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Flow Equalization and Neutralization

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1. INTRODUCTION

Flow equalization and chemical neutralization and are two important components of water and wastewater treatment. Chemical neutralization is employed to balance the excess acidity or alkalinity in water, whereas flow equalization is a process of controlling flow velocity and flow composition. In a practical sense, chemical neutralization is the adjustment of pH to achieve the desired treatment objective. Flow equalization is necessary in many municipal and industrial treatment processes to dampen severe variations in flow and water quality. Both these processes have been practiced in the water and wastewater treatment field for several decades. Thtis chapter will present an overview of these two processes, the chemistry behind neutralization, design considerations, and their industrial application.

2. FLOW EQUALIZATION

Flow equalization is used to minimize the variability of water and wastewater flow rates and composition. Each unit operation in a treatment train is designed for specific wastewater characteristics. Improved efficiency and control are possible when all unit operations are carried out at uniform flow conditions. If there exists a wide variation in flow composition over time, the treatment efficiency of the overall process performance may degrade severely. These variations in flow composition

could be due to many reasons, including the cyclic nature of industrial processes, the sudden occurrence of storm water events, and seasonal variations. To dampen these variations, equalization basins are provided at the beginning of the treatment train. The influent water with varying flow composition enters this basin first before it is allowed to go through the rest of the treatment process. Equalization tanks serve many purposes. Many processes use equalization basins to accumulate and consolidate smaller volumes of wastewater such that full scale batch reactors can be operated. Other processes incorporate equalization basins in continuous treatment systems to equalize the waste flow so that the effluent at the downstream end can be discharged at a uniform rate.

Various benefits are ascribed by different investigators to the use of flow equalization in wastewater treatment systems. Some of the most important benefits are listed as follows (1–6):

1. Equalization improves sedimentation efficiency by improving hydraulic detention time.
2. The efficiency of a biological process can be increased because of uniform flow characteristics and minimization of the impact of shock loads and toxins during operation.
3. Manual and automated control of flow-rate-dependent operations, such as chemical feeding, disinfection, and sludge pumping, are simplified.
4. Treatability of the wastewater is improved and some BOD reduction and odor removal is provided if aeration is used for mixing in the equalization basin.
5. A point of return for recycling concentrated waste streams is provided, thereby mitigating shock loads to primary settlers or aeration basin.

Sometimes it is thought that equalization tanks also serve the purpose of dilution. However, the United States Environmental Protection Agency (US EPA) does not consider the use of equalization tanks as an alternative to achieve dilution. The US EPA's viewpoint is that dilution is mixing of more concentrated waste with greater volumes of less concentrated waste such that the resulting wastewater does not need any further treatment.

Equalization basins in a treatment system can be located in-line or off-line. Figures 1a,b depict the typical layouts of both types of equalization practice with respect to the rest of the unit operations. In in-line equalization, 100% incoming raw wastewater directly enters into the equalization basin, which is then pumped directly to other treatment units (e.g., primary treatment units). However, for side-line or off-line equalization, the basin does not directly receive the incoming wastewater. Rather, an overflow structure diverts excess flow from the incoming raw wastewater into the basin. Water is pumped from the basin into the treatment stream to augment the flow as required.

Two basic configurations are recommended for an equalization basin: variable volume and constant volume. In a variable volume configuration, the basin is designed to provide a constant effluent flow to the downstream treatment units. However, in the case of a constant volume basin, the outflow to other treatment units changes with changes in the influent. Both configurations have their uses in different applications. For example, variable volume type basins are used in industrial applications where a low daily volume is expected. Variable volume equalization basins can also be used for municipal wastewater treatment applications.
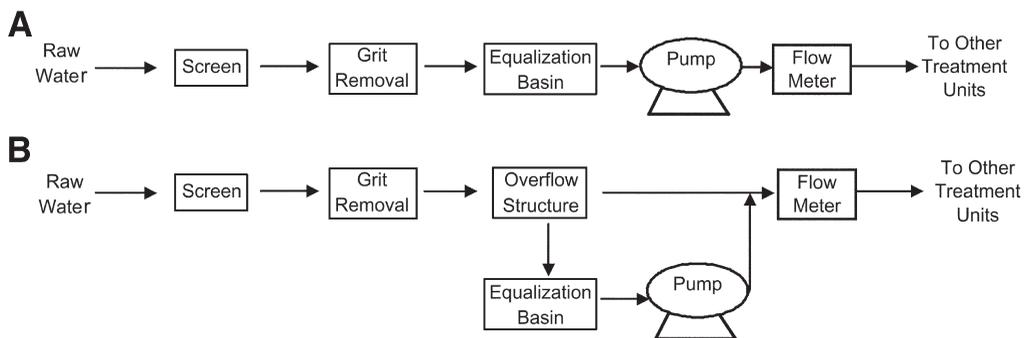
Fig. 1. (a) In-line and (b) off-line flow equalization.
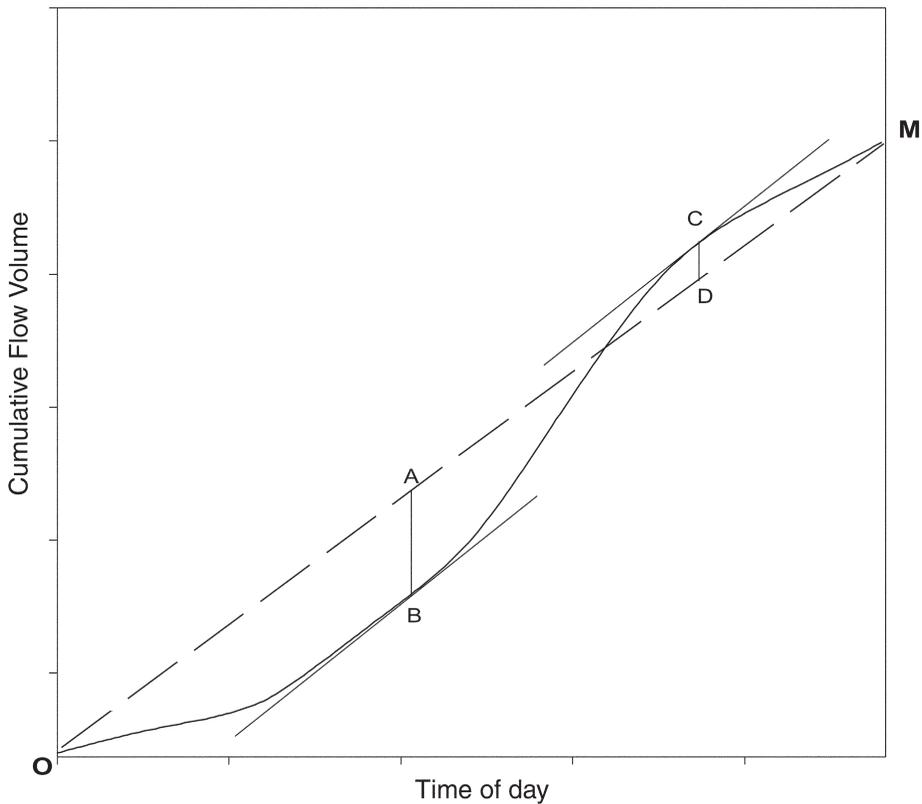
2.1. *Flow Equalization Basin Calculations*

Computation of the volume of an equalization basin is the key design requirement and is based on inflow variation over time. There are two methods used to compute equalization volume. One procedure is based on the characteristic diurnal flow pattern, whereas the other is based on the mass loading pattern of a particular constituent.

The first method relies on computing the equalization volume based on the excess daily average flow storage. The required volume is determined graphically by constructing a hydrograph. The function of the basin is to store flows in excess of the average daily flow and to divert this flow during times when the inflow is less that the average daily flow. The second method computes the volume based on mass loading variations within an acceptable range.

