CHAPTER 10

Process Kinetics and Product Stability

INTRODUCTION

Kinetics is the study of rates or velocities of reactions. Kinetics must be distinguished clearly from the related subject of thermodynamics. The latter deals with energy changes accompanying chemical reactions but does not reveal how fast these reactions occur. For example, glucose oxidation is exothermic, but in the form of cellulose its biological oxidation proceeds slowly at best. If one should ignite the cellulose, such as by setting fire to this paper, oxidation proceeds rapidly indeed. The same total energy is released whether the paper is burned or biologically oxidized to carbon dioxide and water. However, the kinetics of the two cases are markedly different.

Substrate biodegradability was studied in Chapter 9 and is important in determining the thermodynamic limits of the system. The mass of biodegradable organic times its heat content determines the *quantity* of energy available to drive the process. This chapter deals with the *rate* at which this energy is released, in other words, the kinetics of the system. This is a subject of vital interest to the design engineer, who must determine the type of reactor and curing systems and the detention times required to achieve a given degree of organic stabilization. Measured rates of decomposition for composting substrates are reviewed along with the factors most responsible for limiting the rates of reaction.

Because kinetics deals with time, the concepts of hydraulic retention time, HRT, and solids residence time, SRT, are introduced. These parameters are important design criteria in achieving a desired product quality. The subject of product stability is also addressed in this chapter. It is included here because a product is "stable" when its rate of decomposition has been reduced to a low level, i.e., low kinetic rate.

MICROBIAL KINETICS

Rates of decomposition vary widely depending on the organic substrate. Chandler et al.[1] studied the anaerobic fermentation of substrates and found significant differences in the rate

of fermentation between substrates. For example, the time required to evolve 90% of the cumulative methane production was 16 days for chicken manure, 33 days for cow manure, and 70 days for wheat straw. The decomposition rate for chicken manure was over four times as fast as that for wheat straw. If all other factors are equal, a composting reactor designed to achieve 90% BVS reduction would require over four times the residence time with wheat straw compared to chicken manure. This should highlight the importance of kinetic rates to facility design.

The discussion will return to field and laboratory measurements made on actual compost substrates, but first the theoretical concepts that govern the kinetics of microbe-substrate systems will be presented. These concepts will provide insight into the manner in which mass transport can be linked to chemical and biochemical reaction kinetics.

Classification of Microbe-Substrate Systems

Microbe-substrate systems are generally divided into two distinct types, homogeneous and heterogeneous. The systems are summarized in Table 10.1. In a homogeneous system, microbes are dispersed in an aqueous solution containing a soluble substrate. The mass of microorganisms is completely dispersed throughout the reactor volume. Concentration gradients of substrate between cells are minimized, and each cell sees virtually the same concentration if the system is well mixed. Such conditions are approximated in many industrial fermentations and waste treatment processes. The activated sludge process is an example of a nearly homogeneous system. It is not completely homogeneous, however, because flocculation causes some degree of separation between substrate and microbes. In addition, concentration gradients may exist inside the floc particle so that each organism is not surrounded by the same substrate concentration. Nevertheless, each floc particle is randomly dispersed in the fluid phase, and from this standpoint the activated sludge process can be viewed as a nearly homogeneous system.

Homogeneous systems are traditionally modeled using the Monod kinetics developed in Chapter 4.[2] The assumption is usually made that mass transport of substrate to the cell is not limiting, so that Equation 4.1 can be applied directly. Other authors have examined the effects of substrate diffusion through suspended flocs of microbes.[3,4]

A heterogeneous system is one in which either the microbes or substrate are separated from the fluid phase containing the other component. Two distinct types of heterogeneous systems are possible. The type most common to liquid waste treatment is a system in which microbes are separated from the fluid phase containing the substrate. The trickling filter, oxidation tower, rotating biological contactor, submerged filter, anaerobic filter, and anaerobic fluidized bed are examples of reactors that employ heterogeneous conditions. Each of these reactors contains an inert medium used to support the growth of microbes. Biological film constitutes one phase of the system, while liquid containing the substrate constitutes the other. A definite interface exists between the microorganisms and the liquid phase. Substrate must move across this interface before it can be used by the biological film. A concentration gradient must exist between the microbial film and the bulk liquid to assure a mass flow of substrate into the film. In addition to the waste treatment reactors described above, several industrial processes employ enzymes isolated from living organisms and immobilized on or within solid supports. Production of high-fructose syrups from corn starch is an example.[3]

A second type of heterogeneous system is one in which the substrate is insoluble and present in a particulate or solid form. Two subcategories of this system can be described: (1) the solid substrate is suspended in a bulk fluid phase, and (2) the aqueous phase is limited to

Table 10.1. Description of Biological Systems Normally used in Biochemical and Environmental Engineering Practice

System	Description
Homogeneous systems	Individual microbes are uniformly dispersed in a solution of soluble substrate The model is also applied to cases of flocculated microbes in a solution of soluble and fine particulate solids The activated sludge process treating industrial or municipal wastewater is typical of this system
Heterogeneous systems	
Attached microbial growth	Microbes are separated from the aqueous substrate usually by attachment to a solid surface
Falling film	Microbes are attached to a surface which is washed by a falling aqueous film containing the substrate The trickling filter, oxidation tower, and rotating biological contactor are examples
Submerged film	Microbes are attached to a surface with the void spaces filled with fluid containing the substrate The submerged filter, anaerobic filter and fluidized bed reactor are examples
Solid substrates	
Aqueous solution	Solid or insoluble substrate is immersed in an aqueous phase containing microbes, some of which attach to the substrate surface Industrial growth of microbes on insoluble hydrocarbon substrates and anaerobic digestion of sludge solids can be classified in this category The latter is also analyzed using homogeneous kinetics
Limited moisture	Moisture required for microbial growth is limited to that associated with the solid organic substrate Composting of organic residues and decomposition of organic solids in soils are examples

bound water associated with the solid substrate. In either case, microbes must attach to the substrate surface. Hydrolysis of chemical components making up the solid substrate is then necessary before the cell can absorb the solubilized substrate through its cellular membrane. In the limited moisture case, available water is limited to that associated with the solid substrate. Thus, an additional limitation can occur if water levels decrease to a point where they reduce the microbial reaction rates.

Most composting substrates consist of solid organic matter with moisture limited to that bound with the substrate. Thus, composting can be described as a heterogeneous system with solid substrate and limited moisture. Kinetics developed for solid substrate-microbe systems should apply reasonably well to the case of composting.

Heterogeneous Systems — Solid Substrate

The sequence of events involved in metabolizing solid substrates can be conceptually described as follows:

1. release of extracellular hydrolytic enzymes by the cell and transport of the enzymes to the surface of the substrate
2. hydrolysis of substrate molecules into lower molecular weight, soluble fractions
3. diffusion transport of solubilized substrate molecules to the cell

4. diffusion transport of substrate into the microbial cell, floc, or mycelia
5. bulk transport of oxygen (usually in air) through the voids between particles
6. transport of oxygen across the gas-liquid interface and the laminar boundary layers on either side of such an interface
7. diffusion transport of oxygen through the liquid layers bound to the solid substrate
8. diffusion transport of oxygen into the microbial cell, floc, or mycelia
9. aerobic metabolism of the substrate and oxygen within the microbial cell

A rather complicated sequence of events is necessary before substrate can be composted successfully. Because the above events are arranged in series, any one of the events could limit the overall process kinetics. Several of the more important processes are discussed further to gain insight into the rate limitations most common in composting systems.

Kinetics of Solubilization

Consider a hydrolytic enzyme that adsorbs to an active site on a solid substrate surface. The following equilibrium can be described:

$$E + A \underset{k_2}{\overset{k_1}{\leftrightarrow}} EA \overset{k_3}{\leftrightarrow} P + E \tag{10.1}$$

where A is a vacant site on the substrate surface, E is a free hydrolytic enzyme in solution that can adsorb to the surface with a reaction rate constant, k_1, and desorb with rate constant, k_2, and EA is the enzyme substrate complex that can either desorb to the original constituents with a rate constant, k_2, or react irreversibly to yield the original enzyme, E, and the desired product, P, with a rate constant, k_3. If a_o is the total number of adsorption sites per unit volume, then

$$a_o \leftrightarrow a + (ea) \tag{10.2}$$

where

a = number of free sites per unit volume
(ea) = number of sites with an adsorbed enzyme
e = number of free enzymes per unit volume of the reaction mixture

The change in concentration of the enzyme substrate complex can be described as

$$\frac{d(ea)}{dt} = k_1(e)(a) - k_2(ea) - k_3(ea) \tag{10.3}$$

Under steady-state conditions d(ea)/dt will equal zero. Thus,

$$k_1(e)(a) = k_2(ea) + k_3(ea) \tag{10.4}$$

Solving for a:

$$a = \frac{(ea)}{e}\left(\frac{k_2 + k_3}{k_1}\right) = \frac{(ea)}{e}K_a \tag{10.5}$$

Substituting Equation 10.5 into Equation 10.2 and rearranging:

$$(ea) = \frac{a_o(e)}{K_a + e} \tag{10.6}$$

The rate of product formation, v, is given in Equation 10.3 as $k_3(ea)$. Thus,

$$v = k_3(ea) = \frac{k_3(a_o)e}{K_a + e} \tag{10.7}$$

If e is the concentration of free enzyme, it can be related to the total concentration at the start of the experiment, e_o, by,

$$e_o = e + (ea) \tag{10.8}$$

In certain enzyme systems it is often the case that e_o is much greater than a_o. Equation 10.8 then becomes

$$e_o = e \tag{10.9}$$

Substituting Equation 10.9 for e, Equation 10.7 becomes

$$v = \frac{(k_3 a_o e_o)}{(K_a + e_o)} \tag{10.10}$$

Equation 10.10 is similar in form to Equation 4.1 developed for the case of a homogeneous system. In the present case, however, the rate of reaction reaches a maximum value at high enzyme concentrations. Physically, this corresponds to essentially complete adsorption of enzyme on the available substrate surface. Equation 10.10 has been used to describe kinetics of solid substrate-enzyme systems with reasonable success. Data on enzyme-solid substrate reactions are presented in Figures 10.1 and 10.2. The latter is a Lineweaver-Burke double reciprocal plot ($1/v$ vs $1/e_o$). From Equation 10.10 the reciprocal plot should be linear, which is the case in Figure 10.2.

The form of Equation 10.10 probably can be adapted to the case of microbes growing on a solid substrate. The concentration of extracellular enzymes, e_o, is likely a function of the mass concentration of microbes, X. Also, the total number of absorption sites, a_o, is likely related to the available surface area per unit volume, A_v. Substituting these terms into Equation 10.10 and dropping unnecessary subscripts:

$$v = -\frac{dS}{dt} = \frac{kA_v X}{K_x + X} \tag{10.11}$$

where

dS/dt = rate of hydrolysis of solid substrate
k = maximum rate of solid substrate hydrolysis that occurs at high microbial concentration

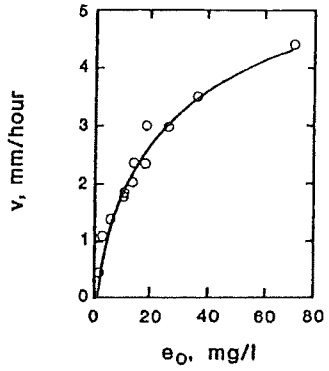

Figure 10.1. Dependence of the rate of disappearance of solid substrate (thiogel) on the concentration e_0 of enzyme in solution. From Tsuk and Oster.[5]

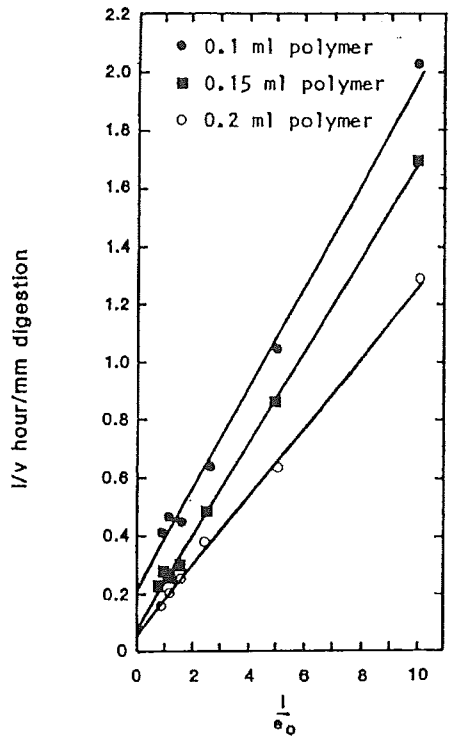

Figure 10.2. Double reciprocal plot for digestion of an insoluble substrate (poly-B-hydroxybutyrate particles) by an enzyme (depolymerase of *P. lemoignei*) in solution. From McLaren and Packer.[6]

K_x = half velocity coefficient equal to the microbial concentration where $ds/dt = k/2$

The general form of Equation 10.11 is graphically illustrated in Figure 10.3. In the limiting cases where X is very high ($X >> K_x$) and where X is very low ($X << K_x$), Equation 10.11 is approximated by the following discontinuous functions:

$$\frac{dS}{dt} = -kA_v \qquad (X >> K_x) \qquad (10.12)$$

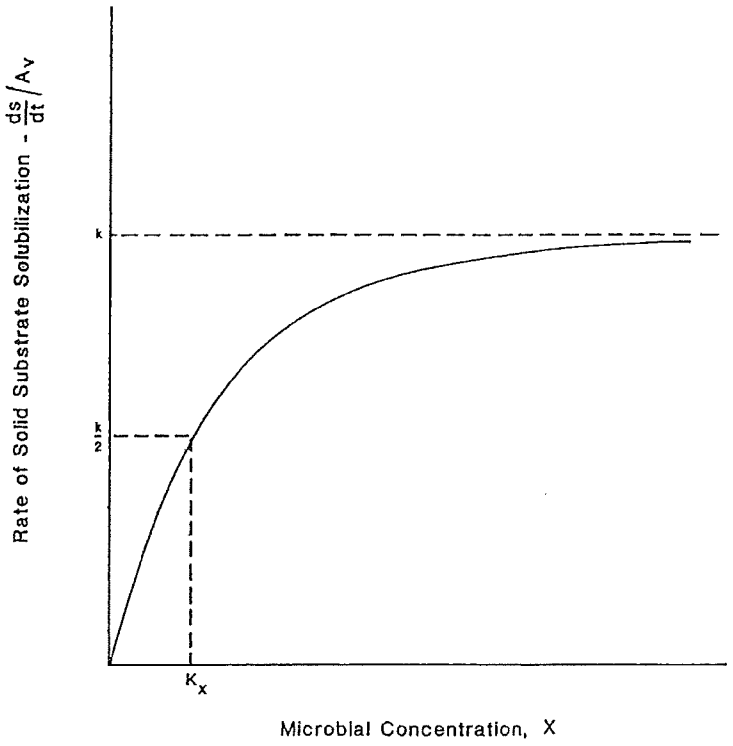

Figure 10.3. Rate of substrate hydrolysis as a function of the microbial concentration for a heterogeneous system with solid substrate.

$$\frac{dS}{dt} = -\frac{k}{K_x} A_v X \qquad (X << K_x) \qquad (10.13)$$

Equation 10.12 is a zero order reaction with respect to microbial concentration while Equation 10.13 is first order.

Actual composting processes are not as "ideal" as pure enzyme systems, and reaction kinetics have not been developed to the same extent as in biochemical engineering. However, the form of Equation 10.11 can be used to explain several phenomena observed in actual composting operations. Jeris and Regan[7] observed considerably lower oxygen consumption rates when composting newsprint compared to mixed refuse. Also, the effect of mechanical and chemical pulping in increasing the rate of degradation of wood and its products was discussed in Chapter 9. Differing rates of decomposition can probably be interpreted as differences in the value of kA_v. Thus, a substrate such as natural wood fiber, which is resistant to enzyme attack, would have a lower kA_v value relative to a substrate more amenable to solubilization by hydrolytic enzymes. This can be interpreted as a lower number of available enzyme binding sites or a lower number of successful enzyme reactions in a more resistant substrate.

