The term anaerobic process refers to a diverse array of biological wastewater treatment systems from which dissolved oxygen and nitrate-N are excluded. In most instances they are operated to convert biodegradable organic matter, both soluble and particulate, to methane and carbon dioxide. Since methane is a sparingly soluble gas, most is evolved and recovered, thereby removing organic matter from the liquid phase and stabilizing any solids present in the influent or produced in the process. Anaerobic digestion of municipal wastewater solids also results in inactivation of pathogens, a step that is usually required prior to ultimate solids disposal. In some cases, anaerobic processes are operated to convert biodegradable particulate organic matter into volatile fatty acids (VFAs), which are subsequently separated from the particulate matter and fed to biological nutrient removal (BNR) systems to enhance their performance.

13.1 PROCESS DESCRIPTION

Anaerobic processes have been used in wastewater treatment systems for more than a century, initially to stabilize the solids produced. These bioreactors, called anaerobic digesters, were simple concrete tanks in which the solids were placed as a slurry and allowed to decompose anaerobically. Hydraulic retention times of 60 days or more were common. Gradually, it was discovered that the decomposition could be accelerated by heating the digester to a consistent temperature of about 35°C and mixing it to provide uniform reaction conditions. These discoveries led to the current high rate anaerobic digestion process, which uses HRTs of 15 to 20 days. Anaerobic digestion remains an extremely popular and widely used solids stabilization process, particularly in municipal wastewater treatment.

Development of high rate anaerobic digestion fostered interest in the use of anaerobic processes to treat high strength industrial wastewaters, leading to the development and use of a wide variety of innovative systems. Some can be classified as either suspended growth or attached growth systems, but many are hybrid systems, incorporating elements of both. All anaerobic processes, regardless of the type of biomass employed, are described in this chapter because of the similarities of the design approaches employed. Additional details on attached growth systems are provided in Chapters 18 and 21.

The purposeful use of anaerobic digestion to inactivate pathogens in municipal wastewater solids is a relatively new and evolving application. Just as in aerobic digestion, pathogen inactivation does not occur as a direct consequence of the di-

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gestion process per se; rather it is a result of the environmental conditions in the
digester. Pathogen inactivation in anaerobic digesters is relatively efficient because of
the elevated temperatures that are typically maintained.

As mentioned above, anaerobic processes are beginning to be used to hydrolyze
and ferment a portion of the biodegradable organic matter in wastewater solids,
producing VFAs. The VFAs are then removed from the solids by elutriation and
used to enhance BNR processes, as discussed in Chapter 11. The solids are then
concentrated prior to subsequent treatment.

13.1.1 General Description

A general description of the microbiology and biochemistry of anaerobic processes
is presented in Chapters 2 and 3, while the kinetics of the transformations are sum-
marized in Section 9.3.2. Although the chemistry, biochemistry, and microbiology of
anaerobic decomposition are quite complex, it can be conceptualized as comprising
three steps, as summarized in Figure 2.3: (1) hydrolysis of particulate organic matter
to soluble substrates; (2) fermentation of those soluble substrates to produce acetic
acid, carbon dioxide, and H₂; and (3) conversion of the acetic acid, the H₂, and a
portion of the carbon dioxide to methane. Methane is a sparingly soluble gas,
which is evolved from solution and collected for subsequent use. The evolution of
methane decreases the chemical oxygen demand (COD) of the waste stream and
provides the mechanism for stabilization of the biodegradable organic matter con-
tained in it. Only minimal COD reduction occurs without methane production, and
it is associated with the formation and evolution of H₂. As discussed in Sections
2.3.2 and 9.3.2, the H₂-oxidizing methanogens are fast growing organisms and are
present in most anaerobic treatment systems, resulting in conversion of most of the
H₂ produced to methane. However, since the greatest proportion of the methane
produced comes from acetic acid, growth of aceticlastic methanogens is required to
achieve significant waste stabilization.

Since COD stabilization in anaerobic processes is directly related to methane
evolution, methane production can be calculated from the COD removed in the
process, just as the oxygen requirement in an aerobic system can be calculated from
a COD balance. As discussed in Section 2.3.2, two moles of oxygen are required to
oxidize one mole of methane to carbon dioxide and water. Thus, the COD equivalent
of methane is 4 kg COD/kg methane. At standard temperature and pressure (0°C and
one atmosphere) this corresponds to 0.35 m³ of methane produced per kg of COD
converted to methane. For municipal primary solids, the methane equivalent is
0.7 m³ of methane produced per kg of volatile solids (VS) destroyed. The carbon
dioxide content of the gas produced in anaerobic processes ranges between about 30
and 50% and varies depending on the nature of the substrate. For example, the carbon
dioxide content is higher when carbohydrates are being treated than when proteins
are treated.

Lema, et al. have summarized those aspects of anaerobic processes that par-
ticularly affect their design. They are:

- The very low growth rates that the microorganisms have during methane
  fermentation.
- The low microbial specific activity, especially at the final step of the process.
• The very low values of the half-saturation coefficients, which means an extraordinary affinity of the microorganisms for their substrates.
• The importance of internal and external resistances to mass transfer.
• The inhibition produced by chemicals present in the wastewater or produced in the process.
• The necessity of keeping the physico-chemical parameters within relatively limited ranges to maximize the activity of the microorganisms.
• The need to design and operate a system that can handle fluctuations in wastewater flow and composition.

These challenges are addressed in the design of anaerobic bioreactors by providing a uniform reactor environment and an SRT that is sufficiently long to ensure the growth of all the necessary microorganisms. The mechanisms by which these objectives are achieved are discussed below.

Figure 13.1 provides a schematic of an anaerobic bioreactor that illustrates its four major components: (1) a closed vessel, (2) a mixing system, (3) a heating system, and (4) a gas–liquid–solids separation system. Table 13.1 relates those components to the aspects identified by Lema et al. Anaerobic bioreactors are typically constructed of either concrete or steel, although earthen basins are used for some low-rate processes. An enclosed vessel is used to exclude dissolved oxygen and ensure the development of anaerobic conditions. The bioreactor is often insulated to minimize heat loss. Mixing is provided to increase the homogeneity of the reaction environment and to reduce the resistance to mass transfer. Uniform bioreactor conditions minimize the impacts of the inhibitory materials produced as metabolic intermediates, keep bioreactor physico-chemical parameters within limited ranges, and minimize the impacts of influent flow and composition fluctuations. Due to the high affinity of the reactions for their substrates, performance is not severely impacted by the uniform bioreactor environment. Several methods are used to mix the bioreactor, including devices such as gas recirculation or mechanical mixers, recirculation of bioreactor effluent to the influent, or bioreactor configurations that use the influent and recirculation flows to mix the contents. Gas evolution during treatment results in a degree of mixing that can be significant in certain bioreactor configurations. The
<table>
<thead>
<tr>
<th>Anaerobic reaction aspect of Lema et al.</th>
<th>Anaerobic reactor component</th>
<th>Closed vessel</th>
<th>Mixing system</th>
<th>Heating system</th>
<th>Gas–liquid–solids separation system</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The very low specific growth rates.</td>
<td>Provides optimum reaction conditions by excluding dissolved oxygen.</td>
<td>Provides intimate contact between microorganisms and their substrates to maximize achievable specific growth rates.</td>
<td>Allows maximum microorganism specific growth rate by maintaining temperature for optimal growth.</td>
<td>Accumulation of active microorganisms allows operation at increased SRT.</td>
<td></td>
</tr>
<tr>
<td>2. The low specific activities.</td>
<td>Provides optimum reaction conditions by excluding dissolved oxygen.</td>
<td>Provides intimate contact between microorganisms and their substrates to maximize achievable specific growth rate.</td>
<td>Allows maximum microorganism activity by optimizing temperature.</td>
<td>Accumulation of active microorganisms allows high total activity, in spite of low specific activity.</td>
<td></td>
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<tr>
<td>3. The very low values of the half-saturation coefficients.</td>
<td></td>
<td>High reaction conversion efficiency possible even though well mixed conditions are typically utilized.</td>
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<tr>
<td>4. The importance of internal and external resistances to mass transfer.</td>
<td>Provides optimum reaction conditions by excluding dissolved oxygen.</td>
<td>Mixing helps to overcome the adverse impacts of internal and external mass transfer resistance.</td>
<td>Allows optimal microorganism activity even though rate is reduced by mass transfer resistance.</td>
<td>Accumulation of active microorganisms and increased SRT can increase total reaction rate and compensate for effects of mass transfer resistances.</td>
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<tr>
<td>5. The inhibition produced by chemicals.</td>
<td>Excludes one reaction inhibitor, oxygen.</td>
<td>Minimizes buildup of reaction intermediates by providing uniform reactor environment.</td>
<td>Minimizes production of reaction intermediates by maintaining temperature for maximum biological activity.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. The necessity of keeping the physico-chemical parameters within relatively limited ranges.</td>
<td>Excludes one reaction inhibitor, oxygen.</td>
<td>Minimizes variations in reactor environment.</td>
<td>Reduces variation in one environmental factor, temperature.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. The need to design and operate a system that can handle fluctuations in wastewater flow and composition.</td>
<td>Excluding oxygen allows optimal reaction rates in spite of fluctuating loading conditions.</td>
<td>Reduces the variation in reactor environmental conditions in spite of variations caused by fluctuating loading conditions.</td>
<td>Allows optimal reactor temperature to be maintained in spite of fluctuating loading conditions.</td>
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<tr>
<td></td>
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<td></td>
<td>Accumulation of active microorganisms allows increased SRT to be maintained, thereby limiting accumulation of reaction intermediates.</td>
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<td></td>
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<td></td>
<td>Accumulation of active microorganisms increases reaction rates in spite of adverse environmental conditions.</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Accumulation of active microorganisms provides increased reactor biomass needed to treat peak process loadings.</td>
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</table>
configuration of the feed distribution system can also encourage mixing. Heating is typically provided to maintain temperatures that are constant and near the optimum values for the biomass. Methane gas produced by the system is generally used to fire boilers that provide the necessary heat.

Relatively long SRTs are required in anaerobic processes because of the low maximum specific growth rates of methanogens. Long SRTs also minimize the build-up of inhibitory reaction intermediates and allow the process to respond better to fluctuations in wastewater flow and composition. In some instances, the necessary SRT is achieved by providing a sufficiently long HRT. In other cases, the necessary SRT is provided by separating solids from the treated effluent and retaining them in the bioreactor, thereby achieving an SRT that is significantly longer than the HRT. The gas–liquid–solids separation device is critical to the performance of such systems because the efficiency of liquid–solids separation determines the extent to which active biomass can be accumulated. Gas separation from the solids is necessary to facilitate liquid–solids separation. Several approaches are used to retain active biomass in anaerobic treatment systems; they are described in Section 13.1.4.

A wide range of bioreactor configurations exists, depending on the type of waste, the type of gas–liquid–solids separation provided, and the treatment objectives. Four different process types are considered: (1) anaerobic digesters, (2) low-rate anaerobic processes, (3) high-rate anaerobic processes, and (4) solids fermentation processes. The first three are used to stabilize organic matter by converting it to methane and carbon dioxide. Solids fermentation processes are used to produce VFAs to enhance the performance of BNR systems.

### 13.1.2 Anaerobic Digestion

Anaerobic digestion (AD) is used for the stabilization of particulate organic matter and Figure 13.2 provides a schematic of the process. An anaerobic digester is well mixed with no liquid–solids separation. Consequently, the bioreactor can be treated as a continuous stirred tank reactor (CSTR) in which the HRT and SRT are identical. An SRT of 15 to 20 days is typically used, although SRTs as low as 10 days have been used successfully and longer SRTs are employed when greater waste
stabilization is required. Many anaerobic digesters are cylindrical concrete tanks with a cone-shaped bottom and steel or concrete covers, although other materials and configurations can be used. Diameters range from 10 to 40 m, and sidewall depths from 5 to 10 m. Mixing is required and is provided by internal mechanical mixers, external mechanical mixers that recirculate the tank contents, gas recirculation systems of various types, or pumped recirculation of the tank contents. Historically, relatively low volumetric power inputs have been used to mix anaerobic digesters. More recent experience suggests, however, that such practices may cause a significant portion of the bioreactor volume to be inactive, as well as in significant short-circuiting of feed to the effluent. In contrast, tracer testing has demonstrated that newer approaches can produce essentially completely mixed conditions, thereby minimizing inactive volume and short-circuiting.

Methane produced by the process is combusted and used to heat the feed stream and digester contents. Bioreactor temperatures in the mesophilic range (−35°C) are typically maintained, although numerous investigations of the use of thermophilic operating temperatures (−55°C) have been conducted. Gas storage is typically provided to accommodate variations in gas production rates, thereby facilitating the operation of boilers and other equipment using the gas as a fuel source. External pressurized storage is sometimes used, but more frequently gas is stored in the digester under a cover that floats on the digester contents, as illustrated in Figure 13.3.

Historically, anaerobic digesters treating municipal wastewater solids have experienced operating problems associated with the accumulation of grit in the bottom and floating scum on the surface. Consequently, bioreactor configurations have been developed that have improved mixing characteristics and reduced potential for grit and scum accumulation. One is the egg-shaped digester, illustrated in Figure 13.4. Developed in Germany, it is receiving increasing interest in the United States, where several full-scale installations currently exist. The large height-to-diameter ratio and the steeply sloped lower and upper sections of the vessel result in improved mixing, reduced grit and scum accumulation, and easier removal of any

![Figure 13.3](image-url) Gas storage covers for anaerobic digesters: (a) floating cover; (b) gas holder cover.
Anaerobic Processes

in the recycle of significant quantities of suspended solids to the liquid treatment process train, thereby causing adverse impacts on its performance.

- Significant advances have been made in recent years in solids thickening technology, particularly for suspended growth biomass. This technology is mechanically reliable, allows the consistent production of a thickened solids with a concentration of 50 g/L or more, and is cost-effective.
- Thickening the feed solids prior to anaerobic digestion results in a significant reduction in required tank volume and associated capital cost. Operating costs are also reduced since the volume of feed that must be heated is significantly reduced.
- The recycle of poor quality digester supernatant is eliminated.

Consequently, current practice is to thicken the feed solids prior to single-stage, high-rate anaerobic digestion, which is the process illustrated in Figure 13.2.

13.1.3 Low-Rate Anaerobic Processes

Low-rate anaerobic processes are slurry bioreactors that utilize a combination of solids sedimentation and accumulation to increase the SRT relative to the HRT. They often use earthen basins (Figure 13.5), although rectangular concrete vessels have also been used (Figure 13.6). Mixing is typically provided simply by the addition of influent wastewater and by gas evolution. As a consequence, well mixed conditions are not generally provided and suspended solids settle and accumulate in the bioreactor. Some systems have incorporated settled solids recycle from a downstream settling zone to an upstream reaction zone, as indicated in Figure 13.6. Historically, materials in the wastewater were allowed to float to the surface and form a scum mat that provided some insulation and odor control, although gas would pass through it and escape to the atmosphere. More recently, membranes and similar materials have been used to trap and collect the gas for use elsewhere. Heating is not typically provided. Consequently, either the process is used to treat wastewaters that are already warm or a sufficiently long SRT is maintained to allow treatment to occur at ambient temperature.

Environmental conditions within low-rate processes are not well regulated and, even though active biomass accumulates, accurate control of the SRT is not generally

![Figure 13.5 Low rate anaerobic process using an earthen basin.](image-url)
Figure 13.6 Low rate anaerobic process using a rectangular concrete structure.

possible. As a result, designs rely on experience with similar systems and waste-
waters, and on the replication of HRTs and organic loading rates (expressed as kg
BOD$_3$ or COD/(m$^3$.day)) found to be successful. HRTs in the 5 to 15 day range are
often appropriate, with longer values required in some cases. Organic loading rates
of 1 to 2 kg COD/(m$^3$.day) are often found to be appropriate. Process performance
varies, but approaches that achieved by high rate anaerobic processes, discussed
below. Further discussion of anaerobic lagoons is presented in Chapter 14.

13.1.4 High-Rate Anaerobic Processes

High-rate anaerobic processes utilize bioreactor configurations that provide signifi-
cant retention of active biomass, resulting in large differences between the SRT and
the HRT.$^{16,23,68}$ Three mechanisms are used to retain biomass: (1) the formation of
settleable particles that are retained by sedimentation, (2) the use of reactor config-
urations that retain suspended solids, and (3) the growth of biofilms on surfaces
within the bioreactor. In many instances, more than one mechanism is operating in
a bioreactor. Consequently, high-rate anaerobic processes represent a spectrum of
bioreactor types ranging from suspended growth to attached growth, with hybrid
bioreactors, which contain significant quantities of both suspended and attached bio-
mass, in between. Six bioreactor types that span this range are described in this
section: (1) anaerobic contact (AC), (2) upflow anaerobic sludge blanket (UASB),
(3) anaerobic filters (AF), (4) hybrid UASB and anaerobic filters (UASB/AF), (5)
downflow stationary fixed film (DSFF), and (6) fluidized bed/expanded bed (FB/EB).

Hall$^{23}$ has summarized the typical performance of high rate anaerobic processes,
as presented in Table 13.2. A relatively high level of biodegradable organic matter
removal can be achieved, as indicated by typical BOD$_3$ removal efficiencies of 80
to 90%. Biogas production is about 0.5 m$^3$/kg COD removed, corresponding to a
Table 13.2 Typical High-Rate Anaerobic Process Performance

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>BOD₅ removal, percent</td>
<td>80 to 90%</td>
</tr>
<tr>
<td>COD removal, mass</td>
<td>$1.5 \times$ BOD₅ removed</td>
</tr>
<tr>
<td>Biogas production</td>
<td>0.5 m³/kg COD removed</td>
</tr>
<tr>
<td>Methane production</td>
<td>0.35 m³/kg COD removed</td>
</tr>
<tr>
<td>Biomass production</td>
<td>0.05-0.10 g VSS/g COD removed</td>
</tr>
</tbody>
</table>

*Adapted from Hall.*

methane production of 0.35 m³/kg COD removed. Solids production is low, typically ranging from 0.05 to 0.10 kg VSS/kg COD removed. These performance levels can be achieved by all of the processes discussed in this section if appropriate organic loading rates are used.