In general, the first method is regarded as a flow balance approach and the second method is regarded as a composition balance approach. Flow balance is the most common method for computing equalization basin volume. The selection of a particular method depends on the type of flow, flow variations, and overall composition of the flow. Flow balance is used when the composition of incoming water is relatively constant but the flow varies over time. The composition balance method is used when the rate of inflow is fairly constant and the composition varies with time.

In the flow balance method, a plot of cumulative volume versus time is developed, which is the well-known Rippl diagram (7). The steps required to create a Rippl diagram and to use this diagram to calculate the equalization volume are outlined as follows:

- The first step is to draw a cumulative volume curve based on the wastewater flow. The volume that flows within a specified periodic time period is calculated based on the flow. The cumulative volume is obtained by adding the volume at the start of a preselected time period to the volume in the next time period. The resulting volume is then added to the volume in the subsequent time period. This process is continued until a cycle of low-flow and high-flow is completed (typically 24 h).
- The second step is to determine the required equalization volume by drawing a line parallel to the average flow rate and tangent to the cumulative influent flow diagram. The equalization volume is calculated by the vertical distance from the point of tangency to the straight line. There could be several points of tangency on the cumulative influent flow curve. However, care should be taken in selecting the points to be taken into consideration for equalization volume calculations.

Fig. 2. Volume calculation of equalization basin.

The theory behind the method is explained with Fig. 2, which shows a typical cumulative influent volume curve for the average daily flows. In this figure, the cumulative volume is plotted on the *y*-axis against the time of day. The resulting graph is shown by an irregularly shaped curve. If the curve is linear, then the flow is constant. When the tail end (O) of this cumulative influent volume curve is joined with the top end (M), the average flow curve (shown by dotted line) is obtained. Lines parallel to average daily flow line (dotted line) and tangent to mass flow curve are then drawn. The points of tangency are (B) and (C). From these points of tangency, vertical straight lines are drawn until these vertical lines intersect the average daily flow line. The points of intersection are given at (A) and (D). The required equalization volume will be equal to sum of the vertical distances AB and CD. At the first point (B) of tangency, the storage basin is empty and beyond this point, the basin begins to fill and continues until the basin becomes full at upper point (C) of tangency.

The volume calculated based on the hydrograph method is the theoretical volume. In practice, the volume will be always greater than the theoretical because of the following reasons:

- A minimum volume of water is always required in an equalization basin for mixing and aeration equipment inside the basin to operate.
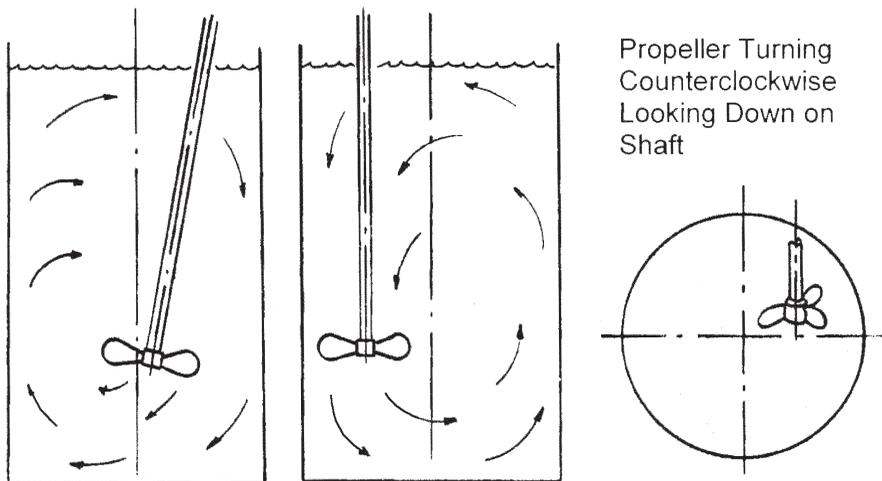
Fig. 3. Illustration of mixer (9).

- Sometimes, concentrated waste downstream in the treatment plant is returned to the equalization basin. To avoid odor problems, dilution of such returned waste is needed and the diluted water is stored in the equalization basin.
- Some free board is always provided to accommodate unforeseen changes in diurnal flow.

Flow equalization is more routinely employed in industry than at municipal facilities because many industries use batch production processes (2,3). However, there are now also a large number of municipal equalization basin installations.

2.2. *Mixing and Aeration Requirements*

Mixers are often employed in equalization basins to achieve homogeneity in and to aerate the wastewater. Various types of mixers are available. The classification of mixers depends on the flow pattern the mixers produce. The commonly used mixers have either axial or radial patterns, with axial mixers most prevalently used in industries (8).

Axial mixers can further be subdivided into other categories, the most common of which are propeller mixers and turbine mixers. Propeller mixers are used primarily when rapid mixing is needed. The axial propeller mixer can be either fixed or portable, depending on the mixer size and application. The size of top-entering propeller mixers range from 0.37 to 2.24 kW, although many industrial designs limit the size to 0.75 kW and a maximum shaft length of 1.83 m (8). Propeller mixers are usually mounted angularly off center. The advantage with this type of arrangement is that complete top to bottom mixing can be achieved. Typically the maximum water volume that is recommended for a propeller mixer is 3.785 m^3 (1000 gal). As shown in Fig. 3, the mixer shaft should enter at 15° from vertical and at a point off the centerline.

The speed ranges for both portable and fixed mounted propeller mixers are 1750 rpm and 350–420 rpm, respectively. The high speed provides a high degree of shear with low draft velocity, causing instant mixing. Low speeds provide less shear force and may allow selective setting of larger and heavier particles.
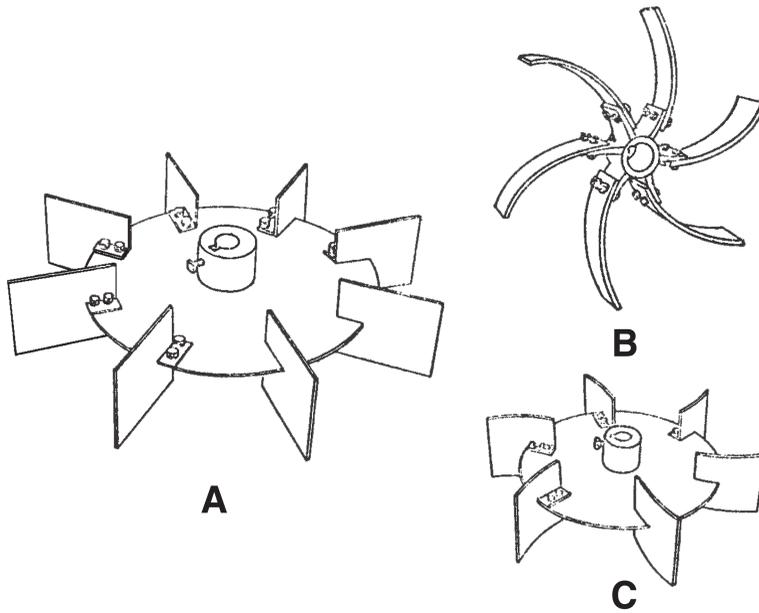
Fig. 4. Typical Radial Turbine Impeller: (a) flat blade; (b) spiral backswept; (c) curved Blade (9).

Other classes of axial mixers include turbine mixers. They can induce both axial as well as radial flow. Axial turbine impellers are pitched blade or fan turbines, whereas radial turbine impellers are flat blade, curved blade, or with a spiral backswept blade (shown in Fig. 4). The curved and spiral backswept impellers are used in high viscous applications such as sodium hydroxide or soda ash neutralization. Axial turbines are used for large scale mixing involving liquid solid suspensions. Turbines mixers are usually fixed mounted, vertically in fully baffled tanks. Turbine impeller diameters are generally one third of the tank diameter.

2.3. Mixer Unit

The design of an economically feasible mixer unit requires an assessment of power requirements, laboratory scale up studies, and the selection of either a batch or continuous system, hydraulic retention time, vessel geometry, and type of mixing unit (6). The following sections discuss some of these design considerations.