The composting of most substrates is characterized by an initial period of high oxygen uptake followed by a longer period of low oxygen uptake. Complex substrates, such as refuse and sludges, are composed of a mixture of organics of varying kA_v values. During early stages, substrates with high values of kA_v are decomposing and the microbial population is increasing. Eventually the concentration of these "high rate" substrates is exhausted. However, substrates with low kA_v values continue to decompose at lower rates for a longer period of time.

Table 10.2. Comparison of Thermophilic Actinomycete in Various Seeding Materials

Material	Organism Count (number of colonies per gram of material)
Commercial inoculum	15.8×10^7
Rich soil	13.4×10^7
Poor soil	1.6×10^7
Horse manure	15.0×10^7

Source: Adapted from McGauhey and Gotaas.[10]

Klass et al.[8] studied the effect of particle size on the anaerobic decomposition of grasses. Fine graded grass, which passed a No. 30 sieve having 0.6 mm openings, decomposed faster than coarser grades. This was attributed to the higher surface area, A_v, of the fine grass which promoted faster solubilization of the solid substrate. Total gas production was about the same for all size fractions, only the rates of decomposition were effected by particle size. This observation is consistent with the form of Equation 10.11.

The Effect of Microbial Concentration

Referring to Equation 10.11, increasing the mass concentration of microbes, X, should increase the rate of solubilization as long as $X < K_x$. If the concentration increase much beyond K_x, however, the rate will approach a maximum value. This may have practical applications with many composting substrates.

The concentration of microbes necessary to avoid rate limitations has been a subject of controversy for many years. There is no question that most organic wastes will decompose through activity of the indigenous microbial flora. However, this does not assure that the microbial concentration is not limiting, particularly in the early stages of composting. In fact, lag periods are often observed at the start of batch composting operations, although the lag could also be caused by other factors such as oxygen availability, low starting temperatures, or poor feed conditioning. Certainly if the waste material is sterile, seeding with microbes should increase the kinetics according to Equation 10.11.

Golueke[9] distinguished between "minute" inoculation and "mass" inoculation with microbes. "Minute" inoculation referred to the introduction of a relatively minute quantity of microbes into a large quantity of substrate. The comparative number of thermophilic actinomycete isolated in various seeding materials is shown in Table 10.2. Consider a commercial inoculum consisting of 1 l of a 10^6 bacteria/ml suspension added to 1 ton of a substrate such as refuse. Compared to the background number of microbes for the substrates of Table 10.2, it seems inconceivable that such a small commercial inoculum could significantly increase the mass concentration of microbes unless the starting substrate is sterile. Use of such small additions of inoculum to increase the rates of reaction has generally been discounted. Results of a comparative study of inoculated and uninoculated composting material is shown in Figure 10.4. The striking similarity between the temperature curves indicates that the inoculum had minimal effect. Golueke[9] concluded that if the addition of "minute" inoculum contributed anything to facilitate the compost process it was so minute as to be undetectable. Even if the feed material were sterile it would seem that rich soil or horse manure would be as effective as a commercial inoculum.

Mass inoculation refers to addition of large quantities of microbial culture. This is generally accomplished by recycling compost product or using a completely or partially mixed reactor.

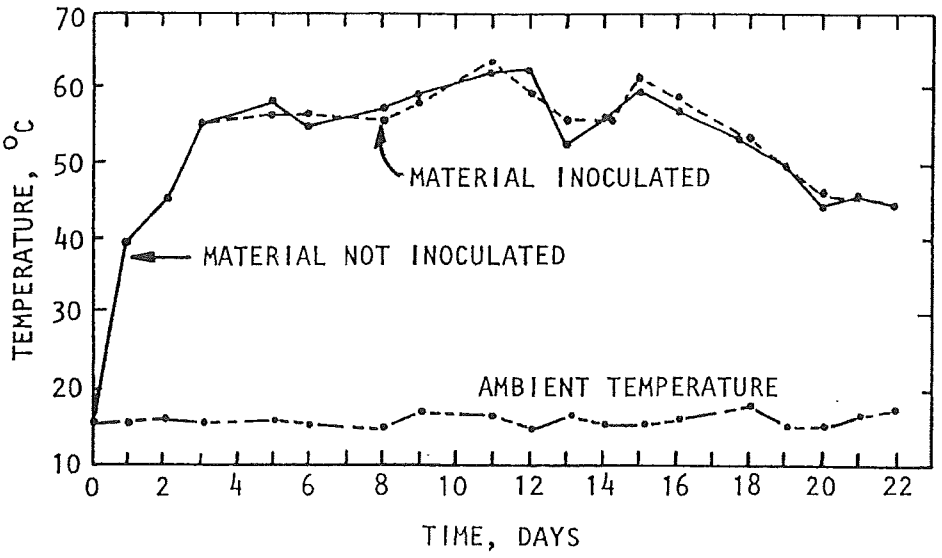

Figure 10.4. Temperature curves showing similarity between "minute" inoculated and uninoculated aerobically composting material. Feed material was composed of shredded vegetable trimmings and paper. Inoculum was purported to be a culture high in thermophilic actinomycete. From McGauhey and Gotass.[10]

In the latter case the infeed is continually inoculated with the microbial population developed in the reactor. Using continuous composters operated on refuse materials, Regan and Jeris[11] examined the effect of seed recycle rates of 25, 50, and 75%, equivalent to R_d values of 1.3, 2.0, and 4.0, respectively. Referring to Figure 10.5 at 50 to 53°C, the composting rates with 25 and 50% seed were 10 and 90%, respectively, of the maximum rates with 75% seed. During these tests other environmental factors such as moisture, temperature, FAS, and aeration were held under conditions previously determined to be optimum. Therefore, the observed effect of recycle can probably be ascribed to the increased microbial concentration and not to other environmental factors influenced by product recycle.

In deference to the above, the literature contains conflicting reports on the utility of mass inoculation by compost recycle. Golueke[9] reported no significant acceleration of windrow refuse composting through product recycle. McGauhey and Gotass[10] examined the effect of product recycle, addition of soil, and addition of up to 30% horse manure to refuse. They concluded that none had any measurable effect on the rate of composting or the composition of the final product. On the other hand, product recycle is generally considered beneficial in sludge composting systems. However, the effect may be related more to improved structural conditioning than to increased microbial concentrations. Senn[12] observed that recycle of at least 10% of finished product during composting of raw manure greatly facilitated production of a relatively odorless material that did not attract or produce fly larvae. Without product recycle, similar composting temperatures developed, but the final product was odorous and developed fly larvae on rewetting. The APWA[13] also suggested that 1 to 10% recycle is beneficial to continuous reactor systems using refuse.

From the above discussion it is evident that the literature is unclear regarding the mass concentration of microbes required to avoid rate limitations. Indeed, values of K_x are likely a function of the type of substrate and should increase as the number of active sites per unit volume increases. Nevertheless, once the active sites on a substrate are saturated with enzymes ($e_o >> K_a$ in Equation 10.10 or $X >> K_x$ in Equation 10.11) the rate of solubilization should become constant. However, there are a number of other ways to further increase the rate of

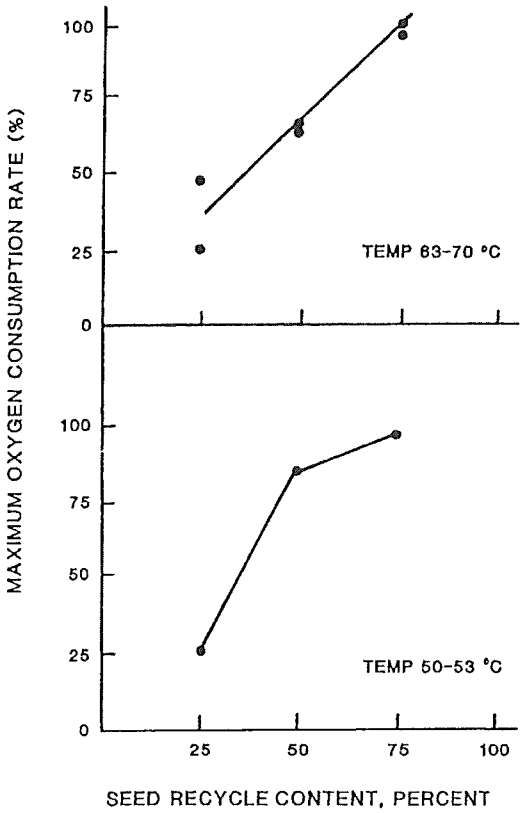

Figure 10.5. Effect of product recycle on the oxygen consumption rate measured during bench-scale composting of refuse. From Regan and Jeris.[11]

reaction. The value of k in Equation 10.11 should be a function of temperature and moisture content. The operator can provide proper conditions for each and also avoid other rate limitations such as low oxygen concentration. Beyond this, however, there is little else that can be done to improve the rate of solubilization except by altering the substrate molecule itself. The effect of chemical and mechanical pulping on cellulose degradation was discussed previously. Both pulping techniques serve to increase the susceptibility of the wood structure to enzyme attack. Grinding the substrate to increase the number of sites per unit volume should also increase the rate of reaction. For example, Pfeffer and Liebman[14] noted that smaller particle sizes resulted in faster rates of reaction during anaerobic digestion of refuse slurries.

Chemical techniques are also available to solubilize certain substrates and make the remaining solids more amenable to biological attack. Alkaline and enzymatic treatment to hydrolyze cellulosic material has been used to produce fermentable sugars. Gossett and McCarty[15] noted that heat treatment of refuse improved its degradability under anaerobic conditions. However, economic and practical considerations will likely limit the application of such techniques to composting.

The Role of Curing

As discussed above, solubilization of the solid substrate is probably a significant rate controlling mechanism during composting. Consider the composting of raw and digested sludges. During anaerobic digestion of municipal sludge ~50% of the solid organic substrate that enters the digester is solubilized and fermented. The solubilization reactions apparently

proceed fast enough to prevent this step from limiting the overall reaction sequence.[3] Indeed, most kinetic models of anaerobic digestion assume that the subsequent fermentation to methane and carbon dioxide is rate-controlling. The point is that the outfeed from the digester has not been solubilized and has resisted hydrolytic attack in the anaerobic reactor. Such resistance is likely maintained in the aerobic composting environment and, therefore, the rate of hydrolysis is likely a serious rate-controlling step with digested sludge. Raw sludge, on the other hand, contains the resistant fraction characteristic of digested sludge as well as the fraction more conducive to hydrolysis. Therefore, rates of reaction may not be limited by solubilization in the early stages of composting, but they may become so in later stages after the readily hydrolyzed fraction has been degraded.

All composting substrates are likely to contain a fraction of solids resistant to hydrolytic enzymes, such as cellulose fiber and certain proteins. Furthermore, microbes synthesized on the feed organic will themselves contain resistant fractions, such as the cell wall structure. If these organic structures become saturated with microbes ($X >> K_x$) the rate of hydrolysis will become constant at $dS/dt = -kA_v$ (Equation 10.12). If the product of kA_v is small for the particular substrate, solubilization will require a considerable period of time. There is little the engineer can do to increase the rate other than to assure all environmental conditions are optimum to keep kA_v as large as possible. No particular reactor design or special inoculum of microbes is likely to reduce the time required as long as $X > K_x$. Therefore, the function of the curing phase is to allow time for the more resistant reactions to occur. There would appear to be little that can be done to shorten the time required for these resistant reactions to complete themselves.

Kinetics in the Aqueous Phase

Once the solid substrate has been solubilized, individual molecules can be transported by diffusion to the cell. The substrate is then transported across the cell wall and is biochemically metabolized by the cell. Diffusion resistance across the cell wall, any internal diffusion resistances, and the actual kinetics of metabolism are incorporated into the Monod kinetic model described in Chapter 4. Given the close proximity between microbes and substrate in the heterogeneous composting system, diffusion resistance through solution is likely low. Therefore, microbial kinetic rates defined by the Monod expression (Equation 4.1) probably govern:

$$\frac{dS}{dt} = -\frac{k_m SX}{K_s + S} \tag{4.1}$$

In the aqueous phase the rate of substrate use is a linear function of the microbial concentration, X, but nonlinear with substrate concentration. As explained in Chapter 4, zero order kinetics result when $S >> K_s$ as a result of saturation of the microbial metabolic system to the point where substrate is processed at the maximum possible rate. This is exactly opposite to the kinetics of the heterogeneous system as represented by Equation 10.11. For the heterogeneous system, the kinetic rate is a linear function of the number of active sites, A_v, and nonlinear with the microbial concentration.

Whang and Meeneghan[16] applied the Monod equation to data developed from batch composting of cattle manure. The authors concluded that their results were reasonably modeled by the Monod expression. Using their data and assuming reasonable values for the

manure characteristics, the product of $k_m X$ ranged from 0.005 to 0.014 day^{-1}. Operating conditions were not specified so the temperatures corresponding to these rate constants are not known. The development of similar rate constants from respirometric data will be discussed later in this chapter.

Kinetics of Oxygen Transport

Along with the organic substrate, oxygen must be available to complete aerobic metabolism. To supply this oxygen, air must first be supplied to the airspace within the composting mixture. Oxygen will then transport to the gas/liquid interface, diffuse across the interface, and then diffuse through the liquid phase to the microbes. Consumption of the oxygen by the microbial population produces a concentration gradient causing further diffusion from the airspace. Conversely, metabolic end products such as CO_2, H_2O, and NH_3 will be at elevated concentrations in the liquid phase and will diffuse toward the airspace and ultimately be removed with the gas flow.

Mass transfer across a gas/liquid interface is widely analyzed using the two-film model developed by Lewis and Whitman in 1924. An illustration of the idealized system is presented in Figure 10.6. Two laminar films are envisioned adjacent to the interface and provide resistance to mass transport of the gas molecules. Applying Fick's Law of molecular diffusion,

$$\frac{dF}{dt} = -AD_l\left(\frac{dS}{dz}\right)_l = -AD_g\left(\frac{dS}{dz}\right)_g \qquad (10.14)$$

where

dF/dt = mass rate of substrate transfer, mass/time
A = surface area, length^2
D_l = diffusion coefficient in the liquid phase, length^2/time
D_g = diffusion coefficient in the gas phase, length^2/time
dS/dz = substrate gradient in a direction perpendicular to the surface layer, mass/volume/length

Assuming linear concentration gradients as shown in Figure 10.6, Equation 10.14 becomes

$$\frac{dF}{dt} = -AD_l\left(\frac{C_i - C_l}{\delta_l}\right) = -AD_g\left(\frac{P_g - P_i}{\delta_g}\right) \qquad (10.15)$$

Gas phase diffusion coefficients are typically greater than those in the liquid phase by a factor of ~10^4. For slightly soluble gases, therefore, it has been shown that essentially all resistance to mass transfer lies on the liquid film side.[3] Under these conditions oxygen transport in the liquid phase becomes rate limiting and any resistance in the gas phase can be neglected.