**Anaerobic Contact.** Anaerobic contact systems, illustrated in Figure 13.7, consist of a completely mixed suspended growth bioreactor, a degassifier, and a liquid–solids separation device where the bioreactor effluent is separated into a relatively clear process effluent and a concentrated slurry of biosolids that is recycled to the bioreactor. Therefore, AC is essentially an anaerobic activated sludge system. The degassifier is a device that facilitates removal of carbon dioxide and methane to allow settling of the biosolids in the liquid–solids separator. If the gas is not removed, bubbles attach to the solids, preventing their settling and subsequent recycle to the bioreactor. A variety of devices can be used to degassify the bioreactor effluent, as illustrated in Figure 13.8. The bioreactor is often configured like an anaerobic digester, and the heating and gas handling systems provided are similar. Completely mixed conditions are achieved by mechanical mixing systems similar to those used in anaerobic digestion. Conventional clarifiers or plate settlers are often used as the liquid–solids separation device.

The AC process is designed and operated to maintain a desired SRT, which is accomplished by adjusting the solids wastage rate. As indicated in Section 9.3.2, SRTs in the 10 to 20 day range are required. Just as with the activated sludge process,
the range of HRTs associated with this range of SRTs is dependent on the strength of the wastewater and the concentration of active biosolids that can be attained in the bioreactor. Bioreactor suspended solids concentrations may range from 4 to 6 g/L as VSS to as high as 25 to 30 g/L as VSS, depending on the settleability of the solids that develop. The lower range of concentrations represents typical operation. Clarifier hydraulic loading rates on the order of 5 to 6 m/day are often used, with a solids recycle rate equal to the influent flow rate. Volumetric organic loading (VOL) rates often range between 0.5 and 10 kg COD/(m³·day).

**Upflow Anaerobic Sludge Blanket.** The UASB process uses suspended growth biomass, but the gas-liquid-solids separation system is integral with the bioreactor. More importantly, the environmental conditions created in the bioreactor can result in the development of large, dense, readily settleable particles called granules, which allow very high concentrations of suspended solids, on the order of 20 to 30 g/L as VSS, to be accumulated. These high suspended solids concentrations allow significant separation between the SRT and HRT, and operation at relatively short HRTs, often on the order of two days or less. Figure 13.9 provides a schematic of the process.

Influent wastewater enters the bottom of the bioreactor through a distribution system that is designed to provide relatively uniform flow across its cross section. A dense slurry of granules forms in the lower portion of the bioreactor, and the combined effects of the influent wastewater distribution and gas production result in mixing of the influent wastewater with the granules. Treatment occurs within the dense blanket of granules. For some wastewaters, a much less dense flocculent sludge also develops, and this accumulates on top of the blanket of granules. Other wastewaters contain suspended solids that are not trapped in the granular sludge, and these solids also accumulate as a flocculent sludge blanket overlying the granules. Treated effluent exits the granular and flocculent sludge zones and flows upward into the gas-liquid-solids separator. A variety of configurations can be used for this device, and the one illustrated in Figure 13.9 is only meant to represent the basic concepts used by several manufacturers. The device often consists of a gas collection hood.
with a settler section above it. Gas bubbles cause some granular and flocculent solids (particularly small granules) to rise through the bioreactor and enter the gas–liquid–solids separator. Gas separation occurs in the hood area, thereby allowing some of this suspended material to return directly to the solids blanket. Gas collects in the upper inverted V section of the hood and is removed from the bioreactor. Liquid with some entrained solids flows out of the hood into the settler section where liquid–solids separation occurs. Clarifier effluent overflows the weirs and is discharged while separated solids settle back into the reaction zone. Design of the gas–liquid–solids separation device requires insight into the physical processes occurring there and experience with specific devices in a variety of applications.

Bioreactor dimensions are affected by process loadings, constraints on maximum upflow velocities, wastewater type, and the settling characteristics of the solids that develop in the process. The solids inventory increases as treatment occurs and new biomass is grown. Consequently, provisions must be made for solids wastage, as illustrated in Figure 13.9. The relative proportions of flocculent and granular sludge can be controlled by the wasting locations used. Bioreactor HRTs in the 0.2 to 2 day range are typical, along with VOL rates of 2 to 25 kg COD/(m³·day), depending on wastewater characteristics and whether granular or flocculent solids develop.

Anaerobic Filter. Anaerobic filter systems use upflow bioreactors that are filled with media. The packing is the same as that used with aerobic plastic media trickling filters (TFs), discussed in Chapter 19. Example media are illustrated in Figure 13.10; the specific surface area is typically 100 m²/m³ with a void volume of 90 to 95%. The presence of packing allows for the growth of some attached biomass, but the primary role of the media is to retain suspended growth. The media may be thought of as performing like a set of tube settlers, which provide enhanced liquid–solids separation and retention of suspended biomass within the bioreactor. Gas–solids separation is also facilitated within the packed section. Although several types have been used successfully in AF systems, direct comparisons indicate ad-
Figure 13.10 Typical media used in anaerobic filters: A. crossflow; B. tubular; C. pall rings. (From J. C. Young, Factors affecting the design and performance of upflow anaerobic filters. Water Science and Technology 24(8):133–156, 1991. Copyright © Elsevier Science Ltd.; reprinted with permission.)

Advantages for the crossflow modular media because of its superior gas–liquid–solids separation capabilities.

Figure 13.11 provides a schematic of the overall AF process. Influent wastewater and recirculated effluent are distributed across the bioreactor cross-section and flow upward through the media. Treatment occurs as a result of the suspended and fixed biomass retained by the media. Effluent exits the top of the media section and is collected for discharge. Gas is collected under the bioreactor cover and is conveyed to subsequent use. Effluent is typically recirculated to maintain a reasonably uniform hydraulic loading on the bioreactor in spite of varying influent flow rates, thereby maintaining uniform bioreactor hydrodynamic conditions. Although performance is determined by the SRT maintained, accurate assessment of the bioreactor suspended solids inventory is not generally possible. Consequently, bioreactor designs are based on the HRTs and VOLs used successfully in other applications. Hydraulic retention times between 0.5 and 4 days are typical, along with VOLs in the 5 to 15 kg COD/(m³·day) range. The biomass inventory is typically controlled by the hydrodynamic conditions that develop in the media as a result of the influent (wastewater plus recirculation) flow applied. Excess biomass is washed out of the system as it develops.
and becomes a part of the effluent. In some instances the capability to remove settled solids from the bioreactor bottom may be provided since heavy solids and precipitates can accumulate there. Solids removal from this location does not constitute an SRT control mechanism, however, because most of the active biomass is retained within the media section.

**Hybrid Upflow Anaerobic Sludge Blanket/Anaerobic Filter.** Hybrid UASB/AF systems combine aspects of the UASB process with aspects of the AF process. As illustrated in Figure 13.12, influent wastewater and recirculated effluent are distributed across the bioreactor cross-section and flow upward through granular and flocculent sludge blankets where anaerobic treatment occurs. The effluent from the sludge blanket zone then enters a section of media identical to that used in AF systems where gas–liquid–solids separation occurs. Treated effluent then exits the media section and is collected for discharge from the bioreactor. Gas collects under the bioreactor cover and is transported to storage and/or use. The hybrid UASB/AF process primarily uses suspended biomass, and process loadings are similar to those used with the UASB process. The solids removal system is similar to that used with the UASB process.

**Downflow Stationary Fixed Film.** Downflow stationary fixed film systems use media just like an AF system, but flow is in the downward rather than the upward direction. As a consequence, suspended biomass tends to be conveyed through the media rather than retained by it, and the process depends to a large extent on attached rather than suspended biomass. As illustrated in Figure 13.13, influent wastewater and recirculated effluent are distributed evenly across the bioreactor and flow downward through the media. Biomass growing on the media surface and that portion of the suspended biomass that is trapped within the media accomplish treatment of the applied wastewater. Solids removal systems are not generally provided because of the reduced importance of suspended biomass. However, the capability to remove heavy solids from the bottom of the DSFF bioreactor may be provided, just as with the AF process, but such provisions may be less useful as effluent is already being removed from this section of the bioreactor. Treated effluent exits the media zone and is collected for recirculation and discharge. Gas produced in the media flows upward and is collected under the bioreactor cover for transport to...
Storage and/or use. The media used in DSFF systems is similar to that used in AF systems, although higher specific surface area media (on the order of 140 m²/m³) may be advantageous because of the importance of attached growth. As with many other high-rate anaerobic treatment processes, loadings are generally expressed in terms of both HRT and VOL. Typical HRTs for the DSFF process range from 0.5 to 4 days and VOLs range from 5 to 15 kg COD/(m³·day), both of which are similar to the AF process.

**Fluidized Bed and Expanded Bed.** Fluidized bed and expanded bed systems differ from those previously considered in that they are essentially attached growth systems with little or no suspended growth. As illustrated in Figure 13.14, FB/EB systems use upflow bioreactors, just like the UASB, AF, and hybrid UASB/AF processes, but the upflow velocities are much higher, resulting in minimal retention of suspended biomass. Instead, the biomass grows attached to granular carrier particles that are fluidized by the upflow of influent wastewater and recirculated effluent. Fluidization is discussed in Section 18.2. The carrier particles are often silica sand with a diameter in the 0.2 to 0.5 mm range and a specific gravity of 2.65 or granular...
activated carbon. In FB/EB systems upward flow rates are sufficient to support the individual carrier particles with their attached biomass (bioparticles), resulting in expansion of the bed volume in comparison to its resting volume. In expanded beds the upflow velocity is sufficient to expand the bed by 15 to 30%. At this degree of expansion the bioparticles are supported partly by the fluid and partly by contact with adjacent bioparticles and, consequently, they tend to remain in the same relative positions within the bed. In fluidized beds a higher upflow velocity is used, resulting in further expansion of the bed to between 25 and 300% of its resting volume. Under these conditions the bioparticles are fully supported by the upward flowing fluid and move freely in the bed. Gas production also results in turbulence that tends to mix the bioreactor contents. Gas—solids separation devices are provided in some cases to allow the bioparticles to be retained in the bioreactor.

The turbulence created by the upward fluid flow and the gas production allows small carrier particles to be used without bioreactor plugging. It also encourages high mass transfer rates. The use of small carrier particles results in a high specific surface area and a high active biomass concentration. For expanded bed bioreactors, the specific surface area of the carrier particles is in the 9,000 to 11,000 m²/m³ range, with a void volume of 45 to 55%. For fluidized bed systems the specific surface area is in the 4,000 to 10,000 m²/m³ range, with void volumes of 50 to 90%, depending on the degree of expansion. These specific surface areas are approximately two orders of magnitude greater than those provided in AF or DSFF bioreactors. The high specific surface areas allow high biomass concentrations to develop, on the order of 15 to 35 g/L as VSS, which are similar to those achieved with the UASB process. The high biomass concentrations allow operation at relatively low HRTs and high VOLs while maintaining adequate SRTs for efficient treatment. HRTs in the 0.2 to 2 day range are used, depending on the concentration of the wastewater. Volumetric organic loadings over 20 kg COD/(m³·day) are common with FB/EB systems.

As with any other biological process, excess biomass must be removed from the bioreactor to control the biomass inventory. As discussed in Section 18.2.2, accumulation of biomass on the carrier particles increases the bioparticle diameter and decreases its density. The result of these two contrasting factors is a decrease in the settling velocity of the bioparticles and the tendency for bioparticles with more biomass to accumulate in the upper portion of the bioreactor. As a consequence, solids wasting is generally from there. The bioparticles are conveyed to a device where biomass is sheared from the carrier particles. The carrier particles are then returned to the bioreactor and the biomass is taken to further processing or ultimate disposal. Several devices are available for this purpose, but they often consist of a rubber lined pump where the biomass is sheared from the carrier particles and a centrifugal separation device where the lighter biomass is separated from the denser media particles. Many of the commercially available devices are proprietary in nature. Fluidized beds are discussed in detail in Chapters 18 and 21.

The basic process options described in this section can also be combined in a variety of ways to produce a wide range of additional anaerobic treatment systems. For example, interest currently exists in the use of membranes as a means of further separating the SRT and the HRT, thereby producing an even more compact anaerobic process.
13.1.5 Solids Fermentation Processes

Solids fermentation processes are used to solubilize particulate organic matter in primary solids and ferment the soluble products to VFAs, particularly acetic and propionic acid, for use in BNR processes.\textsuperscript{66,76} The objectives of solids fermentation processes are different from those of the anaerobic stabilization processes discussed previously. They are to maximize the production of VFAs and recover them in a stream that can be delivered to a BNR system. The first objective is achieved by controlling the SRT to a value that allows the growth of hydrolytic and fermentative bacteria but prevents the growth of aceticlastic methanogens, which would consume the VFAs.\textsuperscript{18,19,66} As indicated in Figure 9.5, at 35°C this requires an SRT in the 2 to 3 day range. In general, the feed solids and bioreactor contents are not heated, so the SRT must be increased to compensate for the lower temperature. Some methane will be produced as a result of the growth of H\textsubscript{2}-utilizing methanogens, but the amount will be small. The second objective is achieved when the VFAs are separated from the residual primary solids by passing the bioreactor effluent through a liquid–solids separation step.

Figure 13.15 illustrates schematically the concepts of fermentation systems. Feed-solids are fed to a mechanically mixed bioreactor where fermentation occurs. The SRT is controlled by adding dilution water in sufficient quantities so that the HRT, which equals the SRT, is maintained at the desired value. The use of gravity sedimentation to achieve liquid–solids separation is illustrated in Figure 13.15. The option of adding elutriation flow to the bioreactor effluent is provided to ensure sufficient supernatant to effectively recover the produced VFAs. Typically, the settled solids are removed from the settler and taken to further processing. However, the capability to recycle a portion of those solids to the bioreactor may be provided to increase its SRT above its HRT.

Figure 13.16 illustrates how the concepts in Figure 13.15 have been implemented at several full-scale wastewater treatment plants. In an activated primary clarifier, primary solids are accumulated in a sludge blanket where fermentation occurs. The settled solids are then recycled to an upstream mixing/elutriation tank where the soluble VFAs are washed from the fermented primary solids and into the

![Figure 13.15](image-url)  
**Figure 13.15** Solids fermentation process.
Figure 13.16 Alternative configurations for the solids fermentation process: A. activated primary tanks; B. complete mix fermenter; C. single-stage fermenter/thickener; D. 2-stage complete mix/thickener fermenter. (From Water Environment Federation, *Use of Fermentation to Enhance Biological Nutrient Removal*, Proceedings of the Conference Seminar, 67th Annual Conference and Exposition, Water Environment Federation, Alexandria, Virginia, 1994. Copyright © Water Environment Federation; reprinted with permission.)
primary clarifier effluent. The SRT is controlled by wasting settled solids from the process. In the completely mixed fermenter, solids are removed from the primary clarifier and fermented in a separate bioreactor. However, the fermented solids are then recycled to the primary clarifier where VFAs are removed by the wastewater flow and fermented solids are wasted to control the SRT. In the single-stage fermenter/thickener, primary solids are added to an oversized gravity thickener where both solids fermentation and liquid–solids separation occur. Solids wasting is controlled to achieve the desired SRT, and VFAs are removed in the overflow. Finally, in the two-stage completely mixed thickener/fermenter system, the fermentation and solids thickening steps are separated into two unit operations. Optional primary effluent addition points provide operational flexibility to control the SRT and VFA elutriation. This option is functionally identical to the prototype solids fermentation process illustrated in Figure 13.15.

All the options presented in Figure 13.16 use gravity liquid–solids separation. Relatively poor solids thickening has been experienced in some instances, probably as a result of the gases produced. Such operating problems have been controlled in some cases by operation at a reduced fermentation reactor solids concentration and/or by dilution of the bioreactor effluent prior to gravity separation. Alternatively, centrifuges have been used.\(^9\) Other options include static fermenters or fermentation basins upstream of biological reactors.

Primary solids fermentation is a developing technology and many process configurations are being evaluated for full-scale application. However, all operate according to the basic principles described in this section. Details of the process configurations developed to date are presented elsewhere.\(^7\)

### 13.1.6 Comparison of Process Options

Table 13.3 summarizes the primary benefits and drawbacks of the anaerobic treatment systems used to stabilize organic matter. Anaerobic digestion is suitable for a wide range of wastewaters, particularly those with high concentrations of suspended solids. Well mixed conditions are provided within the bioreactor, resulting in a uniform environment that produces predictable and stable performance. Process performance is not dependent on solids settleability since anaerobic digesters use completely mixed bioreactors with no biomass recycle. The long HRTs required to achieve adequate SRTs result in large bioreactor volumes which can effectively dilute toxic materials. However, they can cause high capital costs. Effluent quality can be poor if the influent contains high concentrations of nonbiodegradable organic matter. Process stability will be good if a sufficient SRT is provided, but it will be poor at shorter SRTs. The process requires a separate mixing system.

