 53.1 \text{ ft/hr} = 53.1 \text{ ft}^3/(\text{ft}^2)(\text{hr})$$

The overflow rate in gal/(day)(ft²) is

$$53.1 \text{ ft}^3/(\text{ft}^2)(\text{hr}) \times 7.48 \text{ gal/ft}^3 \times 24 \text{ hr/day}$$

$$\therefore V_s = 9533 \text{ gal}/(\text{day})(\text{ft}^2)$$

Step 2. The horizontal cross-sectional area is (for 100% removal)

$$A = Q/V_s = \frac{1,000,000 \text{ gal/day}}{9533 \text{ gal}/(\text{day})(\text{ft}^2)} = 105 \text{ ft}^2$$

With this area, 100% removal is obtained. For 70% removal the residence time (and thus the cross-sectional area) is reduced by 30%. The cross-sectional area is

$$A = 105 \times 0.7 = 73.5 \text{ ft}^2$$

Under these circumstances, the settling velocity for 100% removal is

$$1,000,000/73.5 = 13,605 \text{ gal}/(\text{day})(\text{ft}^2)$$

Note: Check on percent removal. Since the settling velocity is 9533 gal/(day)(ft²), fixed by the particle diameter as determined from Fig. 3.4, percentage removal is 9533/13,605 = 0.70 (70%). Referring to Fig. 3.6 the particles removed are those which at the end of inlet zone, along vertical line *xt*, are already at distance *h* (or less than *h*) from the bottom of the sedimentation zone, where [from Eq. (3.18)]

$$V_s = 13,605 \text{ gal}/(\text{day})(\text{ft}^2) \quad (100\% \text{ removal})$$

$$V_1 = 9533 \text{ gal}/(\text{day})(\text{ft}^2) \quad (70\% \text{ removal})$$

$$\therefore h/H = 0.70$$

SOLUTION: Part 2 If there is a distribution of particle diameters instead of uniform diameter *d* = 0.07 mm, one reads from Fig. 3.4 the diameter, which is larger than 0.07 mm, for which the settling velocity corresponds to 13,605 gal/(day)(ft²). Therefore, the abscissa in Fig. 3.4 is

$$(13,605/9533) \times 0.45 \text{ cm/sec} = 0.45/0.7 = 0.642 \text{ cm/sec}$$

From Fig. 3.4 [for $V_s = 0.642 \text{ cm/sec}$ and $s = 2.65$ ($t = 20^\circ\text{C}$)], read $d = 0.085 \text{ mm}$ (100% removal). If distribution of particle diameter in the influent is known, one can calculate the % removal corresponding to each group of particles for a given diameter (Example 3.2).

SOLUTION: Part 3 The scour velocity to sweep all particles of lower settling velocity than those to be completely removed is calculated from Eq. (3.21).

$$V_c = [8 \times 0.04 \times 9800 \times 0.07(2.65 - 1)/0.03]^{1/2} = 110 \text{ mm/sec}$$

Assuming that the sand contains only two particle sizes, e.g., 0.07 and 0.085 mm, the scour velocity $V_c = 110.0 \text{ mm/sec}$ sweeps away all particles of $d = 0.07 \text{ mm}$, leaving behind those of $d = 0.085 \text{ mm}$. The value of V_c in practical units is

$$V_c = 110 \text{ mm/sec} \times \text{ft}/304.8 \text{ mm} = 0.36 \text{ ft/sec}$$

The vertical cross-sectional area is calculated from Eq. (3.13).

$$A' = \frac{1,000,000 \text{ gal/day} \times \text{day}/86,400 \text{ sec} \times \text{ft}^3/7.48 \text{ gal}}{0.36 \text{ ft/sec}} = 4.3 \text{ ft}^2$$

Any practical combination of length, width, and depth is used to satisfy the requirements $A = 73.5 \text{ ft}^2 = LW$ and $A' = 4.3 \text{ ft}^2 = WH$.

Example 3.2

Suppose that for Example 3.1 instead of a uniform particle size, there is a distribution of diameters. Assume the same specific gravity and temperature as in Example 3.1, i.e., $s = 2.65$ and $t = 20^\circ\text{C}$. Assume that for each 100 lb of grit the following distribution of particle sizes applies (see tabulation below)

(1) Group no.	(2) lb of each particle size	(3) Particle size, <i>d</i> (mm)
1	50	0.085
2	20	0.070
3	20	0.060
4	10	0.050
	100	

The settling velocities for each group of particles are read from Fig. 3.4. This is indicated in column (4) of Table 3.2. Percent removals are then calculated [column (5)] and expressed as fractions of unity in column (6). The

TABLE 3.2
Calculations for Example 3.2

(1) Group no.	(2) lb of each particle size	(3) Particle size, <i>d</i> (mm)	(4) V_s (Fig. 3.4)	(5) % removal = $\frac{(4)}{0.642} \times 100$	(6) Fraction removed = (5) ÷ 100	(7) lb removed (7) = (2) × (6)
1	50	0.085	0.642	(0.642/0.642)100 = 100 ^a	1.00	50.0
2	20	0.070	0.450	(0.45/0.642)100 = 70 ^a	0.70	14.0
3	20	0.060	0.350	(0.35/0.642)100 = 54.5	0.545	10.9
4	10	0.050	0.220	(0.22/0.642)100 = 34.3	0.343	3.43
	100					78.3

^a Already calculated in Example 3.1.

weight of sand removed by settling for each group of particles is computed in column (7). Therefore 78.3% of the weight of the original particles is removed by settling.

In this example, if the vertical cross section A' is taken equal to 4.3 ft^2 (value calculated in Example 3.1), all particles of $d = 0.07 \text{ mm}$ and smaller are scoured away (groups 2, 3, and 4). Therefore, the net removal is of only 50 lb per 100 lb of total grit, i.e., the particles with $d = 0.085$ (group 1). This indicates a net removal by weight of 50%.

If A' is taken larger than 4.3 ft^2 the net removal is greater, since there is less scouring. Examining calculations for Example 3.1, it follows that if A' is taken as 8.6 ft^2 (twice 4.3 ft^2) the value of V_c is 0.18 ft/sec (instead of 0.36 ft/sec). This corresponds to

$$V_c = 55 \text{ mm/sec} \quad (\text{instead of } 110.0 \text{ mm/sec})$$

Since from Eq. (3.21), V_c is proportional to $d^{1/2}$, it follows that d is $0.07/4 = 0.0175 \text{ mm}$, so as to yield $V_c = 55 \text{ mm/sec}$ (half of 110.0 mm/sec). Therefore, only particles with $d = 0.0175 \text{ mm}$ or smaller are removed by scouring. Since for the given distribution the smallest particle diameter is 0.05 mm , there is no removal by scouring. Consequently, the net removal is 78.3 lb from every 100 lb of sand, or 78.3% by weight.

If this value is adopted,

$$A = 73.5 \text{ ft}^2 = LW$$

$$A' = 8.6 \text{ ft}^2 = WH$$

Selecting $H = 4 \text{ ft}$, then

$$W = 8.6/4 = 2.15 \text{ ft}$$

$$L = 73.5/2.15 = 34.2 \text{ ft}$$

This indicates specification of a narrow settling channel 34.2 ft long, 2.15 ft wide, and 4 ft deep.

3.5. FLOCCULENT SETTLING

Flocculent settling takes place when settling velocity of the particles increases due to coalescence with other particles. A diagram of flocculent sedimentation profiles is shown in Fig. 3.8. The settling paths of the particles are curves, rather than straight lines as for discrete settling.

Design criteria for systems exhibiting flocculent settling are established by a laboratory settling analysis. A typical laboratory settling column is shown in Fig. 3.9.

Concentration of suspended solids is kept uniform throughout the column at the beginning of the test by means of a portable stirrer. The depth of the column is approximately the same as that of the settling tank to be designed. Temperature is kept constant during the test. A practical design of a settling column (Fig. 3.9) is 8 ft deep, with sampling ports at depths of 2, 4, 6, and 8 ft.

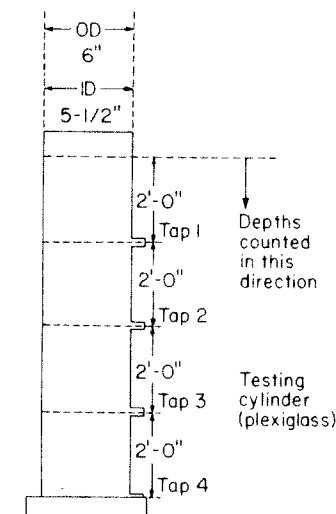


Fig. 3.9. Laboratory settling column.

Data taken at 2-, 4-, and 6-ft depths are utilized to determine settling velocity and detention time relationships. Data from the 8-ft port are used for sludge concentration and compaction determinations.

Step 1. Fill the column with wastewater, maintaining a uniform concentration of suspended solids throughout. A portable stirrer is used for this purpose.

Step 2. Remove the stirrer from the cylinder. At each sampling port, the concentrations of suspended solids are measured at predetermined times.

Examples 3.3 and 3.4 illustrate the procedure from data treatment to the design of a clarifier.

Example 3.3

The suspension being tested has an initial suspended solids concentration of 430 mg/liter (SS_0). The suspended solids (hence abbreviated as SS) concentrations in Table 3.3 are measured at the indicated times at the 2-, 4-, and 6-ft sampling ports. Perform treatment of the data arriving at curves for (a) % SS removal vs. detention time (min), (b) % SS removal vs. overflow rate [$\text{gal}/(\text{day})(\text{ft}^2)$], and (c) % SS remaining (fraction of particles with less than stated velocity) vs. settling velocity (ft/hr).

Step 1. Calculate fraction of solids remaining in suspension for each sample [Eq. (3.22)].

$$x = SS/SS_0$$

or in %

$$y = SS/SS_0 \times 100 \quad (3.22)$$

TABLE 3.3
Laboratory Sedimentation Data (Example 3.3)

Time (min)	SS concentrations at indicated depths		
	2 ft (Tap 1)	4 ft (Tap 2)	6 ft (Tap 3)
5	356.9	387.0	395.6
10	309.6	346.2	365.5
20	251.6	298.9	316.1
30	197.8	253.7	288.1
40	163.4	230.1	251.6
50	144.1	195.7	232.2
60	116.1	178.5	204.3
75	107.5	143.2	180.6

Then calculate for each sample the fraction of solids removed

$$1 - x$$

or in %

$$z = 100 - y \quad (3.23)$$

A sample of these calculations (for a 2-ft depth) is shown in Table 3.4. Similar calculations are performed for 4- and 6-ft depths.

TABLE 3.4
Calculation of Fraction of Solids Remaining and Removed for a 2-ft Depth

(1) Time (min)	(2) SS remaining (mg/liter) (Table 3.3)	(3) Solids remaining (%) $y = (SS/SS_0) \times 100$	(4) Solids removed (%) $z = 100 - y$
5	356.9	83.0	17.0
10	309.6	72.0	28.0
20	251.6	58.5	41.5
30	197.8	46.0	54.0
40	163.4	38.0	62.0
50	144.1	33.5	66.5
60	116.1	27.0	73.0
75	107.5	25.0	75.0

Step 2. In order to smooth the experimental data construct a graph of % SS removed vs. time. This plot is shown in Fig. 3.10 for the 2-, 4-, and 6-ft depths.

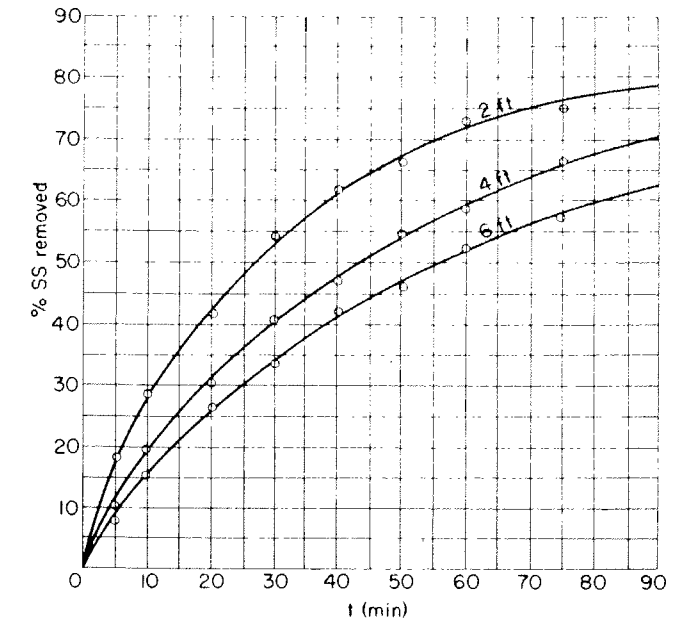


Fig. 3.10. Suspended solids (% SS) removed vs. time.