As oxygen diffuses through the aqueous phase it will be consumed to support the biochemical oxidation of the substrate. This produces a concentration gradient allowing further mass transport into the composting matrix. Because oxygen is in the aqueous phase, its rate of consumption should be governed by the Monod kinetic model. However, application of such a model is difficult without better information on the active microbial concentration, X. Instead, a more simplified approach can be used to provide an order of magnitude estimate of

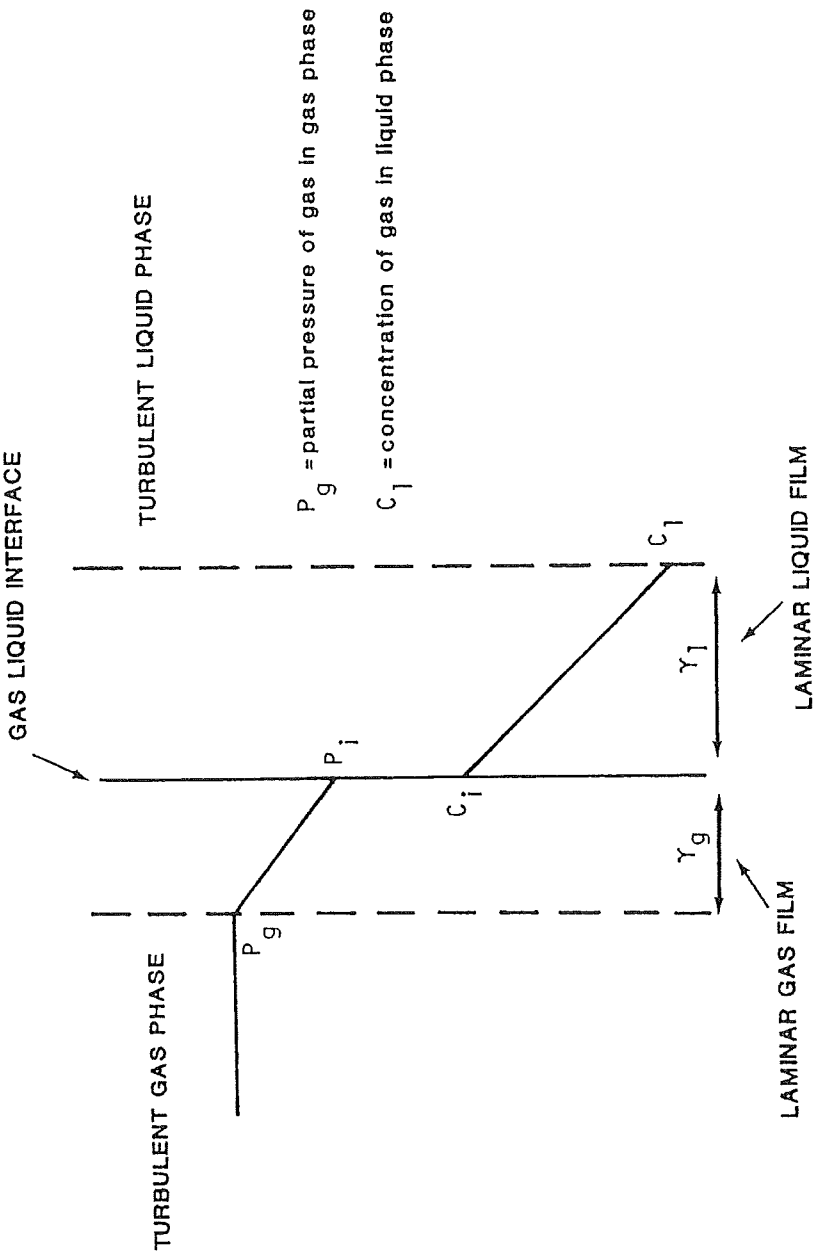

Figure 10.6. Idealized two-film model for mass transfer from the gas to the liquid phase.

the mass transfer rate for oxygen. The calculated rates can then be compared with measured oxygen consumption rates to indicate the conditions under which oxygen supply can be rate-limiting.

The diffusion coefficient is an important parameter in mass transport. It determines the rate at which substrate materials diffuse into the matrix and the rate at which metabolized end products diffuse out of that matrix. Flow conditions within a composting particle are likely to be very quiescent. Therefore, mixing by turbulent or eddy diffusion should be negligible. The actual diffusion coefficient should approach the value of the molecular diffusion coefficient, the limiting value imposed solely by molecular motion of the diffusing materials.

Experimentally determined values for the molecular diffusion coefficient of nonelectrolytes such as oxygen can be found in Reid and Sherwood[17] and Perry and Chilton.[18] Values for dilute solutions can also be estimated from the Wilke-Chang Equation:[18]

$$D = \frac{7.4 \times 10^{-8} T_k (FM)^{0.5}}{n(V_o)^{0.6}} \qquad (10.16)$$

where

D = diffusion coefficient, cm^2/sec
n = solvent viscosity, cP
F = association factor for solvent, 2.6 for water
M = solvent molecular weight
V_o = solute molal volume at normal boiling point, 25.6 cm^3/g-mole for oxygen
T_k = temperature, °K

Equation 10.16 can be used to estimate the molecular diffusion coefficient for small molecules in low-molecular-weight solvents, usually to better than 10 to 15% accuracy.

The actual diffusion coefficient in a composting particle and its water layer may be less than the molecular diffusion coefficient through water alone. Blocking of the diffusing molecules by particulate matter or by changes in the viscosity of the fluid itself can reduce the diffusion coefficient. If molecules are forced to diffuse around particulate matter, such as a bacterial cell, the diffusion coefficient decreases because of the increased path length. If viscosity of the fluid increases, as might occur if the bacteria secreted a slime layer or extracellular polysaccharide, the resistance to passing molecules would increase and the diffusion coefficient decrease.

A substantial amount of work has been conducted to determine diffusion coefficients through biological materials. Most of the measured values for biological materials approximate the values found for water.[19-25] Atkinson et al.,[26] working with glucose oxidation by a fixed film growth, assumed that the diffusion coefficient within the film was equal to the molecular diffusion coefficient for glucose. The assumption worked well under their experimental conditions. Mueller[4] experimentally determined the oxygen diffusivity through pure culture flocs of *Zoogloea ramigera*. Oxygen diffusion values ranged from 0.1 to 2 times that of the molecular diffusion coefficient, primarily because of difficulty in measuring the surface area of the floc particles. However, when the nominal diameter of the floc particle was used to determine the surface area, experimental values were reasonably close to the molecular diffusion coefficient. In detailed experiments by Williamson and McCarty[27,28] diffusion coefficients were measured for NH_4^+, NO_2^-, NO_3^-, and O_2 through nitrifying films. Values ranged

from 80 to 100% of corresponding values through water. It was concluded that a value of 80 to 90% of the molecular diffusion coefficient in water would be a reasonable estimate of the actual coefficient in the biofilm.

The simplified model shown in Figure 10.7 can be used to estimate oxygen diffusion rates through a water-saturated matrix of solid substrate and microbes. Diffusion is assumed to occur from both sides of the particle. The oxygen concentration decreases linearly from a saturation value at the outer interface to zero at the particle midpoint. Obviously, such a model is a greatly simplified version of the actual composting matrix. However, it is unlikely that a more complex model would yield improved results because of the numerous ill-defined factors and unknown kinetic coefficients. The simple model of Figure 10.7 is used in the following example to determine the importance of oxygen diffusion as a rate-controlling mechanism.

Example 10.1

Using the simplified model of Figure 10.7a, estimate the oxygen flux at 60°C for a particle thickness of 0.05 cm. Assume a saturation oxygen concentration of 6 mg/L at the gas-particle interface. Estimate the time required to supply the stoichiometric oxygen quantity assuming the matrix to be 50% TS ($S_m = 0.5$), with 50% VS content ($V_m = 0.5$) and degradability of 50% ($k_m = 0.5$).

Solution

1. Estimate the liquid phase diffusion coefficient D_l for oxygen using the Wilke-Chang correlation. Assume the viscosity of water at 60°C to be 0.45 cP:

$$D_l = \frac{7.4\times10^{-8}(273+60)}{0.45}\left\{\frac{[2.6(18)]^{0.5}}{25.6^{0.6}}\right\}$$

$$D_l = 4.62\ \text{cm}^2/\text{day}$$

2. Estimate the specific gravity and bulk weight of the particle using Equations 6.1 and 6.3:

$$\frac{1}{G_s} = \frac{0.50}{1.0} + \frac{1-0.5}{2.5}$$

$$G_s = 1.43$$

$$\delta_s = \frac{1.0}{\frac{0.5}{1.43}+1-0.5} = 1.18\ \text{g/cm}^3$$

3. Determine the flux across the interface. The gradient of oxygen is given by

$$\frac{dS}{dz} = -\left(\frac{6\ \text{mg/L}}{0.025\ \text{cm}}\right) = -240\ \text{mg/L-cm}$$

Using Equation 10.15 and considering 1 cm^2 of area on each side of the particle:

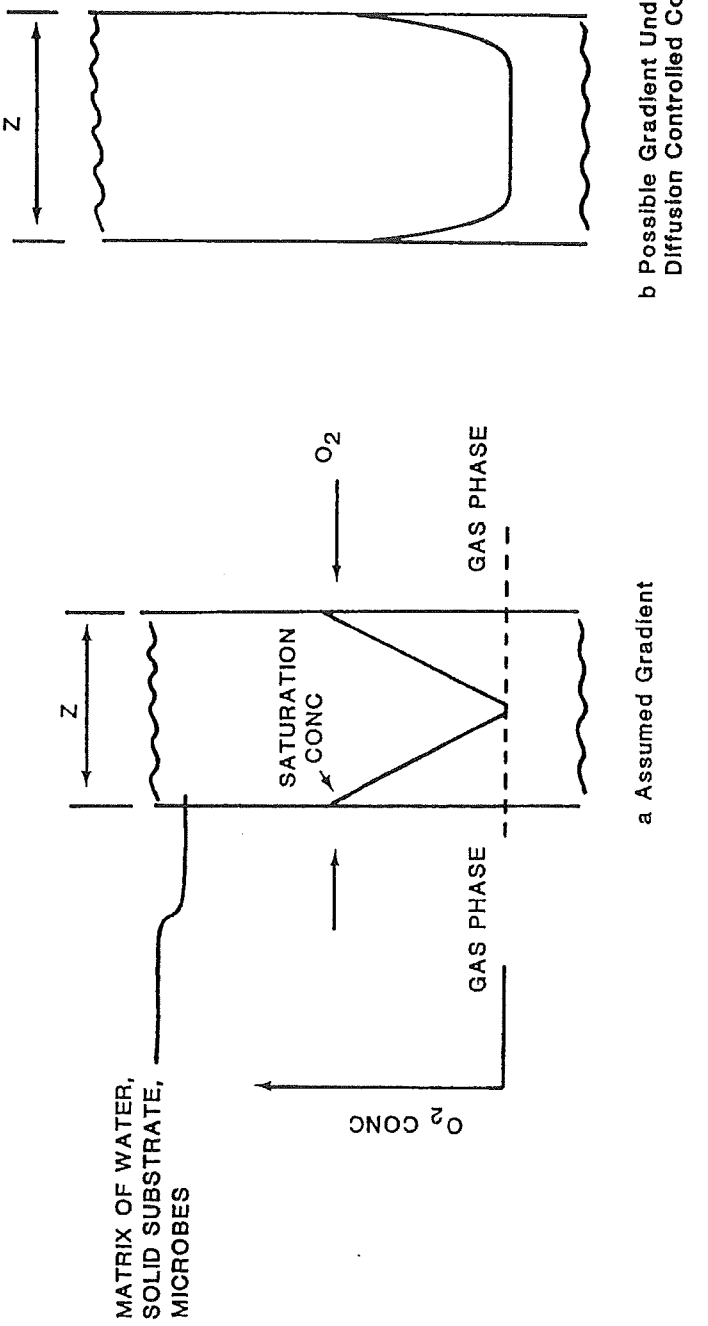

Figure 10.7. Simplified model of gas transfer used to estimate oxygen transport rates through a saturated matrix of solid substrate and microbes.

$$\frac{dF}{dt} = -(2.0\ cm^2)(4.62\ cm^2/day)(-240\ mg/L-cm)\frac{1\ L}{1000\ cm^3}$$

$$\frac{dF}{dt} = 2.22\ mg\ O_2/day$$

4. Each cm^2 of particle surface will contain 1.0(0.05) = 0.05 cm^3 of volume. The matrix mass in this volume is 1.18(0.05) = 0.059 g. The mass of volatile solids VS is

$$VS = 0.059(V_m)(S_m)$$

$$VS = 0.059(0.5)(0.5)$$

$$VS = 0.0148\ gm$$

The oxygen flux can then be expressed as

$$\frac{dF}{dt} = \frac{2.22}{0.0148} = 150\ mg\ O_2/g\ VS-day$$

5. The time required to satisfy the stoichiometric demand can be estimated assuming about 2 g O_2/g VS (see Equation 7.1) and 50% degradability:

$$\text{stoichiometric demand} = 0.0148(0.5)(2.0) = 0.0148\ g\ O_2$$

$$\text{time required} = \frac{0.0148(1000)}{2.22} = 6.6\ days$$

Oxygen flux and time requirements were calculated for various particle sizes using the same approach and assumptions as in Example 10.1. Results are presented in Figure 10.8 along with the observed range of oxygen demands discussed later in this chapter. Oxygen flux is shown to decrease as the particle thickness increases. This obviously leads to an increase in the time required to supply the stoichiometric oxygen requirement. Conditions imposed by the model may be overly severe because the diffusion gradient decreases as particle size increases. In actual fact the gradient may remain constant, leading to the concentration profile shown in Figure 10.7b. Such a profile would be expected when process kinetics are diffusion controlled. Under such conditions the flux may no longer be a function of particle thickness. However, time required to satisfy the oxygen demand would still increase with increasing particle thickness, but at a lower rate than shown in Figure 10.8.

Despite the modeling uncertainties, it appears that diffusion transport of oxygen can match the oxygen consumption rate if the particle size is sufficiently small. Particle size on the order of 1.0 cm appears to result in large diffusion resistances which would dominate the process kinetics. Particle sizes of about 0.10 cm and lower appear to be small enough that diffusion supplied oxygen can balance the observed rates of oxygen demand. If particle thickness decreases below about 0.05 cm, oxygen diffusion would have a negligible effect on process kinetics. Golueke[9] noted that complete aeration of all particles "would involve reducing all particles to a size less than a millimeter or two, because by its very dimensions a particle any

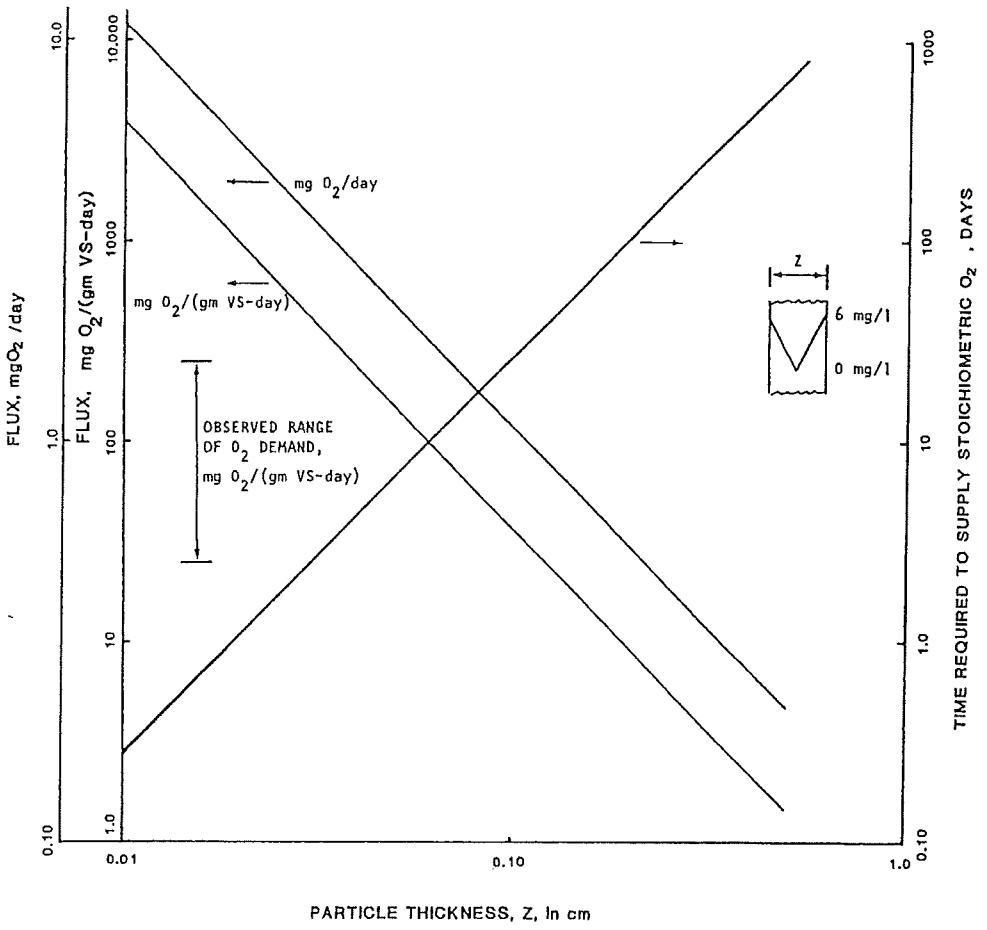

Figure 10.8. Effect of particle thickness on oxygen flux and time needed to satisfy the stoichiometric oxygen requirement. Values were calculated using the simplified model of Figure 10.7a and the procedure and assumed values of Example 10.1.

larger could be anaerobic in its interior." Although no data were supplied to support this statement, the general agreement with the simplified model presented here is interesting.