Low rate anaerobic processes are simple and economical to construct, and are suitable for a wide range of wastewaters, including those with high concentrations of suspended solids. The low VOLs used result in large bioreactors for the dilution of toxic inputs. These processes are also capable of accepting the waste solids from downstream post-treatment aerobic systems, but large bioreactors are required, along with relatively large land areas. Good performance is possible, and is not dependent on the development of a readily settleable sludge. However, because process control techniques are limited, the conditions within the bioreactor are poorly controlled, which can lead to reduced efficiency.
Table 13.3 Anaerobic Treatment Process Comparison—Organic Stabilization

<table>
<thead>
<tr>
<th>Process</th>
<th>Benefits</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anaerobic digestion (AD)</td>
<td>• Suitable for a wide range of wastewaters</td>
<td>• Requires separate mechanical mixing</td>
</tr>
<tr>
<td></td>
<td>• Efficiently handles high suspended solids wastewaters</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Easy to mix, thereby creating uniform reaction environment</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Large bioreactor volume to dilute inhibitors</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Performance not dependent on sludge settleability</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Capable of accepting waste aerobic biomass</td>
<td></td>
</tr>
<tr>
<td>Low-rate anaerobic processes</td>
<td>• Simple and relatively economical construction</td>
<td>• Relatively large bioreactor volumes required</td>
</tr>
<tr>
<td></td>
<td>• Suitable for a wide range of wastewaters</td>
<td>• Large land area required</td>
</tr>
<tr>
<td></td>
<td>• Efficiently handles high suspended solids wastewaters</td>
<td>• Poorly controlled conditions within bioreactor reduce efficiency</td>
</tr>
<tr>
<td></td>
<td>• Large bioreactor volume to dilute inhibitors</td>
<td>• Limited process control capability</td>
</tr>
<tr>
<td></td>
<td>• Good performance possible</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Performance not highly dependent on solids settleability</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Capable of accepting waste aerobic biomass</td>
<td></td>
</tr>
<tr>
<td>Anaerobic contact (AC)</td>
<td>• Suitable for concentrated wastewaters</td>
<td>• Biomass settleability critical to successful performance</td>
</tr>
<tr>
<td></td>
<td>• Easy to mix, thereby creating uniform reaction environment</td>
<td>• Most suitable for wastes with low to moderate levels of suspended solids</td>
</tr>
<tr>
<td></td>
<td>• Relatively high effluent quality achievable</td>
<td>• System is relatively complex mechanically</td>
</tr>
<tr>
<td></td>
<td>• Reduced bioreactor volume compared to AD</td>
<td>• Shorter bioreactor HRTs mean less equalization and dilution of inhibitors</td>
</tr>
<tr>
<td></td>
<td>• Capable of accepting waste aerobic biomass</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Significant process control capability available</td>
<td></td>
</tr>
<tr>
<td>Upflow anaerobic sludge blanket (UASB)</td>
<td>• High biomass concentrations and long SRTs achievable</td>
<td>• Performance dependent on development of dense, settleable solids</td>
</tr>
<tr>
<td></td>
<td>• Small bioreactor volumes due to high volumetric organic loading rates</td>
<td>• Much lower process loading required if wastewater contains suspended solids</td>
</tr>
<tr>
<td></td>
<td>• High-quality effluent achievable</td>
<td>• Special bioreactor configuration required which is based on experience</td>
</tr>
<tr>
<td></td>
<td>• Mechanically simple</td>
<td>• Little process control possible</td>
</tr>
<tr>
<td></td>
<td>• Compact system, relatively small land area</td>
<td>• Shorter bioreactor HRTs mean less equalization and dilution of inhibitors</td>
</tr>
<tr>
<td></td>
<td>• Well mixed conditions produced</td>
<td></td>
</tr>
</tbody>
</table>
### Table 13.3 - Anaerobic Filters and Hybrid UASB/AF

<table>
<thead>
<tr>
<th>Process</th>
<th>Benefits</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anaerobic filter</td>
<td>High biomass concentrations, high volumetric organic loading rates, and long SRTs achievable</td>
<td>Not suitable for high suspended solids wastewaters, not generally impacted by high suspended solids, less equalization and dilution of inhibitors</td>
</tr>
<tr>
<td>Downflow stationary fixed film (DSFF)</td>
<td>High biomass concentrations, high volumetric organic loading rates, and long SRTs achievable</td>
<td>Lower process loadings required, less equalization and dilution of inhibitors</td>
</tr>
<tr>
<td>Hybrid UASB/AF</td>
<td>High biomass concentrations, high volumetric organic loading rates, and long SRTs achievable, well mixed conditions produced in bioreactor</td>
<td>High cost for media and support, development not dependent on inhibitors</td>
</tr>
</tbody>
</table>

**Table 13.3 - Continued**

<table>
<thead>
<tr>
<th>Process</th>
<th>Benefits</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anaerobic filter</td>
<td>High biomass concentrations, high volumetric organic loading rates, and long SRTs achievable</td>
<td>Not suitable for high suspended solids wastewaters, not generally impacted by high suspended solids, less equalization and dilution of inhibitors</td>
</tr>
<tr>
<td>Downflow stationary fixed film (DSFF)</td>
<td>High biomass concentrations, high volumetric organic loading rates, and long SRTs achievable</td>
<td>Lower process loadings required, less equalization and dilution of inhibitors</td>
</tr>
<tr>
<td>Hybrid UASB/AF</td>
<td>High biomass concentrations, high volumetric organic loading rates, and long SRTs achievable, well mixed conditions produced in bioreactor</td>
<td>High cost for media and support, development not dependent on inhibitors</td>
</tr>
</tbody>
</table>

**Benefits**
- High biomass concentrations
- High volumetric organic loading rates
- Long SRTs achievable
- Well mixed conditions produced in bioreactor
- Compact system, relatively small land area

**Drawbacks**
- Not suitable for high suspended solids wastewaters
- Not generally impacted by high suspended solids
- Less equalization and dilution of inhibitors
- Lower process loadings required
- Less equalization and dilution of inhibitors
- High cost for media and support
- Development not dependent on inhibitors
Table 13.3 Continued

<table>
<thead>
<tr>
<th>Process</th>
<th>Benefits</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluidized bed/expanded bed</td>
<td>• High biomass concentrations and long SRTs achievable</td>
<td>• Lengthy start-up period required</td>
</tr>
<tr>
<td>(FB/EB)</td>
<td>• Small bioreactor volumes due to high volumetric organic loading rates</td>
<td>• High power requirements for bed fluidization and expansion</td>
</tr>
<tr>
<td></td>
<td>• Excellent mass transfer characteristics</td>
<td>• Not suitable for high suspended solids wastewaters</td>
</tr>
<tr>
<td></td>
<td>• High-quality effluent achievable, often better than other high-rate processes</td>
<td>• Mechanically more complex than other high-rate processes</td>
</tr>
<tr>
<td></td>
<td>• Most compact of all high-rate processes; requires smallest land area</td>
<td>• Increased process control required</td>
</tr>
<tr>
<td></td>
<td>• Performance not dependent on development of settleable solids</td>
<td>• Cost of carrier media is high</td>
</tr>
<tr>
<td></td>
<td>• Very well mixed conditions generally produced in bioreactor</td>
<td>• Shorter bioreactor HRTs mean less equalization and dilution of inhibitors</td>
</tr>
<tr>
<td></td>
<td>• Increased process control capability relative to other high-rate processes</td>
<td></td>
</tr>
</tbody>
</table>

All high-rate anaerobic processes share certain characteristics. High biomass concentrations are maintained, thereby allowing long SRTs to be achieved while keeping the HRTs short. The high biomass concentrations allow high VOLs to be applied, resulting in relatively small bioreactors, and the long SRTs provide good process stability. Although the systems are compact and require relatively small land areas, a high-quality effluent can generally be achieved. Well mixed conditions are typically produced in the bioreactor, resulting in a uniform reaction environment. High-rate processes are best suited for the treatment of wastewaters containing soluble organic matter (SOM), and are adversely impacted by the presence of high concentrations of influent suspended solids. The relatively short HRTs possible with these systems mean that less equalization is provided and less dilution is available for toxic inputs. Important differences also exist among the various high rate processes.

Anaerobic contact processes are suitable for a wide range of wastewaters; are easy to mix, thereby creating a uniform reaction environment; can tolerate moderate suspended solids loadings, including the waste solids from coupled aerobic treatment systems; and provide the capability for significant process control. In contrast, their performance is dependent on the development of a settleable biomass, they best accommodate wastewaters with low to moderate concentrations of suspended solids, and they are mechanically complex.

Upflow anaerobic sludge blanket systems are mechanically simple and easy to operate, but their performance is dependent on the formation of dense, settleable
Anaerobic Processes

savings in operating cost more than offset the increased capital investment. For example, at current unit costs it is often found that anaerobic digestion is not cost-effective in wastewater treatment plants with capacities less than 40,000 to 100,000 m³/day. Nevertheless, because cost relationships and available options were different in the past, they are often found in many older wastewater treatment plants with lower capacities. The increased availability of alternative approaches to solids management and stabilization has reduced the use of anaerobic digestion. However, it remains a viable solids stabilization technology, and continues to be widely used.

Low-rate anaerobic processes can be applied to wastewaters with a range of strengths, including those with high concentrations of suspended solids. They are most often applied to the treatment of wastewaters with biodegradable COD concentrations in the 20,000 to 30,000 mg/L range and to those with high concentrations of suspended solids. A main limitation, however, is the amount of land that must be available for their construction.

High-rate anaerobic processes are applied most often for the treatment of moderate to high strength wastewaters (those with biodegradable COD concentrations up to about 20,000 mg/L) containing mostly SOM. However, there are differences among them regarding their applications. Anaerobic contact and DSFF systems are not generally affected by influent suspended solids to the same extent as the others. Such solids can be accumulated to a certain degree in AC systems and sufficient SRT can be provided to allow their hydrolysis and stabilization to occur. While suspended solids will not adversely impact the performance of DSFF systems, they will generally pass through them with little stabilization.

If a wastewater contains solids that require stabilization, two options exist for handling them if a high-rate anaerobic process is to be used to treat the wastewater: they can be removed either before or after treatment. An advantage of the latter option is that solids produced during anaerobic treatment will also be removed, but some systems are not amenable to that alternative. For example, prior removal is generally required for AF and FB/EB systems, in which case the removed solids can be processed in a separate anaerobic digester designed specifically for that purpose. Sedimentation is also often used prior to UASB and hybrid UASB/AF systems, but a larger bioreactor could be provided to allow operation at a lower organic loading rate to encourage hydrolysis and stabilization of the solids that accumulate. Stabilization of the accumulated solids can be further encouraged by periodically diverting wastewater away from the bioreactor to allow them to digest and/or by periodically increasing the bioreactor temperature to increase the rates of hydrolysis and acidogenesis. This may be particularly attractive if wastewater is not continuously applied to the treatment system.

Low-rate and high-rate anaerobic processes are widely used around the world, with several thousand installations in place. Their use to treat liquid waste streams is a newer application of anaerobic technology than anaerobic digestion of solids. Consequently, their development is ongoing. Each of the anaerobic technologies described above has a significant number of installations and a well developed experience base upon which to base process designs and evaluate potential applications. Some aspects of these technologies are proprietary, particularly the media and gas—liquid—solids separation devices. The suppliers of this equipment can be contacted to obtain installation lists and summaries of operating and performance experience.
Several recent symposia summarize current experience with the use of low- and high-rate anaerobic processes to treat municipal and industrial wastewaters.\textsuperscript{7,17,24,30,63}

Fermentation of organic solids to produce VFAs for BNR systems is an evolving technology with relatively few installations. However, it is expected that the cost-effectiveness and popularity of BNR systems, coupled with their need for sufficient quantities of VFAs, will result in continued development of fermentation systems. Particular challenges include fermentation in smaller treatment plants where the wastewater is relatively fresh and may contain few VFAs, and where the absence of primary clarifiers means that no primary solids are available to feed to a fermenter. The proceedings of a workshop sponsored by WEF\textsuperscript{76} provides a summary of current experience.

\section*{13.2 FACTORS AFFECTING PERFORMANCE}

Many factors affect the performance of anaerobic treatment systems. These range from process loading factors such as the SRT, VOL, and hydraulic loading rate; to environmental factors such as temperature, pH, nutrient supply, and the presence of toxics; to operational factors such as mixing and the characteristics of the waste being treated. Historically, the stability and performance of anaerobic treatment systems have been considered to be poor in comparison to aerobic systems. However, with improved understanding of the factors that affect their performance, it has been possible to obtain stable and reliable performance. Consequently, a thorough understanding of these factors is critical to successful design and operation.

\subsection*{13.2.1 Solids Retention Time}

The role of the SRT in controlling the performance of anaerobic processes is discussed briefly in Chapter 9 and has been referred to in previous sections of this chapter. Solids retention time controls the types of microorganisms that can grow in the process and the extent to which various reactions will occur. While SRT is the fundamental control parameter, it is difficult to routinely determine it in some anaerobic processes. Determination of the SRT is straightforward in flow-through systems such as anaerobic digesters, where it simply equals the HRT. Its calculation is also straightforward in anaerobic contact systems; the rate of solids wastage is controlled to achieve the desired SRT in the same fashion as in the activated sludge process. The SRT can also be measured and controlled in fluidized and expanded bed systems. The bioreactor bed is sampled to determine the VS inventory, and the biomass control device is adjusted to achieve the desired SRT. The SRT can also be measured and controlled in UASB and hybrid UASB/AF systems, but more often solids are simply wasted to maintain a set level for the granular and flocculent sludge layers. While it is possible to determine the solids inventory in low-rate anaerobic processes, solids wastage control is less certain. Likewise, while it is possible to determine the biomass concentration in pilot-scale AF and DSFF systems by removing sections of the media, this is not a practical approach for routine operation of full-scale systems. Consequently, it is not generally possible to control the operating SRT in low-rate, AF, and DSFF systems. Instead, process control is achieved by controlling the VOL, as discussed in the next section.
When the SRTs in pilot-scale anaerobic treatment systems are calculated, it is not unusual to find values of 30 to 40 days, with some systems ranging up to over 100 days.\textsuperscript{23,32,68} Such values are significantly higher than required for wastewater treatment, and represent the accumulation of excess biomass. Experience indicates that very stable performance can be obtained from some anaerobic treatment systems, particularly if long SRTs are used. It also indicates that anaerobic systems can be shut down for extended periods of time (up to several months) and that good performance can be restored shortly after they are restarted.\textsuperscript{23,32,68} In spite of these desirable features, it is possible that these long SRTs represent underloaded systems that could have been constructed more economically using shorter SRTs, while still achieving acceptable performance.

One benefit of increased SRTs is increased hydrolysis and stabilization of particulate organic matter. This can be particularly important for the stabilization of certain types of wastewater solids. More information will be provided on this topic in Section 13.2.9.

### 13.2.2 Volumetric Organic Loading Rate

Even though the VOL is not a fundamental parameter determining the performance of anaerobic treatment systems, it is related to the SRT through the active biomass concentration in the bioreactor. It is also a relatively easy parameter to calculate, and it has been used historically to characterize the loading on anaerobic treatment systems. Knowledge of the VOLs that can typically be achieved for a particular process quantifies how effectively the bioreactor volume is being utilized. Used in this fashion, the VOL provides useful information for the design and operation of anaerobic processes. The volumetric organic loading rate, $\Gamma_{vs}$, can be calculated in units of kg COD/(m$^3$·day) as:

$$\Gamma_{vs} = \frac{F(S_{so} + X_{so})}{V}$$  \hspace{1cm} (13.1)

where $(S_{so} + X_{so})$ is the influent wastewater strength in g COD/L (kg COD/m$^3$), $F$ is the influent wastewater flow rate in m$^3$/day, and $V$ is the bioreactor volume in m$^3$. Substitution of Eq. 4.15 into Eq. 13.1 relates the VOL to the HRT:

$$\Gamma_{vs} = \frac{S_{so} + X_{so}}{\tau}$$  \hspace{1cm} (13.2)

This shows that the VOL is inversely proportional to the HRT, as illustrated in Figure 13.18. As discussed throughout Section 13.1, VOLs typically range from 1 to 2 kg COD/(m$^3$·day) for low-rate processes to between 5 and 40 kg COD/(m$^3$·day) for high-rate processes.

The SRT is defined by Eq. 5.1, just as for all other biochemical operations. However, we saw in Section 9.4.1 that it is often convenient to use the net process yield to relate the biomass inventory to the mass input rate of substrate and the SRT. Rearranging that equation and expressing the biomass concentration and net yield on a VSS basis gives:
Figure 13.18 Effects of HRT and influent wastewater concentration on the volumetric organic loading of an anaerobic process.

\[ \Theta_c = \frac{X_{M,V} \cdot V}{Y_{n,V} \cdot F(S_{SO} + X_{SO})} \]  

Combining Eqs. 13.2 and 13.3 gives:

\[ \Theta_c = \frac{X_{M,V}}{Y_{n,V} \cdot \Gamma_{V,S}} \]  

Thus, it can be seen that the SRT and the VOL are inversely proportional to each other. Equation 13.4 also shows that for a fixed SRT, the VOL is increased as the biomass concentration is made larger, thereby allowing the bioreactor to be made smaller.