Step 3. From Fig. 3.10 construct a settling profile graph (Fig. 3.11). This is done by reading from the smoothed curves of Fig. 3.10 the abscissas (t , min) corresponding to selected values of % SS removed (e.g., 5, 10, 20, ..., 70, 75%) for each one of the three depths. These values are tabulated (Table 3.5) and utilized for construction of Fig. 3.11.

Step 4. Calculate % removal of SS and overflow rate [gal/(day)(ft²)]. Before the procedure described here is fully understood, some preliminary considerations must be made. An effective settling velocity V_s is defined as the effective depth (6 ft in this example) divided by the time (detention time, t) required for a given particle to travel this distance, i.e. [Eq. (3.24)],

$$V_s = H/t \quad (3.24)$$

If a suspension contains particles with different settling velocities, the efficiency of removal by sedimentation is obtained by performing a settling column test as just described. Let SS be the concentration of solids remaining for one specific sample and time. Thus

$$x_0 = SS/SS_0 = \text{fraction of solids remaining}$$

and

$$1 - x_0 = 1 - SS/SS_0 = y_0 = \text{fraction of solids removed}$$

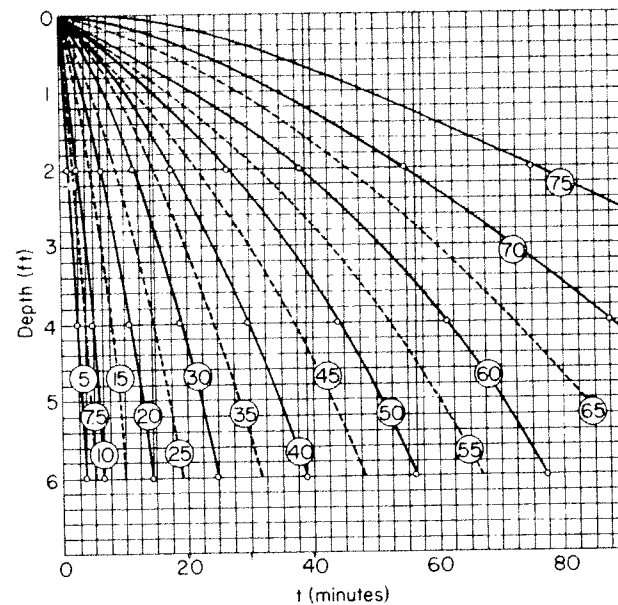


Fig. 3.11. Settling profile. Encircled numbers are % SS removed.

TABLE 3.5
Values for Plotting Fig. 3.11

% SS removed	t (min)		
	2 ft	4 ft	6 ft
5	1.2	2.5	3.7
10	2.5	5.0	6.5
20	6.7	11.0	14.5
30	11.7	19.0	25.0
40	18.0	30.0	39.0
50	27.0	44.0	56.5
60	38.5	61.5	77.5
70	55.0	87.5	—
75	75.0	—	—

Particles with a settling velocity V_S or higher (where $V_S = H/t$) are completely removed. Particles with a lower settling velocity V_1 ($V_1 < V_S$) are removed at a ratio given by Eq. (3.18).

A typical graph like the one in Fig. 3.12 is plotted by analysis of data obtained with the sedimentation column. The details for construction of such

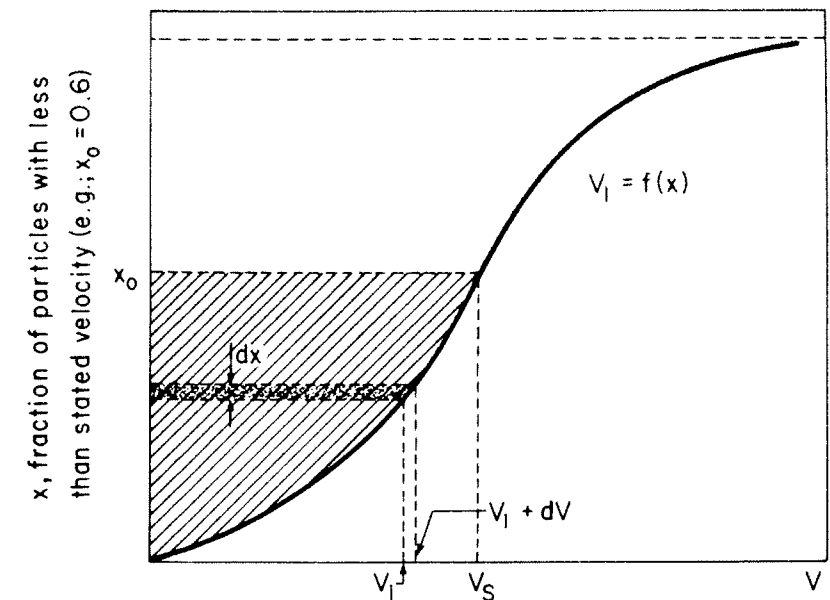


Fig. 3.12. Determination of overall removal.

a graph from experimental data are discussed later in Step 4(d). However, for understanding the calculation procedure described next, it is convenient to assume that this graph is already available.

Figure 3.12 is a plot of the fraction of particles with less than the stated velocity vs. the settling velocity in question. Notice that the fraction of particles with less than the stated velocity (if $V_S = H/t$) corresponds to the fraction of particles *not* completely removed. For example, if 40% of the particles in a specific case are completely removed, then $x_0 = 0.6$ is the ordinate corresponding to the settling velocity $V_S = H/t$.

For particles with settling velocities between V_1 and $V_1 + dV$ (where $V_1 < V_S$), the fraction removed is V_1/V_S . Similarly, for particles with settling velocities between $V_1 + dV$ and $V_1 + 2dV$, the fraction removed is $(V_1 + dV)/V_S$.

The overall removal of suspended solids is

$$\text{Overall removal} = (1 - x_0) + \int_0^{x_0} (V_1/V_S) dx \quad (3.25)$$

In Eq. (3.25) V_1 is a variable ($0 \leq V_1 \leq V_S$) with $V_1 = f(x)$ portrayed by the curve in Fig. 3.12. Term $(1 - x_0)$ is the fraction completely removed, corresponding to particles with velocities $\geq V_S$. The second term in Eq. (3.25), i.e.,

$$\int_0^{x_0} (V_1/V_S) dx = 1/V_S \int_0^{x_0} V_1 dx$$

which is the fraction of removal corresponding to particles with velocities less than V_s (calculated by graphical integration as indicated by the hatched area in Fig. 3.12). The differential area of width dx , indicated in Fig. 3.12, corresponds to particles with settling velocities between V_1 and $V_1 + dV$.

Combining Eqs. (3.18) and (3.25) the final expression for the overall removal is obtained [Eq. (3.26)].

$$\begin{aligned} \text{Overall removal} &= (1 - x_0) + \int_0^{x_0} (V_1/V_s) dx = (1 - x_0) + (1/V_s) \int_0^{x_0} V_1 dx \\ &= (1 - x_0) + \int_0^{x_0} (h/H) dx \end{aligned} \quad (3.26)$$

After these considerations return to discussion of Step 4.

Step 4(a). From Fig. 3.11 for a depth of 6 ft read the values t (min) corresponding to 5, 10, 20, 30, 40, 50, and 60% removal, and calculate the corresponding settling velocities V_s (ft/hr). These values are tabulated in Table 3.6.

TABLE 3.6
Settling Velocities ($H = 6$ ft)

Constant % removal	t (min) $H = 6$ ft	Settling velocity (ft/hr) $V_s = H/t = 6/(t/60) = 360/t$
5	3.7	97.2
10	6.5	55.2
20	14.5	24.8
30	25.0	14.4
40	39.0	9.2
50	56.5	6.35
60	77.5	4.64

Step 4(b). Calculate % removal of SS. Calculations for % removal of SS and overflow rate for a 25-min settling time (fourth entries in Table 3.6) are illustrated next. Similar calculations are also performed for the other settling times listed in the second column of Table 3.6. For $t = 25$ min for the settling depth $H = 6$ ft, 30% of the suspended solids are completely removed. Consider next the particles in each additional 10% range. Start with those in the range 30–40% removal in Fig. 3.11. Particles in this range are removed in the proportion V_1/V_s or in the proportion of average settled depth (h_1) to the total settling depth (H). The average settled depth (h_1) is estimated by drawing (by interpolation) a curve corresponding to 35% constant removal in Fig. 3.11, and reading from it the depth h_1 corresponding to $t = 25$ min. Therefore for this first interval, the % solids removal is $(h_1/H) \times 10 = (4.2/6) \times 10 = 7.0\%$.

In a similar manner for succeeding 10% intervals, the curves for constant % removal of 45, 55, 65, and 75% are drawn and the average settled depths of 2.4, 1.4, 0.84, and 0.28 ft are read for $t = 25$ min. The calculations for $t = 25$ min are indicated below.

Settling velocity: $V_s = H/t = 6.0/(25/60) = 14.4$ ft/hr

Percent solids removal (for $t = 25$ min)

100% removal (at 30%)	30.00%
1st interval (35%): $(4.2/6.0) \times 10 =$	7.00%
2nd interval (45%): $(2.4/6.0) \times 10 =$	4.00%
3rd interval (55%): $(1.4/6.0) \times 10 =$	2.33%
4th interval (65%): $(0.84/6.0) \times 10 =$	1.40%
5th interval (75%): $(0.28/6.0) \times 10 =$	0.46%
	45.19%
Total removed after 25 min	45.2%

Beyond the fifth interval the % removals are negligible, so calculations are stopped at that point. In general, if 10% intervals are selected, the total % removal is given by

$$\text{Total \% removal} = X_{\text{total}} + (h_1/H) \times 10 + (h_2/H) \times 10 + (h_3/H) \times 10 + \dots \quad (3.27)$$

Equation (3.27) is simply an approximation of Eq. (3.26). $(1 - x_0)$ corresponds to X_{total} and the integral $\int_0^{x_0} (h/H) dx$ is replaced by a finite summation of terms.

$$\sum (h_{\text{ave}}/H) \times \Delta x$$

where h_{ave} is the average settled depth for each selected interval. The Δx 's in this example are selected arbitrarily as a 10% range. The smaller the Δx selected, the closer the approximation between the finite summation and the integral.

Similar calculations are performed for the other residence times listed in the second column of Table 3.6. The final results are summarized in Table 3.7.

TABLE 3.7
SS (%) Removed vs. Detention Time

$t = (25 \text{ ft})^2 / (V_s)$	(1) t (min)	(2) % SS removal
	3.7	13.4
	6.5	20.1
	14.5	33.9
	25.0	45.2
	39.0	55.0
	56.5	64.3
	77.5	71.1

From Table 3.7 a graph of % SS removed vs. detention time is prepared (Fig. 3.13).

Step 4(c). Prepare a plot of % SS removed vs. overflow rate. Calculations needed to prepare this plot are presented in Table 3.8.

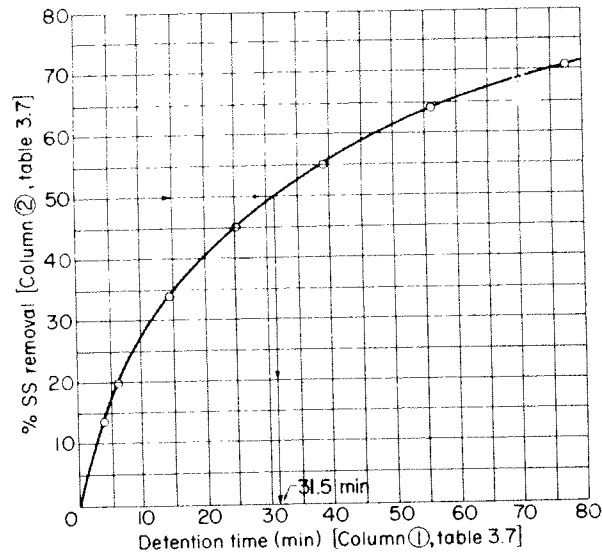


Fig. 3.13. Suspended solids removal (% SS) vs. detention time.