Several other observations can be drawn from the model results. The fact that oxygen is present in the pore spaces between composting particles does not mean that oxygen diffusion is not rate-limiting. Oxygen is required *in* the matrix of water, substrate, and microbes. The fact that oxygen is present in the pore space does not necessarily mean that the flux rate of oxygen into the particles is not rate-limiting. It is common practice to use oxygen probes to measure the oxygen content of gases in the composting material. This is a useful practice but it only assures that oxygen is present in the pore space. It should not be interpreted to mean that all oxygen rate limitations have been removed. Indeed, process kinetics could still be controlled by diffusion transport within the compost particles.

The fact that diffusion transport is enhanced by smaller particle size leads to an unavoidable paradox for systems that rely on natural draft ventilation for aeration. Referring to Chapter 7, it was concluded that (1) natural draft was a primary ventilation mechanism in nonaerated windrow composting systems and (2) that natural ventilation is enhanced by larger particle sizes that increase the dimensions of the void spaces. Ventilation is enhanced by larger particle size whereas diffusion transport is not, an interesting paradox. A balance between these competing effects is necessary to assure that diffusion transport is not overly enhanced at the sake of oxygen supply, or vice versa.

Finally, it should be noted that the model assumed a particle with a continuous matrix of water/substrate/microbes and no void spaces within the particle itself. With wet substrates, such as sludges, wet manures, and wet sawdust, the water will fill many of the voids and pores within the substrate particles. The model assumptions would seem to be reasonable in this case. As composting proceeds, however, water will be removed from the micropores and voids within the substrate. Evaporation or absorption of excess water by recycled product, bulking agent, or amendment could be responsible for the moisture removal. Other substrates, such as dry wood fiber, will contain a significant volume of open micropores within the particle. As previously noted, diffusion coefficients through a gaseous phase are about four orders of magnitude greater than through the liquid phase. Therefore, diffusion through small gas pores within the substrate particle itself should occur rapidly. Also, the interfacial area for transfer into the liquid phase will be greatly increased by the micropores. Thus, diffusion transport of oxygen will be a more controlling factor with wet substrates and assume less significance with dry substrates or as moisture is removed from wet ones.

Potential Rate Limitations

The previous sections examined a number of possible rate limitations, including solubilization of the solid substrate and mass transport of both oxygen and the solubilized substrate to the cell. The effect of moisture content on the mass transport of oxygen was also discussed. However, even if oxygen and a solubilized and degradable substrate are available to the cell, there are a number of other factors that can limit microbial kinetics. Microbial reaction rates can be limited by at least the following:

- lack of degradable organics
- very low or high process temperatures
- low moisture conditions
- lack of free air space
- low oxygen content
- imbalanced pH conditions
- lack of inorganic nutrients
- lack of microbes (sterile substrate)
- the presence of toxic substances

Structural conditioning to adjust FAS and chemical conditioning to remove nutrient and pH rate limitations were discussed in Chapter 6. Aeration needs to reduce oxygen limitations were discussed in Chapter 7. Energy conditioning to assure an adequate supply of degradable organics was discussed in Chapters 8 and 9. The use of product recycle for seeding was discussed previously in this chapter and can be used to reduce rate limitations from a lack of sufficient microbial mass. Most composting substrates do not contain toxic substances in sufficient quantity to limit process kinetics. Therefore, the present discussion will address the effects of moisture and process temperature.

Moisture

The effect of excessive moisture on reducing FAS and limiting the mass transport of oxygen has already been discussed. The opposite case, lack of sufficient moisture, can also limit the reaction kinetics. A number of factors probably combine to account for this effect.

First, most biological reactions during composting are mediated by bacteria that require an aqueous environment. Second, mass transport limitations for soluble components may be encountered under low moisture conditions. In general, moisture contents should be maintained as high as possible without violating requirements for minimum FAS.

Literature data on the effect of moisture content on oxygen consumption rates for various composting materials are presented in Figure 10.9. The trend toward decreasing reaction rates at low moisture content is clearly evident. Below 20% moisture very little, if any, biological activity occurs. From that point rates of oxygen uptake increase in a more or less linear fashion to maximum values that begin at about 50 to 70% moisture. Rates begin to decrease again at high moisture contents, undoubtedly from loss of FAS. This points out the difficulty in isolating effects of moisture alone in such experiments because of the relationships between moisture, bulk weight, and FAS. This probably accounts for much of the data scatter in Figure 10.9, as well as the slightly different trends observed for the various composting materials.

Composting tends to be a drying environment. Even if the initial mixture is conditioned to a proper moisture content, supplemental water addition may be necessary at periodic intervals to avoid rate limitations. This is particularly true with dry substrates, but it may also be true with wet substrates that are "energy rich". The provision for supplemental water addition should be considered during design of any composting system.

Process Temperatures

All organisms have a temperature range over which biochemical functions can be maintained. Within certain limits the rate of these biochemical reactions about doubles for each 10°C rise in temperature. However, excessively low or high process temperatures can limit the overall process kinetics.

Microbial rates of reaction are markedly reduced as the temperature is decreased from 20 to 0°C. If the starting substrates are very cold or frozen and the input air is also cold, a significant lag period may be observed before thermophilic temperatures are developed. In extreme cases, the pile may fail to show any significant temperature rise. This phenomenon is occasionally observed in actual operations in cold climates. When all feed temperatures are low (i.e., near 0°C), newly formed, batch operated piles have been observed to sit with little temperature development. Recourse in such situations has often been to apply additional insulating layers to the pile and reduce the air flowrate. These measures would be effective if the problem were one of process thermodynamics. Unfortunately, it is not, and the above procedures will have only a marginal effect.

The problem with low substrate temperatures is primarily a kinetic problem. Reaction rates are so slow that the rate of heat generation is less than the rate of heat loss to the cold surroundings. The energy is still available within the substrate, but it is not released in significant amounts because of the low rate of biological activity. The pile sits and appears to do nothing. The author has observed composting operations where frozen substrates are piled and then aerated with sub-zero air with the expectation that the pile will elevate in temperature. There is a very good chance that it will not. One must remember that freezing is a method of preservation because it so greatly reduces microbial reaction rates. In effect, the energy to perform the composting task is thermodynamically present, but the spark is slow to ignite the process.

The best approach to overcome low temperature kinetic limitations in cold climates is to assure that any heat in the feed substrates is conserved to give as high a starting temperature as possible. If the substrates are frozen and the air supply is subzero it will be difficult to "ignite" the process. Therefore, efforts should be made to avoid loosing heat from the substrate. For example, sewage sludges should be stored adiabatically or processed as soon as

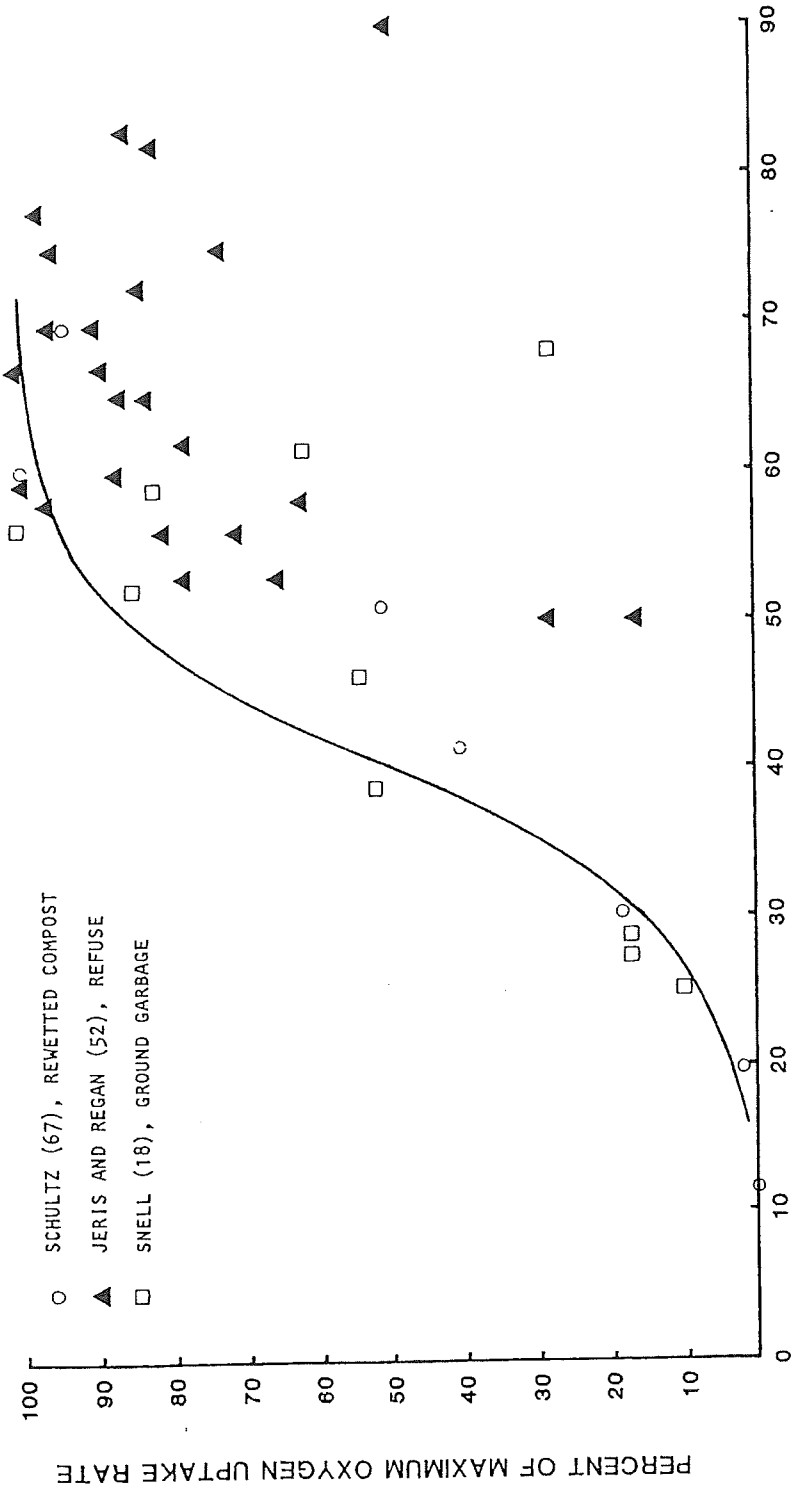

Figure 10.9. Effect of low and high moisture contents on oxygen consumption rates measured for various composting materials.

possible to avoid losing temperature. If this is not sufficient it may be necessary to heat the substrates or preheat the air supply during the initial lag period until the process "ignites". Once started, further heating should be unnecessary. Air preheat could be supplied from conventional fuel sources or by heat exchange with hot exhaust gases.

The potential for cold weather effects on process kinetics highlights a distinction between batch and continuous feed, well-mixed processes. Infeed temperature in a well-mixed system has very little impact on process kinetics because it is the reactor temperature that governs. As long as reactor temperatures are thermophilic, the cold feed will be mixed with the hot reactor contents and low temperature kinetic problems are avoided. This is a significant advantage for compost operations in very cold climates.

If extremely cold temperatures can impose kinetic limitations, so too can very high process temperatures. In a mixed population of microbes, a natural transition from mesophilic to thermophilic temperatures can be expected. Reaction kinetics will tend to increase exponentially with temperature. However, there is an upper limit to the exponential increase with temperature. At some point even the thermophilic microbes cannot overcome the effects of thermal denaturation of their enzymes. At this point, rates of reaction will decrease with further increases in temperature. The temperature corresponding to the maximum reaction rate has been the subject of much debate. Different investigators have reported optimum values during composting ranging from as low as 40 to as high as 70°C. It should be noted, however, that nature's microbes are extremely resilient. Clark[29] reported isolating extreme thermophiles from deep sea hydrothermal vents with temperature optima of 85°C and maximum growth temperatures as high as 110°C.

The point to remember here is that extremely high temperatures do not necessarily imply a high rate of reaction. This is a common mistake because one is inclined to measure composting effectiveness by high temperature elevation. Should temperatures develop to the range of 75 to 85°C, rates of reaction are likely depressed because of the high temperature. Process kinetics would be improved by reducing the temperature. To accomplish this, generated heat must be removed at a greater rate. Increasing the aeration rate will increase the rate of heat loss and is the most effective approach.

The problem of high process temperatures is not unique to composting. Many industrial fermentations also face the problem of high heat generation rates. Because industrial fermentations are usually conducted in aqueous solution, cooling tubes can be placed in the fermenter to remove the excess heat. Unfortunately, this is not practical in a composting system.

RATES OF BIODEGRADATION

Background Data

Oxygen consumption rates during composting have been investigated extensively by numerous researchers using a variety of experimental procedures and feed materials. Both batch and continuous composters have been used. Most data have been developed using controlled, laboratory or bench scale composters where various factors, such as temperature, pH, moisture, and free airspace, can be held reasonably constant. Many studies have focused on garbage and refuse materials, probably because of the universal concern over their proper management. Results of some of the more notable studies will be presented here.

Among the more thorough studies of oxygen uptake rate were those conducted by Schulze.[30-33] His experiments are a good example of the protocols required for such studies. Continuous

composters were operated to achieve steady state conditions. Each composter consisted of a 55-gal rotating drum that was normally filled to about two thirds of its volume. Feed materials consisted of various garbage/sludge mixtures. Feed material was added every 1 to 2 days and the composter was rotated for about 5 min before and after each feeding. Thus, conditions expected in a semicontinuous feed, well-mixed reactor were simulated. Data were collected after establishment of steady state conditions within the reactor.

Schulze examined a number of feed mixtures composed of one or more of the following: (1) shredded garbage consisting primarily of table scraps; (2) dewatered, digested sewage sludge containing 70 to 80% moisture conditioned with about 4% $FeCl_3$ and 12% lime on a dry-weight basis; (3) air-dried digested sludge; (4) air-dried compost; (5) shredded wastepaper, mostly newsprint; and (6) vermiculite, an expanded mica consisting of particles 0.6 to 1.3 cm in size. The vermiculite served as a bulking agent in the same way that wood chips are used in the static pile process. Data on the average composition of the substrate mixtures are presented in Table 10.3.

During initial testing it was found that plain ground garbage, a mixture of garbage and dewatered sludge, or dewatered sludge cake by itself, would not successfully compost. Material in the drum became too dense and formed large balls that impeded oxygen transfer. Because the drum was rotated only intermittently, the tumbling action was apparently insufficient to supply oxygen to the wet material. Schulze then conditioned the wet substrates using the dry amendments noted above to reduce the mixture moisture content to 50 to 60%. For all mixtures listed, the FAS ranged from about 40 to 60%. It is felt that bulk weight measurements recorded by Schultz may have been low, particularly for dewatered sludge cake. Therefore, the values of FAS shown in Table 10.3 may be higher than those actually present in the drum reactor.

Schulze concluded that ground food waste and dewatered sludge cake are too high in bulk weight and moisture to compost as such and that "those materials have to be mixed with a dry and bulky component such as refuse, waste paper, corncobs, wood shaving, rice hulls, etc. in order to obtain a suitable moisture content and bulkweight." This was a prophetic statement made in 1962, a decade before the successful sludge composting operations by the Los Angeles County Sanitation Districts, which began in 1972 and pioneered the use of product recycle for conditioning, and by the U.S. Department of Agriculture at Beltsville, Maryland, which began in 1973 and pioneered the use of bulking agents.

Average operating data observed during the test periods are presented in Table 10.4 and Figures 10.10 to 10.12. Residence times varied between 7 and 18 days and volatile solids, VS, destructions from 37 to 45%. Detention times were estimated from the total weight of ash in the reactor divided by the daily input of ash. Moisture content of the outfeed approximated that of the infeed, indicating that air supply was adjusted primarily to the stoichiometric demand rather than that required for drying. Temperatures remained constant in the thermophilic range between 43 and 68°C.