A similar approach is used for solids stabilization systems, such as anaerobic digesters, except that the VOL is expressed in terms of the mass of volatile solids applied, rather than COD, typically having units of kg VS/(m$^3$·day). Figure 13.18 also presents the relationship between the anaerobic process HRT, the influent volatile solids concentration, and the resulting volatile solids VOL. For single-stage, anaerobic digestion processes, i.e., systems operated without solids recycle, the HRT and the SRT are identical. In these instances, the volatile solids VOL simply indicates how effectively the digester volume is being utilized. For two-stage digestion systems, which incorporate solids recycle, the SRT will be greater than the HRT and the volatile solids VOL indicates both the anaerobic digester volume utilization efficiency and the overall process loading. In both instances volatile solids VOLs typically range from 2 to 6 kg VSS/(m$^3$·day).46,72,75

Interestingly, experience indicates that a maximum COD stabilization activity of 1 kg COD/(kg VSS·day) is achieved in a wide variety of anaerobic treatment processes.23 Although higher values have been reported, especially in conjunction with the treatment of wastewaters rich in acetate, this value can be used to develop an initial estimate of the capability of a particular anaerobic process to stabilize organic matter.
13.2.3 Total Hydraulic Loading

In contrast to the suspended growth systems considered in Part II and the rest of Part III, some of the high-rate anaerobic processes are influenced by the total hydraulic loading (THL) applied to them. This is characteristic of the attached growth processes considered in Parts IV and V, and a detailed discussion of the effects of THL on them is presented in Chapters 16, 18, 19, and 21. This section presents the most important impacts of THL on UASB, AF, hybrid UASB/AF, DSFF, and FB/EB processes. With the exception of UASB systems, all of these anaerobic processes contain attached growth biomass. However, because of the physical similarity between UASB granules and the bioparticles in FB/EB systems, UASB systems also behave like attached growth systems.

The THL is simply the total flow applied to the bioreactor (including recirculation) divided by the bioreactor cross-sectional area perpendicular to the flow. It is calculated as:

$$\text{THL} = \frac{F + F_R}{A_c}$$

where $F_R$ is the recirculation flow rate and $A_c$ is the cross-sectional area. The THL is a superficial velocity, i.e., a theoretical velocity based on the empty bed cross-sectional area.

The THL affects process performance in several ways. For upflow processes with sludge blankets, such as UASB, hybrid UASB/AF, and FB/EB systems, maximum allowable values of the THL correspond to the settling velocity of the particles to be retained in the bioreactor. If the THL exceeds these values, the particles will be washed out of the bioreactor. As a result, the desired biomass inventory and associated SRT cannot be maintained, and the process will fail. Procedures for calculating maximum THL values for FB/EB processes are presented in Section 18.2.2 and typical values are presented in Section 21.2.3.

For UASB and hybrid UASB/AF processes, the maximum allowable THL depends on the nature of the solids developing in the bioreactor. For granular solids, the daily average THL should not exceed 72 m/day when treating fully soluble wastewater, and 24 to 30 m/day when treating partially soluble wastewater. The THL can be temporarily increased to 144 m/day for fully soluble wastewaters and 48 m/day for partially soluble wastewaters. For flocculent solids, the daily average THL should not exceed 12 m/day and the maximum THL should not exceed 48 m/day. The factors that lead to development of granular versus flocculent solids are discussed in Section 13.2.9. Knowledge concerning appropriate values of the THL for these bioreactor types continues to evolve, and the reader is urged to consult the literature for the most recent information.

For some bioreactors, a minimum THL must be maintained for various reasons. For AF and DSFF processes a minimum THL is needed to achieve uniform distribution of flow across the bioreactor cross section to minimize short circuiting. For AF processes, values in the range of 10 to 20 m/day appear to be appropriate. For FB/EB processes, a minimum THL must be maintained to fluidize or expand the bed, as discussed in Chapters 18 and 21. As with the UASB and hybrid UASB/AF processes, THL criteria for these processes continue to evolve and the reader should consult the literature for further information.
THL constraints can affect the configuration of the anaerobic bioreactor. The bioreactor cross-sectional area must be adjusted to produce THL values within the necessary range. In some instances, recirculation must be initiated to maintain minimum required THLs. The impacts of the THL constraints on the design of anaerobic processes is discussed briefly in Section 13.3.2 and in substantially more detail in Chapters 19 and 21 for other attached growth systems.

13.2.4 Temperature

As with all biological processes, the performance of anaerobic processes is significantly affected by operating temperature. Best performance is typically obtained by operation in the optimal region of one of the two higher temperature ranges, i.e., 30°C to 40°C for mesophilic or 50°C to 60°C for thermophilic, and most anaerobic processes are designed to do so. These two regions generally represent the optima for growth of the methanogens. Nevertheless, it is possible to grow methanogens at lower temperatures, provided that longer SRTs are used to compensate for the lower maximum specific growth rates. Although anaerobic activity can be sustained at temperatures approaching 10°C, operating temperatures in the 20°C to 25°C range appear to be the lower limit from a practical perspective.37,46,49,58,62,68

Although the preceding paragraph focussed on methanogens, operating temperature affects hydrolytic and acidogenic reactions as well. For wastewaters consisting largely of simple, readily biodegradable organic matter, the effect of temperature on methanogenesis is the primary concern. However, for wastewaters consisting largely of complex organic compounds or particulate materials, the effects of temperature on hydrolysis and acidogenesis will be the primary concern. Table 13.4 presents μ and Ks values for biodegradation of VFAs at temperatures of 25°C, 30°C, and 35°C. These data may be used to characterize the impact of temperature on the anaerobic biodegradation of simple organic compounds.

Figure 13.19 shows the combined effects of SRT and temperature on the anaerobic digestion of municipal primary solids. Essentially complete stabilization of biodegradable volatile solids is achieved at an SRT of 10 days when operating at a temperature of 35°C. A moderate increase in SRT to about 15 days is required when operating at a temperature of 25°C, but the stabilization is not complete as indicated by a residual VS concentration at SRT values as long as 60 days. The required SRT

| Table 13.4 Average Values of Kinetic Parameters for Anaerobic Enrichment Cultures Grown on Various Volatile Fatty Acids* |
|-----------------|--------------|-----------------|-----------------|-------------------|-------------------|
|                 | 35°C         |                 | 30°C           | 25°C             | 25°C             |
| Volatile fatty acid | μ (day⁻¹) | Ks (mg/L as COD) | μ (day⁻¹) | Ks (mg/L as COD) | μ (day⁻¹) | Ks (mg/L as COD) |
| Acetic          | 0.36        | 165             | 0.26          | 356              | 0.24         | 930               |
| Propionic       | 0.31        | 60              | —             | —                | 0.38         | 1145              |
| Butyric         | 0.38        | 13              | —             | —                | —             | —                 |

*Adapted from Lawrence.37
increases to about 25 days when operating at a temperature of 20°C, and a higher residual VS concentration is observed. At 15°C an SRT of about 30 days is required to obtain stable operation, and only about one-half of the biodegradable volatile solids are destroyed at SRTs as long as 60 days. The curves showing the correspondence between VS destruction and methane production suggest that hydrolysis of the solids is generally the rate limiting step at these temperatures. Taken together, these data suggest that a temperature of about 25°C is the practical minimum for the anaerobic stabilization of municipal primary solids.

Temperature variations are also of concern, and it is typically recommended that systems be designed and operated to achieve variations of less than ±1°C each day. Some research indicates that anaerobic processes are capable of reacting successfully to temperature variations; although reaction rates decrease when the temperature is reduced, activity is restored quickly when the temperature returns to the optimum value. In contrast, experience with full-scale systems indicates that performance is adversely impacted by rapid temperature variations of as little as 2°C.
to 3°C. This may be because of factors such as mixing and stratification within the bioreactor. Regardless of the mechanism, it appears prudent to adhere to recommended practice and to design and operate anaerobic processes to minimize short-term temperature variations.

Opinions vary concerning the benefits of operation under thermophilic conditions. Potential benefits include increased stabilization rates, resulting in smaller bioreactors; improved solids dewatering properties, which benefits downstream processing; and increased inactivation of pathogenic organisms, which increases the options for disposing of treated solids. Potential drawbacks include the increased energy required to achieve thermophilic operating temperatures and decreased process stability. Increased stabilization rates and increased methane production sufficient to meet the increased heating requirements have been demonstrated by some workers, but not by others. Likewise, improved solids dewatering properties have been observed by some, but not by others. However, increased pathogen inactivation is certain to be observed as a result of thermophilic operation. Decreased process stability because of increased VFA concentrations, increased sensitivity to temperature variations, increased ammonia toxicity, increased foaming, and increased odor potential are all areas of concern. Because of its uncertain benefits and numerous drawbacks, designs based on thermophilic operation should be approached with caution unless site-specific pilot test results and/or full-scale experience are available.

13.2.5 pH

Like all biochemical operations, pH has a significant impact on the performance of anaerobic processes, with activity decreasing as the pH deviates from an optimum value. This effect is particularly significant for anaerobic processes because the methanogens are affected to a greater extent than the other microorganisms in the microbial community. As a consequence, there is a greater decrease in methanogenic activity as the pH deviates from their optimum value. A pH range of 6.8 to 7.4 generally provides optimum conditions for the methanogens, whereas a pH between 6.4 and 7.8 is considered necessary to maintain adequate activity. pH will also affect the activity of the acidogenic bacteria; however, the effect is less significant and primarily influences the nature of their products. A decrease in pH increases the production of higher molecular weight VFAs, particularly propionic and butyric acid, at the expense of acetic acid. As discussed in Section 2.3.2, one mechanism causing this is the buildup of H₂ in the system. As its utilization by methanogens is slowed, it begins to accumulate, which then slows down the production of acetic acid by the acidogens and shifts their metabolism toward other VFAs. The activity of the hydrolytic microorganisms is affected the least by pH deviations from neutrality.

The pH sensitivity of the methanogens, coupled with the fact that VFAs are intermediates in the stabilization of organic matter, can result in an unstable response by anaerobic systems to a decrease in pH. The unstable response may be triggered by a high VOL that results in an increase in the production of VFAs by the acidogenic bacteria. If the increased VFA production rate exceeds the maximum capacity of the methanogens to use acetic acid and H₂, excess VFAs will begin to accumulate, decreasing the pH. The decreased pH will reduce the activity of the methanogens, thereby decreasing their use of acetic acid and H₂, causing a further
accumulation of VFAs and a further decrease in the pH. If this situation is left uncorrected, the result is a precipitous decrease in the pH, the accumulation of higher molecular weight VFAs, and a near cessation of methanogenic activity. This condition is known as a “sour” or “stuck” anaerobic process. It can be corrected in its early stages by resolving the environmental factors causing the imbalance between the acidogenic bacteria and the methanogens. In the case considered above, this could be accomplished by reducing the VOL to the point where the VFA production rate is less than their maximum consumption rate. This will allow consumption of the excess VFAs in the system, thereby causing the pH to return to neutrality and the activity of the methanogens to increase. The VOL can then be increased as the process recovers until the full loading capability is utilized. In extreme cases, decreases in loading must be coupled with the addition of chemicals for pH adjustment, as discussed below.

For an anaerobic process functioning within the acceptable pH range, the pH is controlled primarily by the bicarbonate buffering system. Bicarbonate alkalinity is produced by the destruction of nitrogen-containing organic matter and the reaction of the released ammonia-N with the carbon dioxide produced in the reaction. This is illustrated by Eq. 13.6 for the conversion of primary solids (represented as $C_{10}H_{19}O_{3}N$) to methane, carbon dioxide, biomass, and ammonium bicarbonate:\n
$$C_{10}H_{19}O_{3}N + 4.69 \text{H}_2\text{O} \rightarrow 5.74 \text{CH}_4 + 2.45 \text{CO}_2$$
+ $0.2 \text{C}_3\text{H}_7\text{O}_2\text{N} + 0.8 \text{NH}_4\text{HCO}_3$ \hspace{1cm} (13.6)

As illustrated, bicarbonate alkalinity is produced in direct relation to the ammonia-N released. A strong base is needed to react with the carbon dioxide produced in the system to form the bicarbonate. In most instances, ammonia is the strong base, although the cations associated with soaps or the salts of organic acids can also serve to maintain electroneutrality in the reaction with carbon dioxide.

The concentration of bicarbonate alkalinity in solution is related to the carbon dioxide content of the gas space in the bioreactor and the bioreactor pH:

$$S_{\text{BA}k} = 6.3 \times 10^{-4} \left( \frac{P_{\text{CO}_2}}{10^{-\text{pH}}} \right)$$ \hspace{1cm} (13.7)

where $S_{\text{BA}k}$ is the bicarbonate alkalinity expressed as mg/L as CaCO$_3$ and $P_{\text{CO}_2}$ is the partial pressure of carbon dioxide in the gas space expressed in atmospheres.$^{10,48,58}$

This relationship is presented in Figure 13.20 and illustrates that typical anaerobic processes operate with bicarbonate alkalinities in the range of 1,000 to 5,000 mg/L as CaCO$_3$ and carbon dioxide partial pressures of 25 to 45%.

When VFAs begin to accumulate in an anaerobic process, they are neutralized by the bicarbonate alkalinity present. Consider for example, acetic acid. Acetic acid is released by the acidogenic bacteria in nonionized form, but exists as acetate ion at neutral pH. The reaction of acetic acid with bicarbonate alkalinity to convert it to acetate is:

$$\text{HCO}_3^- + \text{HAc} = \text{H}_2\text{O} + \text{CO}_2 + \text{Ac}^-$$ \hspace{1cm} (13.8)

where HAirepresents nonionized acetic acid and Ac$^-$ represents acetate ion. When a pH end point of 4.0 is used in the alkalinity analysis, acetate will be partially converted to acetic acid and will, therefore, register as alkalinity. Thus, if VFAs are
present, the total alkalinity will represent the concentration of both bicarbonate ion and VFAs. If the concentration of VFAs is known and is expressed as acetic acid, the bicarbonate alkalinity can be calculated from the total alkalinity as:

\[ S_{\text{BAIK}} = S_{\text{TALK}} - 0.71(S_{\text{VFA}}) \]  

where \( S_{\text{TALK}} \) is the total alkalinity expressed as CaCO\(_3\) and \( S_{\text{VFA}} \) is the concentration of VFAs expressed as acetic acid. The factor 0.71 converts the VFA concentration expressed as acetic acid to CaCO\(_3\) and corrects for the fact that approximately 85% of the VFA anions are titrated to the acid form at a pH of 4.0. Other organic and inorganic bases, such as sulfides, can also be titrated to their acid form and, consequently, measured as alkalinity. The concentrations of these anions are typically small relative to the bicarbonate concentration, but the potential for such interferences with bicarbonate alkalinity measurement should be recognized.

As discussed above, under stable operating conditions, bicarbonate is the primary form of alkalinity in anaerobic processes. However, under unstable operating conditions VFAs will react with bicarbonate alkalinity, both reducing its concentration and producing carbon dioxide (see Eq. 13.8), which increases the carbon dioxide content of the gas space. Reference to Figure 13.20 illustrates that both of these changes act to decrease the pH in the bioreactor. Stable operation of anaerobic processes is generally achieved by the maintenance of a relatively high concentration of bicarbonate alkalinity so that increased VFA production can be tolerated with a minimal decrease in bioreactor pH.

![Figure 13.20](image_url)  
**Figure 13.20** Effect of pH on the relationship between the bicarbonate alkalinity of the liquid phase and the carbon dioxide content of the gas phase in an anaerobic process. (From G. F. Parkin and W. F. Owen, Fundamentals of anaerobic digestion of wastewater sludges. *Journal of the Environmental Engineering Division, ASCE* 112:867–920, 1986. Copyright © American Society of Civil Engineers; reprinted with permission.)
Adverse pH conditions can be corrected by the addition of appropriate chemicals, but, care must be exercised in their selection because of the complex interactions that can occur and the potential for adding toxicants. Commonly used chemicals include sodium bicarbonate, sodium carbonate, lime, sodium or potassium hydroxide, and ammonia.

Sodium bicarbonate is preferred for pH adjustment because its impact is longer lasting and its toxicity potential is low. It adjusts the pH by the direct addition of bicarbonate ions which, as illustrated in Figure 13.20, will result in a direct increase in the pH without affecting the carbon dioxide content of the gas space.

The addition of hydroxide ions by adding lime, sodium hydroxide, or potassium hydroxide, adjusts the pH because the hydroxide ion reacts with carbon dioxide to form bicarbonate alkalinity. Using lime as the example pH adjustment chemical gives:

\[
\text{Ca(OH)}_2 + 2\text{CO}_2 \rightarrow \text{Ca}^{+2} + 2\text{HCO}_3^- \quad (13.10)
\]

This reaction is accompanied by a decrease in the carbon dioxide content of the gas space, which further contributes to the rise in the bioreactor pH. Unfortunately, further production of carbon dioxide by the microorganisms in the process will restore the original gas space carbon dioxide content and reduce the pH.

The use of carbonate based chemicals reduces the magnitude of the pH variation, as follows:

\[
\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{Na}^+ + 2\text{HCO}_3^- \quad (13.11)
\]

Comparison to Eq. 13.10 illustrates that only one mole of carbon dioxide is required to produce two moles of bicarbonate from carbonate while two moles of carbon dioxide are required to produce two moles of bicarbonate from hydroxide. Thus, when carbonate-based chemicals are used for pH adjustment, the immediate consumption of carbon dioxide from the gas space is one-half of that when hydroxide-based chemicals are used.