TABLE 3.8
SS (%) Removed vs. Overflow Rate

(1) t (min)	(2) Settling velocity, V_s (ft/hr) (Table 3.6)	(3) Overflow rate $\left[\frac{\text{gal}}{(\text{day})(\text{ft}^2)} \right]$ $V_s \left[\frac{\text{ft}}{\text{hr}} \times \frac{24 \text{ hr}}{\text{day}} \times \frac{7.48 \text{ gal}}{\text{ft}^3} \right] =$ $V_s \times 24 \times 7.48 = 179.5 V_s$	(4) % SS removal [column (2) of Table 3.7]
3.7	97.2	17,450	13.4
6.5	55.2	9,908	20.1
14.5	24.8	4,452	33.9
25.0	14.4	2,585	45.2
39.0	9.2	1,651	55.0
56.5	6.35	1,140	64.3
77.5	4.64	833	71.1

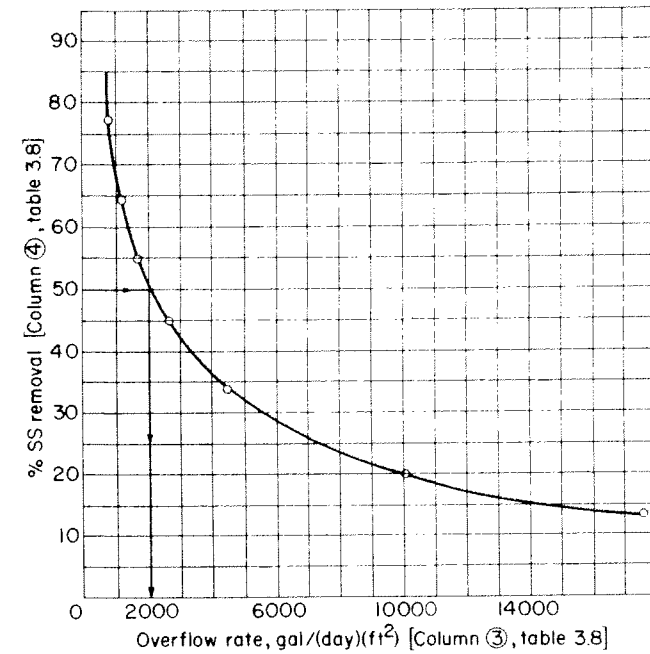


Fig. 3.14. Suspended solids removal (% SS) vs. overflow rate.

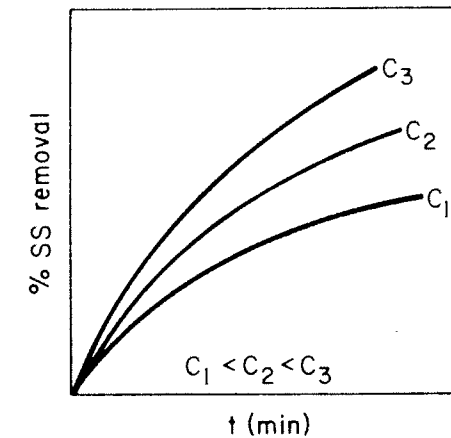


Fig. 3.15. Suspended solids removal (% SS) vs. detention time for different initial SS concentrations.

The plot of % SS removed vs. overflow rate is presented in Fig. 3.14. All calculations are performed for an initial suspended solids concentration SS_0 of 430 mg/liter. If similar calculations are performed for other values of these concentrations (C_1, C_2, C_3, \dots), the data plotted in Figs. 3.13 and 3.14 yield families of curves, as indicated in Figs. 3.15 and 3.16.

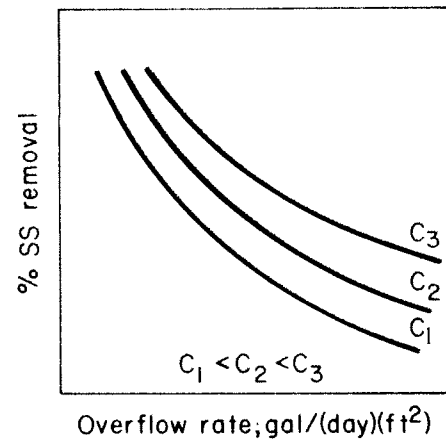


Fig. 3.16. Suspended solids removal (% SS) vs. overflow rate for different initial SS concentrations.

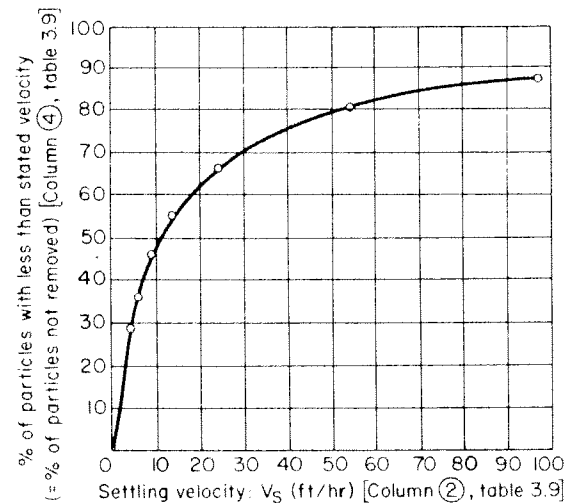


Fig. 3.17. Percentage of particles with less than stated velocity vs. settling velocity.

Step 4(d). Prepare a plot of percentage of particles with less than stated velocity (percentage not removed) vs. settling velocity (ft/hr). Calculations needed to prepare Fig. 3.17 are presented in Table 3.9. Figure 3.17 is not required for the design calculations; it is shown because a typical graph of this type was utilized in developing Eq. (3.26). The plot is presented in Fig. 3.17.

TABLE 3.9
Percentage of Particles with Less Than Stated Velocity vs. Settling Velocity

(1) t (min)	(2) V_s (ft/hr) (Table 3.6)	(3) % SS removal (Table 3.7)	(4) Percentage not removed: $100 - (\% \text{ SS removal})$
3.7	97.2	13.4	86.6
6.5	55.2	20.1	79.9
14.5	24.8	33.9	66.1
25.0	14.4	45.2	54.8
39.0	9.2	55.0	45.0
56.5	6.35	64.3	35.7
77.5	4.64	71.1	28.9

3.5.1. Design Calculations from Laboratory Data

For purposes of scale-up, the fact that the efficiency of the process in an actual settling tank is reduced owing to the effect of parameters such as turbulence, short circuiting, and interference of the inlet and outlet must be taken into account. The net effect of these factors results in a decrease of the overflow rate and an increase in the detention time over values derived from the laboratory analysis. For design purposes, it is customary to divide the overflow rate obtained from the laboratory analysis by a factor ranging between 1.25 and 1.75, and to multiply the detention time by a factor in the same range [3]. Table 3.10 presents some commonly used design values.

TABLE 3.10
Design Values (Primary Clarifiers)

Depth: 7-12 ft
Detention time: 1-2 hr
Flow-through velocity, $V = 1-5$ ft/min
Overflow rate: 900-1200 gal/(day)(ft ²)
Efficiencies
SS removal: 40-60%
BOD removal: 30-50%

Design procedure of a primary clarifier is illustrated by Example 3.4.

Example 3.4

It is determined by field observation that a raw wastewater has an average of 430 mg/liter suspended solids at a flow of 1.0 Mgal/day. Data shown in Table 3.3 are obtained from laboratory settling tests.

1. Design a settling tank of circular cross section, i.e., calculate its diameter and effective depth, to remove 50% of the suspended solids at the flow rate of 1.0 Mgal/day.

2. For the tank designed in (1), what is the removal if flow is doubled to 2.0 Mgal/day?

3. For the flow of 1.0 Mgal/day, calculate the daily accumulation of sludge in lb/day and the average pumping rate in gal/min. Sludge concentration is estimated as 1.5% solids from tests made with samples withdrawn from Tap 4 of the laboratory settling column (Fig. 3.9). A plot of % solids for the compacted sludge vs. settling time is constructed from data obtained from samples withdrawn from Tap 4 (Fig. 3.9). A typical plot of this type is shown in Fig. 3.18.

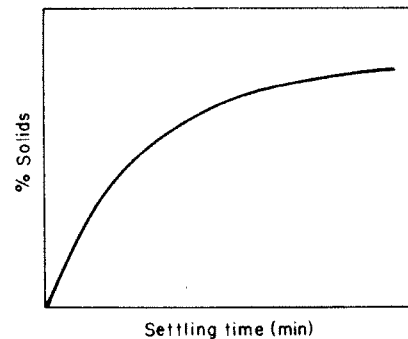


Fig. 3.18. Typical plot of % solids in the sludge vs. detention time.

SOLUTION: Part 1

Step 1. Determine the material balance for SS (see Fig. 3.19).

Influent: 430 mg/liter

Removal: $(0.50)(430) = 215$ mg/liter

Effluent: $430 - 215 = 215$ mg/liter

Step 2. Determine the overflow rate. From Fig. 3.14 read overflow rate corresponding to a 50% removal, $2000 \text{ gal}/(\text{day})(\text{ft}^2)$. Using a 1.75 scale-up factor, take a design overflow rate of $2000/1.75 = 1143 \text{ gal}/(\text{day})(\text{ft}^2)$.

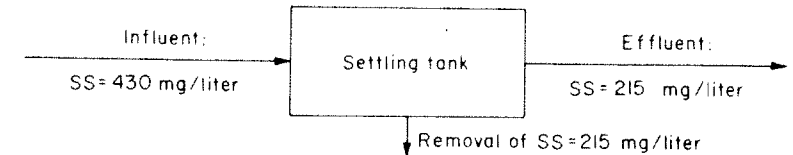


Fig. 3.19. Material balance for primary clarifier (Example 3.4).

Step 3. Determine the detention time. From Fig. 3.13 read detention time corresponding to a 50% removal value, $t = 31.5$ min.* Using a 1.75 scale-up factor, take $t = (31.5)(1.75) = 55.1$ min or $t = 55.1/60 = 0.92$ hr.

Step 4. Calculate required horizontal cross section of clarifier and its diameter. Horizontal cross section of clarifier is

$$A = \frac{1 \times 10^6 \text{ gal/day}}{1143 \text{ gal}/(\text{day})(\text{ft}^2)} = 874.9 \text{ ft}^2$$

and diameter is

$$D = (4A/\pi)^{1/2} = (874.9/0.785)^{1/2} = 33.4 \text{ ft}$$

Step 5. Calculate effective depth of the clarifier.

$$H = \text{volume}/A = Qt/A$$

$$H = \frac{1 \times 10^6 \text{ gal/day} \times \text{ft}^3/7.48 \text{ gal} \times 0.92/24 \text{ day}}{874.9 \text{ ft}^2} = 5.9 \text{ ft}$$

SOLUTION: Part 2 Removal for a flow rate of 2 MGD with the same clarifier

This amounts to doubling the design overflow rate, i.e.,

$$\text{New design overflow rate} = (2)(1143) = 2286 \text{ gal}/(\text{day})(\text{ft}^2)$$

From Fig. 3.14 this corresponds to a removal of 47.5% of the suspended solids.

SOLUTION: Part 3 Daily accumulation of sludge and average pumping rate for flow of 1.0 MGD

Step 1. Determine the daily accumulation of sludge.

$$\text{Removal of SS} = 215 \text{ mg/liter} \rightarrow 215 \times 10^{-6} \text{ lb SS/lb liquor}$$

Therefore, the daily accumulation of sludge in lb/day is

$$\begin{aligned} &1 \times 10^6 \text{ gal liquor/day} \times 8.34 \text{ lb liquor/gal liquor} \times 215 \times 10^{-6} \text{ lb SS/lb liquor} \\ &= 1793 \text{ lb SS/day} \end{aligned}$$

* From this value of the residence time ($t = 31.5$ min), the % solids in the sludge is estimated as 1.5% from a curve of the type in Fig. 3.19.

Step 2. Calculate the average pumping rate. Notice that 1.5% solids corresponds to 1.5 g SS/100 g of liquor = 15 g SS/1000 g of liquor \approx 15 g SS/liter = 15,000 mg/liter = ppm = 15,000 $\times 10^{-6}$ lb SS/lb liquor = 15,000 $\times 8.34 \times 10^{-6}$ lb SS/gal liquor. Since accumulation is 1793 lb SS/day, pumping rate in gal/day is

$$\frac{1793 \text{ lb SS/day}}{(15,000 \times 8.34 \times 10^{-6}) \text{ lb SS/gal liquor}} = 0.0143 \times 10^6 \text{ gal/day}$$

or

$$(0.0143 \times 10^6)/(24 \times 60) = 9.93 \text{ gal/min}$$

Since pumping rate is low, intermittent pumping is used.