Rates of oxygen consumption were determined throughout run 2c which used a mixture of garbage, sludge cake, and vermiculite. Results are shown in Figure 10.13. Oxygen consumption was a function of temperature and followed the relationship

$$w_{O_2} = 0.11(1.066)^T \tag{10.17}$$

where

w_{O_2} = rate of oxygen consumption, mg O_2/g VS-h
T = temperature, °C

Table 10.3. Average Analytical Data for Raw Materials and Mixtures Used by Schulze [30]

Item	Moisture (% fresh weight)	Ash (% dry weight)	pH	Wet Bulk Weight (g/L)	Specific Gravity (g/cm^3)	Dry Bulk Density (g/cm^3)	Porosity (%)	Free Airspace[a] (%)
Ground garbage	63	10	5.9	740	1.064	0.237	77.7	27.4
Moist sludge cake	72	50	8.2	660	1.43	0.185	87.1	39.6
Dry sludge cake	6.0	50	8.4	390	1.43	0.367	74.3	72.0
Vermiculite	1.0	100	7.5	90	2.5	0.09	96.4	96.3
Dry compost	10	60	8.0	290	1.563	0.261	83.3	80.4
Shredded paper	8.0	8.0	5.0	25	1.0	0.023	97.7	97.5
Mixture A[b]	47.8	31.3	6.7	642	1.23	0.353	72.8	42.1
Mixture B[c]	56.5	49.4	5.9	410	1.42	0.178	87.4	64.3
Mixture C[d]	50.5	22.1[e]	6.2	410	1.154	0.203	82.4	61.7
Mixture D[f]	60.0	17.3[e]	6.0	410	1.152	0.164	85.8	61.2
Mixture D_1[g]	57.0	23.2	6.0	410	1.153	0.177	84.7	61.3

[a] Recalculated from original data according to Equation 7.10.
[b] Mixture A = 20 lb garbage, 10 lb air-dry sludge cake.
[c] Mixture B = 20 lb garbage, 10 lb moist sludge cake, 3 lb vermiculite.
[d] Mixture C = 20 lb garbage, 5 lb air-dry sludge cake, 4 lb paper.
[e] Computed from average data for components.
[f] Mixture D = 20 lb garbage, 10 lb moist sludge cake, 5 lb paper.
[g] Mixture D_1 = 20 lb garbage, 10 lb moist sludge cake, 5 lb paper, 2.5 lb air-dry compost.

Table 10.4. Average Operating Data Observed During Continuous Thermophilic Composting

	Run No. 1	Run No. 2	Run No. 2c	Run No. 3b
Feed mixture	A	B	B	D,D_1
Feed cycle, days	1	2	1	2
Test duration, days		52	75	167
Data collected, days[a]	11	34	23	35
Residence time, days	8.9	12.7	7.0	18.3
Red. in vol. mat., %	36.8	43.1	42.4	45.2
Moisture, %				
In	47.8	56.5	58.6	57.0
Out	51.3	55.2	58.4	56.9
pH				
In	6.7	5.9	5.6	6.0
Out	7.6	7.8	6.6	8.1
Wet weight, g/L				
In	642	410	404	412
Out	657	567	587	611
Free airspace, %[b]				
In	42.1	64.0	64.8	61.1
Out	42.4	52.8	50.6	44.3
Air supply, m^3/kg VS-day	0.28	0.55	0.73	0.31
Temperature range range, °C	43–64	53–68	59–68	62–68

Source: Schulze.[30]

[a] Indicates time over which data were collected. For Run 2b, e.g., data collection began on day 18 and was completed on day 52.
[b] Recalculated from original data according to Equation 6.11.

The rate of oxygen consumption continued to increase with temperatures up to 68°C, which was the maximum observed in run 2c. Experience has shown, however, that the oxygen consumption rate would be expected to decrease at higher temperatures.

The pH of the reactor contents was consistently above 7, except for run 2c as shown in Figure 10.12. In this case about 25% of the volatile matter in the reactor was replaced with each daily feeding, the highest feed rate attempted. Apparently, the high loading rate shifted the process into the acidic range, which indicates that the reactor output was not as close to a finished compost as material produced at lower feed rates.

Material removed from the drums was stored in open bins and for several days developed temperatures near 40°C. After 2 to 3 weeks of storage, temperatures generally decreased to ambient and the compost reportedly had a pleasant greenhouse odor. Odor from the sewage sludge was reported to be absent. Thus, a curing phase was required even after continuous thermophilic composting at residence times from 7 to 18 days.

Jeris and Regan[7,11,34,35] conducted an interesting set of experiments using both batch and continuous composters fed with mixed refuse, newsprint, and compost produced from mixed refuse at the circular, agitated bed reactor system at Altoona, Pennsylvania (see Chapter 2). The batch experiments were conducted using the Warburg respirometer and shaker flasks. The continuous composters were similar in concept to those used by Schultz, but differed in that process temperatures were artificially maintained constant by heating rods compared to the self-heating and, therefore, somewhat variable conditions used by Schultz. The mixed refuse was a simulated mix of cafeteria and supermarket wastes (meat and fish scraps, lettuce, and other vegetable trimmings) and newsprint. The mixture contained 60 to 70% paper and was considered a high cellulosic substrate. Because of the high paper content, nitrogen and phosphorus were added to provide supplemental nutrients. Tap water was added to adjust the

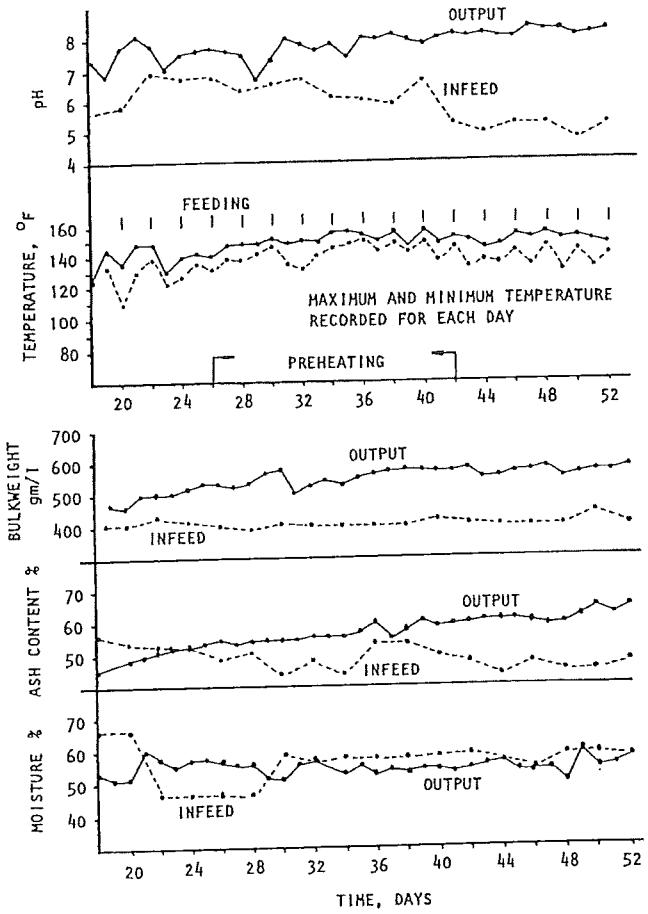

Figure 10.10. Average operating data recorded by Schulze[30] during continuous composting of a garbage/sludge mixture. Feeding was on a 2-day cycle. Data correspond to Run No. 2b, using Mixture B as identified in Table 10.3. Air supply was approximately 6.5 mg O_2/g VS-h with a detention time based on an ash balance of 12.7 days. The data indicate that reasonably steady state conditions were achieved.

moisture content. It was assumed that the tap water supplied any necessary trace elements. The materials were shredded to a particle size no greater than 0.25 inch.

Oxygen consumption rates measured on the various substrates are presented in Figure 10.14. The compost and newsprint showed oxygen consumption rates about one order of magnitude less than freshly mixed refuse. This illustrates that compost may be stable, but it is certainly not inert. It will continue to decompose, but at greatly reduced rates. The low rates observed for newsprint are caused by the structural resistance of mechanically pulped wood products. Jeris and Regan[11] developed best-fit equations for their data over the temperature range from 35 to 70°C. These were adjusted for units and are as follows:

Newsprint

$$w_{O_2} = -0.00147(T^2) + 0.1413(T) - 2.907 \qquad (10.18)$$

Composted mixed refuse

$$w_{O_2} = -0.00133(T^2) + 0.1013(T) - 1.587 \qquad (10.19)$$

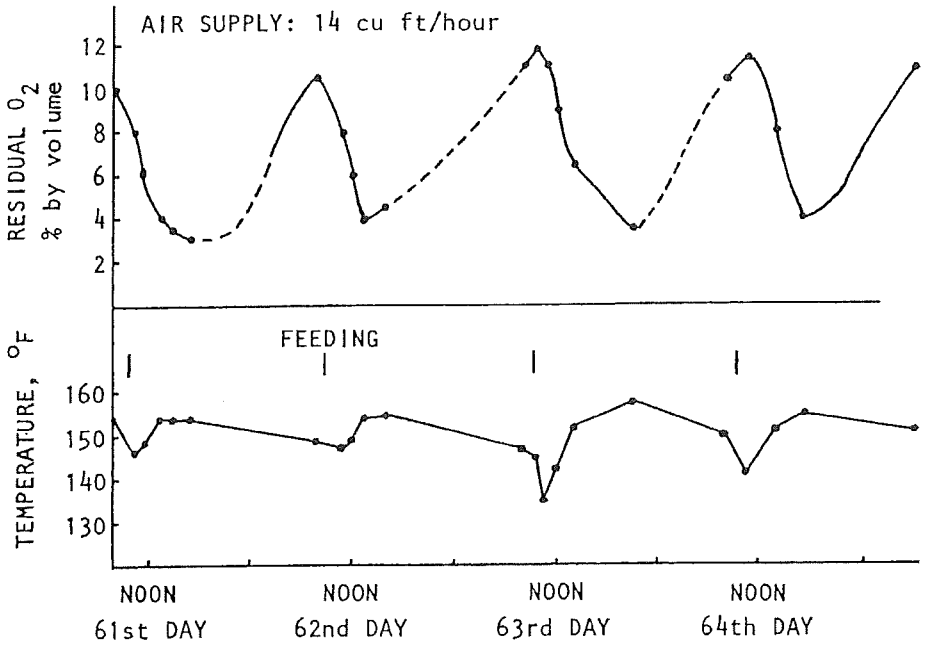

Figure 10.11. Relationship between feed cycle, temperature, and residual oxygen during continuous composting as determined by Schulze.[30] Data correspond to Run No. 2c, Mixture B, as defined in Table 10.3.

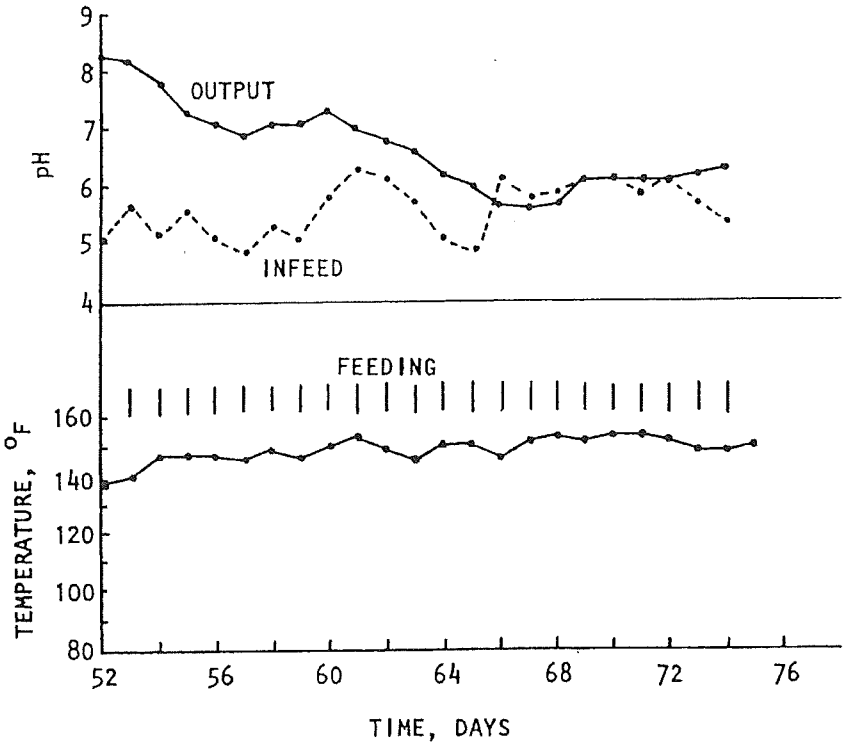

Figure 10.12. Effect of high organic loading on product pH. Data correspond to Run No. 2c, Mixture B, as defined in Table 10.3. The daily feed schedule reduced the detention time to 7 days. Apparently, at the high loading rate the rate of organic acid production exceeded the rate of acid consumption and the pH shifted from the slightly alkaline range to the acid range. From Schulze.[30]

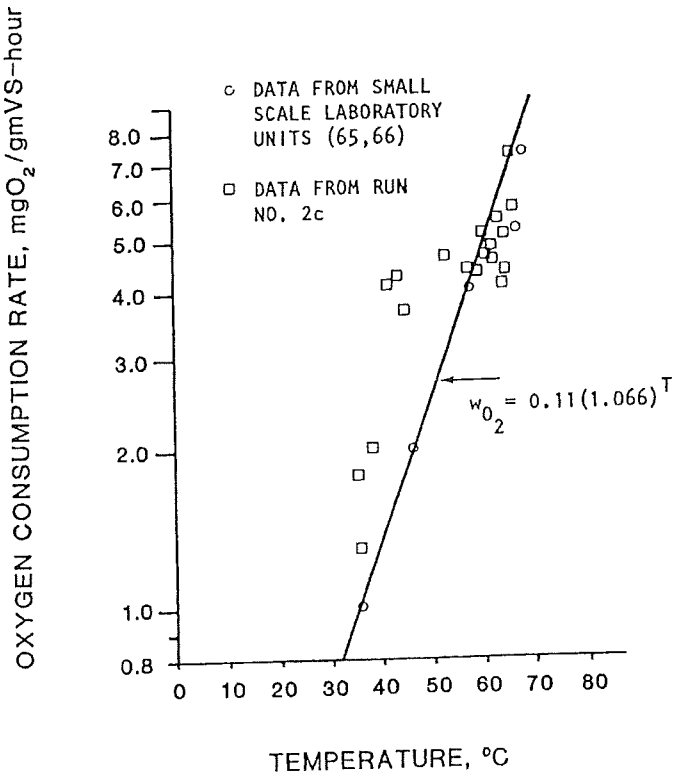

Figure 10.13. Relationship between temperature and oxygen consumption rate observed by Schulze[30] during continuous composting experiments with garbage and digested dewatered sludge cake.

Fresh mixed refuse

$$W_{O_2} = -0.0387(T^2) + 4.560(T) - 117.9 \qquad (10.20)$$

Jeris and Regan determined optimum temperatures for each substrate by differentiating Equations 10.18 to 10.20. Optimum temperatures were 38°C for the composted mixed refuse, 48°C for the newsprint, and 59°C for the fresh mixed refuse. When the process temperature was maintained within 5 to 10°C of the optimum value for each material, 95% of the maximum respiration rate was obtained. The lower temperature optima for the newsprint and compost compared to the fresh mixed refuse was attributed to the higher fractions of cellulose remaining in these materials. The authors felt that this confirmed literature reports[36] that the predominate number of species of microbes capable of utilizing cellulose operate most efficiently within the 45 to 50°C range. This may also explain the lower temperature optima for the fresh mixed refuse compared to the mixtures of garbage and sludge used by Schulze which were lower in cellulose content.