These changes in pH are illustrated in Figure 13.21. Consider an initial condition represented by a gas phase carbon dioxide content of 40% and a bicarbonate alkalinity of 500 mg/L as CaCO₃ (point 1), which corresponds to a pH of about 6.3. The addition of sufficient sodium bicarbonate to elevate the bioreactor bicarbonate alkalinity to 2,100 mg/L as CaCO₃ would directly increase the bioreactor pH to about 6.9 (point 2). The addition of an equivalent amount of hydroxide-based chemical will result in not only an increase in the bicarbonate alkalinity to 2,100 mg/L as CaCO₃, but also in an immediate decrease in the carbon dioxide content of the gas space as it is removed to produce the bicarbonate (Eq. 13.10). The actual decrease in the carbon dioxide content of the gas will depend on the relative gas and liquid volumes in the bioreactor. If the requirement for carbon dioxide is large relative to the amount available, a negative pressure can be created, causing air to be drawn into the gas space, creating an explosive mixture of methane and oxygen. Furthermore, under extreme conditions, removal of carbon dioxide can cause a sufficiently strong negative pressure to collapse the structure. However, for the purposes of this example a decrease to 10% is assumed, and no other adverse consequences are experienced. This results in a pH of approximately 7.5 immediately after addition of the chemical (point 3). However, as additional carbon dioxide is produced by the biomass, the carbon dioxide content of the gas space will increase to its equilibrium...
value of 40\% and the pH will decrease to 6.9, as illustrated by line 3-2 in Figure 13.21. This dramatic variation in pH, from 6.3 (point 1) to 7.5 (point 3) to 6.8 (point 2), can be detrimental to the process. Moreover, it makes pH control difficult from an operational perspective because the relationship between chemical addition and the resulting pH is not straightforward. The effect of adding a carbonate chemical, such as sodium carbonate, is illustrated by point 4 in Figure 13.21, where it is observed that the pH immediately after its addition will be about 7.1. The pH will decrease to 6.9 as carbon dioxide is produced and the carbon dioxide content of the gas is increased back to 40\% (point 2). Thus, it can be seen that the addition of carbonate chemicals causes less drastic swings in pH than addition of hydroxide chemicals.

The cations associated with pH adjustment chemicals can also impact the anaerobic process. Use of lime increases the calcium concentration and if it becomes too high, calcium carbonate can precipitate and reduce the effective volume of the bioreactor. As discussed in Section 13.2.6, sodium, potassium, and calcium are toxic if concentrations become high enough. Ammonia can also be used to adjust the pH because it reacts with carbon dioxide to form ammonium bicarbonate:

$$\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{NH}_4\text{HCO}_3$$ (13.12)

However, this results in the same variations in pH produced by the addition of hydroxide chemicals. Moreover, as discussed in Section 13.2.6, ammonia is also toxic at high concentrations. Thus, it can be seen that no ideal pH adjustment chemical exists and that some degree of care is required when any of them are used.

The control of pH by the removal of carbon dioxide from the gas space has been suggested. As illustrated by point 5 in Figure 13.21, this would require re-
duction of the carbon dioxide content of the gas to about 10% on a sustained basis to achieve the same pH as achieved by increasing the bicarbonate alkalinity to 2,100 mg/L as CaCO₃. This would require continuous removal of carbon dioxide from the gas phase.

13.2.6 Inhibitory and Toxic Materials

As discussed in Section 13.1.1, one characteristic of anaerobic processes is their sensitivity to inhibition by chemicals present in the wastewater or produced as process intermediates. As discussed in Section 3.2.7, inhibition causes a reduction in the maximum specific growth rate of microorganisms, thereby requiring an increase in the SRT of a biochemical operation to produce the same effluent that would be produced in the absence of the inhibitor. However, if the inhibitor concentration is increased sufficiently, a toxic response is exhibited and the microorganisms are killed, causing total process failure. Unfortunately, the literature has not always made a clear distinction between inhibition and toxicity. Consequently, in the information that follows the two terms should not be interpreted strictly. However, it should be recognized that, in general, inhibition precedes toxicity as the concentration of a compound is increased. Several inorganic materials can cause an inhibitory response; the materials of greatest concern are light metal cations, ammonia, sulfide, and heavy metals. In addition, sulfate interferes with methane production by providing an alternate electron acceptor. Not only does the sulfide produce an offensive and dangerous gas, but soluble sulfide exerts an oxygen demand that reduces the amount of COD stabilized. Finally, many organic compounds are also inhibitory, particularly to methanogens.

**Light Metal Cations.** The light metal cations include sodium, potassium, calcium, and magnesium. They may be present in the influent, released by the breakdown of organic matter (such as biomass), or added as pH adjustment chemicals. They are required for microbial growth and, consequently, affect specific growth rate like any other nutrient. Consequently, they must be available if anaerobic treatment is to occur. Nevertheless, their inhibitory nature has been known for over three decades. While moderate concentrations stimulate microbial growth, excessive amounts slow it, and even higher concentrations can cause severe inhibition or toxicity. Table 13.5 indicates the concentration ranges over which these various responses occur.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Stimulatory</th>
<th>Moderately inhibitory</th>
<th>Strongly inhibitory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>100–200</td>
<td>3,500–5,500</td>
<td>8,000</td>
</tr>
<tr>
<td>Potassium</td>
<td>200–400</td>
<td>2,500–4,500</td>
<td>12,000</td>
</tr>
<tr>
<td>Calcium</td>
<td>100–200</td>
<td>2,500–4,500</td>
<td>8,000</td>
</tr>
<tr>
<td>Magnesium</td>
<td>75–150</td>
<td>1,000–1,500</td>
<td>3,000</td>
</tr>
</tbody>
</table>

*Adapted from McCarty.*
The light metal cations exhibit complex interactions in their effects on microbial growth. For example, inhibition can be increased when two light metal cations are present at their moderately inhibitory concentrations. This is known as a synergistic response because the combined effects of the two light metal cations exceeds that of either individually. Secondly, the inhibition caused by one light metal cation can be increased if the other light metal cations are present at concentrations below their stimulatory concentrations. Finally, the presence of one light metal cation at its stimulatory concentration can reduce the inhibition of another. This phenomenon is known as antagonism, since the effect is reduced. Table 13.6 summarizes antagonistic responses for the light metal cations and ammonia.

**Ammonia.** Ammonia-N is a required nutrient and stimulates bacterial growth at low concentrations. For anaerobic processes, ammonia concentrations between 50 and 200 mg/L as N are generally within the stimulatory range. However, ammonia is inhibitory at higher concentrations, and toxic if the concentration is high enough. Ammonia may be present in the influent wastewater, or it may be formed as a result of the breakdown of organic materials that contain nitrogen, such as proteins. The production of ammonia by the breakdown of primary solids is illustrated in Eq. 13.6.

Ammonia is a weak base and dissociates in water:

\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \quad (13.13) \]

Both species are inhibitory, but at significantly different concentrations. Free ammonia (NH$_3$) is more inhibitory and can cause a toxic response at concentrations of about 100 mg/L as N. On the other hand, ammonium ion (NH$_4^+$) concentrations as high as 7,000 to 9,000 mg/L as N have been successfully treated without a toxic response with an acclimated culture, although concentrations as low as 1,500 mg/L as N have been reported to be toxic. This type of response has been observed for many materials that can ionize and the nonionized species is often the more inhibitory of the two. As noted in Table 13.6, ammonium ion is also an antagonist for inhibition by potassium.

The pK$_a$ for the dissociation of ammonia is approximately 9.3, so ammonia is present primarily as the ionized species at the pH values typically occurring in anaerobic processes. However, if the total ammonia (NH$_3$ + NH$_4^+$) concentration is high enough, a sufficient concentration of free ammonia can be present to cause an inhibitory or toxic response. The proportion of total ammonia that is present as free ammonia increases with both pH and temperature. As illustrated in Figure 13.22, vastly different total ammonia concentrations can result in a toxic free ammonia concentration.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Antagonist</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>K$^+$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>Na$^+$, Ca$^{+2}$, Mg$^{+2}$, NH$_4^+$</td>
</tr>
<tr>
<td>Ca$^{+2}$</td>
<td>Na$^+$, K$^+$</td>
</tr>
<tr>
<td>Mg$^{+2}$</td>
<td>Na$^+$, K$^+$</td>
</tr>
</tbody>
</table>

*Adapted from Kugelman and Chin.*
concentration (100 mg/L as N), depending on the pH and temperature. For mesophilic conditions (25°C and 35°C), the total ammonia concentration can exceed 10,000 mg/L as N and the free ammonia concentration will still be below 100 mg/L as N at pH values of about 7. However, for thermophilic conditions (55°C) the total ammonia concentration must be maintained below 2,000 mg/L as N to keep free ammonia concentrations below toxic levels. Even for mesophilic operating conditions, total ammonia concentrations of about 2,000 mg/L can result in toxic free ammonia concentrations (100 mg/L as N) as the pH approaches 7.5 to 8.0.

Three strategies are available for reducing ammonia inhibition in anaerobic processes: (1) reduce the temperature, (2) reduce the pH, or (3) reduce the total ammonia concentration. As discussed in the preceding paragraph, Figure 13.22 illustrates the impact of mesophilic versus thermophilic operating temperatures on allowable total ammonia concentrations. This difference should be carefully considered when selecting the temperature range. Moreover, a reduction in operating temperature within a temperature range must also be carefully evaluated. For example, reducing the temperature from 35°C to 25°C causes a noticeable increase in the allowable total ammonia concentration. However, a temperature decrease of this magnitude would also result in a significant reduction in the maximum specific growth rate of the anaerobic biomass, which may be more detrimental to the process than the reduced inhibition associated with the reduction in free ammonia concentration. As further indicated in Figure 13.22, if pH values are relatively high, significant reductions in ammonia toxicity can result from their decrease. High pH values can occur when high-strength wastewaters or solids are treated because of the
high concentrations of bicarbonate alkalinity that result. If such wastewaters also contain high concentrations of ammonia or organic nitrogen, then the concentration of total ammonia will be elevated as well. The pH in such a bioreactor can be decreased by the addition of an acid. Hydrochloric acid is the ideal chemical for this purpose because chloride ion has little or no impact on anaerobic biomass. In addition, the total ammonia concentration can be reduced by dilution of the wastewater or solids with clean water. Care must be exercised if this is done because the larger flow rate may compromise the SRT of the system. However, if an adequate SRT can be maintained, this approach can be used quite successfully.

**Sulfide.** Sulfide is produced in an anaerobic process through the reduction of sulfate present in the influent and by the degradation of sulfur-containing organic matter (e.g., proteins). Only soluble sulfides are inhibitory and concentrations greater than 200 mg/L cause strong inhibition, while concentrations up to 100 mg/L can be tolerated with little or no acclimation. Concentrations between 100 and 200 mg/L may be tolerated after acclimation. Sulfide reacts with heavy metal cations, including iron, forming highly insoluble precipitates. In fact, iron sulfide gives anaerobic processes their characteristic black color. Consequently, the concentration of soluble sulfide can be reduced by the addition of iron to the bioreactor, thereby reducing sulfide inhibition.

Hydrogen sulfide is a weak acid and, consequently, at neutral pH is present in equilibrium with the sulfide anion. Hydrogen sulfide is sparingly soluble in water, so it will partition between the liquid and gas phases. Hydrogen sulfide increases the corrosivity of anaerobic process gas and results in the formation of sulfur oxides when the gas is burned. Consequently, control of the hydrogen sulfide content of the product gas is desirable. This too can be done by adding iron to the bioreactor to precipitate the sulfide anion as iron sulfide.

Sulfate itself is not inhibitory to anaerobic bacteria, but it impacts anaerobic processes by providing an electron acceptor that can be used by sulfate reducing bacteria, allowing them to compete with methanogens for the electrons available in the organic matter. This has several effects. First, it produces sulfide, which is inhibitory, as discussed above. Second, it reduces the amount of methane produced because the electrons used to reduce the sulfate are not available for the reduction of carbon dioxide to methane. Third, it reduces the value of the product gas, as discussed above. Fourth, it decreases the removal of COD from the wastewater being treated. Although the organic matter is still oxidized to carbon dioxide, much of the sulfide produced remains in the process stream, where it represents an oxygen demand. Approximately two mg of carbonaceous COD are consumed by sulfate reducing bacteria for each mg of sulfate-S reduced to sulfide-S, but any of that sulfide that is still present in the liquid phase exerts a COD. This can have a major impact when anaerobic processes are used to treat relatively dilute wastewaters.

The competition between methanogens and sulfate reducing bacteria is very complex and is influenced by many factors. Consequently, the conversion of sulfate to sulfide may not be complete. Nevertheless, in the absence of other specific information, when judgements are being made about the potential for inhibitory sulfide levels being formed, it is generally prudent to assume that all of the influent sulfate will be reduced to sulfide. Some of the produced sulfide will be precipitated by heavy metals and some will partition into the gas phase. Both of these mechanisms will reduce the soluble sulfide concentration and, consequently, the potential
for the development of an inhibitory sulfide concentration. Nevertheless, when the influent COD is low relative to the influent sulfate concentration, insufficient methane gas may be produced to strip the sulfide produced from the liquid phase, resulting in soluble sulfide concentrations that are inhibitory or toxic. Experience suggests that inhibitory soluble sulfide concentrations may develop when treating wastewaters with a COD/SO₄²⁻ ratio less than about 7.5.²³ Hall²³ lists sulfide control strategies that can be applied in such cases, including, adding iron salts to precipitate sulfide from solution, purging hydrogen sulfide from the bioreactor liquid, scrubbing hydrogen sulfide from the biogas and recirculating it to the bioreactor to remove sulfide, and using biological sulfide oxidation and sulfur recovery.

**Heavy Metals.** As with other biochemical operations, heavy metals have strong effects on anaerobic processes, as indicated in Table 13.7 by the low concentrations causing 50% inhibition. Fortunately, only the soluble metal ions are inhibitory and the metal sulfides are extremely insoluble, giving residual heavy metal concentrations much less than the concentrations in Table 13.7. Consequently, heavy metal inhibition to anaerobic processes is often prevented by the sulfide produced in the process. In situations where inadequate sulfide is produced, sulfur can be added. Approximately 0.5 mg of sulfide is needed to precipitate one mg of heavy metal.⁴⁶⁵⁸ Ferrous sulfide is an ideal chemical to provide supplemental sulfide. Table 13.7 shows that ferrous iron is much less inhibitory than other heavy metals. In addition, the sulfide precipitates of the more inhibitory heavy metals are more insoluble than ferrous sulfide, and consequently the added sulfide will maintain the concentration of those heavy metals at low concentrations. Furthermore, the presence of residual iron will maintain soluble sulfide concentrations at low values. Finally, as long as the pH is 6.4 or above, any excess iron will precipitate as iron carbonate, thereby preventing any inhibition caused by soluble iron.

**Volatile Acids.** It is uncertain whether VFAs are inhibitory to methanogens.⁴⁶⁵⁸ Although early evidence suggested that VFA concentrations above 2,000 mg/L were inhibitory to methanogens, when the pH was held near neutral, neither acetic nor butyric acid inhibited methane formation at concentrations up to 10,000 mg/L⁻¹.⁹ Propionic acid was inhibitory at a concentration of 6,000 mg/L at neutral pH, but this is an extremely high concentration that is unlikely to be found in an anaerobic

<table>
<thead>
<tr>
<th>Cation</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe⁺²</td>
<td>1 to 10</td>
</tr>
<tr>
<td>Zn⁺²</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>Cd⁺²</td>
<td>10⁻⁷</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>10⁻¹²</td>
</tr>
<tr>
<td>Cu⁺²</td>
<td>10⁻¹⁶</td>
</tr>
</tbody>
</table>

*Adapted from Mosey and Hughes.⁵⁶
process at neutral pH. Andrews and coworkers have suggested that it is the non-
ionized form of the VFAs that is actually inhibitory, with concentrations on the order
of 30 to 60 mg/L having an effect. Volatile fatty acids are weak acids that are
largely dissociated at neutral pH. For example, a total acetic acid concentration of
approximately 5,500 mg/L is required to produce a nonionized acetic acid concen-
tration of 30 mg/L at pH 7. On the other hand, at pH 6.5 a total acetic acid concen-
tration of only 1,800 mg/L produces the same nonionized acetic acid concentration,
showing that pH and VFA concentration are interrelated in their effects. Furthermore,
some evidence suggests that the early observations of VFA inhibition were actually
a result of the accumulation of H₂ during anaerobic process upsets. While this
controversy has not been fully resolved, it appears that inhibition caused by VFAs
will be of little concern as long as the pH remains within the normal range for the
growth of methanogens (6.8 to 7.4). For pH values below this range, pH impacts
themselves will be significant and will be compounded by any inhibition caused by
nonionized VFAs.