2.3.1. Power Requirements

Under turbulent hydraulic conditions (i.e., when the Reynolds number is greater than 10^5), the following formula can be used to determine the power requirements of an impeller mixer (6),

$$P = \rho K_T n^3 D^5 \qquad (1)$$

where P = power requirement, N-m/s, ρ = density of the fluid, kg/m^3, K_T = constant dependent on impeller size and shape, n = impeller revolutions per second, s^{-1}, D = diameter of impeller, m.

Table 1
Values of K_T for Impeller Design

Impeller type	K_T
Propeller (square pitch, three blades)	0.32
Propeller (pitch of two, three blades)	1.0
Turbine (six flat blades)	6.30
Turbine (six curved blades)	4.80
Turbine (six arrowhead blades)	4.00
Fan Turbine (six blades)	1.65
Flat paddle (two blades)	1.70
Shrouded turbine (six curved blades)	1.08
Shrouded turbine (with stator, no baffles)	1.12

Source: Ref. 6.

Some of the typical K_T values for design purposes are given in Table 1 (6). These K_T values are for mixing impellers rotating at the center of cylindrical tanks with a flat bottom, four baffles at the tank wall, baffle width of 10% of the tank diameter, and impeller diameter equal to one-third of the tank diameter.

The Camp and Stein mean velocity gradient, G, is used to describe the intensity of mixing in the tank. G is related to the amount of power dissipated in the tank and typically ranges from 500 to 1500 s^{-1} for rapid mixing (2). G can be calculated as follows:

$$G = \left(\frac{P}{V\mu} \right)^{\frac{1}{2}} \tag{2}$$

where V = mixing tank volume, m^3, μ = absolute viscocity of the fluid, N-s/m^2.

To ensure adequate mixing, the tank is sized to obtain a detention time, t_d, in the range of 5–30 s for rapid mixing. This results in $G \times t_d$ values of at least 2500, where

$$G \times t_d = \left(\frac{P}{V\mu} \right)^{\frac{1}{2}} \times \frac{V}{Q} = \frac{1}{Q} \left(\frac{PV}{\mu} \right)^{\frac{1}{2}} \tag{3}$$

where Q = flow rate, m^3/s.

2.3.2. *Laboratory Scale Up*

The usual practice involves the determination of design parameters in laboratory scale experiments and then generalizing these parameters for full-scale applications. Problems are often encountered during the scaling up of laboratory parameters for full-scale applications. Careful considerations should be given while selecting design parameters from laboratory experiments. The selection should be based on experience, similarity, and testing accuracy. If budget permits, it is always beneficial to test the design parameters found in laboratory experiments and in pilot-scale experiments. Once these parameters prove their suitability in pilot-scale experiments, they can further be used for full-scale operations.

2.3.3. *Vessel Geometry*

Vessel geometry plays a significant role in achieving overall mixing efficiency. However, the selection of vessel geometry is dictated by process considerations. As a general rule, circular tanks are more efficient in achieving proper mixing than square or rectangular tanks. For circular tanks, a liquid depth equal to tank diameter is generally employed. For tanks less than 4000 L, compact turbine mixers are the most practical.

3. NEUTRALIZATION

Neutralization is a common practice in wastewater treatment and waste stabilization. If a waste stream is found to be hazardous because of corrosivity, neutralization is the primary treatment used. Moreover, neutralization is used as a pretreatment system before a variety of biological, chemical, and physical treatment processes. Since many chemical treatment processes, such as metal precipitation, coagulation, phosphorus precipitation, and water softening are pH dependent, the pH of these processes is adjusted to achieve maximum process efficiency. Furthermore, the pH of the effluent wastewater from different industrial activities also requires adjustment prior to its discharge into receiving water bodies. The US EPA has set pH standards for different types of water; for example, the pH range required to protect marine aquatic life is 5–9 (10).

Neutralization is the process of adjusting the pH of water through the addition of an acid or a base, depending on the target pH and process requirements. Some processes such as boiler operations and drinking water standards need neutral water at a pH of 7. Water or wastewater is generally considered adequately neutralized if (1) its damage to metals, concrete, or other materials is minimal; (2) it has little effect on fish and aquatic life; (3) it has no effect on biological matter (i.e., biological treatment systems).

In chemical industrial treatment, neutralization of excess alkalinity or acidity is often required. One of the critical items in neutralizing the water is to determine the nature of the substances that cause acidity and alkalinity. This is generally achieved in laboratory-scale experiments by preparing titration curves showing the quantity of alkaline or acidic material necessary to adjust the pH of the target wastewater. The nature of titration curves obtained in these experiments is critical in determining the proper chemical type and dose. Methods used for pH adjustment should be selected on the basis of costs associated with the neutralizing agent and equipment requirements for dispensing the agent.

In neutralization, several parameters need to be assessed and evaluated before the actual pH adjustment is carried out. These parameters are discussed in the following sections.

3.1. *pH*

pH is the reference indicator for neutralization. Many chemical processes, such as metal precipitation and water softening, which are involved in neutralization, are pH dependent. pH is the negative logarithm of the H^+ ion activity in solution

$$pH = -\log\{H^+\} \tag{4}$$

If the ionic strength of the waters is not very high (less than 0.01 *M*), the activity of hydrogen ions can be replaced with the molar concentration of hydrogen ions,

If the ionic strength is high, correction factors using the Debye–Hückel equation or Davies equation can be commonly used (10).

In most practical applications, the pH scale ranges from 1 to 14. In pure water and in the absence of materials other than H^+ and OH^-, water behaves ideally and activity equals molar concentration. Under these conditions, $[H^+]$ equals $[OH^-]$ as required by electroneutrality. At 25°C, the ion product of water ($K_w = [H^+][OH^-]$) is 10^{-14}.

The process of neutralization is not only limited to bringing the pH to 7; it is invariably used in the processes, where pH adjustment to other than 7 is required depending on the chemical process in question. For example, some processes like biological wastewater treatment require pH to be near neutral, whereas other processes like metal precipitation require pH to be in the alkaline range. Some of the important chemical processes, where pH plays a significant role and where pH adjustment through neutralization is often required, are metal adsorption and biosorption, chemical precipitation, water softening, coagulation, water fluoridation, and water oxidation (11–14).

3.2. Acidity and Alkalinity

Alkalinity is the capacity of water to neutralize acids, whereas acidity is the capacity of water to neutralize bases. The amount of acid or base to be used in the neutralization process depends upon the respective amount of acidity and alkalinity.

The most important source of both alkalinity and acidity in natural waters is from the carbonate system. However, if the wastewater comes from industrial sources, OH^- or H^+ is also a major contributory factor to alkalinity or acidity, respectively. For example, water from acid mine drainage contains a large amount of acidity because of the presence of sulfuric acid produced from the oxidation of pyrite. Both acidity and alkalinity are expressed in terms of acid/base equivalents. In water and wastewaters where the predominant ions controlling pH are $[H^+]$, $[OH^-]$, $[HCO_3^-]$, and $[CO_3^{2-}]$, the forms of alkalinity encountered are hydroxide, carbonate, and bicarbonate. These three forms of alkalinity altogether constitute total alkalinity.

Alkalinity and acidity are determined by titration. For wastewater samples whose pH is above 8.3, titration is made in two steps. In the first step, the pH is brought down to 8.3; in the second step, the pH is brought down to about 4.5. When the pH of wastewater is below 8.3, a single titration curve is made. When the pH of wastewater reaches 8.3, all carbonate present in wastewater converts to bicarbonate according to the following reaction;

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \tag{5a}$$

As titration proceeds, bicarbonate goes to carbon dioxide when the pH reaches at 4.5. Carbon dioxide and water together form weak carbonic acid:

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \tag{5b}$$

If it is assumed that carbonate species and OH^- are the only chemical constituents causing alkalinity, the three forms of alkalinity can be defined based on pH. When pH of water is above 8.3, all three forms of alkalinities are present. As a rule of thumb, caustic alkalinity is absent if the pH of the water is below 10, and carbonate alkalinity is absent if the pH is below 8.3.