3.6. ZONE SETTLING

Zone settling occurs in clarifiers of activated or chemically coagulated sludge when the concentration exceeds 500 mg/liter. The sludge blanket exhibits several distinct zones. Each zone is characterized by a specific sludge concentration and settling velocity. Consider what happens when a suspension which initially has a uniform sludge concentration C_0 (mg/liter) is placed in a settling cylinder (Fig. 3.20).

Sludge begins to settle out and an interface (interface 1) is established between the surface of the blanket of settling sludge and the clarified liquid above. The zone below the clarified liquid is called the interfacial zone. Concentration of the sludge in this zone is uniform, and it settles as a blanket with a constant velocity (V_s). Simultaneously with formation of interface 1

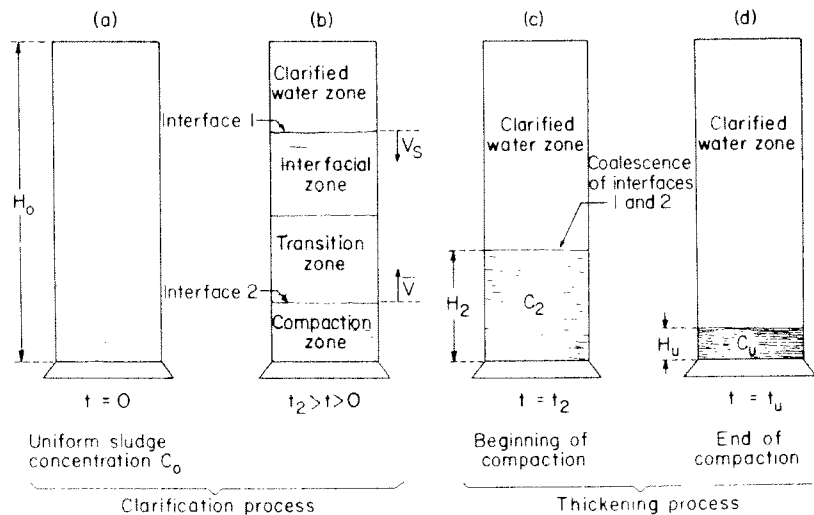


Fig. 3.20. Zone settling.

and interfacial zone, compaction of suspended solids starts at the bottom of the cylinder (compaction zone). In this zone concentration of SS is also uniform, and the interface bordering this zone (interface 2) rises in the cylinder with a constant velocity (\bar{V}).

Between the interfacial and compaction zones there is a transition zone. There, the velocity of settling solids decreases owing to increase of viscosity and density of the suspension. In this same zone, sludge changes gradually in concentration from that of the interfacial zone to that of the compaction zone.

Consider interfaces 1 and 2 in Fig. 3.20(b). Interface 1 moves downward with a constant velocity V_s , whereas interface 2 moves upward with a constant velocity \bar{V} . Eventually, interfacial and compaction zones meet, at which time (t_2) the transition zone fades away [Fig. 3.20(c)]. At this time, the settled sludge exhibits a uniform concentration C_2 , which is termed the critical concentration. Compaction starts and the sludge begins to thicken, eventually reaching an ultimate concentration C_u [Fig. 3.20(d)]. Sedimentation velocity at time t_2 corresponds to a value V_2 , which is given by the slope of the tangent to the settling curve at C_2 , as indicated in Fig. 3.21 where $V_2 < V_s$.

Procedure for designing clarifiers operating under conditions of zone settling:

1. Calculate the minimum surface area required to allow for clarification of sludge.
2. Calculate the minimum surface area required to provide for thickening of sludge to the desired underflow concentration.
3. Take the larger of these two areas as the design area for the clarifier.

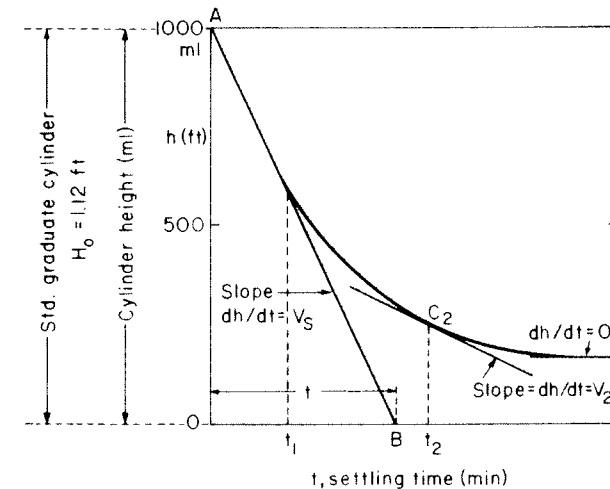


Fig. 3.21. Sludge settling curve.

3.6.1. Laboratory Measurements

To obtain the parameters necessary for design of the clarifier, a settling test for the sludge is performed in the laboratory using a 1000-ml graduated cylinder (a standard graduate cylinder has a height of 1.12 ft). The cylinder is filled with the slurry to be studied. At the beginning of the experiment ($t = 0$), slurry concentration is uniform throughout the cylinder. Height of interface 1 is recorded at selected time intervals. This yields the type of settling curve shown in Fig. 3.21.

It is important to stir the suspension at a rate of about 5 rph. This stirring simulates the action of the mechanical rakes utilized in sludge removal and prevents stratification of the sludge.

Figure 3.21 shows that from the start of the experiment up to a time t_1 , interface 1 falls with a constant velocity V_S given by the slope of the tangent, which essentially coincides with the settling curve from $t = 0$ to $t = t_1$. After $t = t_1$ this velocity decreases appreciably. At time $t = t_2$, the velocity is V_2 given by the slope of the tangent at C_2 . At t_2 compaction starts and the velocity is further reduced until it becomes essentially zero, the tangent being parallel to the abscissa.

Zone settling velocity (ZSV) corresponds to the velocity at which the suspension settles prior to reaching the critical concentration C_2 , and is given by the slope of the tangent AB in Fig. 3.21 [Eq. (3.28)].

$$V_S = \overline{OA}/\overline{OB} = H_0/t = 1.12 \text{ ft/min} \quad (3.28)$$

3.6.2. Determination of Minimum Surface Area Required to Allow Clarification of the Sludge

Minimum surface area A_c required for clarification depends on velocity V_S at which the suspension settles before reaching the interfacial critical concentration C_2 . Under continuous flow conditions, velocity of the liquor over the overflow weir cannot exceed V_S if clarification is to take place. This follows directly from the basic concept of the ideal sedimentation tank [Section 3.4, Eqs. (3.17) and (3.19)].

Therefore,

$$A_c = Q/V_S \quad (3.29)$$

where Q is the flow rate (ft^3/min); V_S the settling velocity (ft/min); and A_c the minimum surface area required for clarification (ft^2).

The value of the zone settling velocity V_S is determined from Fig. 3.21 and Eq. (3.28). Value of t is read directly from the abscissa of Fig. 3.21 (point B). V_S is then calculated from Eq. (3.28) and A_c obtained from Eq. (3.29).

3.6.3. Determination of Minimum Surface Area Required for Thickening of the Sludge

Consider settling of a sludge under zone settling conditions in a cylinder (Fig. 3.20). At start of the experiment, let C_0 be the uniform sludge concentration throughout the cylinder. Total weight of solids in the cylinder is $C_0 AH_0$, where A is the cross-sectional area of the cylinder. Let t_2 be the time counted from the beginning of the experiment, when interfacial and compaction zones merge together [Fig. 3.20(c)]. Let C_2 be the critical concentration which is uniform throughout this sludge zone formed by the merging of interfacial and compaction zones.

A graphical procedure has been proposed [7] for determining t_2 . Consider the settling curve in Fig. 3.22. Draw two tangents (AB and CD) to the two branches of the curve. Tangent AB corresponds to the constant velocity

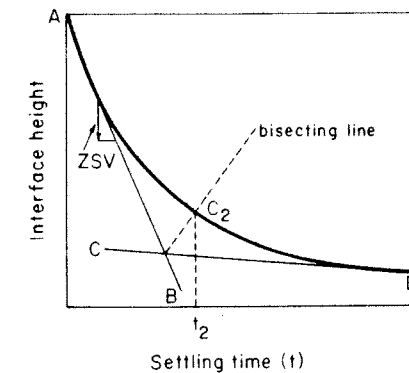


Fig. 3.22. Determination of t_2 .

of settling V_S for the interfacial zone (zone settling velocity, ZSV), and tangent CD corresponds to the settling velocity for the compacted sludge. Point C_2 (corresponding to time t_2) is obtained by bisecting the angle formed by tangents AB and CD. The abscissa of the point where the bisecting line cuts the settling curve corresponds to the desired value of t_2 .

Consider now the thickening process.

1. Start of thickening [Fig. 3.20(c)]. Time, t_2 ; concentration of SS in sludge zone, C_2 ; height of sludge zone, H_2 .
2. End of thickening [Fig. 3.20(d)]. The compacted sludge reaches desired underflow concentration C_u . The time at which this occurs is designated as t_u . Height of the sludge zone is H_u .

Consider separately the sludge zone at the start and end of thickening (Fig. 3.23). Since the total mass of sludge in the cylinder is constant, the

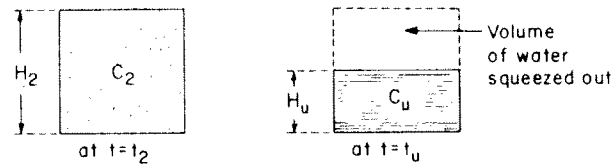


Fig. 3.23. Thickening process.

following material balance equation [Eq. (3.30)] is written, neglecting the amount of suspended solids in the clarified water zone.

$$C_0AH_0 = C_2AH_2 = C_uAH_u \quad (3.30)$$

or

$$C_0H_0 = C_2H_2 = C_uH_u \quad (3.31)$$

Consider Fig. 3.23. The volume of water which is squeezed out and discharged over the overflow weir is calculated from Eq. (3.32).

$$V = A(H_2 - H_u) \quad (3.32)$$

The time interval required to discharge this volume of water is $t_u - t_2$. Average rate of flow Q' (ft^3/min) over the weir is [Eq. 3.33]

$$Q' = V/(t_u - t_2) = A(H_2 - H_u)/(t_u - t_2) \quad (3.33)$$

Solving for $t_u - t_2$,

$$t_u - t_2 = A(H_2 - H_u)/Q' \quad (3.34)$$

Consider now the settling curve and determine graphically the settling velocity V_2 at time t_2 (tangent at point C_2). This is shown in Fig. 3.24.

Let H_1 be the intercept of this tangent. Settling velocity at t_2 is shown in Eq. (3.35).

$$V_2 = \tan \alpha = (H_1 - H_2)/t_2 \quad (3.35)$$

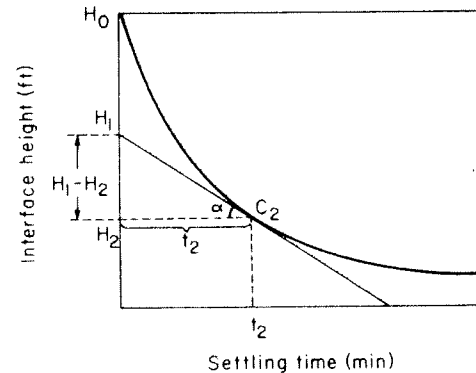


Fig. 3.24. Determination of velocity V_2 .

Under continuous flow conditions the velocity of the liquor over the weir cannot be greater than V_2 if thickening is to take place. Therefore, the flow rate Q' at time t_2 when thickening starts is

$$Q' = AV_2 = A[(H_1 - H_2)/t_2] = \text{ft}^3/\text{min} \quad (3.36)$$

Substitution of Q' given by Eq. (3.36) in Eq. (3.34) yields after simplification and rearrangement Eq. (3.37).

$$(H_2 - H_u)/(t_u - t_2) = (H_1 - H_2)/t_2 \quad (3.37)$$

This equation is the basis for the graphical procedure for determination of t_u illustrated by Fig. 3.25.