Other Organic Compounds. As with aerobic processes, a wide range of or-
ganic compounds can inhibit anaerobic processes. Also like aerobic processes, signif-
ificant biodegradation of these chemicals can occur with sufficient acclima-
tion. Table 13.8 summarizes inhibitory concentrations of some typical organic
compounds, while Table 13.9 compares the relative effects of several organic com-
ounds on anaerobic processes. The concentration ranges presented in these tables
represent the response of anaerobic cultures upon initial exposure to the compounds.
However, it has been found that, with acclimation, anaerobic cultures can tolerate
concentrations of 20 to 50 times those values while successfully metabolizing the
compounds. Table 13.10 demonstrates the biodegradative capability of anaerobic
systems by summarizing petrochemical wastewater components that were inhibitory
initially, but biodegradable following acclimation. During acclimation, the activity
of a methanogenic community may nearly cease. However, even after long periods
of inactivity (50 days or more), a community capable of degrading the target com-
 pound can develop. This suggests that some organisms survived and served as seed
for the development of a healthy community capable of degrading the target com-
 pound. Procedures have been developed to assess the effects of compounds on ana-
erobic cultures, and they may be used to determine the concentration range over

<p>| Table 13.8 | Concentrations of Organic Compounds Reported to be Inhibitory to Anaerobic Processes* |</p>
<table>
<thead>
<tr>
<th>Compound</th>
<th>Inhibitory concentration mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>50–200</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.5</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>200–1,000</td>
</tr>
<tr>
<td>Ethylene dibromide</td>
<td>5</td>
</tr>
<tr>
<td>Kerosene</td>
<td>500</td>
</tr>
<tr>
<td>Linear ABS (detergent)</td>
<td>1% of dry solids</td>
</tr>
</tbody>
</table>

*Adapted from Parkin and Owen.
### Table 13.9 Relative Inhibition of Selected Organic Compounds to Anaerobic Processes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration causing 50% inhibition, mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Chloropropene</td>
<td>0.1</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.1</td>
</tr>
<tr>
<td>Acrolein</td>
<td>0.2</td>
</tr>
<tr>
<td>1-Chloropropane</td>
<td>1.9</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>2.4</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>2.6</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>3.2</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>4</td>
</tr>
<tr>
<td>3-Chlorol-1,2-propanediol</td>
<td>6</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>6.5</td>
</tr>
<tr>
<td>2-Chloropropionic acid</td>
<td>8</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>8</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>10</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>11</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>12</td>
</tr>
<tr>
<td>Catechol</td>
<td>24</td>
</tr>
<tr>
<td>Phenol</td>
<td>26</td>
</tr>
<tr>
<td>Aniline</td>
<td>26</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>29</td>
</tr>
<tr>
<td>Propanal</td>
<td>90</td>
</tr>
</tbody>
</table>

*Adapted from Parkin and Owen.*

### Table 13.10 Petrochemicals Metabolized by Enriched Methanogenic Cultures

<table>
<thead>
<tr>
<th>Petrochemical</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>Formaldehyde</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>Formaldehyde</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>Adipic acid</td>
<td>Formic acid</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>1-Amino-2-propanol</td>
<td>Formic acid</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>4-Aminobutyric acid</td>
<td>Fumaric acid</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>Glutaric acid</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>Butanol</td>
<td>Glycerol</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>Glycerol</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>Butyric acid</td>
<td>Glutaric acid</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>Catechol</td>
<td>Glycerol</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>Methyl acetate</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>Crotonic acid</td>
<td>Methyl acetate</td>
<td>Phthalic acid</td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>Methyl ethyl ketone</td>
<td>Tert-butanol</td>
<td></td>
</tr>
<tr>
<td>Ethyl acrylate</td>
<td>Nitrobenzene</td>
<td>Tert-butanol</td>
<td></td>
</tr>
<tr>
<td>Ethyl acrylate</td>
<td>Phenol</td>
<td>Tert-butanol</td>
<td></td>
</tr>
</tbody>
</table>

*Adapted from Parkin and Owen.*
Anaerobic Processes

digesters are often in the range of 5 to 8 kW/1000 m³, but successful performance has been obtained at inputs as low as 1 kW/1000 m³. The importance of the configuration and efficiency of the mixing system is illustrated by the fact that power densities as high as 20 kW/1000 m³ have been ineffective in some instances. Egg-shaped digesters, shown in Figure 13.4, have superior mixing characteristics and can be properly mixed using lower than normal volumetric power inputs.

Specialized techniques are now routinely used to determine the mixing pattern within full-scale anaerobic digesters. The most frequently used technique involves the pulse addition of lithium into the digester and the monitoring of its concentration in the effluent for at least 3 SRTs. The results are then analyzed as discussed in Section 4.3.2 to determine the residence time distribution, from which the effective volume of the bioreactor and the proportion of the feed that short-circuits can be estimated. Application of this technique allows the effectiveness of various mixing systems to be determined and compared. It has revealed that significant differences exist in the effectiveness of such systems.

13.2.9 Waste Type

The nature of the wastewater being treated significantly affects its performance in an anaerobic process. One consideration is the relative amounts of soluble and particulate organic matter. Some anaerobic processes are better suited to treat wastewaters containing primarily particulate matter, while others are ideally suited to remove soluble substrates. For example, anaerobic digesters and solids fermentation systems were developed specifically to handle particulate organic matter, while the low-rate processes and some of the high-rate ones, such as AC, AF, and DSFF, can tolerate high concentrations of it. They all effectively retain the particulate material and allow the slow hydrolysis reactions to proceed. On the other hand, FB/EB, UASB, and hybrid UASB/AF systems do not retain particulate organic matter as effectively, allowing it to pass through the bioreactor with little hydrolysis and stabilization. They are better for soluble wastes.

Soluble organic matter can be further subdivided into readily and slowly biodegradable components. Slowly biodegradable soluble substrate consists of high molecular weight and/or recalcitrant materials requiring significant metabolism to convert them to the simple VFAs that are the substrates of the acidogenic bacteria. Examples include polymers such as carbohydrates and proteins, as well as the complex organic compounds found in many industrial wastewaters. Long SRTs may be required to metabolize these materials. One characteristic of high-rate processes is their ability to accumulate high concentrations of biomass, which allows maintenance of long SRTs even though their HRTs are short. Thus, effective metabolism of slowly biodegradable soluble organic matter can be achieved in them. Long HRTs are required to degrade such substrates in anaerobic processes that are unable to achieve such an effective separation of SRT and HRT. Examples include the low-rate anaerobic processes as well as AC and DSFF systems. In contrast, a wide range of bioreactor types and process loadings can be used to treat wastewaters containing primarily soluble, readily biodegradable substrates.

The nature of the wastewater has a strong impact on the performance of UASB systems because it affects granule development and its characteristics. Research is still underway to characterize all of the factors that affect the development of granules, but an inter-
An interesting model has been developed by researchers at the University of Capetown.\textsuperscript{78} It suggests that separation of acidogenesis and methanogenesis, along with a deficiency of the amino acid cysteine, causes the formation of excessive quantities of proteins by the H\textsubscript{2}-utilizing methanogen \textit{Methanobrevibacter}. The protein provides a polymeric matrix that results in the formation of granules. Several other researchers have speculated on the role of the filamentous methanogen \textit{Methanoseta} (formerly \textit{Methanothrix}) in determining the structure of UASB granules. While further research will undoubtedly define the conditions that facilitate granule formation, experience indicates that it is encouraged during the treatment of wastewaters consisting primarily of carbohydrates and retarded during the treatment of wastewaters consisting primarily of VFAs or proteins.\textsuperscript{42,43} Granule formation may also be impeded when the wastewater contains a large proportion of particulate or slowly biodegradable organic matter.

The extent and rate of biodegradation of organic solids varies, and this can affect the performance of anaerobic digesters. Approximately 70\% of the organic matter in municipal primary solids, measured as either COD or VS, is biodegradable in an anaerobic environment.\textsuperscript{37,58,72} In contrast, the biodegradability of waste solids from aerobic biochemical operations depends on how much stabilization they have undergone in the operations from which they came. For example, Gossett and Belser\textsuperscript{21} found that the biodegradable fraction of waste activated sludge under anaerobic conditions is equal to the active fraction, as defined in Section 5.1.3. Furthermore, the active biomass degraded under anaerobic conditions in a first order manner, with a rate coefficient of 0.22 day\textsuperscript{-1} at 35\°C. In short, the anaerobic stabilization of waste activated sludge is qualitatively and quantitatively similar to its aerobic stabilization, as described in Chapter 12. However, the rate coefficient for waste activated sludge is lower than the rate coefficient for primary solids. Moreover, because the active fraction of waste activated sludge is often on the order of 50\%, and only about 80\% of the active mass will be stabilized, i.e., \(1 - \phi_p\), only a small fraction of the total organic matter in waste activated sludge will be stabilized during anaerobic digestion. These effects are illustrated in Figure 13.23 where the COD reduction efficiencies of municipal primary solids, waste activated sludge, and a mixture of primary solids and waste activated sludge are plotted as a function of anaerobic digester SRT.

### 13.3 PROCESS DESIGN

As we saw in Section 13.1, a wide range of anaerobic process options exists. Although the various processes operate according to a unified set of principles, they differ in many ways. In some, such as anaerobic digestion, the bioreactor functions as a CSTR without biomass recycle so that the SRT is equal to the HRT. In others, significant quantities of biomass are accumulated, allowing long SRTs to be maintained at relatively short HRTs. However, because of the mechanisms used to accumulate biomass in some anaerobic processes, it is impossible to calculate the resulting biomass concentration or SRT. In these instances, empirical correlations between the VOL and the performance must be used for design purposes. In short,
Figure 13.23 Effect of SRT on the stabilization of primary solids and waste activated sludge. (From G. F. Parkin and W. F. Owen, Fundamentals of anaerobic digestion of wastewater sludges. *Journal of the Environmental Engineering Division, ASCE* 112:867–920, 1986. Copyright © American Society of Civil Engineers; reprinted with permission.)

A wide range of design procedures must be used to accommodate the wide range of anaerobic processes.

### 13.3.1 Anaerobic Digestion

The design of an anaerobic digester to stabilize solids is quite straightforward. Since anaerobic digesters are simple CSTRs, the SRT is equal to the HRT. Consequently, the process design consists simply of selecting an appropriate SRT and calculating the bioreactor volume directly from the solids flow rate and the definition of HRT, as given by Eq. 4.15. Principal concerns in choosing the SRT include the degree of stabilization and pathogen inactivation required, digester mixing efficiency, requirements for equipment and digester redundancy, and variations in solids flow rates.

Several factors must be considered when selecting the minimum acceptable SRT, including washout of methanogens, hydrolysis of particulate organic matter, and pathogen inactivation. As indicated in Figure 9.5, growth of aceticlastic methanogens can be maintained at SRTs as low as 5 days at 35°C, which is the most common digester operating temperature. While full-scale digesters have been suc-
cessfully operated at SRTs this low,\textsuperscript{75} it really is a lower limit and operation at such an SRT places the digester at risk for rapid washout of methanogens and process failure. Furthermore, the hydrolysis of particulate organic matter and its conversion to acetic acid will generally be the rate limiting steps when treating complex organic material. Consequently, longer SRTs are usually used.

A distinction must be made between the design of anaerobic digesters for treatment of primary solids and waste activated sludge, as discussed in Section 13.2.9. Figure 13.19 demonstrates that for municipal primary solids, an SRT of 8 to 10 days is needed at 35°C to ensure reasonably complete stabilization. Figure 13.24 presents

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fate-components-anaerobic-digestion.png}
\caption{Fate of various components of municipal primary solids during anaerobic digestion at 35°C. (From A. W. Lawrence, Application of process kinetics to design of anaerobic processes. In \textit{Anaerobic Biological Treatment Processes}, ACS Advances in Chemistry Series 105:163–189, 1971. Copyright © American Chemical Society; reprinted with permission.)}
\end{figure}
information about the degradation of the various components of those solids and shows that the overall performance is limited by the degradation of lipids. This is consistent with Figure 9.5, which shows that anaerobic oxidation of long and short chain VFAs requires an SRT of about 10 days. The data presented in Figures 13.19 and 13.24 are also consistent with Figure 13.23, where it is observed that an SRT of 10 days results in reasonably complete stabilization of primary solids. Thus, an SRT of at least 10 days is needed to stabilize primary solids at 35°C. However, the hydrolysis of the biomass in waste activated sludge occurs at a slower rate than the hydrolysis of primary solids. As a consequence, a longer SRT is required if waste activated sludge is to be stabilized. Using Figure 13.23 as a guide, an SRT on the order of 15 to 20 days is required to achieve substantial stabilization of waste activated sludge. These conclusions are consistent with observations at full-scale plants.\textsuperscript{72,75}

Pathogen control is a relatively new requirement for anaerobic digesters. It has been known for some time that digestion reduces the concentration of indicator organisms. In fact, that is one reason anaerobic digestion has been used. However, the purposeful design of digesters to achieve a specific degree of pathogen control is new, and few data exist upon which to base such a design. Currently, U.S. regulations require a minimum SRT of 15 days for anaerobic digesters operating at 35°C to ensure effective reduction of pathogens in municipal wastewater solids.\textsuperscript{70} Operation of anaerobic digesters in series also increases pathogen destruction, just as it does in aerobic digesters. Continued evolution of procedures to design anaerobic digesters to control pathogens is expected.

Once the SRT, i.e., HRT, has been selected, the effective volume of the digester is calculated by multiplying the design solids flow rate by the SRT. The design solids flow rate should be for the month or week in which the highest volume of solids is produced to allow the digester to function properly under all reasonable operating conditions. Variations in both the mass of solids produced and the performance of upstream solids thickening devices should be considered in choosing that flow rate. The total volume is then calculated considering the relationship between the effective and total volumes. The effective volume is less than the total volume because of ineffective mixing, leading to the accumulation of grit in the bottom and scum at the top of the digester. In digesters with older style mixing systems, the effective volume can be less than 50% of the total volume, but in digesters with modern mixing systems the effective volume is generally at least 90% of the total volume. Volume should also be allocated to grit and scum accumulations. Typical designs allocate the volume of the floor cone (see Figures 13.2 and 13.3) to grit accumulation and the top 0.6 m of the digester to scum accumulation.\textsuperscript{52,72,75} Minimal grit and scum accumulations occur in egg shaped digesters (Figure 13.4), so the total and effective volumes can generally be assumed to be the same.

Once the total bioreactor volume has been determined, the number of individual units and their dimensions must be selected. Provisions must be made for units to be removed from service for maintenance, so a minimum of two units should be provided. The impacts on performance of having a unit out of service must also be considered, and this may dictate the number of units provided and/or the total volume. In doing so, it may be assumed that the unit will be removed from service during average, rather than peak, solids production. The gas production rate is estimated based on the mass of volatile solids stabilized and the conversion factor of
cessfully operated at SRTs this low, it really is a lower limit and operation at such an SRT places the digester at risk for rapid washout of methanogens and process failure. Furthermore, the hydrolysis of particulate organic matter and its conversion to acetic acid will generally be the rate limiting steps when treating complex organic material. Consequently, longer SRTs are usually used.

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![Figure 13.24 Fate of various components of municipal primary solids during anaerobic digestion at 35°C. (From A. W. Lawrence, Application of process kinetics to design of anaerobic processes. In Anaerobic Biological Treatment Processes, ACS Advances in Chemistry Series 105:163–189, 1971. Copyright © American Chemical Society; reprinted with permission.)](image)
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![Figure 13.24](image-url)

**Figure 13.24** Fate of various components of municipal primary solids during anaerobic digestion at 35°C. (From A. W. Lawrence, Application of process kinetics to design of anaerobic processes. In *Anaerobic Biological Treatment Processes*, ACS Advances in Chemistry Series 105:163–189, 1971. Copyright © American Chemical Society; reprinted with permission.)
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d. What volatile solids destruction efficiency and methane production rate would be achieved under the three loading conditions with all units in service?

The volatile solids destruction efficiencies for the primary solids and waste activated sludge must be estimated separately and then combined to obtain the overall digester performance. From Figure 13.23, the COD destruction efficiency for primary solids, which equals the volatile solids destruction efficiency and methane production rate...
efficiency, will be about 60% for SRTs of 15 to 20 days. The effect of SRT over that range is so small that it need not be considered. Although the volatile solids (or COD) destruction efficiency of waste activated sludge depends on its biodegradable fraction, which depends in turn on the operating conditions of the activated sludge system, we will assume that the curve in Figure 13.23 is applicable. It suggests that the volatile solids destruction efficiency of the waste activated sludge would be 20 to 25% at an SRT of 15 to 20 days. Consequently, to be conservative, we will use 20%. Using this information, the overall volatile solids destruction efficiency can be calculated as shown in Table E13.4. It would be around 41% for all three situations and would represent stable solids, as defined in Section 12.1.1.

Table E13.3 Required Total Digester Volumes Under Various Conditions with All Units in Service for Example 13.3.1.1

<table>
<thead>
<tr>
<th>Flow rate</th>
<th>SRT</th>
<th>Effective volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>m³/day</td>
<td>days</td>
<td>m³</td>
</tr>
<tr>
<td>Average</td>
<td>567</td>
<td>20</td>
</tr>
<tr>
<td>Maximum month</td>
<td>708</td>
<td>20</td>
</tr>
<tr>
<td>Maximum week</td>
<td>1,020</td>
<td>15</td>
</tr>
</tbody>
</table>

Table E13.4 Estimation of the Volatile Solids Destruction Efficiency and Methane Production Rate for the Anaerobic Digester in Example 13.3.1.1

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Maximum month</th>
<th>Maximum week</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary solids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total solids, kg/day</td>
<td>18,000</td>
<td>22,500</td>
<td>27,000</td>
</tr>
<tr>
<td>Volatile solids, kg/day</td>
<td>13,500</td>
<td>16,875</td>
<td>20,250</td>
</tr>
<tr>
<td>Volatile solids destroyed, kg/day</td>
<td>8,100</td>
<td>10,125</td>
<td>12,150</td>
</tr>
<tr>
<td>Methane, m³/day</td>
<td>5,670</td>
<td>7,090</td>
<td>8,505</td>
</tr>
<tr>
<td>Waste activated sludge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total solids, kg/day</td>
<td>16,000</td>
<td>20,000</td>
<td>24,000</td>
</tr>
<tr>
<td>Volatile solids, kg/day</td>
<td>12,000</td>
<td>15,000</td>
<td>18,000</td>
</tr>
<tr>
<td>Volatile solids destroyed, kg/day</td>
<td>2,400</td>
<td>3,000</td>
<td>3,600</td>
</tr>
<tr>
<td>Methane, m³/day</td>
<td>1,680</td>
<td>2,100</td>
<td>2,520</td>
</tr>
<tr>
<td>Total solids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total solids, kg/day</td>
<td>34,000</td>
<td>42,500</td>
<td>51,000</td>
</tr>
<tr>
<td>Volatile solids, kg/day</td>
<td>25,500</td>
<td>31,875</td>
<td>38,250</td>
</tr>
<tr>
<td>Volatile solids destroyed, kg/day</td>
<td>10,500</td>
<td>13,125</td>
<td>15,750</td>
</tr>
<tr>
<td>Percent</td>
<td>41</td>
<td>41</td>
<td>41</td>
</tr>
<tr>
<td>Methane, m³/day</td>
<td>7,350</td>
<td>9,190</td>
<td>11,025</td>
</tr>
</tbody>
</table>

0.75 × Total solids.
0.6 × Volatile solids.
0.7 m³/kg VS destroyed.
0.2 × Volatile solids.
Furthermore, by assuming that destruction of 1 kg of VS results in the formation of 0.7 m³ of methane under standard conditions, the methane production rate can also be estimated, as shown in the table. The average production rate would be 7,350 m³/day. This information can be used to plan for use of the methane.