Mathematically, alkalinity can be expressed by considering the volume of acid required to drop the pH from or above 10 to 8.3 and then to 4.5. If the initial water composition requires V_p mL of acid to reach 8.3 and V_c is the volume of acid required to reach pH 4.5, then following holds true (30):

If $V_c = 0$, alkalinity is due to [OH$^-$] only
If $V_c = V_p$, alkalinity is only due to carbonate
If $V_p > V_c$, major alkalinity specie are hydroxide and carbonate
If $V_p < V_c$, major alkalinity species are bicarbonate and carbonates.

In general mathematical terms, the total alkalinity can be expressed using the following equation:

$$\text{Total alkalinity in eq/L} = 2\left[CO_3^{2-}\right] + \left[HCO_3^-\right] + \left[OH^-\right] - \left[H^+\right] \tag{6}$$

The terms on the right-hand side of Eq. (6) are in mol/L. Alternatively, alkalinity can be expressed in terms of mg/L as $CaCO_3$ (13). Alkalinity of individual species is calculated by

$$\text{Alkalinity of species}_i \left(\text{mg/L as } CaCO_3\right) = \text{species}_i \left(\text{mg/L}\right) \times \frac{EW_{CaCO3}}{EW_{\text{species}_i}} \tag{7}$$

where EW is the equivalent weight. EW values of $CaCO_3$, CO_3^{2-}, HCO_3^-, OH^-, and H^+ are 50, 30, 61, 17 and 1, respectively. Therefore Eq. (6) is revised to:

$$\text{Total alkalinity in mg/L as } CaCO_3 = \left(CO_3^{2-}\right) + \left(HCO_3^-\right) + \left(OH^-\right) - \left(H^+\right) \tag{8}$$

The terms on the right-hand side of Eq. (8) are in mg/L as $CaCO_3$.

The acidity of water is defined in a similar fashion. In the case of acidity also, there are two equivalence points, one at pH 4.5 and the other at pH 8.3. Depending on the pH, the water can have mineral acidity, CO_2 acidity, and total acidity. When pH of the water sample lies below 4.5, the amount of base added to raise the pH to 4.5 is the mineral acidity. In the same way, the amount of base required to raise the solution pH to 8.3 is called CO_2 acidity. Total acidity corresponds to the amount of base added to raise the pH to the carbonate equivalence point (above 8.3). Mathematically, the total acidity can be expressed as follows:

$$\text{Total acidity in eq/L} = 2\left[H_2CO_3\right] + \left[HCO_3^-\right] + \left[H^+\right] - \left[OH^-\right] \tag{9}$$

The terms on the right-hand side of Eq. (9) are in mol/L. The ranges of acidity and alkalinity are shown in Fig. 5.

3.3. Buffer Capacity

The word "buffer" stands for the stubbornness against any change. In environmental chemistry, buffers are always defined in the context of pH. pH buffers are those that resist any changes in solution pH when an acid or a base is added into the solution. They are very important in chemical neutralization processes. Buffers generally contain a mixture of weak acid and their salts (conjugate base) or weak bases and their conjugate acid. A solution buffered at a particular pH will contain an acid that can react with an externally added base and vice versa. The overall efficiency and
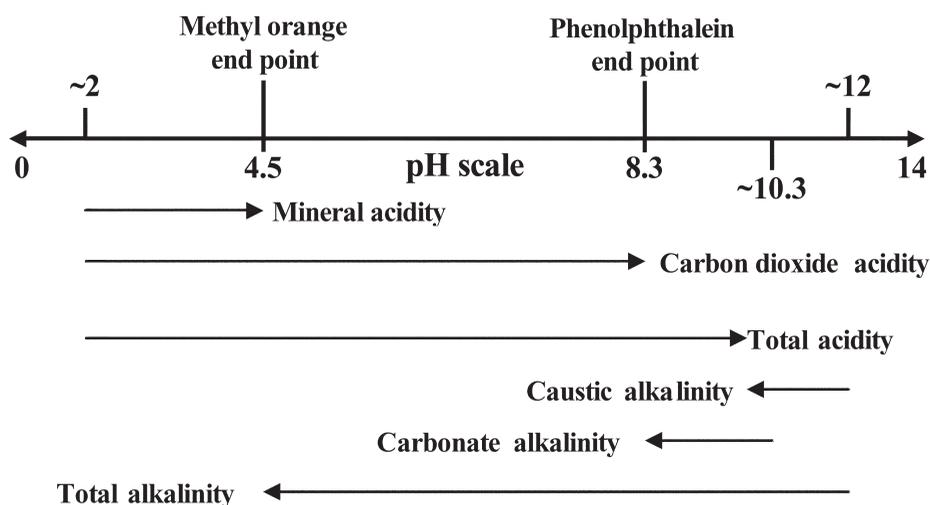
Fig. 5. Ranges of acidity and alkalinity.

chemical cost of the neutralization process depend on the presence of pH buffers in wastewaters.

To define the theory behind how pH buffers act, let us take an example. Consider a solution containing $0.06\,M$ acetic acid and $0.06\,M$ sodium acetate. When a small amount of hydroxide is added in form of sodium hydroxide, the acetic acid present in the solution ionizes to produce H^+, which reacts with the hydroxide added. In similar fashion, if an acid is added to the solution, the acetate takes up the added H^+ to form acetic acid.

In natural waters and wastewaters, the buffering capacity arises due to the presence of phosphates, carbonates, and other weak organic acids. The mineral composition of natural waters is regulated by a buffer system involving natural clay minerals such illite and kaolinite. Careful consideration should be given while neutralizing such waters. If the buffering capacity of the water or wastewater to be neutralized is not taken into account, the actual amount of neutralizing chemical required may vary widely and causes operational problems.

3.4. Hardness

Hardness in waters arises from the presence of multivalent metallic cations (30). The principal hardness-causing cations are calcium, magnesium, ferrous iron, and manganous ions. This parameter is important in water-softening processes. The part of the total hardness that is chemically equivalent to the bicarbonate plus carbonate alkalinities is called carbonate hardness. When both hardness and alkalinity are expressed in mg/L as $CaCO_3$, these two are be related as follows:

When alkalinity < total hardness,

Carbonate hardness (in mg/L) = alkalinity (in mg/L)

When alkalinity > total hardness,

Carbonate hardness (in mg/L) = total hardness (in mg/L)
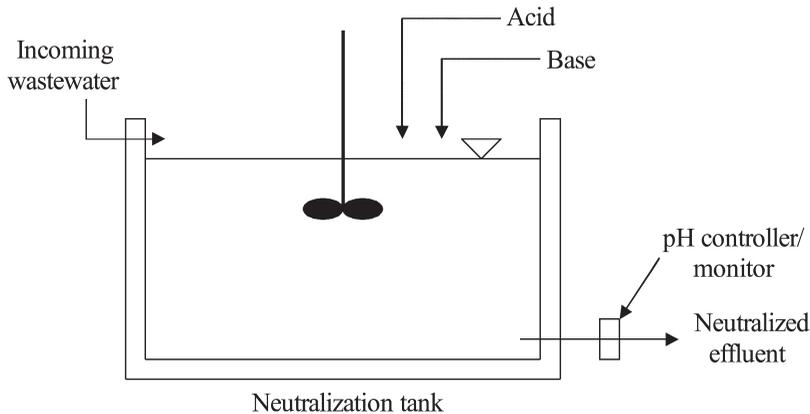
Fig. 6. Continuously operated neutralization tank.

4. NEUTRALIZATION PRACTICES

Neutralization can be carried out in either batch or continuous mode. In batch mode, the effluent is retained until its quality meets specifications before release. Several processes can be simultaneously carried out when the process is performed batchwise. Batch processes are good for small scale treatment plants or small waste volume. For large volumes, a continuous neutralization process is typically used. Figure 6 shows a typical schematic of a continuous neutralization reactor. The use of a batch neutralizing system or continuous flow system depends upon several considerations. In general, continuous flow-through systems are used when

- Influent flow is relatively constant and sudden variations are not expected.
- The influent flow characteristics are essentially constant.
- Effluent chemistry is not very critical. An example is when the process is a part of multi-stage neutralization process.