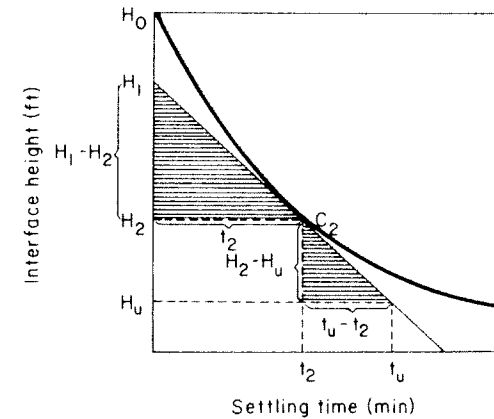


Fig. 3.25. Determination of t_u .

To summarize the steps in the graphical procedure for determination of t_u :

1. Draw the tangent to the settling curve at C_2 .
2. From material balance [Eq. (3.31)]

$$H_u = H_0 C_0 / C_u \quad (3.38)$$

Calculate H_u from Eq. (3.38).

3. Mark distance H_u on the ordinate axis of Fig. 3.25. Draw the horizontal dotted line from H_u until its intersection with the tangent to C_2 . The abscissa of this intersection is the value of t_u . This can be seen by inspection of Eq. (3.37) and consideration of the two cross-hatched similar triangles in Fig. 3.25.

Minimum surface area required for thickening (A_t) is obtained from the following considerations. Average rate at which the layer of concentration C_u forms (in lb/min) is

$$C_u H_u A_t / t_u \quad (3.39)$$

Since from Eq. (3.31) $C_u H_u = C_0 H_0$, then Eq. (3.39) is rewritten as

$$C_0 H_0 A_t / t_u \quad (3.40)$$

Under conditions of continuous flow and steady state, the rate at which the layer of concentration C_u is formed must equal that at which suspended solids enter in the influent (QC_0). Therefore

$$QC_0 = C_0 H_0 A_t / t_u \quad (3.41)$$

Solving for A_t ,

$$A_t = Qt_u / H_0 \quad (3.42)$$

where $H_0 = 1.12$ ft.

The design procedure for clarifiers under zone settling conditions is illustrated by Example 3.5.

Example 3.5

Design a secondary settling tank to produce an underflow concentration of 10,900 mg/liter from an influent containing 2510 mg/liter of suspended solids. Wastewater flow is 1.2 MGD. Calculate the clarifier area required.

The data tabulated below are obtained in a laboratory test of the slurry.

t (min)	Interface height H (m)
0	1000
1	850
2	725
3	600
5	450
8	350
12	280
16	240
20	220
25	210

SOLUTION

Step 1. Settling curve is plotted from available data (Fig. 3.26).

Step 2. Minimum surface area required for clarification (A_c) is determined.

1. Draw tangent AB. Read $t = 7.5$ min. Then $V_s = H_0/t = 1.12/7.5 = 0.149$ ft/min.

2. Area required for clarification:

$$A_c = \frac{1,200,000 \text{ gal/day} \times \text{ft}^3/7.48 \text{ gal} \times \text{day}/1440 \text{ min}}{0.149 \text{ ft/min}} = 748 \text{ ft}^2$$

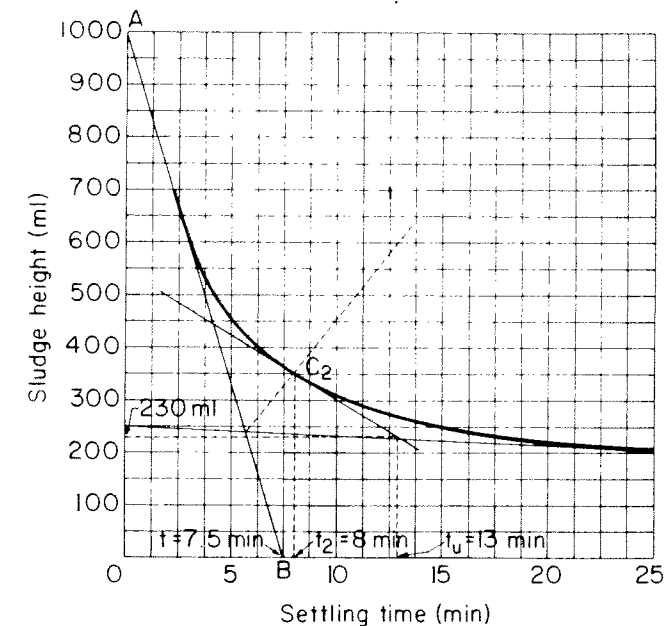


Fig. 3.26. Graph for Example 3.5.

Step 3. Minimum surface area required for thickening (A_t) is calculated.

1. Determine t_2 by the graphical procedure studied. From Fig. 3.26 read $t_2 = 8.0$ min.

2. Determine time t_u . Draw the tangent to the settling curve at C_2 and calculate H_u from Eq. (3.28).

$$H_u = (1000 \times 2510) / 10,900 = 230 \text{ ml}$$

3. Determine t_u by the graphical procedure described. From Fig. 3.26 read $t_u = 13$ min.

4. Calculate A_t from Eq. (3.42).

$$A_t = \frac{1,200,000 \text{ gal/day} \times \text{ft}^3/7.48 \text{ gal} \times \text{day}/1440 \text{ min} \times 13 \text{ min}}{1.12 \text{ ft}} = 1293 \text{ ft}^2$$

Step 4. Take $A = A_t = 1293 \text{ ft}^2$. Required diameter for a sedimentation tank of circular cross section is

$$d = (4A/\pi)^{1/2} = (1293/0.785)^{1/2} = 40.6 \text{ ft}$$

3.7. TYPES OF CLARIFIERS

Clarifiers are classified according to geometry of their horizontal cross section as (1) rectangular and (2) circular: (a) center and (b) peripheral feed. Sketches of typical clarifiers are shown in Figs. 3.27(a), (b), and (c).

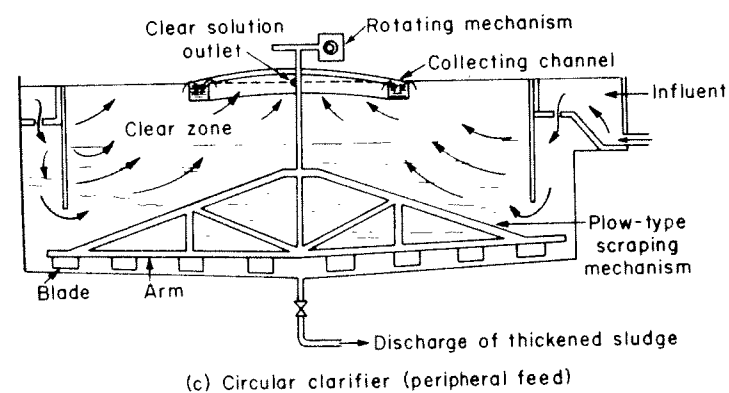
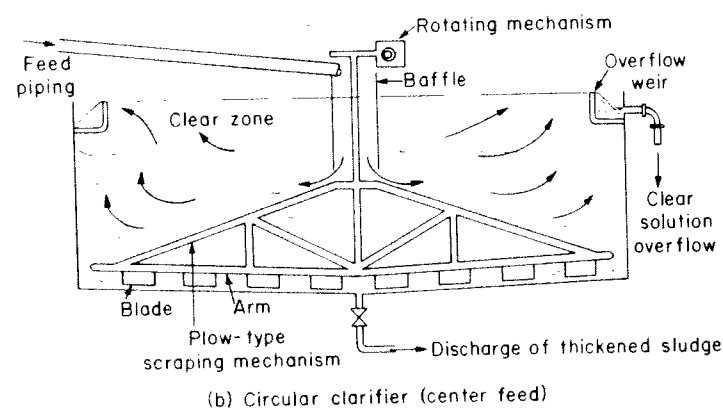
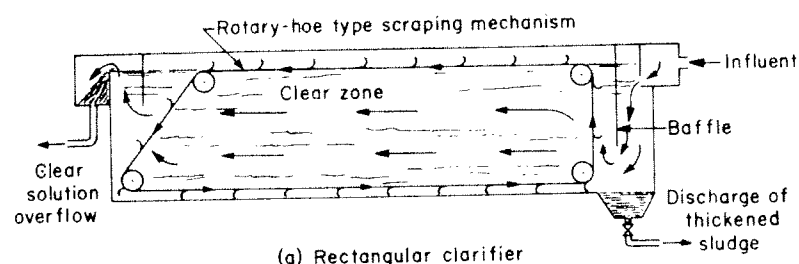


Fig. 3.27 Types of clarifiers (a), (b), and (c).

1. Rectangular clarifier [Fig. 3.27(a)]

In the type shown in Fig. 3.27(a), scraped sludge is moved toward the inlet end of the tank. Some other designs move sludge toward the effluent end of the tank.

Scraping mechanism shown is of rotary-hoe type, consisting of a series of short scrapers mounted on an endless chain, which make contact with the bottom of the tank. It moves slowly at speeds of approximately 1 ft/min.

2a. Circular clarifier with center feed [Fig. 3.27(b)]

Feed is at the center and clear solution overflows to a collecting channel at the periphery. The bottom of the clarifier has a minimum slope of 1 in./ft. Scraping mechanism is of plow type to overcome inertia and prevent adherence of sludge to the bottom of the tank.

2b. Circular clarifier with peripheral feed [Fig. 3.27(c)]

The feed is at the periphery and the clear solution overflows to a collecting channel at the center. The other details are similar to those for the type shown in Fig. 3.27(b).

The inlet section should be carefully designed for a uniform flow distribution across the width and depth of the tank. Similarly, the outlet section should be designed to collect the effluent uniformly.

A good design of inlet and outlet sections reduces possibilities of flow short circuiting, which lead to poor performance of the clarifier. Proper positioning of weirs and baffles, as indicated in Fig. 3.27, prevents short circuiting.

4. Flotation

4.1. INTRODUCTION

Flotation is a process for separating low density solids or liquid particles from a liquid phase. Separation is brought about by introduction of gas (usually air) bubbles into the liquid phase. The liquid phase is pressurized to an operating pressure ranging from 30 to 60 psia (2–4 atm) in presence of sufficient air to promote saturation of air in the water. Then, this air-saturated liquid is depressurized to atmospheric pressure by passage through a pressure-reducing valve. Minute air bubbles are released from the solution because of depressurization. Suspended solids or liquid particles, e.g., oil, are floated by these minute air bubbles, causing them to rise to the surface of the tank. Concentrated suspended solids are skimmed off by mechanical means from the tank surface. Clarified liquor is withdrawn near the bottom, and part of it may be recycled [Fig. 3.28(b)]. A flotation system without recycle is shown diagrammatically in Fig. 3.28(a).

In the field of wastewater treatment, flotation is used for the following purposes: (1) separation of greases, oils, fibers, and other low density solids from wastewaters; (2) thickening of the sludge from the activated sludge

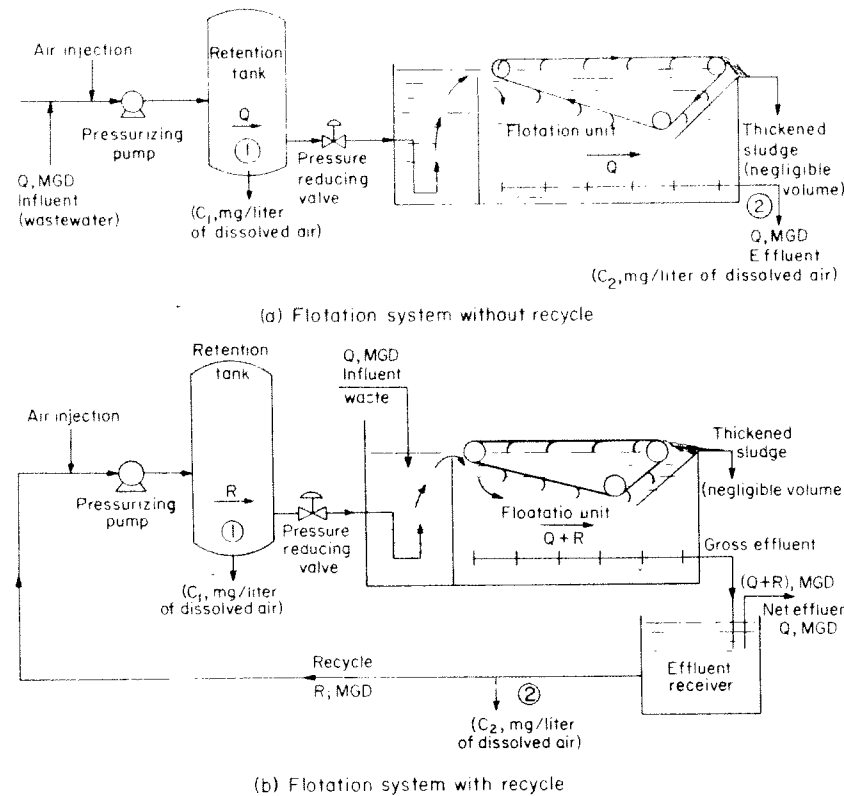


Fig. 3.28. Flotation systems (a) and (b).

process; and (3) thickening of flocculated chemical sludges resulting from chemical coagulation treatment. Superior effluent quality, i.e., effluent containing lower percentage of suspended solids, and economy in power are achieved by flotation systems with recycle.