Another important design consideration for anaerobic digesters is the feeding frequency. Wastewater sludges are thixotropic, and they contain grit, rags, and other debris that can clog piping if adequate velocities are not maintained. Furthermore, the presence of debris requires the use of minimum pipe diameters of 10 cm. The need to maintain minimum velocities in sludge piping often precludes continuous feeding of digesters. Fortunately, because of the relatively long SRTs and HRTs used, periodic feeding will not adversely impact digester performance if the time between feedings is sufficiently short. A feeding frequency of several times per day spaced relatively uniformly will provide acceptable performance.

13.3.2 Low- and High-Rate Anaerobic Processes

Low- and high-rate anaerobic processes are used primarily to treat industrial wastewaters and occasionally to treat municipal wastewaters. Because of the mechanisms that some use to accumulate active biomass, it is often impossible to precisely determine the degree of biomass accumulation and the resulting SRT. Consequently, process performance is commonly correlated with the volumetric organic loading rate. In many instances, this is done by operating a pilot plant for a particular bio-reactor type treating a specific wastewater. In other instances, the correlation can be based on experience. Further information on the use of these procedures and detailed examples are presented in Chapter 21.

The general procedure used to design a low- or high-rate anaerobic process is as follows:

- Characterize the wastewater to be treated. Characterization involves determination of conventional wastewater parameters such as total and soluble BOD₅ and COD, total and volatile solids, total and volatile suspended solids, pH, alkalinity, temperature, and nutrient concentrations. It also involves assessment of the nature of the organic matter present, i.e., readily or slowly biodegradable; carbohydrate, protein, or synthetic organic compounds of a particular type, and the potential presence of inhibitory materials.
- Summarize experience with treatment of the particular type of wastewater in the low- or high-rate anaerobic process.
- Compare the subject wastewater with the characteristics of the low- or high-rate anaerobic process. Some preliminary cost analyses may be conducted to help discriminate among the various process options. Based on the available information, the option or options most appropriate for treating the subject wastewater can then be selected.
- Determine the need for bench or pilot-scale studies of treatment of the subject wastewater in the selected process(es). This will depend on the available knowledge base.
- Conduct bench or pilot-scale studies, as appropriate.
Develop a correlation between process performance (generally COD removal efficiency) and the VOL, or some other measure of loading. Also characterize other pertinent design parameters such as HRTs, THLs, and bioreactor geometry.

Use the process performance relationships developed above to size and configure the bioreactor.

Calculate the methane production rate using the stoichiometric relationship 0.35 standard m³ of methane per kg of COD stabilized.

Perform a heat balance and determine the need to insulate the bioreactor and/or to provide supplemental heat. If supplemental heat is needed, size the system.

Determine the need for any ancillary facilities such as nutrient addition, pH adjustment or alkalinity addition, iron addition to control sulfide, or sulfur addition to control heavy metal toxicity.

Summarize the results of the process design in a succinct table of process loadings and required facilities.

Several procedures are used to size and configure low- and high-rate anaerobic processes. Many anaerobic processes are directly analogous to other suspended and attached growth systems discussed elsewhere in this book, and the procedures used to size and configure them are similar.

AC systems are analogous to the activated sludge process, as described in Chapters 9 and 10. Thus, the general design procedures described in Section 9.4 are applicable to AC systems. The design SRT is selected and used to calculate the necessary bioreactor suspended solids inventory and waste solids mass flow rate. The bioreactor MLSS concentration is then chosen considering the trade-off between the sizes of the bioreactor and clarifier, and the bioreactor is sized. Finally, the methane production rate is calculated with Eq 9.6.

Upflow anaerobic sludge blanket, hybrid UASB/AF, and FB/EB processes are designed using the procedures for submerged attached growth bioreactors described in Chapter 21. Upflow anaerobic sludge blanket and hybrid UASB/AF processes behave essentially as upflow packed bed bioreactors, and can be sized and configured using the procedures described in Section 21.3.2. FB/EB processes can be designed using the procedures outlined in Section 21.3.3. These procedures involve selection of appropriate VOLs and THLs and determination of the necessary bioreactor volume, cross-sectional area, and recirculation flow rates (for FB/EB processes) using these criteria. The waste solids mass flow rate and methane production rate can be calculated using the procedures described above for the AC process.

Anaerobic filter and DSFF processes are similar in configuration to trickling filters, and are designed using procedures like those described in Chapter 19. Volumetric organic loading and THL criteria are used most often, so the approach presented in Section 19.3.2 is appropriate. Anaerobic lagoons are generally sized and configured using VOL and HRT criteria, as discussed in Chapter 14. Again, the waste solids mass flow rate and methane production rate can be calculated using the procedures described above for the AC process.

Rather than repeat information presented in greater detail elsewhere, the reader is referred to the appropriate sections of this book for detailed descriptions of the process design procedures. Further information on the design of anaerobic processes is provided in recent books devoted entirely to anaerobic systems.47,68
13.3.3 Fermentation Systems

The primary objective of most anaerobic processes is stabilization of biodegradable organic matter through its conversion to methane. In contrast, the objective of fermentation processes is conversion of biodegradable organic matter to VFAs and the harvesting of those VFAs for addition to biological nutrient removal systems.

Several differences exist between fermentation systems and other anaerobic processes. The first is the SRT. Conversion of biodegradable organic matter to VFAs is accomplished by operation at SRTs that allow the growth of hydrolytic and acidogenic bacteria but preclude the growth of aceticlastic methanogens. The latter is necessary because acetic acid is the most desirable VFA for nutrient removal systems, and thus we do not want it to be converted to methane. Analysis of Figure 9.5 suggests that growth of Hz-utilizing methanogens is likely at the SRTs used, so that some methane will be produced. This results in the loss of some COD in the form of methane, but this loss is beneficial because the consumption of Hz minimizes its partial pressure in the bioreactor and allows the fermentation reactions to proceed with acetic acid as the main product. Suppression of the growth of sulfate reducing bacteria is also desirable since they will consume acetic acid. Experience with full-scale fermentation systems indicates that their growth can also be controlled by appropriate selection of the SRT.

A second difference is that fermentation bioreactors are generally operated at ambient temperature without heating. Since only limited quantities of methane are produced, heating generally requires an external energy source. Because fermentative bacteria can grow at significantly lower SRTs than aceticlastic methanogens, the economic benefit of reduced bioreactor volume as a result of elevated temperature is much less for fermentation systems. Operation at reduced temperature also makes it easier to limit the growth of aceticlastic methanogens and maximize the production of VFAs.

Another difference is the operating pH. Since the primary objective of a fermenter is production of VFAs, the bioreactor pH will be significantly less than the pH in methanogenic anaerobic processes. pH values are typically less than 6, and may be less than 5. Reduced pH values also aid in controlling the growth of aceticlastic methanogens.

Although the production of methane is limited, other gases are produced. Significant quantities of carbon dioxide are generated in the hydrolytic and acidogenic reactions, along with some Hz, which will be converted to methane by Hz-utilizing methanogens. Limited quantities of hydrogen sulfide will be produced if sulfate reducing bacteria are able to grow, and nitrogen may also be present because of the entrance of air into the bioreactor or the reduction of any nitrate-N present. Thus, the gas produced will consist primarily of carbon dioxide with small quantities of methane and trace quantities of nitrogen, Hz, and hydrogen sulfide. Consequently, the gas will not generally be combustible.

The typical feed to a fermentation process is primary solids collected from the influent wastewater. At the SRTs and temperatures used, only a portion of the biodegradable organic matter in those solids is converted to VFAs, with yields on the order of 0.05 to 0.3 g VFA produced/g VS fed to the fermenter. Consequently, the solids still contain significant quantities of biodegradable organic matter that must be stabilized prior to final disposal. Primary solids also contain inert suspended solids
(both volatile and fixed). Thus, the VFAs are normally separated from the solids stream for addition to the BNR process, while the remaining solids are sent for further treatment in the solids processing train.

As illustrated in Figure 13.16, gravity settling is often used for liquid–solids separation in fermentation systems, with the overflow carrying the VFAs for use in the downstream BNR system. Since the concentration of VFAs, which are soluble, is the same in the overflow and underflow from the settler, the recovery of VFAs will be equal to the fraction of flow leaving the settler via the overflow. However, because the solids in the bioreactor are highly concentrated, little additional concentration can occur in the settler, which means that, without dilution, the overflow rate will be a small fraction of the inflow rate, thereby limiting VFA recovery. This problem is overcome by adding an elutriation stream to increase the total flow and make the overflow a larger fraction of the total.

The design of a two-stage completely mixed thickener/fermenter, shown schematically in Figures 13.15 and 13.16, illustrates the solids fermentation processes. It is presented in the following example.

**Example 13.3.3.1**

A primary solids flow of 385 m³/day at a solids concentration of 25 g/L (75% volatile) is to be fermented to produce VFAs to add to a BNR process. A two-stage completely mixed thickener fermenter is to be used, as illustrated in Figure 13.16. The process will be sized based on the following assumptions: primary solids are added directly to the fermenter, no overflow from the primary clarifier is added to the fermenter, no thickened solids are recycled from the thickener to the fermenter, and overflow from the primary clarifier is added to the fermenter effluent to dilute it prior to the thickener. Experience with fermentation of these solids indicates that a conversion efficiency of 0.12 g VFA/g VS fed can be achieved at an SRT of 5 days. In addition, the fermented solids will thicken to 40 g/L. Design the system for 80% recovery of the VFAs produced.

a. What is the volume of the fermenter?

At the design condition the completely mixed fermenter operates as a CSTR. For a CSTR the volume is just the flow rate times the SRT. Therefore:

\[ V = (385)(5) = 1,925 \text{ m}^3 \]

b. How many kg/day of VFAs will be produced?

The mass of volatile solids fed to the process is:

\[ (25)(385)(0.75) = 7,220 \text{ kg VS/day} \]

\[ \text{VFA production} = (0.12)(7,220) = 866 \text{ kg VFA/day} \]

c. What volume of overflow from the primary clarifier must be added to the fermenter effluent if 80% of the VFAs are to be recovered in the gravity thickener overflow?

The thickened solids concentration will be 40 g/L. Minimal destruction of solids will occur in the fermenter. Therefore, the mass of solids in the thickener underflow will be approximately equal to the solids fed to the process. From a mass balance, the thickened solids flow rate will be:

\[ \text{Thickened solids flow} = \frac{(385)(25)}{40} = 241 \text{ m}^3/\text{day} \]
To achieve 80% VFA recovery, the thickener overflow must be 80% of the total flow leaving the thickener and the thickened solids flow must be the other 20%. Since the total flow out must equal the flow in, the flow to the thickener must be:

\[
\text{Thickener influent flow} = \frac{241}{0.2} = 1205 \text{ m}^3/\text{day}
\]

The thickener influent flow consists of primary solids plus overflow from the primary clarifier. Thus, the primary overflow required is:

\[
\text{Primary overflow} = 1205 - 385 = 820 \text{ m}^3/\text{day}
\]

### 13.3.4 Other Design Considerations

Once the process design is completed, the design of the other components of the system can commence. Mixing and recirculation systems must be selected and sized, with the type depending on the particular anaerobic process being designed. A heat balance must also be done, as discussed previously. If that balance shows that more methane will be produced than is needed to heat the process, then plans can be made for use of the gas. One potential use is in an engine-driven electric generator, with waste heat from the engine being used to heat the anaerobic process. Alternatively, excess gas can be used directly for various heating purposes at the facility, or it can be processed and sold as a fuel. Insulation of the bioreactor will reduce its heat requirements, and the cost of the insulation can be compared to the value of the extra gas made available to determine whether insulation is justified.

Materials selection is of particular concern in the design of anaerobic processes. Corrosion of process components is minimal as long as the environment in which they are housed remains completely anaerobic. For example, concrete inside of anaerobic digesters that have been in service for several decades is generally in excellent condition because the environment has consistently been anaerobic. However, corrosion can be excessive at interfaces between anaerobic and aerobic environments because reduced anaerobic reaction products can be oxidized to acidic products as they come in contact with oxygen. One example is hydrogen sulfide, which can be oxidized to sulfuric acid that will attack metal and concrete bioreactor components, causing rapid deterioration. Care must also be exercised in the handling of anaerobic process gas because a combustible mixture can result if it mixes with air. Standard safety equipment is available to prevent atmospheric air from entering anaerobic bioreactors and to suppress an explosion if one begins. However, these devices are not foolproof, and care must be exercised in anaerobic bioreactor design and operation. Further details on the physical design of anaerobic processes are available elsewhere.\textsuperscript{52,72,75}

### 13.4 PROCESS OPERATION

The great variety of anaerobic processes results in a corresponding multiplicity of process monitoring and control techniques, as well as numerous operating problems. Nevertheless, because all of the processes employ similar microbial communities, a
number of similarities exist between the monitoring and control techniques used and the operating problems encountered. These similarities are discussed below.

13.4.1 Process Monitoring and Control

Control of anaerobic processes is accomplished primarily by maintaining appropriate loadings and operating conditions. Loadings are controlled by controlling the rate at which biodegradable organic matter is added to the process. Operating conditions of particular concern include temperature and pH. As discussed in Section 13.2.4, temperature must be maintained in an optimum range, but, more importantly, changes in temperature must be held to less than 1°C per day. Optimum performance is generally obtained at pH values between about 6.8 and 7.4. Lower pH values lead to inhibition of methanogens, while higher pH values can lead to ammonia toxicity because of increased free ammonia concentrations. Fortunately, most anaerobic processes operate naturally within this pH range as a result of the carbonate/bicarbonate buffering system. The pH may deviate from this desirable range during process upsets, and pH adjustment chemicals must be added as discussed in Section 13.2.5. Process upsets can result from temporarily high loadings, deviations in the environment provided, or the presence of toxic or inhibitory materials in the bioreactor influent. While pH adjustment is necessary to prevent process failure, the root cause of the upset should be identified and corrected to ensure long-term process stability.

Several parameters can be monitored to assess anaerobic process performance. As indicated by the previous discussion, deviations in bioreactor pH are associated with process upsets. However, both experience and theoretical analysis indicate that pH is not a good indicator of process upsets.\textsuperscript{1,77} Because of the buffering capacity inherent in the system, by the time that a noticeable decline in bioreactor pH occurs, the upset may be well under way. Other indicators, such as the relative proportions of VFAs and alkalinity, or the methane production rate, are better indicators of impending failure.

The ratio of VFAs to alkalinity indicates the relative proportion of compounds acting to lower the pH and of buffering capacity acting to maintain it. Any change that suggests an increase in acids or a decrease in buffering capacity indicates an imbalance between the acid forming and consuming microbial populations and an impending upset. Alkalinity concentrations are generally measured by titration, whereas VFA concentrations can be measured directly by gas chromatography or by titration.\textsuperscript{1} The VFA to alkalinity ratio and the bioreactor pH should be plotted chronologically to allow detection of trends indicative of an impending upset and to assist in the identification of potential causes.

Methane production is another good indicator of process performance because it is proportional to the mass of biodegradable organic matter stabilized.\textsuperscript{48,58,71,77} It is also a direct indicator of the activity of the methanogens. Various specific indicators have been used to quantify process performance. One is the methane content of the gas produced. A decrease in this parameter suggests a decrease in the activity of the methanogens. Another parameter is the volume of methane produced per unit of COD or VS fed to the bioreactor. As long as the composition of the bioreactor feed remains constant, then a fixed proportion of it should be converted into methane if operating conditions remain constant. Therefore, deviations in this ratio suggest deviations in operating conditions. Methane production will change more quickly than...
bioreactor effluent COD or VS concentrations, and consequently, the ratio of methane produced to COD or VS fed provides an early indication of decreased bioreactor performance. This ratio can also be plotted chronologically and the trends used to identify the onset of upsets.

For many anaerobic processes, the collection of operating data and calculation of process performance indicators on a daily basis is adequate. For these, the HRT is on the order of several days, causing process changes to occur over the course of days. For the high-rate processes, however, HRTs are just a few days and significant changes can occur from one day to the next. These processes benefit from the increased data collection and analysis frequency provided by on-line analysis. Research is ongoing to evaluate the use of various on-line control strategies, such as those based on gas-flow rate and composition, and bicarbonate alkalinity measurements.12,27,54

13.4.2 Common Operating Problems

Two of the most common operating problems in anaerobic processes are foaming and the formation of precipitates. Two types of foaming can occur in anaerobic processes. One can occur in all of them. It is associated with incomplete metabolism of the influent organic matter, which leads to the production of intermediates with surfactant properties. Because of the surfactants, the gas produced by the process forms bubbles, to which particulate matter attaches, forming a foam. The foam can plug gas piping, interfering with proper operation of the bioreactor, and can escape from the bioreactor, resulting in unsightly and unsafe operating conditions. Moreover, the removal of active biomass by the foam reduces the SRT, thereby decreasing the treatment capacity. A downward spiral of performance can result as the decreased treatment capacity causes more surfactant production, which produces more foaming, thereby removing more biomass, causing more surfactant production, etc. The primary corrective measure in such instances is to reduce the organic loading to a value that allows complete treatment to occur so that intermediates with surfactant properties are no longer produced.