Use of a continuous composter is necessary to determine temperature effects under steady state conditions. However, many composting systems are operated on a batch basis and true steady state conditions are never achieved. Numerous studies of oxygen consumption have been conducted using batch reactors. An example of the type of data derived from such studies is shown in Figure 10.15 based on the work of Snell.[37] Small, bench scale composters were used with temperature and moisture conditions held constant. Moisture control became difficult at higher temperatures and the samples became dried, which likely introduced a

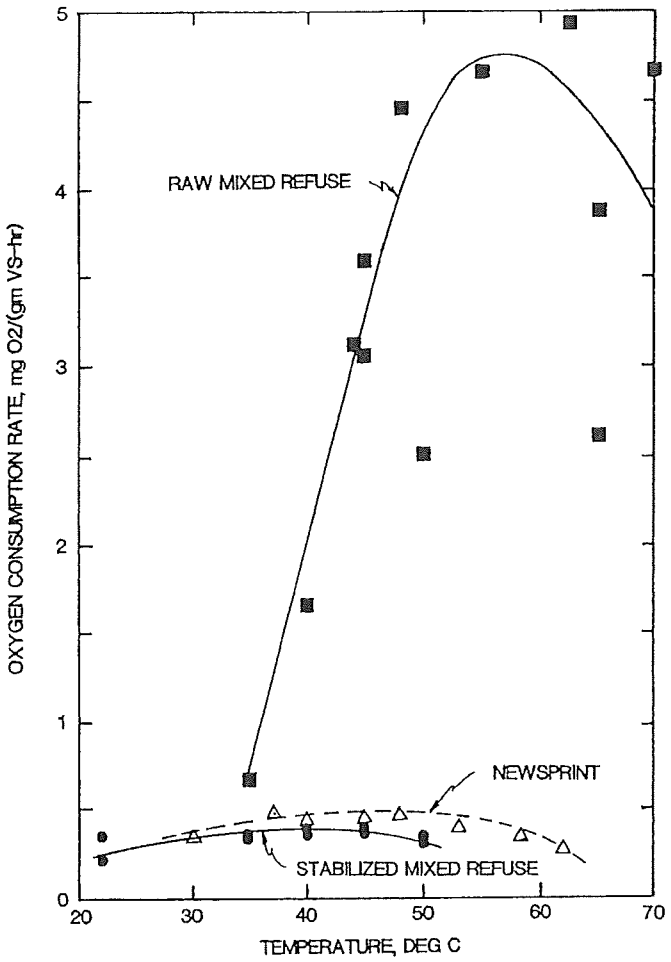

Figure 10.14. Relationships between temperature and oxygen consumption rates observed by Regan and Jeris[11] during continuous composting experiments with mixed refuse, newsprint, and compost made from mixed refuse. All substrates were high in cellulose content.

moisture rate limitation. No seeding or reseeding was practiced and the feed material consisted of ground garbage. Because of the batch nature of the process, a characteristic lag period was observed at the start of composting. As long as 8 days was required to achieve maximum rates of oxygen uptake. The maximum rate would hold for several days and then begin to decrease as the more readily degradable feed components were exhausted.

A temperature curve typical of a batch windrow system is shown in Figure 10.16. The windrow consisted of a large mass of aerobically composting refuse. The difference between temperature curves for batch and continuous reactors can be seen by comparing Figures 10.10 and 10.16. If the feed schedule is continuous or semicontinuous, and if the reactor contents are well mixed, feed material will be quickly inoculated with the mixture of microbes developed for the particular steady state conditions. The material will also quickly be brought to conditions of temperature, pH, moisture, and FAS established in the reactor. Thus, the lag period common to batch systems can be reduced or eliminated with continuous composters. Notice in Figure 10.16 that the temperature curve does not hesitate at the transition from mesophilic to thermophilic temperatures. In smaller masses of compost there is sometimes a temporary temperature plateau as the mesophilic population declines and the thermophilic population develops. In large piles where heat loss from the interior is slow, the effect is dampened.

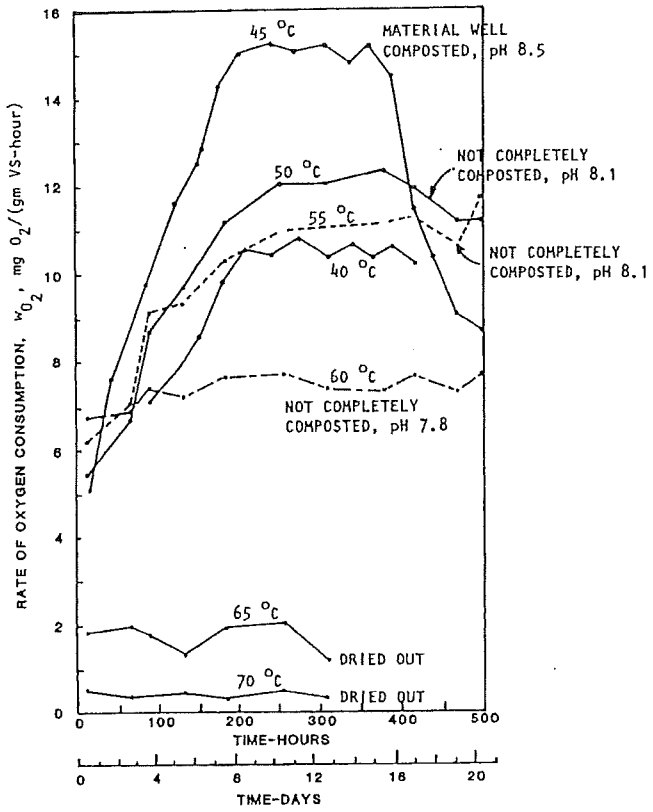

Figure 10.15. Rate of oxygen consumption for various temperatures using a batch composter with ground garbage. Note the somewhat linear increase in oxygen uptake rate to a maximum value for each temperature. Peak values are plotted in Figure 10.17. From Snell.[37]

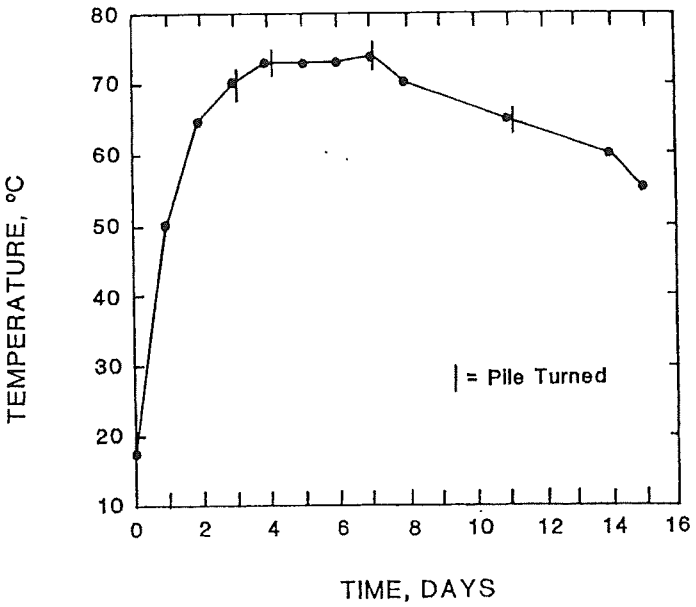

Figure 10.16. Temperature curve typical of a large mass of refuse material during aerobic composting in a batch operated windrow system. From McGauhey and Gotaas.[10]

Wiley and Pearce[38] and Wiley[39-41] studied the rates of CO_2 evolution from samples of mixed garbage and refuse with a paper fraction estimated to be at least 50%. Samples were ground to a size <5/8 in. Batch composters with a 1.5 ft^3 working volume were used. The composters were insulated and no external heating or cooling was applied. Air was supplied at a constant rate to each composter and the exhaust gas analyzed to determine the rate of CO_2 evolution. Thus, the substrate self-heated to a point where heat production was balanced by heat loss. Over 245 data points relating temperature and CO_2 production rate were developed, which spanned the temperature range from 15 to 70°C. A best fit equation developed from their CO_2 data can be converted to an equivalent O_2 consumption rate by assuming 1 mol O_2/mol CO_2. The latter ratio is applicable to a largely cellulosic substrate. With these assumptions, the data of Wiley can be represented as

$$w_{O_2} = 0.3432(1.0429)^T \tag{10.21}$$

A summary of some of the available data on oxygen uptake rates is presented in Figure 10.17. Despite the variety of procedures and feed materials, the data are reasonably consistent. All studies show an increase in the rate of oxygen uptake with increasing temperature. Some of the studies show maximum rates at intermediate temperatures of 40 to 60°C, while others show consistently increasing rates to ~70°C. All studies show decreasing rates at temperatures higher than the optimum temperature. As Regan and Jeris[11] suggest, the differences in temperature optima may in part be due to differences in the cellulosic content of the substrate.

In any composting system, the aeration system must be capable of meeting the maximum oxygen consumption rate demanded by the microbial population. From Figure 10.17, a maximum rate in the range of 4 to 14 mg O_2/g VS-h would appear to be sufficient in all but the most extreme cases. This equates to about 460 to 1620 ft^3/ton VS-h (14 to 50 m^3/metric ton VS-h). These values represent *peak* stoichiometric demands. Higher aeration rates would be required to remove the heat released from consumption of the oxygen (see Chapter 7).

First Order Reaction Rates

The shape of the oxygen consumption curves from the long term respirometric tests presented in Figures 9.7 and 9.8 strongly suggest a first order rate equation of the form

$$\frac{d(BVS)}{dt} = -k_d(BVS) \tag{10.22}$$

where

BVS = the quantity of biodegradable volatile solids, usually kg or lbs
t = time, days
k_d = rate constant, g BVS/(g BVS-day) or day^{-1}

According to Equation 10.22, the rate of BVS oxidation, d(BVS)/dt, is a function of the quantity of remaining BVS. The negative sign indicates that the quantity of BVS decreases with time.

The assumption of first order kinetics has worked well in describing numerous processes involving biological oxidation. Included among these is the familiar first order expression for organic oxidation in such wide ranging systems as biological oxygen demand (BOD) bottles

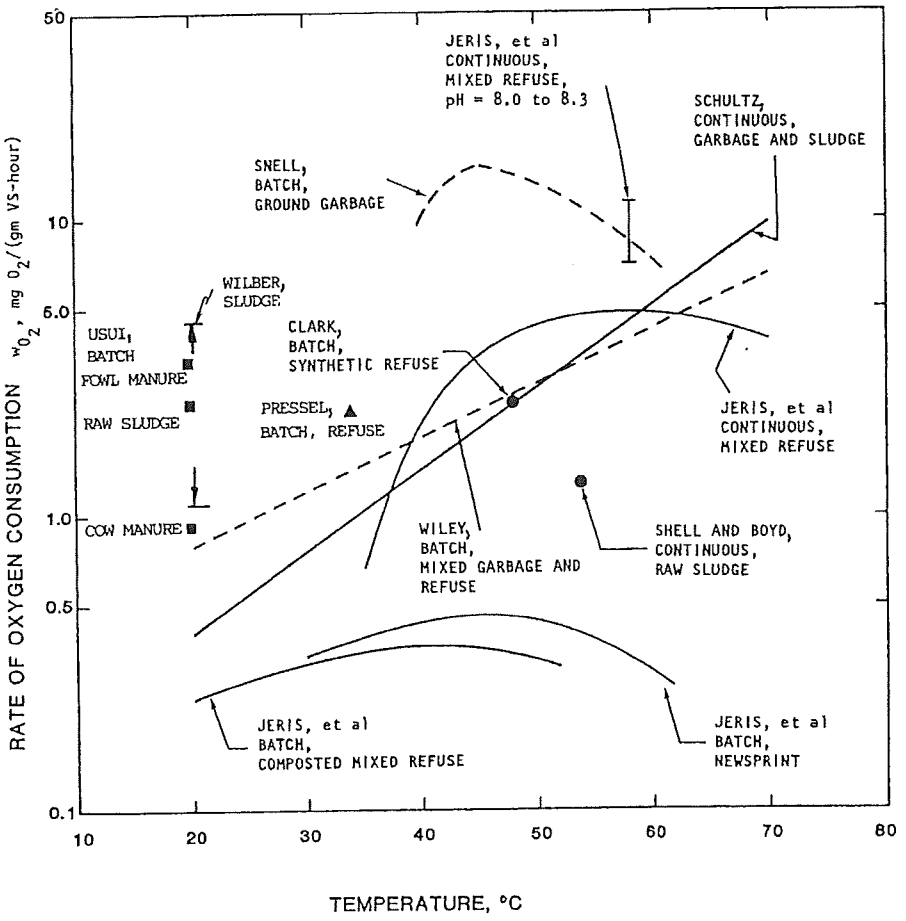

Figure 10.17. Observed oxygen consumption rates for various composting mixtures and reactor types as a function of temperature. Each curve represents the best fit of observed data.

and streams. The approach has also worked well in describing more complex processes such as activated sludge, trickling filters, submerged filters for nitrification, anaerobic filters, and aerobic digesters.

Nolan[42] studied the decomposition of papermill sludges and other substrates in the soil to determine their reaction rate constants. The substrate/soil mixtures were incubated under controlled conditions at 25°C and optimum moisture. CO_2 free air was passed through the incubator and CO_2 evolution observed. Test runs were usually 30 to 60 days duration. Nolan used a first order rate equation to model the data, but divided the substrate VS content into "fast" and "slow" fractions each with their own first order rate constants. It was found that in some cases this provided a better fit to the experimental data. Complex substrates contain a mixture of organics, some of which are likely to degrade faster than others. Therefore, dividing the substrate into faster and slower fractions would seem to be a reasonable assumption.

The first order rate constants and the fast and slow fractions developed by Nolan are presented in Table 10.5. It is interesting to note that the rate constants for grass often exceed those for digested and raw sludges. This is the reason that grass must be carefully handled to avoid odor conditions. It is also interesting to note that crude oil has a relatively high rate constant for decomposition. It is only necessary that moisture, nutrients, microbes, and a support matrix such as soil or compost be provided to increase the oil/water interface area.

The use of respirometers to measure substrate degradability was discussed in Chapter 9. Oxygen uptake curves for several substrates were presented in Figures 9.7 and 9.8. First order

Table 10.5. First Order Rate Constants (base e) at 25°C for Various Substrates Incubated with Soil

Substrate	k_d (day^{-1})		Percent	
	Fast	Slow	Fast	Slow
Digested Sludge				
(Average)[a]	.0282	.0037	34	66
(Standard Deviation)	.0169	.0029	12	12
Limed Raw Sludge				
(Average)[b]	.0293	.0045	32	68
(Standard Deviation)	.0164	.0075	10	10
Primary papermill sludge				
(Average)[c]		.0033	0	100
(Standard Deviation)		.0006		
Primary papermill sludge	.0333	.0060	26	74
Kraft papermill sludge				
(Average)[d]		.0015	0	100
(Standard Deviation)		.0002		
Sawdust	.0100	.0016	20	80
Crude oil	.0170	.0110	35	65
Wheat straw		.0029	0	100
Wood bark		.0004	0	100
Bermuda grass	.0383	.0132	40	60
Rye grass	.0699	.0172	28	72

Source: Adapted from Nolan.[42]

[a] Average of 31 60-day composite samples collected from the same facility over a 5-year period.
[b] Average of 17 60-day composite samples collected from the same facility over a 5-year period.
[c] Average of 4 samples.
[d] Average of 4 samples.

rate constants can be developed from such data using procedures described by Haug and Ellsworth.[43] An analysis for the raw sludge sample identified as Run A in Figure 9.7 is presented in Figure 10.18. Regression analysis on the data projected an ultimate oxygen uptake of 0.778 g O_2/g BVS. Degradability was estimated at 45.8% based on a sample COD of 1.70 g COD/g VS. The best fit of experimental data resulted when the BVS was divided into a 19% "fast" fraction with rate constant 0.15 day^{-1} and an 81% "slow" fraction with rate constant 0.05 day^{-1}. Projected oxygen uptake curves for the fast and slow fractions and the summation of the two are presented in Figure 10.18. The summation curve corresponds closely to the experimental data.

A similar analysis for a hardwood sawdust, shown in Figure 9.8, is presented in Figure 10.19. A significant lag period was observed with the hardwood substrate, probably due to the need to acclimate the seed microbes. In actual practice such lag periods can usually be avoided by using product recycle to supply an acclimated seed. Therefore, the lag period is removed as shown in Figure 10.19. Regression analysis projects an ultimate degradability of 78.4%. In this case the data is modeled to acceptable accuracy by use of a single rate constant of 0.0081 day^{-1}. A summary of fast and slow fractions and associated rate constants developed by Haug and Ellsworth[43] is presented in Table 10.6.