Basic components of a flotation system are (1) pressurizing pump; (2) air injection facilities; (3) retention tank (to provide air-liquid contact); (4) pressure-reducing valve; and (5) flotation tank.

4.2. EVALUATION OF FLOTATION VARIABLES FOR PROCESS DESIGN

4.2.1. Parameter A/S

For design of flotation systems, a fundamental parameter commonly utilized is a dimensionless air to solids ratio (A/S) defined by Eq. (3.43).

$$A/S = \frac{\text{lb/day of air released by depressurization}}{\text{lb/day of solids in the influent}} \quad (3.43)$$

4. Flotation

This parameter is estimated from studies with a laboratory-scale flotation cell of pilot-plant data. The value of A is obtained from determinations of dissolved air (mg/liter) at sampling locations indicated as (1) and (2) in Fig. 3.28(a) and (b). Thus [Eq. (3.44)]

$$A = A_1 - A_2 \quad (3.44)$$

where A is the lb/day of air released by depressurization; A_1 the lb/day of dissolved air at (1) [Fig. 3.28(a) and (b)]; and A_2 the lb/day of dissolved air at (2) [Fig. 3.28(a) and (b)].

For flotation systems without recycle [Eq. (3.45)],*

$$A_1 = Q \frac{\text{Mgal liquor}}{\text{day}} \times C_1 \frac{\text{lb air}}{\text{Mlb liquor}} \times 8.34 \frac{\text{lb liquor}}{\text{gal liquor}} = 8.34QC_1 \quad (\text{lb air/day}) \quad (3.45)$$

Similarly [Eq. (3.46)]

$$A_2 = 8.34QC_2 \quad (\text{lb air/day}) \quad (3.46)$$

Therefore

$$A = A_1 - A_2 = 8.34Q(C_1 - C_2) \quad (\text{lb/day of air released}) \quad (3.47)$$

For flotation systems with recycle the corresponding equation is

$$A = A_1 - A_2 = 8.34R(C_1 - C_2) \quad (\text{lb/day of air released}) \quad (3.48)$$

If S_i is the concentration of suspended solids (mg/liter) in the influent, the value of S [denominator of Eq. (3.43)] is

$$S = Q \frac{\text{Mgal liquor}}{\text{day}} \times \frac{8.34 \text{ lb liquor}}{\text{gal liquor}} \times S_i \frac{\text{lb SS}}{\text{Mlb liquor}} = 8.34QS_i \quad (\text{lb SS/day}) \quad (3.49)$$

Substitution of Eqs. (3.47) [or Eq. (3.48)] and (3.49) in Eq. (3.43) leads to Flotation systems without recycle

$$A/S = (C_1 - C_2)/S_i \quad (3.50)$$

Flotation systems with recycle

$$A/S = (R/Q)(C_1 - C_2)/S_i \quad (3.51)$$

4.2.2. Correlation of Flotation Variables to Parameter A/S

By use of a laboratory flotation cell or pilot-plant data, it is possible to correlate mg/liter of suspended solids contained in liquid effluent to parameter A/S . A typical correlation curve for a wastewater has the shape indicated in Fig. 3.29.

* Notice that C_1 mg of air/liter of liquor = C_1 lb of air/Mlb of liquor.

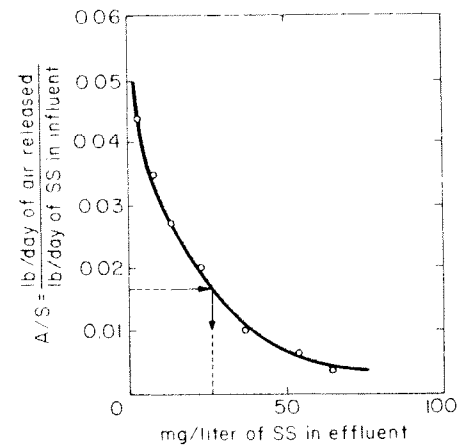


Fig. 3.29. Typical correlation of parameter A/S vs. concentration of SS in effluent.

For a given influent, the lb/day of suspended solids (term S in ratio A/S) is fixed. Ratio A/S increases by operating at higher air rates, which results in increase of air released (A). From Fig. 3.29 it follows that a higher quality effluent is obtained.

Graphs like Fig. 3.29 permit selection of the A/S ratio for a required degree of effluent clarification. These curves indicate that increasing the A/S ratio beyond an optimum value does *not* result in substantial reduction in effluent suspended solids.

Judicious selection of the A/S ratio involves an economical balance between equipment and maintenance costs and desired effluent quality. Typical range of A/S ratios for thickening of sludges in wastewater treatment is 0.005–0.060.

4.2.3. Alternative Expressions for Parameter A/S [2]

Consider Eq. (3.46) for A_2 , where C_2 is the solubility of air in water in mg/liter. Frequently, the solubility of air is expressed in terms of cm^3 of air/liter of water. It is assumed that conditions at (2) [Figs. 28(a) and (b)] are atmospheric pressure and ambient temperature. Solubility of air in water in cm^3 of air/liter of water [hence denoted as S_a] is presented in Table 3.11 for atmospheric pressure at several temperatures.

This concentration of dissolved air in cm^3 of air/liter of water is converted to the value C_2 (mg air/liter of water) [Eq. (3.52)].

$$S_a \text{ cm}^3 \text{ air/liter water} \times \rho_a \text{ mg air/cm}^3 \text{ air} = C_2 \quad (\text{mg air/liter water}) \quad (3.52)$$

TABLE 3.11
Solubility of Air in Water at Atmospheric Pressure at Several Temperatures [6]

Temperature ($^{\circ}\text{C}$)	S_a (cm^3/liter)
0	29.2
10	22.8
20	18.7
30	15.7

Utilize for the density of air ρ_a a mean value of 1.2 mg/cm^3 . (This corresponds to the value at 1 atm and 20°C .) Then [Eq. (3.53)]

$$C_2 = 1.2S_a \quad (3.53)$$

Consider now Eq. (3.45), where C_1 is the solubility of air in mg/liter. The cm^3 of air/liter of water at the retention tank [point (1)] is shown in Eq. (3.54).

$$\varphi S_a \quad (\text{cm}^3 \text{ air/liter water}) \quad (3.54)$$

where φ is the ratio of solubility of air in water at the pressure in the retention tank [at (1)] to the solubility at atmospheric pressure [at (2) in Figs. 28(a) and (b)] [Eq. (3.55)].

$$\varphi = C_1/C_2 \quad (\varphi > 1.0) \quad (3.55)$$

It is found experimentally that for a specific design of the retention tank, and within ordinary pressure ranges utilized in flotation operations, ratio φ is proportional to the pressure

$$\varphi = fP \quad (3.56)$$

where f is the proportionality factor and P the pressure in retention tank in atmospheres.

At 20°C for pressure range 30–60 psia utilized in most flotation systems and for baffled retention tanks, the value of f in Eq. (3.56) is approximately 0.5. Consequently, values of φ vary from

$$30 \text{ psia} (= 30/14.7 = 2.04 \text{ atm}) = 0.5 \times 2.04 = 1.02$$

$$60 \text{ psia} (= 60/14.7 = 4.08 \text{ atm}) = 0.5 \times 4.08 = 2.04$$

Therefore for the pressure range from 30 to 60 psia at 20°C , solubility of air in baffled retention tanks varies from 1.02 to 2.04 times its saturation value at 20°C and 1 atm. Since from Eq. (3.55)

$$C_1 = \varphi C_2 \quad (3.57)$$

substitution of φ and C_2 by their values given by Eqs. (3.56) and (3.53) yields

$$C_1 = fP(1.2S_a) \quad (3.58)$$

Substitution of values of C_1 and C_2 given, respectively, by Eqs. (3.58) and (3.53) in Eqs. (3.50) and (3.51) leads to

Flotation systems without recycle

$$A/S = 1.2S_a(fP - 1)/S_i \quad (3.59)$$

Flotation systems with recycle

$$A/S = (R/Q)1.2S_a(fP - 1)/S_i \quad (3.60)$$

4.3. DESIGN PROCEDURE FOR FLOTATION UNITS WITHOUT AND WITH RECYCLE

4.3.1. Flotation Systems without Recycle

From Eq. (3.59) it follows that if a ratio A/S is selected, f being fixed for a selected type of retention tank and S_i from characteristics of the influent, this amounts to specification of operating pressure P , which is calculated from Eq. (3.59) as

$$P = (1/f)[(A/S)S_i/1.2S_a + 1] \quad (3.61)$$

Design of flotation systems without recycle involves calculating the required operating pressure [Eq. (3.61)] and determining the cross-sectional area of the flotation unit. This area is calculated from a selected value of the overflow rate, usually a value between 2 and 4 gal/(min)(ft²) (Example 3.6).

Example 3.6

Laboratory flotation tests for a given wastewater indicate optimum air/solids ratio (A/S) as 0.04 lb air/lb solids. Flow of wastewater is 1.0 MGD and it contains 250 mg/liter of suspended solids. Laboratory flotation tests (without recycle) indicate for a ratio $A/S = 0.04$ an optimum effluent containing 25 mg/liter of suspended solids. Take $f = 0.50$ for retention tank and an operating temperature of 20°C. Design a flotation system without recycle for this service.

SOLUTION

Step 1. Select $A/S = 0.04$, as stated.

Step 2. Calculate P from Eq. (3.61).

$$P = (1/0.5)(0.04 \times 250/1.2 \times 18.7 + 1) = 2.9 \text{ atm}$$

Step 3. Select an overflow rate,

$$OR = 3 \text{ gal}/(\text{min})(\text{ft}^2)$$

Step 4. Calculate required surface area,

$$Q = 1.0 \text{ MGD}$$

or

$$Q = 1,000,000 \text{ gal/day} \times \text{day}/24 \text{ hr} \times \text{hr}/60 \text{ min} = 695 \text{ gal/min}$$

$$\text{Surface area (ft}^2\text{)} = Q/OR = \frac{695 \text{ gal/min}}{3.0 \text{ gal}/(\text{min})(\text{ft}^2)} = 232 \text{ ft}^2$$

4.3.2. Flotation Systems with Recycle

It follows from Eq. (3.60) that for a specific application (i.e., for fixed values of f and S_i) one must specify not only the A/S ratio but also the recycle before the operating pressure P becomes fixed. The usual procedure is to specify an operating pressure P and an A/S ratio and calculate the required recycle from Eq. (3.60), which solved for R yields Eq. (3.62).

$$R = (A/S)QS_i/1.2S_a(fP - 1) \quad (3.62)$$

The design procedure for flotation systems with recycle is illustrated by Example 3.7.

Example 3.7

For the application in Example 3.6 design a flotation system with recycle, taking an operating pressure of 2.9 atm.

SOLUTION

Step 1. Select $A/S = 0.04$, as stated.

Step 2. Calculate R from Eq. (3.62).

$$R = (0.04)(1.0)(250)/1.2 \times 18.7(0.5 \times 2.9 - 1) = 0.99 \text{ MGD} \approx 1.0 \text{ MGD}$$

This means that recycle ratio R/Q is approximately unity.

Step 3. Select an overflow rate

$$OR = 3 \text{ gal}/(\text{min})(\text{ft}^2)$$

Step 4. Required surface area is defined as

$$Q + R \approx 2.0 \text{ MGD}$$

or

$$2,000,000 \text{ gal/day} \times \text{day}/24 \text{ hr} \times \text{hr}/60 \text{ min} = Q + R = 1390 \text{ gal/min}$$

$$\text{Surface area (ft}^2\text{)} = (Q + R)/OR = 1390/3.0 = 464 \text{ ft}^2$$

Surface area is twice as large as for the unit without recycle. However, an effluent of superior quality (i.e., SS < 25 mg/liter) is obtained.