The second type of foaming occurs in anaerobic digesters that are stabilizing solids from activated sludge systems containing significant quantities of the nuisance microorganism Nocardia (see Section 10.4.2). Nocardia is a branched, filamentous microorganism that causes foaming in activated sludge systems. When the waste solids from such a system are added to an anaerobic digester, the Nocardia retains its physical integrity and characteristics, thereby causing foaming in the digester.28,73 The effects are similar to those described in the preceding paragraph. In severe cases, significant disruption of the digestion process can occur. Correction of anaerobic digester foaming caused by the presence of Nocardia requires its elimination from the feed solids. This requires correction of the conditions causing the Nocardia to grow in the upstream activated sludge system.

The other major operational problem in anaerobic processes is the formation of precipitates resulting from the liberation of inorganic constituents during stabilization of complex organic matter like wastewater solids. This follows from the high feed concentrations to many anaerobic processes, which result in high concentrations of inorganic constituents. Precipitation of metal sulfides and their impact on heavy metal solubility were discussed in Section 13.2.6. Other precipitates can form in
large quantities, forming scale on surfaces and clogging pipes. Two precipitates of particular concern are struvite (MgNH₄PO₄) and calcium carbonate (CaCO₃).

Struvite precipitation occurs most frequently when waste biomass and vegetable matter are digested because their stabilization releases inorganic cell constituents, including magnesium, ammonia, and phosphate. Struvite is moderately soluble (pK_{sp} of 12.6 at 25°C), but the high biomass concentrations in the feed to many anaerobic digesters result in a supersaturated solution with respect to struvite precipitation. The kinetics of struvite precipitation are slow and precipitation does not occur immediately or uniformly. Instead, it begins at some location within the digester system, and further precipitation occurs rapidly at that location, resulting in the formation of a scale. Struvite precipitates frequently occur at points of turbulence, such as in overflow structures, in piping immediately adjacent to pumps, and in heat exchangers or heat exchanger piping. These points of turbulence strip carbon dioxide, resulting in a localized increase in pH. Struvite solubility decreases with increasing pH, thereby increasing the degree of supersaturation and the propensity for a precipitate to form.

Work is ongoing to characterize the precise conditions under which struvite precipitation occurs. Research is also ongoing to determine how the recycle of nitrogen and phosphorus to anaerobic digesters from solids handling systems can be minimized. Design features to minimize the impacts of struvite precipitation include the use of polyvinyl chloride (PVC) or glass-lined pipes to minimize the adherence of precipitates, the design of piping systems with long radius elbows and other features to minimize turbulence, and the incorporation of features to allow easy cleaning of piping.

Calcium carbonate precipitates can form when treating high-strength wastewaters that also contain high concentrations of calcium (for example, dairy wastes). Carbonate formed as a result of stabilization of the organic matter reacts with the calcium to form the precipitate. The precipitate may form on surfaces, but it may also form within biomass flocs or biofilms. For example, calcium carbonate precipitates have been observed in the granules in UASB systems. These precipitates may or may not cause operating problems. However, they introduce a nonreactive solid phase that reduces treatment capacity by reducing the unit activity of the biomass in the process. These effects must be accounted for in the process design.

13.5 KEY POINTS

1. Anaerobic processes stabilize biodegradable organic matter by converting it to methane gas. At standard temperature and pressure, 0.35 m³ of methane are produced per kg of chemical oxygen demand (COD) removed. For primary solids this is equivalent to 0.7 m³ of methane per kg of volatile solids (VS) removed.

2. Anaerobic processes consist of four major components: (1) a closed bioreactor, (2) a mixing system, (3) a heating system, and (4) a gas–liquid–solids separation system.

3. Anaerobic processes can be grouped into four principal types: (1) anaerobic digesters, (2) low-rate anaerobic processes, (3) high-rate anaerobic processes, and (4) solids fermentation processes.
4. Anaerobic digesters are used to stabilize biodegradable organic matter and inactivate pathogens in slurries that contain high concentrations of particulate matter. They are completely mixed bioreactors with no cell recycle and can be characterized as single continuous stirred tank reactors (CSTRs).

5. Low-rate anaerobic processes are generally mixed only by the gas produced in the bioreactor. Consequently, solids settle and accumulate within the bioreactor, resulting in some difference between the solids retention time (SRT) and the hydraulic retention time (HRT). Covers can form as a result of the accumulation of scum and other floating materials, or membrane covers can be provided to capture the methane produced.

6. High-rate anaerobic processes incorporate a variety of biomass retention mechanisms, including: the formation of readily settleable particles which are retained by sedimentation, the use of bioreactor configurations that retain suspended solids, and the growth of biofilms on surfaces. High-rate anaerobic processes are generally able to remove 80 to 90% of the 5-day biochemical oxygen demand (BOD₅) applied (COD removed is approximately 1.5 times the mass of BOD₅ removed), to produce 0.35 m³ of methane per kg COD removed, and to produce 0.05 to 0.10 kg of biomass (as volatile suspended solid [VSS]) per kg COD removed.

7. The various high-rate anaerobic processes differ in their ability to successfully treat wastewaters with high concentrations of particulate matter and in the volumetric organic loadings (VOLs) applied. Anaerobic contact (AC) processes can effectively treat wastewaters with high concentrations of particulate matter. Anaerobic filter (AF) systems can treat wastewaters with moderate levels of suspended solids, while suspended solids will generally pass through downflow stationary fixed film (DSFF) bioreactors. Upflow anaerobic sludge blanket (UASB), hybrid UASB/AF, and fluidized bed/expanded bed (FB/EB) bioreactors do not generally respond well to wastewaters containing high concentrations of particulate matter. High VOLs can be applied to UASB, hybrid UASB/AF, and FB/EB bioreactors if the wastewater contains primarily soluble organic matter (SOM).

8. Solids fermentation systems differ from other anaerobic processes since their objective is the production of volatile fatty acids (VFAs) and their separation from the waste stream for feeding to biological nutrient removal processes.

9. Anaerobic processes are generally competitive with aerobic processes for the treatment of wastewaters with biodegradable COD concentrations greater than 1,000 mg/L, and are usually the process of choice when the biodegradable COD concentration exceeds 4,000 mg/L. Factors affecting the choice include waste strength, flow rate, and temperature. Combustion of the methane produced and recovery of heat from the effluent can be used to achieve the temperatures required for effective anaerobic treatment.

10. The SRT is the primary factor determining the performance of anaerobic processes. An SRT of 15 to 20 days is generally required to achieve stable, reliable performance at 35°C. Many high-rate processes have SRTs in
excess of 30 to 50 days, and sometimes even 100 days. These very high SRTs may partially account for their stability.

11. It is not possible to precisely determine the SRT for some bioreactors. In such cases, the VOL is used to characterize process performance. The VOL is related to the SRT through the process yield and the biomass concentration.

12. The performance of some high-rate anaerobic processes, such as AF, UASB, hybrid UASB/AF, DSFF, and FB/EB, is affected by the total hydraulic loading (THL). The THL is the total bioreactor influent flow rate, including recirculation, divided by the cross-sectional area perpendicular to the flow. Total hydraulic loading criteria include maximum values to prevent biomass washout and minimum criteria to fluidize/expand media or to ensure good flow distribution.

13. Optimum performance of anaerobic processes is generally achieved by operation at a temperature near the optimum for mesophilic (30°C to 40°C) or thermophilic (50°C to 60°C) microorganisms. Acceptable performance can be achieved at temperatures below these values if an increased SRT is provided and if sufficient time is allowed for acclimation. Short term temperature fluctuations must be avoided, with a typical goal of no more than 1°C/day.

14. The optimum pH range for growth of aceticlastic methanogens is 6.8 to 7.4, with their activity decreasing significantly at pH values below this range. In contrast, the growth of acidogenic bacteria is much less sensitive to low pH. This difference in pH sensitivity can result in a downward spiral in process performance in which retardation of the aceticlastic methanogens causes reduced consumption of VFAs relative to their formation, which results in further reductions in pH, etc. This condition can be resolved by pH adjustment and reduction of the loading.

15. The pH in anaerobic processes is determined by the bicarbonate buffering system. Excess carbon dioxide is generally produced, and the quantity of bicarbonate is determined by the concentration of strong base available to react with it. Ammonia-N present in the wastewater or produced through biodegradation of nitrogen-containing organic matter is the base carbon dioxide reacts with most often.

16. Sodium bicarbonate is the most desirable chemical for pH adjustment. Other options result in pH variations as the added chemical reacts with carbon dioxide, removing it from the gas space. When the carbon dioxide balance is restored through continued metabolic activity, a second pH shift occurs. Addition of calcium based chemicals can also cause the precipitation of calcium carbonate.

17. The light metal cations sodium, potassium, calcium, and magnesium are required nutrients in anaerobic processes and their presence at low concentrations causes a stimulatory effect on microbial growth. However, elevated concentrations can cause moderate inhibition, and even higher concentrations can cause severe inhibition or toxicity. Interactions between the light metal cations can cause either increased or decreased inhibition.
matter and control of pathogens. Design procedures must also consider variations in influent flow rates and requirements to periodically remove units from service for maintenance.

28. Low- and high-rate anaerobic processes are often designed using VOLs and other parameters based on pilot-scale and full-scale experience. Pilot tests may be needed to design a specific installation, or previous experience with the subject wastewater in anaerobic processes may provide sufficient information for design. The procedures used to design many anaerobic process options are analogous to those used to design other processes considered in this book.

29. Several solids fermentation process configurations are available. In general, fermentation processes are operated at SRTs that are short enough to preclude the growth of aceticlastic methanogens.

30. Control procedures for anaerobic processes generally require monitoring the bioreactor pH, the volatile acids to alkalinity ratio, and the methane production rate.

31. Foaming removes active biomass from the liquid phase in the bioreactor, thereby interfering with anaerobic treatment. It can be caused by incomplete metabolism of influent organic matter or by the presence of Nocardia. Foaming caused by incomplete metabolism can be reduced by reducing the process loading. Foaming caused by Nocardia requires its elimination from the feed by appropriate control of the activated sludge system producing it.

32. Precipitates can form in anaerobic processes and cause scaling of surfaces and plugging of piping. One frequently encountered precipitate is struvite ($\text{MgNH}_4\text{PO}_4$). It is encountered when complex wastes are degraded, resulting in releases of high concentrations of magnesium, ammonia, and phosphate. Calcium carbonate can form when wastes that are high in calcium (such as dairy wastes) are treated.

13.6 STUDY QUESTIONS

1. Prepare a table summarizing the advantages and disadvantages of anaerobic digestion compared to aerobic digestion for the stabilization of waste solids.

2. Prepare a table summarizing the advantages and disadvantages of low-rate and high-rate anaerobic wastewater treatment processes relative to aerobic processes. When is each typically used? When might either be used?

3. Discuss the roles of $\text{H}_2$ utilizing and aceticlastic methanogens in anaerobic processes.

4. Prepare a table summarizing the typical design criteria for the various low-rate and high-rate anaerobic processes. Contrast those processes in terms of the fate of soluble and particulate organic matter within them.

5. List the principal biomass retention mechanisms used in each of the low-rate and high-rate anaerobic processes.
6. Prepare a table summarizing the advantages and disadvantages of mesophilic versus thermophilic anaerobic processes.

7. Discuss the impact of SRT on the reactions occurring in anaerobic processes. What SRT should be selected for various applications, and why?

8. A wastewater with a biodegradable COD concentration of 20 g/L is being treated in an anaerobic process operated at an HRT of 5 days. What is the VOL? If the bioreactor biomass concentration is 10 g VSS/L, what is the SRT? What net yield value did you use in the calculation of the SRT, and why?

9. An anaerobic digester is treating waste solids with a volatile solids concentration of 40 g/L. If the VOL is 3 kg VS/(m³·day), what is the HRT?

10. Municipal primary solids with characteristics similar to those used to develop Figure 13.19 are to be treated in an anaerobic digester. A minimum of 70% of the biodegradable organic matter is to be converted to methane. What SRT is required to achieve this objective at temperatures of 35°C, 25°C, and 20°C? Should somewhat larger SRTs be used in some cases to increase process stability? If so, when and why?

11. An anaerobic digester treating municipal primary solids with a volatile solids concentration of 60 g/L has an HRT of 25 days. If it is operating at 35°C, what volatile solids destruction efficiency would be expected? Explain how you arrived at your answer.

12. Prepare a diagram demonstrating the downward spiral that occurs as a "stuck" or "sour" anaerobic process develops.

13. An anaerobic process is operating with a bicarbonate alkalinity concentration of 750 mg/L as CaCO₃ and a gas carbon dioxide content of 40%. What is the bioreactor pH?

14. For the anaerobic process described in Study Question 13, how much sodium bicarbonate, lime, sodium carbonate, or ammonia must be added to the bioreactor to adjust the pH to 7.0?

15. For the anaerobic process described in Study Question 13, to what value must the gas carbon dioxide content be adjusted to produce a bioreactor pH of 7.0?

16. Describe what is meant by "stimulatory" and "inhibitory" concentrations of a chemical. Describe what is meant by "synergistic" and "antagonistic" interactions of inhibitors.

17. Discuss the relationship between temperature and pH as it affects ammonia toxicity in anaerobic processes.

18. A wastewater with a flow rate of 1,000 m³/day and a biodegradable COD concentration of 25 g/L is to be treated in an anaerobic process. Assuming typical performance for a high-rate anaerobic process, what will the methane production rate be?

19. A second waste stream with a flow rate of 300 m³/day, a sulfate concentration of 5 g SO₄²⁻/L, and a biodegradable COD concentration of 1,000 mg/L is to be added to the anaerobic process described in Study Question 18. If all of the sulfate is reduced to sulfide and the sulfide is precipitated with iron, how will the addition of this waste stream affect the methane production rate from the anaerobic process?
20. What can be done to reduce the dissolved sulfide concentration in an anaerobic process?
21. Heavy metal toxicity is occurring in an anaerobic process. What chemicals can be added to eliminate this toxicity? What are the relative advantages and disadvantages of these chemicals?
22. A wastewater with a biodegradable COD concentration of 20 g/L is to be treated in an anaerobic process. What concentrations of ammonia-N and phosphorus are required to achieve efficient treatment?
23. The primary solids and waste activated sludge from a wastewater treatment plant are to be stabilized by anaerobic digestion. For the primary solids, 75% of the total solids are volatile and 70% of the volatile solids are biodegradable. For the waste activated sludge, 80% of the total solids are volatile and 40% of the volatile solids are biodegradable. The solids masses and thickened solids concentrations are given in Table SQ13.1. For this plant, do the following:
   a. Select an appropriate SRT to stabilize the biodegradable organic matter and inactivate pathogens, and calculate the total digester effective volume required under average, maximum month, and maximum week conditions. Assume that the operating temperature is 35°C.
   b. Evaluate options that provide two, three, or four digesters and determine the option that requires the minimum total bioreactor volume. Assume that digester cleaning occurs only under average loading conditions.
   c. Calculate the methane production rate under all loading conditions.
24. Reconsider Study Question 23. The SRT in the activated sludge system is to be reduced, resulting in a 25% increase in the mass of biodegradable volatile solids in the waste activated sludge (WAS) stream. How much more methane will be produced when the solids are anaerobically digested?
25. Discuss when treatability tests and a pilot study should be conducted prior to the design of an anaerobic process to treat an industrial waste. When would it not be necessary to conduct treatability tests or a pilot study?
26. Consider a wastewater with a flow of 125,000 m³/day and a TSS concentration of 200 mg/L (75% volatile). Primary treatment of this wastewater results in removal of 60% of the TSS. Solids are removed from the primary clarifier at a concentration of 10 g/L. A completely mixed/thickener fermenter is to be designed to produce VFAs to add to a BNR

<table>
<thead>
<tr>
<th>Type of solids</th>
<th>Average Mass kg/day</th>
<th>Conc. g/L</th>
<th>Maximum month Mass kg/day</th>
<th>Conc. g/L</th>
<th>Maximum week Mass kg/day</th>
<th>Conc. g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>25,000</td>
<td>50</td>
<td>27,500</td>
<td>50</td>
<td>30,000</td>
<td>40</td>
</tr>
<tr>
<td>WAS</td>
<td>20,000</td>
<td>45</td>
<td>22,500</td>
<td>40</td>
<td>25,000</td>
<td>35</td>
</tr>
</tbody>
</table>
system. The fermented primary solids can be gravity thickened to 25 g/L. You wish to recover 85% of the VFAs produced. Do the following:
a. Size the completely mixed fermenter.
b. Determine the flow rate of any elutriation streams required.
c. Determine the mass of VFAs formed in the process and the mass elutriated for addition to the BNR system.

REFERENCES

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a. Size the completely mixed fermenter.
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REFERENCES


77. Water Pollution Control Federation, *Operation of Municipal Wastewater Treatment Plants*, Manual of Practice No. 11, Water Pollution Control Federation, Alexandria, Virginia, 1990.


1. **PROCESS DESCRIPTION**

Anaerobic processes are one of the oldest forms of bioremediation and have been in use in some form for more than 3,000 years. Anaerobic processes are generally used to treat a wide variety of industrial and municipal wastewaters. In a conventional system of anaerobic treatment in a wastewater treatment plant, the effluent is usually discharged to surface waters and the waste is returned to the plant. However, this mechanical simplicity masks a delicate and biologically complex system, unparalleled by other biochemical processes. The factors that affect process performance and efficiency have often been underestimated, yet are critical to the successful operation of an anaerobic treatment system.