Batch neutralization systems are used when:

- There are large fluctuations in influent properties (i.e., flow and pH).
- The influent wastewater contains concentrated acids or bases.
- The effluent quality has stringent discharge limits.

Neutralization tanks should be constructed with a corrosion-resistant material or should be lined to prevent corrosion. Addition of an acid or an alkali should be controlled by continuous pH measurement, either by withdrawing samples periodically and measuring the pH or by installing an online pH meter that gives continuous pH readings.

4.1. Neutralization of Acidity

The most widely used methods to balance acidity by adding a proper alkaline solution are outlined below (6):

- Mixing alkaline and acidic wastes such that the net effect is nearly neutral pH.
- Passing the acidic water through a limestone bed. This water should not contain limestone-coating substances such as metal salts or sulfuric or hydrofluoric acids.

- Mixing acid waste with lime slurries or dolomitic slurries.
- Supplementing acidic wastewater with proper amounts of caustic soda or soda ash (Na_2CO_3).

Acidic wastes are neutralized either by adding lime alkalis or by adding sodium alkalis. The most commonly used lime alkalis are quicklime (CaO) and hydrated or slaked lime ($Ca(OH)_2$) (13–15). Sodium alkalis involve the use of caustic soda (NaOH) or soda ash (Na_2CO_3). Calcium and magnesium oxides are considerably less expensive than sodium alkalis and are used more widely (6). Because these oxides are moderately soluble in water, they are typically slurried. Calcium or magnesium alkalis produce more sludge than do sodium alkalis.

Sodium alkali rapidly reacts with acidic wastes and produces soluble neutral salts when combined with most acidic wastewaters. Between the two types of sodium alkalis, caustic soda is a stronger alkali than soda ash. Caustic soda is available in anhydrous form at various concentrations. Soda ash can be purchased as dry granular material. Liquid caustic soda is produced and supplied in a concentration range of 50–73%. Most industries use a 50% caustic soda solution. The specific gravity ranges from 1.47 to 1.53 depending on the temperature. Caustic soda is very corrosive in nature. Hence all containers and lines that come in to contact with caustic soda during use or shipment should be carefully selected.

Soda ash, when used as sodium carbonate monohydrate, contains 85.48% sodium carbonate and 14.52% water of crystallization. Hydrated soda ash loses water of crystallization when heated. Heptahydrated and decahydrated are other forms of soda ash used in neutralization practices. Dissolving monohydrated soda ash in water generates heat while heptahydrate and decahydrate absorbs heat in contact with water. Bagged soda ash should not be stored in humid places. Furthermore, excessive air circulation should be avoided. Soda ash contains 99.2% sodium carbonate when shipped.

4.2. *Neutralization of Alkalinity*

Lowering the pH of a solution is sometimes necessary in some treatment processes or when wastewater is to be discharged in open streams. Discharge of effluent with a pH greater than 8.5 is undesirable and lowering the pH is generally achieved either by adding an acid or by adding carbon dioxide. The process of adding carbon dioxide is called recarbonation and is often practiced in industrial wastewater neutralization. The commonly used acids for pH adjustment of alkaline wastewaters are sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3). Among them, sulfuric acid is the most widely used neutralizing agent. Use of nitric acid is restricted because of more stringent nutrient effluent limitations. There is no direct relationship between pH and alkalinity. Hence, titration curves should be established in laboratories before the design of an alkaline wastewater neutralization system. Sulfuric acid used in wastewater treatment could be 77.7% concentration or 97% concentration with an approximate specific gravity of 1.83 (1,8,9). Sulfuric acid releases a significant amount of heat when added to water. Precautionary measures must be taken to avoid any chemical accident due to the heat generated when practicing neutralization with sulfuric acid. Hydrochloric acid has an average specific gravity of 1.17 and an acid content of 33% by weight. Properly lined tanks should be used to store this classification of hydrochloric acid. Generally polyvinyl chloride tanks or lined steel tanks are used.

4.3. Common Neutralization Treatments

The application of neutralization varies from industry to industry. The most common application includes neutralization of acidic waste from mining industries, in chemical precipitation, water softening, wastewater coming out from electronic manufacturing plants, and coagulation and flocculation in wastewater-treatment plants. Neutralization is also required for treated wastewater if the pH of such water is found to be higher or lower than the permissible discharge limits. Some of the applications of neutralization are discussed in the following sections.

4.3.1. Water Softening

As explained earlier, hardness of water is caused by the presence of polyvalent metal cations. The major disadvantages of using this type of water are the increased consumption of soap required to produce lather when bathing or washing clothes and the formation of scales in boilers if this hard water is used for generating steam. Chemical precipitation is commonly employed to soften the water, where alkalis are added to the water to raise the pH and precipitate the metal ions in the forms of hydroxides and carbonates.

The softened waters usually have high pH values in the range of 10.5 and are supersaturated with calcium carbonate and magnesium hydroxide. For further use of such high pH waters, acid neutralization is applied. Adjustment of pH toward neutrality is accomplished either by recarbonation or by adding sulfuric acid (30).

pH adjustment by recarbonation can proceed in two different ways: one-stage recarbonation or two-stage recarbonation. In one-stage recarbonation, enough CO_2 is passed only one time to drop the pH to the desired level. When sulfuric acid is used in place of CO_2 in one-stage recarbonation, the process is simply called one-stage neutralization. In two-stage recarbonation, CO_2 is added to water at two different points after excess lime treatment. At the first point of addition, the CO_2 is passed to precipitate calcium carbonate. In the next step, CO_2 is added to adjust pH to acceptable levels. Figure 7 shows a schematic of one-stage and two-stage recarbonation.

4.3.2. Metal Precipitation

Metal precipitation through formation of metal hydroxide is one of the common methods of metal removal in industries. At high pH, most of the metal hydroxides are insoluble and come out of the solution in the form of metal hydroxide precipitates. Metals are precipitated as the hydroxides through the addition of lime or another base to raise pH to an optimum value (10–12,30–32). Metal carbonate precipitates can also be formed once soluble carbonate solutions such as sodium carbonate are added into metal solutions. Because pH is the most important parameter in precipitation, control of pH is crucial to the success of the process.

4.3.3. Mine Drainage

The wastewater coming out of mining industries is highly acidic due to the presence of sulfuric acid in appreciable quantities. Acid water coming out of mining industries is one of the common problems prevalent in United States and around the world. Sulfide minerals, mainly pyrite (FeS_2), which are often present in mine waste, can generate acid mine drainage when the waste comes in contact with water and air. Pyrite oxidizes to

A

B
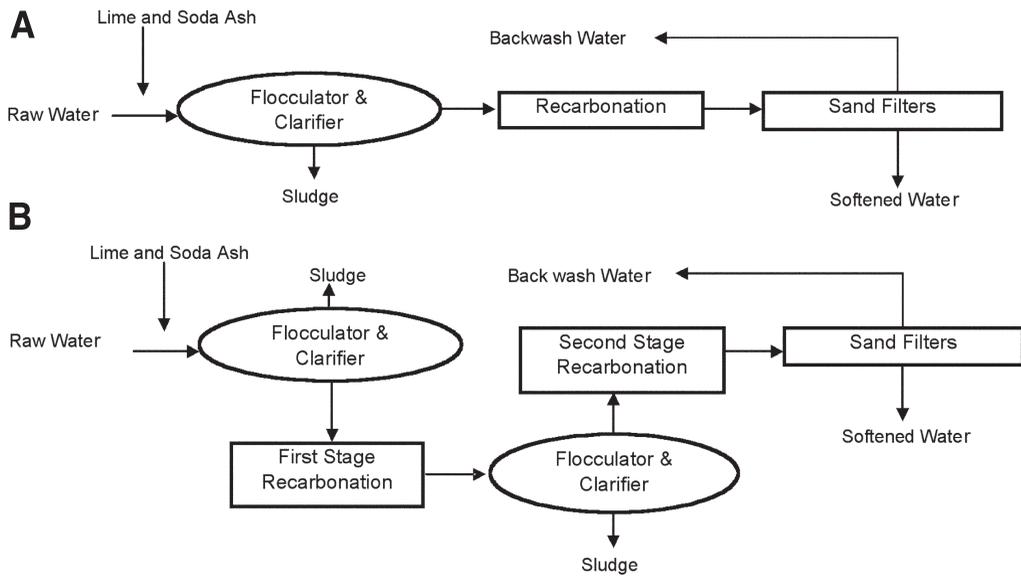
Fig. 7. Recarbonation in water treatment: (a) one-stage recarbonation; (b) two-stage recarbonation.

release sulfuric acid into water, resulting in a pH decrease that can be lower than 2. Most of the metals coming in the mine waste dissolve at this pH, resulting in water that is toxic to aquatic life. Chemical treatment by neutralization and subsequent precipitation is often applied to acid mine drainage. The pH range for point source discharge set by the US EPA is in the range of 6–9. The alkali comparison for acid mine drainage is given in Table 2 (8).