5. Neutralization (and Equalization)

5.1. NEUTRALIZATION IN THE FIELD OF WASTEWATER TREATMENT

Neutralization treatment is often utilized in the following cases arising in wastewater treatment:

1. Prior to discharge of the wastewater into a receiving water. The justification for neutralization is that aquatic life is sensitive to pH variations beyond a narrow range around pH 7.

2. Prior to discharge of industrial wastewaters to the municipal sewer system. Specification of the pH of industrial discharges into municipal sewer systems is frequently made. It is more economical to neutralize industrial wastewater streams prior to the discharge into the municipal sewer, rather than attempting to perform neutralization of the larger volume of combined domestic and industrial sewage.

3. Prior to chemical or biological treatment. For biological treatment, pH of the system is maintained within the range 6.5–8.5 to ensure optimum biological activity. The biological process itself provides a neutralization and buffer capacity as a result of production of CO_2 , which forms carbonates and bicarbonates in solution. The degree of preneutralization required for biological treatment depends on two factors: (1) the alkalinity or acidity present in the wastewater and (2) the mg/liter BOD to be removed in the biological treatment. The latter is related to the production of CO_2 , which may provide for partial neutralization of alkaline wastes.

5.2. METHODS FOR NEUTRALIZATION OF WASTEWATERS

Methods for neutralization of wastewaters include (1) equalization, which consists of mixing acidic and alkaline waste streams available in the plant and (2) direct pH control methods, which consist of addition of acids (or bases) for neutralization of alkaline (or acidic) wastewater streams.

5.3. EQUALIZATION

When utilized for purpose of neutralization, equalization involves mixing wastewater streams of acidic and alkaline nature in an equalization basin. Equalization is often used for purposes other than neutralization such as (1) to smooth out individual wastewater stream flow variations, so that a composite stream of relatively constant flow rate is fed to the treatment plant; and (2) to smooth out variations in influent BOD to the treatment facilities. Constant and variable level equalization basins are utilized.

1. *Constant level equalization basins.* This arrangement is illustrated in Fig. 3.30. The level in the equalization basin is held constant. Therefore as

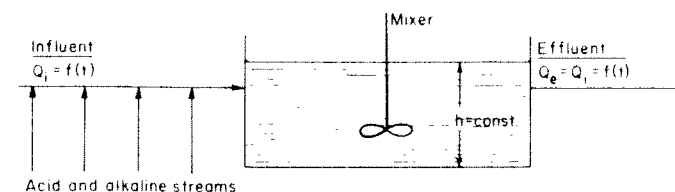


Fig. 3.30. Constant level equalization basin.

the rate of flow of influent varies, that of effluent is equally affected. Consequently, this is not a technique of flow equalization, simply a method of neutralization. If fluctuations in the flow rate are too great, the effluent from the constant level equalization basin is fed to another equalization basin having as objective flow equalization.

2. *Variable level equalization basins.* In this method of equalization, the effluent is taken out at a constant rate, and since the flow rate of influent varies with time, the level of the equalization basin is variable. This method is also utilized for the purpose of flow equalization, as well as providing for neutralization. A diagram of a variable level equalization basin is shown in Fig. 3.31.

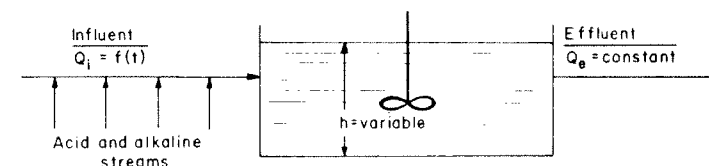


Fig. 3.31. Variable level equalization basin.

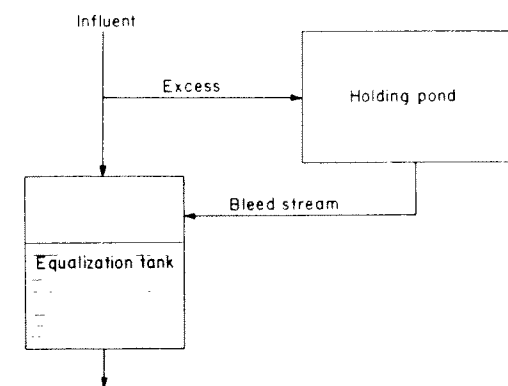


Fig. 3.32. "Holding pond" method of equalization.

Another method of equalization consists of diverting the "excess" of the incoming stream to a holding pond, from which a bleed stream is fed to the equalization tank. This method is not used for neutralization purposes, but only for equalization of BOD content or flow rate. This is illustrated by Fig. 3.32.

5.4. DIRECT pH CONTROL METHODS: NEUTRALIZATION OF ACIDIC WASTES BY DIRECT pH CONTROL METHODS

The following methods of direct neutralization of acidic wastes are the most commonly employed: (1) limestone beds, (2) slurried lime neutralization, (3) caustic soda (NaOH) neutralization, (4) sodium carbonate neutralization, and (5) ammonia neutralization.

A few specific comments about these methods are as follows:

Slurried lime neutralization is the most common method and is discussed in Section 5.6. Design of limestone beds is described in Section 5.5.

Caustic soda (NaOH) is more expensive than lime. It offers an advantage with respect to uniformity of the reagent, ease of storage and feeding, rapid reaction rate, and the fact that the end products of neutralization (sodium salts) are soluble.

Sodium carbonate (Na_2CO_3) is not as reactive as caustic soda and presents frothing problems owing to release of carbon dioxide.

Ammonia (NH_4OH) presents the disadvantage of being a contaminant; consequently its use may be ruled out by pollution control standards.

Factors guiding selection of a neutralization reagent are (1) purchase cost, (2) neutralization capacity, (3) reaction rate, and (4) storage and disposal of neutralization products.

5.5. LIMESTONE BEDS

5.5.1. Types of Equipment

Both upflow and downflow types of limestone beds are employed. For wastewaters containing H_2SO_4 , limestone beds should not be used if concentration of H_2SO_4 exceeds 0.6%. The reason for this limitation is that the limestone becomes covered with an insoluble coat of CaSO_4 , rendering it ineffective. In addition, evolution of CO_2 causes frothing problems.

Upflow type arrangement is preferable to downflow type since in upflow units, CaSO_4 tends to be flushed out before precipitation on the limestone. Also, escape of CO_2 generated by the neutralization reaction is easier in upflow type units. For these reasons, maximum hydraulic rate for downflow systems is limited to approximately 50 gal/(hr)(ft²).

Presence of metallic ions (e.g., Al^{3+} , Fe^{3+}) in the wastewater reduces

effectiveness of the limestone bed owing to coating of limestone with precipitated hydroxides. Finally, if dilution of the acid in the wastewater is increased, higher residence times are required for neutralization.

5.5.2. Design Procedure for Limestone Beds

In this section, the laboratory procedure recommended by Eckenfelder and Ford [3] for obtaining the basic design data is described. A numerical example is presented to illustrate design of an actual limestone column. A model of a laboratory limestone neutralization column is shown in Fig. 3.33. Bench-scale columns operate with heights of limestone of 1.0–5 ft, which is the actual range of heights for plant-scale units. Column diameter is approximately 6 in., and rates of flow [gal/(hr)(ft²)] are comparable to those for plant operation.

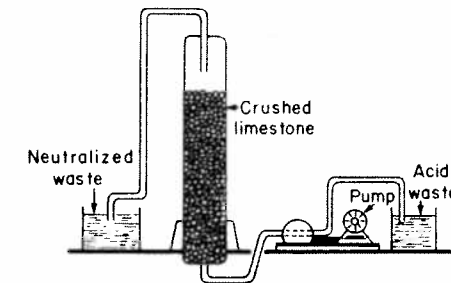


Fig. 3.33. Laboratory model of limestone neutralization column.

Step 1. Fill neutralization columns with limestone (after washing and screening) to depths of 1, 2, 3, 4, and 5 ft (5 columns).

Step 2. Adjust upward flow rate of acid wastewater for each column. Flow rates varying from 50 to 1000 gal/(hr)(ft²) are used.

Step 3. Check effluent pH from each column at each flow rate utilized until it is stabilized.

Step 4. After each run replace limestone used in the columns.

Step 5. Plot terminal pH as a function of rate of flow [gal/(hr)(ft²)] for each depth of limestone. A typical plot of this type is shown in Fig. 3.34.

Purposes of the design procedure are (1) to select the most economical height of column for a specified pH of the effluent. This is the column height corresponding to a maximum allowable flow rate, expressed in terms of volume of limestone utilized, i.e., gal of liquor/(hr)(ft³ of limestone); and (2) to calculate annual requirement of limestone under these conditions, which corresponds to a minimum requirement of limestone.

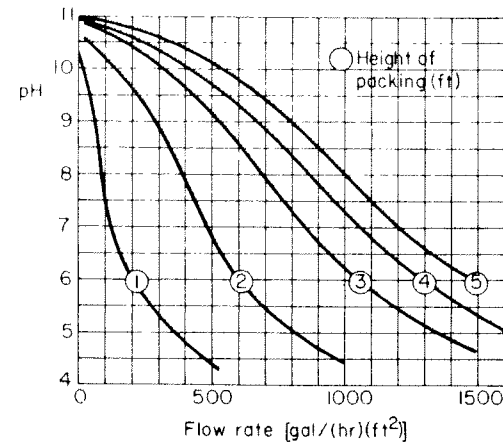


Fig. 3.34. Limestone neutralization data.

Example 3.8

It is desired to neutralize a wastewater acid stream containing 0.1 N HCl to a pH of 7.0 through a limestone bed. Laboratory tests with the wastewater yield data plotted in Fig. 3.34. Design a neutralization system for 100 gal/min (6000 gal/hr) of wastewater and estimate annual limestone requirement for the most economical operation.

SOLUTION

Step 1. For pH 7 read from Fig. 3.34 rates of flow [gal/(hr)(ft²)] corresponding to each column depth. Then calculate cross-sectional area, volume of limestone bed required, and flow rate in gal/(hr)(ft³ of limestone bed) (Table 3.12).

TABLE 3.12
Calculations for Example 3.8

(1) Depth (ft)	(2) Flow rate [gal/(hr)(ft ²) [From Fig. 3.34 for pH 7]	(3) Cross section (3) = $\frac{6000 \text{ gal/hr}}{(2)}$	(4) Volume of limestone (ft ³) (4) = (1) × (3)	(5) Flow rate [gal/(hr)(ft ³)] (5) = $\frac{6000 \text{ gal/hr}}{(4)}$
1.0	118	51	51	118
2.0	492	12.2	24.4	246
3.0	845	7.1	21.3	282
4.0	1047	5.73	22.9	262
5.0	1200	5.0	25.0	240

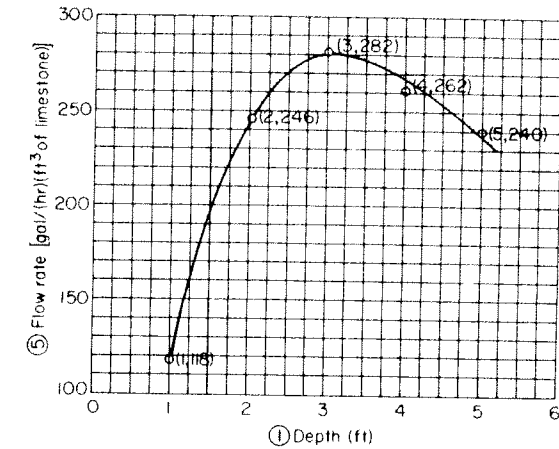


Fig. 3.35. Determination of optimum bed depth.

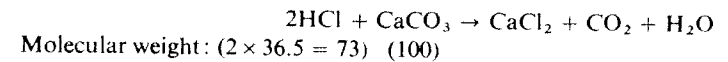
Step 2. Plot flow rates [gal/(hr)(ft³)] from column (5) of Table 3.12 vs. depths [column (1)]. This plot is shown in Fig. 3.35 and indicates that a 3-ft limestone bed is the most economical, corresponding to a maximum on the curve. The cross-sectional area in this case (see Table 3.12 for a depth of 3.0 ft) is 7.1 ft², corresponding to a diameter of 3.0 ft.