The oxygen uptake rates summarized by Equation 10.17 can be used to predict reaction rate constants as a function of temperature. The feed material used in deriving Equation 10.17 consisted of a mixture of ground garbage and dewatered, digested sludge cake. Oxygen

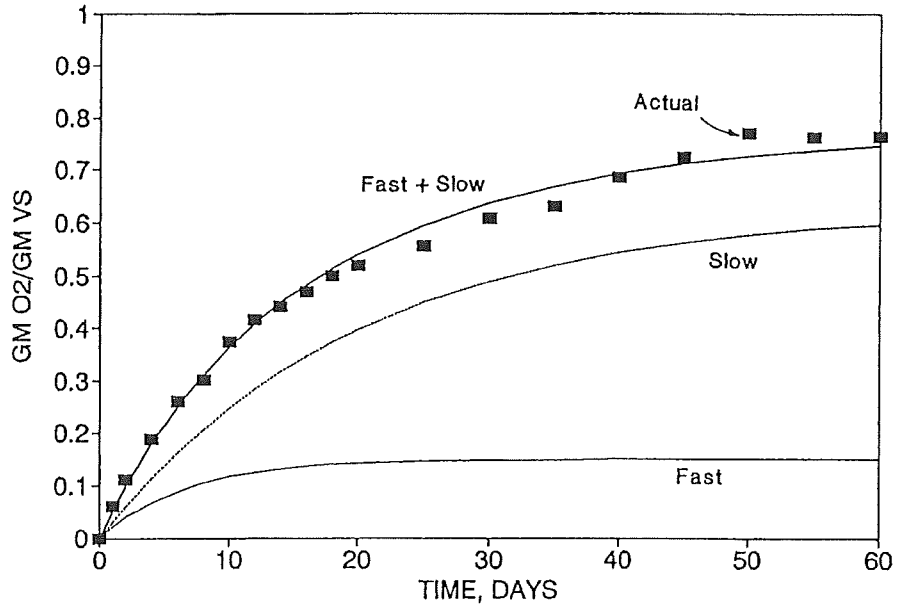

Figure 10.18. Oxygen uptake data for raw sludge compared to a first order reaction rate model. The data were developed using the constant pressure respirometer of Figure 9.5. The data were modeled assuming 19% of the BVS with a rate constant of 0.15 day^{-1} and 81% at 0.05 day^{-1}. From Haug and Ellsworth.[45]

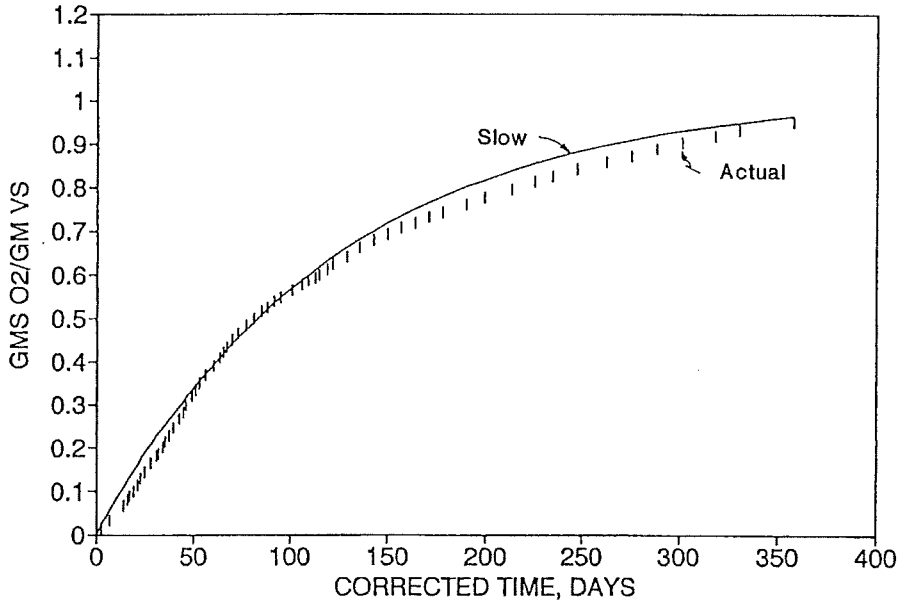

Figure 10.19. Oxygen uptake data for hardwood sawdust compared to a first order reaction rate model. The data were developed using the constant pressure respirometer of Figure 9.5. The data were modeled assuming one rate constant at 0.0081 day^{-1}. From Haug and Ellsworth.[43]

equivalent of the organics was not presented but was estimated from the original data to be about 1.5 g O_2/g VS oxidized. Using this factor, Equation 10.17 can be converted to a rate constant with the following form:

$$k_d = 0.00632(1.066)^{T-20} \text{ (g BVS oxidized/g VS – day)} \qquad (10.23)$$

Table 10.6. First Order Rate Constants (base e) at 20 to 25°C and Substrate Degradabilities Determined by Long Term Respirometry

Substrate	Test Duration (days)	Ultimate Degradability[a] (%)	k_d, day^{-1}		Percent	
			Fast	Slow	Fast	Slow
Raw sludge[b]	60	45.8	0.15	0.05	19	81
Raw sludge	242	66	0.015	0.004	40	60
Pulpmill sludge	200	44.1	—	0.0095	0	100
Sawdust, pine softwood	90	11.2	0.15	0.02	71	29
Sawdust, hardwood	368	78.4	—	0.0081	0	100

Source: Haug and Ellsworth.[43]

[a] Ultimate degradability determined by projection of the oxygen uptake data.
[b] Raw primary and secondary sludge from Plattsburgh, NY.

Examination of Schulze's original data indicates a reduction in volatile matter ranging from about 37 to 45%. Assuming the degradable fraction to be 50% of the total, Equation 10.23 becomes

$$k_d = 0.0126(1.066)^{T-20} \text{ (g BVS oxidized/g BVS} - \text{day)} \tag{10.24}$$

Units on the rate constant in Equation 10.24 are now appropriate to the present analysis. At 20°C the rate constant per Equation 10.24 is 0.0126 day^{-1} (base e), which is consistent with the range of values reported in Tables 10.5 and 10.6. Equation 10.24 can be applied up to about 68°C, the maximum temperature tested by Schultz.

Equation 10.21 was developed from Wiley's experiments conducted on garbage and refuse with a high paper fraction. Using similar assumptions as above, an equation for the reaction rate constant can be developed as

$$k_d = 0.0254(1.0429)^{T-20} \text{ (g BVS oxidized/g BVS} - \text{day)} \tag{10.25}$$

The range of rate constants predicted from Equations 10.24 and 10.25 are consistent with the values presented in Tables 10.5 and 10.6. Equation 10.25 predicts a higher rate constant than Equation 10.24 at 20°C. However, the rate constants at 50°C become essentially equivalent because of the larger temperature coefficient in Equation 10.24.

Several observations can be made from the above data and equations. First, the first order kinetic model appears to accurately describe the decomposition of many composting substrates, even in long term respirometer studies spanning over 800 days duration. Second, the accuracy of fit can sometimes be improved by dividing the substrate into fractions with different rate constants. Third, the rate constants for composting substrates are typically less than for other liquid wastes. For example, the first order rate constant for the BOD test on municipal sewage is typically taken to be about 0.23 day^{-1} (base e) at 20°C and may be considerably higher for simple substrates such as glucose. By comparison, the rate constant for many composting substrates is on the order of 0.01 day^{-1} at 20°C. This rather remarkable difference in reaction rates is due to two factors; the nature of the organic matter and the ability of the organisms to utilize the organic matter. Organic matter that exists in true solution is generally readily available, whereas solid substrates must await hydrolytic action before they

can diffuse into the bacterial cells. This suggests that the rate of hydrolysis is the controlling factor in composting kinetics. Also, composting substrates commonly contain lignin and other compounds that are resistant to microbial attack. These factors combine to make the rate constants for solid substrates considerably less than for the more soluble substrates common to wastewater treatment. As a result, the residence times required to produce a stable compost product are considerably longer than for most other biological treatment processes.

HYDRAULIC AND SOLIDS RETENTION TIMES

The rate of biochemical reaction determines the speed at which composting can proceed. The same decomposition can be achieved by a fast reaction rate operating over a short time or a slower reaction rate operating over a longer time. Because kinetics deals with rates of reaction, the concept of time is important to the design and operation of composting systems. In this section, the concepts of hydraulic retention time, HRT, and solids residence time, SRT, are developed and applied to the composting process.

Distinction Between HRT and SRT

For liquid phase systems, two detention times can be defined, one based on liquid retention time and one based on solids residence time. Detention time based on liquid retention time is usually termed "hydraulic retention time". Detention time based on the average residence time of solids in the system is usually termed "solids residence time". For a reactor without recycle of solids, the HRT and SRT are equivalent. If solids are recycled, however, the SRT will be greater than the HRT.

The distinction between SRT and HRT is an important concept. For homogeneous, liquid phase systems, the efficiency of BVS decomposition is determined by the system SRT. The minimum HRT is determined primarily by time constraints imposed by oxygen transfer and the ability to maintain the required microbial concentration. The same concepts can be applied to solid phase composting systems. The extent of microbial decomposition is determined by the system SRT, whereas reactor or process stability is largely determined by HRT.

Concepts of HRT and SRT for liquid phase systems with recycle are presented in Figure 10.20. The single pass hydraulic retention time is defined as

$$HRT = \frac{V}{Q+q} \tag{10.26}$$

where

HRT = single pass, hydraulic retention time
V = volume of reactor or system
Q = volumetric flowrate of material, excluding recycle
q = volumetric flowrate of recycle material

SRT for a liquid phase system is defined as

$$SRT = \frac{V}{Q} \tag{10.27}$$

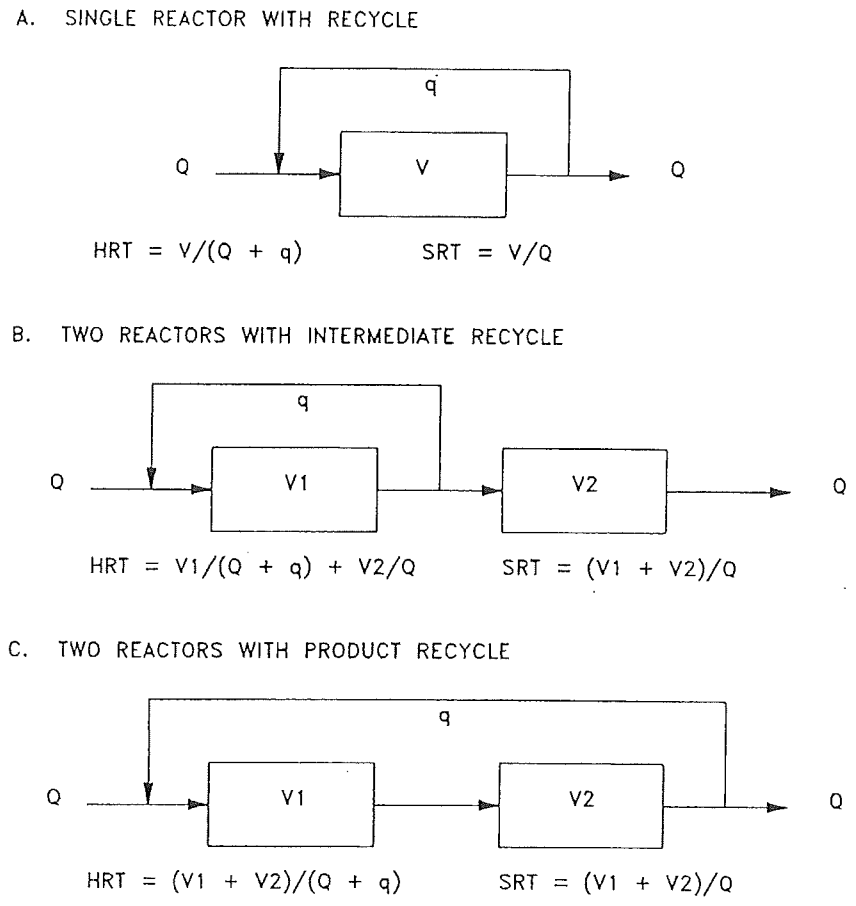

Figure 10.20. Concepts of hydraulic retention time (HRT) and solids residence time (SRT) for liquid phase systems with recycle.

where

SRT = mean solids residence time

For liquid phase systems, the volumetric flowrate remains essentially constant across the reactor, simplifying the calculation of average residence time. The equations for HRT and SRT presented in Figure 10.20 apply to liquid phase systems, but can be adapted to apply to composting systems.

Concepts of HRT and SRT can be defined for composting systems analogous to the concepts used for liquid phase systems. HRT for a composting system is defined as follows: *HRT is the single pass, mean residence time of the mixed materials including recycle.* This definition is equivalent to Equation 10.26 as applied to liquid phase systems. SRT for a composting system is defined as follows: *SRT is the mean residence time of the feed solids excluding recycle.* This definition is equivalent to Equation 10.27.

The volume of mixed materials entering a composting reactor does not remain constant with time. Moisture is lost by evaporation and BVS solids are lost by microbial decomposition. As a result, mixture volume usually decreases across the system. Recall that mass is conservative but volume is not. To account for the volumetric changes that occur during composting, the basic equations for HRT and SRT can be modified to

$$HRT = \frac{V}{\left[\frac{(Q+q)_{in} + (Q+q)_{out}}{2}\right]} \quad (10.28)$$

$$SRT = \frac{V}{\left[\frac{Q_{in} + Q_{out}}{2}\right]} \quad (10.29)$$

A number of alternative mathematical formulations to Equation 10.29 can be developed to estimate SRT from the general definition given above. Gossett[44] used an equation of the form

$$SRT = HRT\left(\frac{W_1}{W_2}\right) \quad (10.30)$$

where

W_1 = weight of reactor outfeed
W_2 = weight of reactor outfeed less the weight of recycle

The important points here are the definitions of HRT and SRT and the distinction between the two. The mathematical approach used for estimation is developed further in Chapter 11.

Design Criteria

HRT is an important parameter that affects composting temperature, output solids content, and the stabilization of BVS. These factors are quantitatively discussed in Chapter 12. In summary, process stability is favored by longer detention times. A minimum design HRT of 10 to 20 days is reasonable for continuous, well-mixed reactor systems, because the process is stable over a wide range of conditions and high output solids contents and BVS reductions are possible. Longer detention times produce smaller improvements in these parameters for a comparable increase in reactor volume. Many reactor systems are designed for an HRT of 14 to 28 days which is consistent with the above discussion. Batch processes may require longer detention times because of the lag phase encountered at the start of composting.

SRT is the most important factor in determining the stability of the compost product. Again, the effect of SRT on product stability and quality is quantitatively discussed in Chapters 12 to 14. The minimum system SRT for design is a function at least the following:

1. the types of substrates and amendments used and their corresponding reaction rate constants
2. the extent of process control incorporated into the design and the processes used for the high-rate and curing phases
3. the extent to which kinetic rate limitations are avoided
4. the end use of the product

The operating records of a number of composting systems, using a variety of substrates, were reviewed. These data, together with the simulation model results in Chapters 13 and 14

and the discussion on product stability presented later in this Chapter, suggest that a minimum system SRT of about 60 to 180 days is required to produce compost with sufficient stability and maturity to avoid reheat and phytotoxic effects. This assumes that the feed materials are properly conditioned to close the energy balance and reduce kinetic limitations. It further assumes a reasonable level of process control to prevent excessive rate limitations during the process.

Design Approach

The minimum system SRT, SRT_{min}, is a key process criteria that should be established at the beginning of the design phase. System SRT should also be monitored by the operator of an existing facility to guide operational practices and measure system performance. SRT_{min} can be established by a review of similar facilities and/or by simulation modeling to determine the required SRT to produce a given product quality. The latter approach is discussed in Chapters 11 through 14.

Once SRT_{min} is established, the next step is to define the desired HRT for the first stage, high rate phase, HRT_r. If a reactor (in-vessel) system is used for the first stage, the minimum reactor HRT should be in the range of 12 to 20 days. A minimum HRT of 20 to 30 days is typically used with the aerated static pile and windrow processes. The proper ratio of mixture components for structural, chemical, and energy conditioning is then determined using the procedures of Chapters 6 and 8. The required volume of reactor, REACVOL, aerated piles, or windrows can then be determined using Equation 10.28.

Once the volume of the first stage is known, the corresponding SRT in the first stage, SRT_r, can be determined from Equation 10.29 or 10.30. The difference between the minimum system SRT and the SRT of the first stage equals the additional SRT, which must be provided by the second stage, curing phase, SRT_c. In other words, $SRT_c = SRT_{min} - SRT_r$. Once SRT_c is determined, Equation 10.29 can be used to determine the volume required for the curing phase, CUREVOL, and Equation 10.28 to determine the curing HRT, HRT_c.