4.3.4. Metal Sorption

Activated carbons have successfully been used for metal removal (16–18). They are normally used for filtration of suspended solids, as well as adsorption of both organic and metal substances. Removal of heavy metal ions from waste streams by inexpensive recyclable biosorbents has emerged as an innovative technique in the last two decades (11,19). The major advantage is the high removal efficiencies for metal ions. This

Table 2
Alkali Comparison for Treatment of Acid Mine Drainage

Alkali	Formula	Molecular weight	Equivalent weight	Factor[a]
Ca Neutralizers				
Hydrated lime	$Ca(OH)_2$	74.10	37.05	1.35
Quicklime	CaO	56.08	28.04	1.78
Limestone	$CaCO_3$	100.08	50.04	1.00
Mg neutralizers				
Dolomitic lime	$Mg(OH)_2$	58.03	29.15	1.72
Na neutralizers				
Caustic soda	$NaOH$	39.99	39.99	1.25
Soda ash	Na_2CO_3	105.99	53	0.94

[a]Factor to convert CaO to $CaCO_3$ equivalence.

process is normally termed as biosorption. Normally biodegradation isn't involved as most biosorbents are inactive. The term "biosorption" is used simply because the biosorbents are made from organisms, such as bacteria and seaweed.

Numerous studies have shown that the sorption of metal ions from aqueous solutions is strongly pH dependent. An increase of the solution pH results in a decrease of positive surface charge and an increase of negatively charged sites and, eventually, an increase of metal ion binding. Normally the pH effect becomes less important when the pH is above 4–6. The metal ion adsorption onto activated carbon increases from 5% to 99% from pH 2.0 to 5.5 (16–18). Sorption experiments using calcium alginate beads (a biosorbent) demonstrated that the metal removal percentages increased from 0 to almost 100% (for metal concentrations < 0.1 m*M*) from pH 1.2 to 4 and a plateau was established at a pH > 4 (11). Therefore, neutralization pretreatment must be performed if the initial pH value of metal waste stream is less than 6.

5. pH NEUTRALIZATION PRACTICES

5.1. Passive Neutralization

In most cases, wastewater equalization is used to dampen out short-term extreme pH variations and allow excess acid to neutralize excess base materials, and vice versa, wherever possible. The equalization can be either on-line or off-line depending on the magnitude of the flows involved.

Off-line equalization is frequently practiced for small flow batch-wise release such as those associated with the regeneration of a plant's process water ion exchange columns. The isolation and off-line blending of the acid and caustic regeneration streams allow an industry to minimize the amounts of neutralization agents required to produce a wastewater that is suitable for downstream processes. The schematic of a typical industrial neutralization process is shown in Fig. 8.

5.2. In-Plant Neutralization

Industrial facilities that generate a continuous wastewater stream that is consistently acidic or basic can practice in-plant neutralization by metering a known quantity of the opposite neutralization agent into the sewer system. The combination of mixing that occurs in the pipe lines and in on-site equalization tanks can be sufficient to avoid costly pH adjustment systems.

5.3. Influent pH Neutralization

Industrial wastewaters produced by non-continuous processes that are characterized to be outside the allowable range for either direct discharge to a treatment plant or on-site treatment must be collected and the pH adjusted with a neutralization system. The most common influent pH adjustment chemicals are sulfuric acid, carbon dioxide, sodium hydroxide, calcium hydroxide, and magnesium hydroxide.

Carbon dioxide is frequently used as an in-pipe neutralization agent because of its rapid dissolution rate. The addition rate of the carbon dioxide is controlled by an in-line pH sensor in combination with a proportional pH controller and a wastewater flow meter.

The remaining neutralization agents are normally applied using a flowthrough neutralization tank containing a mechanical agitator capable of providing vigorous
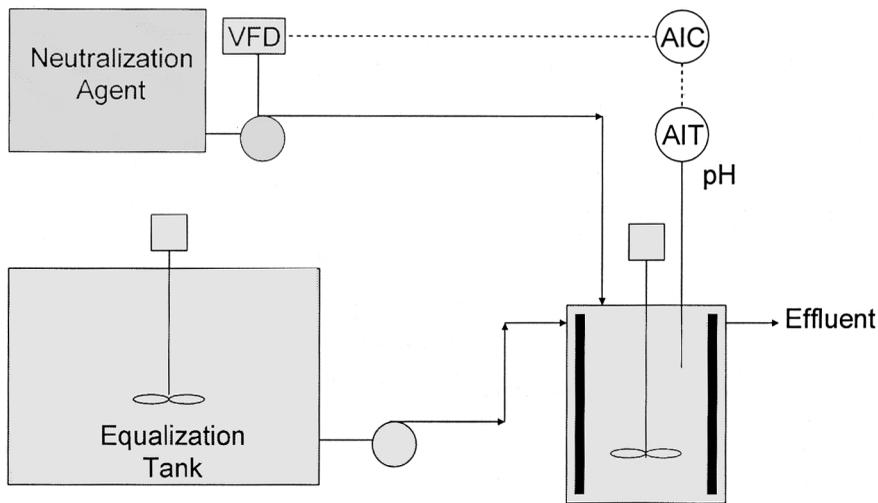
Fig. 8. Industrial neutralization practice.

agitation and instantaneous blending of wastewater and the neutralization agent. The neutralization tank contains a pH sensor that is connected to a proportional pH controller that sends a control signal to either a neutralization metering pump or control valve that is used to precisely meter the required amount of chemical to meet the instantaneous demand. These systems operate best when there is a constant (i.e., pumped) flow rate entering the neutralization tank and upstream equalization is practiced. Variable influent flow rate and a dynamic influent pH range present difficult neutralization problems that increase the complexity and cost of the neutralization equipment.

If the pH of the influent wastewater is typically more than 2 pH units away from the desired set point, the system is normally designed with two pH tanks in series. The first tank is designed to provide a rough pH adjustment and the second provides the fine tuning of the wastewater's pH.

Typical neutralization tank design provides for a hydraulic residence time between 10 and 20 min. The 20-min design factor is normally for systems that use either calcium or magnesium hydroxide slurries for base addition. The additional time is required to allow complete dissolution of the solids and to avoid downstream pH creep associated with post-neutralization tank reactions.

In some cases, the influent neutralization system is designed to raise the pH high enough to provide the needed alkalinity for a downstream process such as biological nitrification.

5.4. In-Process Neutralization

In well-mixed and buffered biological systems, the designer may elect to practice pH adjustment within the biological system's aeration basin. Under these circumstances, the designer must be careful to design redundant pH sensors and a control system that will protect the bacteria from malfunctioning mechanical or instrumentation systems.

Such systems are normally applied where the neutralization agent demand is low and continuous in nature such that the addition system can meet the demand but cannot rapidly shift the pH of the system.