Step 3. Calculate the lb of acid to be neutralized per day (acid contained in the 6000 gal/hr of the 0.1 N solution of HCl). Since this is a dilute acid solution, calculation is based on the density of water, taken as 8.34 lb/gal. A 0.1 N solution of HCl contains 3.65 g/liter of HCl, or approximately 3.65 lb of acid per 1000 lb of solution. Therefore

$$\text{Mass flow rate: } 6000 \text{ gal/hr} \times 24 \text{ hr/day} \times 8.34 \text{ lb/gal} = 1.2 \text{ Mlb/day}$$

$$\text{Acid content: } 3.65 \times (1,200,000/1000) = 4380 \text{ lb/day}$$

Step 4. Calculate limestone (CaCO₃) required. The neutralization equation is



Therefore limestone required is

$$4380 \times 100/73 = 6000 \text{ lb/day of limestone}$$

This is the theoretical amount of limestone assuming 100% reactivity. For design purposes, assume an 80% reactivity. Limestone required is then

$$6000/0.8 = 7500 \text{ lb/day or } 2.738 \times 10^6 \text{ lb/year}$$

5.6. SLURRIED LIME TREATMENT

5.6.1. Equipment for Slurried Lime Systems

Slurried lime is the most commonly used reagent for neutralization of acid wastewaters, the low cost of lime being the main reason for its widespread utilization. A flowsheet of a two-stage slurried lime neutralization system is shown in Fig. 3.36.

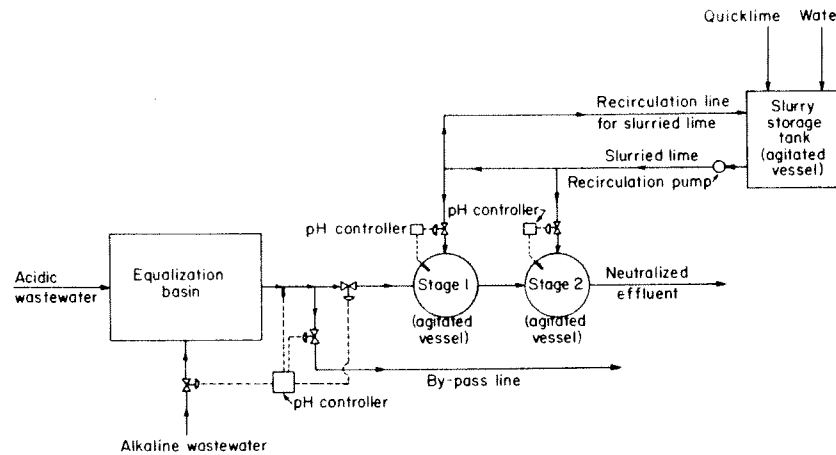


Fig. 3.36. Flow diagram of a two-stage slurried lime neutralization system.

Stepwise addition of lime is recommended. For highly acidic wastes a minimum of two stages is desirable, the first (bulk neutralization) to raise pH to a value of 3.0–3.5, and the second (fine tuning) to adjust pH to desired effluent value. Sometimes a third stage is desirable.

Automatic control of this process is not simple because the relationship between pH and amount of lime added is highly nonlinear, particularly in the vicinity of the neutralization point (pH 7). This is appreciated by inspection of a typical neutralization curve of an industrial wastewater, shown in Fig. 3.37.

In the vicinity of the neutralization point, the pH becomes exceedingly sensitive to small additions of lime, varying in an ordinary operation of slurried lime systems at a rate as fast as one pH unit per minute. Also, fluctuation in flow rate of influent complicates operation of the process. Use of an equalization tank is indicated to dampen fluctuations, as shown in Fig. 3.36. A relatively small amount of reagent is thoroughly mixed with a large liquid volume in a short time interval. Mechanical mixers are provided for this purpose.

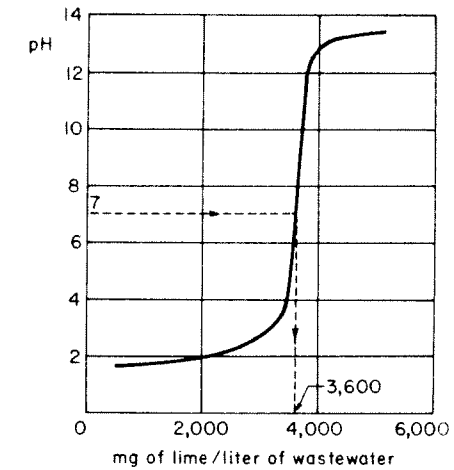


Fig. 3.37. Typical neutralization curve for an industrial wastewater.

5.6.2. Design Procedure for Slurried Lime Neutralization Systems

The procedure recommended by Eckenfelder and Ford [3] is summarized in this section and illustrated by a numerical example. Basic information required is (1) neutralization curve for the wastewater (see Fig. 3.37), and (2) power consumption data, i.e., a curve of level of agitation vs. detention time for a desired terminal pH (see Fig. 3.38). This basic information is obtained by simple laboratory procedures [3].

Purposes of the design procedure illustrated by Example 3.9 are (1) to select the number of stages of neutralization and to size neutralization reactors, and (2) to select appropriate mixing equipment.

Example 3.9

200 gal/min of an acidic industrial wastewater are neutralized to pH 7.0. From laboratory tests, the neutralization curve is plotted (Fig. 3.37). Also, a curve of level of agitation vs. detention time is obtained for this neutralization (Fig. 3.38). Design a lime slurry neutralization system.

SOLUTION

Step 1. From the neutralization curve in Fig. 3.37, lime slurry requirement for neutralizing the wastewater to a pH of 7 is read as 3600 mg/liter.

Step 2. Calculate lime slurry requirement for 200 gal/min wastewater flow. Since

$$3600 \text{ mg lime/liter waste} = 3600 \times 10^{-6} \text{ lb lime/lb waste}$$

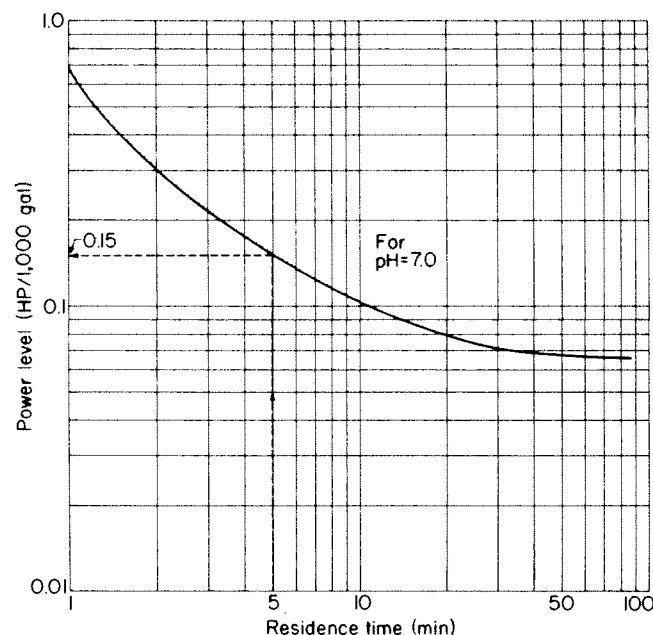


Fig. 3.38. Level of agitation vs. detention time.

then

$$200 \text{ gal waste/min} \times 60 \text{ min/hr} \times 24 \text{ hr/day} \times 8.34 \text{ lb waste/gal waste} \\ \times 3600 \times 10^{-6} \text{ lb lime/lb waste} = 8647 \text{ lb lime/day}$$

Step 3. Neutralize acid in two steps as indicated by flow diagram in Fig. 3.36, the first stage for bulk neutralization, and the second for fine tuning.

Step 4. Select a detention time and size the reactors.

$$\text{Volume of reactor (gal)} = Q \text{ (gal/min)} \times t \text{ (min)} \quad (3.63)$$

Selection of the optimum detention time is arrived at by an economical balance.

1. Assume a residence time (usually a value between 5 and 10 min).
2. Size the reactor [Eq. (3.63)].
3. From Fig. 3.38 for the assumed residence time, determine power level required.
4. Select mixers (as shown in Step 5) from knowledge of power level [item (3)].

5. Estimate total costs (capital and operating) corresponding to this assumed residence time. Main items in the column of capital costs are the reactors themselves (and auxiliary equipment) and the mixers. Energy requirement is the variable item among operating costs.

6. Repeating steps (1)–(5), a curve of total cost per year vs. a series of selected residence times is plotted. This curve passes through a minimum which corresponds to the optimum detention time. Capital costs are expressed on a yearly basis by estimating equipment life and utilizing the current value for interest rate.

Assume for Example 3.9 that optimum residence time is estimated by this procedure as 5 min. Then

$$\text{Volume of each reactor (gal)} = 200 \text{ gal/min} \times 5 \text{ min} = 1000 \text{ gal}$$

or

$$1000 \text{ gal} \times \text{ft}^3/7.48 \text{ gal} = 134 \text{ ft}^3$$

Selecting a reactor depth of 5 ft, required cross-sectional area is

$$\text{Area} = 134 \text{ ft}^3/5 \text{ ft} = 26.8 \text{ ft}^2$$

corresponding to a diameter of 5.84 ft.

Step 5. Select mixers. From Fig. 3.38, power level required for 5-min detention time is

$$0.15 \text{ HP/1000 gal}$$

Since each tank has a volume of 1000 gal, specify one 0.15-HP mixer for each tank.

5.7. NEUTRALIZATION OF ALKALINE WASTES

In principle, any strong acid can be used to neutralize alkaline wastewaters. Cost considerations limit choice to H_2SO_4 (the most common) and HCl . Reaction rates are essentially instantaneous. The basic design procedure for alkaline wastes is similar to that for acidic wastes described in Section 5.6.

Flue gases containing 14% or more of CO_2 are used for neutralization of alkaline wastewaters. When bubbled through the wastewater the CO_2 forms carbonic acid, which reacts with the base. Reaction rate is slow but sufficient if pH need not be adjusted below 7 or 8. Either bubbling through a perforated pipe or using spray towers is satisfactory.

Problems

I. *Sedimentation (discrete settling).* A particle size distribution is obtained from a sieve analysis of sand particles. For each weight fraction an average settling velocity is calculated. Data [6] are presented in the following tabulation.

Settling velocity (ft/min)	Weight fraction remaining
10.0	0.55
5.0	0.46
2.0	0.35
1.0	0.21
0.75	0.11
0.50	0.03

1. Prepare a plot of fraction of particles with less than stated velocity vs. settling velocity (ft/min).
2. For an overflow rate of 100,000 gal/(day)(ft²), calculate overall removal utilizing Eq. (3.26).

II. Sedimentation (floculent settling). A laboratory settling analysis gave the results tabulated below.

Time Time (min)	% suspended solids removed at indicated depth		
	2 ft	4 ft	6 ft
10	40	25	16
20	54	37	28
30	62	47	37
45	71	56	46
60	76	65	53

1. Perform analysis of the data and arrive at curves for % SS removal vs. detention time (min), and % SS removal vs. overflow rate [gal/(day)(ft²)].
2. If the initial concentration of the slurry is 430 ppm, design a settling tank (i.e., calculate diameter and effective depth of the tank) to remove 70% of the suspended solids for a 1 Mgal/day flow.
3. What removal is attained if flow is increased to 2 Mgal/day?
4. For the flow of 1 Mgal/day calculate daily accumulation of sludge in lb/day and average pumping rate in gal/min. Assume sludge concentration to be 1.5% solids ($\approx 15,000$ mg/liter).

III. Sedimentation (zone settling). It is desired to design a secondary settling tank to produce an underflow concentration of 15,000 mg/liter from a mixed liquor solids content of 3750 mg/liter in the influent. Wastewater flow is 2.0 Mgal/day. Calculate clarifier area required. Data below are obtained in a laboratory test of the slurry.

t (min)	Interface height, H (ml)
0	1000
2	920
4	840
6	760
8	690
10	600
15	400
20	300
25	280
30	270

IV. Flotation. A pilot-plant flotation operation indicated optimum air/solid ratio to be 0.04 lb air/lb of solids.

1. If a wastewater to be treated has 250 ppm suspended solids, compute the % recycle to be pressurized to 60 psia at 20°C. Take $f = 0.68$.
 2. For a wastewater flow of 1.0 Mgal/day and an overflow rate of 4.0 gal/(min)(ft²) compute surface area required.
- V. Neutralization.** For the 3-ft limestone bed designed in Example 3.8 prepare a plot of volume of limestone required vs. a range of selected values of pH for the effluent (select pH = 5, 6, 7, 8, 9, and 10).

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