This design approach is developed further in Chapters 11 to 14. The procedure allows the designer to integrate the first stage, high rate phase and the second stage, curing phase into an overall system design. For example, decreasing the size of the first stage process will increase the size of the second stage process required to achieve the same SRT_{min}. This approach to the problem of design allows for optimization of individual processes, based on site specific constraints, while maintaining minimum system requirements.

PRODUCT STABILITY

Definition and Purpose

The term "stabilization" refers to the oxidation of organic matter or its conversion to a more refractory form. When an organic substrate is oxidized by microbes, a portion of the released energy is captured and used to support the synthesis of new cell material from the substrate. When the microbe dies the cell material becomes food for other microbes and a further transformation to CO_2, H_2O, and cell matter occurs. Each time this process is repeated a portion of the remaining organic matter is very resistant to microbial attack. This is commonly called humus. As composting proceeds, the readily degradable organics in the substrate are oxidized and gradually replaced by increasingly less degradable humus materials. The more

stable compounds that remain at the end of composting are still degradable, but at a much reduced rate compared to the original feed substrate.

The question that arises is, how much stabilization is enough? There is no precise answer to this question. For example, anaerobically digested sludge is generally considered stable. In the liquid or cake form, digested sludge can be applied to land in controlled amounts without producing nuisance conditions. On the other hand, if digested sludge cake is allowed to sit in open piles, septic and odorous conditions can often develop. As another example, raw sludge can be heat dried and stored for long periods without producing odorous conditions. The low moisture content limits the rate of biological activity resulting in a "pseudostable" material. In the dried state, raw sludges are even bagged and sold by nurseries, perhaps the most demanding market in terms of product quality. When the material is rewetted, normal rates of biological activity will resume. By this time, however, the material should be incorporated into the soil, thus reducing the nuisance potential.

Another aspect of stabilization is the effect of the organics on plant growth. Numerous researchers have observed that "immature" composts can contain metabolites that are toxic to plants (phytotoxicity). Zucconi et al.[45] noted that the introduction of decomposing organic matter in the soil may damage existing plant roots and inhibit growth. If the organic matter has a high C/N ratio and decomposes rapidly, it can rob the soil of the nitrogen needed to support plant growth. If the organic matter has a low C/N ratio, released ammonia can be phytotoxic. Metabolic products of biodegradation, particularly organic acids such as acetic acid, can also exhibit a toxic effect on plant growth. Zucconi et al.[46] composted MSW fractions using mechanically agitated windrows. Samples collected throughout the process were tested for phytotoxicity. Toxicity was associated with the initial 3 to 4 weeks of composting. Following this stage, toxicity rapidly decreased, although it had not completely disappeared after 60 days of composting.

The purpose of composting is to produce an organic soil amendment that is beneficial to plants. All compost facilities should be designed and operated to produce a stable product that is beneficial to plants and not phytotoxic. Tuttle[47] has noted the truism that "if it kills plants, it's *not* compost." This does not necessarily mean that the compost must be fully cured on site. Wheeler[48] reported that the City of Hamilton, Ohio pays a soil blender to remove uncured, sludge compost immediately upon exit from their reactor system. Subsequent storage and dilution with soil materials apparently produces an acceptable product.

We come back to the original question, how much stabilization is enough before the product can be termed a compost? Certainly, there is no such thing as complete stabilization as long as any organic matter remains, because it will continue to decompose at some rate. In a strict sense, complete stabilization would require the oxidation of all organic matter to CO_2 and H_2O. However, complete stabilization is not desirable because the value of compost as a soil amendment depends in part on its organic content. The following working definition of compost is suggested: *Compost is an organic soil conditioner that has been stabilized to a humus-like product, that is free of viable human and plant pathogens and plant seeds, that does not attract insects or vectors, that can be handled and stored without nuisance, and that is beneficial to the growth of plants.* Such a definition is not precise, but it is practical. Stabilization must be sufficient to reduce the nuisance potential and phytotoxic metabolites, but not so complete that organics are unnecessarily lost from the final product. Stabilization is sufficient when the rate of oxygen consumption is reduced to the point that anaerobic or odorous conditions are not produced to such an extent that they interfere with storage or end use of the product and phytotoxic compounds have been metabolized.

Measuring Stability

A number of approaches have been used to measure the degree of stabilization and to judge the condition of the compost product. Included among these are:

1. decline in temperature at the end of batch composting or curing
2. a low level of self-heating (reheat) in the final product
3. organic content of the compost as measured by VS content, chemical oxygen demand (COD), carbon content, ash content, or C/N ratio
4. oxygen uptake rate
5. the effect on seed germination and plant growth
6. the presence of particular constituents such as nitrate and the absence of others such as ammonia, sulfides, organic acids, and starch
7. lack of attraction of insects or lack of development of insect larvae in the final product
8. characteristic changes in odor during composting and odor producing potential of the final product upon rewetting
9. rise in the redox potential
10. experience of the operator

Some of these approaches are qualitative while others are at least semiquantitative. Most can provide the operator a comparative tool by which to judge the compost product.

Temperature Decline

A temperature decline back to near ambient conditions at the end of composting is a good indication that the process is nearing completion. The proviso is that the temperature drop is not caused by thermal kill, oxygen shortage, low moisture, lack of FAS, or lack of sufficient pile insulation. This approach is based on the fact that the rate of heat production is proportional to the rate of organic oxidation, which decreases after the more degradable material is decomposed. A declining temperature is inevitable as the energy balance adjusts to the decreasing rate of heat input. Conversely, composting material that is still in a thermophilic condition is probably not stable and not yet mature.

Reheat Potential

Reheating potential of the product is another useful but comparative tool. In a method proposed by Niese,[49] the sample is adjusted to optimum conditions and placed in a Dewar flask. The flask is placed in a special incubator equipped with temperature control circuits to maintain a constant temperature difference between the incubator and the Dewar flask. Niese observed temperatures >70°C with raw refuse, 40 to 60°C with partly stable refuse, and <30°C with fully stable material. Willson and Dalmat[50] noted that the decline in temperature in windrows and piles is actually a large scale variation of Niese's lab test, but lacks its precision due to variable heat loss parameters. One difficulty with this approach is that apparent "stability" may result in part from other rate limitations such as low moisture content or lack of FAS. Willson tried the technique but judged the results as too erratic to be useful.

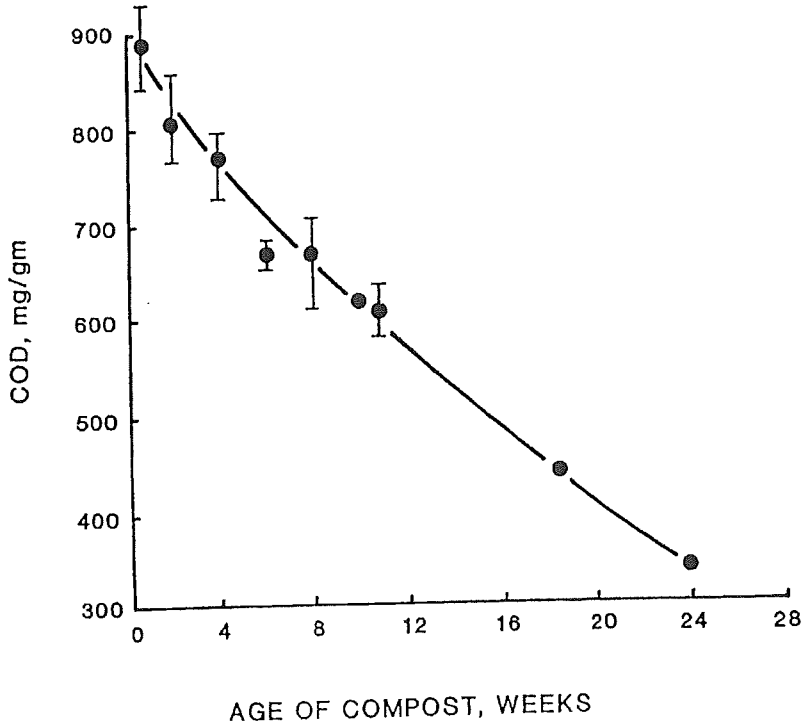

Figure 10.21. Effect of compost age on the COD of samples collected during windrow composting of refuse. From Lossin.[51]

Organic Content

The organic content of a compost will depend largely on the organic characteristics of the feed substrate. Therefore, organic content can provide a measure of stability for a particular feed, but should not be used to compare composts produced from different feed substrates. A number of chemical tests have been used to either directly or indirectly measure the organic fraction, including VS, ash or carbon contents, COD, and C/N ratio. The COD of composting samples reported by Lossin[51] during windrow composting of refuse is presented in Figure 10.21. The compost was considered stable and ready for use after eight weeks, which corresponded to a COD <700 mg/g compared to about 900 mg/g for fresh refuse. If the refuse is assumed to be primarily cellulose, the final COD corresponds to a VS content of ~70% (1 g glucose = 1.07 g COD). By contrast, compost produced from a windrow composed of digested sludge conditioned solely with product recycle usually has a VS content of only 30 to 40%. This emphasizes the point that organic content can be a useful measure when applied to a particular feed substrate, but should not be used to compare composts produced from different starting substrates. It is interesting to note from Figure 10.21 that the VS content after 24 weeks was about 30 to 40%.

Chemical Characteristics

Particular constituents in compost are often characteristic of the level of stability. Ammonia is usually present in the early stages of composting as organic nitrogen is decomposed. The ammonia concentration is eventually reduced through volatilization or oxidation to the nitrate form. Thus, the presence of nitrate and absence of ammonia are indicative of a stabilized condition. Lossin[52] reported on the use of starch content as a measure of stability. The rationale

Table 10.7. Acetic Acid Concentrations during Windrow Curing of Refuse Compost from the Dano facility at Ghent, Belgium

	Acetic Acid in Extract (ppm)	
Windrow Curing Time (days)[a]	Turned Windrow[b]	Nonturned
1	25,980	18,500
5	25,570	20,630
9	21,400	27,800
13	14,600	15,500
36	12,400	14,800
68	400	690
120	0	0

Source: DeVleeschauwer et al.[53]

[a] The curing time followed 3 days in a Dano drum.
[b] One windrow was turned frequently by means of a bulldozer. The other was left undisturbed — neither windrow was force ventilated.

rests on the assumption that most feed substrates contain a measurable quantity of starch. Because starch is easily broken down and metabolized, it should be degraded before the compost is considered acceptable. The test procedure involves formation of a colored starch-iodine complex in an acid extract from the compost material. Lossin reported that well-stabilized compost never gave a positive starch reaction with this test.

DeVleeschauwer et al.[53] studied the phytotoxicity of compost produced from town refuse at a Dano facility in Ghent, Belgium. The refuse spent about 3 days in the Dano stabilizer followed by windrow curing. Phytotoxicity was correlated with the organic acid content of the composting material. Acetic, propionic, isobutyric, butyric, and isovaleric acids were quantified by extraction into 50 ml of water added to 10 gms of compost and acidified to pH 2. Phytotoxicity was measured by bioassays with cress seed. Acetic acid was determined to be the primary organic acid present and was responsible for most of the phytotoxic effect. Phytotoxic effects began when the acetic acid concentration in the extract was above 300 ppm. Above ~2000 ppm, no seed germination was observed. Acetic acid concentrations determined during the composting cycle are presented in Table 10.7. Very high concentrations were observed during the first month of composting. It took 120 days of windrow curing to reduce acetic acid concentrations below the phytotoxic level. No seed germination was noted until the day 120 samples. The authors concluded that at least 4 months composting would be required before the product could be used safely in horticulture or agriculture.

Plant Bioassays

Perhaps the most direct method to determine whether the compost product has been cured sufficiently from the standpoint of phytotoxicity is to determine its effect on plant growth. Potting studies could be conducted but these require considerable time before the results are known. Several researchers have worked on ways of reducing the time required for testing. Most have used the germination rate of a test seed, usually cress seed *Lepidium sativum*, because of its rapid response. Spohn[54] described a procedure that measured the germination and growth of cress seed planted in beds of compost that required 5 days.

Zucconi et al.[45,46] developed a 24-h bioassay test that measured germination and root elongation in an aqueous extract from the compost. In the water extract 6 to 8 cress seeds are incubated for 24 h in the dark at 27°C, 10 to 15 replicate samples are recommended. The water

Moisture is limited to that associated with the solid substrate. In such a case, a rather complex sequence of events is necessary for metabolism of the substrate. Solubilization of substrate by exocellular enzymes, mass transport of oxygen to the cell, and utilization of the solubilized substrate and oxygen by the cell are likely the predominant rate-controlling steps during aerobic composting. Kinetic models can be developed for each of these steps. A model of substrate solubilization suggests that the kinetics for this step are a function of the mass concentration of microbes, X, at concentrations of X less than a constant, K_x. The rate becomes independent of X at higher concentrations where $X > K_x$. Under the latter conditions the rate of solubilization becomes constant at a given temperature. This means that for materials resistant to solubilization, longer time periods are required to allow solubilization and decomposition. This appears to be the function of the curing stage commonly used in composting systems.

Particle thickness on the order of 1 cm can result in large oxygen mass transport limitations which would dominate and slow the process kinetics. Particle thickness of about 0.1 cm or less is small enough that diffusion supplied oxygen can match the peak rates of oxygen demand. The fact that oxygen is present in the pore spaces of a composting material does not by itself assure that oxygen diffusion is not rate-limiting, because oxygen must still be transported within the composting particle. The moisture content of individual composting particles is significant because diffusion coefficients through a gaseous phase are much greater than through the liquid phase. Thus, diffusion transport of oxygen may be a controlling factor when particle moisture contents are high and assume less significance as moisture is removed from the particle.

A number of other factors can limit microbial reaction rates during composting. These include lack of degradable organics, very low or high process temperatures, low moisture conditions, lack of free air space, low oxygen content, imbalanced pH conditions, lack of inorganic nutrients, lack of microbes (sterile substrate), and the presence of toxic substances. The effect of these potential rate limitations can be controlled by assuring proper structural, chemical, and energy conditioning of the feed mixture, supplying adequate air to the process, and using some product recycle to seed the feed mixture if it is suspected that microbial concentrations are low.

Rates of oxygen consumption have been measured in both batch and continuous composting reactors on a variety of feed materials. In general, rates of oxygen utilization increase exponentially with temperature up to a peak value. Further temperature increases result in decreased rates of reaction from thermal inactivation. Temperature optima from 40 to 70°C have been reported. Data suggest that cellulosic substrates may have a temperature optima in the 45 to 50°C range because of a larger number of microbial species capable of utilizing cellulose in this temperature range. Maximum rates of oxygen consumption are likely to range from 4 to 14 mg O_2/g VS-h. These values represent *peak* stoichiometric demands.

Organic decomposition during composting can be modeled as a first order reaction. The accuracy of the model can sometimes be improved by dividing the substrate into fractions with different first order rate constants. The rate constants for most composting substrates are typically lower than for more solubilized substrates in the liquid phase. This suggests that the rate of hydrolysis may be the controlling factor in composting kinetics. Because of the slower kinetic rates, the residence times required to produce stable composts are considerably longer than for most other biological treatment processes.

Concepts of hydraulic retention time (HRT) and solids residence time (SRT) can be defined for composting systems analogous to the concepts used for liquid phase systems. HRT for a composting system is defined as the single pass, mean residence time of the mixed materials

including recycle. SRT for a composting system is defined as the mean residence time of the feed solids, excluding recycle. The recommended design approach is to establish the minimum system SRT necessary to produce a given product quality. Volumes of the high rate and curing phases can then be adjusted as necessary to achieve the minimum system SRT. This approach to design allows for optimization of individual processes, based on site specific constraints, while maintaining minimum system requirements.

The purpose of composting is to produce an organic soil amendment that is beneficial to plants. All compost facilities should be designed and operated to produce a stable, mature compost. To be defined as compost, the organic substrates must be stabilized to a humuslike product that is free of viable human and plant pathogens, plant seeds, and insect eggs, that can be handled and stored without nuisance, and that is beneficial to the growth of plants. A number of test procedures have been developed to measure the degree of stabilization. Data from these tests indicate that curing is essential to produce a stable product. System SRTs from 60 to over 180 days are generally necessary to stabilize organics and reduce phytotoxic effects in high rate composting systems. Longer SRTs may be required in less controlled processes.

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