5.5. *Effluent Neutralization*

Effluent neutralization is not normally required for a biological treatment system discharging to either a sewage treatment plant or an outfall. Normally, effluent neutralization would only be required for a physicochemical treatment system discharging to an NPDES outfall. Effluent neutralization maybe required by a sewage treatment plant if the receiving plant has an excess of alkalinity in the influent wastewater. Negotiations can frequently result in a pretreatment permit that allows discharge of treated wastewater with a pH as high as 10 (20,21).

5.6. *Chemicals for Neutralization*

It may be difficult to hold a pH of 6–8 as a slight change in hydrogen concentration can bring about wide swings in pH. Acidic industrial water can be neutralized by slaked lime [also called hydrated lime, calcium hydroxide, $Ca(OH)_2$], caustic soda (sodium hydroxide, NaOH), and soda ash (sodium carbonate, Na_2CO_3) (15).

As calcium hydroxide is less expensive than others, it is commonly applied for pH neutralization. High calcium quicklime known as calcium oxide (CaO) and dolomitic quicklime (a mixture of CaO and MgO) are typical commercial limes. The composition is very much dependent on their sources and manufacturing procedures. High calcium quicklime produces a high calcium hydrated lime that contains around 70% CaO; a dolomitic hydrate from a dolomitic quicklime has around 45% CaO and 34% MgO.

Selection of the above neutralizing agents depends on a series of factors, including their cost, expense of transportation, handling in plant, preparation for usage, and investment in facility, storage, safety, and labor costs. Caustic soda is poisonous, thus must be carefully handled. Emergency eyewashes and showers must be provided close to the chemical storage and operation area in case of an accident.

Lime may lose its efficiency as the solution pH approaches 7. In addition, the presence of organics can cause a significant amount of sludge, which is classified as a hazardous waste and must be treated. Thus, caustic soda as the principal neutralizing agent can be used in order to reduce the sludge production rate (15). However, the operational cost will be increased due to its high purchase expense. Lime can be used first to bring up the water to a slightly higher pH and subsequently caustic soda can be applied, resulting in the reduction of total operational cost.

Titration experiments are highly recommended to obtain the optimal dosage of neutralizing agents. However, if the composition of wastewater is known, one can use commercially available computer stimulation programs to get the dosage. MINEQL is one of the programs and has been widely used (22). In the program, chemical reactions, including solution reactions, precipitation and sorption reactions, in conjunction with the mass balances of different species are considered and solved numerically. It has been successfully used for many cases, including adsorption of heavy metals and metal pollution of groundwater (16,23).

5.7. *Encapsulated Phosphate Buffers for* In Situ *Bioremediation*

During *in situ* bioremediation of subsurface sediments and groundwater, changes in pH could be neutralized by the environmentally controlled release into the subsurface of phosphate buffers encapsulated in a polymer coating (24,32). The capsules are not designed or expected to move through the aquifer to specific contaminated areas. During *in situ* applications, it is anticipated that the encapsulated buffers would be added through a series of monitoring wells or drive points at specific locations. As groundwater flows through those points, the pH of the groundwater would be modified. This system would be analogous to that of *in situ* treatment walls in which a reactive barrier is created through which the groundwater flows. The reactive barrier is not mobile. Once the capsules have been used up, more could be added as necessary and any management of the introduction system, such as de-fouling, could be accomplished during that time.

The capsules are designed to release buffer (KH_2PO_4 or K_2HPO_4) into sediment pore water as a function of the polymer material used as the outer coating. Polymer coatings can be designed to dissolve at specific pH levels, releasing the buffer only when necessary and mediating not only processes that increase pH, but those that decrease pH as well.

The KH_2PO_4 microcapsules designed for application have an average diameter of 1 mm and are coated with a polymer that dissolves at pH levels above 7.0. It was shown that the encapsulated KH_2PO_4 buffer controlled pH under denitrification conditions in activated sludge suspended culture. The pH rise from 7.0 to 8.6 after 2 d of incubation was mediated to 7.0 ± 0.2 pH units in microcosms containing the encapsulated buffer (25).

Encapsulation technology has been examined for *in situ* bioremediation of subsurface environments. Vesper et al. encapsulated sodium percarbonate as 0.25–2.0 mm grains in order to provide a source of oxygen (from hydrogen peroxide) to enhance aerobic biodegradation of propylene glycol in soil (26). Encapsulated bacteria added to 0.2-μm dialysis bags and lowered into contaminated subsurface sediment have been used to enhance remediation of atrazine (27). dos Santos et al. reported the use of co-immobilized nitrifiers and denitrifiers to remove nitrogen from wastewater systems (28). Lin et al. co-immobilized fungal cells, cellulose co-substrate, and activated carbon in alginate beads in order to concentrate pentachlorophenol for microbial degradation (29). Encapsulation in environmental systems usually entails applications such as these, in which bacteria or slow release compounds are used to directly enhance biodegradation.

6. DESIGN OF A NEUTRALIZATION SYSTEM

The engineering design of a successful neutralization system involves several steps. Engineering design should be based on several factors such as optimum process parameters, laboratory-scale tests and their results, and, finally, cost analysis. Practical aspects such as availability of neutralizing agent in the near vicinity and thus reduced transportation costs play an important role in process design. The important steps involved in neutralization process design are outlined below.

All neutralization process, irrespective of type of waste, share several basic features and operate on the principle of acid–base reaction. Successful design of a neutralization process should consider the following;

- Influent wastewater parameters
- Type of neutralizing agent used
- Availability of land
- Laboratory scale experimental results

The overall design of neutralization process involves the design of the following features:

1. Neutralization basin
2. Neutralization agent requirements based on theoretical and treatability studies
3. Neutralization agent storage (e.g., silo, silo side valve, dust collector, and foundation design)
4. Neutralization agent feeding system
5. Flash mixer design

7. DESIGN EXAMPLES

7.1. *Example 1*

The flow rate at different time levels is given in Table 3. Calculate the volume of an equalization basin based on the characteristic diurnal flow.

Solution

The example asks for equalization basin volume based on diurnal flow. Hence, the hydrograph method described above is used for the calculation. It is assumed that the rate of inflow between any two consecutive time events is constant. The first step is to calculate the total volume entering the basin on an hourly basis by multiplying the flow rate in gal/min with 60 min. Then the cumulative flow is calculated as shown in Table 3 with the corresponding hydrograph shown in Fig. 9.

As explained in the previous section, the equalization volume will be sum of the vertical distances between the points of tangency of cumulative volume curve and the average daily flow. In this example, there are three such vertical distances. In Fig. 9, these distances are shown by AB, CD, and EF. However, close observation reveals that the equalization basin starts filling up at point B and continues until the cumulative volume curve reaches at point E. The equalization basin fills up to point C also, and continues beyond this point until it reaches point E. Hence the equalization volume is given by summation of AB and EF.

$$\text{Equalization volume} = AB + EF = 6000 + 40{,}000 = 46{,}000 \text{ gal.}$$

7.2. *Example 2*

Design a neutralization basin with 20 min detention time and a complete neutralization system for an industrial effluent with the following characteristics: flow rate = 0.792 MGD, pH = 3.5, acidity as mg/L $CaCO_3$ = 605, sulfate = 1300 mg/L, suspended solids = 65 mg/L.

Solution

Neutralization basin
Assume water depth = 5 ft and detention time period = 20 min:

Table 3
Wastewater Flow Variation with Time

Time	Flow rate (gpm)	Total volume (gal)	Cumulative volume (gal)
8 AM	70	4200	4200
9 AM	90	5400	9600
10 AM	235	14100	23700
11 AM	315	18900	42600
12 PM	279	16740	59340
1 PM	142	8520	67860
2 PM	85	5100	72960
3 PM	110	6600	79560
4 PM	78	4680	84240
5 PM	148	8880	93120
6 PM	234	14040	107160
7 PM	300	18000	125160
8 PM	382	22920	148080
9 PM	202	12120	160200
10 PM	78	4680	164880
11 PM	60	3600	168480
12 PM	68	4080	172560
1 AM	57	3420	175980
2 AM	42	2520	178500
3 AM	72	4320	182820
4 AM	77	4620	187440
5 AM	47	2820	190260
6 AM	57	3420	193680
7 AM	30	1800	195480

$$\text{Required volume} = 0.792 \times 10^6 \, \frac{\text{gal}}{\text{d}} \times \frac{1 \, \text{d}}{24 \, \text{h}} \times \frac{1 \, \text{h}}{60 \, \text{min}} \times 20 \, \text{min}$$

$$= 11 \times 10^3 \, \text{gal} = 1470 \, \text{ft}^3$$

$$\text{Surface area required} = \frac{1470 \, \text{ft}^3}{5 \, \text{ft}} = 294 \, \text{ft}^2$$

The neutralization basin can be of square, rectangular, or circular cross section. For a square basin, each side should be 17.1 ft.

Lime Requirement (Theoretical)
Lime requirement will be calculated based on the amount of acidity present in water. Assuming 70% lime efficiency, theoretical lime required is

$$\text{Theoretical daily lime requirement} = 605 \, \frac{\text{mg}}{\text{L}} \times \frac{1 \, \text{mol Ca(OH)}_2}{1.35 \, \text{mol CaCO}_3} \times \frac{1}{0.7}$$

$$= 640 \, \frac{\text{mg Ca(OH)}_2}{\text{L}}$$
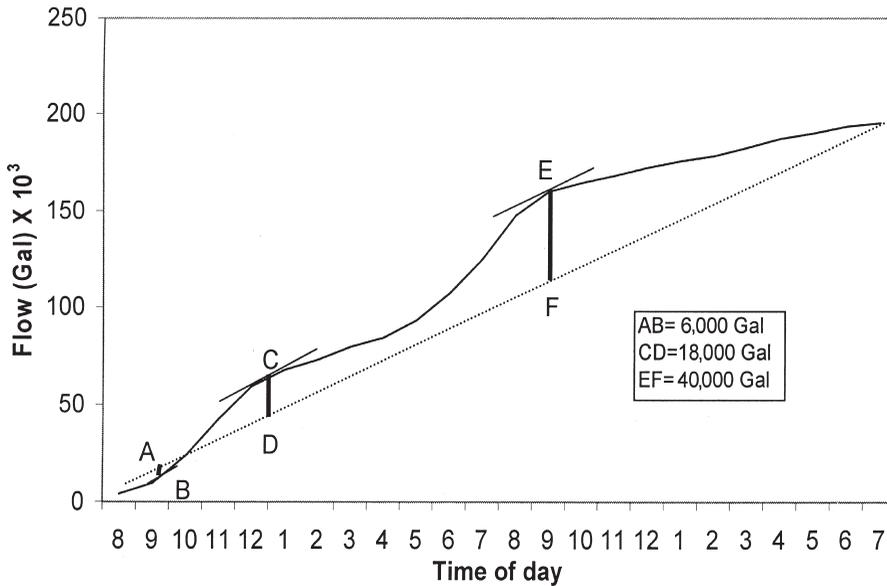
Fig. 9. Hydrograph for volume calculation of equalization basin.

$$\text{In terms of lb/d, the amount required} = 640\,\frac{\text{mg}}{\text{L}}\times 0.792\times 10^6\,\frac{\text{gal}}{\text{d}}\times 3.79\,\frac{\text{L}}{\text{gal}}$$

$$\times\frac{1\,\text{kg}}{10^6\,\text{mg}}\times\frac{\text{lb}}{0.45\,\text{kg}}=4270\,\frac{\text{lb}}{\text{d}}$$

To assess the actual lime requirement, laboratory-scale titration experiments need to be performed. In general, the actual lime requirements are always higher than the theoretical requirement, because of other chemicals present. In this particular example, 15% extra is added to fulfill that requirement:

$$\text{Actual lime requirement} = 4270\,\frac{\text{lb}}{\text{d}}\times 1.15 = 4910\,\frac{\text{lb}}{\text{d}}$$

The above calculation gives a preliminary estimate of the amount of lime to be used. Although it is a good estimate, a treatability study must be performed when designing a large plant. A firmer estimate of the amount to be purchased on a regular basis will depend on actual usage. Once the amount of lime required is calculated, further design requires the selection of the type of lime used. The most common forms of lime used in industries are quicklime, limestone, and hydrated lime. In this example, quicklime is used, because this is the most widely used form of lime:

$$\text{Quicklime required} = 4910\,\frac{\text{lb}}{\text{d}}\times\frac{56\,\text{g quick lime}}{74\,\text{g hydrated lime}}=3720\,\frac{\text{lb}}{\text{d}}$$

The actual total quicklime requirement will depend on the average efficiency of the slaker. Let us assume a 90% slaker efficiency:

$$\text{Actual CaO requirement} = 3720\,\frac{\text{lb}}{\text{d}}\times\frac{1}{0.9}=4130\,\frac{\text{lb}}{\text{d}}$$

Design of Lime Silo

Silo is designed for a storage capacity for 7 d:

$$\text{Silo capacity} = 4130 \frac{\text{lb}}{\text{d}} \times 7 \text{ d} = 28,900 \text{ lb}$$

Using the density of quick lime of 30 lb/ft^3,

$$\text{the silo volume required} = \frac{28,900 \text{ lb}}{30 \frac{\text{lb}}{\text{ft}^3}} = 960 \text{ ft}^3$$

Assuming a diameter of 8 ft, the required side wall height is 19.1 ft. Provide a side wall height of 20 ft with a 60° hopper angle.

Other Silo Equipment

Design of other silo parts such as bin activator, dust collector, and bin level indicators is based on personal judgment and experience of designer. In general, bin activators are sized one half of the silo diameter, and the dust collector size varies with the module.

Lime Feeding, Slurry, and Tank

The hourly rate of lime required is

$$4130 \frac{\text{lb}}{\text{d}} \times \frac{1\text{d}}{24 \text{ h}} = 172 \frac{\text{lb}}{\text{h}}$$

In practice, a 10–15% slurry is desired. Let us assume a 15% slurry. To calculate the slurry volume and water requirements, the specific gravity of the slurry can be determined experimentally in the laboratory or can be obtained from the supplier. If the slurry specific gravity is 1.05, then the slurry has a unit weight of 8.8 lb/gal, of which 15% is due to the lime. Thus, the slurry flowrate required is

$$\text{Slurry flowrate} = 172 \frac{\text{lb CaO}}{\text{h}} \times \frac{\text{gal}}{8.8 \text{lb slurry}} \times \frac{1 \text{ lb slurry}}{0.15 \text{ lb CaO}} = 130 \frac{\text{gal}}{\text{h}}$$

If a 30-min detention time is provided, the required tank volume is

$$130 \frac{\text{gal}}{\text{h}} \times 0.5 \text{h} = 65 \text{ gal} = 8.7 \text{ ft}^3$$

If we use a cylindrical tank with diameter equal to height, we obtain $D = H = 2.2$ ft.

Flash Mix Tank

Assume a detention time of 3 min:

$$\text{Volume} = \frac{3}{60} \text{h} \times \left(\left(0.792 \times 10^6 \frac{\text{gal}}{\text{d}} \times \frac{1 \text{ d}}{24 \text{ h}} \right) + 130 \frac{\text{gal}}{\text{h}} \right) = 1660 \text{ gal} = 222 \text{ ft}^3$$

If we use a cylindrical tank with diameter equal to height, we obtain $D = H = 6.6$ ft.

NOMENCLATURE

D	diameter of impeller, m
G	mean velocity gradient, s^{-1}
K_T	constant dependent on impeller size and shape

n	impeller revolutions per second, s^{-1}
P	power requirement, N-m/s
Q	flow rate, m^3/s
V	mixing tank volume, m^3
t_d	detention time, s
V_p	volume of acid added to a solution to reach a pH of 8.3 during titration, mL
V_c	volume of acid added to a solution to reach a pH of 4.5 during titration, mL
ρ	density of the fluid, kg/m^3
μ	absolute viscocity of the fluid, $N\text{-}s/m^2$

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